

Complexes of Cu(II), Ni(II) & Co(II) with 3,5-Dimethyl-1-nitroguanylpirazole

NITYANANDA SAHA* & N. C. GAYEN

Department of Pure Chemistry, University College of Science, Calcutta 700009

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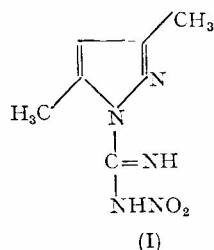
The solid complexes of Cu(II), Ni(II) and Co(II) with 3,5-dimethyl-1-nitroguanylpirazole (LH) have been isolated both in the hydrated and anhydrous forms and characterized on the basis of analytical data, electronic spectra (diffuse reflectance and solution), magnetic susceptibilities at room temperature, IR spectra and TGA studies. A change in stereochemistry on dehydration is suggested. The blue $\text{Cu(II)L}_2 \cdot 2\text{H}_2\text{O}$ on dehydration yields the violet $[\text{Cu(II)L}_2]$, which has probably a tetragonal configuration. The $\text{Ni(II)L}_2 \cdot 2\text{H}_2\text{O}$ is blue and paramagnetic and is assigned a *trans*-octahedral structure with D_{4h} symmetry, while Ni(II)L_2 is orange red and diamagnetic and is square-planar as expected. The $\text{Co(II)L}_2 \cdot 3\text{H}_2\text{O}$ is probably five coordinate as suggested by spectral data, magnetic moment and TGA studies. The anhydrous Co(II)L_2 complex has a polymeric octahedral structure. The IR data indicate possible deprotonation of NH group on complexation.

THE metallic complexes of pyrazole-derived ligands have been recently reviewed by Trofimenko¹. In this paper, we have investigated the chelating ability of the bidentate ligand 3,5-dimethyl-1-nitroguanylpirazole. Thus Cu(II), Ni(II) and Co(II) chelates with this ligand have been isolated in the solid state both in hydrated and anhydrous forms and have been characterized on the basis of elemental analyses, magnetic susceptibilities, electronic (diffuse reflectance) and vibrational spectral data and thermogravimetric studies.

Materials and Methods

3,5-Dimethyl-1-nitroguanylpirazole (I) was prepared according to the method described in the literature² and recrystallized as white needles from ethanol, m.p. 126° (lit² m.p. 126°).

The electronic diffuse reflectance spectra were recorded on a Zeiss PMQII spectrophotometer (at the University of New South Wales, Australia). Electronic spectra in AR grade solvents were recorded on a Spectromom '20' (Hungarian) spectrophotometer using a 2 cm cell unless otherwise stated. The IR spectra were recorded on a Beckman-20 IR-spectrophotometer using KBr plates.



Magnetic susceptibilities³ were measured at room temperature by Gouy's method using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant. Thermogravimetric experiments were carried out in air in a thermobalance of local design in the temperature range $25\text{-}400^\circ$ with a heating rate of $7^\circ/\text{min}$.

General method for the preparation of the complexes — A solution of the ligand (0.004 mole, 0.73 g) in ethanol (30 ml) was added to an ethanolic solution of corresponding metal (II) chloride hydrate (0.002 mole). To this was added with stirring a dilute solution of ammonia dropwise till the coloured precipitate was obtained ($\text{pH} \approx 5$). It was filtered, washed with water and ethanol and dried in a vacuum desiccator. The anhydrous compounds were obtained by heating the hydrated varieties in an oven at $130\text{-}40^\circ$ for 2-3 hr.

Results and Discussion

The elemental analyses and room temperature magnetic data support the formulations of all the complexes recorded in Table 1. The electronic absorption spectra both in the solid state and in DMSO at $25\text{-}30^\circ$ are given in Table 2.

All the complexes $\text{ML}_2 \cdot \text{XH}_2\text{O}$ and ML_2 (LH = 3,5-dimethyl-1-nitroguanylpirazole) are either insoluble or slightly soluble in water and non-solvating organic solvents. All the compounds are, however, soluble in coordinating solvents often accompanied by change in colour.

Cu(II) complexes — The magnetic moment of 2.01 BM for the blue $[\text{Cu(II)L}_2] \cdot 2\text{H}_2\text{O}$ is well within the range of octahedral species⁴. The reflectance spectrum of the solid complex shows a broad band at $\sim 16,500\text{ cm}^{-1}$, while in DMSO, the main band is shifted to $15,630\text{ cm}^{-1}$ with a shoulder at $16,940\text{ cm}^{-1}$. The broad asymmetric band in each case indicates that more than one transitions are

*To whom all correspondence should be made.

