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Electronic Structure and Magnetic Coupling of Two Dinuclear Trigonal Bipyramidal Cobalt(II) Complexes

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The EPR spectra of zinc-doped (bis(N-methylsalicylaldiminato)cobalt(II), (Zn, Co) SALMe, which was found to be dinuclear, and of zinc-doped bis-(N,N-bis(2-(diethylamino)ethyl)-2-hydroxyethylamino-O)dicobalt(II)diperchlorate, (Zn, Co)n$_3$o, were recorded at liquid helium temperature and X-band frequency.

The polycrystalline powder spectra of (Zn, Co)-SALMe were interpreted within an effective $S = 1/2$ spin hamiltonian formalism with $g_1 = 1.8$, $g_2 = 2.7$, $g_3 = 6.2$, while those of (Zn, Co)n$_3$o showed only one band at $g = 6.9$. The single crystal spectra for the latter yielded $g_1 = 0.31(4)$, $g_2 = 0.84(4)$, $g_3 = 6.86(2)$. The electronic structure of the complexes was calculated using the AOM, and the lowest Kramers doublet for CoSALMe was found to be ±1/2 while a ±3/2 doublet was found for Con$_3$o. The temperature dependence of the magnetic susceptibility of Co-SALMe was measured between 295 and 4.2 K. The data were fitted with two different methods which either took into account or neglected the zero-field splitting of single ions. The coupling was found to be antiferromagnetic with $J = 9.8(2)$ cm^{-1} (J is defined through the hamiltonian $\mathcal{H} = JS_1 \cdot S_2$). The extent of the magnetic interaction between the metal ions for both the complexes was discussed on the basis of a structural analysis.

Introduction

Continuing our interest in the characterization of the electronic structure of high spin cobalt(II) complexes, both mononuclear [1–3] and dinuclear [4–5], we decided to study the extent of magnetic coupling in bis(N-methylsalicylaldiminato)cobalt(II), Co-SALMe, which was found to be dinuclear [6], with two trigonal bipyramidal cobalt(II) complexes bridged by two oxygen atoms. The compound was reported to follow the Curie–Weiss law in the range 291–79 K, with $\theta = 24$ K [7]. In order to obtain more accurate data we extended the magnetic susceptibility measurements down to 4.2 K, and also recorded EPR spectra of both the Zn-doped cobalt complex and of the cobalt-doped zinc complex in order to have information on the electronic structure of the single ion. In view of the current interest in the exchange interactions in cobalt(II) complexes [8–10], we also recorded the polycrystalline powder and single crystal EPR spectra of zinc-doped bis(N,N-bis(2-(diethylamino)ethyl)-2-hydroxyethylamino-O)-dicobalt(II) diperchlorate, (Zn, Co)n$_3$o, which was reported to be dinuclear [11], in order to obtain information on the electronic structure of the metal ion also in this case and to discuss the variation of the extent of the magnetic coupling between the two cobalt ions.

Experimental

The complexes were prepared as reported previously [12, 13]. They were analyzed satisfactorily for C, H. N.

The EPR spectra were recorded at X-band frequency on a Varian E-9 spectrometer, equipped with an Oxford Instruments E9 continuous flow cryostat for measurements at 4.2 K.

Magnetic susceptibility measurements were performed on a Faraday balance equipped with a Cahn R-100 microbalance, a Bruker electromagnet and an Oxford Instruments CF 200 cooling apparatus.

Results

The temperature dependence of the magnetic susceptibility of CoSALMe from 295 K to 4.2 K is shown in Fig. 1. The magnetic susceptibility goes through a maximum at ~25 K, below which it decreases rapidly.

The polycrystalline powder EPR spectrum of (Zn, Co)SALMe at 4.2 K and X-band frequency is shown in Fig. 2. It is typical of high spin cobalt(II) complexes and can be interpreted within an effective $S = 1/2$ spin hamiltonian formalism with $g_1 = 1.8$, $g_2 = 2.7$, $g_3 = 6.2$. Attempts to grow doped single crystals suitable for EPR studies were totally unsuccesful.

