



SPECTROSCOPIC STUDIES OF HOMOBINUCLEAR AND BIVALENT TRANSITION METAL COMPLEXES

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Abstract

A new series of symmetric tetradentate cyclic ligand and their transition metal complexes have been synthesized and characterized. Macrocyclic ligand has been synthesized by the condensation reaction of the thiodiglycolic acid and 2,6 diammino pyridine or 2,6 diammino phenylene in the molar ratio of 1:1. Light yellow colored ligand was precipitated out. The synthesis of the ligand was confirmed by ir, and mass spectral data. The cobalt complexes were prepared by using the ligand and the metal salt in the ratio of 1:2. Colored cobalt complexes were synthesized and characterized by elemental analysis, molar conductance, IR, Electronic and EPR spectral studies in DMSO/DMF solutions. Six coordinated octahedral geometry were proposed for the complexes.

Introduction:

Macrocyclic complexes and their chemistry has attracted the interest of both bioinorganic and organic chemists in the recent years. This enormous growth of the macrocyclic complexes is due to their synthesis of large number of synthetic macrocycles which behaves as coordinating agents for metal ions. The macrocyclic ligands and their metal complexes in the coordination chemistry is important because of its various applications in the biological processes such as photosynthesis and dioxide transport catalytic properties, potential applications as metal extractants and radio therapeutic agents[1-6]. The importance of macrocyclic complexes is due to their resemblance with the natural occurring biological molecules like haemoglobin, myoglobin etc. The macrocyclic ligands and their complexes are of great interest because of their properties in bacterial and fungal growth, analytical, industrial and medical applications[7-11].

This paper describes the synthesis and characterization of the homobinuclear cobalt (II) complexes.

Material and methods

Reagent grade commercially available chemicals (sigma-Aldrich) were used to perform all the experimental work.

Elemental analysis and physical measurements

The C and H analysed on the Carlo-Erba 1106 elemental analyzer. Kjeldahl method was used to determine the nitrogen content in the ligand and the complexes. ELICO (CM82T) conductivity bridge was used to measure the molar conductance and Sherwood scientific magnetic susceptibility Guoy balance (model no. MK1) at room temperature is used to determine the magnetic susceptibility of the complexes. Shimadzu UV-1601 spectrophotometer is used to record the electronic spectra of the complexes in the range of 200-1100nm. FT-IR spectrum BX-II spectrophotometer was used to record the IR spectra of the complexes as KBr pellets in the region 4000-200 cm^{-1} . The X band EPR spectra of the complexes were recorded at 77K (LNT) by using the frozen DMSO glass as the matrix on E4-EPR spectrometer using DPPH as the g marker.

Procedure for the synthesis of the complexes

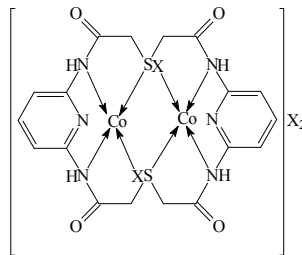
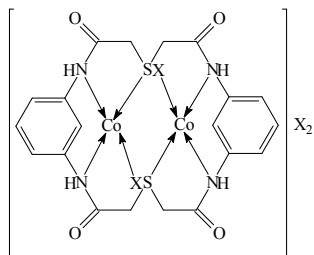
A template method was adopted to prepare the complexes. A hot ethanolic solution of divalent metal salt was mixed with the hot ethanolic solution of 2,6 diamminopyridine/ 2,6 diamminophenylene in the molar ratio of 2:1. To this solution the hot ethanolic solution of thiodiglycolic acid in the molar ratio of one was mixed and the resultant solution was refluxed for 6-9 hrs. The colored complexes were precipitated out on cooling the solution. They were collected by filtration, washing and recrystallized with ethanol and dried over anhydrous calcium chloride. The purity of the complexes were checked by TLC.

Result and Discussion

The general composition of the complexes was found to be M_2LX_2 (where M = Co (II) and X= Cl^{-1} , NO^{-3} , NCS^{-1}). All the complexes have C H and N composition in good agreement with those of the calculated. The result of the elemental analysis, melting point and color of the complexes given on the **table-4**. Molar conductance values of the complexes show the electrolytic nature of the complexes. The cobalt complexes reported shows the magnetic moment values in the range of 4.72-4.95 B.M. given in **table-1** indicates the octahedral nature of the complexes[12-14]. The experimental values were higher than the spin only values due to the orbital angular momentum contribution in d7 system. The absence of band in the IR spectra of the complexes in the range of 3400 cm^{-1} confirmed the absence of free amino group in the complexes and the condensation of the amino to thiodiglycolic acid group. The appearance of band at 450-480 cm^{-1} in the spectra indicate the metal was bonded to the azomethine nitrogen[15]. The IR spectra showed a strong band at 1609-1696 cm^{-1} assigned to (CO) stretching frequency. The presence of bands at 2050-2080 cm^{-1} indicates that both thiocyanate groups were N-bonded given in **table-3**. The electronic spectra of the complexes shows transitions: ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$.

