overlapping region. Here again the main spikes are recorded, but, in general, specific assignments are not possible. The ionization of the most stable lone pairs of fluorine in $(CF_3)Ge(CH_3)_3$, or sets of orbitals for the other two species, stands out clearly in all spectra, emphasizing that again in this region there is essentially a superimposition of ionizations for each CF_3 group. The shift of 0.7 from 16.9 eV in $(CF_3)_3Ge(CH_3)$ to 16.2 eV in $(CF_3)Ge(CH_3)_3$ is very similar to that observed between the fluorine 1s orbitals (694.65 and 694.0 eV, respectively). This demonstrates that where there is no appreciable change in the makeup of an orbital, the valence levels show the same trends to the same degree as the core levels. The principal features of the remaining lone pairs of fluorine can be seen in the He II spectra to correspond to those in $(CF_3)_4Ge$ or other (trifluoromethyl)germanes[3,4] apart from a slight progressive shift. The counterparts to these features can be detected in the He I spectra, allowing the remainder of the envelope to be assigned in a general fashion to the CH_3 bonding orbitals.

The CF_3 bonding orbitals show approximately the same tendency toward stabilization from $(CF_3)Ge(CH_3)_3$ to $(CF_3)_3Ge(CH_3)$ as do the fluorine lone pairs, and the intensity of the peak around 19 eV is in the same proportion to the fluorine lone pairs, so no particularly unusual features appear. For $(CF_3)Ge(CH_3)_3$ the band splits into the expected e and a components, and an assignment of the rather sharp band at 18.8 eV is in accord with the spectra of CF_3 halides.[19] In $(CF_3)_2Ge(CH_3)_2$ and $(CF_3)_3Ge(CH_3)$ the band structure gets more complex but hardly broadens so that there is again essentially a superimposition of the spectrum of one bonding CF_3 group.

The evidence for the Ge (4s) ionization is not good. It is assumed to occur between 15.8 (as in $Ge(CH_3)_4$) and 18.5 eV (as in $(CF_3)_4Ge$), and high-energy shoulders on the most stable F (2p) lone pair are assumed to arise from this ionization, placing it at 17.0 eV for $(CF_3)Ge(CH_3)_3$ and 17.5 eV for $(CF_3)_2Ge(CH_3)_2$.

The spectra above 21 eV are noisy, but the main feature, which is assumed to correspond to ionization from the C (2s) levels, does shift progressively from the highest energy in $(CF_3)_3Ge(CH_3)$ to the lowest in $(CF_3)Ge(CH_3)_3$. In this it is of course reflecting the general trends in both the valence and the core-level binding energies of these molecules.

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Registry No. $Ge(CH_3)_4$, 865-52-1; $(CF_3)Ge(CH_3)_3$, 21907-59-5; $(CF_3)_2Ge(CH_3)_2$, 66348-20-7; $(CF_3)_3Ge(CH_3)$, 66348-19-4; $(CF_3)_4Ge$, 55642-43-8.

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ESR Spectra of Low-Symmetry High-Spin Cobalt(II) Complexes. 10.[1] Five-Coordinated Trigonal-Bipyramidal Complexes

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The EPR spectra of the five-coordinated complexes $[CoX(Me_6tren)]Y$ (Me_6tren = tris[2-(dimethylamino)ethyl]amine; X = Cl, Br, I; Y = Cl, Br, I, BPh_4) and $[CoX(np_3)]Y$ (np_3 = tris[2-(diphenylphosphino)ethyl]amine; X = Cl, Br, I; Y = PF_6, BPh_4) have been recorded. The Me_6tren complexes were found to yield $g_\parallel \approx 2$ and $g_\perp \approx 4$, in agreement with a ground $\pm^1/_2$ Kramers doublet. No ^{59}Co hyperfine was resolved. The np_3 complexes were found to give a g value in the range 6-7, but no other signal could be detected in the range 0-1.40 T. Single-crystal analysis showed that the g = 6-7 value is found parallel to the cobalt-axial ligand direction. The angular dependence of the spectra confirmed that the other two g values must be smaller than 0.45 and therefore outside the range available to our spectrometer. These data have been interpreted as indicative of a ground $\pm^3/_2$ Kramers doublet. The spin Hamiltonian parameters of the two sets of complexes have been justified on an angular overlap model.

