

Synthesis & Structural Studies of 1,3,5-Trisubstitutedphenyl-2S-benzylisobiuret with Oxovanadium(IV), Cobalt(II), Nickel(II) & Copper(II)

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Complexes of oxovanadium(IV), Co(II), Ni(II) and Cu(II) with 1,3,5-trisubstitutedphenyl-2S-benzylisobiuret, $\phi N = C(SCH_2\phi)N(\phi)C(=O)NH\phi$ (TPBB), have been prepared and characterized on the basis of analytical data, molar conductance, magnetic susceptibility, electronic, EPR, infrared spectral and X-ray powder diffraction measurements. Some of these complexes have been subjected to antifungal screening also.

Recently Shoukry *et al.*¹ and Satpathy *et al.*² have isolated complexes with ligands containing S, N and O donor atoms from alkaline and neutral media. The $>N-C-S-$ moiety in these compounds has been shown to be responsible for pesticidal³ and fungicidal activities. A literature survey revealed that there is no previous work on the metal complexes of 1,3,5-trisubstitutedphenyl-2S-benzylisobiuret (TPBB), a ligand containing S, N and O donor sites, with transition metals. In this paper we report the synthesis, structural characterization and antifungal activity of oxovanadium(IV), Co(II), Ni(II) and Cu(II) complexes with the above mentioned ligand.

Materials and Methods

All the chemicals used in this study were BDH reagents or reagents of equivalent grade. TPBB was prepared following the literature procedure for substituted isobiurets⁴, m.p. $230 \pm 1^\circ\text{C}$. [Required for TPBB: C, 74.15; N, 9.61; H, 5.26. Found: C, 74.14; N, 9.70; H, 5.31%].

Synthesis of complexes

The complexes $ML(CH_3COO)_2$ [$M = \text{Co(II), Ni(II)}$] were prepared by the addition of a hot solution of respective metal acetate (1 mmol) in 10 ml of aqueous ethanol to a hot ethanolic solution of the ligand (2 mmol) in 20 ml ethanol with constant stirring. $\text{CoL(CH}_3\text{COO)}_2$ and $\text{CuL(CH}_3\text{COO)}_2$ were precipitated immediately while $\text{NiL(CH}_3\text{COO)}_2$ precipitated on heating on a water bath. All the complexes were digested on a water bath for about 1 hour to complete the reaction. The precipitates thus obtained were filtered, washed repeatedly with water, hot ethanol and finally with ether and dried *in vacuo*. VOL_2SO_4 and $\text{MLCl}_2(\text{H}_2\text{O})_n$ [$M = \text{Co(II), Ni(II)}$ and

Cu(II) ; $n = 1$ or 2] were obtained by mixing together the appropriate metal salt (1 mmol) in 15 ml methanol or ethanol and the ligand (2 mmol) in 15 ml ethanol with constant stirring. The reaction mixture was heated on a water bath and precipitation of complexes was effected by raising the pH to ~ 7 with NaOH solution. The complexes thus obtained were filtered, washed with water, hot ethanol and finally with ether and dried *in vacuo*.

The metals in the complexes were analysed using standard literature procedures⁵. Chloride was estimated as AgCl, sulphur as BaSO_4 and nitrogen microanalytically. The analytical data are given in Table 1.

Experimental details pertaining to the measurements of molar conductance ($10^{-3} M$ in DMF), magnetic susceptibility, electronic and IR spectra, X-ray powder diffraction and antifungal activity of $[\text{L, CoL(CH}_3\text{COO)}_2, \text{CuL(CH}_3\text{COO)}_2]$ against *Rhizoctonia solani* Kühn have been described in our previous paper⁶. Magnetic moment values are included in Table 1. EPR spectra were recorded on an Eline EPR spectrophotometer in DMF solution at room and liquid nitrogen temperature (LNT) using TCNE as g marker. The EPR parameters are given in Table 2.

Results and Discussion

$\text{CuL(CH}_3\text{COO)}_2$ melts at 240°C and VOL_2SO_4 does not melt or decompose upto 300°C while all the other complexes decompose between 230 and 240°C . The loss of water molecules at comparatively higher⁷ temperatures (150 - 160°C) in hydrated complexes, the presence of a band characteristic of coordinated water in 760 - 820 cm^{-1} region in the IR spectra of the hydrated complexes and its absence in anhydrous complexes show clearly that water molecules are

Table 1—Analytical, Colour, Melting Point and Magnetic Moment Data of TPBB Complexes

