Complexes of Iron(II), Cobalt(II), Nickel(II) & Copper(II) with 1-(2-Pyridylazo)-2-naphthol & -2-Phenanthrol & 1-(2-Quinolylazo)-2-phenanthrol

R C KHULBE & R P SINGH

Department of Chemistry, University of Delhi, Delhi 110 007

and

Y K BHOON*

Sri Venkateswara College, Dhaula Kuan, New Delhi 110 021

Complexes of the types [Cu(LigX], [Cu(Lig)₂] and [M(Lig)₂] [where Lig = deprotonated 1-(2-pyridylazo)-2-naphthol (PAN), 1-(2-pyridylazo)-2-phenanthrol (PAPL) and 1-(2-quinolylazo)-2-phenanthrol (QAPL); X = Cl⁻, Br⁻, I⁻; and M = Ni(II), Co(II) and Fe(II)] have been prepared and characterized on the basis of electronic spectral and magnetic susceptibility measurements. The copper(II) complexes have been studied also by EPR in polycrystalline form and in solution at room temperature, and at liquid nitrogen temperature. From the ESR parameters, covalency in the complexes has been evaluated. The anisotropy in g suggests the presence of low symmetry components of ligand field.

In continuation of our earlier studies[1-7] on transition metal complexes of 2-pyridylazo compounds, we have now synthesized 1-(2-quinolylazo)-2-phenanthrol, (QAPL, I), a new member of this series, and this paper describes the magnetic and spectral properties of complexes of the types [M(QAPL-H)₂], {where M = Cu(II), Ni(II), Co(II), Fe(II)} and [Cu(II) (QAPL-H) X] (where X = Cl⁻ and Br⁻). The copper(II) complexes have been studied by EPR technique also both at room temperature in polycrystalline state and solution, and at liquid nitrogen temperature in frozen state.

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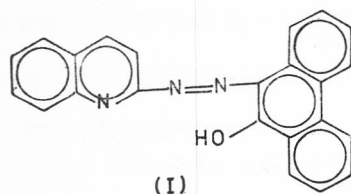
Materials and Methods

[Cu^{II} (PAN-H) X] and [Cu^{II} (PAPL-H) X] (where X = Cl⁻, Br⁻ and I⁻) are the same as reported by us earlier[4].

QAPL was synthesized by the condensation of 2-hydrazinoquinoline with 9,10-phenanthraquinone. 2-Hydrazinoquinoline (7.95 g, 0.05 mol), prepared by the method reported earlier[8], was dissolved in 100 ml ethanol and the solution was added to a boiling ethanolic solution of 9,10-phenanthraquinone (10.4 g, 0.05 mol). To the resulting solution, 5 ml conc. HCl was added and it was refluxed for 30 min.

The yellow colour of phenanthraquinone changed to red; the solution was neutralized with 1 : 1 ammonia when the product precipitated. It was washed with water, ethanol, and finally recrystallized from a mixture of benzene and chloroform (70 : 30). The reddish crystalline needles melt with decomposition at 235°C. [Found : C, 78.98; N, 11.89; H, 4.08. Calc. : C, 79.08; N, 12.03; H, 4.29%].

[Cu^{II}(QAPL-H)Cl] and [Cu^{II}(QAPL-H)Br] were prepared by mixing aqueous solution of CuCl₂.2H₂O (0.17 g, 0.001 mol) or CuBr₂ (0.2258, 0.001 mol) with a boiling DMF solution of QAPL (0.35 g, 0.001 mol). The mixing resulted in the immediate change of orange colour to dark violet-red to blue in each case. The resulting solution was refluxed on a water-bath and its volume was reduced to one-third by distilling off excess of the solvent under reduced pressure. Dark coloured compound separated out in each case which was filtered off, washed successively with water and acetone and dried *in vacuo* over P₄O₁₀.

A complex of composition Cu(QAPL-H)₂ was obtained while attempting to prepare Cu(QAPL-H) I by the above method using Cu₂I₂ dissolved in liquor ammonia. However, Ni^{II} (QAPL-H)₂, Fe^{II} (QAPL-H)₂ and Co^{II} (QAPL-H)₂ were also prepared using the above method but taking the metal chloride and the ligand in 1 : 2 molar ratio.