Pursuing our project for characterizing the EPR spectra of low-symmetry high-spin cobalt(II) complexes,[1-3] we wish to report here the EPR spectra of some five-coordinate complexes formed with tripod ligands, which, although distorted to some extent, can be in every case loosely described as trigonal bipyramidal. In particular we have studied $[CoX(Me_6tren)]Y$ (Me_6tren = tris[2-(dimethylamino)ethyl]amine; X = Cl, Br, I; Y = Cl, Br, I, BPh_4) and $[CoX(np_3)]Y$ (np_3 = tris[2-(diphenylphosphino)ethyl]amine; X = Cl, Br, I; Y = PF_6, BPh_4). For these complexes the crystal structures are available,[4-6] which have shown that the Me_6tren complexes can be more closely described as trigonal bipyramidal,[4] while for the np_3 complexes the distortion toward a tetrahedral structure is quite remarkable.[5-7] The electronic spectra of the above complexes

Table I. Spin Hamiltonian Parameters for Some Five-Coordinate Trigonal-Bipyramidal Cobalt(II) Complexes

complexes	g_1	g_2	g_3
$[CoCl(Me_6tren)]Cl$	2.29	4.25	
$[CoBr(Me_6tren)]Br$	2.27	4.30	
$[CoI(Me_6tren)]I$	2.10	4.30	
$[CoBr(Me_6tren)]BPh_4$	*a*	4.70	6.30
$[CoCl(np_3)]PF_6$	*b*	*b*	6.70
$[CoBr(np_3)]PF_6$	*b*	*b*	6.50
$[CoI(np_3)]BPh_4$	*b*	*b*	6.40

[a] A broad signal in the g = 2 region is present, but a precise g value cannot be obtained. [b] No other signals could be detected in the range 0-1.40 T. g_1 and g_2 may be estimated to be smaller than 0.45.

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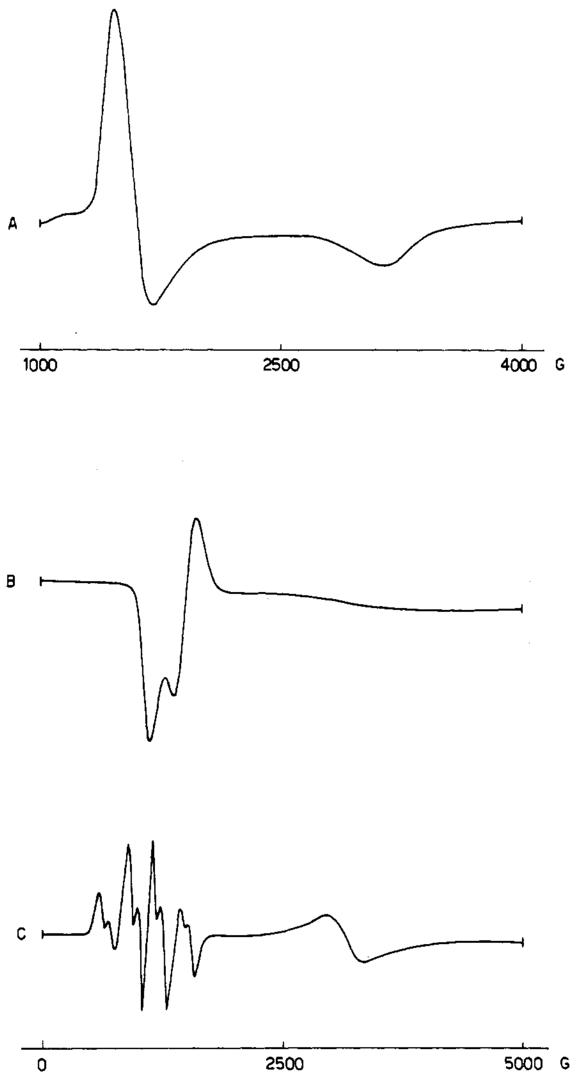

Figure 1. Polycrystalline powder EPR spectra recorded at 4.2 K and 9 GHz: A, [CoBr(Me$_6$tren)]Br; B, [CoBr(Me$_6$tren)]BPh$_4$; C, [CoI(np$_3$)]BPh$_4$.

have been thoroughly studied on single crystals,[8,9] with use of polarized light, and the angular overlap parameters[10] that are relevant for them have been obtained.

