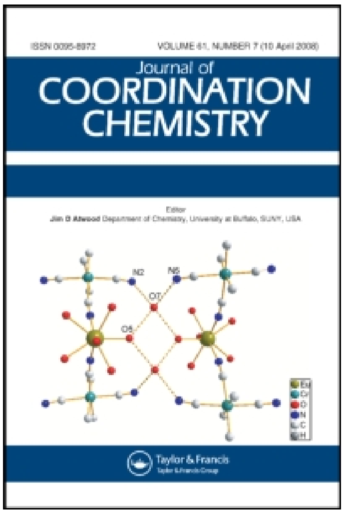

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MAGNETIC EXCHANGE INTERACTION AND SPIN-STATE EQUILIBRIUM IN COBALT(II) COMPLEXES OF 1(2-PYRIDYLAZO)-2-PHENANTHROL

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MAGNETIC EXCHANGE INTERACTION AND SPIN-STATE EQUILIBRIUM IN COBALT(II) COMPLEXES OF 1-(2-PYRIDYLAZO)-2-PHENANTHROL

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1-(2-Pyridylazo)-2-phenanthrol forms two distinct complexes with cobalt(II). Isolation from ethanolic medium yields green coloured $CoL_2 \cdot 4C_2H_5OH$, which shows antiferromagnetic interaction between cobalt(II) ions of $S = 1/2$ ($J = 49\ cm^{-1}$). The green coloured complex dissolves in chloroform to give a pink solution yielding pink crystals of $CoL_2 \cdot 4C_2H_5OH \cdot 1/3\ CHCl_3$, which involves temperature dependent equilibrium between doublet ($S = 1/2$) and quartet ($S = 3/2$) states.

INTRODUCTION

Cobalt(II) attains a variety of stereochemical configurations in its complexes. The coordination sphere of the ion is labile and equilibrium between different stereochemistries in solution is quite common. However, the factors which determine obtaining of a particular stereochemistry are not yet understood.[1,2] Even more interesting feature of the coordination chemistry of cobalt(II) is the occurrence of equilibrium between different spin-states involving same ligand field symmetry.[3–7] Speculations about existence of such an equilibrium to explain the "anomalous" magnetic moment values were made as early as 1933,[2] but a systematic study of the phenomenon leading to conclusive proof was first reported only in 1961[4] by Stouffer *et al.* Relevant data are still rare.

In the course of our investigations on the electronic structures of the metal-chelates of 1-(2-pyridylazo)-2-phenanthrol (PAPhen), the cobalt(II) system showed the following features:

i) Two distinct complexes are formed. Isolation from ethanolic medium yields green complex, $CoL_2 \cdot 4C_2H_5OH$ which dissolves in chloroform to give pink solution yielding pink complex, $CoL_2 \cdot 4C_2H_5OH \cdot 1/3CHCl_3$. The conversion is reversible.

$$\underset{\text{(green)}}{CoL_2 \cdot 4C_2H_5OH} \xrightleftharpoons[C_2H_5OH]{CHCl_3} \underset{\text{(pink)}}{CoL_2 \cdot 4C_2H_5OH \cdot 1/3CHCl_3}$$

ii) Magnetic measurements on the green complex reveal doublet ground state of the cobalt(II) ion involving antiferromagnetic interaction.

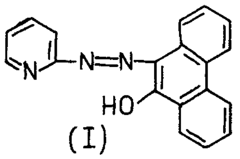
iii) The pink complex shows magnetic properties indicating a Boltzmann distribution between cobalt(II) ions of doublet and quartet spin states.

PAPhen[8] is a new member of a well known series of 2-pyridylazo compounds used extensively as analytical reagents. The ligand molecule (I) has three coordination centres to be used suitably for obtaining a four-coordinate planar (II) or a six-coordinate octahedral (III) stereochemistry, proposed respectively for the green and pink complexes under discussion.

