Asian Journal of Chemistry Vol. 22, No. 7 (2010), 5601-5606

Synthesis and Spectral Characterization of Mixed-Ligand Chelates of Chromium(III) and Manganese(III) with Heterocyclic Thioamide Ligands

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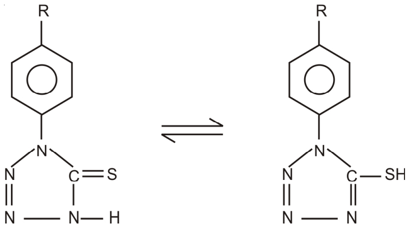
Some trivalent metal chelates of heterocyclic thioamide ligands have been synthesized and characterized by elemental analysis, magnetic, conductance, electronic, infrared and ^{1}H NMR spectral studies. IR spectral data provide unambiguous evidence for the coordination through nitrogen (M-N) and sulphur (M-S) of the ligands. The crystal filed parameters have been calculated and ^{1}H NMR observation are consistent with IR spectral data.

Key Words: Cr(III) and Mn(III) chelates, Thioamide ligands, IR, UV-vis and ^{1}H NMR spectra.

INTRODUCTION

In continuation of our studies on the metal complexes of 1-substituted tetrazoline-5-thione[1-3], we report preparation and spectral characterization of metal-chelates of Cr(III) and Mn(III) with *p*-substituted derivatives of 1-substituted phenyl tetrazoline-5-thione (**I**).



(R = CH_3-, CH_3O-, CH_3CH_2O-, OH-)

(**I**)

EXPERIMENTAL

All chemicals used were of CP grade or AR grade 1-*p*-tolyl (m.p. = 149 °C), 1-*p*-methoxy phenyl (m.p. = 160 °C), 1-*p*-ethoxy phenyl (m.p. = 205 °C) and 1-*p*-hydroxyl phenyl (m.p. = 161 °C) derivatives of 1-substituted tetrazoline-5-thione were prepared by the method described by Lieber *et al.*[4].

The precursor compounds manganese(III) acetate dihydrate[5] and chromium(III) acetate hexahydrate[6] were prepared by the methods reported in the literature. The complexes were prepared using a general method. An aqueous solution of metal acetate was mixed with methanolic solution of ligand in the desired metal-ligand molar ratios. The mixture was refluxed on water bath for 2 h and there after its pH was adjusted to 8 with help of aquous NaOH or pyridine and glacial acetic acid solutions. The mixture was then taken in a beaker and stirred on magnetic stirrer at 100 °C for 2 h. A green-yellow precipitate with Cr(III) and yellow-brown precipitate with Mn(III) were obtained. The crystal that separated was washed thoroughly with hot water, methanol and ether to make free from excess metal-ion or ligand. It was then dried in an electric oven at 60-70 °C for 2 h.

The magnetic moments of the complexes were measured at 300 K using Gouy balance. The IR spectra of ligands and complexes were recorded by means of Perkin-Elmer 521 spectrophotometer using KBr pellets. The electronic spectra were recorded with zeiss (Jena) model of automatic recording system. ^{1}H NMR spectra of ligands and complexes were recorded with 90 MHz NMR spectrophotometer in $CDCl_3$ solution using TMS as the internal indicator in the range of 0-10 ppm. Molar conductance of complexes were measure in DMF using Wiss-Werkstatter Weithen Obb type conductivity meter.

RESULTS AND DISCUSSION

The analytical data of the complexes are given in Table-1. The ligand interacts with Cr(III) and Mn(III) in basic medium with deprotonation of imino hydrogen and acts as bidentate. The different metal-ligand ratio gives different products with Cr(III) on complexation (Table-1). All isolated solid products are stable solid and non-electrolyte in DMF (10^{-3} M) solution. When hydroxo complexes $[CrL(OAc)(OH)(H_2O)_2]\cdot 2H_2O$ were treated with N/10 HCl solution and kept for 8 h then replacement hydroxyl group occurs and chloro complexes having general formula $[CrL(OAc)Cl(H_2O)_2]\cdot 2H_2O$ yielded. All complexes loses crystal water at 110 °C and two molecules of water were eliminated complelety per mole of complex as a result of dehydration and the colour of the residue changed to yellow. The deportonated ligand also coordinates with Mn(III) acetate and forms *bis*-chelates of general formula $[MnL_2(OAc)X]$ (X = H_2O/Py; LH = ligand).

