

Synthesis and Characterization of the Metal Complexes of Thiourea Derived from 3-Amino-5-Methylisoxazole

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The complexes of Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with ligands derived from 3-amino-5-methylisoxazole and benzoyl thiocyanate have been synthesized and their structural characterization carried out by elemental analysis, conductance, thermal, magnetic and infrared, electronic and ESR spectral data. Relevant conclusions with respect to the ligating behaviour of the ligands and the geometry of the metal complexes together with the nature of metal-ligand bonding present in them have been drawn based on the data obtained.

INTRODUCTION

Isoxazole thiourea systems composed of biologically potent isoxazole and thiourea moieties¹⁻⁴ are expected to be more promising in terms of biological activity. Since the biological activity of organic compounds has been attributed, in most of the cases, to their ability to form complexes with metals present in biosystem, it is considered worthwhile to prepare metal complexes of some isoxazole thiourea systems and characterize them structurally. In the present investigation, the complexes of Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with ligands N-benzoyl-N'-(5-methylisoxazol-3-yl) thiourea (BMIT), N-p-methylbenzoyl-N'-(5-methylisoxazol-3-yl) thiourea (MBMIT) and N-p-nitrobenzoyl-N'-(5-methylisoxazol-3-yl) thiourea (NBMIT) (Fig. 1) have been synthesized and characterized.

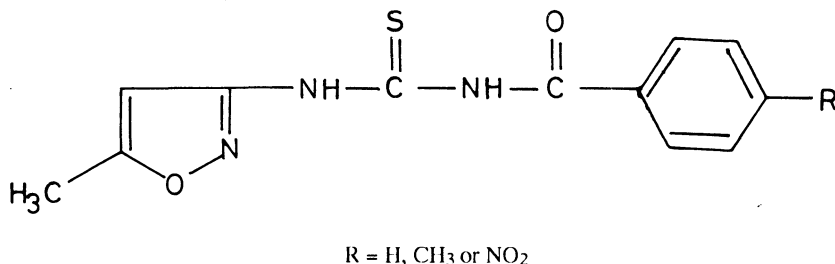


Fig. 1 N-Aroyl-N'-(5-methylisoxazol-3-yl) thiourea.

EXPERIMENTAL

Preparation of the ligands

*N-Aroyl-N'-(5-methylisoxazol-3-yl) thioureas*⁵: To ammonium thiocyanate

(10.0 mmol) dissolved in acetone, aroyl chloride (10.0 mmol) was added and the contents were heated on a water bath for 10 min. The reaction mixture was cooled and a solution of 3-amino-5-methylisoxazole† (10.0 mmol) in acetone was added to it. The reaction mixture was stirred for 10 min. and then poured in cold water. The solid that separated was filtered, dried and recrystallized from petroleum ether-benzene mixture to give corresponding N-aroyle-N'-(5-methylisoxazol-3-yl)-thiourea. BMIT, m.pt. 158°C (reported 158°C); MBMIT m. pt. 190°C (reported 190°C) and NBMIT, m.pt. 183°C (reported 183°C).

Preparation of the metal complexes

The Fe(III) complexes with all the three ligands were prepared using anhydrous ferric chloride while the complexes of Co(II), Ni(II), Cu(II) and Zn(II) were prepared using corresponding metal acetates.

In the preparation of all the metal complexes, the metal and the ligand were combined in 1 : 2 mole ratio using required quantities of methanol for the metal salts and acetone for the ligands so as to effect their solubility. The mixture was refluxed on a hot water bath for 60–90 min. The solid that separated out was filtered, washed with water, methanol and acetone in succession and was dried in vacuum over fused CaCl₂.

RESULTS AND DISCUSSION

The ligands BMIT, MBMIT and NBMIT are non-hygroscopic and are stable at normal conditions. They are insoluble in water but are soluble in organic solvents such as acetone and methanol. The Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes of BMIT, MBMIT and NBMIT are, as well, stable at normal conditions and are non-hygroscopic. Upon heating, the complexes decompose without melting. The complexes are insoluble in water and common organic solvents but are soluble in DMF and DMSO.

The analytical and conductance data and colours of the complexes are presented in Table 1. The molecular formulae of the complexes have been worked out based on the analytical data obtained. All the complexes, with the exception of those of Fe(III), show only residual molar conductance values (8–16 ohm⁻¹ cm² mol⁻¹) and hence they may be considered non-electrolytic. This implies that the acetates associated with these complexes are present inside the coordination sphere. The values (Table 1) observed for Fe(III) complexes, however, correspond to 1 : 1 electrolyte type⁶.