TABLE 1 — CHARACTERIZATION DATA OF THE COMPLEXES

Complex*	Colour	N (%)		M (%)		μ_{eff} (BM) (299°K)
		Calc.	Found	Calc.	Found	
CuL ₂ ·2H ₂ O	Deep blue	30.20	29.97	13.70	13.80	2.01
CuL ₂	Violet	32.75	32.60	14.55	14.67	1.90
NiL ₂ ·2H ₂ O	Light blue	30.49	30.30	12.79	12.99	3.13
NiL ₂	Orange-red	33.12	33.24	13.89	13.98	Diamagnetic
CoL ₂ ·3H ₂ O	Light yellow	29.68	29.45	12.37	12.50	4.70
CoL ₂	Deep violet	33.10	33.60	13.95	14.10	4.30

*Satisfactory C and II analyses were obtained for the complexes.

TABLE 2 — ELECTRONIC ABSORPTION SPECTRA OF METAL COMPLEXES

Complex	State	λ_{max} (cm ⁻¹) (ϵ molar for solution)
CuL ₂ ·2H ₂ O	Reflectance	16,500
	In DMSO	15,630 (93.56); 16,940 (sh)
CuL ₂	Reflectance	18,200; 15,630 (sh)
	In DMSO	15,380 (101.30); 16,660 (sh)
NiL ₂ ·2H ₂ O	Reflectance	9,100; 13,200; 16,600; 23,800 (sh); 27,390
	In DMSO	9,090 (10.56); 15,630 (11.65); 25,950 (15.50)
NiL ₂	Reflectance	21,040
	In DMSO	16,000 (24.5); 27,000 (6.7)
CoL ₂ ·3H ₂ O	Reflectance	6,600; 15,000; 16,200 (sh); 20,000 (sh)
	In DMSO	9,100 (9.5); 15,630 (2.08); 16,660 (4.16); 19,610 (13.18); 20,410 (14.25)
CoL ₂	Reflectance	8,620; 20,000
	In DMSO	8,700 (20.09); 19,750 (14.4)

contained in the absorption envelope. A distorted octahedral structure is suggested for the blue complex with a symmetry lower than O_h (ref. 5).

The reflectance spectrum of the violet [Cu(II)L₂] is characterized by a strong band at 18,200 cm⁻¹ with considerable asymmetry on the low energy side and a well-defined shoulder near 15,630 cm⁻¹. Although no Gaussian analysis is attempted in the present case, the main band and the shoulder can be assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions respectively, in D_{4h} symmetry^{6,7}.

Ni(II) complexes — The reflectance spectrum and room temperature magnetic moment (3.13 BM) of the light blue Ni(II)L₂·2H₂O are characteristic of Ni(II) in a tetragonal 6-coordinate environment, with local symmetry of the coordination sphere of the metal ion approximating D_{4h} . In this symmetry, the split components of the ${}^3T_{2g}$ level (in O_h) become 3E_g and ${}^3B_{2g}$ causing the splitting of the first band⁸. The marked splitting of the ν_1 band (Table 2) and broadening of the ν_2 band in the present case strongly suggests a trans-octahedral structure for the complex with water groups occupying the *trans*-positions. Electronic spectrum of the complex in DMSO (green solution) shows three bands (Table 2) typical of distorted octahedral Ni(II) complex. The shift of the absorption bands as compared with the solid

state spectrum suggests some solvation. The low molar extinction coefficients are usual for pseudo-octahedral geometry⁹.

An interesting change in stereochemistry is noticed by heating the blue paramagnetic dihydrate [Ni(II)L₂]·2H₂O at 130° for 2-3 hr, when orange-red diamagnetic [Ni(II)L₂] is formed. The behaviour is very similar to β -ketoenolate complex of Ni(II) (ref. 10). The reflectance spectrum of this orange-red complex exhibits one ligand field band at 21,040 cm⁻¹ which has been assigned to the transition ${}^1A_{1g} \rightarrow {}^1A_{2g}$ as suggested by the earlier workers¹¹⁻¹³ for square planar Ni(II) complexes. When the electronic spectrum of this orange-red Ni(II) complex was taken (Hilger Watt Uvispeck spectrophotometer with 1 cm cell) in DMSO (green solution), the band at $\sim 21,040$ cm⁻¹ disappeared and two new bands appeared around 16,000 and 27,000 cm⁻¹. Such a behaviour in coordinating solvents in the case of Ni(II) complexes has been ascribed^{10,14} to change in geometry from square planar to octahedral.