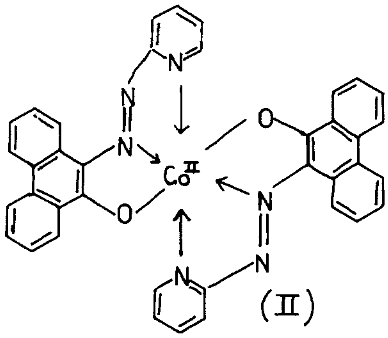
EXPERIMENTAL

(a) Preparation of Compounds

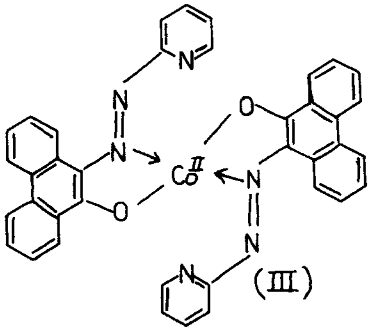
i) 1-(2-pyridylazo)-2-phenanthrol (PAPhen)[9]*:* PAPhen was prepared by the condensation of pyridylhydrazine with phenanthraquinone in acidic medium and precipitated by neutralization with 1:1 ammonia.



(I)



(II)



(III)

It was purified by recrystallization from dry benzene. Purity of the compound was checked by thin layer chromatography.

ii) The green coloured complex: A mixture of 1.0 g ascorbic acid and 0.90 g of PAPhen in 500 ml ethanol was refluxed in a round bottom flask to get a clear solution, while passing nitrogen to make the solution air-free. 0.35 g of $CoCl_2 \cdot 6H_2O$ (solid) was then added and the contents refluxed for about an hour. Intense bluish green colour developed. On concentration, green coloured complex separated out. It was filtered, washed with hot water and ethanol and dried in an electric oven at 30°C. Analysis: Co = 7.00, C = 63.8, H = 5.67 and N = 9.80%; $Co(C_{19}H_{12}N_3O)_2 \cdot 4C_2H_5OH$ requires Co = 7.02, C = 65.8, H = 5.72 and N = 10.0%.

iii) The pink coloured complex: The green coloured complex was dissolved in chloroform and the solution was concentrated, when pink coloured complex separated out. It was filtered, washed with hot water and chloroform and dried in an electric oven at 30°C. Analyses, Co = 6.53, C = 61.8, H = 5.50, N = 9.00 and Cl = 3.88%; $Co(C_{19}H_{12}N_3O)_2 \cdot 4C_2H_5OH \cdot 1/3CHCl_3$ requires Co = 6.70; C = 63.3, H = 5.50, N = 9.56 and Cl = 4.40%.

Tendency of metal chelates of PAPhen to crystalize with the solvent molecules has been observed earlier[9] also.

b) Physical Measurements

Magnetic susceptibility measurements on solid complexes were made by Gouy method using mercury tetrathiocyanatocobaltate(II) as calibrating agent ($\chi_g = 16.44 \times 10^{-6}$ c.g.s. units).

RESULTS AND DISCUSSION

a) Green Coloured Complex, $CoL_2 \cdot 4C_2H_5OH$

The magnetic susceptibility data on the complex is given in Table I. The room temperature magnetic moment value for the complex is near the moment expected for a doublet ground state. For cobalt(II), S = 1/2 is obtained either in a low-spin octahedral complex, $(t_{2g})^6(eg)^1$, ^2E_g, where spin orbit coupling leads to a value of about 1.86 B.M. or in a four coordinate square-planar complex, $(t_{2g})^2(eg)^4(a_{1g})^1$, $^2A_{1g}$, where values in the range 2.1–2.8 B.M. are observed.

But the susceptibility measurements at low temperature reveal that the magnetic moment is temperature-dependent, showing decrease with decreasing temperature. This indicates the presence of antiferro-

TABLE I
Magnetic susceptibility data and some derived parameters for the green complex, $CoL_2 \cdot 4C_2H_5OH$

