

this investigation are in agreement with our observation since the copper catalysts were also observed to have superior activities compared to the cobalt catalysts. In the case of the copper catalysts the effect of pH is not as significant as was the case with the cobalt complexes as can be seen from Figures 4.8 and 4.9. Although the activities of the copper catalysts at pH 3 were slightly lower than activities observed at pH 6, the drop in activity was not as great as observed for the cobalt systems. In the latter case activities at pH 3 were approximately half those observed at pH 6 indicating that the cobalt catalysts are much more sensitive to very acidic pH values compared to the copper complexes.

The investigation conducted by Ray et al. [9] also showed a pronounced impact on the product distribution which depended on both the nature of the metal centre as well as the pH of the reaction medium. It was observed that a very similar ratio of HQ to CT was obtained with copper catalysts within the pH range studied, whereas cobalt and nickel catalysts appeared to be much more selective at different pH values producing one of the dihydroxybenzenes preferentially over the other [9]. This phenomenon is also observed in the catalytic experiments conducted here, which showed copper catalysts producing the dihydroxybenzenes in either a 1:2 or a 1:1.5 (HQ:CT) ratio over the pH range studied with little or no deviation from these distributions with change in pH. Although similar ratios to these are obtained for the cobalt catalysts at pH 3, under more basic conditions an increase in the formation of CT is observed which results in ratios of roughly 1:3 and 1:5 (HQ:CT) being obtained for the mononuclear catalysts and metallodendritic catalysts, respectively.

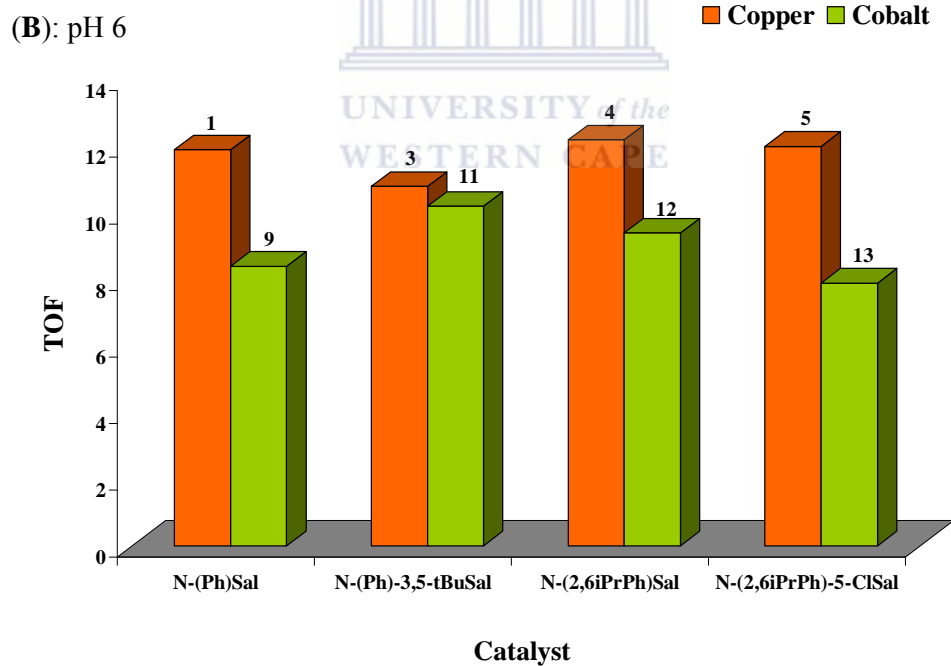
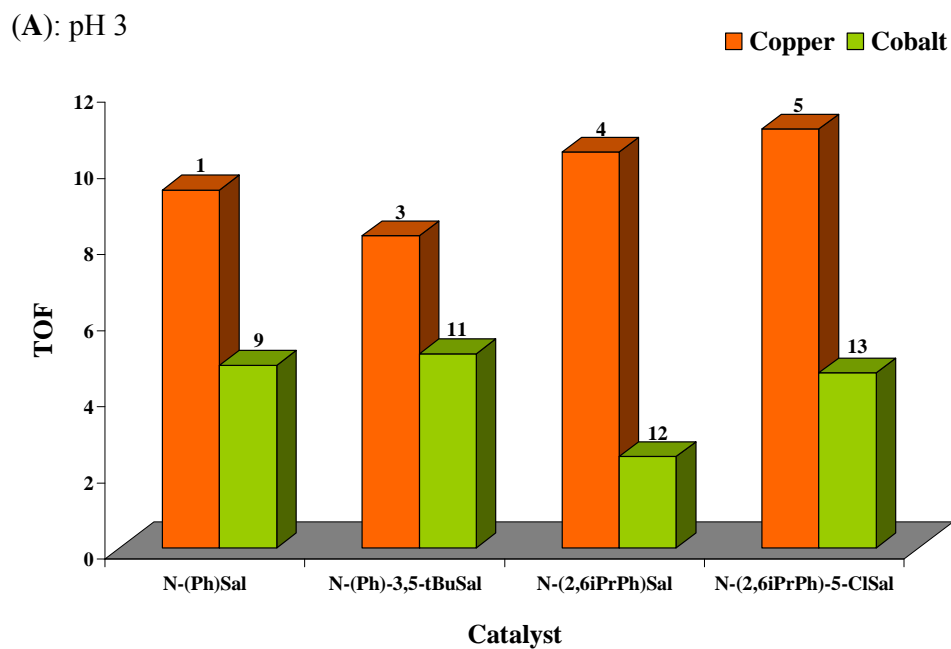


Figure 4.8: Comparison of the activity of Cu(II) and Co(II) mononuclear complexes derived from the same *N*-(aryl)salicylaldimine ligands at pH 3 (A) and pH 6 (B). (*x*-axis indicates the ligand from which the metal complex is derived).

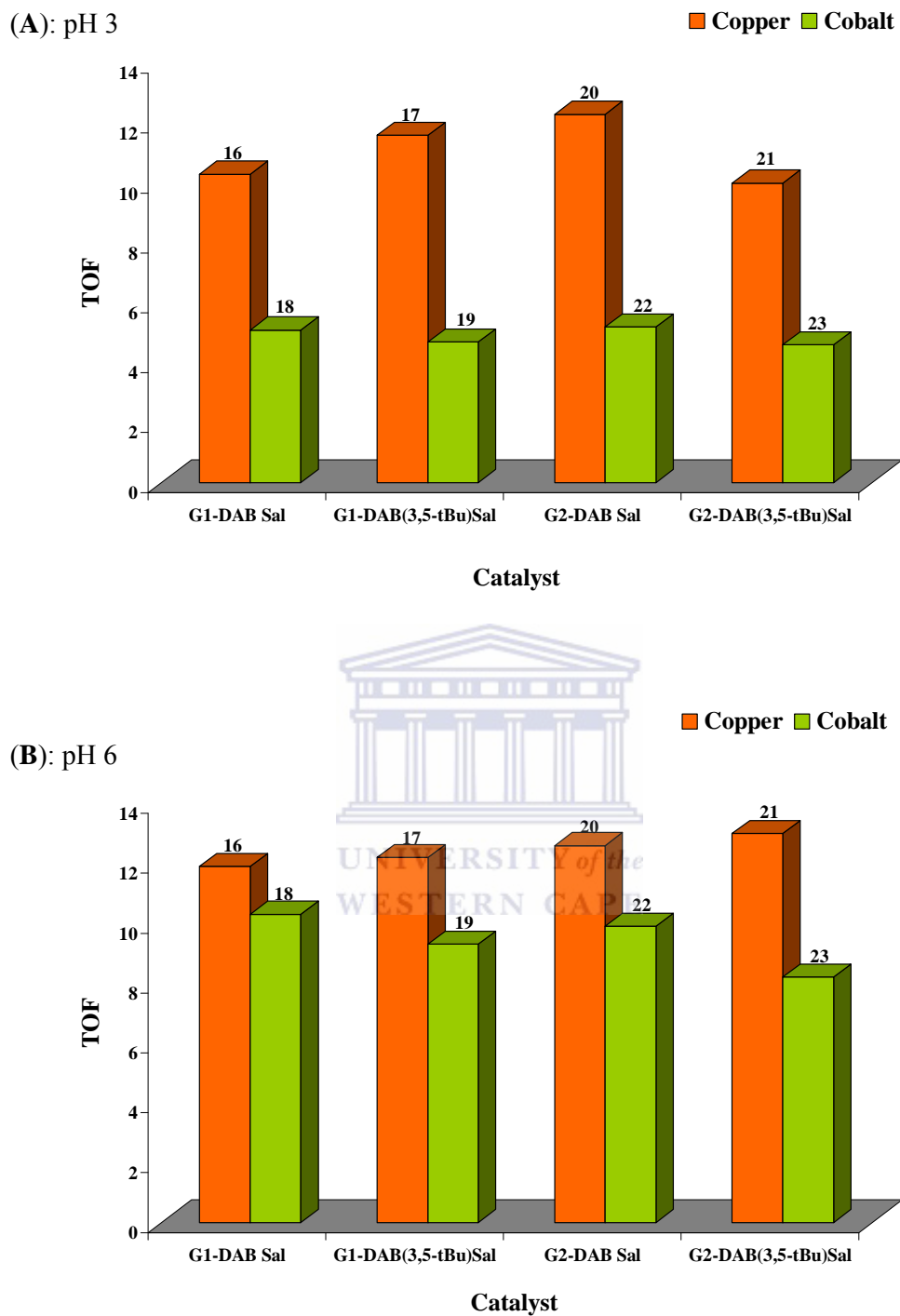


Figure 4.9: Comparison of the activity of Cu(II) and Co(II) metallodendrimers derived from the same salicylaldehyde dendritic functionalised ligands at pH 3 (A) and pH 6 (B). (x-axis indicates the ligand from which the metal complex is derived).

4.2.4 The effect of immobilization of complexes on activity and product selectivity.

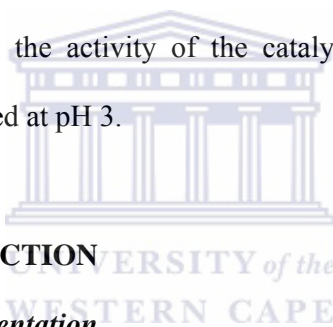
On comparing the performance of the mononuclear catalysts versus the dendritic immobilized systems of both copper and cobalt it was observed that under the conditions investigated the activities of the catalysts are in general comparable. However in the case of the copper catalysts it was found that the G2 catalyst **21** performed the best and the only catalyst derived from *N*-(aryl)salicylaldimines which produced comparable activity was bimetallic catalyst **8**. In the case of the cobalt systems mononuclear catalyst **14** produced the best overall activity and the G1 catalyst **18** was the only metallodendrimer which showed a comparable conversion. It was thus observed that the mononuclear cobalt systems performed slightly better than the dendrimeric systems.

For the copper catalysts it was found that the dendritic systems showed a higher formation of HQ than the mononuclear catalysts in the pH range investigated, the exception being **1** which showed a similar product distribution as the metallodendrimers. In the case of the cobalt catalyst, aside from **9**, which only showed the formation of CT it was observed that the product distribution of the dendritic immobilized catalysts was similar to that of the mononuclear catalysts. For instance at pH 3 the catalysts showed a 1:1.5 HQ to CT ratio, while at pH 6 either none of the two dihydroxybenzenes were produced or a higher selectivity to CT was observed.

4.3 CONCLUSIONS

The catalytic activity of copper(II) and cobalt(II) complexes derived from *N*-(aryl)salicylaldimines as well as those derived from peripheral functionalised dendritic salicylaldimine ligands were evaluated in the hydroxylation of phenol in aqueous media

under pH-controlled conditions. All the catalysts investigated were observed to be active for the oxidation process with the major products detected being HQ and CT. All the catalysts appeared to be more selective towards the formation of CT. In the case of the *N*-(aryl)salicylaldimine copper(II) catalysts a CT:HQ ratio of roughly 2:1 was observed for all catalysts except catalyst **1** which showed a slightly higher formation of HQ producing a CT:HQ distribution of 1.5:1. The copper(II) metallodendrimers also showed a higher formation of HQ resulting in a similar CT:HQ ratio as obtained for catalyst **1**. For the copper catalysts there was no significant pH effect observed in terms of catalyst activity and only a slight pH effect was observed favouring the formation of CT for all catalysts. The cobalt systems however showed a much more significant pH dependence of activity since the activity of the catalysts roughly doubled at pH 6 compared to activities observed at pH 3.



4.4 EXPERIMENTAL SECTION

4.4.1 Material and Instrumentation

Phenol, catechol, hydroquinone, benzoquinone and formic acid were purchased from Sigma-Aldrich Ltd and 30 % H₂O₂ (w/w) was obtained from Merck Chemicals Ltd. All chemicals were used without further purification. Oxidation reactions were performed on a 12 place RADLEY's Heated Carousel Reaction Station fitted with a reflux unit as well as a gas distribution system with glass reaction vessels. High-pressure liquid chromatography (HPLC) was performed on a HP 1090 liquid chromatograph equipped with a ZORBAX[®] C18 column of dimensions 4.6 x 150 mm and a UV detector using a solvent system consisting of 0.1% formic acid (v/v) and acetonitrile. The pH of the buffers was measured at 25 °C using a Metrohm Limited 744 pH meter.

4.4.2 General procedure for the hydroxylation of phenol

A 12 place RADLEY's Heated Carousel Reaction Station fitted with a reflux unit as well as a gas distribution system was used to perform the hydroxylation reactions. In a typical reaction, phenol (1 mmol) and the appropriate catalyst (0.1 mmol) was placed in a 50 mL glass reaction vessel followed by the appropriately buffered solution which was saturated with oxygen (10 mL) for approximately 15 minutes prior to use. The temperature of the reaction mixture was brought to 110 °C under an oxygen atmosphere and the mixture stirred at this temperature for 15 min. A 30% H₂O₂ (w/w) solution (1 mmol) was added and the reaction mixture was stirred at 110 °C under an oxygen atmosphere for a further 6 hours. The reaction mixture was cooled to room temperature and a 1 mL sample withdrawn, filtered through a syringe filter and diluted 20 times. The consumption of phenol and the oxidation products obtained were analyzed by HPLC. Detection of the products was performed with a dual wavelength UV detector (254 and 275 nm). The mobile phase used was a mixture of 0.1% formic acid solution and acetonitrile.

4.5 REFERENCES

1. C. J. Pereira, *Chem. Eng. Sci.* **1999**, *54*, 1959.
2. M. T. Hassenein, S. S. Gerges, M. A. Abdo, S. H. El-Khalafy, *J. Porphyrins Phthalocyanines* **2005**, *9*, 621.
3. D.C. Sherrington, *Pure & Appl. Chem.* **1988**, *60*, 401.
4. H-Q. Zeng, Q. Jiang, Y-F. Zhu, X-H. Yan, X-B. Lang, H-Y. Hu, Q. Liu, W-Y. Lin, C-C. Guo, *J. Porphyrins Phthalocyanines* **2006**, *10*, 96.
5. A. Zombeck, R. S. Drago, B. B. Corden, J. H. Gaul, *J. Am. Chem. Soc.* **1981**, *103*, 7580.

