

Chapter-6

Metal assisted synthesis of mixed nitrogen-sulfur donor set.

6.1 MACROCYCLIC COMPLEXES OF MANGANESE(II), NICKEL(II), COBALT(II) AND COPPER(II) WITH N₂S₂ DONOR SET

6.1.1 INTRODUCTION

The design and synthesis of macrocyclic compounds incorporating sulfur as a donor atom have been a fascinating area of research.¹⁻⁶ Recently a large number of workers⁷⁻¹⁵ are engaged for the synthesis of macrocyclic complexes incorporating sulfur and nitrogen mixed donor atoms. Macrocyclic complexes containing sulfur and nitrogen as donor atoms are of much biological significance¹⁶⁻¹⁸ and have a large number of industrial applications.^{19,20} They are used as ionophores²¹, receptor molecules²², chemical sensors in catalysis²³, as models²⁴ for protein metal binding sites, metalloenzymes, pigments and vitamin B₁₂. In biomedical systems^{25,26} they are used as therapeutic reagents, anti-HIV agents, cyclic antibiotics and radiopharmaceuticals.

The present study was undertaken with an objective to design and synthesise macrocyclic compounds incorporating sulfur and nitrogen as mixed donor atoms and a series of dithiadiaza macrocyclic complexes [MLX₂], (M = Mn(II) and Co(II); X = Cl or NO₃) and [ML]X₂, (M = Ni(II) and Cu(II); X = Cl or NO₃) has been reported.

6.1.2 MATERIALS AND METHODS

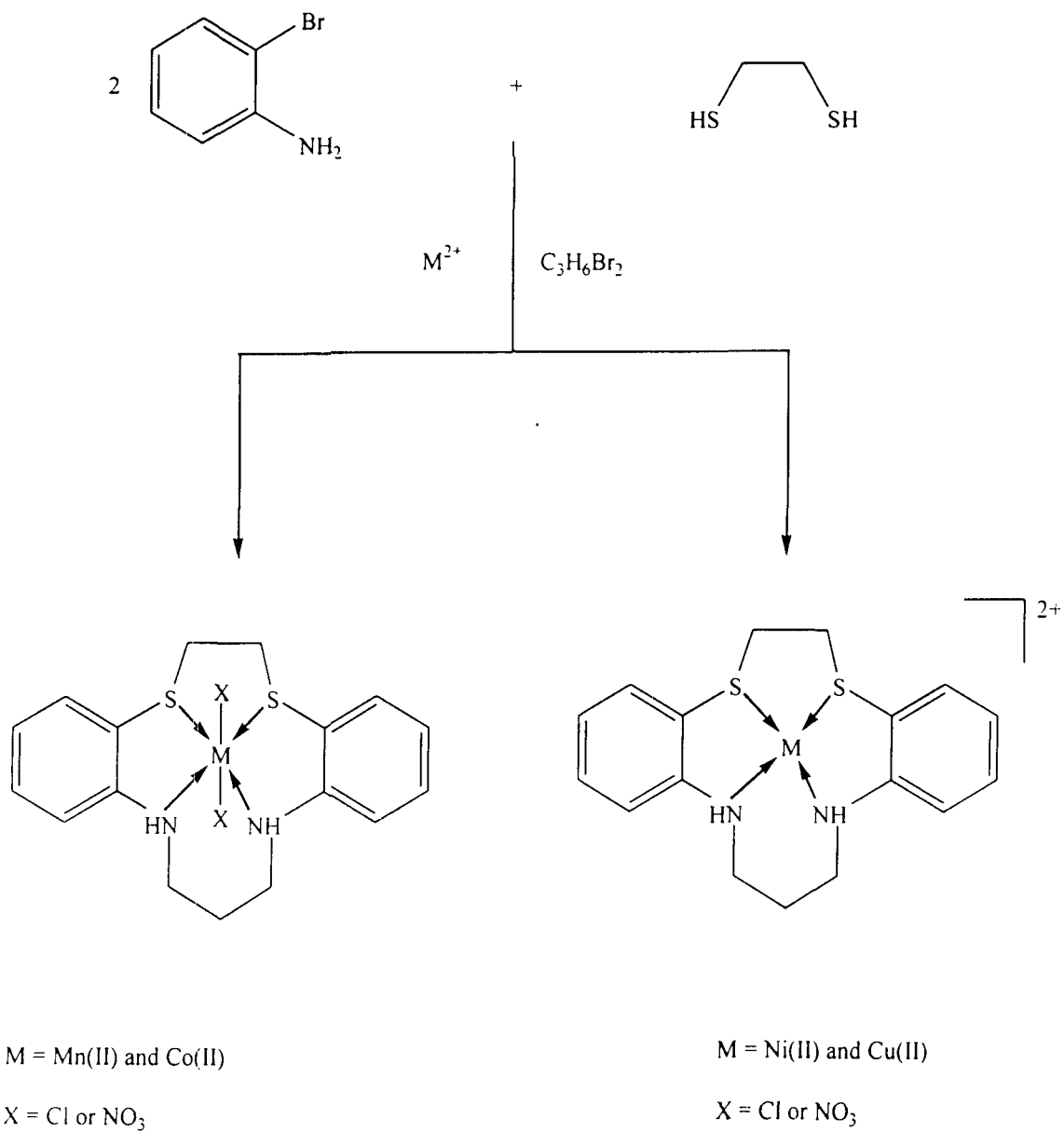
o-Bromoaniline (Merck), 1,2-ethanedithiol (Fluka) and 1,3-dibromopropane (Merck) were used as received, metal salts, $MnX_2 \cdot 4H_2O$, $CoX_2 \cdot 6H_2O$, $NiX_2 \cdot 6H_2O$ and $CuX_2 \cdot 2H_2O$ ($X = Cl$ or NO_3) were commercially available pure samples.