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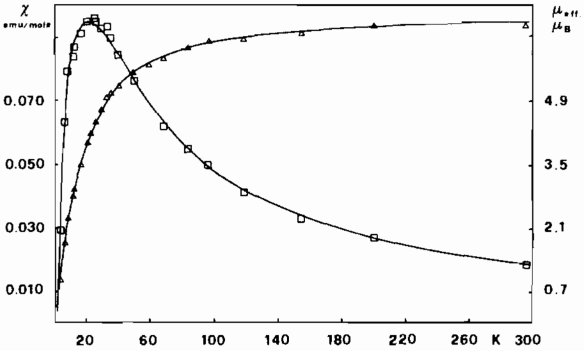

Fig. 1. Temperature dependence of the magnetic susceptibility (□) and of the effective magnetic moment (△) of Co SALMe. Solid lines are the curves calculated with the Bleaney–Bowers equation for two identical S = 3/2 ions.

The polycrystalline powder EPR spectrum of (Zn, Co)n$_3$o at 4.2 K and X-band frequency is shown in Fig. 2. Only one feature is resolved at $g = 6.9$ without any hyperfine splitting. The spectra are substantially unchanged if the pure cobalt complex is doped with zinc.

Single crystal spectra of the doped complex were recorded by rotating the static magnetic field in three orthogonal planes. The angular dependence of g^2 is shown in Fig. 3. The principal g values and directions were obtained through a least-squares procedure using Schonland's method [14]. The principal g values are: $g_1 = 0.31(4)$, $g_2 = 0.84(4)$, $g_3 = 6.86(2)$. The crystals were found to be monoclinic with $a = 12.099(5)$, $b = 18.869(3)$, $c = 8.941(4)$ Å, $\beta = 109.16(3)$. They are not isomorphous to either the nickel and copper analogues [13, 15], whose crystal structures were previously reported. Therefore it is not possible to orient the experimental g tensor in the molecular frame.

Discussion

In order to discuss the mechanism of the exchange interaction between the two cobalt(II) ions, the electronic structure of the single ions is a necessary prerequisite. It can be estimated using both electronic and EPR spectra, together with structural data.

The electronic spectra of CoSALMe show bands at 5,500, 11,400, 15,800, and 19,600 cm^{-1}, which are assigned as previously reported [7]. The electronic structure of the complex was calculated using the Angular Overlap Model [2, 16]. The geometrical parameters for the ligands were those seen in the crystal structure of the zinc analogue [6]. We tried to fit simultaneously the electronic transitions and the g values. The parameters we used are: e_σ^N and e_π^N for the nitrogen donors; e_σ^O, $e_{\pi\parallel}^O$, $e_{\pi\perp}^O$ for the oxygen donors (⊥ and ∥ refer to orthogonal and parallel to the M–O–N plane respectively; for the nitrogen donors only the π interaction orthogonal to that