6. A. Haikarainen, J. Siplilä, P. Pietikainen, A. Pajunen, I. Mutikainen, *Bioorg. Med. Chem.* **2001**, *9*, 1633.
7. W. Zeng, Z. Mao, X. Wei, J. Li, Z. Hong, S. Qin, *J. Supramol. Chem.* **2002**, *2*, 501.
8. M. Stiborová, V. Suchá, M. Mikšanová, J. Páca Jr., J. Páca, *Gen. Physiol. Biophys.* **2003**, *22*, 167.
9. S. Ray, S. F. Mapolie, J. Darkwa, *J. Mol. Catal. A: Chem.* **2007**, *267*, 143.
10. Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, Volume 13, Page 996, Wiley Interscience Publications.
11. J. A. Martens, P. Buskens, P. A. Jacobs, A. V. D. Pol, J. H. C. van Hooff, C. Ferrini, H. W. Kouwenhoven, P. J. Kooyman H. van Bekkum, *Appl. Catal. A: Gen.*, **1993**, *99*, 7.
12. F. Luck, *Catalysis Today* **1999**, *53*, 81.
13. S. S. Lin, C. L. Chen, D. J. Chang, C. C. Chen, *Water Research* **2002**, *36*, 3009.
14. A. Cybulski, J. Trawczyński, *Appl. Catal. B: Environ.* **2004**, *47*, 1.
15. H. Zhang, X. Zhang, Y. Ding, L. Yan, T. Ren, J. Suo, *New J. Chem.* **2002**, *26*, 376.
16. W. Zhu, Y. Bin, Z. Li, Z. Kiang, T. Yin, *Water Research* **2002**, *36*, 1947.
17. A. Santos, P. Yustos, A. Quintanilla, F. García-Ochoa, *Topics in Catalysis* **2005**, *33*, 1.
18. A. Dubey, V. Rives, S. Kannan, *J. Mol. Catal. A: Chem.* **2002**, *181*, 151.
19. Y.H. Hue, A. Gedeon, J.L Bonardet, N. Melush, J.B. D’Espinose, J. Fraissard, *Chem. Commun.* **1999**, 1967.
20. C. Liu, Y. Shan, X. Yang, X. Ye, Y. Wu, *J. Catal.* **1997**, *168*, 35.
21. L. Wang, A. Kong, B. Chen, H. Ding, Y. Shan, M. He, *J. Mol. Catal. A: Chem.* **2005**, *230*, 143.

22. J.N. Park, J. Wang, K.Y. Choi, W.-Y. Dong, S.-J. Hong, C.W. Lee, *J. Mol. Catal. A: Chem.* **2006**, 247, 73.
23. Q. Xie, J-Z. Li, X-G. Meng, C-W. Hu, X-C. Zeng, *Trans. Met. Chem.* **2004**, 29, 388.
24. J. Zhang, Y. Tang, J-Q Xie, J-Z. Li, W. Zeng, C-W. Hu., *J. Serb. Chem. Soc.* **2005**, 70, 1137.
25. Z-W. Yang, Q-X. Kang, H-C. Ma, C-L. Li, Z-Q. Lei, *J. Mol. Catal. A: Chem.* **2004**, 213, 169.
26. E. Schön, D.A. Plattner, P. Chen, *Inorg. Chem.* **2004**, 43, 3164.
27. K.C. Gupta , A.K. Sutar, *J. Mol. Catal. A: Chem.* **2007**, 272, 64.



CHAPTER 5

CATALYTIC OXIDATION OF CYCLOHEXENE USING SALICYLALDIMINE COMPLEXES AS CATALYSTS

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5.1. INTRODUCTION

As mentioned in Chapter 1, catalysis is one of the key factors identified in developing *greener* chemical processes to diminish environmental impact and improve sustainability of current industrial chemical processes [1]. Recent years have thus seen considerable research efforts to develop suitable immobilized catalysts especially in the area of oxidation, which are able to utilise cheap oxidants such as hydrogen peroxide and molecular oxygen [2-5]. This strategy addresses two problems viz. catalyst-product separation and waste minimization by utilizing environmentally friendly oxidants. Developing catalysts which are able to produce oxygenated compounds with a high degree of selectivity remains an area of interest due to the complexity of oxidation processes and the limitations in controlling or terminating the oxidation at different stages. Achieving selectivity in the oxidation of organic substrates with peroxides is particularly difficult due to the fact that the reactions proceed via a radical mechanism which is generally described by the Haber-Weiss cycle [6]. Moreover the radical species generated during the oxidation process are highly reactive and thus achieving selective oxidation is not always possible.

The oxidation of cyclohexene has received considerable attention recently. This is most likely due to the propensity of this substrate to undergo allylic oxidation as opposed to epoxidation particularly in the presence of peroxides. Cyclohexene is thus often used as a model substrate to investigate the activity and selectivity of transition metal complexes in the oxidation of substrates which typically show preferential attack at the allylic position as opposed to epoxide formation. It has widely been established that the reaction parameters such as the type of solvent, reaction temperature, oxidant to substrate ratio and the nature of the metal has a pronounced impact on the activity of the

catalyst as well as the distribution of the oxidation products. Recent investigations which have focussed on immobilized catalysts have also indicated that the nature of the support has an influence on the activity of the catalyst as well as product distribution.

It has been shown for oxidation processes catalysed by transition metal catalysts that the mechanism of oxygen transfer is very important to achieve selectivity. In order to achieve selective oxygen transfer it has widely been established that generation of an active transition metal intermediate such as the species depicted in Figure 5.1 is required. The mechanistic aspects of selective oxidation via metal-peroxo complexes have been extensively reviewed by Modena, Sherrington and Jørgensen [7-9]. Recently Yudanov also investigated the mechanistic aspects of oxygen transfer with metal-peroxo species using DFT methods [10].

Porphyrins, phthalocyanines and salicylaldehyde metal complexes are very capable of generating the metal oxo species, especially in the presence of oxidants such as iodosylbenzene and sodium hypochlorite [11]. In the presence of peroxides these transition metal systems have also been reported to produce the metal-peroxo complex [12]. The ability of the metal to produce these active species generally depends on the ability of the ligand systems to stabilise these active intermediates. This in turn depends on the resistance of the ligand system itself to oxidation.

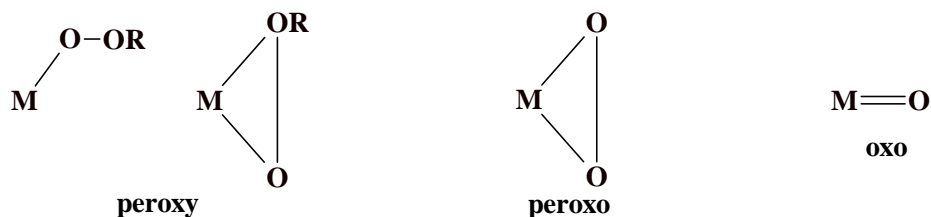
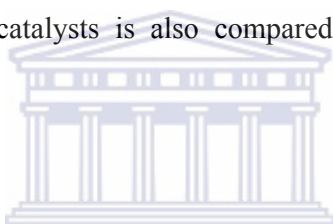


Figure 5.1: Active transition metal intermediates for selective oxygen transfer in oxidation processes.

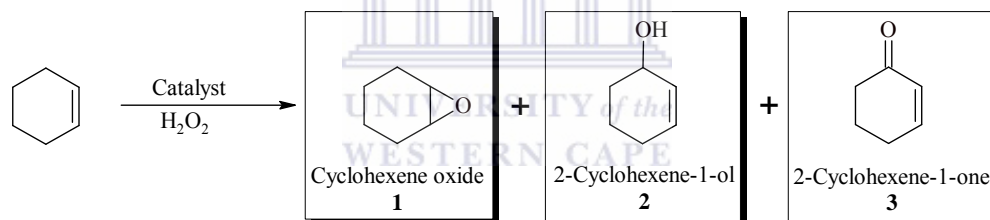
In this chapter the oxidation of cyclohexene using typical mononuclear Co(II) complexes based on *N*-(aryl)salicylaldimines and multinuclear Co(II) complexes based on peripheral functionalised dendritic salicylaldimines is discussed. The efficiency of the dendrimer immobilized catalysts is also compared against typical mononuclear systems.



5.2. RESULTS AND DISCUSSION

The catalytic oxidation of cyclohexene using H_2O_2 as oxidant under an oxygen atmosphere at ambient pressure was investigated using the mononuclear (Fig.5.2) and the multinuclear (Fig 5.8) complexes discussed in Chapter 2 and Chapter 3 as catalyst precursors. Due to the multinuclear nature of the metallodendrimers, the catalytic runs were performed in such a way as to ensure that the metal concentration was the same irrespective of the catalyst used. Initially a preliminary investigation of the mononuclear and dendrimeric cobalt catalysts was performed in acetonitrile, tetrahydrofuran (THF) and neat cyclohexene. This study was conducted under standard conditions which consisted of refluxing cyclohexene (10 mmol), 0.1 mol% Co(II) and 30% (w/w) H_2O_2 (10 mmol) at a temperature of 60°C for 6 hours. However the catalysts only exhibited good activity in THF and in neat cyclohexene and thus

subsequent investigations focused on the performance of the metal complexes in these two reaction media. The standard conditions employed in the preliminary investigation were also utilised to establish a base-line to investigate the effect of reaction parameters such as the oxidant to substrate ratio as well as the metal concentration on the performance of the catalysts as well as the distribution of oxidation products. The consumption of cyclohexene as well as the oxidation products formed in the catalytic runs were analysed and quantified with gas chromatography (GC) using toluene as internal standard. The major products detected under the conditions of analysis for the oxidation process were the oxygenated compounds 2-cyclohexene-1-ol (**2**) and 2-cyclohexene-1-one (**3**) with the epoxide, cyclohexene oxide (**1**) observed as a minor product often in trace quantities (Scheme 5.1).



Scheme 5.1: Oxidation products obtained in the oxidation of cyclohexene.

5.2.1. Catalytic oxidation of cyclohexene using mononuclear catalysts.

The cobalt(II) *N*-(aryl) salicylaldiminato complexes investigated (**9-15**) in the oxidation of cyclohexene showed good activity under the base-line conditions as can be seen from Table 5.1 and Table 5.2 which show the results obtained for reactions performed in neat cyclohexene and THF respectively. Data in these tables also illustrate the effect of changing the cyclohexene to H₂O₂ ratio to 3:1 as well as increasing the Co(II) concentration to 0.2 mol%. The performance of the catalysts under the different

reaction conditions are also graphically represented in Figure 5.3 and Figure 5.4, which show the activity of the catalyst in neat cyclohexene and THF respectively.

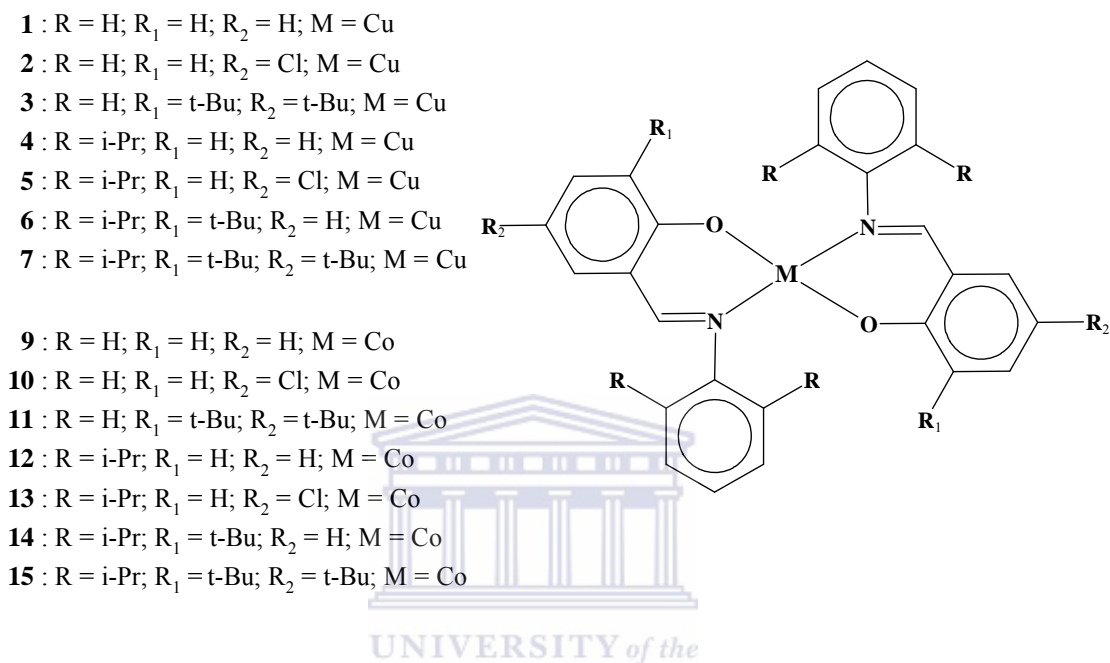


Figure 5.2: Salicylaldiminato metal complexes evaluated in the oxidation of cyclohexene.

5.2.1.1. Catalyst activity.

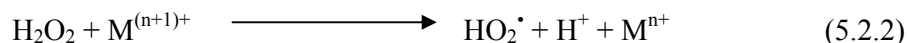
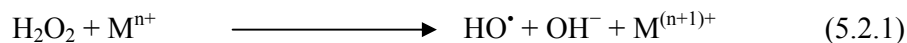
It can clearly be seen that the catalysts performed very differently under the various reaction parameters in the two reaction media investigated (Fig. 5.3 and Fig. 5.4). In the case where the reactions were carried out in neat cyclohexene the catalysts generally performed the best under the base-line conditions with catalyst **10** being the most active resulting in a substrate conversion of 73%. However the activity of the catalyst when a higher metal loading (0.2 mol%) was used, was only slightly lower than activities observed under the base-line conditions. In fact catalyst **11** showed the same activity

when the reaction was performed with 0.1 mol% Co(II) as when performed with 0.2 mol% Co(II). It was also observed that catalyst **15** showed slightly better activity with a loading of 0.2 mol% Co(II). Reactions where the oxidant to substrate ratio was reduced to 1:3 showed a significant drop in activity for all the catalysts.

In the presence of peroxides, transition metal catalysts are known to exhibit Fenton type chemistry which can generally be summarized by the two equations in Scheme 5.2 [13]. In the event that the metal is unable to return to its original oxidation state the decomposition of the peroxide is stoichiometric since a catalytic cycle cannot be formed. The catalytic nature of this process thus depends on returning the metal centre to its original oxidation state as described by Equation 5.2.2. For cobalt catalysts the ability of the metal to switch between the oxidation states $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ is well known and thus the oxidation processes mediated by the cobalt catalysts investigated here are expected to decompose hydrogen peroxide by the equations described in Scheme 5.2.

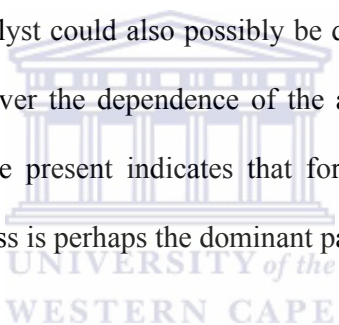
In the cases where the reactions were performed in neat cyclohexene, the observation that such a significant drop in activity when the hydrogen peroxide to substrate ratio was reduced, suggests that the decomposition of hydrogen peroxide is perhaps largely stoichiometric. The slight drop in activity in the case where 0.2 mol% Co(II) was used could be attributed to catalyst deactivation possibly due to dimerization as a result of the higher catalyst loading. The slightly higher activity observed with **15** is most likely due to the fact that deactivation of the catalyst via dimerization does not occur as readily due to steric constraints imposed by the highly substituted ligand systems. The stoichiometric nature of the decomposition reaction thus also explains the significant drop in activity when the amount of oxidant is reduced. This indicates that for the

oxidation reactions investigated in neat cyclohexene that the decomposition of the hydrogen peroxide is an important step in the oxidation process.



Scheme 5.2: Metal catalyzed hydrogen peroxide decomposition.

The oxidation could also be catalyzed by a metal-peroxo species and thus it is possible that the active species in this process are both the radicals produced by hydrogen peroxide decomposition as well as a metal-peroxo complex. In the case of catalyst **15** the higher activity of the catalyst could also possibly be due to the generation of stable metal-peroxo species. However the dependence of the activity of the process on the amount of hydrogen peroxide present indicates that for reactions performed in neat cyclohexene the radical process is perhaps the dominant pathway.