Magnetic moment and electronic spectra: The effective magnetic moment of Cr(III) complexes were observed in the range of 3.45-3.48 BM in contrast to the spin-only value of 3.87 BM for d^3-system[7] indicating appreciable spin-orbit coupling and probably distortion of the octahedral symmetry. The reflectance spectra of complexes display two intense bands at 17600-17650 and 24790-25400 cm^{-1} assigned to $^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$ transitions and a shoulder at 36700-37000 cm^{-1} due to $^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$ transition for octahedral structure[8]. Broomhead *et al.*[9] have observed two *d-d* transition bands in the same region as observed in the present for Cr(III) chelates. The value of crystal field parameters were obtained using

TABLE-1
ANALYTICAL, PHYSICAL AND ELECTRONIC SPECTRAL DATA OF COMPLEXES

S. No.	Complex/(colour)	μ_{eff} (BM)	Ligand field parameters			Analysis found/calcd (%)			
			Dq (cm^{-1})	B	β	C	H	N	M
1	$[CrA_2(OAc)(H_2O]\cdot 2H_2O$ (Green)	3.46	1760	733	0.71	39.51 (39.48)	4.32 (4.20)	20.31 (20.47)	9.81 (9.50)
2	$[Cr(A)(OAc)(OH)(H_2O)_2]\cdot 2H_2O$ (Greenish yellow)	3.45	1765	735	0.71	3.68 (3.69)	4.56 (4.60)	14.51 (14.32)	13.52 (13.30)
3	$[CrA(OAc)Cl(H_2O)_2]\cdot 2H_2O$ (Green)	3.48	1750	730	0.70	29.32 (29.30)	4.40 (4.39)	13.70 (13.69)	12.80 (12.69)
4	$[CrB_2(OAc)(H_2O)]\cdot 2H_2O$ (Greenish yellow)	3.48	1755	731	0.70	37.25 (37.17)	4.32 (4.30)	19.52 (19.27)	9.11 (8.95)
5	$[CrC_2(OAc)(H_2O)]\cdot 2H_2O$ (Greenish yellow)	3.44	1760	733	0.71	40.01 (39.53)	4.45 (4.44)	18.50 (18.45)	9.01 (8.56)
6	$[CrD_2(OAc)(H_2O)]\cdot 2H_2O$	3.47	1765	735	0.71	35.00 (34.84)	3.08 (3.01)	20.35 (20.32)	9.55 (9.43)
7	$[MnA_2(OAc)(Py)]$ (Brown yellow)	4.85	–	–	–	48.01 (48.00)	3.85 (3.82)	23.11 (22.91)	9.86 (9.56)
8	$[MnB_2(OAc)(Py)]$ (Brown yellow)	4.56	–	–	–	45.46 (45.32)	4.01 (3.94)	20.40 (20.68)	9.23 (9.03)
9	$[MnC_2(OAc)(H_2O)]$ (Brown-yellow)	4.87	–	–	–	42.21 (41.81)	3.92 (4.00)	19.82 (19.52)	10.00 (9.58)

*: HA = 1-*para*-tolyl-tetrazoline-5-thione (*p*-CH_3-$C_7H_5N_4S$), HB = 1-paramethoxy-tetrazoline-5-thione (*p*-CH_3O-$C_7H_5N_4S$), HC = 1-*para*-ethoxy-tetrazoline-5-thione (*p*-CH_3CH_2O-$C_7H_5N_4S$), HD = 1-*para*-hydroxyl-tetrazoline-5-thione (*p*-OH-$C_7H_5N_4S$).

Tanabe-sugano diagrams for d^3-system[10] and found to be $\nu_1/\nu_2 = 0.71$; Dq/B = 2.41, B = 735 cm^{-1}, Dq = 1760 and β = 0.70 indicating octahedral stereochemistry around Cr(III) ion[11]. The appearances of ν_3 at 37000 cm^{-1} as compared to calculated value 37960 cm^{-1} indicates that the environment in complexes is not exactly octahedral. The low value of β indicates that all the derivatives of 1-substituted tetrazoline-5-thione are strong chelating ligands and the expansion of d electrons charge on complexation reduces the inter electronic repulsions having high degree of covalent character in Cr-L sigma bond.

The magnetic moment value of Mn(III) complexes were found to be 4.87 BM indicating $T^3_{2g}e_g$ configuration for octahedral surrounding is subject to a Jahn-Teller distortion[12]. The three electronic spectral bands at 13460, 17600, 20800, 36100 cm^{-1} are consistent with hexa coordinate octahedral environment around Mn(III) ion[13]. The first band (13460 cm^{-1}) assignable to $^5B_{1g} \rightarrow {}^5E_g$ is most convincing evidence for D_{4h} symmetry. The other bands are attributed due to $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$, respectively. The higher energy band (36100 cm^{-1}) in the complexes may be assigned to charge transfer band. Moreover, it is difficult to interpret in all their details the spectra of octahedral Mn(III) presumably because both steric and dynamic Jahn-

Teller effects perturbs the simple picture based on fixed and perfect octahedral symmetry[12]. However, on the basis of magnetic moment value and electronic spectral bands position distorted octahedral structure all Mn(III) complexes may be tentatively assigned[14].

