Asian Journal of Chemistry Vol. 9, No. 2 (1997), 275–277

Mixed Chelates of Chromium(III) containing Salicylaldehyde Thiosemicarbazone, Glycine and Nitrogen, Oxygen or Sulphur Donor Ligands

D.S. NAIK and K.M. PUROHIT*
Department of Chemistry
Regional Engineering College, Rourkela-769 008, India

Mixed chelates of the type [Cr(Stsc)(Gly)L] (where H_2Stsc = salicylaldehyde thiosemicarbazone, GlyH = glycine and L = γ-picoline (γ-pic), isoquinoline (IQ), pyridine-N-oxide (PyNO), triphenyl-phosphene oxide (TPPO) or thiourea (Tu) have been synthesised and characterised by elemental analyses, molar conductance, magnetic moment, infrared and electronic spectral data. The complexes are paramagnetic, non-electrolyte and have octahedral geometries.

INTRODUCTION

In continuation of our earlier studies on mixed chelates[1–5] we now report the preparation and characterisation of some mixed chelate chromium(III) complexes containing salicylaldehyde thiosemicarbazone (H_2Stsc), glycine (GlyH) and γ-picoline (γ-pic)/isoquinoline (IQ)/pyridine-N-oxide (PyNO), triphenyl phosphine oxide (TPPO) and thiourea (Tu).

EXPERIMENTAL

All chemicals used were of A.R. grade. Salicylaldehyde thiosemicarbazone was prepared by known method[6]. All other ligands were used as such.

[Cr(Stsc)(Gly)*(H_2O)]*: Aqueous solution of chromium(III) nitrate, ethanolic solution of salicylaldehyde thosemicarbozone and aqueous solution of glycine were mixed in 1 : 1 : 1 molar ratio. To this reaction mixture was added a dilute solution of ammonium hydroxide dropwise with stirring till the mixture attained a pH *ca.* 8. The mixture was digested on a water bath for 20 min. The solid complex obtained was filtered, washed with 50% ethanol followed by ether and dried in vaccum.

[Cr(Stsc)(Gly)L]: (where L = γ-pic, IQ, PyNO, TPPO and Tu.) [Cr(Stsc)-(Gly)H_2O] was treated separately with γ-pic, IQ, PyNO, TPPO and Tu, in 1 : 1 molar ration in ethanolic medium. The resulting mixture was refluxed for 2 h. The separated complexes were filtered under suction and washed with ethanol, ether and dried under reduced pressure.

Chromium and sulphur were estimated by standard methods.[7] Carbon and hydrogen were estimated using semimicro methods, Molecular weight was determined by using Rast's method. The magnetic susceptibilities were determined at room temperature using solid specimen and Gouy's balance with Hg [$Co(NCS)_4$] as calibrant. Diamagnetic corrections were made using Pascal's constants. The molar conductances of a 10^{-3} m solution was measured using a systronic direct reading conductivity meter 303. IR spectra were recorded on a Shimadzu-480A spectrophotometer and electronic spectra were recorded on a Shimadzu 160A spectrophotometer. The characterisation data are presented in Table-1.

TABLE-1
ANALYTICAL DATA OF Cr(III) COMPLEXES

Complex	% Analysis, Found (Calcd.)				
	Cr	C	H	N	S
[Cr(Stsc)(Gly)(γ-Pic)]	11.97 (12.90)	45.72 (47.80)	4.30 (4.72)	12.68 (14.02)	7.23 (7.52)
[Cr(Stsc)(Gly)(IQ)]	10.27 (11.25)	48.47 (51.52)	4.02 (4.32)	14.20 (15.15)	5.98 (6.92)
[Cr(Stsc)(Gly)(PyNO)]	11.82 (12.14)	43.72 (44.86)	3.89 (4.20)	16.00 (16.35)	6.88 (7.47)
[Cr(Stsc)(Gly)(TPPO)]	7.66 (8.51)	55.65 (56.95)	3.98 (4.58)	8.87 (9.16)	5.02 (5.23)
[Cr(Stsc)(Gly)(Tu)]	11.39 (12.71)	35.00 (35.20)	3.90 (4.15)	19.63 (20.53)	15.22 (15.64)

RESULTS AND DISCUSSION

The elemental analyses correspond to the stoichiometries of the compounds as indicated in Table-1.

The molecular weight data indicate the compounds to be monomeric. The low molar conductance values indicate their non-electrolytic nature. Magnetic susceptibility measurements suggest that all the complexes are paramagnetic with three unpaired electrons as expected for a d^3 system of chromium(III).