Magnetic susceptibility measurements were carried out on a Gouy balance using Hg [Co(NCS)₄] as the calibrant.

The EPR spectra were recorded on a Varian E-4 EPR spectrometer operating in X-band frequency (9.5 MHz). The absorption spectra were recorded

in nujol mull on a DMR-21 UV-ViS-NIR spectro-photometer.

Results and Discussion

The results of elemental analyses and magnetic measurements are presented in Table 1. From the analysis, it is obvious that chloro and bromo Cu(II) complexes are of the type 1 : 1 (metal : ligand) while the third Cu(II) complex which was synthesized with the intention of getting [Cu^{II} (QAPL-H) I] is in fact [Cu^{II}(QAPL-H)$_2$].

Octahedral and square-planar copper(II) complexes[9-13] show magnetic moments in the range 1.73- 2.03 B.M. while tetrahedral copper(II) comp-lexes are expected to show magnetic moments above 2.00 B.M. The magnetic moments of the present three copper(II) complexes with QAPL fall in the range expected for tetrahedral complexes. The magnitudes of magnetic moment values, indicate appreciable amount of orbital contribution which could possibly arise from the lesser distortion in the tetrahedral structure and a smaller degree of delocali-zation of the unpaired electron to the ligand orbitals[14-18]. This behaviour is corroborated by the absorption spectra of the complexes recorded in nujol mull. In [Cu^{II}(QAPL-H)$_2$], the absorption around 8340 cm^{-1} cannot be taken to correspond to $^2E_g \rightarrow \, ^2T_{2g}$ transition of octahedral copper(II) be-cause 10 Dq for the present ligand will be even less than that for H$_2$O and, therefore, in this complex the ligand is supposed to act as a bidentate ligand, coordinating through the phenolic O and the nitrogen of the azo group while the quinoline part of the molecule remains uncoordinated. However, the chloro and bromo complexes are tetrahedral and QAPL behaves as a terdentate ligand coordinating through the nitrogen of quinoline ring, nitrogen of the azo group and oxygen of the phenanthrol part. [Cu^{II}(QAPL-H) Cl] and [Cu^{II}(QAPL-H) Br] show absorption bands at 11110, 16800 and 11110, 15384 cm^{-1} respectively. The variation in the position of second band indicates that it is not a charge-transfer band; rather it has a ligand field origin. From the values of the magnetic moments, it could be conclud-ed that the distortion of the tetrahedral structure increases in the following order : [Cu^{II}(QAPL-H)$_2$]> [Cu^{II}(QAPL-H)Br] > [Cu^{II}(QAPL-H)Cl]. ESR

spectra of the complexes discussed below also favour this conclusion.

[Cu^{II}(PAN-H)X] and [Cu^{II}(PAPL-H)X] (X = Cl$^-$ Br$^-$, I$^-$) are the same compounds as reported by us earlier[4]. We now report the results of ESR studies on the copper(II) complexes of the 2-pyridylazo and 2-quinolylazo compounds.