Synthesis of dichloro/dinitrato (2,3:8,9-dibenzo-4,7-dithia-1,10-diazacyclotridecane) (L) metal (II), $[MLX_2]$ ($M = Mn(II)$ and $Co(II)$; $X = Cl$ or NO_3) and (2,3:8,9-dibenzo-4,7-dithia-1,10-diazacyclotridecane) (L) metal(II) dichloride/dinitrate, $[ML]X_2$, ($M = Ni(II)$ and $Cu(II)$; $X = Cl$ or NO_3).

Methanolic solution of o-bromoaniline (10 mmol, 0.172 g) was taken in a two-necked round bottom flask and methanolic solution of ethanedithiol (5 mmol, 0.429 mL) was added to this solution. Then methanolic solution of 1,3-dibromopropane (5 mmol, 0.517 mL) and respective metal salt (5 mmol) were mixed simultaneously and the mixture was stirred for 8 hours. A coloured solid product was obtained which was filtered, washed with methanol and dried over fused $CaCl_2$ in a desiccator.

6.1.3 RESULTS AND DISCUSSION

A series of dithiadiaza complexes $[MLX_2]$ ($M = Mn(II)$ and $Co(II)$; $X = Cl$ or NO_3) and $[ML]X_2$ ($M = Ni(II)$ and $Cu(II)$; $X = Cl$ or NO_3) have been prepared by the template reaction of o-bromoaniline, 1,2-ethanedithiol and 1,3-dibromopropane with metal salt in 2:1:1:1 molar ratio (Scheme 14). The analytical results (Table 13) suggest that the proposed macrocyclic complexes



Scheme 14

Table 13. Melting point(°C), yield%, Colour, elemental analyses and molar conductance value of the compounds

Compound	M.P. (°C)	Yield (%)	Colour	Found calcd (%)				Molar Conductivity ($\text{cm}^2\Omega^{-1}\text{mol}^{-1}$)		
				M	C	H	N		S	Cl
[MnLCl ₂]	195	36	Brown	12.0 (12.4)	46.5 (46.1)	4.6 (4.5)	6.6 (6.3)	14.0 (14.4)	16.5 (16.0)	12
[MnL(NO ₃) ₂]	205	28	Black	11.1 (11.0)	41.0 (41.2)	4.2 (4.0)	11.0 (11.3)	12.7 (12.9)	-	13
[CoLCl ₂]	240	34	Brown	13.0 (13.2)	45.5 (45.7)	4.6 (4.5)	6.4 (6.2)	14.0 (14.3)	15.4 (15.8)	18
[CoL(NO ₃) ₂]	218	32	Brown	11.4 (11.8)	40.4 (40.8)	4.2 (4.0)	11.0 (11.2)	12.6 (12.8)	-	24
[NiL]Cl ₂	270	28	Brown	13.3 (13.1)	45.4 (45.7)	4.6 (4.5)	6.4 (6.2)	14.0 (14.3)	15.3 (15.8)	118
[NiL](NO ₃) ₂	280	30	Black	11.5 (11.7)	40.2 (40.9)	4.3 (4.0)	11.0 (11.2)	12.6 (12.8)	-	111
[CuL]Cl ₂	260	41	Brown	14.3 (14.0)	45.7 (45.2)	4.8 (4.4)	6.7 (6.2)	14.6 (14.2)	15.2 (15.7)	105
[CuL](NO ₃) ₂	250	32	Gray	12.3 (12.6)	40.8 (40.5)	3.5 (3.9)	11.5 (11.1)	12.2 (12.7)	-	116

