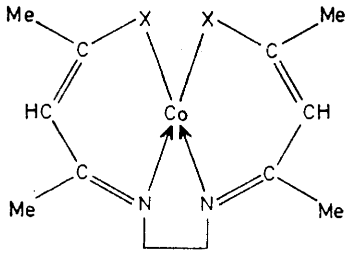
Paramagnetic Anisotropy and Electronic Structure of *NN'*-Ethylenebis(acetylacetoneiminato)cobalt(II) and *NN'*-Ethylenebis(thioacetylacetoneiminato)cobalt(II)

By **Keith S. Murray*** and **Robert M. Sheahan**, Chemistry Department, Monash University, Clayton, Victoria Australia 3168

Magnetic-susceptibility measurements have been made on single crystals of the title complexes, [Co(acacen)] and [Co(tacacen)], over the range 100—300 K. Both complexes exhibit anisotropy typical of planar low-spin cobalt(II) species, with [Co(tacacen)] being much less anisotropic in the *xy* ligand plane than [Co(acacen)]. The anisotropy in both is dominated by the close approach of the d_{yz} orbital to the d_{z^2} ground-state orbital. The temperature-dependent principal susceptibilities have been fitted to a recently developed model for low-spin Co^{II} which takes into account excited doublet and quartet states. In conjunction with e.s.r. parameters, it is found that quartet-state components lie only a few thousand wavenumbers in energy above the ground state. Correlations are made between the energies of out-of-plane metal π orbitals and the ability of the chelates to bind molecules such as pyridine and O_2.

THE Schiff-base complex *NN'*-ethylenebis(acetylacetoneiminato)cobalt(II), [Co(acacen)], has been used extensively by Basolo and his co-workers [1-3] and Busetto *et al.*[4] as a simple model for natural oxygen carriers. The solution properties of [Co(acacen)] and its 1 : 1 oxygen adduct, usually in the presence of axial bases, have been studied in considerable detail with e.p.r. measurements being used as the chief structural and electronic probe. It is now generally accepted that the odd electron in this low-spin d^7 system resides in a d_{z^2} orbital, while in the oxygenated species it is localized on the O_2 molecule.[5] In order to define more completely the electronic structure of these interesting molecules we have made susceptibility measurements on single-crystal samples of $[Co(acacen)]\cdot C_6H_6$, (Ia), and of its thio-analogue [Co(tacacen)],



(Ia) X=O [Co(acacen)]
(Ib) X=S [Co(tacacen)]

---

[1] A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 55.

[2] B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.

[3] M. T. Carter, P. D. Rilleme, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 392.

[4] C. Busetto, F. Cariati, P. Fantucci, D. Galiziolli, F. Morazzoni, and V. Valenti, *Gazzetta*, 1972, **102**, 1040.

[5] B. M. Hoffman, T. Szymanski, and F. Basolo, *J. Amer. Chem. Soc.*, 1975, **97**, 673.

(Ib). E.p.r. spectra have been reported for [Co(acacen)]–[Ni(acacen)] powders [4,6] and for [Co(acacen)] in nematic solvents,[7] but with some disagreements in interpretation.

EXPERIMENTAL

The complex [Co(acacen)] was synthesized by the literature method and crystallized slowly from benzene in a sealed tube.[8] Well formed translucent orange crystals developed on standing. The crystals were extremely sensitive to the atmosphere and were coated with silicone grease for all subsequent handling. Magnetic measurements were made on freshly coated crystals. In contrast, the crystals of [Co(tacacen)] [9] were stable in the atmosphere.

Magnetic-anisotropy and average-susceptibility measurements were made as described previously.[10] Crystal axes were located by *X*-ray goniometry.

Crystal Structures.—The benzene solvate of [Co(acacen)] is monoclinic, with two formula units per unit cell.[11] Each [Co(acacen)] molecule is perfectly planar, as required by a crystallographic mirror plane. The complex [Co(tacacen)] is orthorhombic,[12] the four molecules in the unit cell being slightly distorted from planarity.