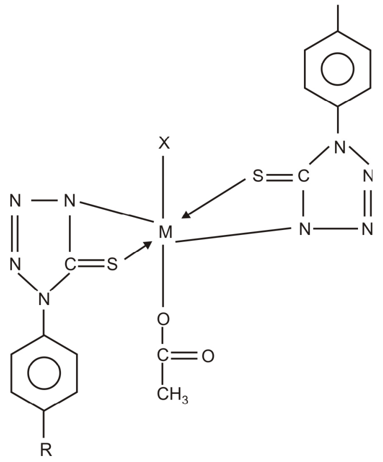
IR Spectra: A close examination of infrared spectra of ligands and complexes indicates simultaneous metal-S and metal-N bonding in all complexes. The ν(S-H) 2550 and ν(N-H) 3145 cm^{-1} bands of ligands disappears from the spectra of complexes indicating deprotonation of imino proton on complexation and formation of metal-N bond. All ligands contain a thioamide group and give rise to four characteristic thioamide bands[15-17] in the region of 1500 (band I), 1300 (band II), 1000 (band III) and 800 cm^{-1} (band IV). Considering normal coordinate analysis (NCA) of thioamides performed by Agarwala *et al.*[18] and Suzuki[19], these bands are mixed band having contributions from ν(C=S), ν(C-N), δ(C-H) and δ(N-H) modes. The blue shift of thioamide band II (30 cm^{-1}), red shift of band IV (40-60 cm^{-1}), band III (15-30 cm^{-1}) and band I (15-20 cm^{-1}) indicates simultaneous metal-S and metal-N bond on complexation[20-22]. These observations are further supported by the presence of new bands ν(M-N) (425 cm^{-1}) and ν(M-S) (370-341 cm^{-1}). The band in the complexes observed at 410 cm^{-1} is stonger in intensity than ν(M-N) band.

The additional bands for the complexes were observed in the region 1585-1567 and 1367-1352 cm^{-1} attributable to ν_{as} (COO) and ν_s (COO) modes of vibrations of the acetato group, respectively. The frequency difference between symmetric and antisymmetric stretches (Δν) *ca.* 210 cm^{-1} is typical monodentate coordination of acetato group[23,24].

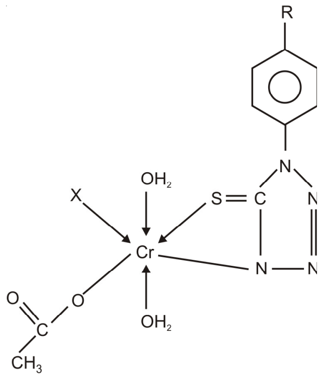
The presence of coordinated pyridine (S. No. 7 and 8) is indicated by the four ν(C=C) and ν(C=N) pyridine skeletal bands observed at 1610-1590 (band I), 1580-1560 (band II), 1490-1455 (band III) and 1445-1430 (band IV). On coordination to Mn(III), these bands are not shifted appreciably but in-plane-ring deformation (604 cm^{-1}) and out-of-plane-ring deformation (405 cm^{-1}) are shifts to higher frequencies 15-20 and 20-30 cm^{-1}, respectively[24] indicating pyridine nitrogen coordinations. The non-ligand bands at 3460, 1605 and 810 cm^{-1} in aquo-complexes assigned to ν(H_2O), δ(H_2O) and π(H_2O) of coordinated water molecules[25].

^{1}H NMR spectra: All complexes display broad multiplet in the region δ 7.42-7.74 ppm due to phenyl protons in complexes. The broad nature of peak may be due to large quadrupole resonance broadening effect of tetrazoline nitrogen atoms[26]. The resonances due to imino proton in the ligands observed at δ 1.25 ppm is absent in the spectra of complexes suggesting the formation of metal-N bond and deportonation of N-H group on complexation. The methoxy proton observed as a sharp singlet at δ 3.74 ppm in complexes concides with that of methoxy group proton in literature[27]. The signal at δ 2.4 ppm assigned to methyl proton of coordinated ligand.