Due to the low solubilities of the complexes in chloroform, we have studied the EPR spectra of these compounds in DMF both at room temperature (RT) and in the frozen solution at liquid nitrogen temperature (LNT). All the complexes in solution at RT show a four-line pattern (Fig. 1) due to Cu hyperfine structure, and the line-width is spin-dependent. The lines in the low field region are quite broad probably due to the bulky size of the tumbling complex species. However, the lines in the high-field region are quite sharp and intense. g_{iso} in all the cases is found to be centred at 2.123 $\pm$ 0.002 The spectra have also been recorded by freezing the same solution at LNT. The spectra are anisotropic (Fig. 2) and yield g_{xx}, g_{yy} and g_{zz}; g_{zz} in all the
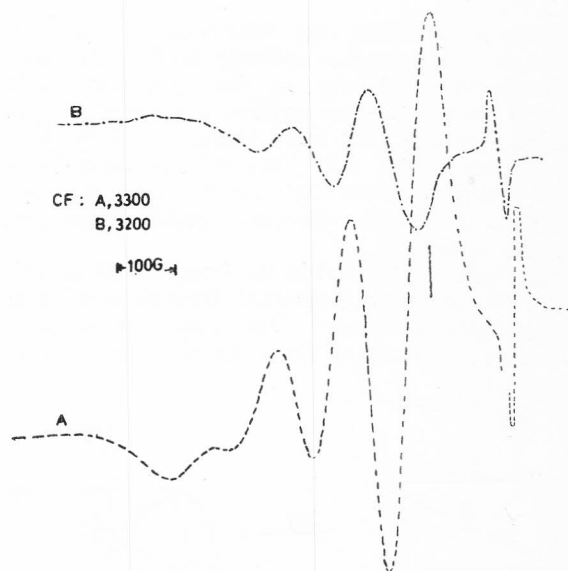

Fig. 1 — ESR spectra of complexes at RT {– – – – –, [Cu^{II} (PAN-H)Cl]; .—.—.—.—., [Cu^{II}(PAPL-H)Cl]}.

Table 1—Elemental Analyses and Magnetic Moment Data for the Complexes

Compound	Found (Calc.), %					μ_{eff} (B.M.)
	M	C	N	H	X	
[Cu^{II} (QAPL-H)Cl]	14.05 (14.21)	61.69 (61.74)	9.21 (9.39)	3.09 (3.13)	7.89 (7.94)	2.29
[Cu^{II} (QAPL-H)Br]	7.38 (7.42)	55.94 (56.03)	8.47 (8.53)	2.67 (2.83)	16.14 (16.24)	2.24
[Cu^{II} (QAPL-H)$_2$]	8.19 (8.36)	72.58 (72.67)	10.98 (11.06)	3.56 (3.68)	—	2.20
[Co^{II} (QAPL-H)$_2$]	7.68 (7.80)	73.05 (73.12)	10.98 (11.12)	3.67 (3.71)	—	5.31
[Ni^{II} (QAPL-H)$_2$]	7.56 (7.78)	73.05 (73.14)	11.05 (11.13)	3.69 (3.69)	—	3.28
[Fe^{II} (QAPL-H)$_2$]	7.29 (7.43)	73.19 (73.42)	11.17 (10.91)	3.65 (3.72)	—	4.18
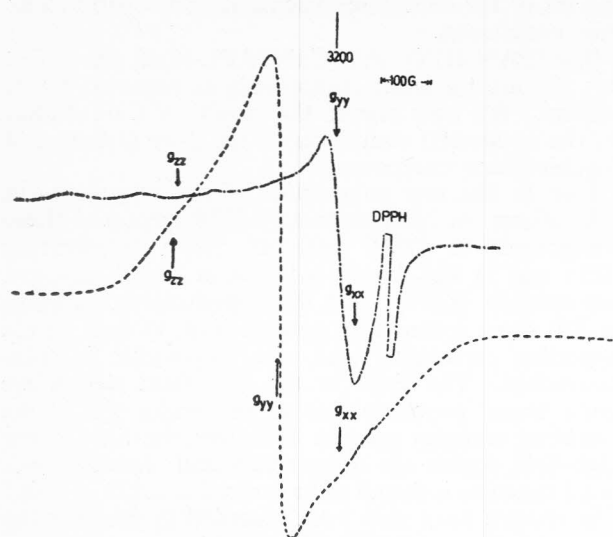
Fig. 2 — ESR spectra of [Cu^{II} (PAN-H)I] in DMF frozen solution at LNT {– – – –, scan range 2000 G; .—.—.—.— scan range 400 G}.

Fig. 3 — ESR spectra of complexes in DMF frozen solution at LNT {– – – – –, [Cu^{II} (QAPL)$_2$]; —.—.—. [Cu^{II} (QAPL-H) Br]}.

cases shows splitting into four components equally spaced due to hyperfine splitting by Cu. g_{yy} shows superhyperfine splitting; in the spectrum of [Cu (PAN-H) I] a nine-line pattern appearing in three bunches, each having three lines, is clearly visible. The appearance of nine lines reflects the non-equivalent nature of the two coordinating nitrogens. The two equivalent nitrogens should have given only five lines.