The trend in the performance of catalysts **10**, **12** and **13** when the reactions were studied in THF under the different conditions was essentially the same as that in neat cyclohexene. Catalyst **10** was still amongst the best performing catalysts. However catalyst **13** showed a vast improvement in activity in THF under the base-line conditions as well as under the other conditions investigated. All the other mononuclear catalysts showed deviation from the trend observed in neat cyclohexene. In THF catalyst **15** was observed to be the most active amongst the investigated complexes. The best activity for this catalyst (**15**) was observed with a reduced oxidant to substrate ratio, however the activity observed with the base-line conditions was only slightly lower. In the case of **9** it was found that the complex performed the best with a reduced oxidant to substrate ratio. In addition, for this catalyst, better activity was also observed

with a metal loading of 0.2 mol% than with the lower metal loading of 0.1 mol%. Catalyst **11** exhibited its best activity with a catalyst loading of 0.2 mol% and it was observed that with a oxidant to substrate ratio of 1:3 better activity than with the base-line conditions was obtained. The difference in the performance of the catalyst in THF as compared to neat cyclohexene is possibly due to the better solubility of hydrogen peroxide in the solvent which should allow for easier formation of the metal-peroxo intermediate.

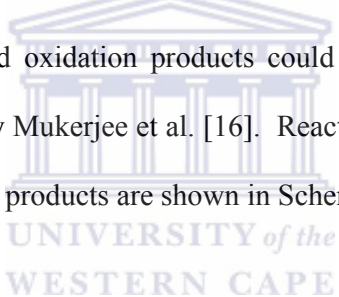
In order to evaluate the effect of the nature of the metal centre on activity and product selectivity copper analogues of the cobalt systems were also investigated. The activities of the copper systems were evaluated by performing the catalytic runs under the same conditions as the base-line reaction used for the cobalt catalysts (10 mmol cyclohexene, 0.1 mol% Cu and 10 mmol 30% H₂O₂ (w/w)) in THF for 6 hours. Results obtained for the catalytic experiments conducted for the mononuclear copper complexes (**1-7**) are shown in Table 5.3.

In general the activity of many of the copper catalysts was observed to be slightly lower than the cobalt analogues. However for catalysts **1**, **4** and **6** slightly better activity was observed than analogous cobalt systems. It is generally expected that the decomposition reaction of hydrogen peroxide with a copper system should be slower since it has a lower redox potential than cobalt. It is known that metals with a higher redox potential switch between oxidation states more easily and thus decomposition of H₂O₂ occurs faster [14]. Thus the observation that comparable activity is observed supports the proposal that in THF oxidation occurs via a metal-peroxo species to a much greater extent than in cyclohexene. Thus the slightly better activity observed with some of the

copper complexes may be due to the fact that the metal-peroxo species formed are slightly more stable than analogous cobalt complexes.

5.2.1.2. *Distribution of oxidation products.*

The oxidation products produced under the different reaction parameters for the reactions performed in bulk was predominantly the allylic oxidation products. Thus the oxidation products formed also indicate that the oxidation proceeds via a radical pathway. The oxidation of cyclohexene via a radical mechanism is well established for peroxide and is expected to occur as depicted by the mechanism shown in Scheme 5.3. However under aerobic conditions this mechanism has also been shown to be operable [15]. Moreover the observed oxidation products could also be formed via a metal-peroxo species as proposed by Mukerjee et al. [16]. Reaction mechanisms which depict the formation of the oxidation products are shown in Schemes 5.4 and 5.5.



In neat cyclohexene the major product formed was the ketone and only catalysts **11** and **14** were observed to form small quantities of epoxide (Fig. 5.5). When the oxidant to substrate ratio was reduced the catalyst still produced the ketone as major product, however higher levels of alcohol were observed and all the catalysts except **15** produced the epoxide. This indicates that under a reduced hydrogen peroxide content oxidation may also proceed via the metal-peroxo species. When the catalyst loading was increased it was once again observed that higher quantities of alcohol was formed and the formation of the epoxide is also observed for catalysts **10**, **12** and **13**.

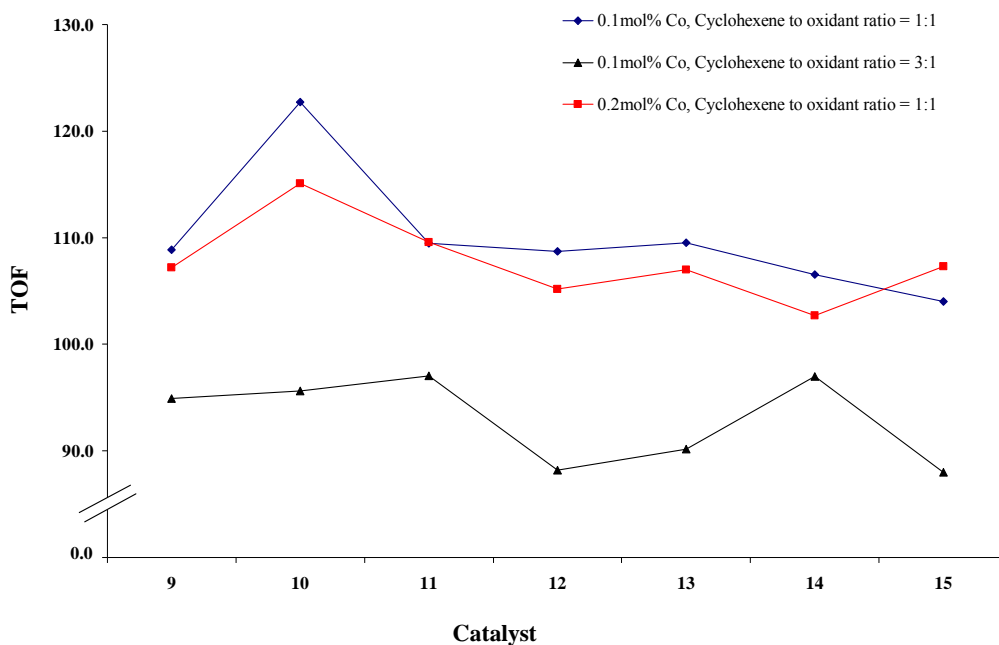


Figure 5.3: The effect of reaction parameters on activity of catalysts 9-15 for reactions performed in neat cyclohexene.

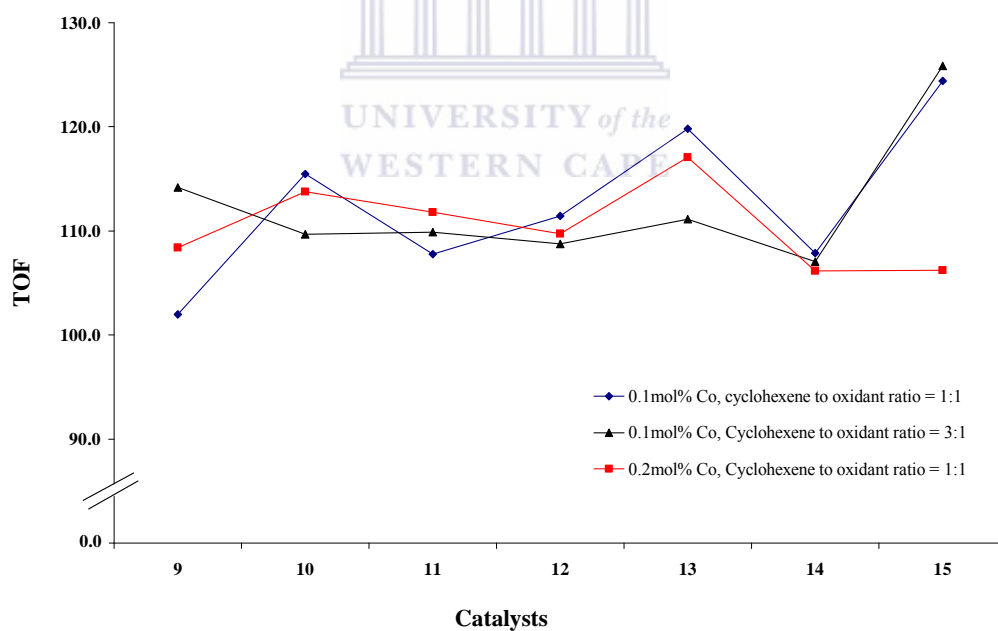


Figure 5.4: The effect of reaction parameters on activity of catalysts 9-15 for reactions performed in THF.

Table 5.1: Evaluation of mononuclear cobalt complexes in neat cyclohexene^a.

Entry	Catalyst	%Conversion	%Selectivity			TOF ^e
			Oxide ^f	Alcohol ^g	Ketone ^h	
1 ^b	9	65.3	0	30	70	108.9
2 ^c		57.0	2	27	71	94.9
3 ^d		64.3	0	31	69	107.2
4 ^b	10	73.6	0	38	62	122.7
5 ^c		57.4	2	30	68	95.6
6 ^d		69.0	1	26	73	115.1
7 ^b	11	65.7	1	27	72	109.5
8 ^c		58.2	4	30	66	97.0
9 ^d		65.7	0	30	70	109.6
10 ^b	12	65.2	0	31	69	108.7
11 ^c		52.9	6	35	59	88.2
12 ^d		63.1	5	39	56	105.2
13 ^b	13	65.7	0	29	71	109.5
14 ^c		54.1	4	33	63	90.1
15 ^d		64.2	2	25	73	107.0
16 ^b	14	63.9	1	24	75	106.5
17 ^c		58.2	4	39	57	97.0
18 ^d		61.6	0	39	61	102.7
19 ^b	15	62.4	0	36	64	104.0
20 ^c		52.8	0	45	55	88.0
21 ^d		64.4	0	48	52	107.3

^a Reactions performed in neat cyclohexene at 60°C for 6 hours under O₂ atmosphere (1atm)

^b 0.1 mol% Co; Cyclohexene:H₂O₂ ratio = 1:1

^c 0.1 mol% Co; Cyclohexene:H₂O₂ ratio = 3:1

^d 0.2 mol% Co; Cyclohexene:H₂O₂ ratio = 1:1

^e TOF = mmol substrate converted per mmol cobalt per hour

^f Cyclohexene oxide; ^g 2-Cyclohexene-1-ol; ^h 2-Cyclohexene-1-one

Table 5.2: Evaluation of mononuclear cobalt complexes using THF as solvent^a.

Entry	Catalyst	%Conversion	Selectivity			TOF
			Oxide ^f	Alcohol ^g	Ketone ^h	
1 ^b		61.2	5	48	47	102.0
2 ^c	9	68.5	5	41	53	114.2
3 ^d		65.0	6	41	54	108.4
4 ^b		69.3	5	33	62	115.5
5 ^c	10	65.8	4	38	58	109.7
6 ^d		68.3	6	40	54	113.8
7 ^b		64.7	5	39	56	107.8
8 ^c	11	65.9	5	44	51	109.9
9 ^d		67.1	6	47	47	111.8
10 ^b		66.9	5	39	57	111.4
11 ^c	12	65.3	4	43	53	108.8
12 ^d		65.8	6	43	51	109.7
13 ^b		71.9	4	34	62	119.8
14 ^c	13	66.7	5	44	52	111.1
15 ^d		70.2	6	41	53	117.1
16 ^b		64.7	5	37	58	107.9
17 ^c	14	64.2	5	52	43	107.1
18 ^d		63.7	0	59	41	106.2
19 ^b		74.6	6	44	50	124.4
20 ^c	15	75.5	5	52	44	125.8
21 ^d		63.7	5	53	42	106.2

^a Reactions performed using 2 mL THF as solvent at 60°C for 6 hours under O₂ atmosphere (1atm)

^b 0.1 mol% Co; Cyclohexene:H₂O₂ ratio = 1:1

^c 0.1 mol% Co; Cyclohexene:H₂O₂ ratio = 3:1

^d 0.2 mol% Co; Cyclohexene:H₂O₂ ratio = 1:1

^e TOF = mmol substrate converted per mmol cobalt per hour

^f Cyclohexene oxide; ^g 2-Cyclohexene-1-ol; ^h 2-Cyclohexene-1-one

Table 5.3: Evaluation of copper(II) mononuclear and metallodendritic catalysts in the oxidation of cyclohexene^a.

Catalyst	%Conversion	%Selectivity			TOF ^b
		Oxide ^c	Alcohol ^d	Ketone ^e	
1	62.2	6	53	41	103.6
2	62.3	5	51	44	103.8
3	62.0	0	56	44	103.3
4	68.4	5	46	49	114.0
5	62.2	0	52	48	103.7
6	67.2	5	50	45	112.1
7	62.2	0	54	46	103.6
16	61.5	8	57	35	102.5
17	70.6	12	50	37	117.6
20	61.1	9	55	36	101.8
21	63.9	8	51	42	106.5

^a Reactions performed using 2 mL THF as solvent at 60°C for 6 hours under O₂ atmosphere (1atm) with 0.1 mol% Cu and a cyclohexene:H₂O₂ ratio = 1:1

^b TOF = mmol substrate converted per mmol cobalt per hour

^c Cyclohexene oxide; ^d 2-Cyclohexene-1-ol; ^e 2-Cyclohexene-1-one

The distribution of oxidation products supports the proposal that the oxidation process occurs via two different mechanisms simultaneously. In the case of a radical pathway the oxidation products are expected to be primarily ketone and alcohol, whereas for the process via the metal-peroxo species all three oxidation products shown in Scheme 5.2 could be expected.

The oxidation products obtained for the reactions performed in THF were also mostly the allylic oxidation products. However a very different picture is observed when comparing the product distribution under the different reaction conditions to the distribution of oxidation products observed for reactions performed in neat cyclohexene. Under the base-line conditions, as for the neat reactions, the ketone is still observed to

be the major oxidation product. However higher levels of alcohol are observed and all the catalyst are also observed to produce the epoxide. The amount of epoxide produced by the catalysts was observed to be fairly similar. The observed product distribution supports the suggestion that when the reactions are performed in THF the oxidation perhaps proceeds via the metal-peroxo species to a greater extent. The investigation conducted by Mukerjee et al. [16] showed that when the reactions were performed with hydrogen peroxide the ketone was also formed in higher levels than the alcohol due to further oxidation of the alcohol. Thus for the reactions performed in THF it is possible that further oxidation does not occur as readily as when the reactions were performed neat, thus leading to higher levels of alcohol being observed.

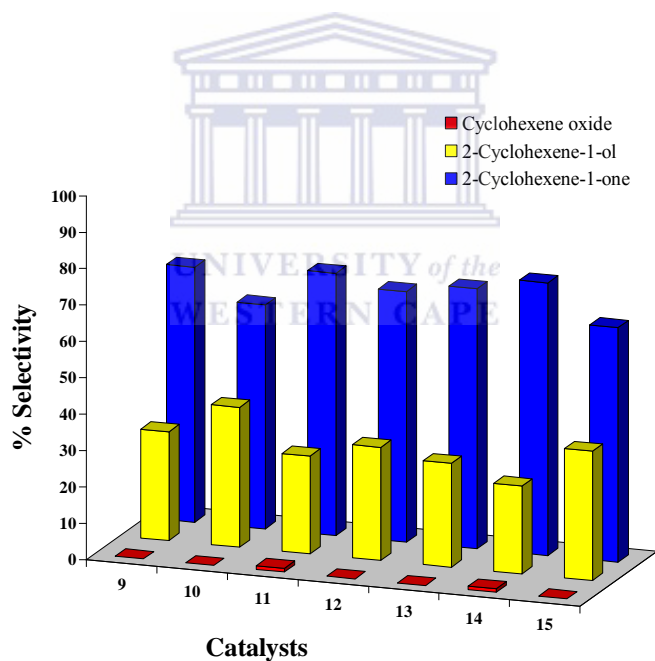


Figure 5.5: Product distributions for mononuclear Co(II) catalysts for reactions performed with 0.1 mol% Co and a 1:1 cyclohexene to H₂O₂ ratio in neat cyclohexene.