The thermograms of the complexes of NBMIT reveal that the complexes are not associated with water-either lattice or coordinated. A sharp decomposition associated with the loss of ligand moiety starts at 180, 190, 200, 230 and 240°C in the case of Fe, Co, Ni, Cu, and Zn complexes respectively, the final product of decomposition above 550, 750, 750, 510 and 650°C for the order just given corresponding to the respective metal oxide. Taking the decomposition

†Obtained from Aldrich Chemical Co., Inc., USA.

temperatures as a measure of thermal stability, the stability order of the present complexes may be computed as Zn-NBMIT > Cu-NBMIT > Ni-NBMIT > Co-NBMIT > Fe-NBMIT.

The ligands BMIT, MBMIT and NBMIT each show a medium intensity band around 3100 cm^{-1} which may be assigned to $\nu(\text{NH})$. This band undergoes no perceptible shift in the spectra of the metal complexes suggesting that there is no interaction between nitrogen of this group and the metal ions⁷. The $\nu(\text{C}=\text{O})$ frequency that appears as a sharp band around 1700 cm^{-1} in the ligands suffers, on the other hand, a negative shift by $30\text{--}50\text{ cm}^{-1}$ in the complexes indicating coordination through oxygen of this group⁸. The ligands display a sharp band around 1650 cm^{-1} assignable to $\nu(\text{C}=\text{N})$. This band remains unshifted in the spectra of the complexes ruling out bonding through nitrogen of this group⁹. A low or medium intensity band that appears around 1080 cm^{-1} in the ligands has been assigned to $\nu(\text{C}=\text{S})$ with a contribution from $\delta(\text{C}-\text{N})$ ¹⁰. This band undergoes, in the complexes, a lower shift by $40\text{--}60\text{ cm}^{-1}$ indicating that the thione sulphur is involved in coordination¹¹. Further, the Co(II), Ni(II), Cu(II) and Zn(II) complexes of all the ligands reveal medium or small intensity bands around 1520 and 1340 cm^{-1} which may be assigned respectively to $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ vibrations of the coordinated acetate ions. A fairly large separation of these two frequencies suggests unidentate nature of acetate ions¹². The coordination through oxygen of C=O group and sulphur of C=S group in all the complexes and additionally through chloride in Fe(III) complexes is further substantiated by the appearance, in the complexes, of sharp, non-ligand bands around 500 , 350 and 300 cm^{-1} assignable respectively to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{S})$ and $\nu(\text{M}-\text{Cl})$ vibrations¹³⁻¹⁵. Thus, it may be inferred that BMIT, MBMIT and NBMIT act as neutral, bidentate ligands coordinating through oxygen of C=O group and sulphur of C=S group.

The magnetic and electronic spectral behaviour of the complexes formed of a particular metal with all the ligands is the same.

Fe(III), Co(II), Ni(II) and Cu(II) complexes are found to be paramagnetic with μ_{eff} values around 5.60, 4.95, 3.00 and 1.80 B.M. corresponding to five, three, two and one unpaired electrons respectively. The values observed for Fe(III) and Co(II) complexes are diagnostic of the presence of high-spin configuration in them. Zn(II) complexes are diamagnetic in nature.

The electronic spectra of Fe(III) complexes each show two sharp and weak bands around 18000 and 25000 cm^{-1} . Since the bands observed are weak, they may be assigned to the spinforbidden transitions of octahedral geometry, the lower energy band corresponding to ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}}(\text{G})$ and the other to ${}^6\text{A}_{1\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}(\text{G})$ ¹⁶. The proposition of octahedral geometry for the Fe(III) complexes is supported by their magnetic moment values.

The Co(II) complexes show each three peaks at or around 8900 , 16100 and 20000 cm^{-1} assignable respectively to the transitions ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{2\text{g}}(\text{F})$, ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{A}_{2\text{g}}(\text{F})$ and ${}^4\text{T}_{1\text{g}}(\text{F}) \rightarrow {}^4\text{T}_{1\text{g}}(\text{P})$, characteristic of octahedral geometry¹⁷.

The frequencies observed for Ni(II) complexes at or around $9,300$, $16,000$ and $25,900\text{ cm}^{-1}$ assignable respectively to ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{2\text{g}}(\text{F})$, ${}^3\text{A}_{2\text{g}}(\text{F}) \rightarrow {}^3\text{T}_{1\text{g}}(\text{F})$

and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ suggest that the Ni(II) ion in the complexes is present in an octahedral environment¹⁷.

The Cu(II) complexes reveal three peaks around 15000, 18000 and 22000 cm^{-1} that could be assigned in the order of increasing energy to the transitions ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$. Based on these observations and the analytical data, the complexes have been assigned square-planar geometry.¹⁸

Zn(II) (d^{10}) complexes show no d-d bands and on the basis of analytical, conductance and infrared spectral data obtained, these complexes have been assigned tetrahedral geometry-the most preferred geometry for a tetracoordinated d^{10} system.