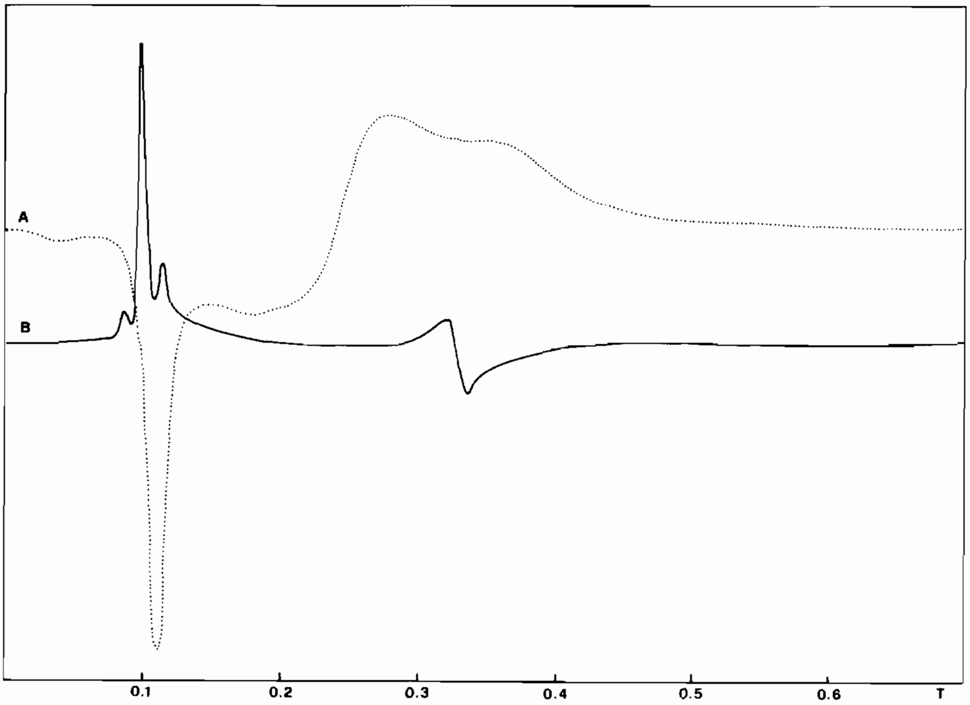

Fig. 2. Polycrystalline powder EPR spectra of (Zn, Co)SALMe (A; ...) and of (Zn, Co)n$_3$o (B; ——) at 4.2 K and X-band frequency.

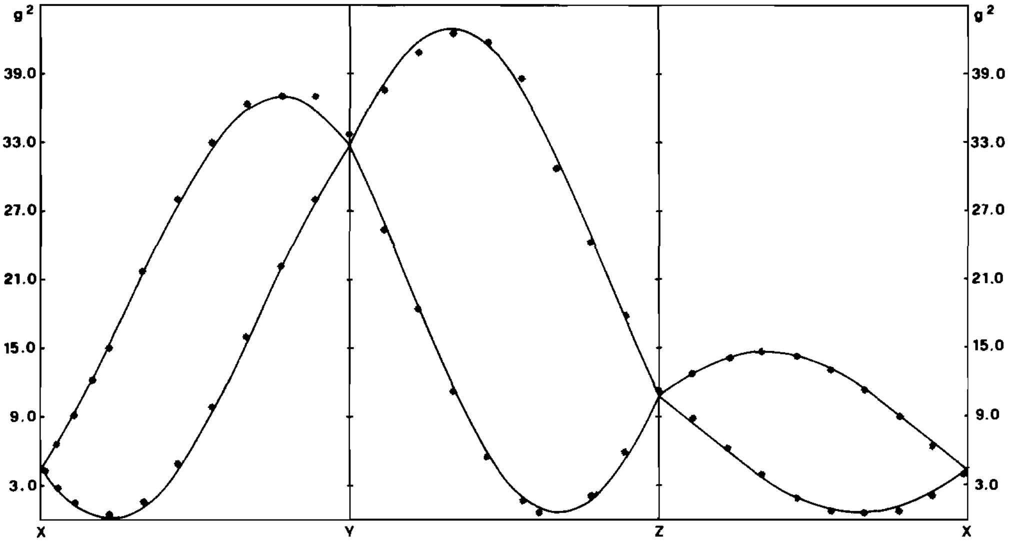

Fig. 3. Angular dependence of g^2 values of (Zn, Co)n$_3$o at 4.2 K in three orthogonal planes. The curves correspond to the least-squares fit of the experimental points.

plane was considered) [17, 18]; k, the orbital reduction factor, while the spin orbit coupling constant, ξ, was kept fixed at the free ion value. The best fit values were found to be: $e_\sigma^{N} = 3345$ cm^{-1}, $e_\pi^{N} = 270$ cm^{-1}, $e_\sigma^{O} = 4100$ cm^{-1}, $e_{\pi\perp}^{O} = 545$ cm^{-1}, $e_{\pi\parallel}^{O} = 190$ cm^{-1}. Our e_σ values compared well with those reported for salycilaldiminato complexes, while the previously reported e_π values support a stronger interaction than in our case, even if they confirm the out-of-plane interaction to be stronger than the in-plane one [17, 18]. The calculated transitions are at 5,300, 11,400, 16,200, and 19,300 cm^{-1} and the calculated g values are $g_1 = 1.75$, $g_2 = 2.70$, $g_3 = 6.25$, in good agreement with the experimental data. The calculated principal directions (expressed as direction cosines referred to be *a*bc* crystallographic frame) are: −0.1744, 0.7723, 0.6108 for g_1; 0.9799, −0.2028, 0.0232 for g_2; 0.1060, 0.6020, 0.7914 for g_3. The ground spin quartet is thus calculated to be split by 35 cm^{-1}, with the lowest Kramers doublet which can be loosely described as ±1/2 [16]. In fact the above results can be recast in the formalism of $S = 3/2$ spin hamiltonian and the results are: $g_x = 2.28$, $g_y = 2.37$, $g_z = 2.15$, $D = 15.94$, $\lambda = E/D = 0.27$, where D and E are the usual zero–field splitting parameters and the g_i's are the *true g* values relative to the spin quartet [19]. The energies of the d orbitals corresponding to the best fit are given in Fig. 4. The overall symmetry is not far from axial, the largest splitting (1,300 cm^{-1}) being calculated for the predominantly xy and $x^2 - y^2$ orbitals.