The position of the bands indicates that the cobalt (II) complexes have an octahedral geometry. Various ligand field parameters and Dq values have been calculated. The values of nephelauxetic parameter lies in the range of 0.40-0.56 indicate the poor covalent character of the complexes given in **table- 2**.

Conclusions: Results indicates that all the complexes were ionic and high spin in nature. Spectral studies suggested six coordinated octahedral geometry for the cobalt (II) complexes.



COMPLEXES OF COBALT WITH LIGAND L1
WITH LIGAND L2

COMPLEXES OF COBALT

Table- 1 Magnetic moments electronic spectral bands of binuclear cobalt(II) complexes

Complexes	μ_{eff} (B.M.)	Electronic spectral bands (cm^{-1})
$[\text{Co}_2\text{L}_1\text{Cl}_2]\text{Cl}_2$	2.01	10661, 24452
$[\text{Co}_2\text{L}_1(\text{NO}_3)_2](\text{NO}_3)_2$	2.03	10112, 23719
$[\text{Co}_2\text{L}_1(\text{SO}_4)_2]$	2.05	11101, 24708
$[\text{Co}_2\text{L}_1(\text{SCN})_2](\text{SCN})_2$	2.06	12000 23972
$[\text{Co}_2\text{L}_2\text{Cl}_2]\text{Cl}_2$	2.02	10001, 23122
$[\text{Co}_2\text{L}_2(\text{NO}_3)_2](\text{NO}_3)_2$	2.03	10512, 24572
$[\text{Co}_2\text{L}_2(\text{SO}_4)_2]$	2.03	10000, 24891
$[\text{Co}_2\text{L}_2(\text{SCN})_2](\text{SCN})_2$	2.05	10615, 24663

Table- 2 ESR Spectral data of Binuclear Co(II) complexes

[Co ₂ L ₁ Cl ₂]Cl ₂	1029	427	0.39	82.7	2.86	3.52
[Co ₂ L ₁ (NO ₃) ₂](NO ₃) ₂	1039	413	0.52	85.3	2.87	3.54
[Co ₂ L ₁ (SO ₄) ₂]	1131	419	0.51	63.5	2.88	3.54
[Co ₂ L ₁ (SCN) ₂](SCN) ₂	1137	373	0.35	65.7	2.85	3.55
[Co ₂ L ₂ Cl ₂]Cl ₂	1039	353	0.39	92.5	2.76	3.50
[Co ₂ L ₂ (NO ₃) ₂](NO ₃) ₂	1107	367	0.43	89.3	2.78	3.51
[Co ₂ L ₂ (SO ₄) ₂]	1053	419	0.51	77.7	2.83	3.50
[Co ₂ L ₂ (SCN) ₂](SCN) ₂	1123	423	0.47	63.5	2.88	3.54

Table- 3 IR Spectra bands of Binuclear Cu(II) complexes

Complexes	$\nu(\text{N-H})$	Amide-I	Amide-II	Amide-III	Amide-IV	$\nu(\text{M-N})$	Anion
[Co ₂ L ₁ Cl ₂]Cl ₂	3437	1637	1575	1237	621	415	–
[Co ₂ L ₁ (NO ₃) ₂](NO ₃) ₂	3431	1661	1577	1233	676	409	1421, 1313, 1035
[Co ₂ L ₁ (SO ₄) ₂]	3423	1627	1582	1235	681	413	1026, 619
[Co ₂ L ₁ (SCN) ₂](SCN) ₂	3427	1635	1579	1239	687	419	2083
[Co ₂ L ₂ Cl ₂]Cl ₂	3433	1649	1585	1253	703	415	–
[Co ₂ L ₂ (NO ₃) ₂](NO ₃) ₂	3419	1667	1567	1249	625	406	1426, 1317, 1036
[Co ₂ L ₂ (SO ₄) ₂]	3415	1647	1555	1251	709	427	1026, 619
[Co ₂ L ₂ (SCN) ₂](SCN) ₂	3417	1625	1548	1235	769	423	2091

Table- 4 Molar conductance and elemental analysis data of binuclear Co(II) complexes