TABLE 1
ANALYTICAL AND CONDUCTANCE DATA AND COLOUR OF THE COMPLEXES

Complex	Found (Calc.) %				Molar cond. ($\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$)
	M	C	H	N	
[Fe(BMIT) ₂ Cl ₂]Cl (Mustard)	7.95 (8.16)	41.78 (42.09)	3.12 (3.25)	12.46 (12.28)	63
[Fe(MBMIT) ₂ Cl ₂]Cl (Mustard)	7.63 (7.84)	43.55 (43.81)	3.76 (3.68)	11.58 (11.79)	65
[Fe(NBMIT) ₂ Cl ₂]Cl (Brown)	7.08 (7.29)	36.93 (37.20)	2.64 (2.61)	14.52 (14.47)	72
[Co(BMIT) ₂ (OAc) ₂] (Brown)	8.28 (8.43)	48.33 (48.07)	4.22 (4.04)	11.89 (12.02)	12
[Co(MBMIT) ₂ (OAc) ₂] (Mustard)	8.26 (8.10)	49.18 (49.52)	4.33 (4.44)	11.64 (11.55)	10
[Co(NBMIT) ₂ (OAc) ₂] (Light brown)	7.28 (7.47)	42.25 (42.59)	3.12 (3.33)	13.98 (14.20)	13
[Ni(BMIT) ₂ (OAc) ₂] (Light green)	8.23 (8.40)	47.78 (48.08)	3.96 (4.04)	11.92 (12.02)	10
[Ni(MBMIT) ₂ (OAc) ₂] (Light green)	7.91 (8.07)	49.66 (49.53)	4.28 (4.44)	11.27 (11.56)	14
[Ni(NBMIT) ₂ (OAc) ₂] (Light green)	7.32 (7.44)	42.30 (42.60)	3.48 (3.33)	13.93 (14.20)	16
[Cu(BMIT)(OAc) ₂] (Grey)	14.11 (14.35)	42.88 (43.39)	3.96 (3.88)	9.28 (9.49)	11
[Cu(MBMIT)(OAc) ₂] (Grey)	13.66 (13.91)	44.37 (44.68)	4.00 (4.20)	8.98 (9.20)	9
[Cu(NBMIT)(OAc) ₂] (Grey)	12.84 (13.02)	39.12 (39.38)	3.16 (3.31)	11.26 (11.49)	13
[Zn(BMIT)(OAc) ₂] (Light yellow)	14.32 (14.70)	42.92 (43.21)	3.63 (3.86)	9.16 (9.45)	8
[Zn(MBMIT)(OAc) ₂] (Light yellow)	14.42 (14.25)	44.22 (44.50)	4.02 (4.18)	9.00 (9.16)	8
[Zn(NBMIT)(OAc) ₂] (Light yellow)	13.06 (13.35)	38.88 (39.24)	3.12 (3.30)	11.26 (11.44)	10

The solution ESR spectra of Cu(II) complexes with all the three ligands are anisotropic, each consisting of two peaks, one as a shoulder towards low field region and the other of medium intensity towards high field region. In no case has the splitting due to copper nuclear spin been observed. The ESR parameters calculated for the complexes are presented in Table 2.

TABLE 2
ESR PARAMETERS OF Cu(II) COMPLEXES

Complex	g_{\parallel}	g_{\perp}	K_{\parallel}^2	K_{\perp}^2	$-\lambda$ (cm ⁻¹)
Cu-BMIT	2.25	2.08	0.6750	1.0322	559
Cu-MBMIT	2.25	2.08	0.6805	1.0346	564
Cu-NBMIT	2.26	2.07	0.7003	0.8953	580

A comparison of the g values obtained for the present complexes indicates that $g_{\parallel} > g_{\perp}$ and so the unpaired electron lies predominantly in the $d_{x^2-y^2}$ orbital with ${}^2B_{1g}$ as the ground state—a characteristic feature of a square-planar or an elongated octahedral geometry¹⁹. The g_{\parallel} associated with the complexes is less than 2.3 pointing out that the metal-ligand in them is covalent in character²⁰.

The complexes are supposed to be in-plane π -bonded²¹ since the parallel component of the orbital reduction parameter, K_{\parallel}^2 is less than the perpendicular component, K_{\perp}^2 . Further, the spin-orbit coupling constant of copper ion in the complexes ($-\lambda$) is less than the free ion value ($-\lambda_0 = 828$ cm⁻¹) suggesting considerable mixing of ground and excited states.

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