For the Con$_3$o complex, the geometrical coordinates seen in the structure of the analogous copper(II) complex [15] were used. The two oxygen atoms were considered as equivalent, and so were the two nitrogen atoms which are closer to the central metal

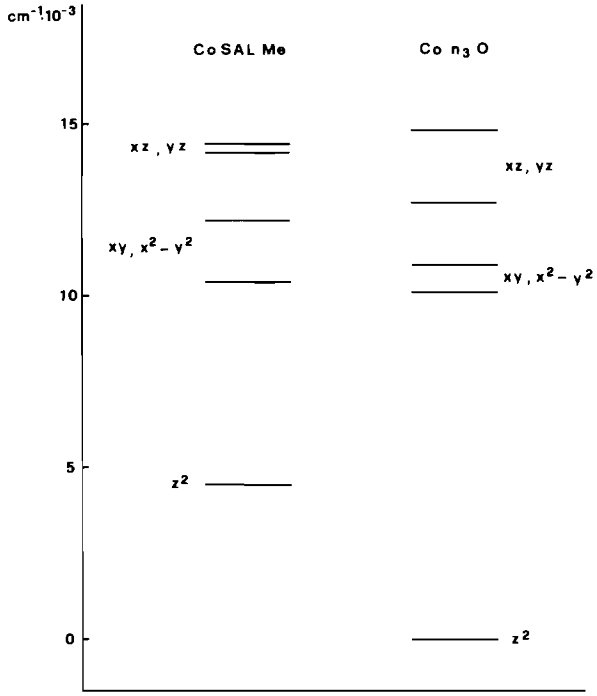

Fig. 4. Energies of d orbitals for the two complexes. The reported values are calculated with the best fit parameters described in the text.

ion. For the nitrogen donors only e_σ^{N} parameters were used, while three parameters, e_σ^{O}, $e_{\pi\parallel}^{O}$, $e_{\pi\perp}^{O}$ were used for the oxygen atoms (∥ and ⊥ refer to the π interaction parallel and normal to the Co–O–Co′ plane). The best fit value were: $e_\sigma^{N} = 5{,}850$ cm^{-1}; $e_\sigma^{N'} = 1{,}000$ cm^{-1}; $e_\sigma^{O} = 6{,}200$ cm^{-1}; $e_{\pi\parallel}^{O} = 710$ cm^{-1}; $e_{\pi\perp}^{O} = 140$ cm^{-1} (N′ is the nitrogen atom with the longer Co–N bond distance). These values compare well with those reported for the analogous copper(II) complex [15]. The calculated transitions are at 7,000, 13,000, 16,600, 20,700 cm^{-1}, to be compared with 6,500, 12,800, 16,900, and 20,400 cm^{-1} seen in the electronic spectra [11]. The g values fitted slightly less satisfactorily, to give $g_1 = 0.60$, $g_2 = 0.78$, $g_3 = 6.92$. The ground spin quartet is split into two Kramers doublets separated by 40 cm^{-1}, the lowest in this case being ±3/2. The calculated true g values are in this case $g_x = 2.15$, $g_y = 2.10$, $g_z = 2.38$, and the zero field splitting parameters $D = 23.16$, $\lambda = 0.10$. The energies of the d orbitals corresponding to the fit are given in Fig. 4. The energy differences are higher than in CoSALMe. Also, in this case the overall symmetry is not too far from axial, but the most largely split orbitals are in this case the xz and yz orbitals (2,120 cm^{-1}).

The difference between the two complexes, determining the opposite pattern of g values and the different sign of D, lies in the geometry which is closer to a trigonal bipyramid for the SALMe complex, while it has a substantial distortion towards the square pyramid for the $\mathrm{n_3o}$ complex [2].