Complexes	M.W. Calc. (Found)	Molar cond. $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$	Colour	Yield %	M.Pt. °C	Elemental analysis Calc. (Found)			
						Co	C	H	N
[Co ₂ L ₁ Cl ₂](Cl) ₂ Co ₂ C ₂₀ H ₂₀ N ₄ S ₂ O ₄ Cl ₂	702 (701.72)	236	Pink	63	211	16.80 (16.92)	34.18 (34.27)	2.84 (2.91)	7.97 (8.07)
[Co ₂ L ₁ (NO ₃) ₂](NO ₃) ₂ Co ₂ C ₂₀ H ₂₀ N ₆ S ₂ O ₁₀	810 (809.81)	248	Light Pink	71	213	14.56 (14.62)	29.62 (29.72)	2.46 (2.53)	13.82 (13.89)
[Co ₂ L ₁ (SO ₄) ₂] Co ₂ C ₂₀ H ₂₀ N ₄ S ₃ O ₈	754 (753.69)	16	Moove	64	215	15.64 (15.69)	31.83 (31.89)	2.65 (2.71)	7.42 (7.51)
[Co ₂ L ₁ (SCN) ₂](SCN) ₂ Co ₂ C ₂₂ H ₂₀ N ₆ S ₄ O ₄	797 (796.69)	236	Soft Pink	69	210	14.80 (14.61)	36.13 (36.23)	2.50 (2.59)	14.05 (14.13)
[Co ₂ L ₂ Cl ₂](Cl) ₂ Co ₂ C ₁₈ H ₁₈ N ₆ S ₂ O ₄ Cl ₂	704 (703.87)	230	Dark Pink	78	212	16.76 (15.72)	30.68 (30.73)	2.55 (2.63)	11.93 (12.01)
[Co ₂ L ₂ (NO ₃) ₂](NO ₃) ₂ Co ₂ C ₁₈ H ₁₈ N ₈ S ₂ O ₁₀	812 (811.23)	234	Lotus Pink	76	211	14.53 (14.61)	26.60 (26.73)	2.21 (2.29)	17.24 (17.31)
[Co ₂ L ₂ (SO ₄) ₂] Co ₂ C ₁₈ H ₁₈ N ₆ S ₃ O ₈	756 (755.37)	22	Dark Pink	62	207	15.60 (15.72)	28.57 (28.65)	2.38 (2.47)	11.11 (11.22)
[Co ₂ L ₂ (SCN) ₂](SCN) ₂ Co ₂ C ₂₀ H ₁₈ N ₈ S ₄ O ₄	860 (859.23)	245	Moove	64	203	13.72 (13.79)	25.11 (25.21)	2.09 (2.17)	16.27 (16.33)

References:

1. P.A. Vigato, S. Tamburim, Coord. Chem. Rev. 248, 1717-2118 (2004).
2. V.P.Daniel, B.Murukan, B.S.Kumari, K.Mohanau, Spectrochim. Acta A. 70, 403-410 (2008).
3. M.N.Al-Jibouri, J. Appl.Chem., 6, 64-73 (2014).
4. D.P. Singh, V.Malik, K.Kumar, R.Kumar, Rasayan J. Chem., 2, 133-138 (2009).
5. S.Shukla, S.Chandra and A.Kumar, European J. of pharmaceutical and Med. Research, 5, 303-309 (2016).
6. D.P.Singh, European. J. Med. Chem. 44, 63-69 (2009).
7. D.P.Singh, R.Kumar, J.Singh,. European. J. Med. Chem., 44, 1731-1736 (2009).
8. R.K.Singh, L.Sharma, D.K. Singh., Bioinorganic Chemistry and Applications, 10, 301-306 (2006).
9. R. Huszank, G. Lendav, O.Horvath., J. Biol. Inorg. Chem. 12, 681-690 (2007).
10. D.P.Singh, R. Kumar, V.Malik, P.tyagi. J. Enz.Inhib. Med. Chem. 22, 177-182 (2007).
11. D.P.Singh, R.Kumar., Trans.Met.Chem., 31, 970-973 (2006).
12. S.Chandra, D.Jain, B.Ratnam. J.Chem. Pharm.Res., 2, 533-538 (2010).
13. ABP Lever., Inorganic Electronic Spectroscopy, 2nd Edition Elsevier, Amsterdam, NewYork, 553-571 (1984).
14. S.Shukla, A.P.Mishra. Der.Pharma.Chemica.,2, 410-418 (2010).
15. K.Kumar, MF Tweedle., Pure and Appl. Chem., 65, 515-520 (1993).

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