

Synthesis, Characterization and Ligand field Parameters of Some bis-Chelates of Transition Metals(III) Ligated by 2-aminothiophenols

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Abstract

Some bis-chelates of Ti(III), Cr Mn(III) Co(III) and ligated by 2-aminothiophenol have been prepared and investigated using elemental analysis, magnetic moment, conductometric, IR, and UV-Vis spectral data. The ligand acts as bidentate (N,S) and trans-octahedral configuration to all complexes have been assigned.

Key words: transition metals, bis-chelates, 2-aminothiophenol.

Introduction

2-Aminothiophenol has interesting coordination sites and used as ligand by several workers¹⁻³. Coordination can occur either through (a) both nitrogen and sulphur, or (b) through nitrogen only, or (c) through sulphur only. The present communication reports synthesis, characterization and ligand field parameters of Ti(III), Cr(III), Mn(III), Co(III) and Ru(III) chelates of this ligand.

Experimental

All the chemicals used were of A.R. grade or CP grade. The ligand, 2-aminothiophenol (Schuchardt, Munchen) was used after redistillation under reduced pressure. The precursor compounds manganese (III) acetate dehydrate⁴ and chromium (III) acetate

hexahydrate⁵ were prepared by the method reported earlier in the literature. The complexes were prepared using our general method⁶.

1. For $[\text{Ti}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$:
Found(%): C 35.32; H 4.0; N 6.92; Ti 12.28.
Calculated(%): C 35.33; H 3.92; N 6.87; Ti 12.26.
2. For $[\text{CrSC}_6\text{H}_4\text{NH}_2)_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})].2\text{H}_2\text{O}$:
Found(%): C 40.56; H 5.01; N 6.82; Cr 12.62.
Calculated(%): C 40.67; H 5.08; N 6.77; Cr 12.56.
3. For $[\text{Mn}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})]$:
Found(%): C 44.26; H 3.48; N 7.88; Mn 14.81.
Calculated(%): C 44.21; H 3.42; N 7.36; Mn 14.47.
4. For $[\text{Co}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$:
Found(%): C 38.08; H 4.18; N 7.52; Co 15.68.
Calculated(%): C 38.05; H 4.22; N 7.39; Co 15.57.
5. For $[\text{Ru}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$:
Found(%): C 34.25; H 3.40; N 6.72; Ru 24.22.
Calculated(%): C 34.18; H 3.79; N 6.64; Ru 24.14.

The magnetic moment of the complexes were measured at 300K using Gouy balance. The IR spectra of ligand and complexes were recorded by means of Perkin-Elmer 521 spectrophotometer using KBr pellets. Reflectance spectra of the complexes were recorded on a Backman D.U. spectrophotometer attached with a standard reflectance attachment. MgO was used as a references. Molar conductance of the complexes were measure in DMF (10^{-3} M) using Wiss-Werkstatter Weithem obb type conductivity meter.

Result and Discussion

2-Aminothiophenol forms bis-chelates with Ti(III), Mn(III), Co(III), and Ru(III) ions and deprotonation of thiol hydrogen occurs at pH=7.5. The complexes are soluble in dimethyl formamide and are probably monomeric. The analytical data are consistent with the proposed stoichiometries of the complexes. Molar conductivity value in DMF (10^{-3} M) reveal non-electrolytic nature of Cr(III) and Mn(III) and uni-uni (1:1) electrolytic nature for Ti(III), Co(III) and Ru(III) chelates.

Magnetic moment and Electronic spectra :

The magnetic moment of Ti(III) complexes found to be 1.76 BM corresponding to d^1 -configuration of Ti(III). One band at 19610 cm^{-1} with a shoulder at 185520 cm^{-1} indicate an octahedral geometry and assigned to ${}^2T_{1g} \rightarrow {}^2E_g$ transition⁷. The broad nature of band suggest John-Teller distortion as expected in d^1 -complexes. The magnetic moment of Co(III) complexes were observed 0.33 BM due to TIP is in agreement with the result reported earlier⁸. This suggests ${}^1A_{1g}$ ground state with low spin

octahedral configuration.

The magnetic moment of Cr(III) complex (3.68BM) are well within the range reported for high spin octahedral complexes⁹. The visible spectra display three bands at $17310\text{ cm}^{-1}(\nu_1) = {}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$
 $23150\text{ cm}^{-1}(\nu_2) = {}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$
 $36150\text{ cm}^{-1}(\nu_3) = {}^4A_{2g}(F) \rightarrow {}^4T_{1g}(P)$

The ν_1 and ν_2 bands are intense but ν_3 appears as shoulder. The crystal field parameters, $\nu_1/\nu_2=1.33$ $Dq/B=2.56$, $Dq=1702\text{ cm}^{-1}$ and $B=0.64$ are in agreement with the reported values for six coordinated octahedral Cr(III) complexes. The lowering of B value from free ion value (1030 cm^{-1}) suggest strong metal ligand covalent bonding. The magnetic moment of Ru(III) complex was observed to be 1.68BM which indicates one unpaired electron and ${}^2T_{1g}$ ground state configuration. The electronic spectral band at 20700 cm^{-1} (${}^2T_{1g} \rightarrow {}^2A_{2g}$) for low spin octahedral structure¹⁰. The other two spin-forbidden bands are observed at 16500 and 22700 cm^{-1} and ligand field parameters, $Dq/B=5.10$, $Dq=3925\text{ cm}^{-1}$ are in good agreement with the available literature for low-spin octahedral structure¹⁰. The magnetic moment of Mn(III) chelates are found to be 4.80 BM indicating ground term 5D and $T^3_{2g\text{eg}}$ configuration for octahedral surrounding is subject to John-Teller distortion¹¹. The electronic spectral bands at 13200 , 17600 , 19500 and 36100 cm^{-1} are consistent with hexa coordinated octahedral environment around Mn(III) ion¹². The first band (13200 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 ${}^5B_{1g} \rightarrow {}^5E_g$