The infrared spectra of the complexes revealed that both the chelates were coordinated to the metal ion. Salicylaldehyde thiosemicarbazone behaves as a dibasic tridentate ligand. Deprotonation of phenolic-OH and coordination through oxygen was indicated by the occurence of ν(C—O) at *ca.* 1350 cm^{-1}. A sharp band at *ca.* 1600 cm^{-1} due to ν(C—N) of the Schiff base indicated the coordination through azomethine nitrogen. The Schiff base had undergone keto ⇄ thioenol tautomerism in alkaline medium and subsequent coordination to the metal ion by the deprotonation of C—SH group was evident by the absence of bands in the region 2800–2650 cm^{-1} in all the complexes[8]. A new band at 660 cm^{-1} characteristic[9, 10] of ν(C—S) also appeared in the complexes. This was further supported by the bands *ca.* 1490 cm^{-1} in all the complexes due to ν(C═N) formed by thioenolisation of the Schiff base in the alkaline medium. The above facts clearly indicate that salicylaldehyde thioemicarbazone behaves as a binegative tridentate (O^-, N, S^-) ligand. It has been found[11] that bidentate glycine absorbs at 1643 cm^{-1} unlike either the ionised monodentate which absorbs at 1610 cm^{-1} or the unionised monodentate which absorbs at 1710 cm^{-1}. The bands due to $\nu_{sym}(COO^-)$, $\nu_{asym}(COO^-)$ and $\nu(NH_2)$ at *ca.* 1360, 1650 and 3360 cm^{-1}

respectively indicated that glycine was coordinated to the metal ion as a uninegative bidentate ligand. The presence of coordinated water molecule in aqua complex [Cr(Stsc)(Gly)H_2O] was indicated by the bands observed at *ca.* 830 and *ca.* 3400 cm^{-1}. However these bands due to water molecule are absent and new bands are observed in the complexes containing monodentate ligands. One of the bands of $\nu(C{=}C) + \nu(C{=}N)$ at 1600 cm^{-1} due to γ-picoline and isoquinoline was found to overlap with the band of salicylaldehyde thiosemicarbazone where as the other one was found at *ca.* 1550 cm^{-1}. This suggests the coordination of these ligands through nitrogen atom[12]. The ν(P—O) band observed at 1070 cm^{-1} for triphenylphosphine oxide indicates participation of its oxygen atom in coordination[13] (1195 cm^{-1} in free ligand). Appearance of bands at 1210 cm^{-1} and 835 cm^{-1} due to ν(N—O) and δ(N—O) respectively indicate the bonding of pyridine-N-oxide through oxygen atom ν(N—O) δ(N—O) at 1265 cm^{-1} and 840 cm^{-1} in free ligand[14]. A negative shift of 20–25 cm^{-1} $\nu(C{=}S)$ in the thiourea complex indicates that thiourea is coordinated through sulphur atom to the metal ion (685 cm^{-1} in free ligand).

The electronic spectra of the complexes exhibit two bands in the region 19200–18500 and 23400–23200 cm^{-1}. These can be assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}$ transition respectively which are typical of octahedral coordination[16].

ACKNOWLEDGEMENTS

The authors are thankful to Head, Dept. of Chemistry and Principal, Regional Engineering College, Rourkela for facilities. One of the authors (DSN) thanks the management of Rourkela Steel Plant, Rourkela for kind permission.

REFERENCES

1. S. Mishra and K.M. Purohit, *J. Indian Chem. Soc.*, **65**, 588 (1988).
2. D.S. Naik and K.M. Purohit, *Acta Cienc. Indica*, **20C**, 66 (1994).
3. _______, *J. Inst. Chemists (India)*, **66**, 99 (1994).
4. _______, *Asian J. Chem.*, **8**, 485 (1996).
5. _______, *Asian J. Chem.*, **8**, 315 (1996).
6. B. Beecroft, M.J.M. Campbell and R. Grzeskowiak, *J. Inorg. Nucl. Chem.*, **36**, 55 (1974).
7. A.I. Vogel, A Text Book of Quantitative Analysis, 3rd Edn., Longmans, London (1962).
8. S.N. Poddar and N. Saha, *J. Indian Chem. Soc.*, **52**, 57 (1975).
9. N.B. Golthup, L.H. Daly and S.E. Wiberly, Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, p. 311 (1964).
10. K.K. Arvindakshan and C.G.R. Nair, *Indian J. Chem.*, **20A**, 684 (1981).
11. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley, New York, p. 310 (1978).
12. A.K. Das and D.V. Raman Rao, *Chem. Ind. (London)*, 186 (1973).
13. L. Donald, *J. Inorg. Nucl. Chem.*, **31**, 236 (1969).
14. I.S. Ahuja and P. Rastogi, *J. Inorg. Nucl. Chem.* **32**, 208 (1970).
15. M.D. Sardar Hassain, S.C. Chakraborty, G.L. Thambe and A.S.R. Murthy, *Indian J. Chem.*, **25A**, 737 (1986).
16. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, p. 277 (1968).

(*Received*: 9 September 1996; *Accepted*: 28 November 1996) AJC-1193