Complex	Colour (m.p., °C)	Found (Calc.), %				$\mu_{\text{eff.}}$ (B.M.)
		Metal	Cl	S	N	
VOL ₂ SO ₄	Green (300)	4.92 (4.918)	—	6.20 (6.17)	7.90 (8.10)	1.83
CoLCl ₂ (H ₂ O) ₂	Blue (230d)	9.45 (9.77)	10.85 (11.77)	5.00 (5.30)	7.10 (6.96)	5.20
NiLCl ₂ (H ₂ O) ₂	Green (230d)	10.03 (9.74)	11.50 (11.78)	4.95 (5.30)	6.93 (6.96)	3.10
CuLCl ₂ ·H ₂ O	Brown (235d)	10.75 (10.77)	12.25 (12.04)	5.03 (5.42)	6.88 (7.12)	1.62
CoL(CH ₃ COO) ₂	Blue (240d)	9.70 (9.59)	—	5.11 (5.21)	6.44 (6.84)	4.92
NiL(CH ₃ COO) ₂	Green (240d)	9.34 (9.56)	—	5.00 (5.21)	6.53 (6.84)	3.21
CuL(CH ₃ COO) ₂	Brown (240)	9.86 (10.26)	—	4.95 (5.17)	6.28 (6.79)	0.86

Table 2—ESR Magnetic Parameters

	CuL(CH ₃ COO) ₂	VOL ₂ SO ₄
$A_{\parallel}(\text{G})$	57.50	96.5
$A_{\perp}(\text{G})$	15	23.2
$A_{\text{iso}}(\text{G})$	29.16	47.6
$g_{\parallel}$	2.1255	1.999
$g_{\perp}$	2.0113	2.012
g_{av}	2.0493	2.0077

coordinated. With the exception of CuL(CH₃COO)₂, CuLCl₂·(H₂O), and VOL₂SO₄, which are more or less soluble in DMF, all the complexes are insoluble in water and common organic solvents. The molar conductance values of CuL(CH₃COO)₂ and CuLCl₂·H₂O (2-6 ohm⁻¹ cm² mol⁻¹) are indicative of their non-electrolytic nature while VOL₂SO₄ (67.5 ohm⁻¹ cm² mol⁻¹) shows 1:1 ionic nature⁸ in solution. The molar conductances of the remaining complexes could not be determined because of their insolubility even in coordinating solvents.

Magnetic and electronic spectral studies

The magnetic moment of VOL₂SO₄ corresponds to one unpaired electron irrespective of stereochemistry but three bands at 15265, 18690 and 21050 cm⁻¹ in its electronic spectrum, assignable to the transition $d_{xy} \rightarrow d_{yz}$, $\rightarrow d_{xz}$ and $\rightarrow d_{x^2-y^2}$ transitions, indicate square pyramidal geometry^{9,10}. Octahedral coordination is indicated for the Co(II) complexes by their $\mu_{\text{eff.}}$ values¹¹ and electronic spectra. Two bands at 15385 and 18180 cm⁻¹ in the spectrum of CoLCl₂(H₂O)₂, and at 18805 and 20000 cm⁻¹ in that of CoL(CH₃COO)₂ have been assigned to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $\rightarrow {}^4T_{1g}(P)$ transitions, respectively, and an additional band at 10990 in CoLCl₂(H₂O)₂ has

been assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition under octahedral¹² environment around the metal ion. Three bands at 9090, 16660 and 21050 cm⁻¹ in the spectrum of NiLCl₂(H₂O)₂ and at 9760, 15385 and 23530 cm⁻¹ in that of NiL(CH₃COO)₂ in conjunction with the magnetic moments of the complexes are indicative of octahedral¹³ stereochemistry of the complexes. The subnormal $\mu_{\text{eff.}}$ values of CuLCl₂·H₂O and CuL(CH₃COO)₂ may be attributed to metal-metal and/or super-exchange interaction¹⁴ through bridging chloride and acetate, respectively. Of the two bands observed at 15625 and 21050 in the spectrum of CuLCl₂·H₂O and at 16000 and 25000 in that of CuL(CH₃COO)₂, the first one may be attributed to ${}^2E_g \rightarrow {}^2T_{2g}(D)$ transition assuming distorted octahedral¹⁵ geometry of the former complex. However, a square pyramidal geometry is more probable for the second complex as adduced from chemical composition and IR studies discussed later. The second band in both the complexes indicates dimeric¹⁶ nature of the complexes.

EPR spectral studies

The DMF glass spectrum of CuL(CH₃COO)₂ shows strong absorption bands at 2962.5, 3015, 3095 and 3117.5 G, and weak absorptions at 3055, 3082.5 and 3135 G which can be tentatively interpreted on the basis of the spin Hamiltonian for the triplet state¹⁷. of these, bands at 2962.5, 3015, 3082.5 and 3135 G may be assigned to copper hyperfine splitting with an average separation of 57.5 G. This is half of the expected value for a monomeric¹⁸ copper(II) complex indicating dimeric nature of the complex. The lesser number of lines than that expected (seven) may be due to overlapping of these lines with perpendicular region. The $g_{\parallel}$ (3050 G) and $g_{\perp}$ (323.5 G) have been evaluated

from the spectra. The trend $g_{\parallel} > g_{\perp} g_e$ (2.0023, free ion value) observed in the complex shows that unpaired electron is in the $d_{x^2-y^2}$ orbital¹⁹ of Cu(II) ion. In frozen solution, EPR spectrum of VOL_2SO_4 is anisotropic and two sets of resonance components, one each due to the parallel and perpendicular features, are observed. The trend $g_{\perp} > g_{av} > g_{\parallel}$ found in oxovanadium(IV) complex indicates that the unpaired electron is present in $b_{2g}^*(D_{xy})$ orbital^{20,21} of oxovanadium(IV).

