

Synthesis, Characterisation of Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) Chelates of Monoprotic Tridentates Possessing N,N,O Moiety

ANIL BHANDARI†, ANJU SHARMA‡, VIMLA CHOUDHARY
and SHOBHA SHARMA*

Department of Chemistry, J.N.V. University, Jodhpur-342 001, India

Solid chelates of Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) with *o*-(N-pyridine-2-methyl imino) benzoic acid (HPB) and β -(N-pyridine-2-methyl imino) propanoic acid (HPP) have been synthesised and characterized by physico-chemical techniques. The ligand acts as monoprotic, tridentate ligand coordinating through nitrogen and oxygen donor sites. The complexes have 1 : 2 (metal-ligand) stoichiometry, in which the bivalent metal showed six coordination number. Magnetic data coupled with electronic and ligand field parameters suggest an octahedral geometry for these chelates.

Key words: Synthesis, Characterization, Cr(II), Mn(II), Co(II), Ni(II), Cu(II), Chelates, Monobasic tridentate ligands.

INTRODUCTION

A perusal of the literature¹⁻³ revealed that no work has been done on Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) with *o*-(N-pyridine-2-methyl imino) benzoic acid (HPB) and β -(N-pyridine-2-methyl imino) propanoic acid (HPP). Hence, the same was undertaken and its findings are reported in the present paper. A variety of polydentates and their metal chelates have been studied in these laboratories⁴⁻⁶.

EXPERIMENTAL

Synthesis of ligand: The ligands HPB and HPP were synthesised by condensation of 2-acetyl pyridine with *o*-amino benzoic acid or β -alanine respectively in presence of a drop of piperidine as the condensing agent. On refluxing the equimolar ethanolic solution of the reagents for 3-4 h, the pale yellow and lemon yellow products were filtered hot, concentrated and cooled when pale yellow (HPB) and lemon yellow (HPP) crystals were obtained. These were recrystallised from ethanol. The authenticity and purity of the ligands were established by elemental analysis, molecular mass, electronic, IR and ¹H NMR spectral data.

HPB: m.p. 210°C. Found: C, 69.90; H, 4.97 and N: 11.46%; calcd. for C₁₄H₁₂N₂O₂: C, 70.00; H, 5.00 and N, 11.66% .

HPP: m.p. 187°C. Found: C, 62.33; H, 6.16 and N: 14.52%; calcd. for C₁₀H₁₂N₂O₂: C, 62.5°C; H, 6.25 and N, 14.58%.

†Department of Pharmacy, L.M. College of Science & Technology, Jodhpur, India.

‡Department of Chemistry, Government College, Nagaur, India.

The apparatus and chemicals employed were the same as reported earlier⁷.

Synthesis of metal-chelates: The solid metal chelates of Cr(II), Mn(II), Co(II), Ni(II) and Cu(II) chelates of HPB or HPP (0.01 mole) solution in 30–50 mL of 80% ethanol and metal(II) acetate (0.005 mole) in 10–15 mole of 80% ethanol were mixed and refluxed in nitrogen atmosphere on steam bath for 3–4 h. The crystalline solid obtained was filtered, washed with ethanol and recrystallised from suitable solvents. (yield 70–75%).

RESULTS AND DISCUSSION

On the bases of elemental analysis and molecular mass (Table-1), it is determined that the solid metal-chelates possess 1 : 2 (metal-ligand) stoichiometry.