RESULTS

The crystal anisotropies and average magnetic susceptibilities for [Co(acacen)]·C_6H_6 and [Co(tacacen)] are given as a function of temperature in Table 1. The crystal measurements for [Co(tacacen)] are limited to the range 220—300 K since the crystals shattered violently on cooling to *ca.* 200 K. However, the powder-susceptibility measurements showed no discontinuity over the range 100—300 K. The room-temperature magnetic moments of [Co(acacen)]·C_6H_6 (χ_g 5.66 × 10^{-6} cm^3 g^{-1}) and the unsolvated form of [Co(acacen)] (χ_g 7.09 × 10^{-6} cm^3 g^{-1}) are the same within experimental error, $\bar{\mu}$ = 2.26 B.M.* E.s.r. measurements on frozen benzene solutions of [Co(acacen)] and [Co(tacacen)] gave only very broad and featureless lines when compared to those in pyridine [2] or when doped into nickel(II) analogues.[4,6]

TABLE 1

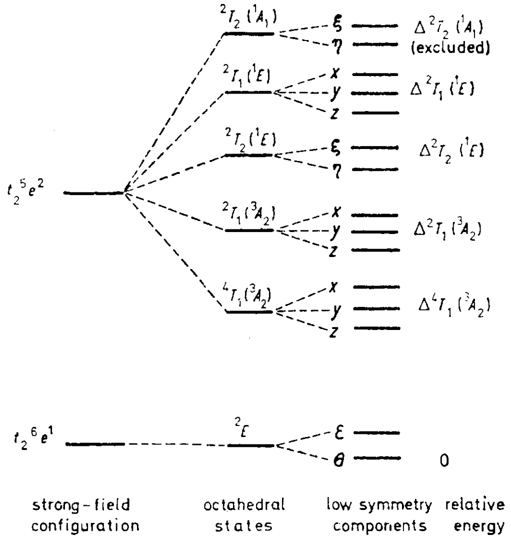
Experimental crystal anisotropies and average susceptibility (10^6 cm^3 mol^{-1})

(*a*) [Co(acacen)]·C_6H_6 (diamagnetism, −205 × 10^{-6} cm^3 mol^{-1})

T/K	b axis (χ_3) vertical ($\chi_2 - \chi_1$)	χ_1 vertical ($\chi_2 - \chi_3$)	$\bar{\chi}$ $\frac{1}{3}(\chi_1 + \chi_2 + \chi_3)$
300	1 540	2 000	2 150
280	1 600	2 120	2 260
260	1 680	2 265	2 400
240	1 795	2 435	2 555
220	1 935	2 615	2 720
200	2 090	2 820	2 905
180	2 265	3 075	3 170
160	2 495	3 400	3 505
140	2 800	3 840	3 900
120	3 210	4 400	4 380
100	3 760	5 240	5 040

(*b*) [Co(tacacen)] (diamagnetism, −150 × 10^{-6} cm^3 mol^{-1})

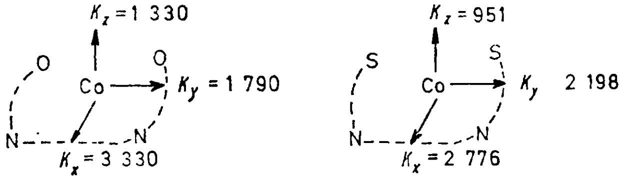
T/K	a axis vertical ($\chi_b - \chi_c$)	b axis vertical ($\chi_a - \chi_c$)	$\bar{\chi}$ $\frac{1}{3}(\chi_1 + \chi_2 - \chi_3)$
300	960	987	1 975
280	985	1 015	2 100
260	1 030	1 064	2 205
240	1 085	1 125	2 340
220	1 115	1 204	2 500
200	Crystals shatter		2 740
180			2 950
160			3 260
140			3 685
120			4 225
100			4 980



Representation (no ordering of states implied) of states which derive from the strong-field configurations t_2^6e and $t_2^5e^2$

TABLE 2

Direction cosines and molecular-susceptibility directions ($K_i/10^6$ cm^3 mol^{-1})



[Co(acacen)]·C_6H_6

	a	b	c *
K_x	0	−1	0
K_y	0.7071	0	0.7071
K_z	0.7071	0	−0.7071

[(Co(tacacen)]

	a	b	c
K_x	0.7545	−0.6487	0.0998
K_y	−0.5090	−0.6744	−0.5349
K_z	−0.4142	−0.3528	0.8390

The derived molecular-susceptibility ellipsoids have K_x and K_y in the ligand plane for both complexes (Figure). These are directed, respectively, between the O, O (or S, S)

---

* 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

[6] C. Busetto, F. Cariati, P. C. Fantucci, D. Gallizioli, and F. Morazzoni, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 313.

