

Chelates of Co(III) & Cu(II) with 1-(2'-Pyridylazo)-2-phenanthrol (PAPL) & 1-(2'-Pyridylazo)-2-naphthol (PAN)

K. B. PANDEYA & R. P. SINGH

Department of Chemistry, University of Delhi, Delhi 110007

and

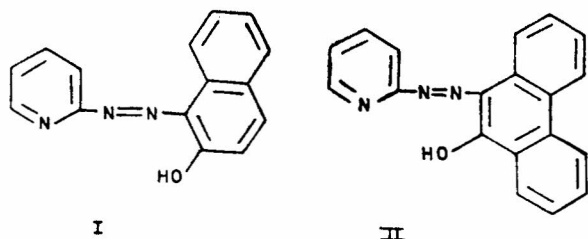
Y. K. BHOON

Sri Venkateshwara College, Delhi

Received 28 July 1975; accepted 20 January 1976

Complexes of 1-(2'-pyridylazo)-2-phenanthrol and 1-(2'-pyridylazo)-2-naphthol with Co(III) ($\text{CoL}_2\text{X}\cdot 2\text{H}_2\text{O}$, X=Cl, Br or ClO_4) and with Cu(II) (CuLX , X=Cl, Br or I) have been prepared and characterized on the basis of analytical, magnetic susceptibility and ESR data. Co(III) complexes show residual paramagnetism of magnitudes varying in the order PAN < PAPL for the ligands and $\text{ClO}_4 < \text{Br} < \text{Cl}$ for the anions. In Cu(II) complexes, change in X shows a regular change in the ESR spectra.

FOR the determination of various metal ions¹⁻⁹, 2-pyridylazo compounds have been extensively used as spectrophotometric reagents. The present paper describes preparation and characterization of Co(III) and Cu(II) complexes of 1-(2'-pyridylazo)-2-naphthol (PAN) (I) and 1-(2'-pyridylazo)-2-phenanthrol (PAPL) (II).



Materials and Methods

The ligands PAN and PAPL were prepared by literature methods^{1,10}.

Preparation of complexes: $\text{CoL}_2\text{X}\cdot 2\text{H}_2\text{O}$ — 15 ml of 0.1M aqueous solution of the cobaltous salt (perchlorate, chloride or bromide) were added to an ethanolic solution of the ligand (750 mg of PAN or 900 mg of PAPL in 500 ml ethanol). pH of the solution was adjusted to 3.0 in each case, by adding dilute sodium hydroxide solution. Intense bluish green colour developed instantaneously. The contents were refluxed on a water-bath for 2 hr. On concentration, the complex separated out in the form of fine flakes. It was filtered, washed successively with water, ethanol and acetone and dried at $\sim 60^\circ$. Results of elemental analyses are presented in Table 1.

All the complexes are insoluble in water, ethanol and acetone but are soluble in other common organic solvents. These do not melt or decompose on heating up to 300° .

CuLX — For CuCl and CuBr complexes, 15 ml of 0.1M ethanolic solution of the required copper

halide were added to an ethanolic solution of the ligand (350/450 mg of PAN/PAPL dissolved in 500 ml ethanol). For CuI, ammoniacal solution of Cu_2I_2 was added to an ethanolic solution of the ligand keeping metal-ligand ratio as 1:1. The contents were refluxed for 2 hr. On concentration, reddish violet complex separated out in each case. The complexes were worked out as in the case of Co(III) complexes. Results of elemental analyses are presented in Table 1. All the complexes are insoluble in water but soluble in common organic solvents. The complexes do not melt or decompose on heating up to 300° .

Magnetic susceptibility measurements on the powdered samples were carried out on a Gouy balance using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as the calibrant.

The EPR spectra of the complexes (powder) were recorded on an X-band Varian V-4502-12 EPR spectrometer.

Results and Discussion

The magnetic susceptibility data for all the complexes are presented in Table 2.

A feeble paramagnetism is shown by all the Co(III) complexes. The Co(II) complexes should show magnetic moments corresponding to three unpaired spins in tetrahedral and high-spin octahedral stereochemistries and one unpaired spin in low-spin octahedral and square-planar stereochemistries. The magnetic susceptibility data in all the cases exclude the possibility of the presence of bivalent cobalt and indicate aerial oxidation during complexation. Co(III) (electron configuration $3d^6$) generally favours d^2s^3 hybridization to give spin-paired diamagnetic complexes¹¹. But, a feeble paramagnetism in Co(III) complexes may arise by two different mechanisms. A temperature-independent contribution to the paramagnetism susceptibility may spring from the high frequency term in Van Vleck formula¹¹⁻¹⁵ and a temperature-

