

TABLE 2 — c.m.c. AND C.S.T. VALUES OF COBALT SOAPS IN DIFFERENT SOLVENTS

Solvent	Cobalt stearate		Cobalt palmitate		Cobalt myristate	
	C.S.T. (0°C)	c.m.c. × 10 <sup>5</sup> (mole/litre)	C.S.T. (0°C)	c.m.c. × 10 <sup>5</sup> (mole/litre)	C.S.T. (0°C)	c.m.c. × 10 <sup>5</sup> (mole/litre)
Benzene	50.0	1.6	46.5	2.7	45.0	4.2
<i>m</i> -Xylene	45.0	2.0	43.5	2.4	42.5	3.3
Toluene	50.0	1.0	49.0	1.4	47.5	3.6
Chlorobenzene	47.0	1.2	44.5	1.9	43.0	2.5
Nitrobenzene	45.0	0.80	43.5	1.2	42.0	2.2
Ethyl methyl ketone	46.5	2.2	43.5	3.3	42.5	4.0

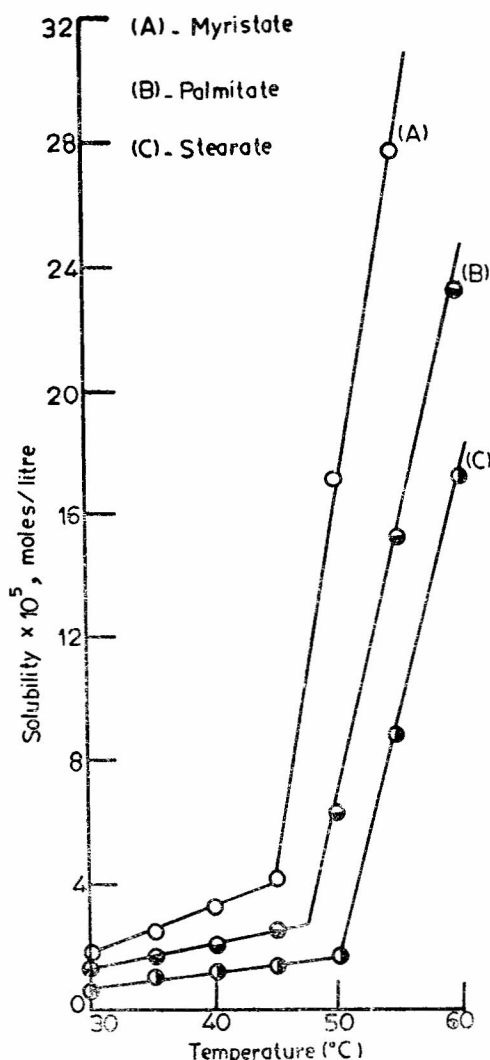


Fig. 1 — Effect of temperature on the solubility of cobalt soap in benzene

sufficiently soluble. Activity measurements were made and solubility determined as already described<sup>1,2</sup>.

The solubility of cobalt soaps (Table 1) indicates that the solubility is more for soaps with smaller carbon chain length. Further, it is obvious that these soaps are sparingly soluble in all solvents and no correlation between the solubility and nature of solvent emerges.

The effect of temperature on the solubility of cobalt soaps in benzene is graphically shown in

Fig. 1. Almost, similar behaviour was observed in other solvents, viz. toluene, *m*-xylene, ethyl methyl ketone, nitrobenzene and chlorobenzene. The solubility of the soaps is quite low at lower temperature but increases gradually as the temperature increases. The Krafft point<sup>4</sup> or the critical solution temperature (C.S.T.) is also very much evident from Fig. 1. The concentration at which significant increase in solubility of cobalt soaps occurs denote the c.m.c. of the soap. The explanation of this significant increase in solubility is obviously due to the fact that the single soap molecule is relatively less soluble whereas the micelle is highly soluble. The c.m.c. and C.S.T. values calculated from the abrupt changes in solubility behaviour are given in Table 2. It is observed that c.m.c. and C.S.T. values are a function of carbon chain length of the soap. Further, the C.S.T. value decreases and c.m.c. value increases as we pass on from cobalt stearate to myristate. Since cobalt myristate has highest solubility (Table 1), we may conclude that higher the solubility of the soap, the lower is its C.S.T. and higher is the c.m.c. value.

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#### Magnetic Properties of Ru(III) Complexes of 1-(2-Pyridylazo)-2-naphthol & 1-(2-Pyridylazo)-2-phenanthrol

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Magnetic susceptibility measurements on Ru(III) complexes of 1-(2-pyridylazo)-2-naphthol and 1-(2-pyridylazo)-2-phenanthrol show antiferromagnetic interactions. Dichloro-bridged structure has been proposed.

THIS note describes the preparation of Ru(III) complexes of 1-(2-pyridylazo)-2-naphthol (PAN) and 1-(2-pyridylazo)-2-phenanthrol (PAPL) and their

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characterization by magnetic susceptibility measurements. The ligands belong to a series of 2-pyridylazo compounds<sup>1</sup> known for their analytical applications, particularly as spectrophotometric reagents. Ruthenium(III) complexes have a possible role to play in homogeneous catalysis.

The ligand PAN<sup>1</sup> and PAPL<sup>2</sup> were prepared and purified by the literature methods. Purity of the compounds was checked by TLC<sup>3</sup>.