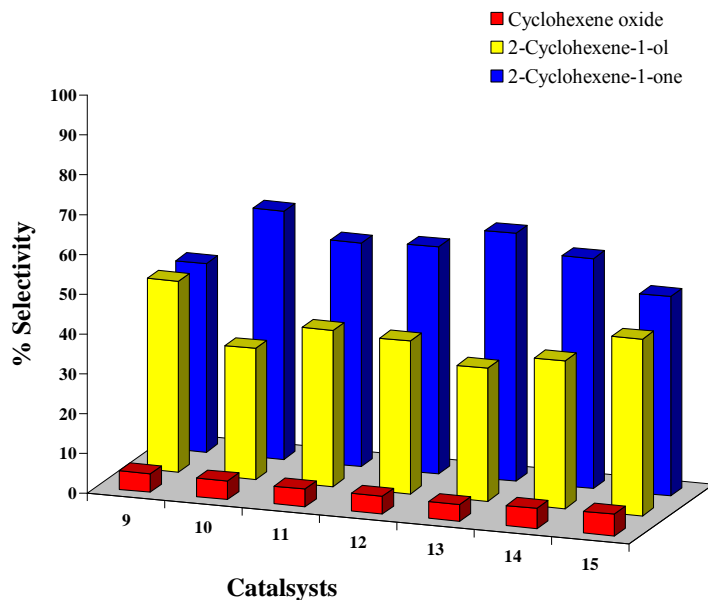


Figure 5.6: Product distributions for mononuclear Co(II) catalysts for reactions performed with 0.1 mol% Co and a cyclohexene to H₂O₂ ratio of 1:1 using THF as solvent.

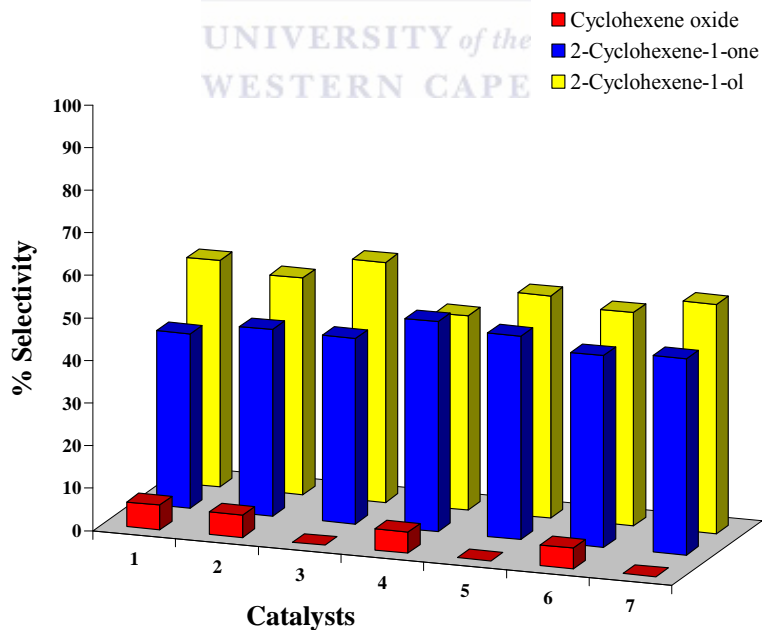
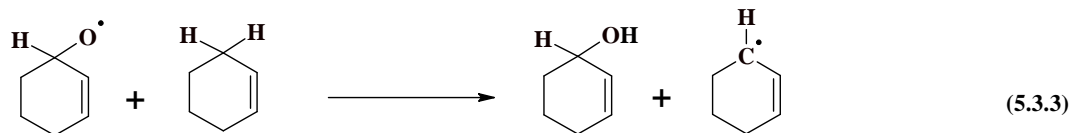
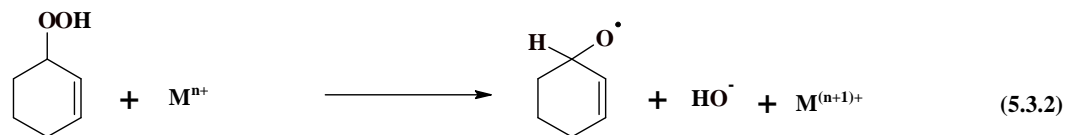
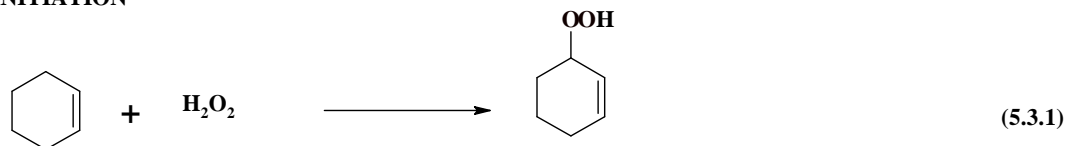
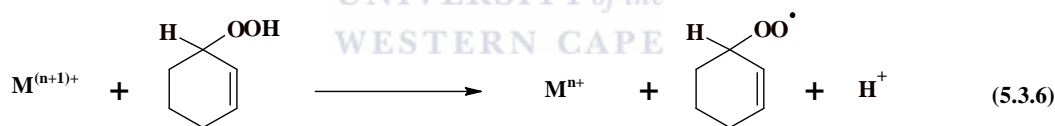
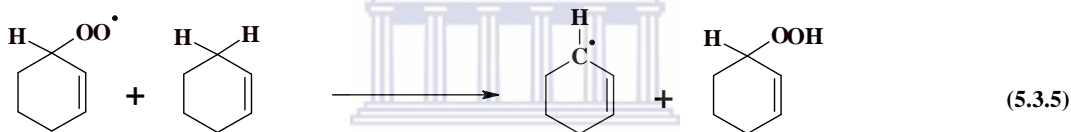
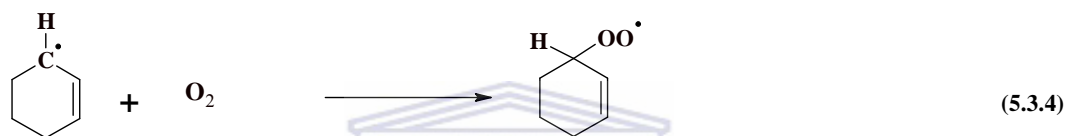


Figure 5.7: Product distributions for mononuclear Cu(II) catalysts for reactions performed with 0.1 mol% Cu and a 1:1 cyclohexene to H₂O₂ ratio using THF as solvent.

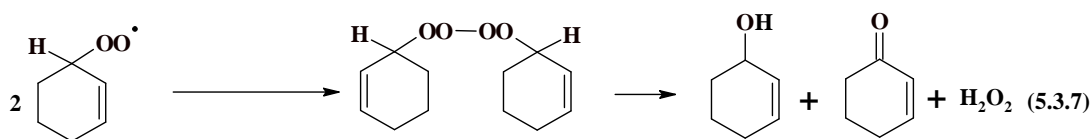
INITIATION



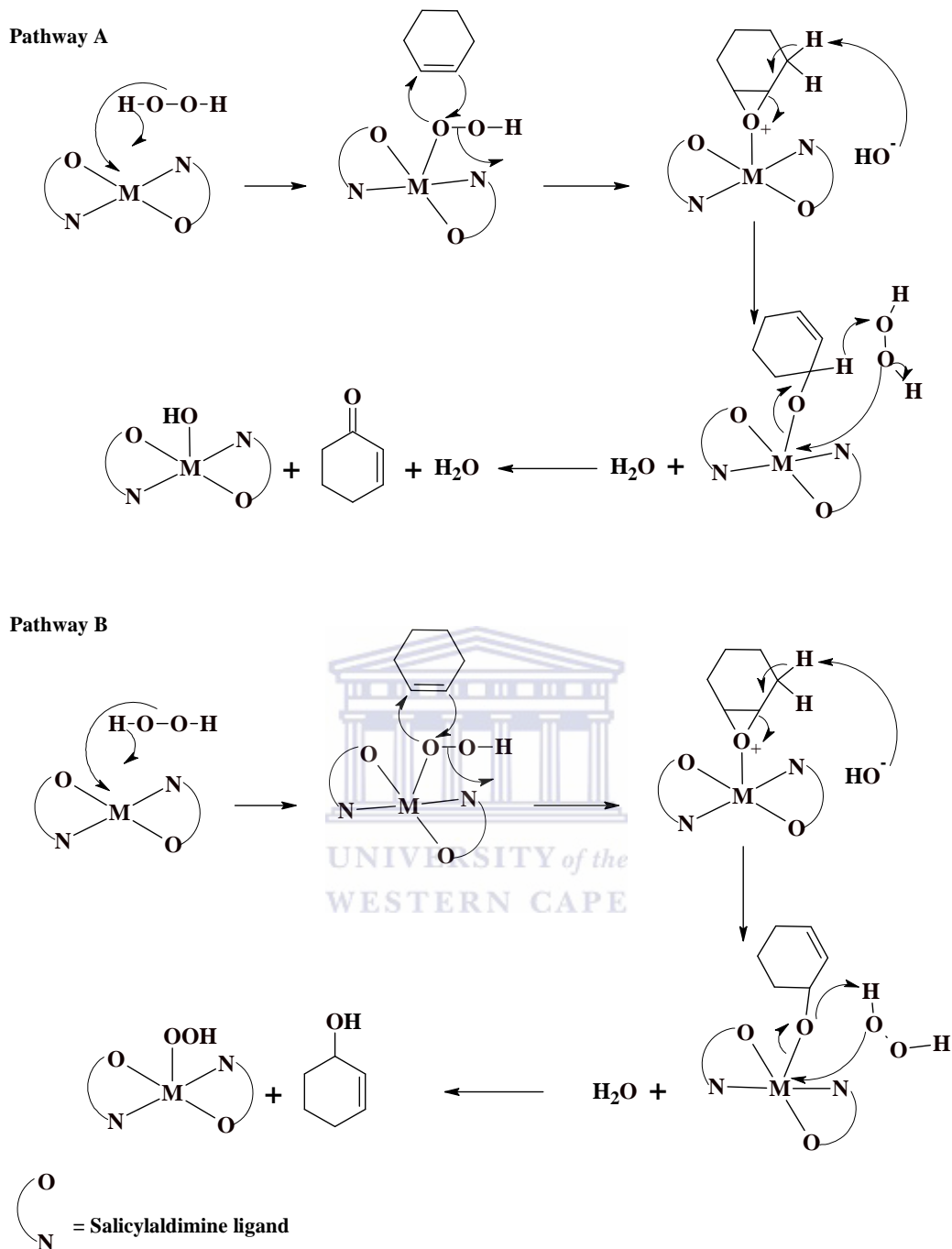
PROPAGATION



TERMINATION

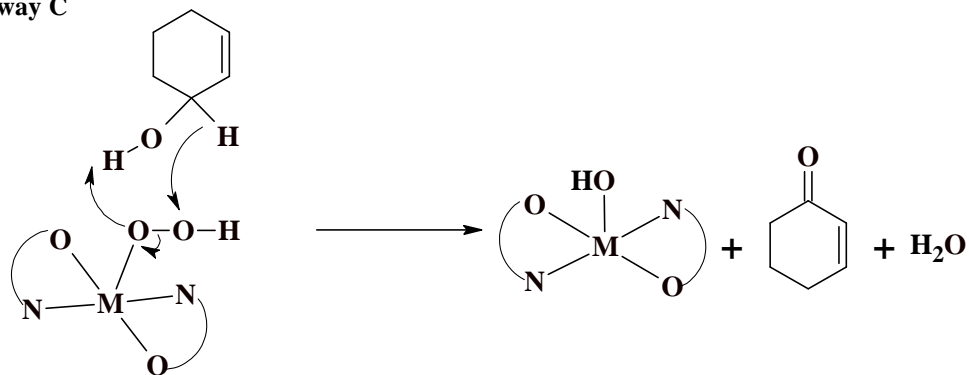


Scheme 5.3: Free radical mechanism for the oxidation of cyclohexene [15].

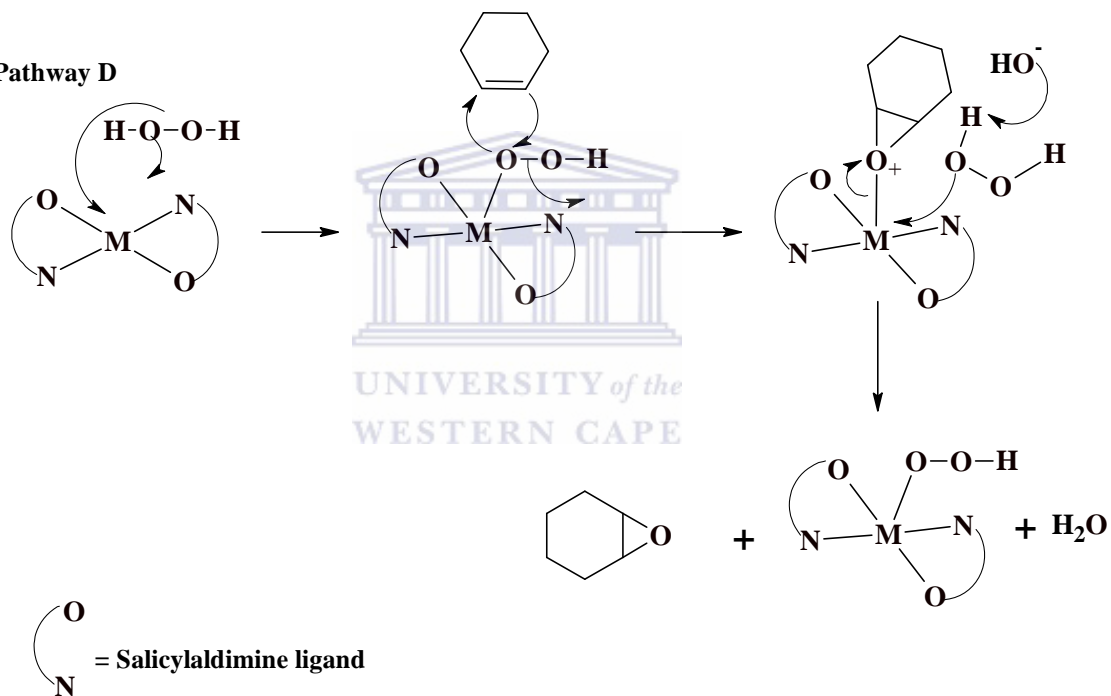


Scheme 5.4: Possible reaction mechanism for the allylic oxidation of cyclohexene which shows the formation of 2-cyclohexene-1-one (Pathway A) and 2-cyclohexene-1-ol (Pathway B) [16].

Pathway C



Pathway D



Scheme 5.5: Possible reaction mechanism which depicts the further oxidation of 2-cyclohexene-1-ol to 2-cyclohexene-1-one (Pathway C) and the formation of the epoxide via a metal-peroxo species [16].

In the case where the hydrogen peroxide to substrate ratio was reduced for the reactions performed in THF it was observed that the levels of alcohol formed were higher than for the reactions performed under the base-line conditions. Both catalysts **14** and **15** showed higher levels of alcohol than ketone. When the metal loading was increased the amount of alcohol formed was once again observed to be slightly higher than for the base-line reactions and catalysts **14** and **15** were found to produce higher quantities of alcohol than ketone. Thus as for the neat reactions an increase in the amount of alcohol with changing the oxidant content and metal loading is also observed. However the majority of the catalysts showed roughly the same levels of epoxide. The exception was catalyst **14** which did not show any epoxide formation with a higher metal loading (entry 18, Table 5.2).

The reaction performed with the copper analogues of the cobalt systems also produced predominantly the allylic oxidation products. However it was observed that the copper catalysts showed better selectivity to the alcohol oxidation product with the ketone being formed to a lesser extent. Several of the catalysts viz. **1**, **2**, **4** and **6** were also observed to produce the epoxide. All three catalysts (**1**, **4** and **6**) which showed slightly better activity than their cobalt counter-parts are amongst the systems producing the epoxide. The distribution of the oxidation products supports the proposal that the oxidation occurs via the metal-peroxo species to a greater extent than the radical pathway. The different product distribution observed is most likely due to the fact that oxidation of the alcohol to the ketone occurs at a much slower rate than with cobalt.