X-Ray powder diffraction studies

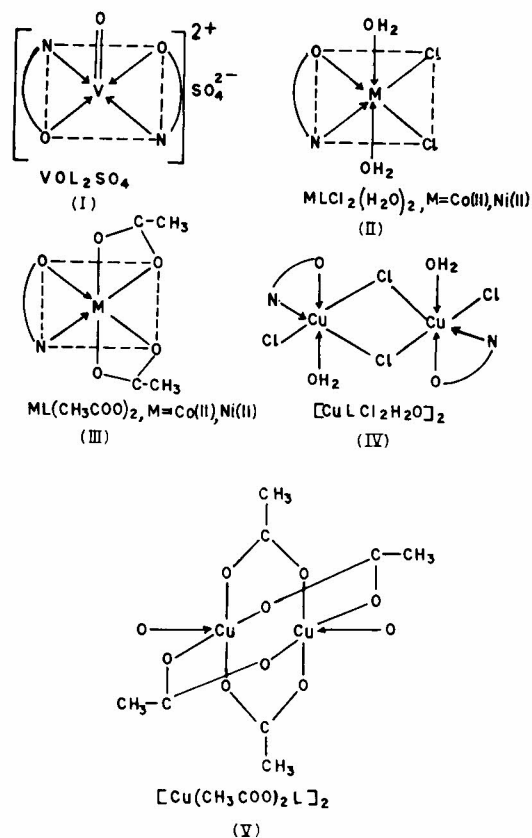
The powder X-ray diffraction photograph of $\text{NiL}(\text{CH}_3\text{COO})_2$ yields no diffraction lines indicating its non-crystalline nature. The diffraction lines for $\text{CuL}(\text{CH}_3\text{COO})_2$ have been successfully indexed for tetragonal symmetry²². The lattice parameters computed for the above symmetry are, $a = b = 20.571 \text{ \AA}$, $c = 31.308 \text{ \AA}$, $\rho = 1.57 \text{ g cm}^{-3}$, $\rho(\text{cal}) = 1.58 \text{ g cm}^{-3}$ and $Z = 12$.

IR spectral studies

IR spectrum of the ligand shows bands at 1640, 1620, 1385 and 1230 cm^{-1} which may be attributed to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$, $\text{S}-\text{CH}_2\varphi$ and $\text{S}-\text{CH}_2$ modes²³, respectively. The $\nu\text{C}=\text{O}$ and $\nu\text{C}=\text{N}$ modes suffer negative shifts of 5-20 and 5-10 cm^{-1} respectively in all the complexes except in $\text{CuL}(\text{CH}_3\text{COO})_2$, which shows negative shift only in $\nu(\text{C}=\text{O})$ (10 cm^{-1}) indicating that both $\text{C}=\text{O}$ and $\text{C}=\text{N}$ groups are coordinated in all the complexes and only carbonyl oxygen is involved in bonding in $\text{CuL}(\text{CH}_3\text{COO})_2$. The positive shift in both $\nu_{as}\text{O}-\text{C}-\text{O}$ (32 cm^{-1}) and $\nu_s\text{O}-\text{C}-\text{O}$ (46 cm^{-1}) in $\text{CuL}(\text{CH}_3\text{COO})_2$, and a negative shift in $\nu_{as}\text{O}-\text{C}-\text{O}$ (28 cm^{-1}) and a positive shift in $\nu_s\text{O}-\text{C}-\text{O}$ (41 cm^{-1}) in $\text{CoL}(\text{CH}_3\text{COO})_2$ and $\text{NiL}(\text{CH}_3\text{COO})_2$ with respect to the positions in sodium acetate indicate bridging²⁴ bidentate behaviour in the former complex and chelating²⁴ bidentate nature in the latter two complexes. The bands appearing in the spectrum of VOL_2SO_4 at 1140 and 970 cm^{-1} indicate ionic²⁵ nature of SO_4^{2-} in oxovanadium(IV) complexes. The presence of a band in the region $3500\text{--}3550 \text{ cm}^{-1}$ in hydrated complexes is attributed to $\nu(\text{OH})$. The bands observed in the regions 400-430, 290-340 and $240\text{--}250 \text{ cm}^{-1}$ in the spectra of the complexes, which are absent in the spectrum of ligand, are tentatively assigned to $\nu(\text{M}-\text{O})$ ²⁶, $\nu(\text{M}-\text{N})$ ²⁶ and $\nu(\text{M}-\text{Cl})$ ²⁷ modes, respectively.

The ligand as well as the complexes are inactive at 50 ppm and 100 ppm except $\text{CuL}(\text{CH}_3\text{COO})_2$ which shows activity at 100 ppm. $\text{CuL}(\text{CH}_3\text{COO})_2$ is found to be physiologically more active and $\text{CoL}(\text{CH}_3\text{COO})_2$ less active than the ligand at 300 ppm.

Based on chemical compositions and physico-chemical studies discussed above the following



structures (I-V) are tentatively proposed for the complexes.

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