TABLE-1
MOLECULAR MASS, ELEMENTAL ANALYSIS AND MAGNETIC MOMENT OF BIVALENT METAL CHELATES OF HPB AND HPP

Compounds	m.w. Found (Calcd.)	% Elemental analysis: Found (Calcd.)				μ_{eff} (BM)*
		Metal	C	H	N	
$\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ (HPB)	230 (240)	—	69.9 (70.0)	4.97 (5.00)	11.48 (11.66)	—
$\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_2$ (HPB)	184 (192)	—	62.33 (62.50)	6.16 (6.25)	14.52 (14.58)	—
$\text{Cr}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2$	514 (530)	8.90 (9.06)	63.21 (63.39)	4.01 (4.15)	10.40 (10.56)	4.20
$\text{Cr}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2)_2$	425 (434)	11.86 (11.98)	55.23 (55.29)	5.02 (5.07)	12.79 (12.90)	4.83
$\text{Mn}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2$	523 (533)	9.47 (9.57)	62.91 (63.03)	3.92 (4.13)	10.37 (10.50)	5.09
$\text{Mn}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2)_2$	429 (437)	12.43 (12.58)	54.74 (54.91)	4.94 (5.03)	12.68 (12.81)	5.61
$\text{Co}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2$	520 (537)	10.14 (10.24)	62.37 (62.57)	3.93 (4.09)	10.26 (10.42)	4.15
$\text{Co}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2)_2$	434 (441)	13.24 (13.38)	54.35 (54.42)	4.84 (4.99)	12.62 (12.69)	4.57
$\text{Ni}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2$	519 (537)	10.06 (10.24)	62.38 (62.57)	3.95 (4.09)	10.34 (1.43)	3.06
$\text{Ni}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2)_2$	437 (441)	13.28 (13.38)	54.34 (54.42)	4.91 (4.98)	12.60 (12.69)	3.20
$\text{Cu}(\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2)_2$	529 (541)	10.66 (10.90)	61.98 (62.11)	3.96 (4.06)	10.05 (10.35)	1.70
$\text{Cu}(\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_2)_2$	434 (445)	14.06 (14.14)	53.88 (53.93)	4.89 (4.94)	12.50 (12.58)	1.79

*Measured at 308 K.

The molar conductance in dioxane was found in the range 4.5 to 15.2 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ suggesting non-electrolytic nature of the metal chelates.

The magnetic moments of Cr(II), Mn(II), Co(II), and Ni(II) (Table-1) indicate their octahedral stereochemistry⁸. In the case of Cu(II) complexes the observed magnetic moments suggest a distorted octahedral geometry in terms of Jahn-Teller effect.

A comparison of IR spectra of the ligands with their bivalent metal-chelates indicated coordination of the ligands through azomethine nitrogen, carboxylic oxygen and pyridine nitrogen in HPB and HPP respectively.

In the IR spectra of HPB and HPP shown, three major peaks were observed in the range 1590-1420, 1650-1500 and 1790-1750 cm^{-1} assignable to pyridine ring nitrogen, $\nu(\text{C}=\text{N})$ and $\nu(\text{COOH})$ respectively.

In the metal chelates of HPB and HPP the band in the region 1790-1750 cm^{-1} disappeared, indicating deprotonation of $-\text{COOH}$ of the ligand molecule due to chelation. However, the spectra of the metal-chelates displayed two new bands in the range 1600-1585 and 1400-1390 cm^{-1} assignable to $\nu_{\text{asym}}(\text{COO}^-)$ and $\nu_{\text{sym}}(\text{COO}^-)$ respectively, indicating involvement of $-\text{COOH}$ in coordination.

In the spectra of metal chelates, the band in the range 1590-1420 and 1650-1500 cm^{-1} decreased appreciably, indicating participation of azomethine nitrogen and pyridine ring nitrogen in chelation. In addition, two new bands appeared in the ranges of 550-520 and 440-400 cm^{-1} assignable to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively.

The absence of an IR band in the range 250-100 cm^{-1} indicated the non-existence of $\text{M}-\text{M}$ band in the complexes.

The electronic spectrum is typical for octahedral coordination observed for Cr(II) complexes corresponded to the transition ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$. The spectra of Mn(II) complexes, which corresponded to the transitions ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{G})$, ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{2g}(\text{G})$ and ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{A}_{1g}(\text{G})$ viz., ν_1 , ν_2 and ν_3 respectively were characteristic of octahedral geometry around the metal ion. The electronic spectra of Co(II) complexes gave three distinct transitions: ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ν_1 ; ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$, ν_2 and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$, ν_3 . These bands were typical for high-spin octahedral Co(II) complexes. The splitting of ν_3 band into two or more compounds in Co(II) complexes was due to lifting of degeneracy of ${}^4\text{T}_{1g}$ level either by the spin-orbital coupling or by the presence of a low-symmetry component in the ligand field; however, the ν_2/ν_1 ratio (2.12-2.15) also confirmed the octahedral geometry.