5.2.2. *Catalytic oxidation of cyclohexene using multinuclear catalysts.*

The Co(II) metallodendrimers were investigated using similar conditions to those utilised in the study conducted with mononuclear Co(II) complexes. As was the case for the mononuclear systems, the metallodendrimers were evaluated using various reaction conditions as well as in different solvents. The solvents investigated were acetonitrile, THF and cyclohexene. The performance of the multinuclear catalysts was observed to be similar to the mononuclear systems. In acetonitrile the catalysts were observed to be completely inactive and while good activity was observed in neat cyclohexene and THF. Thus variation in reaction parameters were also investigated in these two solvents for the metallodendrimers. Results obtained for catalysts **18**, **19**, **22** and **23** which were obtained in cyclohexene and THF are shown in Tables 5.3 and 5.4 respectively.

5.2.2.1. *Catalyst activity.*

The activity of the catalysts under the various reaction conditions in neat cyclohexene is graphically represented in Figure 5.9. In the case of catalysts **18** and **22** the optimum activity is observed under the base-line conditions. A decrease in activity is observed when the metal loading is increased to 0.2 mol%. The reverse is observed for catalysts **19** and **23**. For both these catalysts the best activity was observed with a metal loading of 0.2 mol%.

As for the mononuclear catalysts it was found that the cobalt metallodendrimers also show a significant drop in activity with a reduced hydrogen peroxide content. Therefore in the case of the metallodendrimers the activity of the catalysts also appears to be linked to the amount of hydrogen peroxide present. Thus once again it would appear that the decomposition of hydrogen peroxide is largely stoichiometric when the reactions were performed in neat cyclohexene. The mechanism of oxidation thus also

possibly proceeds primarily via a radical mechanism. Investigations conducted by Yang et al. [18] showed Mn PAMAM metallodendrimers to be active for the oxidation of cyclohexene in the neat reaction medium using molecular oxygen as oxidant. Thus it is possible that oxygen also plays a role in the oxidation process for the catalysts investigated in this thesis.

Table 5.4: Evaluation of dendritic cobalt complexes in neat cyclohexene^a.

Entry	Catalyst	%Conversion	Selectivity			TOF
			Oxide ^f	Alcohol ^g	Ketone ^h	
1 ^b	18	64.5	0	25	75	107.5
2 ^c		53.6	3	19	77	89.3
3 ^d		59.9	0	26	74	99.9
4 ^b	19	61.9	0	31	69	103.1
5 ^c		56.6	7	32	61	94.4
6 ^d		64.1	10	30	60	106.9
7 ^b	22	69.1	0	25	75	115.2
8 ^c		52.4	0	20	80	87.3
9 ^d		62.2	19	17	64	103.6
10 ^b	23	60.3	0	28	72	100.5
11 ^c		50.5	4	23	73	84.2
12 ^d		64.7	3	21	75	107.8

^a Reactions performed in neat cyclohexene at 60°C for 6 hours under O₂ atmosphere (1atm)

^b 0.1 mol% Co; Cyclohexene:H₂O₂ ratio = 1:1

^c 0.1 mol% Co; Cyclohexene:H₂O₂ ratio = 3:1

^d 0.2 mol% Co; Cyclohexene:H₂O₂ ratio = 1:1

^e TOF = mmol substrate converted per mmol cobalt per hour

^f Cyclohexene oxide; ^g 2-Cyclohexene-1-ol; ^h 2-Cyclohexene-1-one

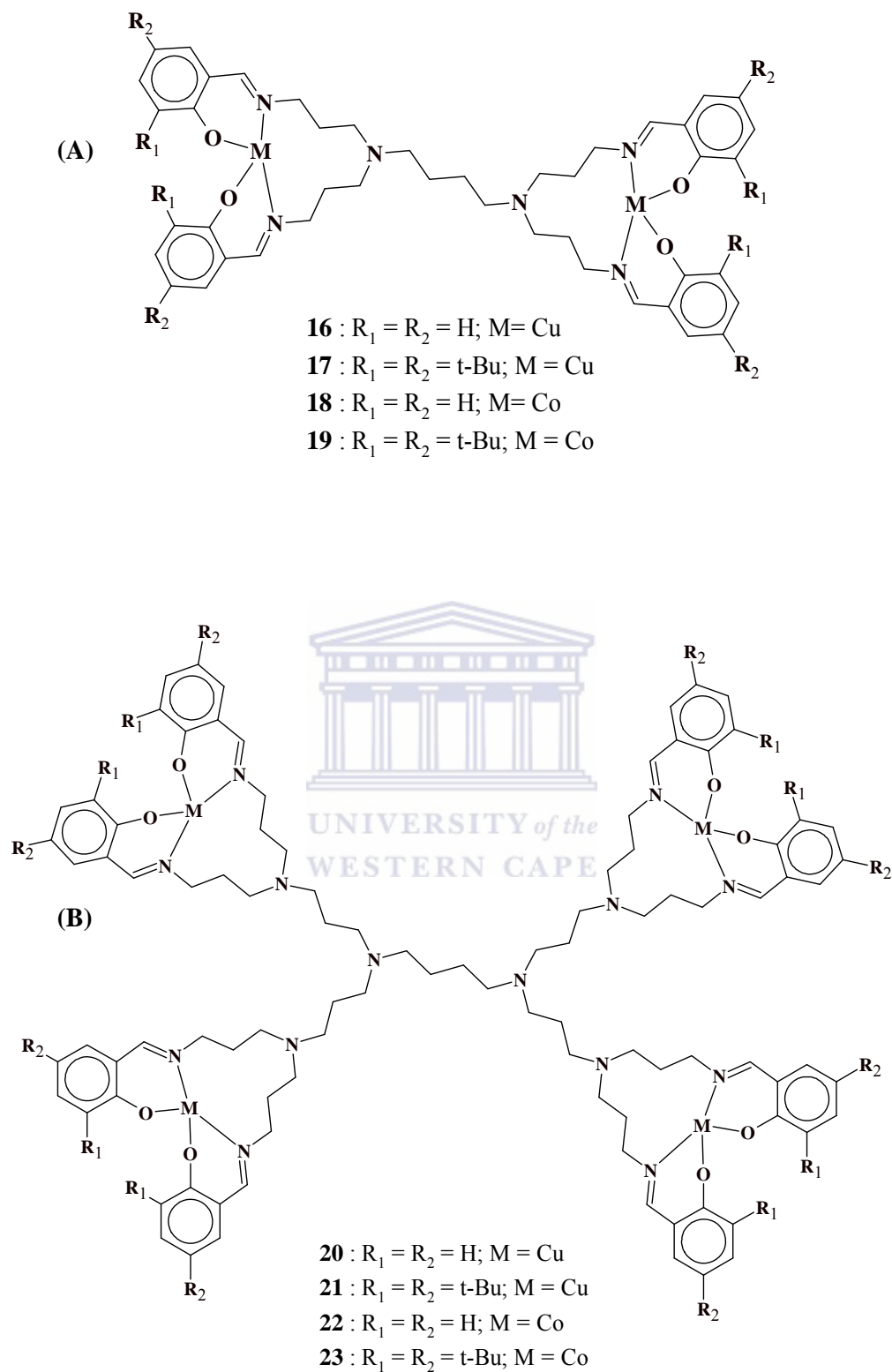


Figure 5.8: First (A) and second (B) generation metallodendrimers evaluated in the oxidation of cyclohexene.

When the reactions were performed in THF the trend in activity of the catalysts were observed to be completely different (Fig 5.12) to the trend observed in neat cyclohexene. It was also found that the catalysts performed much better in THF than in neat cyclohexene. This fact was exemplified by the observation that a conversion of 77% was obtained with catalyst **19** under the base-line conditions. Both G2 catalysts **22** and **23** also exhibit optimum activity under the base-line conditions in THF. Catalyst **18** on the other hand performed the worst of the dendritic catalysts investigated under all the conditions.

Table 5.5: Evaluation of dendritic cobalt complexes using THF as solvent^a.

Entry	Catalyst	%Conversion	Selectivity			TOF
			Oxide ^f	Alcohol ^g	Ketone ^h	
1 ^b		64.1	8	40	52	106.8
2 ^c	18	65.2	4	49	47	108.7
3 ^d		67.7	8	43	49	112.9
4 ^b		77.8	0	29	71	129.6
5 ^c	19	72.4	5	39	57	120.7
6 ^d		68.8	5	37	58	114.6
7 ^b		76.0	4	32	64	126.7
8 ^c	22	70.4	4	47	49	117.3
9 ^d		69.6	4	50	46	116.0
10 ^b		71.8	5	35	60	119.6
11 ^c	23	68.3	4	38	58	113.8
12 ^d		63.0	5	40	55	105.0

^a Reactions performed using 2 mL THF as solvent at 60°C for 6 hours under O₂ atmosphere (1atm)

^b 0.1 mol% Co; Cyclohexene:H₂O₂ ratio = 1:1

^c 0.1 mol% Co; Cyclohexene:H₂O₂ ratio = 3:1

^d 0.2 mol% Co; Cyclohexene:H₂O₂ ratio = 1:1

^e TOF = mmol substrate converted per mmol cobalt per hour

^f Cyclohexene oxide; ^g 2-Cyclohexene-1-ol; ^h 2-Cyclohexene-1-one

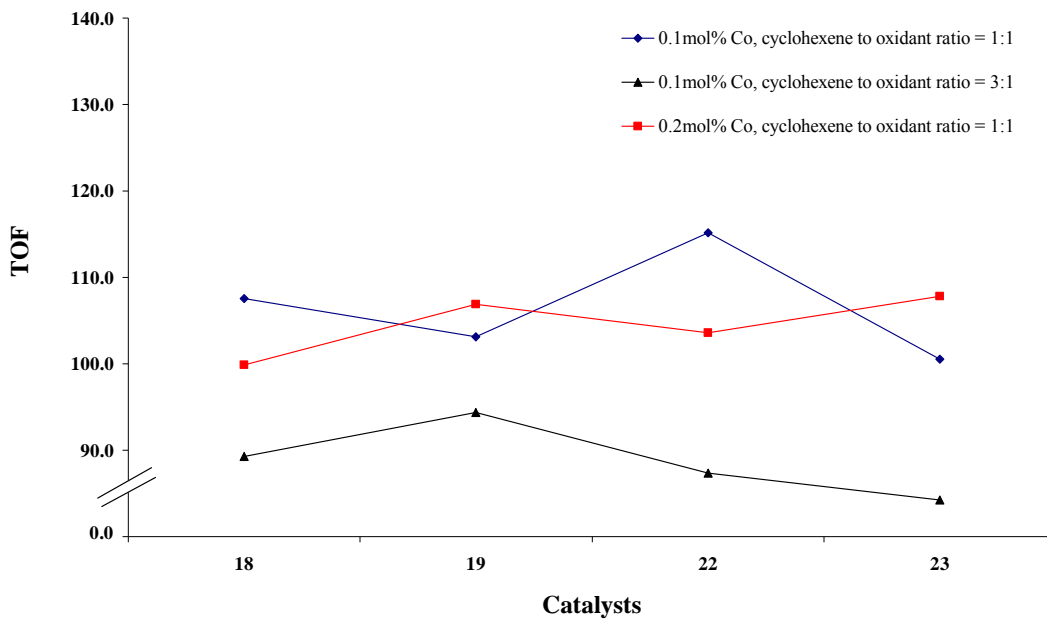


Figure 5.9: The effect of reaction parameters on activity of dendritic catalysts for reactions performed in neat cyclohexene.

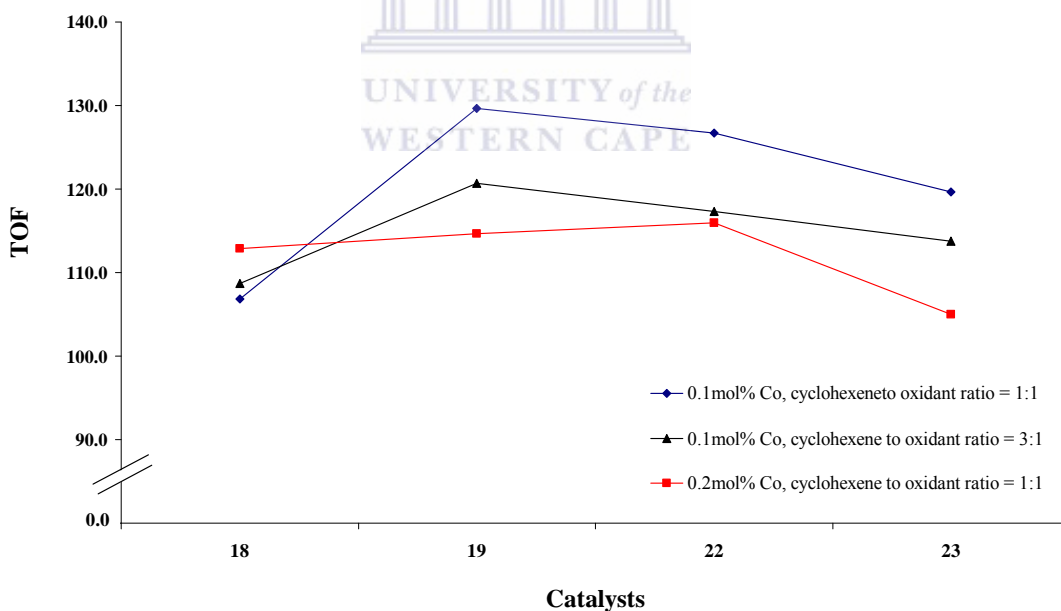


Figure 5.10: The effect of reaction parameters on activity of dendritic catalysts for reactions performed in THF.

In the case where the oxidant to substrate ratio was reduced the activities of the catalysts were lower than those observed under the base-line conditions, however virtually the same trend in activity was observed with catalyst **19** still performing the best. It was found that many of the catalysts showed the lowest activity when the metal loading was increased to 0.2 mol%. In addition it was observed that there is a distinct change in the trend in the activity of the catalysts for reactions performed in THF as compared to those carried out in neat cyclohexene. Under the conditions of higher metal loading **22** showed the best activity, while **18** and **19** showed slightly lower activities. Catalysts **23** showed quite a dramatic drop in activity in comparison to its performance under other reaction conditions as compared with the other dendritic systems investigated. The fact that **19**, **22** and **23** showed lower activity with a metal loading of 0.2 mol% is possibly due to the increased solubility of the complexes in THF and thus deactivation in solution plays a much more significant role as compared to when the reactions were performed in neat cyclohexene, where the solubility of the complexes were relatively poor in comparison.

In order to investigate the influence of the metal centre on the activity of the catalyst, copper analogues were also investigated under the base-line conditions in THF. Results obtained for these complexes are shown in Table 5.3. As for the mononuclear copper catalysts it was found that the copper metallodendrimers were also slightly less active than their cobalt counter-parts. The best activity was observed with catalyst **17**, the copper analogue of cobalt catalyst **19**, which exhibited the best performance under similar conditions amongst the metallodendrimers investigated. The activity of G1 and G2 catalysts **16** and **20** were roughly the same, while catalyst **21** performed slightly better than these two catalysts. Thus in the case of the metallodendrimers it also

appears that the reaction possibly proceeds via the metal-peroxo species since only a slight drop in activity to their cobalt counter part was observed. As mentioned previously, copper has a lower redox potential than cobalt and thus the copper catalysts are expected to decompose H_2O_2 slower since it is known that metals with higher redox potentials switch between oxidation states more easily and thus decompose H_2O_2 faster.

5.2.2.2. Distribution of oxidation products.

As was the case for the mononuclear catalysts the major product using the dendritic catalysts were observed to be the ketone and alcohol, although in some instances the epoxide is also observed. The distribution of the oxidation products observed for the base-line reactions are shown in Figure 5.11 and Figure 5.12 for reactions performed in cyclohexene and THF respectively. In the case of the neat reactions only ketone and alcohol were observed with none of the catalysts producing the epoxide under the base-line conditions. Thus the product distribution supports the idea that the oxidation proceeds largely via a radical pathway.