For preparing the complexes aqueous solution of ruthenium(III) chloride trihydrate and ethanolic solution of the respective ligand were mixed together in the metal-ligand ratio of 1:2. Intense red colouration developed. The contents were refluxed for 2 hr and concentrated, when the complexes, separated out as crystalline granules which were filtered, washed successively with water, ethanol and acetone and dried at ~60°.

Analysis for Ru(III)-PAN complex [Found: Ru, 14.83; C, 55.7; H, 3.18; N, 12.3; Cl, 5.10. Ru(C<sub>15</sub>H<sub>10</sub>N<sub>3</sub>O)<sub>2</sub>Cl.2H<sub>2</sub>O requires Ru, 15.1; C, 53.8; H, 3.60; N, 12.6; Cl, 5.31%]. Analysis for Ru(III)-PAPL complex [Found: Ru, 12.9; C, 60.0; H, 3.90; N, 10.7; Cl, 4.50. Ru(C<sub>19</sub>H<sub>12</sub>N<sub>3</sub>O)<sub>2</sub>Cl.2H<sub>2</sub>O requires Ru, 13.1; C, 59.3; H, 3.64; N, 10.9; Cl, 4.62%].

Complexes are insoluble in water, ethanol and acetone and dissolve in other common organic solvents, viz. chloroform, pyridine, dimethylformamide and nitrobenzene. Conductance measurements in nitrobenzene medium show them to be non-electrolytes.

Magnetic susceptibility measurements (Table 1) on the solid complex were made by Gouy method using mercury tetrathiocyanatocobaltate(II) as calibrating agent ( $\chi_g = 16.44 \times 10^{-6}$  cgs).

Ruthenium(III)<sup>5</sup>, although isoelectronic with Fe(III) and Mn(II), assumes invariably the ground state  $^2T_{2g}(e_g^5)$  in its complexes. Magnetic moments of low-spin octahedral Ru(III) complexes are expected to lie around 2.0 BM ( $\lambda = -1180$  cm<sup>-1</sup>), with very little temperature dependence. However, the complexes under study show room temperature magnetic moments of 1.45 BM for Ru(III)-PAN and 1.77 BM for Ru(III)-PAPL. Also the low temperature magnetic susceptibility measurements on the Ru(III)-PAPL complex reveal that the magnetic moment decrease with decreasing temperature (Table 1). A plot of  $1/\chi$  vs  $T$  shows that the compound obeys Curie-Weiss law ( $\theta = -205^\circ\text{K}$ ) in the temperature range  $300^\circ\text{K} > T > 100^\circ\text{K}$ . Below  $100^\circ\text{K}$  the susceptibility shows a sudden drop. These

observations indicate the presence of antiferromagnetic interactions in the complex with the Neel point of  $100^\circ\text{K}$ . For low-spin Ru(III) complexes involving exchange interactions between the ruthenium atoms of spin  $S_2 = S_2 = \frac{1}{2}$ , the susceptibility may be given by<sup>4</sup>

$$\chi_A = \frac{3K}{T} \frac{1}{3+x^2} + N\alpha$$

where  $x = \exp(J/KT)$ ,  $K = \frac{N g^2 \beta^2}{3K}$  ( $= 0.1251 \text{ g}^2$ ) ( $J$  is the exchange coupling constant). The best fit between the theoretical values and the experimental values in the present case is obtained for  $J = 45$  cm<sup>-1</sup>. However, the value of  $J$  is comparatively smaller, while the value of  $\theta$  is quite large. In fact, use of spin-only two-centre interaction formula in the case of a Ru(III) complex, where spin orbit interaction is quite large ( $\lambda, -1180$  cm<sup>-1</sup>), involves big approximation.

Considering the composition of Ru(III)-PAPL complex and assuming the ligand to be bidentate in nature, it is possible to construct two models, one a binuclear complex involving two chlorine bridges and the other, involving only one chlorine bridge leading to a chain polymer. However, the low value of  $J$  ( $= 45$  cm<sup>-1</sup>) forbids a chain polymer and favours coupling between ions bridged by two chlorine atoms.

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#### Complexes of Zn(II), Cd(II) & Hg(II) with Schiff base Derived from *o*-Vanillin & Aniline

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Solid 1:1, non-electrolytic complexes of Zn(II), Cd(II) and Hg(II) with the Schiff base derived from *o*-vanillin and aniline have been prepared and characterized on the basis of analytical, conductance, electronic and IR spectral data. The complexes are amorphous and reddish-yellow in colour. The IR spectra of the complexes show that coordination takes place through azomethine nitrogen while phenolic group remains undissociated. A chloro-bridged dimeric structure is proposed for the complexes.

IN continuation of our earlier work on the bivalent transition metal complexes of the Schiff bases derived from vanillin<sup>1</sup>, we now report the complexes

TABLE 1 — MAGNETIC SUSCEPTIBILITY DATA OF Ru(III)-PAPL COMPLEX

Temp. (°K)	$\chi_g \times 10^6$ (cgs)	$\chi_{M \text{ corr}} \times 10^6$ (cgs)	$\mu_{\text{eff}}$ (B.M.)
300.0	1.240	1307	1.772
210.0	1.755	1684	1.684
178.0	1.839	1745	1.577
140.0	2.113	1945	1.477
123.5	2.220	2026	1.400
111.0	2.378	2141	1.379
101.0	2.453	2196	1.332
85.5	1.839	1751	1.095