Co(II) complexes — The light yellow Co(II)L₂·3H₂O has a room temperature magnetic moment of 4.7 BM, the most intense bands in the reflectance spectrum occur at 6600 and 15,000 cm⁻¹, but there are weaker bands at 16,200 and 20,000 cm⁻¹. In the light of these data, the present Co(II) complex can be considered as a 5-coordinate species with essentially square-pyramidal geometry in accordance with the available literature^{15,16}. In the absence of crystallographic data, although nothing definitely can be said, yet TG studies give additional support for a 5-coordinate structure of Co(II)L₂·3H₂O which loses two molecules of water quantitatively at 120° while the third water molecule is lost only at 140°. So, a reasonable formulation of the complex might be [Co(II)L₂·H₂O]·2H₂O.

This hydrated Co(II) complex produces a red solution in DMSO. The electronic spectral bands of this solution are indicative of an octahedral geometry for the complex. But the splitting of the main band into closely spaced components (Table 2) suggests a lower symmetry than O_h .

The deep violet Co(II)L₂ has a magnetic moment of 4.3 BM, a value which is significantly lower than those usually observed for octahedral high-spin Co(II) complexes⁴. This lowering in magnetic moment value could be due to the greater deformation from the octahedral symmetry. An axial dis-

tortion will produce lower magnetic moments of T ground terms [as in Co(II) in O_h], since the splittings are of the same order of magnitude as those due to spin-orbit coupling¹⁷. The reflectance spectrum of the complex is characterized by two main bands viz. at 8620 (ν_1) and 20,000 cm^{-1} (ν_3) which can be assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively in O_h symmetry. Thus the anhydrous Co(II) L_2 may be considered to have a polymeric octahedral structure in the solid state.

The anhydrous Co(II) complex gives a red solution in DMSO which shows two main bands, viz. ν_1 and ν_3 bands, characteristic of distorted octahedral structure which might be attained by the coordinating solvent used (Table 2).

Infrared spectra — In view of the X-ray crystallographic studies of several pyrazole metal complexes¹⁸⁻²⁰, pyrazole nitrogen as a bonding site has to be accepted in the present complexes also, although definite IR evidence could not be presented due to limited range of the IR spectrophotometer used. Two strong bands present at 3440 and 3300 cm^{-1} in the ligand, due to $\nu_{\text{as}}(\text{N-H})$ and $\nu_{\text{sy}}(\text{N-H})$ modes²¹ respectively, disappeared in the spectra of Cu(II), Ni(II) and Co(II) complexes and a new band appeared around 3340-3350 cm^{-1} (the broadening of the bands may be due to the inter or intramolecular interaction). This could be explained by assuming that one of N-H groups of the ligand got deprotonated on complexation with the formation of M-N bond. Thus one should not expect intramolecular interaction of the N-H groups in the complexes and thus a single band due to $\nu(\text{N-H})$ should appear in the spectra²². The ligand also shows two absorption bands at 1560 (ω) and 1625 (s) cm^{-1} due to $\nu\text{C}=\text{C}$ and $\nu\text{C}=\text{N}$ (ref. 23). The IR spectra of all the metal chelates show a considerable decrease in $\nu\text{C}=\text{N}$ which indicates coordination of this group to the metal ions through tertiary ring nitrogen. The broad band around 3530-3540 cm^{-1} in the hydrated complexes is due to $\nu\text{O-H}$ of attached water²⁴; this band disappeared in the anhydrous complexes. The hydrated Co(II) complex shows an additional band at 1670 cm^{-1} which is assigned to the bending mode of coordinated and lattice water²⁵.

TGA studies — The weight-loss percentage of the metal chelates, gathered from the thermal analyses at different temperatures, indicate that their thermal stability decreases in the order $\text{NiL}_2 \cdot 2\text{H}_2\text{O} > \text{CuL}_2 \cdot 2\text{H}_2\text{O} > \text{CoL}_2 \cdot 3\text{H}_2\text{O}$. The hydrated complexes start losing their water molecules at $\sim 120^\circ$ and at 140° , the anhydrous species are formed. The TG curve, in each case, reveals that the anhydrous

complexes, thereafter, undergo a continuous loss in weight with no thermally stable intermediates. The complexes undergo a rapid decomposition process from about 300° and complete conversion to the corresponding metal oxides occurs within 400° .

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