However for reactions performed in bulk when the oxidant to substrate ratio was reduced to 1:3 all the catalysts except **22** produced the epoxide which suggests that with a low oxidant content the oxidation possibly proceed via pathway C as shown in Scheme 5.5 to a greater extent. In the case where the catalytic reactions were performed with a higher metal loading all the catalysts except **18** produced the epoxide. For catalyst **22** the amount of epoxide produced was observed to be slightly higher than the amount of alcohol produced (entry 9, Table 5.3). Thus the distribution of oxidation products obtained for reactions performed in neat cyclohexene with a metal loading of

0.2 mol% also suggests that pathway C (Scheme 5.5) occurs to a greater extent under these experimental conditions.

The product distribution for the reactions performed in THF also showed the ketone to be the major product under the base-line conditions, however catalysts **18**, **22** and **23** also formed the epoxide. However when the oxidant ratio was reduced and the metal loading was increased the levels of alcohol formed were observed to increase for all the catalysts. This may possibly be due to fact that further oxidation of the alcohol to the ketone may not occur as readily under these conditions. The copper metallodendrimers produced the alcohol oxidation product in slightly higher quantities than the ketone. This was also the case for the mononuclear copper catalysts. The copper metallodendrimers were also observed to produce the epoxide in levels slightly higher than what was observed for the mononuclear systems.

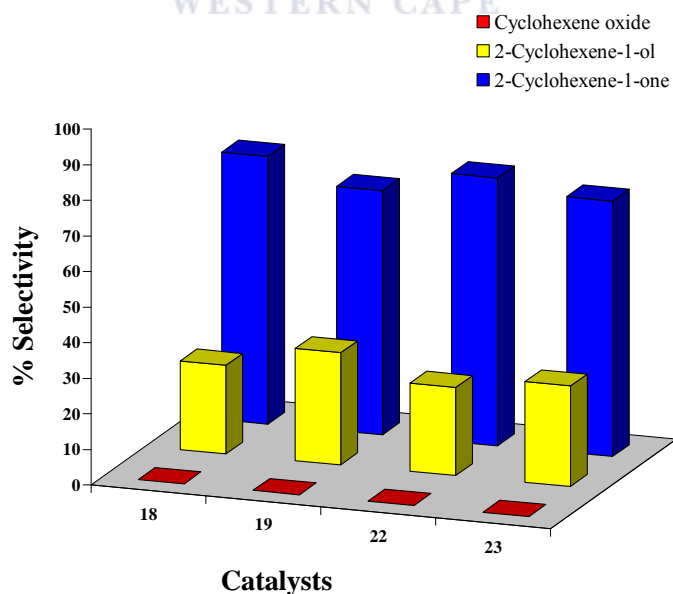


Figure 5.11: Product distributions for Co(II) metallodendritic catalysts for reactions performed with 0.1mol% Co and a 1:1 cyclohexene to H₂O₂ ratio in neat cyclohexene.

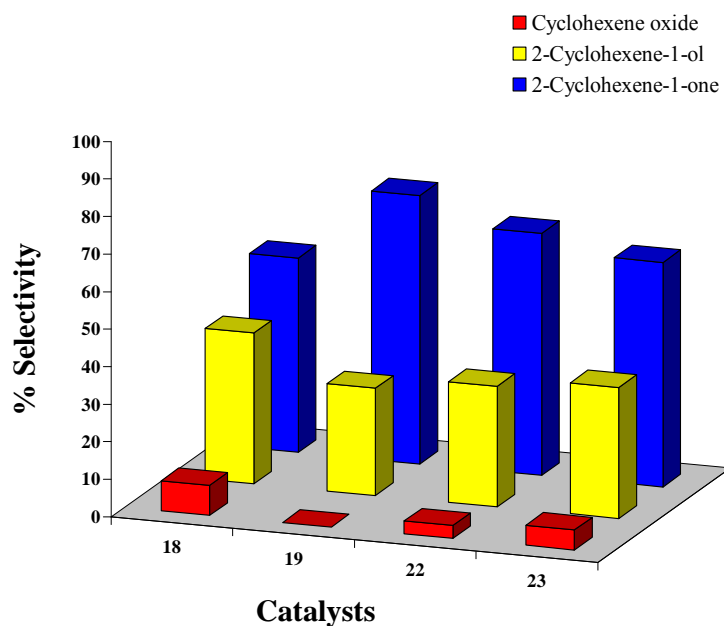


Figure 5.12: Product distributions for Co(II) metallodendritic catalysts for reaction performed with 0.1 mol% Co and a 1:1 cyclohexene to H₂O₂ ratio using THF as solvent.

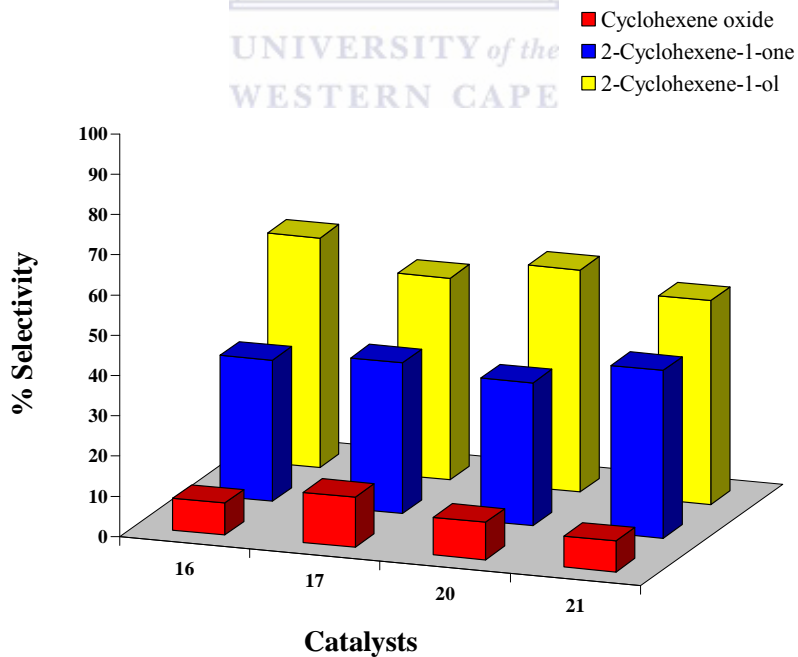


Figure 5.13: Product distributions for Cu(II) metallodendritic catalysts for reactions performed with 0.1 mol% Cu and a 1:1 cyclohexene to H₂O₂ ratio using THF as solvent.

5.2.3. *The effect of solvent on catalyst activity and selectivity.*

The activity of the mononuclear and dendrimeric metal complexes was observed to be significantly different in the reaction media investigated. The inactivity of the metal complexes in acetonitrile could possibly be due to coordination of the solvent to the metal centre which thus prevents the formation of the active oxidation species. It has also been shown by Niasari et al. [19] that the solvent has a profound effect on the activity of salen based catalysts in cyclohexene oxidations. It was shown that the efficiency of the catalysts in the different reaction media decreased in the order cyclohexene > dichloromethane > chloroform > methanol > acetonitrile. A similar observation was made by Kanmani et al. [20] for the epoxidation of cyclohexene, however the study conducted showed benzene to be the best solvent and tetrahydrofuran the worst. The different behaviour of the catalysts in the different reaction media could possibly also be due to the fact that hydrogen peroxide is more soluble in THF and thus the interaction with the metal centre occurs to a greater extent. Alternatively the stability of the metal-peroxo intermediate could be different in the two reaction media. This could lead to a difference in activity of the catalysts and could also account for the difference in the distribution of oxidation products.

5.2.4. *The effect of the nature of the metal on catalyst activity and selectivity.*

In general it was observed that majority of the cobalt catalysts performed better than their copper counter-parts. However catalysts **1**, **4** and **6** show slightly higher activity than analogous cobalt complexes investigated under similar conditions. Research conducted by the group of Salavati-Niasari also indicated that the nature of the metal centre is a factor in developing highly activity catalysts in their investigation of

bis(salicylaldiminato) hydrazone metal complexes in the oxidation of cyclohexene with *tert*-butyl hydroperoxide [19]. A decrease in catalyst activity was observed in the order Mn>Co>Cu>Ni indicating copper(II) analogues also showed lower activity than cobalt systems. A similar trend was also observed by Karandikar et al. in a study which investigated the activity of Cu and Co catalysts in the oxidation of olefins with *tert*-butyl hydroperoxide [21].

The nature of the metal also appears to have an effect on the type of oxidation products formed. Both mononuclear and multinuclear copper systems show the preferential formation of the alcohol oxidation product as can be seen from Figure 5.7 and Figure 5.13. Studies conducted by Mukerjee et al. with copper systems also showed higher selectivity to the alcohol when hydrogen peroxide was used as oxidant [16]. It was also observed that the alcohol was subsequently converted to the ketone as the reaction progressed. However when *tert*-butyl peroxide was used the ketone was observed to be the preferred product. It thus possible that the oxidation of the alcohol to the ketone occurs to a lesser extent in the case of the copper catalysts or alternatively the rate of oxidation of the alcohol to the ketone might be slower.

5.2.5. *The effect of the catalyst immobilization on catalyst activity and selectivity.*

Several investigations have shown that improved catalysts activity is often observed when comparing immobilized catalysts with their homogeneous counter-parts. This improved performance is widely attributed to site-isolation of the coordination systems thus minimizing certain deactivation pathways of the catalysts.

In general only a slight difference in activity was observed in the activities of the mononuclear catalysts and dendritic immobilized systems. In addition it was found that the two different classes of coordination systems exhibit similar trends in activity when the reactions were performed in cyclohexene. Both mononuclear and multinuclear catalysts showed a significant drop in activity with a low oxidant to substrate ratio, while only a slight difference in activity was observed when the metal loading was increased from 0.1 mol% to 0.2 mol%. However when the reactions were performed in THF the trend in activity observed for the mononuclear catalysts appeared to be different to that observed for the metallodendrimer catalysts. It was also observed that the mononuclear systems showed slightly better activity than the dendritic systems when the reactions were performed in cyclohexene.

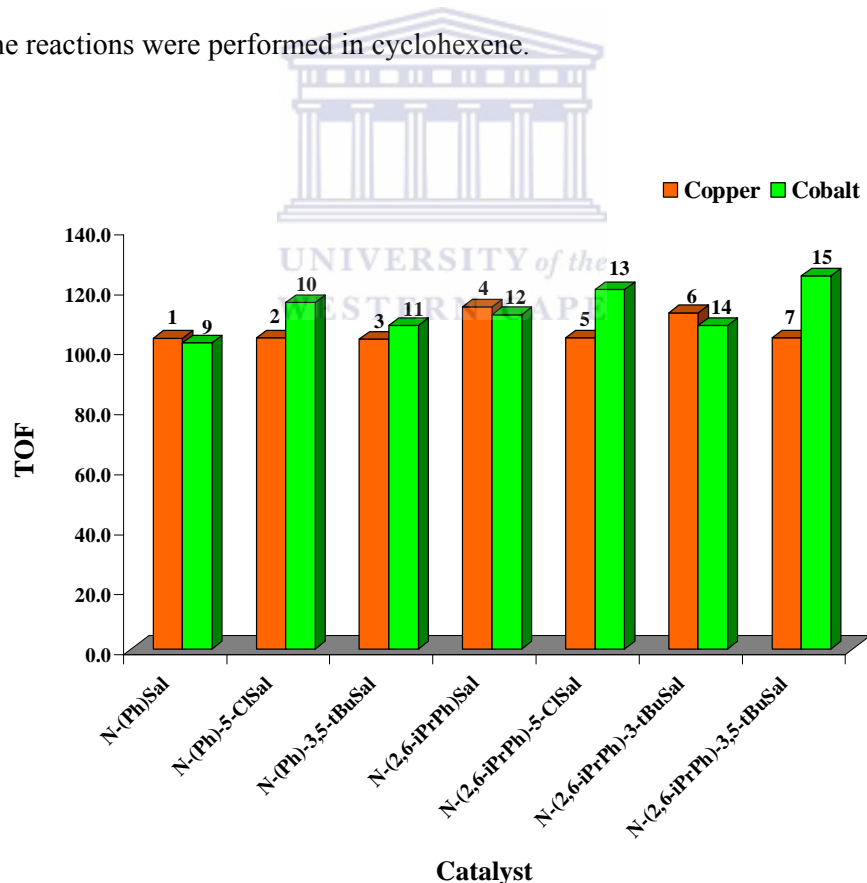


Figure 5.14: Comparison of the activity of mononuclear Cu(II) and Co(II) complexes.

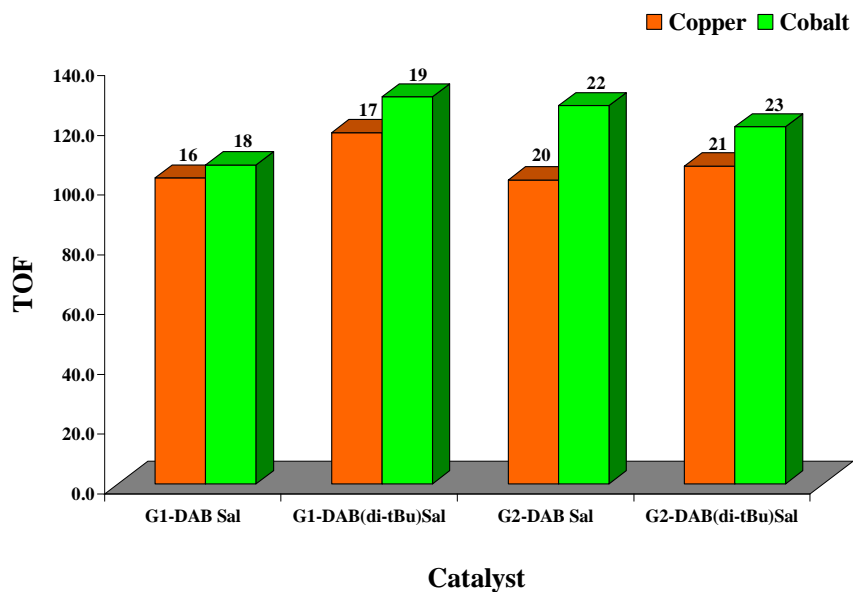


Figure 5.15: Comparison of the activity of dendritic Cu(II) and Co(II) complexes.

However the dendritic catalysts on the other hand showed better activity than the mononuclear catalysts when the reactions were performed in THF. This indicates that the influence of the solvent is slightly different for the two classes of catalysts. The superior performance of the dendritic catalysts in THF may allude to the fact the dendritic ligands are able to stabilise the active intermediate to a greater extent than the monofunctional ligands.

A difference in the activity of the two generations of dendrimeric catalysts was also observed. In the case of the unsubstituted G2 metallodendrimers catalysts, **22** exhibited slightly better activity than **18** in both solvents investigated. The exception was observed with a low oxidant to substrate ratio when the reactions were performed in neat cyclohexene. Catalyst **18** shows a slightly higher activity than **22**. The difference in the performance of the two generations may indicate a slight positive dendritic effect for the unsubstituted catalysts with increase in generation. The superior activity of **22** is

possibly due to greater distribution of active sites. However in the case of the *tert*-butyl substituted complexes G1 catalyst **19** showed slightly better activity than G2 system **23** in the two solvents under various reaction conditions. The only instance where comparable activity was observed for **19** and **23** was with a 0.2 mol% metal loading in neat cyclohexene. In this case there appears to be a slight negative effect on activity which might be due to steric interactions in the case of **23**, since the coordination spheres are closer together than in the G1 system and thus the *tert*-butyl groups might prevent the substrate from accessing the metal sites during the oxidation process.

5.3. CONCLUSIONS

It was found that for catalytic experiment performed in acetonitrile the catalysts were completely inactive in this solvent. However all the metal complexes investigated were found to show good activity when the oxidation reactions were performed in neat cyclohexene or in THF. Comparable activity of the catalysts was observed in the reaction media investigated and it was found that the solvent as well as the reaction conditions have an impact on the activity and product selectivity. The major oxidation product formed for all catalysts was 2-cyclohexene-1-one. However it was found that an increase in the formation of the alcohol was observed when the metal loading was increased as well as when the oxidant to substrate ratio was reduced.