[7] B. M. Hoffman, F. Basolo, and D. L. Diemente, *J. Amer. Chem. Soc.*, 1973, **95**, 6497.

[8] G. T. Morgan and J. D. M. Smith, *J. Chem. Soc.*, 1925, **127**, 2030.

[9] P. R. Blum, R. M. C. Wei, and S. C. Cummings, *Inorg. Chem.*, 1974, **13**, 450.

[10] K. S. Murray and R. M. Sheahan, *Chem. Phys. Letters*, 1973, **22**, 406.

[11] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Chim. Acta*, 1968, **2**, 386.

[12] G. D. Fallon and B. M. Gatehouse, unpublished work.

and O, N (or S, N) donor atom sets; K_z is perpendicular to the metal–ligand plane. The appropriate direction cosines are given in Table 2. In both complexes it was found that $K_x > K_y > K_z$ with [Co(tacacen)] being the least anisotropic. The experimental K_i and μ_i values are given in Table 3 for both complexes over the temperature ranges of the measurements. Both complexes exhibit Curie–Weiss behaviour.

TABLE 3

Principal magnetic susceptibilities (10^6 cm^3 mol^{-1}) and moments (B.M.)

[Co(acacen)]·C_6H_6

(a) Observed

T/K	K_x	K_y	K_z	μ_x	μ_y	μ_z	$\bar{\mu}$
300	3 300	1 790	1 330	2.83	2.07	1.79	2.27
280	3 500	1 900	1 380	2.80	2.06	1.76	2.25
260	3 715	2 035	1 450	2.78	2.06	1.74	2.23
240	3 965	2 170	1 530	2.76	2.04	1.71	2.21
220	4 237	2 302	1 622	2.73	2.01	1.69	2.19
200	4 542	2 452	1 722	2.70	1.98	1.66	2.16
180	4 950	2.685	1 875	2.67	1.97	1.64	2.14
160	5 470	2 975	2 010	2.65	1.95	1.63	2.12
140	6 113	3 313	2 273	2.62	1.93	1.60	2.09
120	6 917	3 707	2 517	2.58	1.89	1.55	2.05
100	8 040	4 280	2 800	2.53	1.85	1.50	2.01

(b) Calculated (without quartet states)

T/K	K_x	K_y	K_z	μ_x	μ_y	μ_z	$\bar{\mu}$
300	3 334	1 791	1 361	2.83	2.07	1.81	2.28
280	3 510	1 884	1 414	2.80	2.05	1.78	2.25
260	3 711	1 990	1 476	2.78	2.03	1.75	2.23
240	3 946	2 114	1 547	2.75	2.01	1.72	2.21
220	4 222	2 260	1 632	2.73	1.99	1.70	2.18
200	4 554	2 435	1 734	2.70	1.97	1.67	2.16
180	4 959	2 650	1 858	2.67	1.95	1.64	2.13
160	5 465	2 918	2 014	2.65	1.93	1.61	2.11
140	6 116	3 262	2 214	2.62	1.91	1.57	2.08
120	6 984	3 721	2 481	2.59	1.89	1.54	2.05
100	8 199	4 364	2 854	2.56	1.87	1.51	2.03

Best-fit parameters: $\zeta = 500$ cm^{-1}

	Δ/cm^{-1}		
	$^2T_1(^3A_2)$	$^2T_1(^1E)$	$^2T_2(^1E)$
x	1 700	1 200	
y	1 900	4 000	
z	5 500	25 000	
ξ			2 000
η			10 000

(c) Calculated (including quartet states)