Table 14. I.R. vibrational frequencies (cm^{-1}) of the compounds.

Compound	$\nu(\text{N-H})$	$\nu(\text{C-N})$	$\nu(\text{M-N})$	$\nu(\text{M-S})$	$\nu(\text{M-O})$	$\nu(\text{M-Cl})$	Ring vibrations
$[\text{MnLCl}_2]$	3260 s	1180 s	410 s	340 s	-	280 m	1440 s, 1070 s, 735 s
$[\text{MnL}(\text{NO}_3)_2]$	3250 s	1170 s	410 s	330 s	240 m	-	1420 s, 1080 s, 720 s
$[\text{CoLCl}_2]$	3270 s	1180 s	430 s	370 s	-	310 m	1450 s, 1100 s, 740 s
$[\text{CoL}(\text{NO}_3)_2]$	3290 s	1200 s	390 s	380 s	230 m	-	1460 s, 1090 s, 735 s
$[\text{NiL}]\text{Cl}_2$	3280 s	1200 s	430 s	360 s	-	-	1410 s, 1080 s, 730 s
$[\text{NiL}](\text{NO}_3)_2$	3310 s	1190 s	410 s	380 s	-	-	1440 s, 1075 s, 730 s
$[\text{CuL}]\text{Cl}_2$	3270 s	1160 s	450 s	380 s	-	-	1425 s, 1070 s, 720 s
$[\text{CuL}](\text{NO}_3)_2$	3280 s	1190 s	420 s	360 s	-	-	1430 s, 1095 s, 725 s

Table 15. Magnetic moment value, electronic Spectra data, their Assignments and EPR data of the compounds.

Compound	μ_{eff} (B.M.)	Band position (cm^{-1})	Assignment	EPR data	
				g_{\parallel}	g_{\perp}
[MnLCl ₂]	5.83	22,600	⁶ A _{1g} → ⁴ T _{2g}	-	-
		18,900	⁶ A _{1g} → ⁴ T _{1g}		
[MnL(NO ₃) ₂]	5.80	22,400	⁶ A _{1g} → ⁴ T _{2g}		
		18,600	⁶ A _{1g} → ⁴ T _{1g}		
[CoLCl ₂]	4.56	21,700	⁴ T _{1g} (F) → ⁴ T _{1g} (P)		
		16,100	⁴ T _{1g} (F) → ⁴ A _{2g} (F)		
[CoL(NO ₃) ₂]	4.61	21,400	⁴ T _{1g} (F) → ⁴ T _{1g} (P)		
		15,950	⁴ T _{1g} (F) → ⁴ A _{2g} (F)		
[NiL]Cl ₂	-	20,100	¹ A _{1g} → ¹ A _{2g}		
		15,200	¹ A _{1g} → ¹ B _{1g}		
[NiL](NO ₃) ₂	-	19,400	¹ A _{1g} → ¹ A _{2g}		
		15,700	¹ A _{1g} → ¹ B _{1g}		
[CuL]Cl ₂	1.80	21,800	² B _{1g} → ² E _g	2.12	2.04
		16,050	² B _{1g} → ² A _{1g}		3.00
		11,500	² B _{1g} → ² B _{2g}		
[CuL](NO ₃) ₂	1.78	21,200	² B _{1g} → ² E _g	2.09	2.03
		16,100	² B _{1g} → ² A _{1g}		3.00
		11,900	² B _{1g} → ² B _{2g}		

have 1:1 (metal to ligand) stoichiometry. An attempt to prepare the corresponding free ligand has been unsuccessful. The observed molar conductance values indicate 1:2 electrolytic nature of the Ni(II) and Cu(II) complexes.