The g values observed in the frozen DMF solution appreciably differ in magnitude from those obtained in polycrystalline state[4]. The difference could be accounted by change of stereochemistry in coordinat-
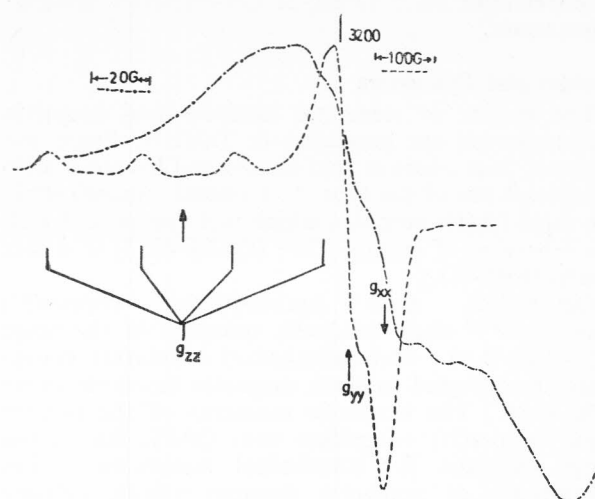
ing DMF solution from planar (II) to octahedral(III). Some of the EPR parameters calculated from the spectra are presented in Table 2. $A_{dipolar} = A_{zz} - A_{iso}$, which is a measure of the d-electron density, has also been evaluated from the LNT spectra in some cases and the covalency follows the order : [Cu^{II} (PAN-H)Cl] > [Cu^{II}(PAN-H)Cl] > [Cu^{II} (PAN-H)I].

The ESR spectrum of [Cu^{II}(QAPL-H)$_2$] recorded (Fig. 3) at LNT shows three g values due to the very low symmetry of the ligand field. The anisotropic nature of g indicates that the possible arrangement of coordinating centres in the complex is as shown in (IV) and not that shown in (V).
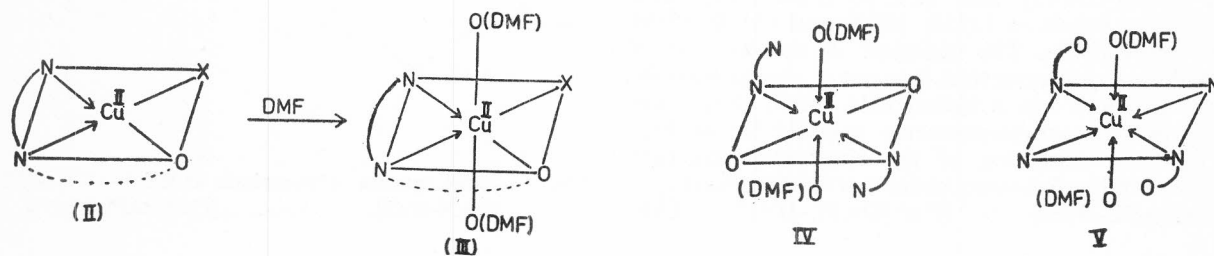

