assigned to all non-hydrogen atoms.

The final disagreement factor defined as $R = \sum|F_o| - |F_c|/|F_o|$ obtained was 0.094. Disorder in the TMPD unit hampered further refinement of the R factor. The hydrogen atoms could not be located from the final difference Fourier maps. There seems to be quite a bit of thermal disorder among the two ion radicals as indicated by the numerous correlation matrix elements (>0.5) obtained during least squares after introduction of the anisotropic thermal parameters. There is also evidence for a large degree of disorder from susceptibility data.

Appendix B

Figure 14 gives two coordinate systems for (TMPD)Ni(mnt)$_2$. The secular and nonsecular contributions from all the neighbors except the two on the chain vary as shown in Figure 15. As is seen, the secular part is much less and unless the system is highly one-dimensional (i.e. $\rho >> 1$) it does not contribute substantially. The off-chain contributions were found to be affected only negligibly by the change in the direction cosines of the **g** tensor.

On the other hand, contributions from the two neighbors on the Ni(mnt)$_2^-$ stack are very sensitive to the orientation of the **g** tensor and the better fit was obtained only when the g_z direction was taken to be along "a", the stack axis. Both positive and negative values of D_e were tried, and the angular variation was better predicted by taking D_e to be negative. The value of ρ indicates the system is quite low dimensional, which is in agreement with the non-Lorentzian line shape observed for $B\|$chain axis.

Registry No. (TMPD)Ni(mnt)$_2$, 85762-15-8.

Contribution from the Istituto Chimica Generale, Facoltã di Farmacia, University of Florence, and ISSECC, CNR, Florence, Italy

π-Bonding Interactions of Nonlinearly Ligating Ligands with Octahedral Cobalt(II) Complexes

A. BENCINI,[1b] C. BENELLI,[1a] D. GATTESCHI,*[1a] and C. ZANCHINI[1a]

Received May 19, 1982

The EPR spectra of several trigonal-octahedral cobalt(II) complexes have been used to obtain information on the π-bonding anisotropic interactions. The pattern of g values is strongly influenced by the difference between the two π-bonding parameters of individual ligands in the angular-overlap model. It was found that in CoO_6 chromophores the larger π interaction is orthogonal to the Co–O–R plane. For CoN_6 chromophores, where N is provided by imidazoles or bipyridine, no evidence of dominant π back-bonding was found, in agreement with previous findings.

In recent years there has been a systematic attempt to investigate low-symmetry components of the ligand field, thanks to the development of the angular-overlap model, AOM.[2–6] As a matter of fact the use of this model gives an effective parameterization of low-symmetry fields by using parameters that are in principle related to the σ- and π-donor ability of the atoms surrounding a central metal ion.[2] It is now currently believed that the values of the parameters obtained from the analysis of several spectroscopic and magnetic data do reflect some chemical sense and that they can be transferred from one complex to another, provided that the necessary caution is observed.[7]

One of the fascinating fields of application of the angular-overlap model is that of the determination of anisotropic π components in the interaction of nonlinearly ligating ligands with transition-metal ions. In fact when the donor atom belongs to a molecule, the M–L moiety does not usually possess cylindrical symmetry so that it is generally to be expected that the π interaction with the metal ion is not isotropic. This has now been established in several cases, in which it was found that a good interpretation of the spectral and magnetic properties of the complexes[9–11] could not be achieved by considering the donor atoms as spherical.

Table I. Observed g and Calculated D^a and γ^a Values for Some Trigonal Cobalt(II) Complexes

	D, cm^{-1}	γ	$g_\|$	$g_\perp$
$Co(H_2O)_6$	397	−1.44	5.82	3.44
$Co(pyO)_6$[b]	−652	−1.16	2.26	4.77
$Co(apy)_6(ClO_4)_2$	−355	−1.46	3.08	4.85
$Co(N\text{-MeIz})_6$[c]	−367	−1.47	3.06	4.87
$Co(Iz)_6(NO_3)_2$	323	−1.38	5.55	3.53
$Co(en)_3(NO_3)_2$	−581	−1.48	2.6	5.0
$Co(bpy)_3Br_2$	−258	−1.25	3.16	4.62

[a] D and γ values are calculated as described in the text to reproduce the observed g values within ±0.005. [b] pyO is pyridine N-oxide. [c] N-MeIz is N-methylimidazole.