Temp. (°K)	$\chi_g \times 10^6$ (cgs)	$\chi_M \times 10^6$ (cgs)	$\chi_M^{corr} \times 10^6$ (cgs)	μ_{eff} (B.M.)	Parameters
299.0	1.500	1259	1770	2.06	
204.5	1.826	1532	2043	1.83	Weiss constant (θ) = 87.5°K
173.2	2.082	1747	2258	1.77	Neel Temperature (T_c) = 87.5°K
153.0	2.347	2015	2526	1.76	Exchange integral (J) = 49 cm^{-1}
135.5	2.612	2192	2703	1.71	Magnetic moment in absence of exchange
121.0	2.735	2295	2806	1.65	(μ_{eff}°) = 2.20 B.M.
110.0	2.744	2302	2813	1.58	
85.5	2.864	2403	2914	1.42	

magnetic interaction. In interaction between two ions of S = 1/2, the expression for μ_{eff} per interacting ions takes the form[10]

$$\mu_{eff} = \mu^0_{eff}[1 + 1/3 \exp(2J/kt)]^{-1/2}$$

where J is the exchange integral and μ^0_{eff} is the magnetic moment in absence of exchange. The susceptibility goes through a maximum at $-5J/4K$, the Neel point. The variation of susceptibility with temperature (χ vs. T and $1/\chi$ vs. T) is shown in Figure 1. The Neel point is obtained at 87.5°K. From this the value of the exchange integral, J, has been calculated as 49 cm^{-1}. Well above the Neel point the system obeys Curie–Weiss Law, the value of Weiss constant, θ, being 87.5°K. The system thus shows the property $T_c = |\theta|$. Number of the nearest neighbours of the metal atom in the exchange lattice comes out to be 2.5.

The value of μ_{eff}, the magnetic moment in absence of exchange, calculated by means of equation $\mu_{eff} = 2.83 [\chi(T + \theta)]^{1/2}$ comes out to be 2.20 B.M. This favours a square-planar stereochemistry around cobalt(II). Also, the planar complexes are prone to magnetic exchange between adjacent molecules because of the absence of ligand groups above and below the plane of the complex.

b) Pink Coloured Complex $CoL_2 \cdot 4C_2H_5OH \cdot 1/3CHCl_3$

The magnetic susceptibility data on the complex are given in Table II. Room temperature magnetic moment of the complex, 3.59 B.M., is intermediate between the values expected for low-spin and high-spin octahedral cobalt(II) complexes (S = 1/2, ^2E_g, μ_{eff} = 1.86 B.M. and S = 3/2 $^4T_{1g}$, μ_{eff} = 5.10 B.M.), indicating, therefore, an equilibrium between the two spin-states. None of the other possibilities, viz., an admixture of cobalt(II) complex with cobalt(III) complex antiferromagnetic interaction between cobalt(II) ions with quartet spin-state, or a considerable amount of $4T_1$ (4F) character to the 2E(2G) level, accounts for the way in which the moment varies with the temperature.

Mole fractions of the quartet and doublet states, N_q and N_d have been calculated for each temperature of experiment, assuming a magnetic moment of 1.86 B.M. for the doublet state and 5.10 B.M. for the quartet state. The results are presented in Table II. A plot of ΔG° (= –RT log K) for the equilibrium,

$$\text{spin-free} \rightleftharpoons \text{spin-paired}$$

as a function of the temperature is shown in Figure 2. The nonlinearity of this curve at lower temperatures may be attributed to alteration in the crystal structure as the fraction of doublet molecules increases.[11,12] The values of ΔH° and ΔS° evaluated from the linear part of the graph are –1.00 kcal/mole and –0.375 e.u., respectively.

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TABLE II
Magnetic susceptibility data and some derived parameters for the pink complex $CoL_2 \cdot 4C_2H_5OH \cdot 1/3CHCl_3$

Temp. (°K)	$\chi_g \times 10^6$ (cgs)	$\chi_M \times 10^6$ (cgs)	$\chi_M^{corr} \times 10^6$ (cgs)	μ_{eff} (B.M.)	N_q	N_d	K	$-\Delta G$ (cal.)
292.0	5.568	4904	5485	3.58	0.420	0.580	1.4	196.3
215.8	5.805	5102	5683	3.13	0.285	0.715	2.5	395.4
162.2	6.103	5364	5945	2.78	0.190	0.810	4.3	473.2
131.7	6.342	5559	6140	2.54	0.136	0.964	6.3	484.9
108.2	7.186	6317	6898	2.41	0.114	0.886	7.8	444.4
84.6	7.341	6455	7036	2.18	0.060	0.940	15.6	464.7

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