Experimental Section

The complexes were prepared according to the methods previously reported.[11,12] The crystals were oriented by Weissenberg techniques.

The EPR spectra down to 4.2 K were recorded with a Varian E-9 spectrometer equipped with the Oxford Instruments ESR 9 continuous-flow cryostat. The crystals were mounted on a Perspex rod and rotated by means of a one-circle goniometer.

Results

[CoX(Me$_6$tren)]Y (X = Cl, Br, I; Y = Cl, Br, I, BPh$_4$). The polycrystalline powder EPR spectra of these compounds are all substantially similar to each other, with $g_\parallel$ close to 2 and $g_\perp$ close to 4 and no metal hyperfine resolved, as shown in Table I and Figure 1. In general, the $g_\parallel$ feature is broader than the $g_\perp$ one. Also an increase of line widths is observed on passing from the chloride to the iodide derivative.

For [CoBr(Me$_6$tren)]BPh$_4$ the EPR spectrum clearly shows that the symmetry of the chromophore is lower than axial. The signal corresponding to $g_\parallel$ is very broad.

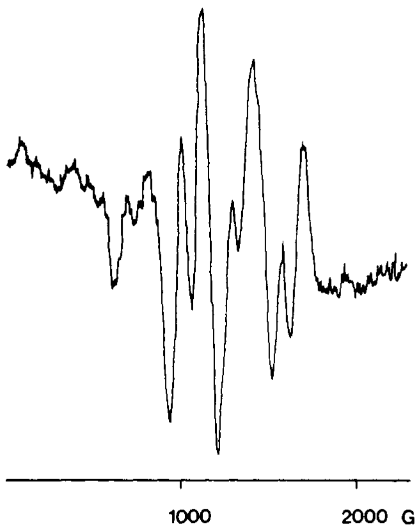

Figure 2. Single-crystal EPR spectrum of [CoI(np$_3$)]BPh$_4$ recorded at X-band frequencies at 4.2 K. The static magnetic field is normal to the (100) face of the crystal.

[CoX(np$_3$)]Y (X = Cl, Br, I; Y = PF$_6$, BPh$_4$). The polycrystalline powder EPR spectra of this series of compounds are similar to each other (Figure 1), and different from the previous one. One feature is well resolved, at g = 6–7 with some hyperfine splitting showing up. The best resolved case is that of [CoI(np$_3$)]BPh$_4$, where the feature at g = 6.4 is split into eight components, which tentatively can be attributed to the interaction of the unpaired electron with ^{59}Co. A confirmation to this is provided by the single-crystal spectra reported below. The hyperfine splitting is about 140 G, which corresponds to $A = 412 \times 10^{-4}$ cm^{-1}. This very large cobalt hyperfine value compares well with that previously found for a square-pyramidal cobalt complex.[13]

No other feature that can be safely attributed to the complex is seen in the range up to 1.4 T. Several preparations of the complexes were used, and in some cases broad signals were detected in the region of g = 1, but they seem to be due to some unknown impurity. Also a sharp signal at g = 0.57, identical for all the complexes, seems to be due to an unknown impurity.[14] Signals at $g \approx 2$ are perhaps due to some low-spin cobalt.

In order to obtain some more experimental information on these complexes, we recorded the single-crystal EPR spectra of [CoI(np$_3$)]BPh$_4$, since it showed the best powder spectra. The complex is known to crystallize in a triclinic lattice;[5] therefore one magnetically nonequivalent site is present in the cell.