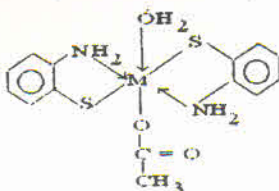
respectively. The higher energy band (36100 cm^{-1}) in the complex may be assigned to CT band. Moreover, it is very difficult to interpret in all their detail the spectra of octahedral Mn(III) because both steric and Dynamic Jahn-Teller effect perturb the simple picture based on fixed and perfect octahedral symmetry¹¹. However, on the basis of magnetic moment value and electronic spectral bands positions, distorted octahedral structure of Mn(III) chelates may be tentatively assigned¹³.

IR Spectra :

The IR spectrum of 2-aminothiophenol shows $\nu_{\text{sym}} \text{NH}_2$ at 33 cm^{-1} and $\nu_{\text{asym}} \text{NH}_2$ at 3460 cm^{-1} . These bands red shift to lower frequency and observed at $3300\text{--}3310\text{ cm}^{-1}$ and $3400\text{--}3410\text{ cm}^{-1}$ on complexation to M(III) ions respectively. This indicate formation of metal-N bond which is further supported by new

bands of medium intensity at $530\text{--}567\text{ cm}^{-1}$ (table 1) due to metal-N stretching modes¹⁴. The $\nu_{\text{S-H}}$ band is present at 2560 cm^{-1} in the spectrum of the free ligand, does not appear in the spectra of all complexes indicating coordination of the metal through deprotonated thiol sulphur³. A weak broad band near $340\text{--}370\text{ cm}^{-1}$ in far IR spectra of complexes supports the formation of metal-sulphur bond and is assigned due to metal sulphur stretching mode. The non-ligand bands for Cr(III) and Mn(III) chelates in the region $1580\text{--}1560\text{ cm}^{-1}$ and $1360\text{--}1350\text{ cm}^{-1}$ attributable to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}} \text{COO})$ modes of vibrations of acetato group respectively. The frequency difference between symmetric and anti symmetric ($\Delta\nu$) Ca. 210 cm^{-1} is typical mono dentate coordination of acetato group¹⁵.

Thus on basis of aforesaid observations the following distorted octahedral structure of all complexes may be tentatively assigned :



dist- Oh structure of $[\text{Mn}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})]$ $\text{M} = \text{Cr(III)}/\text{Mn(III)}$

Table 1

Complex	Deff. (BM)	Molar conductivity $^{\circ}\Omega^{-1}\text{cm}^{-1}\text{mol}^{-1}$	Ligand field parameters			IR Bands (cm^{-1})	
			Dq(cm^{-1})	B(cm^{-1})	B	$\nu_{\text{M-N}}$	$\nu_{\text{H-S}}$
1. $[\text{Ti}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$	1.76	78.34	-	-	-	530m	360w
2. $[\text{CrSC}_6\text{H}_4\text{NH}_2)_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})].2\text{H}_2\text{O}$	3.68	90.32	1702	733	0.64	530m	420w
3. $[\text{Mn}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{CH}_3\text{COO})(\text{H}_2\text{O})]$	4.80	632	-	-	-	530m	470w
4. $[\text{Co}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$	0.33	3.62	1748	437	-	540m	340w
5. $[\text{Ru}(\text{SC}_6\text{H}_4\text{NH}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$	1.68	85.86	3925	775	-	567m	370w

References

1. R. John Wasson, J. Shirley Wasson and M. Gerald Wattermann, *Inorg. Chem.* 9, 1576 (1970).
2. L.F. Larkworthy, J.M. Murphy and D.J. Phillips, *Inorg. Chem.* 7, 1436 (1968).
3. B. singh and R.V. Choudhary, *Indian J. Chem. Vol 13.* 926 (1975).
4. C.T. Christensen Z., *Inorg. Chem.* 27, 325 (1901).
5. G. Brayer, 'A handbook of Preparative Inorganic Chemistry, Vol. 11, P. 1371, Academic Press, New York (1965).
6. R. N. Pandey, Abhijeet Anand, R.K. Singh and Amaresh Kumar, *Asian J. Chem.* Vol. 22(No 7), 5601 (2010).
7. R.N. Pandey, R.K. Singh and Kalpana Shahi, *Asian J. Chem.* Vol. 23(No.6), 2739 (2011).
8. R.N. Pandey, R.K. Singh, Priya and Manoj Ranjan, *Asian J. Chem.* Vol. 22(No.7), 5595 (2010).
9. B.N. Figgis, "Introduction to Ligand Fields", Inc, John Wiley, New York P. 278 (1966).
10. C.L. Jain, P.N. Mundley, Y. Kumar and P.D. Sethi, *J. Indian Chem. Soc.* 66, 431 (1989).
11. J.P. Fackler Jr. and I.D. Chawala, *Inorg. Chem.* 3, 1130 (1964).
12. D.H. Neveess and J.C. Dabrovick, *Inorg. Chem.* 15, 129 (1976).
13. R. Saraswat and V.B. Rana, *J. Ind. Chem. Soc.* 75, 129 (1976).
14. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn., John Wiely and Sons, New York, P. 199 (1986).
15. G.B. Deacon and R.J. Philips. *Coord. Chem. Rev.* 33, 227 (1980).