Octahedral cobalt(II) complexes appear to be extremely well suited for recognizing π-bonding anisotropy, since low-symmetry components of the ligand field are easily monitored through the EPR spectra.[12,13] In particular, trigonal com-

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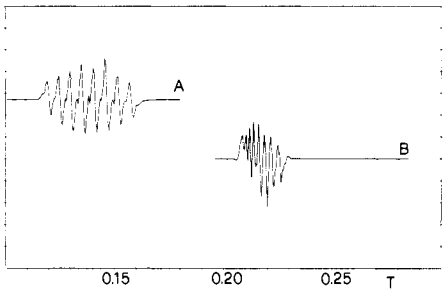

Figure 1. Single-crystal EPR spectra of cobalt(II)-doped $Mg(apy)_6(ClO_4)_2$ at 4.2 K: (A) static magnetic field in the *ab* plane; (B) static magnetic field parallel to *c*.

plexes are highly desirable, since in this case the number of independent parameters required to parameterize the ligand field are reduced to a minimum.

We wish to report here the single-crystal EPR spectra of $Co(apy)_6(ClO_4)_2$ (apy = 1-phenyl-2,3-dimethyl-5-pyrazolone) doped into the corresponding magnesium complex, in which the X-ray single-crystal analysis showed that the metal ion is in a trigonal site symmetry.[14] The comparison of these new data with other data available in the literature and powder spectra obtained by us allows us to discuss critically the values of the angular-overlap parameters.

Experimental Section

All the reagents and ligands were used as purchased without further purification, and the complexes were prepared according to reported procedures.[15,16]

Single crystals of cobalt-doped $Mg(apy)_6(ClO_4)_2$ were grown by slow evaporation of water solutions. The crystals were oriented with a Philips PW 1100 diffractometer. EPR spectra were run with a Varian E9 spectrometer equipped with an Oxford Instruments ESR 9 continuous-flow cryostat.

Results

The polycrystalline powder EPR spectra of $Co(apy)_6(ClO_4)_2$, $Co(en)_3(NO_3)_2$ (en = 1,2-diaminoethane), $Co(Iz)_6(NO_3)_2$ (Iz = imidazole), and $Co(bpy)_3Br_2$ (bpy = 2,2′-bipyridine) were recorded at 4.2 K. They are typical of high-spin cobalt(II) complexes.[12,13] In the doped compounds a ^{59}Co hyperfine structure was also resolved. In the case of $Co(en)_3(NO_3)_2$, the spectra exhibited more transitions than expected, presumably due to intermolecular exchange phenomena. Attempts to obtain magnetically dilute complexes failed, because in each case relatively concentrated solid solutions were obtained. The spin Hamiltonian parameters of these complexes are given in Table I.

The single-crystal EPR spectra of $(Co,Mg)(apy)_6(ClO_4)_2$ were recorded by rotating around the *a* crystal axis. The spectra recorded with the static magnetic field vector parallel to *b* and *c* are shown in Figure 1. The spectra show the presence of forbidden lines, due to quadrupole and/or nuclear Zeeman effects.[17] Also, some exchange interactions are seen to be operative.

The single-crystal data were analyzed through a computer program that takes into account second-order hyperfine effects.[8] The values are only slightly different from those of the powder spectra ($g_\parallel = 3.02$, $g_\perp = 4.70$, $A_\parallel = 0.0042$ cm^{-1}, $A_\perp = 0.0118$ cm^{-1}), namely, $g_\parallel = 3.08$, $g_\perp = 4.85$, $A_\parallel = 0.0034$ cm^{-1}, and $A_\perp = 0.0121$ cm^{-1}.

Discussion

For octahedral cobalt(II) complexes the ground $^4T_{1g}$ level is split by low-symmetry components, and it is this splitting that determines the pattern of *g* values. The simplest way of relating the pattern of *g* values to the sign of the splitting in axial symmetry is that of the Abragam–Pryce model.[18] With this model the *g* values are calculated[19] by using the Hamiltonian

$$H = -\tfrac{1}{3}\gamma k\zeta\, \hat{L}\cdot\hat{S} - Dk^2(\hat{L}_z^2 - \tfrac{2}{3}) + \mu_B B\cdot(kL + g_e\hat{S}) \qquad (1)$$