The IR spectra (**Table 14**) of all the macrocyclic complexes exhibit a strong intensity band in the region 3250-3310 cm^{-1} ascribed to the N-H stretching vibration.²⁷ Bands observed in the region 1160-1200 cm^{-1} may reasonably be assigned to C-N stretching vibrations.²⁸ Appearance of a sharp band in the 390-450 cm^{-1} region may reasonably be assigned to $\nu(\text{M-N})$.²⁸ All the complexes show bands in the 1410-1460, 1070-1100 and 720-740 cm^{-1} regions which can be assigned to phenyl ring vibrations.²⁹ The spectra of nitrate complexes gave additional bands around 1230, 1050 and 850 cm^{-1} regions consistent with the monodentate bonding of this group. Bands at 230-240 and 280-310 cm^{-1} in the nitrate and chloro complexes are assignable³⁰ to $\nu(\text{M-O})$ and $\nu(\text{M-Cl})$ respectively. However a strong intensity band in the region 330-380 cm^{-1} may be assigned to M-S stretching vibration.

The EPR spectra (**Table 15**) of both the Cu(II) complexes at room temperature exhibit a single absorption band. The absence of hyperfine splitting in these complexes is due to the strong dipolar and exchange interactions between the Cu(II) ions in the unit cell. The calculated g_{\parallel} and g_{\perp} values appeared in the range 2.09-2.12 and 2.03-2.04 respectively which supports³¹ that the $d_{x^2-y^2}$ may be the ground state ($g_{\parallel} > g_{\perp} > 2.02$). The

magnitude of the ratio $G = (g_{\parallel} - 2) / (g_{\perp} - 2)$ indicates³² the possibility of the exchange interaction in these complexes. In the present case the G values appeared at 3.00 indicating considerable exchange interaction in these complexes. The g_{\parallel} value ($g_{\parallel} < 2.3$) indicates²³ covalent character of the metal ligand bond.

The electronic spectra (**Table 15**) of the manganese complexes gave two bands in the regions 22,400-22,600 and 18,600-18,900 cm^{-1} which may be assigned³⁴ to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transitions, respectively, suggesting an octahedral environment around the manganese(II) ion. The spectra of the cobalt complexes gave two ligand field bands in the regions 21,400-21,700 and 15,950-16,100 which are assignable³⁴ to the ${}^4T_{1g} (F) \rightarrow {}^4T_{1g} (P)$ and ${}^4T_{1g} (F) \rightarrow {}^4A_{2g} (F)$ transitions, respectively, consistent with the octahedral geometry of the cobalt(II) ion. This has been further confirmed by the appearance of two bands in their electronic spectra centered in the 19,400-20,100 and 15,200-15,700 cm^{-1} regions, which may reasonably be assigned³⁴ to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transitions, respectively, consistent with a square planar geometry around the nickel(II) ion. The electronic spectra of copper complexes showed a broad band centered at ca 16,100 cm^{-1} assignable³⁴ to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions. However, two weak shoulders appearing in the regions 21,200-21,800 and 11,500-11,900 cm^{-1} may be ascribed to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively, suggesting a square planar geometry around the copper(II) ions.

