

Synthetic and structural studies of the transition metal complexes of manganese-, cobalt- and zinc(II) with *m*-nitrobenzaldehydethiosemicarbazone and some neutral ligands

R. K. Parihari, R. K. Patel and R. N. Patel*

Department of Chemistry, Regional Engineering College, Rourkela-769 008, India

Manuscript received 2 July 1999 revised 27 December 1999, accepted 26 February 2000

Complexes of the type MLL'_2X_2 , where $M = Co^{II}, Mn^{II}$, $L = m$ -nitrobenzaldehydethiosemicarbazone (NBTS), $L' =$ quinoline, isoquinoline, pyridine and γ -picoline, $X = Cl^-, Br^-$ and MLL'_1X_2 , where $M = Zn^{II}$ have been synthesized. The Co^{II} and Mn^{II} complexes are paramagnetic and that of Zn^{II} diamagnetic. The ligand coordinates through N and S atoms. Octahedral geometry is suggested for Mn^{II} and Co^{II} complexes and tetrahedral for Zn^{II} complex.

Transition metal complexes with chelating ligands containing sulfur and nitrogen as donor atoms have attracted special attention¹. We report here some new complexes of Mn^{II} , Co^{II} and Zn^{II} with the ligand *m*-nitrobenzaldehydethiosemicarbazone (NBTS) and some neutral ligand.

Results and Discussion

The analytical and physical data of the complexes are given in Table 1. The low molar conductance values ($4.2-8.3 \Omega^{-1} cm^2 mol^{-1}$) for the complexes indicate their non-electrolyte nature. The elemental analysis data suggest the formula as MLL'_2X_2 , where $M = Mn^{II}, Co^{II}$ and MLL'_1X_2 , where $M = Zn^{II}$, $L = NBTS$, $L' =$ neutral ligand, $X = Cl^-, Br^-$. The molecular weight (Rast) data suggest the monomeric nature of the complexes.

Table 1. Analytical and physical data of the complexes*

Compd	Colour	M p °C	Metal % Found(Calcd)
Ligand (NBTS)(C ₈ H ₈ N ₄ O ₂ S)	Yellow	246	
[Mn(NBTS)(γ -pic) ₂ Cl ₂]	White	260	10.94(10.24)
[Mn(NBTS)(Qn) ₂ Cl ₂]	Buff	280	9.03(8.98)
[Mn(NBTS)(Py) ₂ Cl ₂]	Red	260	11.00(10.81)
[Mn(NBTS)(γ -pic) ₂ Br ₂]	Red	>300	8.94(8.78)
[Mn(NBTS)(Qn) ₂ Br ₂]	Pink	>300	8.01(7.87)
[Mn(NBTS)(Py) ₂ Br ₂]	Yellow	>300	9.60(9.20)
[Co(NBTS)(γ -pic) ₂ Cl ₂]	Pink	250	11.21(10.90)
[Co(NBTS)(Qn) ₂ Cl ₂]	Pink	255	10.01(9.62)
[Co(NBTS)(γ -pic) ₂ Cl ₂]	Purple	250	11.21(11.50)
[Co(NBTS)(γ -pic) ₂ Br ₂]	Violet	>275	9.86(9.36)
[Co(NBTSC)(Qn) ₂ Br ₂]	Blue	>275	8.61(8.40)
[Co(NBTSC)(Py) ₂ Br ₂]	Purple	>275	10.10(9.80)
[Zn(NBTSC)(γ -pic)Cl]	White	>250	16.0(15.63)
[Zn(NBTSC)(Qn)Cl]	White	>250	14.59(14.39)
[Zn(NBTSC)(Py)Cl]	White	>250	16.48(16.18)

*All complexes gave satisfactory C, H, N, S and Cl⁻/Br⁻ analyses, Py = pyridine, Qn = quinoline, γ -pic = γ -picoline

The ligand shows IR bands at ~ 3350 and $3480 cm^{-1}$ due to NH_2 group of the thiosemicarbazones². The ligand bands at $3100-3040 cm^{-1}$ (aromatic C-H) remain unchanged in the complexes indicating the presence of free NH_2 group. The broad ligand band at $\sim 1630 cm^{-1}$ (C=N of azomethine N) exhibits a negative shift by $15-25 cm^{-1}$ in the complexes, indicating the coordination of metal through azomethine nitrogen³.

