

Mixed Ligand Complexes Obtained by the Replacement of Coordinated Water in Some Copper(II) & Nickel(II) Complexes Derived from 3-Methyl-4-(*p*-methylphenylazo)pyrazole-5-ones

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Starting from the parent complexes of the types $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{SO}_4$ and $[\text{Ni}(\text{L})(\text{H}_2\text{O})_4]\text{SO}_4$, where L = 3-methyl-4-(*p*-methylphenylazo)pyrazole-5-one ($\text{C}_{11}\text{H}_{13}\text{N}_4\text{O}$), a large number of mixed ligand complexes of the types $[\text{Cu}(\text{L})(\text{am})_2]\text{SO}_4$; $[\text{Ni}(\text{dien})(\text{L})(\text{H}_2\text{O})]\text{SO}_4$; $[\text{Cu}(\text{trien})]\text{SO}_4$ and $[\text{Ni}(\text{trien})(\text{H}_2\text{O})_2]\text{SO}_4$ where am = α -, β - or γ -picoline, dam = ethylene or propylene-diamine, dien = diethylenetriamine and trien = triethylenetetramine, have been obtained, by the replacement of L or H_2O in the original complexes by nitrogen donor ligands. The Cu(II) and Ni(II) complexes are assigned planar and distorted octahedral structures respectively, on the basis of infra-red, magnetic moment and electronic spectral data. An attempt has been made to correlate the replacement of the ligands in the parent complexes with the crystal field strength of the incoming nitrogen donors, as well as the geometry of the product so obtained.

Studies on the preparation of mixed ligand complexes using the ligand replacement reactions have recently been made by us for a large number of different transition metal ions¹⁻⁵. In this note we report the results of studies on the reactions of copper(II) and nickel(II) complexes of the types $[\text{Cu}(\text{L})(\text{H}_2\text{O})_2]\text{SO}_4$ and $[\text{Ni}(\text{L})(\text{H}_2\text{O})_4]\text{SO}_4$, with α -, β - or γ -picoline, ethylenediamine, propylenediamine, diethylenetriamine and triethylenetetramine.

The parent complexes were prepared by treating stoichiometric quantities of copper(II) or nickel(II) sulphate suspended in methanol with 3-methyl-4-(*p*-methylphenylazo)pyrazole-5-one⁶. A known weight of the parent complex was suspended in methanol and treated with α -, β - or γ -picoline or di-, tri- or tetra-amine and the contents were refluxed for 4 hr. The resulting complex was isolated by repeated crystallisations from petroleum ether-ethanol mixture. Charts I and II sum up the reactions undergone by Cu(II) and Ni(II) complexes with various nitrogen donors.

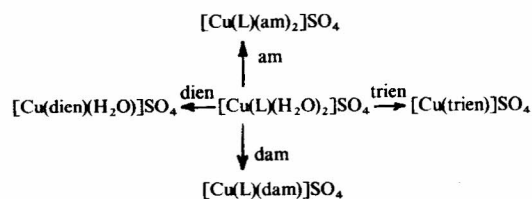


Chart 1

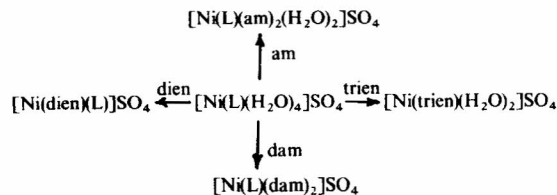


Chart 2

(L = Pyrazole-5-one, am = α -, β - or γ -picoline, dam = ethylene- or propylene-diamine, dien = diethylenetriamine and trien = triethylenetetramine)

The stoichiometries of different complexes have been established on the basis of carbon, hydrogen nitrogen and metal analyses (Table I). The molar conductances of the complexes in nitrobenzene, recorded on a Toshniwal Instrument, showed that all the complexes are ionic in nature.

The purpose of conducting these replacement reactions was to find out whether pyrazole-5-one is replaced on treatment with amine ligands possessing different ligand field strengths. Charts I and II sum up the reactions carried out.

These charts indicate that monodentate and bidentate donors i.e., picolines and diamines, replace the two water molecules from the parent Cu(II) complex leaving ligand (L) intact. The tridentate donor, diene, replaces one water molecule and the bidentate pyrazolone ligand (L). The tetradentate attacking ligand, triethylenetetramine, replaces both L and water molecules. In case of Ni(II) parent complex, similar reactions are undergone with the differences that the tridentate attacking ligand, dien, is not able to replace L and the same is replaced only when the tetradentate ligand trien, is used. The formation of new complexes is supported by their analytical, melting point and spectral data.

In the IR spectra of parent complexes three sharp bands are seen at 3460, 1630 and 1560 cm^{-1} which are due to the $-\text{OH}$, $>\text{C}=\text{O}$ and $-\text{C}=\text{N}$ stretches of coordinated water and pyrazole-5-one⁶⁻⁹. In the product Cu(II) complexes of picolines or diamines and Ni(II) complexes of, di- or tri-amines, the latter two