REFERENCES

1. B. Patel and G. Reid, *J. Chem. Soc., Dalton Trans.*, **2000**, 1303.
2. A. J. Blake, G. Reid and M. Schroder, *J. Chem. Soc., Dalton Trans.*, **1992**, 2987.
3. R. Cammack, *Adv. Inorg. Chem.*, **1988**, 32, 297.
4. K. E. Krakowiak, J. S. Bradshaw and K. D. J. Zamechkakra, *Chem. Rev.*, **1989**, 89, 929.
5. K. R. Adam, M. Antolovich, D. S. Baldwin, L. G. Brigden, P. A. Duckworth, L. F. Lindoy, A. Bashall, M. Mc. Partlin and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, **1992**, 1869.
6. K. R. Adam, M. Antolovich, D. S. Baldwin, P. A. Duckworth, A. J. Leong, L. F. Lindoy, M. Mc. Partlun and P. A. Tasker, *J. Chem. Soc., Dalton Trans.*, **1993**, 1013.
7. I. M. Atkinson, J. D. Chartres, A. M. Groth, L. F. Lindy, M. P. Lowe, G. V. Meehan, B. W. Skeltan and A. H. White, *J. Chem. Soc., Dalton Trans.*, **2001**, 2801.
8. J. D. Chartres, A. M. Groth, L. F. Lindoy and G. V. Meehan, *J. Chem. Soc., Dalton Trans.*, **2002**, 371.
9. I. M. Atkinson, J. D. Chartres, A. M. Groth, L. F. Londoy, M. P. Lowe and G. V. Meehan, *Chem. Commun.*, **2002**, 2428.
10. M. C. Thompsan and D. M. Busch, *J. Am. Chem. Soc.*, **1964**, 86, 3561.
11. L. F. Lindoy and D. H. Busch, *J. Am. Chem. Soc.*, **1969**, 91, 4690.
12. A. M. Groth, L. F. Lindoy and G. V. Meehan, *J. Chem. Soc., Perkin Trans.*, 1, **1996**, 1553.
13. R. Tanaka, T. Yano, T. Nishioka, K. Nakajo, B. K. Breedlove, K. Kimura, I. Kinoshita and K. Isobe, *Chem. Commun.*, **2002**, 1686.
14. M. M. Bernardo, M. J. Heeg, R. R. Schroeder, L. A. Ochrymowycz and D. B. Rorabacher, *Inorg Chem.*, **1992**, 31, 191.
15. M. Shakir, S. P. Varkey and P. S. Hameed, *J. Chem. Res.*, **1993**, 11, 442.
16. A. Bencini, A. Bianchi, M. I. Burguete, P. Dapporto, A. Domench, E. G. Espana, S. V. Luis, P. Paoli and J. A. Ramirez, *J. Chem. Soc., Perkin Trans.*, **1994**, 2, 569.
17. H. Miyake and Y. Kojima, *Coord. Chem. Rev.*, **1996**, 148, 301.
18. J. M. Veauthier, W. S. Cho, V. M. Lynch and J. L. Sessler, *Inorg. Chem.*, **2004**, 43, 1220.

19. H. B. Kagan, "In Fundamental and Technological Application of Organo f-Element Chemistry" Ed; T. J. Marks, Riedel, Dordrecht, **1985**, p. 49.
20. G. J. McCarty, J. J. Rhyme and H. B. Silber, "The Rare Earths in Modern Science and Technology, Plenum; New York, **1977**, Vol. 1; **1979**, Vol. 2; **1981**, Vol. 3.
21. J. B. Love, J. M. Vere, M. W. Glenney, A. J. Blake and M. Schroder. *Chem. Commun.*, **2001**, 2678.
22. P. D. Beer, N. Berry, M. G. B. Drew, O. D. Fox, P. M. E. Tosta and S. Patell, *Chem. Commun.*, **2001**, 199.
23. P. D. Beer, P. A. Gale and G. Z. Chem, *J. Chem. Soc., Dalton Trans.*, **1999**, 1897.
24. J. Costamgna, G. Ferraudi, B. Matsuhiro, M. V. Campos, J. Canales, M. Villagean, J. Vergas and M. J. Anguيرة, *Coord. Chem. Rev.*, **2000**, 196, 125.
25. P. V. Bernhardt and P. C. Sharpe, *Inorg. Chem.*, **2000**, 39, 4123.
26. J. S. Trommel and L. G. Marzilli, *Inorg. Chem.*, **2001**, 40, 4374.
27. M. Shakir, S. P. Varkey and P. S. Hameed, *Polyhedron.*, **1994**, 13, 1355.
28. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds Wiley Interscience", New York, **1970**.
29. M. Shakir, D. Kumar and S. P. Varkey, *Polyhedron.*, **1992**, 11, 2831.
30. M. Shakir, S. P. Verkey, *Transition. Met. Chem.*, **1994**, 19, 606.
31. M. C. Jain, A. K. Srivastava and P. C. Jain, *Inorg. Chim. Acta.*, **1977**, 23, 199.
32. I. M. Proctor, B. J. Hathway and Nicholls, *J. Chem. Soc., A*, **1968**, 1978.
33. D. Kivelson and R. R. Neiman, *J. Chem. Phys.*, **1961**, 15, 149.
34. A. B. P. Lever, "Inorganic Electronic Spectroscopy," 2nd Edn; Elsevier Amsterdam; **1984**, 318.