The single crystals we were able to grow have the (100) face prominent. In the rotation around the {001} direction a low-field extreme was found at g = 6.2 with $A = 430 \times 10^{-4}$ cm^{-1}, very close to the values observed in the powder spectrum. The corresponding spectrum is shown in Figure 2. The hyperfine pattern is rather irregular, as may be expected, considering the presence of intermolecular exchange interactions and of magnetic nuclei around the cobalt ion. The extreme was found close to the b direction. In the crystal the N–Co–I direction, which individuates the "trigonal" axis of the bipyramid, makes an angle of 20° with b, thus showing that the low-field feature

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(14) The shape of this absorption here is of a g feature. A similar feature, at exactly the same g value, had been observed previously[15] but was erroneously attributed to the tetrahedral cobalt complex that was investigated. We have found the same absorption also in several other cases where no cobalt complex was involved.
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of the EPR spectra is associated with the z molecular direction.

When the static magnetic field is rotated from the b direction, a large increase of the line width is observed and the hyperfine splitting is no longer resolved. The signal could be traced down to about $g = 0.6$, until it vanishes. It must be assumed therefore that the high-field extremes are outside the range of values available to our magnet (1.4 T). An approximate analysis of the angular dependence of the g^2 values in these planes suggests the value $g = 0.25$ for the higher field extreme. In the rotation around a a somewhat similar behavior is observed although in this case the number of experimental points that are available for an analysis similar to the above one is too low and no approximate g values can be estimated.

Discussion

The present series of five-coordinate cobalt(II) complexes is interesting since it shows how it is possible to have largely different g-value patterns as a consequence of geometrical distortions and of variations in the ligand field strengths.

In a previous paper[1] we have shown that the ground $^4A_2'$ level, appropriate for high-spin cobalt(II) in D_{3h} symmetry, is split by spin–orbit coupling into two Kramers doublets whose separation in zero magnetic field is usually larger than the energy of the available microwave sources for EPR experiments. As a consequence only transitions within the lowest Kramers doublet can be detected at the very low temperatures required by the fast spin–lattice relaxation times of high-spin cobalt(II).

We also predicted,[1] using an angular overlap formalism we have developed for the study of the EPR spectra of high-spin cobalt, that the sign of the zero-field splitting is strongly dependent on the angle defined by the axial ligand, the cobalt ion, and the equatorial ligand, γ. In particular we calculated that for γ close to 90° D is positive; i.e., the $\pm^1/_2$ Kramers doublet is of lower energy, while the reverse is true when γ becomes closer to the tetrahedral limit, 109.47°. This is not the unique parameter, however, to determine the nature of the ground doublet. At intermediate angles also the e_π/e_σ ratios can be important. The average X–Co–L angle (X = Cl, Br, I; L = N, P) in the series of complexes we have studied is 105° for $[CoCl(np_3)]^+$,[6] 106° for both $[CoBr(np_3)]^+$ and $[CoI(np_3)]^+$,[5] and only 99° for $[CoBr(Me_6tren)]^+$.[4]

The g values of the last compound are clearly indicative of a positive D, with $g_\parallel$ close to 2 and $g_\perp$ close to 4. For the $[CoX(np_3)]^+$ complexes the sign of D is apparently reversed, since the highest g value is found close to the z molecular axis, as would be expected for a $\pm^3/_2$ ground level.[16] That this is actually the case is shown also by the fact that the g_x and g_y values must be smaller than 0.6, the minimum value that we could observe in the crystal. Also the observed signals are of low intensity, as one would expect for a transition within the $\pm^3/_2$ levels. As a matter of fact, if the two Kramers doublets are expressed as

$$|\pm\tilde{3}/2\rangle = (\cos\beta)|\pm 3/2\rangle + (\sin\beta)|\mp 1/2\rangle$$

$$|\tilde{\pm}1/2\rangle = -(\sin\beta)|\pm 3/2\rangle + (\cos\beta)|\mp 1/2\rangle$$

it is easy to show that the transition probabilities within the two Kramers doublets for the oscillating magnetic field parallel to x are given by

$$I(3/2) \propto (\sin^2\beta)(\sin\beta + 3^{1/2}\cos\beta)^2 \qquad I(1/2) \propto \cos^4\beta$$