Table 1—Analytical and Magnetic Moment Data of the Complexes

Compound	Colour	m.p. (°C)	Found (Calc.), %					$\mu_{\text{eff.}}$ (B.M.)
			M	C	H	N	SO ₄	
[Cu(α -C ₆ H ₇ N) ₂ (C ₁₁ H ₁₂ N ₄ O)]SO ₄	Reddish-brown	198	11.02 (11.30)	48.85 (44.15)	4.30 (4.66)	14.60 (14.94)	16.86 (17.08)	2.13
[Cu(β -C ₆ H ₇ N) ₂ (C ₁₁ H ₁₂ N ₄ O)]SO ₄ ·2H ₂ O	Brown	205	12.86 (10.62)	44.68 (46.19)	6.11 (5.05)	13.00 (14.09)	18.83 (16.05)	2.18
[Cu(γ -C ₆ H ₇ N) ₂ (C ₁₁ H ₁₂ N ₄ O)]SO ₄ ·2H ₂ O	Brown	M.D	12.00 (10.62)	44.96 (46.19)	5.29 (5.05)	16.02 (14.04)	18.00 (16.05)	2.20
[Cu(C ₆ H ₈ N ₂)(C ₁₁ H ₁₂ N ₄ O)]SO ₄	Yellowish brown	M.D.	14.15 (14.57)	35.51 (35.82)	4.12 (4.62)	18.11 (19.27)	21.82 (22.03)	1.90
[Cu(C ₃ H ₁₀ N ₂)(C ₁₁ H ₁₂ N ₄ O)]SO ₄	Reddish brown	210	13.00 (14.12)	36.13 (37.37)	4.38 (4.92)	17.30 (19.67)	20.11 (21.34)	1.94
[Cu(H ₂ O)(C ₄ H ₁₃ N ₃)]SO ₄ ·H ₂ O	Green	192	22.35 (18.59)	15.22 (21.08)	5.00 (6.98)	15.78 (16.38)	34.00 (28.09)	1.78
[Cu(C ₆ H ₁₈ N ₄)]SO ₄ ·2H ₂ O	Brown	190	17.58 (18.59)	20.73 (21.08)	5.34 (6.98)	15.21 (16.38)	27.86 (28.09)	1.82
[Ni(α -C ₆ H ₇ N) ₂ (H ₂ O) ₂ (C ₁₁ H ₁₂ N ₄ O)]SO ₄ ·2H ₂ O	Yellow	M.D.	8.02 (9.32)	45.10 (43.90)	4.02 (5.44)	14.27 (13.35)	15.02 (15.26)	3.62
[Ni(β -C ₆ H ₇ N) ₂ (H ₂ O) ₂ (C ₁₁ H ₁₂ N ₄ O)]	Yellow	M.D.	8.92 (9.89)	45.16 (46.57)	4.60 (5.09)	15.04 (14.16)	17.08 (16.18)	3.62
[Ni(γ -C ₆ H ₇ N) ₂ (H ₂ O) ₂ (C ₁₁ H ₁₂ N ₄ O)]SO ₄	yellow	M.D.	9.30 (9.89)	44.25 (46.57)	4.05 (5.09)	13.02 (14.16)	15.01 (16.18)	3.61
[Ni(C ₁₁ H ₁₂ N ₄ O)(C ₂ H ₈ N ₂) ₂]SO ₄	Red	186	10.21 (11.95)	35.80 (36.68)	5.10 (5.74)	21.98 (22.80)	(10.85) (11.55)	3.31
[Ni(C ₁₁ H ₁₂ N ₄ O)(C ₃ H ₁₀ N ₂)]SO ₄ ·H ₂ O	yellow	202	9.68 (0.95)	37.42 (38.01)	6.02 (6.38)	16.26 (17.87)	16.96 (17.87)	3.46
[Ni(H ₂ O)(C ₁₁ H ₁₂ N ₄ O)(C ₄ H ₁₃ N ₃)]SO ₄ ·H ₂ O	Dark green		(10.81) (11.50)	34.20 (35.21)	5.49 (5.73)	18.04 (19.23)	18.46 (18.82)	3.38
[Ni(C ₆ H ₁₈ N ₄)(H ₂ O)]SO ₄ ·4H ₂ O	Yellow		13.66 (14.35)	16.68 (17.62)	3.82 (4.92)	12.58 (13.69)	22.42 (23.48)	3.06

L = C₁₁H₁₂N₄O; M.D. = melts with decomposition.

bands remain intact while the former disappears, and in its place the characteristic bands of amines appear¹⁰⁻¹³. In the case of the triamine complex of Cu(II) and the tetramine complexes of both the metal(II) ions, the pyrazole-5-one bands also disappear and only the amine bands are observed. The OH stretch, however, does not disappear from the picoline and tetramine complex of Ni(II) as expected. These replacements are in accordance with the positions of ligands in the spectrochemical series and their denticities. The formation of product complex [Ni(trien)(H₂O)₂]SO₄ is an outcome of the geometrical requirements of the incoming tetramine ligand, which causes the replacement of L in preference to H₂O. The parent as well as all the product complexes exhibit two sharp bands around 1100 and 650 cm⁻¹ which are assigned to the ν_3 and ν_4 modes of uncoordinated sulphate groups.

All the copper(II) complexes are paramagnetic ($\mu_{\text{eff.}}$ around 1.90); their electronic spectra show a single peak around 700 nm. These observations along with the analytical data of the complexes show the coordination number of the metal to be four and thus suggest a planar geometry⁶. The paramagnetism of

nickel(II) complexes corresponds to two unpaired electrons. In their electronic spectra, three transitions ν_1 , ν_2 and ν_3 are observed in the ranges 9.50-11.20; 14.00-19.50 and 24.50-28.00 kK respectively, which indicate octahedral structures¹⁴⁻¹⁶.

The above discussion thus establishes that the replacement reactions cause no change either in the coordination number of the metal(II) ion or the geometry of the complex, and the nature of the products formed depends upon the relative strength and the density of the secondary ligand used.

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