The temperature-dependence of the magnetic susceptibility of CoSALMe was established using two different procedures. First, the simple Bleaney–Bowers equation relative to the hamiltonian $\mathcal{H} = JS_1\cdot S_2$ for two identical ions with $S = 3/2$ was used [20]. In this case the best fit was found through a least-squares method for $J = 9.8(2)\ \mathrm{cm}^{-1}$; $g = 2.49(1)$. Since the EPR spectra indicate a substantial single ion zero field splitting, a modified version which takes this into account was also used. The best fit was obtained through a trial and error procedure which minimized the function

$$R = \sum_i^n \left[(\chi_i^{\mathrm{ob}} - \chi_i^{\mathrm{calc}})^2 \Big/ \sum_i^n (\chi_i^{\mathrm{ob}})^2 \right]^{1/2},$$

where n is the number of experimental data, χ_i^{ob} and χ_i^{calc} are the observed and calculated magnetic susceptibilities respectively. To evaluate the magnetic susceptibility we used the following hamiltonian which includes the zero field splitting parameters D and E for the single ions:

$$\hat{\mathcal{H}} = J\hat{S}_1\cdot\hat{S}_2 + D\left[\hat{S}_{1z}^2 + \hat{S}_{2z}^2 - \frac{1}{3}\{S_1(S_1+1) + S_2(S_2+1)\}\right] + E[(\hat{S}_{1x}^2 - \hat{S}_{1y}^2) + (\hat{S}_{2x}^2 - \hat{S}_{2y}^2)] \qquad (1)$$

The matrix elements were calculated by means of the method outlined by Scaringe *et al.* [21–23]. The exchange determined zero-field splitting [24] was neglected, in the assumption that it is smaller than the large single ion zero field splitting.

The diagonalization of the 16 × 16 matrix of eqn. (1) in the basis of $S = 3/2$ states for the two cobalt ions allowed to calculate the distribution of the energy levels, and then to evaluate the magnetic susceptibility with the expression [25]:

$$\chi_{\mathrm{mol}} = -\frac{N_{\mathrm{a}}}{B}\,\frac{\sum^{16} \frac{\delta E_n}{\delta B} \exp\left(-\frac{E_n}{kT}\right)}{\sum^{16} \exp\left(-\frac{E_n}{kT}\right)}$$

were N_{a} is Avogadro's number, **B** the magnetic field and k Boltzman's constant.

Using D and E as obtained from the analysis of the EPR spectra the calculated values are: $J = 13$ cm^{-1}, $g = 2.29$, but the fit is significantly worse than that obtained for the simple Bleaney–Bowers equation. On the other hand, letting D and E vary as free parameters, we find a good fit only when they become very small. Since the zero–field splitting is indeed experimentally observed it is possible that the Bleaney–Bowers equation works best due to the cancellation of possible errors. In fact in eqn. 1 beyond the D and E parameters introduced by the exchange interaction, we have also neglected intermolecular exchange effects [20].

A comparison between the calculated J values for CoSALMe and $\mathrm{Con_3o}$ shows that the exchange interaction is significantly larger in the alkoxo than in the phenoxo bridged complex. In fact for the $\mathrm{Con_3o}$ complex, an analysis of the variation of the magnetic susceptibility with temperature in the range 86–291 K gave, using the Bleaney–Bowers approach, $J = 17\ \mathrm{cm}^{-1}$; $g = 2.35$ [11].

A structural analysis is difficult since the structure of CoSALMe is known only through its isomorphous zinc derivative, while for $\mathrm{Con_3o}$ only the copper and nickel complexes are reported but they are not isomorphous. However, for these the M–O–M angles, ϕ, which effectively correlate to J for di-μ-hydroxo bridged copper(II) complexes [26] are very similar for both SALMe and $\mathrm{n_3o}$ derivatives. In fact for the $\mathrm{n_3O}$ complex, ϕ is 103.1° [15] for the copper and 103.9° for the zinc derivative [6]. Since ϕ is smaller for the $\mathrm{n_3O}$ complexes, it seems that this is not the factor determining the larger J value observed for $\mathrm{Con_3o}$, since a larger ϕ would be expected to give a larger antiferromagnetic coupling. On the other hand, the e_σ parameter for the alkoxo ligands is larger than e_σ for the phenoxo donor. Since this extent of the exchange interaction is influenced by the e_σ values for the bridge ligand [27], the larger antiferromagnetic coupling of the alkoxo derivative must be related to its larger ligand field strength. Similar trend of more efficient coupling though alkoxo as compared to phenoxo bridges was previously observed for copper(II) complexes [28].

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