Spectra of Ni(II) complexes were typical of octahedral coordinated Ni(II) in as much as they exhibited three d-d transition bands, viz., ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}(\text{F})$, ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ corresponding to ν_1 , ν_2 and ν_3 bands. These spectral data were utilized to compute the important ligand field parameters 10 Dq, B and λ using the ligand theory of spin allowed transition in d^8 configuration. The high values of 10 Dq and B are consistent with the nitrogen coordination of the azomethine group⁹. The ratio of ν_2/ν_1 lies between 1.63 and 1.67 as expected for octahedral Ni(II) complexes.

The spectra of Cu(II) complexes corresponded to the transitions ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$

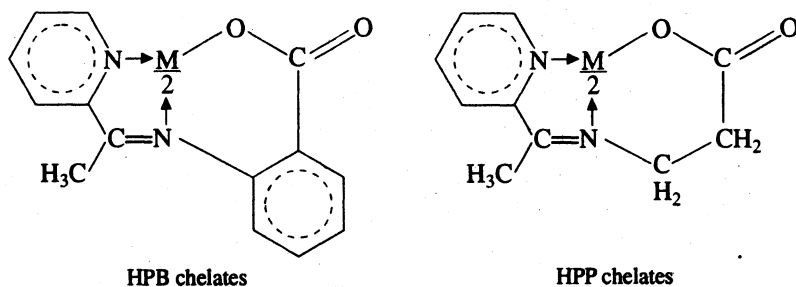
and C → T (charge transfer band). The broadness of the bands and their position indicated distorted octahedral symmetry for these complexes.

To substantiate further bonding in these chelates ¹H NMR spectra of HPB and HPP and their bivalent metal-chelates were recorded in CDCl₃/TMS. The chemical shift values (δ, ppm) of the different protons are as follows.

The signals due to —COOH protons in HPB and HPP appeared at δ 11.8 and 11.4 ppm respectively, but disappeared in the spectra of corresponding metal-chelates. The two signals centred around δ 7.18–7.25 and 8.56–8.60 in free ligands (HPB and HPP) were due to pyridine ring protons. The position of signals due to —CH₂— multiplets in (HPP) and benzene ring multiplets in (HPB) observed at δ 3.07–3.15 and 7.1 ppm remained unchanged in the metal-chelates.

The signals centred in free ligands were due to >C=N and =N—CH₂ protons which were shifted to higher field in metal-chelates indicating involvement of azomethine nitrogen in coordination.

The results obtained conclusively indicate hexa-coordinated octahedral geometry for the bivalent metal-chelates of HPB and HPP (Fig. 1) except the Cu(II) chelates which possess distorted octahedral stereochemistry.



where M = Cr(II), Mn(II), Co(II), Ni(II), or Cu(II).

Fig. 1. Bivalent metal chelates of HPB and HPP

REFERENCES

1. F.A. Cotton, *Progr. Inorg. Chem.*, **7**, 88 (1966).
2. H. Irving and H.S. Rossotti, *J. Chem. Soc.*, 2904 (1945).
3. A. Syamal, *Coord. Chem. Rev.*, **16**, 309 (1975).
4. S. Sharma and A. Sharma, *Oriental J. Chem.*, **16**, 349 (2000).
5. V. Chowdhary, M. Parihar and R.K. Mehta, *Z. Phys. Chem. (Leipzig)*, **271**, 413 (1990).
6. A. Sharma, V. Chowdhary and S. Sharma, *Asian J. Chem.*, **14**, 437 (2002).
7. M. Parihar, V. Gupta, V. Goyal, B.R. Patel and R.K. Mehta, *Nat. Acad. Sci. Lett.*, **13**, 2 (1990).
8. A.B.P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, p. 277 (1968).
9. D.K. Rastogi, S.K. Sahni, V.B. Rana and S.K. Dua, *J. Coord. Chem.*, **8**, 94 (1978)

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