where $\hat{L}$ is an orbital momentum operator within an effective $L = 1$ base, γ ranges from −1.5 to −1, accounting for the admixture of excited states into the ground state, k is the Stevens orbital reduction factor,[20] ζ is the spin–orbit coupling constant, and D is the axial symmetry component of the ligand field. A positive D yields an orbital doublet as the ground level, and $g_\parallel > g_\perp$, while for negative D an orbital singlet lies lowest, and $g_\parallel < g_\perp$. If k and ζ are kept fixed at 1 and the free-ion value, respectively, only two parameters are required to fit the *g* values in axial symmetry. The results of the analysis of the complexes we have reported here and of other selected literature examples are shown in Table I. It is apparent from Table I that the only complexes that have an orbital doublet ground state are $Co(H_2O)_6^{2+}$ and $Co(Iz)_6^{2+}$, while for all the other complexes the orbital singlet lies lowest. The calculated γ values are in general close to the value expected in the weak-field limit,[19] with the exception of $Co(pyO)_6^{2+}$ and $Co(bpy)_3^{2+}$.

The above model fails to give a clear physical interpretation of the value of D, the AOM being better suited to this purpose. In order to apply the AOM, it is necessary to have more structural details. For the complexes with CoO_6 chromophores[14,21,22] the O–Co–O angles are very close to 90°; therefore the orbital splitting can be determined only by anisotropic π interactions, i.e. by the fact that the L–M bond does not have cylindrical symmetry.

When this is the case, it is one of the postulates of the angular-overlap model that it is possible to find a reference frame in which the interaction of a metal with a ligand on the z' axis is diagonal.[2] In this reference frame the parameters required for expressing the d-orbital energies are e_σ, $e_{\pi s}$, and $e_{\pi c}$, neglecting, as usual, the δ contributions. $e_{\pi s}$ and $e_{\pi c}$ are the π interactions parallel to y' and x', respectively. When the symmetry of the M–L moiety is very low, the classification is actually meaningless, and not too much significance can be attached to the calculated parameters. In fact when the symmetry around the M–L axis is lower than orthorhombic, it is not possible to distinguish between σ and π interactions. It is therefore possible to predict the choice of axes that can yield a diagonal perturbation of the metal orbitals. However, it may be hoped that, by looking at a series of complexes, it will be possible to check whether the calculated parameters are consistent with each other.

For the present series of complexes the choice of the diagonal axes can be performed reasonably well for the aqua complex, since in the isomorphous iron complex neutron diffraction studies have shown that the water–metal moiety has to a good approximation C_{2v} symmetry.[22] The axes were chosen therefore with z' parallel to the Co–O direction and x' parallel to the H_2O plane.

In the other two cases, namely, $Co(apy)_6(ClO_4)_2$ and $Co(pyO)_6(ClO_4)_2$, the symmetry around the oxygen atoms is only C_1,[14,21] since the aromatic rings are not in the same plane as N, O, and Co atoms, making angles of 72° in the pyO example and 56° in the apy case. It seems therefore that the only choice

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Table II. Spin Hamiltonian Geometrical and Bonding Parameters for a Series of Trigonal Cobalt(II) Complexes

	$g_{\parallel}$[f]	$g_{\perp}$[f]	$A_{\parallel}$[a,b,f]	$A_{\perp}$[f]	ψ,[c] deg	α,[d] deg	e_{σ}[a]	$e_{\pi s}$	$e_{\pi c}$	ref
$Co(H_2O)_6^{2+}$	5.82	3.44	0.0184	0.0047	2–9	53.77	2920	110	60	18
	5.81	3.43	0.0186	0.0050						
$Co(pyO)_6^{2+}$	2.26	4.77	0.0019	0.0038	72	54.73	3575	608	304	9
	2.26	4.78	0.0017	0.0033						
$Co(apy)_6^{2+}$	3.08	4.85	0.0034	0.0121	78	54.94	2680	202	93	this work
	3.08	4.85	0.0039	0.0129						
$Co(N\text{-}MeIz)_6^{2+}$	3.06	4.87	e	0.0125	0	57.04	3390	85		25
	3.06	4.81	0.0018	0.0120						
$Co(Iz)_6^{2+}$	5.55	3.53	e	e	25	56.08	3650	350		25
	5.54	3.53								
$Co(en)_3^{2+}$	2.6	5.0				57.30	3700			this work
	2.63	4.96								
$Co(bpy)_3^{2+}$	3.16	4.62			40.5	57.20	4300	575		this work
	3.16	4.69								

[a] A values and e_{λ} parameters are in cm^{-1}. [b] All the values are calculated with a P value in the range 0.0220 cm^{-1} and with a κ value in the range 0.30–0.32. [c] See text. [d] The angle between the trigonal axis and Co–L directions. [e] Unresolved. [f] The first value given for each compound is the observed value, and the second, the calculated value.