The resonances in the region 7.72, 8.07 and 8.81 ppm assignable to the proton of the pyridine ligand along with the resonances due to aromatic protons. The pyridine proton resonances exhibited down field (S. No. 7) as compared to that in free ligand indicate the complexation of pyridine nitrogen atom with metal centre[28]. All aquo complexes exhibit singlet signal at δ 1.31 ppm which corresponds to two protons and another multiplet at δ 2.1 ppm corresponding to two protons. This is due to 4-protons of the two coordinated water molecules[29]. Which are in two different magnetic environment. These observation are consistent with the conclusion drawn from IR spectra. Thus, the following distorted octahedral structure of complexes may be assigned.



(X = H_2O/Py; M = Cr/Mn
R = CH_3-; CH_3O-, CH_3CH_2O-, OH-)
(Tentative dist. Oh-str.)



(X = Cl/OH; R = CH_3-,
CH_3O-, CH_3CH_2O-, -OH)
(Dist. Oh-str.)

REFERENCES

1. R.N. Pandey, L.M.R. Choudhary, P. Sharma, A.N. Sahay and R.N. Sharma, *Indian J. Chem.*, **32A**, 450 (1993).
2. R.N. Pandey and S. Kumar, *J. Indian Chem. Soc.*, **70**, 563 (1993).
3. R.N. Pandey, 34th IUAC Congress, Beijing (China), Section-3, Paper No. T-3519 (1993).
4. E. Lieber and J. Ramchandran, *Can. J. Chem.*, **37**, 101 (1959).
5. C.T. Christensen, *Z. Anorg. Chem.*, **27**, 325 (1901).
6. G. Brauer, A Hand Book of Preparative Inorganic Chemsity, Vol. 11, p. 1371, Academic Press, New York (1965).
7. B.N. Figgis, Introduction to Ligand Fields, Inc. John Wiley, New York, p. 278 (1966).
8. B. Singh and R.V. Choudhary, *Indian J. Chem.*, **13**, 926 (1975).
9. J.A. Broomhead, M. Dwyer and N. Maguire, *Inorg. Chem.*, **7**, 1388 (1970).
10. Y. Tanabe and S. Sugano, *J. Phys. Soc. (Japan)*, **9**, 753 (1954).
11. H.S. Verma, Anangal, R.C. Saxena and J.L. Vats, *J. Indian Chem. Soc.*, **59**, 1184 (1982).
12. J.P. Fackler Jr., and I.D. Chawla, *Inorg. Chem.*, **3**, 1130 (1964).
13. D.H. Nevess and J.C. Dabroviak, *Inorg. Chem.*, **15**, 129 (1976).
14. R Sarsawat and V.B. Rana, *J. Indian Chem. Soc.*, **75**, 493 (1998).
15. C.N.R. Rao and R. Venkataraghavan, *Spectrochim. Acta*, **18**, 541 (1962).

16. C.N.R. Rao, R. Venkataraghavan and T.R. Kasturi, *Can. J. Chem.*, **42**, 36 (1964).
17. R.N. Pandey, H.H. Khan, H.N. Tiwari and B. Singh, *Indian J. Chem*., **21A**, 315 (1982).
18. U. Agarwala and P.B. Rao, *Indian J. Pure Appl. Phys*., **7**, 229 (1969).
19. I. Suzuki, *Bull. Chem. Soc. Japan*, **35**, 1419 (1962).
20. R.N. Pandey, R.N. Sharma, L.M.R. Choudhary and Pramila Sharma, *J. Indian Chem. Soc*., **69**, 719 (1992).
21. B. Singh, R. Singh, R.V. Choudhary and K.P. Thakur, *Indian J. Chem*., **11**, 174 (1973).
22. U. Agarwala and B. Singh, *Indian J. Chem*., **7**, 726 (1969).
23. G.B. Deacon and R.J. Philips, *Coord. Chem. Rev*., **33**, 227 (1980).
24. R.J.H. Clark and C.S. Williams, *Inorg. Chem*., **4**, 350 (1965).
25. I. Nakagawa and T. Schimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).
26. E.O. Greaves, C.J.L. Lock and P.M. Maitlis, *Can. J. Chem*., **46**, 3879 (1968).
27. I.C. Douek and G. Wilkinson, *J. Chem. Soc*. *A*, 2604 (1969).
28. O.S. Sisodiya, A.N. Sahay and D.S. Pandey, *Indian J. Chem*., **39A**, 453 (2000).
29. P. Onetal Richard, *Spectrochim. Acta*, **26A**, 659 (1979).

(*Received*: 25 November 2009; *Accepted*: 31 March 2010) AJC-8596