TABLE 1 — ANALYTICAL DATA FOR THE COMPLEXES

Complex	M (%) Found (calc.)	C (%) Found (calc.)	N (%) Found (calc.)	H (%) Found (calc.)	X (%) Found (calc.)
Co(PAN) ₂ Cl ₂ ·2H ₂ O	9.31 (9.41)	56.12 (57.4)	13.01 (13.4)	4.35 (3.83)	5.50 (5.60)
Co(PAN) ₂ Br ₂ ·2H ₂ O	8.70 (8.78)	53.60 (53.70)	12.2 (12.5)	3.86 (3.58)	11.8 (11.9)
Co(PAN) ₂ ClO ₄ ·2H ₂ O	8.40 (8.53)	51.9 (52.1)	11.9 (12.1)	3.30 (3.47)	—
Cu(PAN)Cl	18.31 (17.98)	51.88 (51.62)	12.11 (11.90)	2.88 (2.64)	10.23 (10.02)
Cu(PAN)Br	16.24 (16.05)	46.00 (45.67)	10.72 (10.52)	2.55 (2.42)	20.42 (20.15)
Cu(PAN)I	14.48 (14.28)	41.06 (39.94)	9.58 (9.38)	2.28 (2.04)	28.29 (27.94)
Co(PAPL) ₂ Cl ₂ ·2H ₂ O	8.00 (8.09)	63.00 (62.8)	11.3 (11.6)	4.23 (3.86)	4.79 (4.89)
Co(PAPL) ₂ Br ₂ ·2H ₂ O	7.58 (7.64)	58.19 (59.20)	10.6 (10.9)	3.75 (3.63)	10.10 (10.37)
Co(PAPL) ₂ ClO ₄ ·2H ₂ O	7.70 (7.45)	58.9 (57.7)	10.8 (10.6)	3.68 (3.58)	—
Cu(PAPL)Cl	16.01 (15.91)	57.42 (57.49)	10.58 (10.57)	3.02 (3.21)	8.94 (8.39)
Cu(PAPL)Br	14.40 (14.21)	51.65 (51.42)	9.51 (9.40)	2.72 (2.61)	18.10 (17.93)
Cu(PAPL)I	13.16 (13.01)	46.70 (46.42)	8.60 (8.42)	2.46 (2.28)	26.00 (25.65)

PAN = 1-(2'-pyridylazo)-2-naphthol; PAPL = 1-(2'-pyridylazo)-2-phenanthrol.

TABLE 2 — MAGNETIC SUSCEPTIBILITY DATA OF THE COMPLEXES

Complex	Temp. (°K)	$\chi_g \times 10^6$ (c.g.s.)	$\chi_{corr} \times 10^6$ (c.g.s.)	μ_{eff} (BM)
Co(PAN) ₂ Cl ₂ ·2H ₂ O	296.0	-0.09761	288.9	0.83
Co(PAN) ₂ Br ₂ ·2H ₂ O	294.0	-0.2423	199.9	0.68
Co(PAN) ₂ ClO ₄ ·2H ₂ O	296.0	-0.221	189.0	0.67
Co(PAPL) ₂ Cl ₂ ·2H ₂ O	295.0	+0.2805	591.8	1.18
Co(PAPL) ₂ Br ₂ ·2H ₂ O	292.0	-0.1052	346.2	0.90
Co(PAPL) ₂ ClO ₄ ·2H ₂ O	296.0	-0.244	222.8	0.79
Cu(PAN)Cl	292.0	4.083	1771.0	2.03
Cu(PAN)Br	293.0	3.467	1542.0	1.90
Cu(PAN)I	292.0	2.889	1468.0	1.85
Cu(PAPL)Cl	294.0	3.868	1749.0	2.03
	207.8	5.898	2559.0	2.07
	154.0	8.041	3410.0	2.05
	123.8	10.570	4417.0	2.08
	103.1	12.080	5018.0	2.03
	83.5	14.740	6078.0	2.01
Cu(PAPL)Br	292.5	2.752	1430.0	1.83
Cu(PAPL)I	292.0	2.719	1566.0	1.91

dependent susceptibility may arise if there is a thermally accessible state placed not too high above the magnetically inert ground state. For Co(III) complexes¹¹⁻¹⁵, the value of temperature-independent susceptibility should be of the order of 200×10^{-6} c.g.s. units. This does not account for the magnetic susceptibility of some of the present complexes. Therefore, a contribution from the thermally accessible states also is indicated.

A perusal of the magnetic susceptibility data reveals the following features: (1) The residual paramagnetism of PAPL complexes is higher than that of PAN complexes in all the cases, and (2) with both the ligands, the values with different anions follow the order: Cl > Br > ClO₄.

TABLE 3 — EPR PARAMETERS OF THE COMPLEXES

Complex	g_1	g_2	g_3
Cu(PAN)Cl		2.049	2.138
Cu(PAN)Br		2.078	2.137
Cu(PAN)I	2.045	2.088	2.404
Cu(PAPL)Cl		1.996	2.123
Cu(PAPL)Br		2.044	2.194
Cu(PAPL)I	2.006	2.084	2.442

The expected differences in $^1A_{1g} \rightarrow ^1T_{1g}$ transition-energy values for the two ligands (PAN > PAPL) may not give rise to the observed difference in the magnitude of the paramagnetic susceptibilities. There is a difference, therefore, also in the contributions from the thermally accessible states in the case of the two ligands.