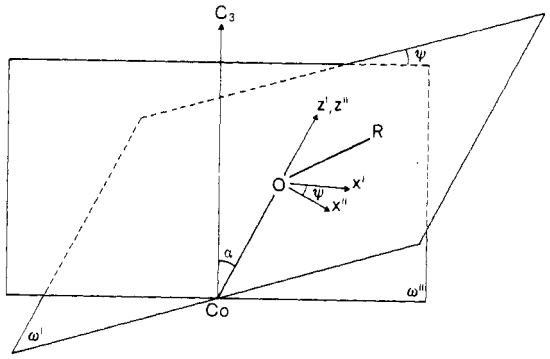

Figure 2. Local axes for oxygen donor complexes. ω' is the plane defined by the Co, O, and R atoms, ω'' is defined by the trigonal axis and the Co–O direction, x' les on ω', and x'' lies on ω''. The corresponding y' and y'' axes are omitted for the sake of simplicity.

that can be systematic is that of referring in each case to the Co–O–R plane, with x' set parallel and y' orthogonal to it as shown in Figure 2.

The energies of the levels will depend on the angle ψ between the ω' and ω'' planes of Figure 2. In the strong-field limit the splitting of the ground $^4T_{1g}$ level is given by the difference in energy in the xy and xz, yz orbitals. In the AOM this is given by

$$D = -3(2 \sin^2 \psi - 1)(e_{\pi s} - e_{\pi c}) \qquad (2)$$

For the complexes we are considering the ψ values range from 0 to 78°. Therefore for the three complexes the following relations are expected to hold:

$$D_{H_2O} = 3(e_{\pi s}^{H_2O} - e_{\pi c}^{H_2O})$$
$$D_{pyO} = -2.43(e_{\pi s}^{pyO} - e_{\pi c}^{pyO}) \qquad (3)$$
$$D_{apy} = -2.74(e_{\pi s}^{apy} - e_{\pi c}^{apy})$$

It is apparent that, if the $e_{\pi s} - e_{\pi c}$ difference retains the same sign throughout the series, D_{H_2O} is expected to have a sign opposite to that in the other two complexes. If the π interactions of these oxygen donors are assumed to be positive, i.e. to give antibonding effects on the metal orbitals, then the experimental pattern of g values can be reproduced by using $e_{\pi c} < e_{\pi s}$. This is exactly the pattern of π values that is expected for the water ligand,[8,23,24] where the in-plane bond pairs of the oxygen atoms are heavily involved in the σ bonding to the hydrogen atoms. Similar results have been previously

Table III. Observed and Calculated Electronic Transitions for Some Trigonal Cobalt(II) Complexes

	obsd[a]	assignt	calcd[a]	B,[b] cm^{-1}	ref
$Co(H_2O)_6^{2+}$	8.1	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	8.0	850	28
	16.0	$\rightarrow {}^4A_{2g}(F)$	16.3		
	19.4	$\rightarrow {}^4T_{1g}(P)$	19.5		
$Co(pyO)_6^{2+}$	7.25, 8.3	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	8.1, 8.5	840	10
	17.7	$\rightarrow {}^4A_{2g}(F)$	17.4		
	18.6, 20.4	$\rightarrow {}^4T_{1g}(P)$	19.1, 20.2		
$Co(apy)_6^{2+}$	6.8	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	7.0	950	
	19.6	$\rightarrow {}^4A_{2g}(F)$	20.0		
	20.6	$\rightarrow {}^4T_{1g}(P)$	20.6		
$Co(en)_3^{2+}$	10.0	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	10.1	810	29
	21.0	$\rightarrow T_{1g}(P)$	20.8		
$Co(bpy)_3^{2+}$	11.0	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	10.6	825	30
	22.0	$\rightarrow {}^4T_{1g}(F)$	21.7		

[a] In units of 10^{-3} cm^{-1}. [b] The other AOM parameters used in the calculations are those reported in Table II.

reported for the pyO ligand,[9,11] and the apy ligand is now found to behave similarly.

This analysis is based on several approximations so that it may have only a semiquantitative meaning. In order to substantiate it better, we used also a program we have previously described[26] and tried to fit both the electronic and the EPR transitions, using the geometrical coordinates of the donor atoms found in the crystal structure determination and e_{σ}, $e_{\pi s}$, $e_{\pi c}$, k, ζ, and B as parameters.