Since β is related to the zero-field splitting parameters through the relation[17]

$$\beta = \tfrac{1}{2}\tan^{-1} 3^{1/2}(E/D)$$

and since the two limit cases correspond to $E/D = 0$ for axial symmetry and $E/D = {}^1/_3$ for maximum rhombic splitting,[18] it is apparent that for axial symmetry the $+^3/_2 \rightarrow -^3/_2$ transition is forbidden, but that even for the maximum allowed rhombicity it is much less allowed than the corresponding $+^1/_2 \rightarrow -^1/_2$ transition. Also the ^{59}Co hyperfine coupling constant is in agreement with a $\pm^3/_2$ ground level. In fact we showed that for negative D values and small E/D ratios, large cobalt hyperfine coupling constants must be expected.

In order to confirm these qualitative conclusions, we performed also some angular overlap model calculations. Since we have previously assigned the electronic transitions of these complexes using AOM parameters,[9] we decided to use them as the starting point for the calculation of the spin Hamiltonian parameters. The calculated values of these parameters for the $[CoI(np_3)]^+$ complex are in accord with a $\pm^3/_2$ ground level, separated by 8.5 cm^{-1} from the excited $\pm^1/_2$ level, the principal g values being $g_z = 6.42$, $g_x = 0.43$, and $g_y = 0.40$, in good agreement with the experimental values. The calculated hyperfine tensor[19] is however a bit different from the experimental data. In fact we calculate $A_z = 148 \times 10^{-4}$ cm^{-1}, $A_x = 16 \times 10^{-4}$ cm^{-1}, and $A_y = 16 \times 10^{-4}$ cm^{-1}. Several attempts to vary the values of the parameters were not able to yield better agreement with experiment.

The calculations for $[CoBr(Me_6tren)]^+$, using the parameters previously reported,[9] are far less satisfactory, since they predict a $\pm^3/_2$ ground level, contrary to the experimental data. It is possible however to restore the correct $\pm^1/_2$ ground level by varying the e_π/e_σ ratio for the bromine donor, keeping its $10Dq = (3e_\sigma - 4e_\pi)$ value constant. In the previous paper[9] we used $e_\pi/e_\sigma = 0.4$ on the basis of squared overlap considerations. However, lower e_π/e_σ ratios for halogen donors have been suggested.[20,21] With use of $e_\pi/e_\sigma = 0.275$, the correct order of the levels is obtained. The calculated g values are $g = 2.17$ and $g = 4.38$ in fair agreement with the experimental values. Also the agreement between calculated and observed electronic transition energies can be considered satisfactory. In fact the energies are reproduced within 500 cm^{-1}, with the exception of the $^4A_2 \rightarrow {}^4A_2(P)$ transition for which the difference between calculated and observed is 900 cm^{-1}. Then ^{59}Co hyperfine in this case is predicted to be small in good agreement with experimental data.

In conclusion, the present data on five-coordinate cobalt(II) complexes of trigonal-bipyramidal geometry show that different g-value patterns in dependence on the distortion exerted by the ligands can be obtained. This can be quantitatively understood on an angular overlap approach. The quantitative agreement is in general satisfactory, except for the cobalt hyperfine of the $[CoI(np_3)]^+$ complexes. It is possible that unresolved interactions with ^{31}P may alter a little the experimental A values. Also it may happen that the disorder seen in the crystal structure[5] demands slightly different atomic coordinates in a unpredictable way.

It is now apparent that the $\pm^3/_2$ Kramers doublet can be of lowest energy in distorted tetrahedral geometries.[16,20] In these cases also a large ^{59}Co hyperfine can be resolved, so that the rejection of a tetrahedral geometry only on the basis of resolving a sizeable cobalt hyperfine splitting is to be considered as dubious.

Registry No. $[CoCl(Me_6tren)]Cl$, 15692-87-2; $[CoBr(Me_6tren)]Br$, 14405-53-9; $[CoI(Me_6tren)]I$, 15750-29-5; $[CoBr(Me_6tren)]BPh_4$, 80422-44-2; $[CoCl(np_3)]PF_6$, 30109-77-4; $[CoBr(np_3)]PF_6$, 34376-74-4; $[CoI(np_3)]PF_6$, 80422-45-3.

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