5.4. EXPERIMENTAL

5.4.1. Materials and instrumentation

Cyclohexene, 2-cyclohexene-1-ol, 2-cyclohexene-1-one were purchased from Sigma-Aldrich Ltd. Cyclohexene oxide was purchased from Fluka. Acetonitrile was purchased

from BDH chemicals Ltd and toluene and 30 % H₂O₂ (w/w) were purchased from Merck Chemicals Ltd. Oxidation reactions were performed on a 12 place RADLEY's Heated Carousel Reaction Station fitted with a reflux unit as well as a gas distribution system with glass reaction vessels. GC analyses were performed on a Varian CP-3800 with a HP PONA column. Oxidation products were identified using authentic samples. Conversion and product yields were determined using toluene as internal standard.

5.4.2. *Catalytic cyclohexene oxidation*

A 12 place RADLEY's Heated Carousel Reaction Station fitted with a reflux unit as well as a gas distribution system was used to perform the oxidation reactions. In a typical reaction, cyclohexene (10 mmol) and the appropriate catalysts (0.1 mol % M) were placed in a 50 mL glass reaction vessel followed by solvent (2 ml). This reaction mixture was brought to a temperature of 60°C under an oxygen atmosphere (1atm). The reaction mixture was stirred under these conditions for approximately 5 minutes after which the reaction was initiated by adding 30% (w/w) H₂O₂ (10 mmol). The resulting reaction mixture was stirred for a period of 6 hour at 60°C under an oxygen atmosphere (1atm). After this time 1 ml of the reaction mixture was withdrawn which was analysed with gas chromatography using toluene (0.2 ml) as internal standard.

5.5. REFERENCES

1. P. T. Anastas, M. M. Kirchhoff, T. C. Williamson, *Appl. Catal. A: Gen.* **2001**, 221, 3
2. Z. P. Pai, A. G. Tolstikov, P. V. Berdnikova, G. N. Kustova, T. B. Khlebnikova, N. V. Selivanova, A. B. Shangina, V. G. Kostrovskii, *Russ. Chem. Bull. Int. Ed.* **2005**, 54, 1847.

3. M. Zimowska, A. Michalik-Zym, J. Połtowicz, M. Bazarnik, K. Bahranowski, E. M. Serwicka, *Catal. Today* **2007**, *124*, 55.
4. M. Cardoso, A. R. Silva, B. de Castro, C. Freire, *Appl. Catal A: Gen.* **2005**, *285*, 110.
5. K. C. Gupta, A. K. Sutar, *J. Mol. Catal. A: Chem.* **2008**, *280*, 173.
6. D. E. De Vos, M. Dams, B. F. Sels, P. A. Jacobs, *Chem. Rev.* **2002**, *102*, 3615.
7. F. Di Furia, G. Modena, *Pure & Appl. Chem.* **1982**, *54*, 1853.
8. D. C. Sherrington, *Pure & Appl. Chem.* **1988**, *60*, 401.
9. K. Jorgensen, *Chem. Rev.* **1989**, *89*, 431.
10. I. V. Yudanova, *J. Struct. Chem.* **2007**, *48*, S111.
11. E. N. Jacobsen, L. Deng, Y. Furukawa, L. E. Martínez, *Tetrahedron* **1994**, *50*, 4323.
12. M. Selke, M. F. Sisemore, J. Selverstone-Valentine, *J. Am. Chem. Soc.* **1996**, *118*, 2008.
13. C. Masters, *Homogeneous Transition-Metal Catalysis: A Gentle Art* **1981**, Chapman & Hall, London, 172.
14. S. Seelan, A. K. Sinha, *Appl. Catal. A: Gen.* **2003**, *238*, 201.
15. R. Wang, Z. Duan, Y. He, Z. Lei, *J. Mol. Catal. A: Chem.* **2006**, *260*, 280.
16. S. Mukherjee, S. Samanta, B. C. Roy, A. Bhaumik, *Appl. Catal. A: Gen.* **2006**, *301*, 79.
17. Z-W. Yang, Q-Z. Kang, H-C. Ma, C-L. Li, Z.-Q. Lei, *J. Mol. Catal. A: Chem.* **2004**, *213*, 169.
18. M. Salavati-Niasari, A. Amiri, *Appl. Chem. A: Gen.* **2005**, *290*, 46
19. A. S. Kanmani, S. Vacheesan, *J. Mol. Catal. A: Chem.* **1999**, *150*, 95.
20. P. Karandikar, K. C. Dhanya, S. Deshpande, A. J. Chandwadkar, *Catal. Commun.* **2004**, *5*, 69.

CHAPTER 6

SUMMARY

Chapter 1 of this thesis provides a brief literature survey of the current status of the application of salicylaldimine metal complexes as homogeneous catalysts as well as heterogenised catalysts. Several different classes of salicylaldimine complexes are discussed and their use in a range of catalytic applications are summarized in this chapter. In addition this chapter also provides a brief overview of the strategies employed to immobilized salicylaldimine catalysts as well as the application of these immobilized systems in some catalytic processes. This part of the thesis thus provides some background for one of the main objectives of this research project viz. the investigation into the use of previously unexplored salicylaldimine complexes as homogeneous as well as dendrimer immobilized catalysts in two catalytic processes (phenol hydroxylation and alkene oxidation) with the intent of identifying suitable catalysts for *greener* chemical processes.

Chapter 2 describes the synthetic approach to several new salicylaldimine ligands and their related metal complexes. From the results reported in this chapter, it can clearly be seen that all ligands and their copper and cobalt complexes have been successfully characterized. Similarly in Chapter 3 the preparation of 8 new dendritic metal complexes is also reported. Once again a comprehensive suite of characterization data for all complexes prepared is presented in this chapter. Characterization techniques employed include, IR and UV-Vis spectroscopy, mass spectrometry, elemental analysis

and thermogravimetric analysis. All of these techniques confirmed the nature of the metal complexes prepared.

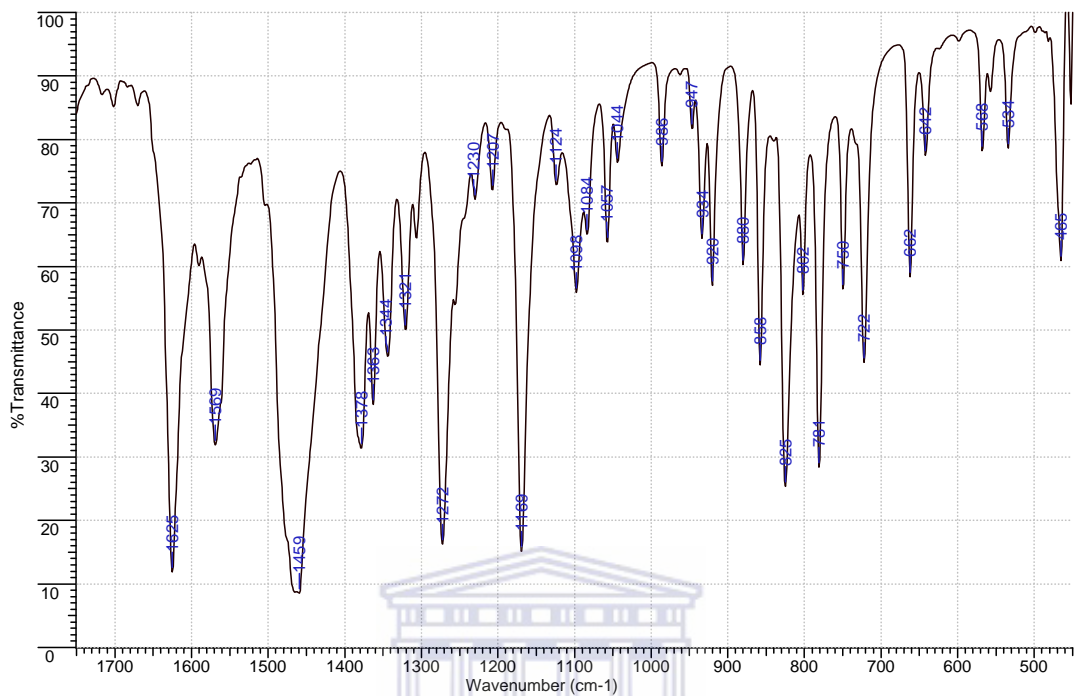
Chapter 4 describes the evaluation of the Cu(II) and Co(II) complexes as catalysts in the hydroxylation of phenol to produce catechol (CT) and hydroquinone (HQ). The catalytic reactions were performed in aqueous media over a range of pH values using hydrogen peroxide as oxidant. All the metal complexes evaluated were active for the oxidation process. The Cu(II) complexes were evaluated in the pH range 3-6 and showed good activity producing both CT and HQ, however CT was observed as the major product. Most of the mononuclear Cu(II) catalysts produced CT and HQ in a ratio of approximately 2:1, which is the typical product distribution of copper catalysts reported in literature. However the Cu(II) metallodendrimers exhibited as slightly higher formation of HQ producing CT and HQ roughly in a 1.5:1 ratio. The investigation of the Cu(II) complexes in the pH range showed only a slight influence of the pH on the activity of the catalyst and product distribution. The Co(II) complexes were only investigated at pH values 3 and 6 and were found to be slightly less active than the Cu(II) complexes under these conditions. The Co(II) complexes were also observed to produce both CT and HQ, with CT once again being produced as the major product. However for the Co(II) complexes a much more significant influence of the pH on the activity of the catalysts as well as the distribution of the oxidation products was observed.

In Chapter 5 the performance of the Cu(II) and Co(II) complexes were evaluated in the oxidation of cyclohexene using hydrogen peroxide as oxidant under aerobic conditions. All the catalysts investigated were found to active for the oxidation process producing

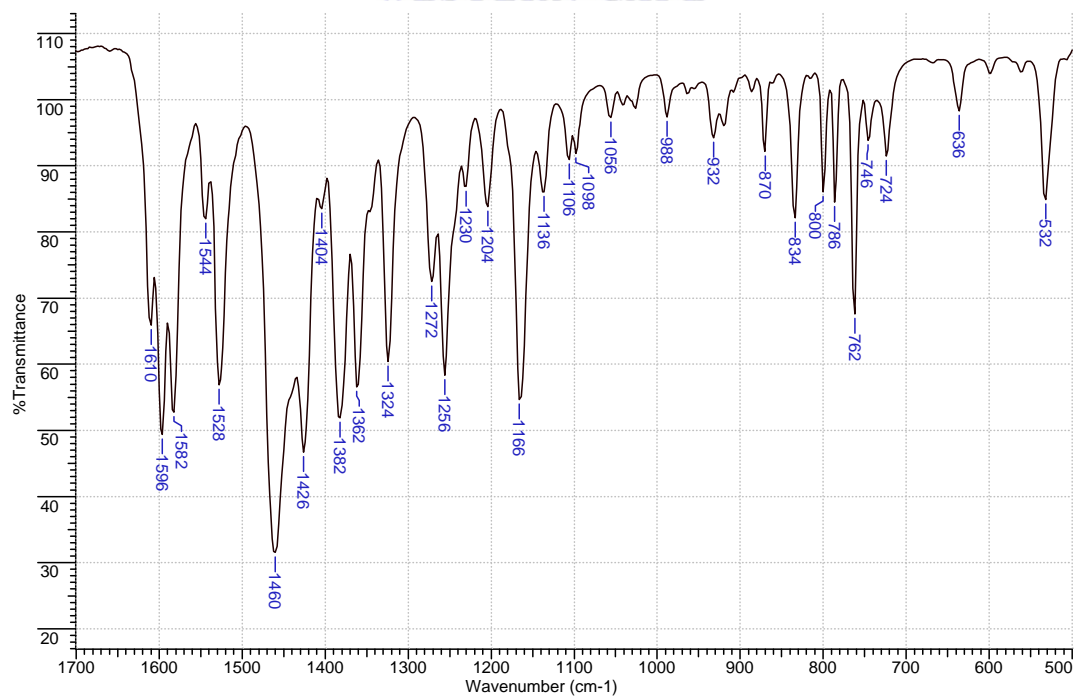
the allylic oxidation products 2-cyclohexene-1-one (ketone) and 2-cyclohexene-1-ol (alcohol) as major products and the epoxide, cyclohexene oxide as a minor product or in trace quantities. All the catalysts were observed to produce the ketone in higher quantities than the alcohol. However it was found that the reaction conditions such as the solvent, oxidant to substrate ratio and the metal loading has an influence on the activity of the catalysts and the distribution of oxidation products.

The successful application of the investigated metal complexes in the oxidation of phenol and cyclohexene is thus described, however further optimization of the process conditions is still required and thus future studies should be focused on a more comprehensive study of reaction conditions. In addition, kinetic as well as mechanistic studies to probe the role of the complexes in the processes investigated should also be performed as this will perhaps provide a clearer picture of oxygen transfer to the substrates as well as the nature of the active species involved in this process for future catalyst development. Future investigation should also include ultrafiltration studies to determine the suitability of the dendrimeric catalysts for continuous catalytic processes.

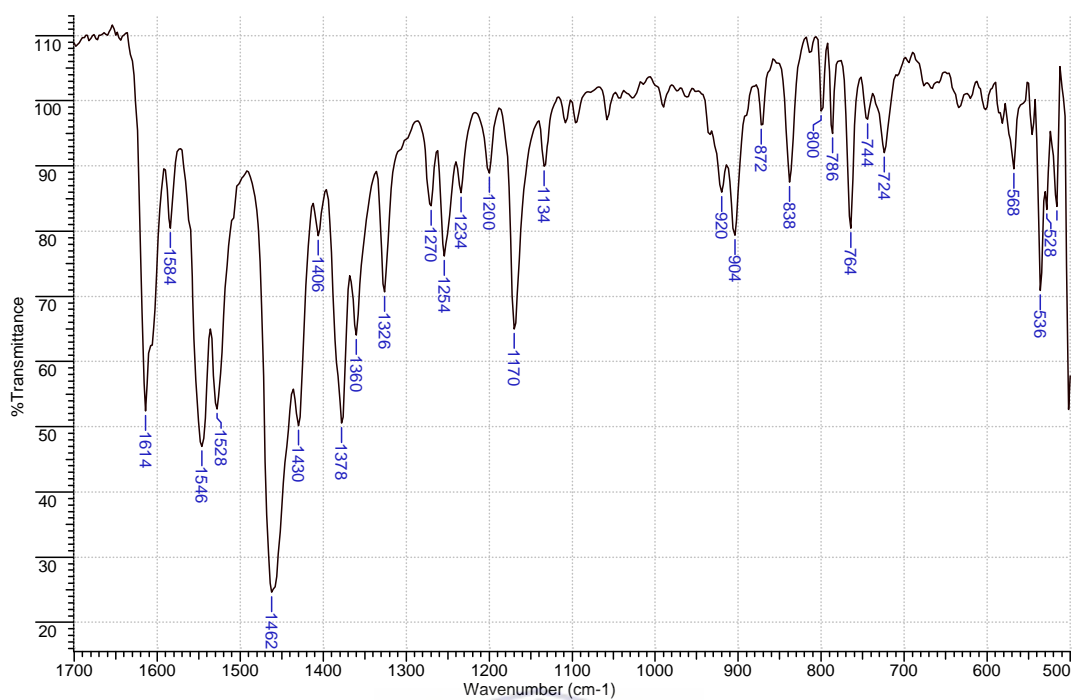
APPENDIX



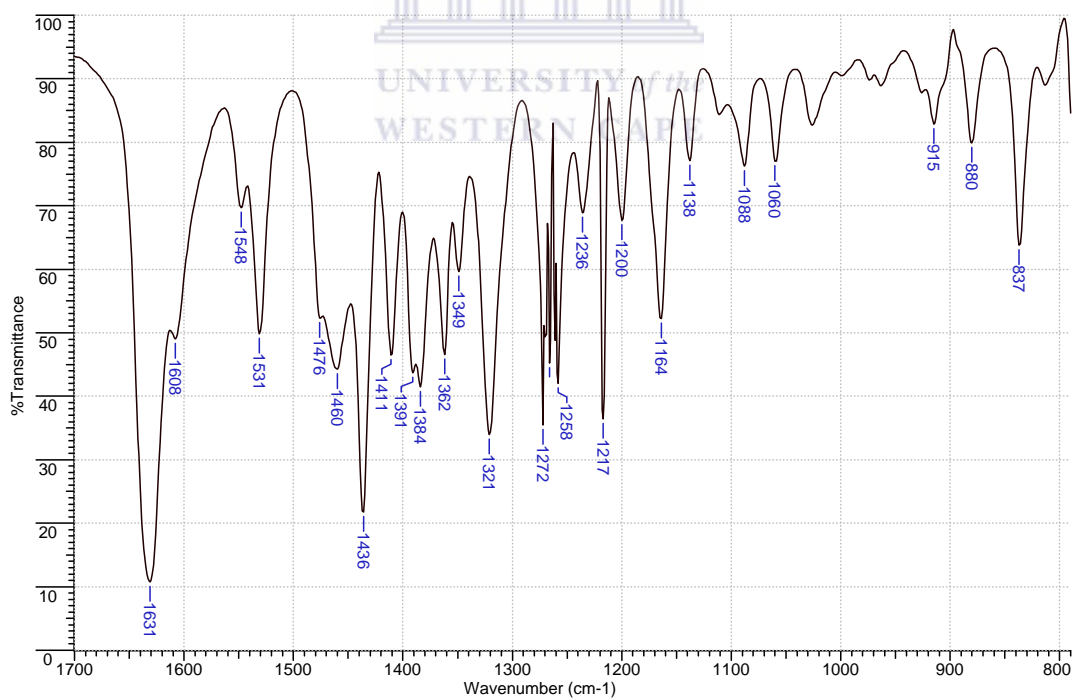
Infrared spectrum of *N*-(aryl)salicylaldimine ligand **HL**⁵