First of all the Dq value of the oxygen donors, defined as $10Dq = 3e_{\sigma} - 2e_{\pi s} - 2e_{\pi c}$, was varied in such a way as to find a reasonable agreement with the electronic transitions. Then the $e_{\pi s}$ and $e_{\pi c}$ values were varied until the g and A values were satisfactorily reproduced. The parameter space was swept accurately. It was found that the observed pattern of g values (either $g_{\parallel} > g_{\perp}$ or $g_{\parallel} < g_{\perp}$) could be reproduced by using either positive or negative e_{π} values but that good numerical agreement between observed and calculated g values could be attained only by using positive e_{π} values. Also the ^{59}Co hyperfine splitting was calculated, and fair agreement with the experimental data was found. The two additional parameters, P and κ[27] required were fixed at values close to the free-ion values. The calculated g and A values are given in Table II, while those for the electronic transitions are given in Table

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III. The best fit parameters reported are not unique, since as shown by eq 2 the g values depend only on the $e_{\pi s} - e_{\pi c}$ difference and not on the individual values.

If the D values calculated with (3) are compared with those calculated with (1), it is found that the agreement is poor, but the two models agree on the sign of the splitting of the ground $^4T_{1g}$ level.

In the case of the CoN_6 chromophores, major distortions are observed from octahedral symmetry, especially with the bidentate ligands.[31-35] Therefore, the σ component of the bonding interaction also becomes relevant in determining the splitting of the ground $^4T_{1g}$ state since the xy, xz, and yz orbitals acquire σ antibonding character. For the bidentate complexes the deviation from octahedral symmetry can be loosely described as trigonal compression, and similar, although less dramatic, deviations are observed also for monodentate complexes, as shown by the value of the angle α of Table II. It should be 54.74° for a regular octahedral geometry.

Calculations show that the effect of the σ contribution for trigonal compression is that of yielding the orbitally nondegenerate state as the ground state, suggesting $g_{\parallel} < g_{\perp}$. As a matter of fact, this is found to be the case for all the complexes except for the imidazole complex, where $g_{\perp} < g_{\parallel}$. In this case the deviation from strict octahedral symmetry is not too large, and π components of the ligand field may still be important in determining the splitting of the ground level. For the en complex, where no π interaction is anticipated,[36] both the electronic and the EPR spectra can be fit with the e_{σ} parameter alone. For the other complexes π components were also taken into account, with e_{π} allowed to be different from zero only in the direction orthogonal to the aromatic plane, if the nitrogen orbitals in the molecular plane are assumed to be involved with the π system of the aromatic ring.[37]

Fits were attempted with both negative and positive e_{π} values (a negative value means substantial π back-bonding from ligand to metal). The bpy complex, which is the most distorted from octahedral symmetry, is the most sensitive to the effects of both σ and π interactions. In no way is it possible to obtain a reasonable fit of the g and A values with negative e_{π}. As a matter of fact, a negative e_{π} tends to split the ground $^4T_{1g}$ state, with the orbital singlet lower in energy; i.e., it tends to have the same effect as that of the σ interaction. Therefore, using negative e_{π} invariably yields $g_{\parallel} < g_{\perp}$, but with an anisotropy much larger than that observed. On the other hand, positive e_{π} tends to place the orbital doublet at lowest energy; therefore, including it will decrease the $g_{\parallel} - g_{\perp}$ anisotropy. The best fit of the spin Hamiltonian parameters is shown in Table I, while the corresponding fit for the electronic transitions is given in Table III.

For the N-MeIz and Iz complexes similar considerations hold. It is sufficient to increase slightly the e_{π} value on passing from N-MeIz to Iz in order to reverse the pattern of g values. Reasonable fits are shown in Table II. A reason why e_{π} should be larger in Iz as compared to its value in N-MeIz is that the metal to nitrogen distance is shorter in the former as compared to that in the latter.[31,38]

It seems safe therefore to conclude that in no case was evidence of π back-interaction of cobalt(II) ions with heterocyclic amine ligands found, in line with previous findings on cobalt–pyridine complexes.[39-42] This of course does not exclude the possibility of π back-interactions with different metal ions.[43-46] For the oxygen donors it seems to now be established that the π interactions orthogonal to the M–O–R plane are stronger than those in the plane.

Registry No. $Co(apy)_6(ClO_4)_2$, 19572-96-4; $Mg(apy)_6(ClO_4)_2$, 15713-41-4; $Co(en)_3(NO_3)_2$, 56928-12-2; $Co(Iz)_6(NO_3)_2$, 31363-22-1; $Co(bpy)_3Br_2$, 15388-66-6.

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