The ligand band at $\sim 1395 cm^{-1}$ is blue-shifted by $80-85 cm^{-1}$ in the complexes indicating the coordination through S-atom of C=S group⁴. The ligand bands at ~ 1540 and $\sim 1340 cm^{-1}$ (nitrogen at *meta*-position of benzene ring) remain unchanged in the spectra of the metal complexes. The shifting of the band⁵ at $\sim 780 cm^{-1}$ to the lower frequency by $50-60 cm^{-1}$ further suggests the coordination of C=S group.

The Mn^{II} complexes show electronic spectral bands at 13500 , 16000 and $19000 cm^{-1}$, which can be assigned to transitions ${}^6A_{1g} \rightarrow {}^4T_{1g} ({}^4G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g} ({}^4G)$ and ${}^6A_{1g} \rightarrow {}^4T_g {}^4A_{1g} ({}^4G)$, respectively. These transitions and magnetic moment values ($5.9-6.1$ B.M.) suggest high-spin octahedral geometry around the metal ion. The bands at $8800-9120$ and $18100-18500 cm^{-1}$ of the Co^{II} complexes may be assigned to the transitions ${}^4T_{1g} (F) \rightarrow {}^4T_{2g} (F) \gamma_1$ and ${}^4T_{1g} (F) \rightarrow {}^4A_{2g} (F) \gamma_2$, suggesting octahedral geometry⁶. The magnetic moment values ($4.01-4.38$ B.M.) support the octahedral geometry for the Co^{II} complexes⁷. A tetrahedral geometry is suggested for the Zn^{II} complexes⁸.

Experimental

All chemicals used were of A.R. grade. The ligand

(NBTS) was prepared by reacting thiosemicarbazide (0.1 mol) dissolved in hot water in presence of glacial acetic acid (~3 drops) and sodium acetate solution with a solution of *m*-nitrobenzaldehyde (0.1 mol) in ethanol. The mixture was stirred for 0.5 h and the resulting light yellow crystalline solid was washed with water, dried (80–100°) and crystallised from methanol, m.p. 246°. It was found insoluble in water but soluble in a few common organic solvents.

The complex was prepared by refluxing a mixture of ethanolic solution of the metal salts, NBTS and pyridine, quinoline, isoquinoline and γ -picoline in 1 : 1 : 2 molar ratio for 0.5 h and the resulting solid was washed with ethanol and dried under reduced pressure.

The metals were analyzed by standard procedure. C, H, N were analyzed by using a CE-440 analyzer. The molar conductance (10^{-3} M nitrobenzene) was measured on a Systronic 303 conductivity bridge. IR spectra were recorded on an Unicam sp-200 spectrophotometer and electronic spectra on an Unicam sp-500 spectrophotometer.

Magnetic susceptibility was measured at room temperature by Guoy's method using diamagnetic correction with Pascal constant.

References

1. S. Padhye and G. B. Kauffman, *Coord. Chem. Rev.*, 1985, **127**, 63; S. D. Dhunwad, K. B. Gudasi, T. R. Goudar, C. T. Goudar and M. P. Chitnis, *Indian J. Chem., Sect. A*, 1995, **34**, 38.
2. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd. ed., Wiley Interscience, New York, 1978; J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", 3rd. ed., Prentice-Hall of India Ltd., New Delhi, 1974.
3. B. Samvel, R. Smaith, C. Sumeford and K. Wade, *J. Chem. Soc. (A)*, 1970, 2019.
4. G. B. Aitken, J. L. Dumcam and G. P. Mcquillen, *J. Chem Soc. (A)*, 1971, 2965.
5. M. L. Patel and P. B. Jani, *J. Indian Chem. Soc.*, 1986, **63**, 276.
6. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968; A. Razik and A. K. A. Hadi, *Transition Met. Chem.*, 1994, 19.
7. B. N. Figgis, "Introduction to Ligand Field", Wiley Eastern, New Delhi, 1976.
8. B. M. Keshari and L. K. Mishra, *Indian J. Chem., Sect. A*, 1981, **20**, 883.