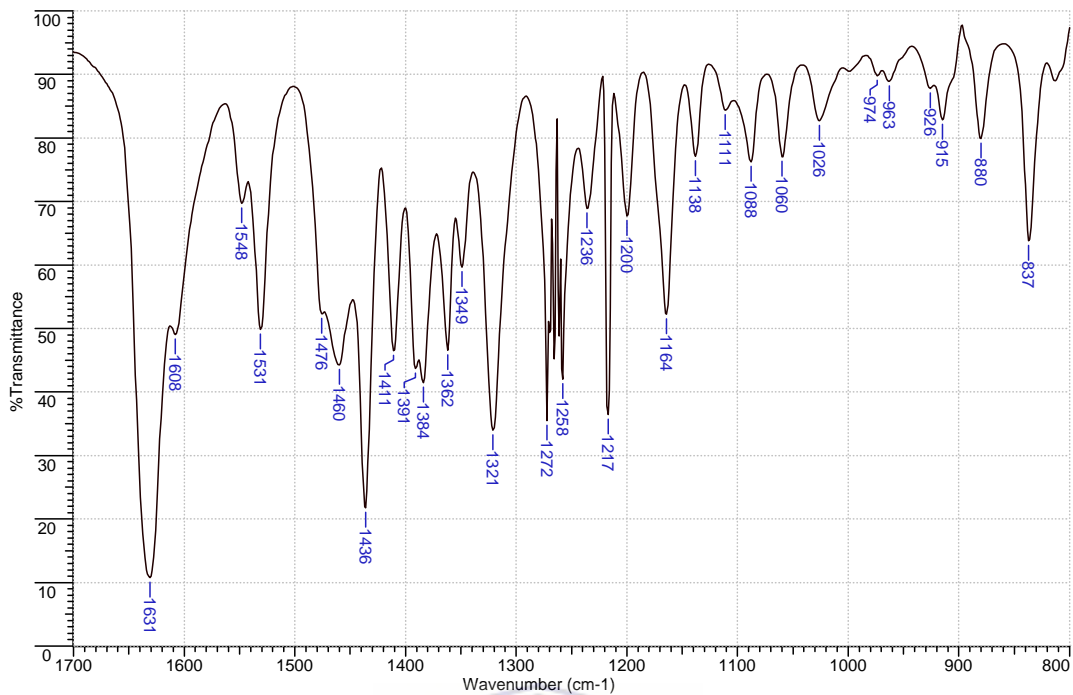
Infrared spectrum of copper(II) salicylaldiminato complex **7**.



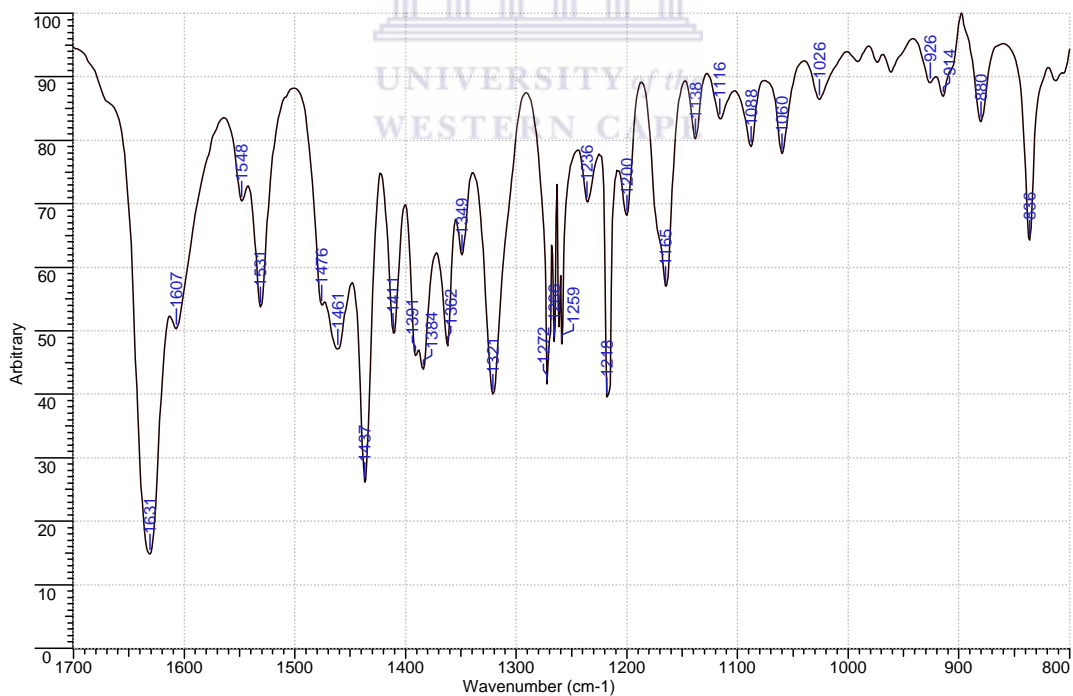
*Infrared spectrum of bimetallic copper(II) complex **8**.*



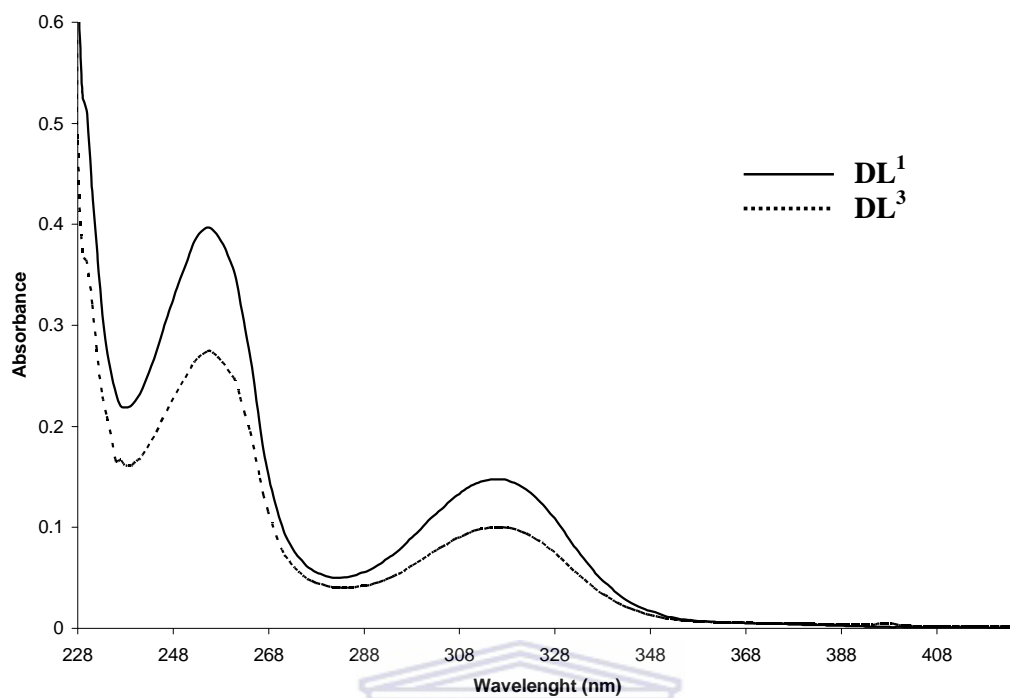
*Infrared spectrum of G2 salicylalimine functionalized poly(propyleneimine) dendrimer **DL⁴**.*



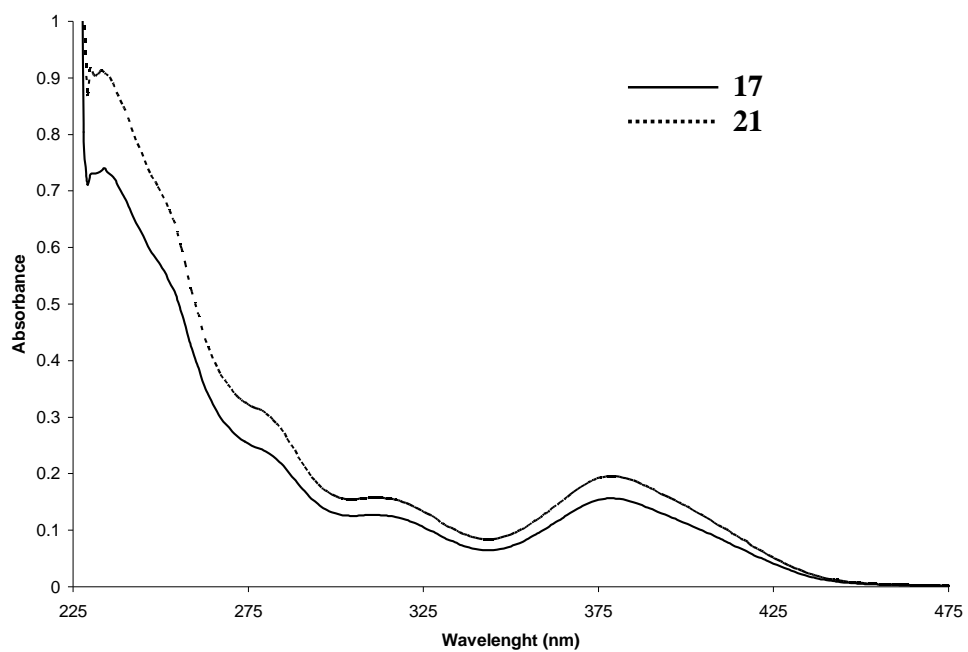
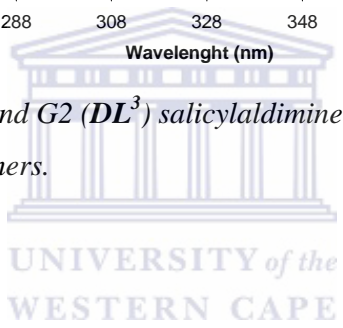
Infrared spectrum of G1 cobalt(II) metallodendrimer 19.



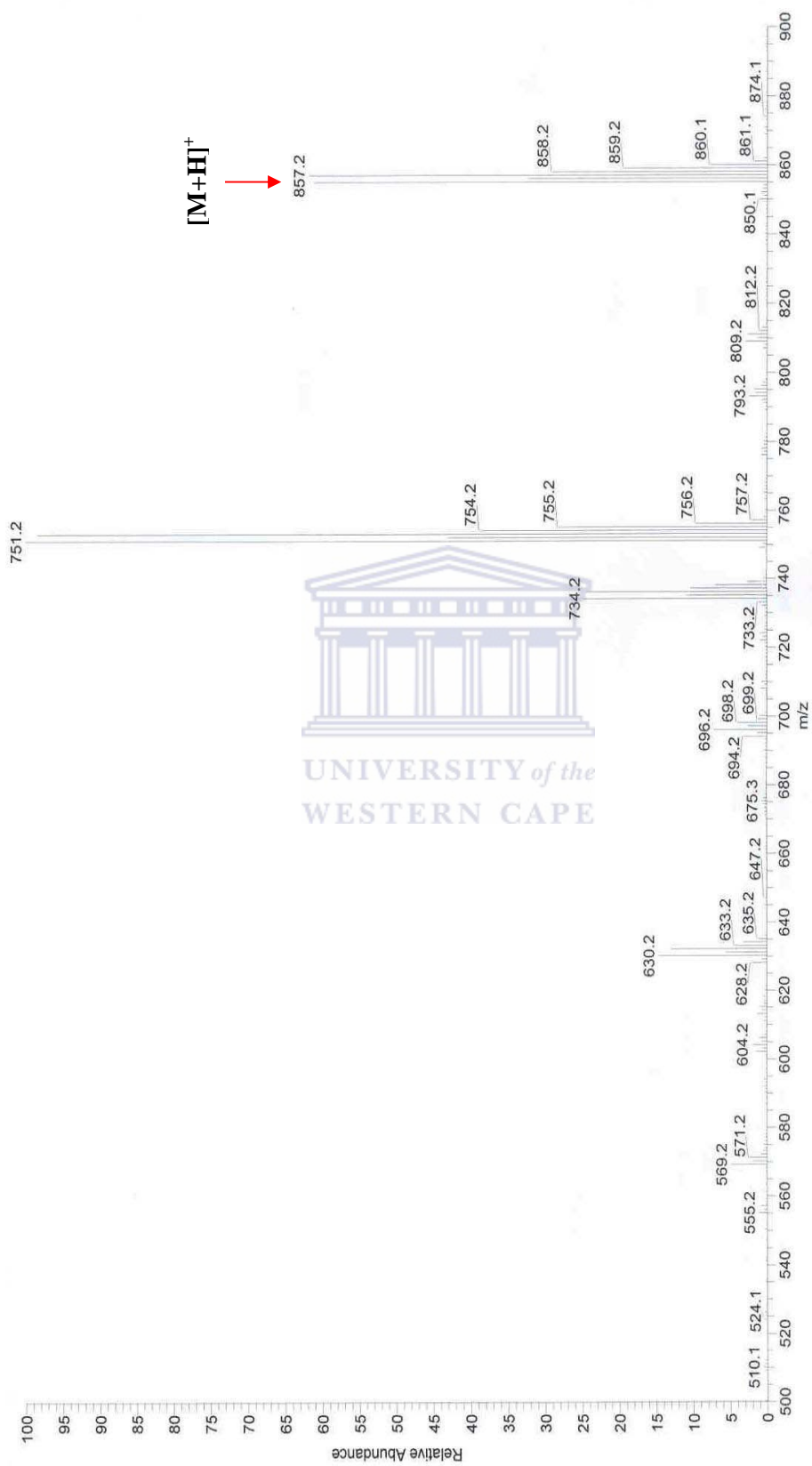
Infrared spectrum of G2 cobalt metallodendrimer 23.



UV-Vis spectra of G1 (DL^1) and G2 (DL^3) salicylaldimine functionalized poly(propyleneimine) dendrimers.



*UV-Vis spectra of G1 (**17**) and G2 (**21**) copper(II) metallodendrimers.*



ESI Mass spectrum of G1 copper(II) metallodendrimer 16.