Measurements on the Cu(II) complexes under study yield normal magnetic moment values (Table 2). That the magnetic moment value is also temperature-independent has been checked in the case of one complex, CuLCl. Curie's law is obeyed. This confirms the monomeric nature of the complexes¹⁶⁻¹⁸.

The g values from the ESR spectra of Cu(II) complexes have been calculated by the method of Kneubühl¹⁹ and are presented in Table 3. As in the case of several planar Cu(II) complexes²⁰⁻²³, spectra of CuLCl and CuLBr yield only two g values as against the expected three. Spectra of CuLI complexes, however, make possible the calculations of all the three values, g_1 , g_2 and g_3 . The variation in g values is in accordance with the variation in inequality between $\mu_{N,X}$ and $\mu_{N,O}$ as we proceed from Cl through Br to I.

The measured value of g can also be used to a reasonable extent to decide the ground state of

the complex. Those with $d_{x^2-y^2}$ ground state are characterized by

$$g_{\parallel} = 2, \quad g_{\perp} = 2 \left(1 - \frac{3\lambda}{\Delta_1} \right)$$

where $\Delta_1 = E(e_g) - E(a_{1g})$ and those with $d_{x^2-y^2}$ ground state by

$$g_{\parallel} = 2 \left(1 - \frac{4\lambda}{\Delta_2} \right), \quad g_{\perp} = 2 \left(1 - \frac{\lambda}{\Delta_3} \right)$$

where $\Delta_2 = E(b_{2g})$ and $\Delta_3 = E(e_g) - E(b_{1g})$.

The results in the present case reveal a $d_{x^2-y^2}$ ground state for the complexes.

Acknowledgement

Our grateful thanks are due to Prof. T. R. Govindachari, Director, CIBA-Geigy Research Centre, Bombay, for micro-analysis, and Dr B. D. Joshi, Bhabha Atomic Research Centre, Bombay, for ESR measurements.

References

- SHIBATA, S., in *Chelates in analytical chemistry*, edited by H. A. Flaska & A. J. Barnard (Jr), Vol. IV (Marcell Dekker Inc., New York), 1972.
- RISHI, A. K., GARG, B. S. & SINGH, R. P., *Curr. Sci.*, **41** (1972), 117.
- RISHI, A. K., GARG, B. S. & SINGH, R. P., *Curr. Sci.*, **41** (1972), 155.
- RISHI, A. K., GARG, B. S. & SINGH, R. P., *Z. Anal. Chem.*, **259** (1972), 288.
- RISHI, A. K., GARG, B. S. & SINGH, R. P., *Indian J. Chem.*, **10** (1972), 1037.
- BHOON, Y. K., PANDEYA, K. B. & SINGH, R. P., *Curr. Sci.*, **43** (1974), 306.
- BHOON, Y. K., PANDEYA, K. B. & SINGH, R. P., *Chimia*, **28** (1974), 659.
- BHOON, Y. K., PANDEYA, K. B. & SINGH, R. P., *J. Indian chem. Soc.*, **51** (1974), 960.
- BHOON, Y. K., PANDEYA, K. B. & SINGH, R. P., *Indian J. Chem.*, **13** (1975), 84.
- CHISWELL, B., LIONS, F. & TOMLINSON, M. L., *Inorg. Chem.*, **3** (1964), 492.
- KAMIMURA, H., KOIDE, S., SUGANO, S. & TANABE, Y., *J. phys. Soc. (Japan)*, **13** (1958), 464.
- BALLHAUSEN, C. J. & ASMUSSEN, R. W., *Acta chem. scand.*, **11** (1957), 479.
- GRIFFITH, J. S. & ORGEL, L. E., *Trans. Faraday Soc.*, **53** (1957), 601.
- KERNAHAN, J. L. & SIENKO, M., *J. Am. chem. Soc.*, **77** (1955), 1078.
- VAN VLECK, J. H., *Electronic and magnetic susceptibilities* (Oxford University Press, Oxford), 1932.
- FIGGIS, B. N. & LEWIS, J., in *Progress in inorganic chemistry*, Vol. 6, edited by F. A. Cotton (Interscience Publishers, New York), 1964, 37.
- KATO, M., JONASSEN, H. B. & FANNING, J. C., *Chem. Rev.*, (1964), 99.
- CARLIN, R. L., *Transition metal chemistry*, Vol. 6 (Marcell Dekker Inc., New York).
- KNEÜBUHL, F. K., *J. chem. Phys.*, **33** (1960), 1074.
- KIVELSON, D. & NEIMAN, R., *J. chem. Phys.*, **35** (1961), 149.
- Electron spin resonance of metal complexes*, edited by T. F. Yen (Plenum Press, New York), 1969, 13.
- ROGERS, R. N. & PAKE, G. E., *J. chem. Phys.*, **33** (1960), 1107.
- MCGARVEY, B. R., *J. phys. Chem.*, **61** (1957), 1232.