Table 2—EPR Parameters for Copper(II) Complexes in DMF Solution

Compound	Temp. (K)	g_{iso}	g_{zz}	g_{yy}	g_{xx}	A_{zz}^{Cu}	A_{iso}^{Cu} (in Gauss)	A dipolar	A^{N}	Covalency (%)
[Cu^{II} (PAN-H)I]	RT	2.123	—	—	—	—	64.00	96.00	—	—
	LNT	—	2.226	2.052	2.012	160	—	—	10.57	53.18
[Cu^{II} (PAPL-H)Br]	RT	—	—	—	—	—	—	—	—	—
	LNT	—	2.377	2.053	2.025	163.3	—	—	11.25	—
[Cu^{II} (PAN-H)Cl]	RT	2.123	—	—	—	—	60.00	92.5	—	54.88
	LNT	—	2.377	2.061	2.031	152.5	—	—	13.0	—
[Cu^{II} (PAPL-H)Cl]	RT	2.125	—	—	—	—	65.00	86.6	—	—
	LNT	—	2.373	2.059	2.019	151.7	—	—	—	57.76
[Cu^{II} (PAPL-H)I]	RT	2.124	—	—	—	—	70.00	—	—	—
	LNT	—	—	—	—	—	—	—	—	—
[Cu^{II} (QAPL-H)Br]	LNT	—	2.315	2.071	2.039	150.0	—	—	—	—
[Cu^{II} (QAPL-H)$_2$]	LNT	—	2.229	2.137	2.045	—	—	—	—	—

The arrangement (V) will give rise to axial symmetry and the ESR spectrum should give only g_{II} and $g_{\perp}$ values and not g_{xx}, g_{yy} and g_{zz}.

This also confirms the fact that quinoline part of QAPL will be uncoordinated when it behaves as a bidentate ligand as in [Cu^{II}(QAPL)$_2$] complex. The tetrahedral geometry of the complexes is not retained in DMF solution and the spectra correspond to octahedral copper(II) complexes where the axial positions are occupied by solvent molecules coordinating through oxygen.

Octahedral nickel(II) complexes which have $^3A_{2g}$ as the ground state show RT magnetic moment values in the range 2.9 - 3.3 B.M. while the tetrahedral complexes with $^3T_1(P)$ as the ground state have moments always more than 3.3 B.M., usually falling in the range 3.4 - 3.9 B.M., which are temperature dependent[19,20]. The nickel(II) complex under study has magnetic moment value of 3.28 B.M. and thus, in view of the elemental analyses and terdentate character of the ligand, the complex could be assigned an octahedral structure which is supported by the absorption spectra of the complex. Out of the three characteristic bands expected in octahedral geometry[21,22] around nickel (II), only those due to the transitions $^3A_{2g} \rightarrow {}^2T_{2g}$ (v_1) and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (v_2) have been identified at 8160 and 12500 cm^{-1}. The third band, $^3A_{2g} \rightarrow {}^3T_{1g}$ (v_3) could not be located due to the appearance of charge-transfer bands in the same region.

Tetrahedral cobalt(II) complexes with $^4A_2$ ground state show magnetic moments close to the spin-only value for three electrons in the range 4.4 - 4.8 B.M. However, in an octahedral crystal field, the magnetic moment values are much higher due to orbital contribution[23]. In the present case, the magnetic moment value is found to be 5.31 B.M. which clearly rules out the possibility of tetrahedral geometry in the complex and supports the octahedral environment around cobalt. Square-planar geometry is also ruled out since the planar cobalt(II) complexes are found to be of low spin type ($S = 1/2$).

The corroboration of the tetrahedral geometry indicated by magnetic moment data cannot be obtained from spectral data because charge-transfer bands obscure the low intensity ligand-field bands.

For octahedral iron(II) compounds, magnetic moment is expected to be around 5.64 B.M. in high-spin state while the low-spin complexes are diamagnetic. The magnetic moment for the present iron(II) compound is 4.18 B.M., which lies between those expected for states with $S = 2$ and $S = 0$. The intermediate value for the magnetic moment could possibly be due to $^5T_{2g} \rightleftharpoons {}^1A_{1g}$ equilibrium which however can be confirmed only by the variable temperature susceptibility data. The absorption spectrum of the complex in nujol mull has three bands at 7690, 9260 and 12500 cm^{-1}. Octahedral Fe(II) ion is characterised by the transition $^5T_{2g} \rightarrow {}^5E_g$. This band appears as a doublet, with a splitting of 1570 cm^{-1} due to Jahn Teller effect[24]. It is difficult to assign the ligand-field bands arising due to low spin iron(II) molecules because of the appearance of charge-transfer bands in the same region. But the lowering in the magnetic moment value as a result of exchange interactions could be ruled out in view of the structure of ligand involving very bulky quinoline and phenanthrene moieties.

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