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ESR Spectra of Low Symmetry High Spin Cobalt(II) Complexes. 8 [1]. Observation of ESR Spectra of Dichloro-Tetrakispyrazole Cobalt(II) Doped into Paramagnetic Nickel(II) Analogue

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We have recently reported the ESR spectra of dichloro-tetrakispyrazole cobalt(II), $Copyz_4Cl_2$, [2]. At that time we were not able to find any suitable diamagnetic host, therefore we recorded the ESR spectra of the pure compound, yielding g_1 = 2.14, g_2 = 4.55, g_3 = 5.83. Intermolecular exchange and dipolar interactions prevented us from observing the cobalt hyperfine splitting.

In an attempt to record the ESR spectra of the nickel(II) analogue, we observed a signal, split into eight components, which could be attributed to some cobalt(II) impurity present in the nickel compound. The latter [3] is isomorphous to the cobalt analogue [2], therefore it is tetragonal octahedral and high spin. Previous magnetic susceptibility data [4] have shown that the $^3A_{2g}$ ground state of octahedral symmetry is split in zero field, so that the M_s = 0 spin level lies below the ±1 levels by approximately 7.2 cm^{-1}. At 4.2 K about 85% of the nickel molecules are in the non magnetic M_s = 0 ground state, giving a good lattice where to dissolve the cobalt impurities. Since each complex in the lattice is surrounded by three couples of nearest neighbours at 722, 834 and 874 pm respectively, the dipolar interactions are very weak. Exchange interaction if any, between nickel(II) and cobalt(II) ions must be smaller than the smallest resolved hyperfine of 120 X 10^{-4} cm^{-1}. The line widths are orientation dependent. The largest signals are recorded when g reaches its minimum. The peak to peak width is ≅50 G, while in correspondence of the low field extreme it is ≅20 G.

The angular dependence of the g_2 values in the three experimental rotations are shown in Fig. 1. The principal g values and directions are given in Table I together with the corresponding A values. The g values are similar to those of the pure cobalt complex, although some variations do occur, which can be attributed to some distortions of the chromophore on passing to a different lattice. The principal directions are within error parallel to those found for the pure complex.

TABLE I. Principal Values and Directions of the g and A Tensors of $(Ni, Co)pyz_4Cl_2$.

g			
1.97(1)	−0.7851[a]	−0.5963	0.1676
4.84(3)	0.4998	−0.4500	0.7400
5.50(1)	0.3658	−0.6648	−0.6513
A^b			
125(2)	−0.8158	−0.5772	0.0352
136(1)	0.2834	−0.4522	0.8457
197(2)	0.5041	−0.6799	−0.5325

[a] For the definition of reference frame see caption to Fig. 1.
[b] cm^{-1} x 10^{-4}.

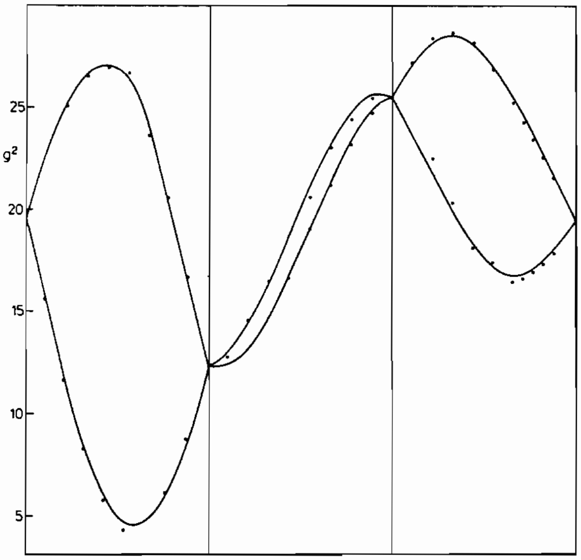

Fig.1. Angular dependence of the g^2 tensor of $(Ni, Co)pyz_4Cl_2$ in the rotations about, from left to right, three orthogonal axes z, y, x. The x axis corresponds to the 101 crystallographic direction, while the y corresponds to the b crystal axis. The curves are calculated by a least squares fit to the experimental points.

In the previous paper we were able to reproduce the g values, using an Angular Overlap Model we have been employing for the interpretation of the ESR spectra of high spin cobalt(II) [5]. Using the same parameters above, we tried to calculate also the A values [6] in order to compare them with the experimental values found in the present work. The calculated values are A_1 = 106 X 10^{-4} cm^{-1}, A_2 = 120 X 10^{-4} cm^{-1} and A_3 = 209 X 10^{-4} cm^{-1} in good agreement with the experiment. In this calculation k = 0.35 and P = 0.0270 cm^{-1} where P k is the isotropic hyperfine term and P = $g_e g_N \beta_e \beta_N \langle r^{-3} \rangle_{av}$. These values of k and P are quite close to the values estimated for the free ion [7].

The present results show that: (*i*) even 'paramagnetic' nickel(II) compounds may yield a suitable lattice for ESR experiments at very low temperatures; (*ii*) the Angular Overlap Model can also reproduce nicely the hyperfine splitting.

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