T/K	K_x	K_y	K_z	μ_x	μ_y	μ_z	$\bar{\mu}$
300	3 330	1 827	1 394	2.83	2.09	1.83	2.29
280	3 504	1 916	1 449	2.80	2.07	1.80	2.26
260	3 704	2 019	1 513	2.78	2.05	1.77	2.24
240	3 937	2 139	1 588	2.75	2.03	1.75	2.21
220	4 212	2 282	1 677	2.72	2.00	1.72	2.19
200	4 542	2 453	1 785	2.70	1.98	1.69	2.16
180	4 945	2 663	1 917	2.67	1.96	1.66	2.14
160	5 448	2 925	2 082	2.64	1.93	1.63	2.11
140	6 096	3 261	2 294	2.61	1.91	1.60	2.08
120	6 959	3 711	2 577	2.58	1.89	1.57	2.06
100	8 167	4 340	2 974	2.56	1.86	1.54	2.03

Best-fit parameters: $\zeta = 500$ cm^{-1}

	Δ/cm^{-1}			
	$^2T_1(^3A_2)$	$^2T_1(^1E)$	$^4T_1$	$^2T_2(^1E)$
x	1 000	1 000	2 000	
y		20 000		
z	4 500	25 000	1 000	
ξ				1 900
η				25 000

TABLE 3 (*Continued*)

[Co(tacacen)]

(a) Observed

T/K	K_x	K_y	K_z	μ_x	μ_y	μ_z	$\bar{\mu}$
300	2 776	2 198	951	2.58	2.30	1.51	2.18
280	2 927	3 322	1 051	2.56	2.28	1.53	2.17
260	3 076	2 429	1 110	2.53	2.25	1.52	2.14
240	3 267	2 563	1 190	2.50	2.22	1.51	2.12
220	3 502	2 717	1 281	2.48	2.19	1.50	2.10

(b) Calculated (without quartet states)

T/K	K_x	K_y	K_z	μ_x	μ_y	μ_z	$\bar{\mu}$
300	2 790	2 202	1 043	2.59	2.30	1.58	2.20
280	2 933	2 306	1 077	2.56	2.27	1.55	2.17
260	3 095	2 424	1 116	2.54	2.25	1.52	2.14
240	3 279	2 560	1 164	2.51	2.22	1.50	2.13
220	3 493	2 718	1 223	2.48	2.19	1.47	2.09

Best-fit parameters: $\zeta = 500$ cm^{-1}, $k_z = 0.6$

	Δ/cm^{-1}		
	$^2T_1(^3A_2)$	$^2T_1(^1E)$	$^2T_2(^1E)$
x	1 000	750	
y		1 250	
z	5 000	25 000	
ξ			6 000
η			15 000

(c) Calculated (including quartet states)

T/K	K_x	K_y	K_z	μ_x	μ_y	μ_z	$\bar{\mu}$
300	2 785	2 194	1 080	2.59	2.29	1.61	2.20
280	2 926	2 302	1 132	2.56	2.27	1.59	2.18
260	3 088	2 425	1 192	2.53	2.46	1.58	2.16
240	3 275	2 568	1 264	2.51	2.20	1.56	2.13
220	3 495	2 737	1 350	2.48	2.19	1.54	2.11
200	3 759	2 939	1 454	2.45	2.17	1.53	2.09

Best-fit parameters: $\zeta = 500$ cm^{-1}, $k_z = 0.5$

	Δ/cm^{-1}			
	$^2T_1(^3A_2)$	$^2T_1(^1E)$	$^4T_1$	$^2T_2(^1E)$
x	1 000	1 000	10 000	
y		2 000		
z	5 000	25 000	1 500	
ξ				4 250
η				10 000

Calculations and Curve Fitting.—We recently outlined our theoretical model [13] and described in detail [14] its application to the magnetic properties of low-spin cobalt(II) species of the [Co(salen)] type [salen = *NN'*-ethylenebis(salicylideneiminato)]. In essence the model involves the effect of ligand-field and spin–orbit coupling perturbations between the ground doublet state from the $t_2^6e^1$ configuration (using octahedral notation for convenience) and the various doublet and quartet states from the first excited configuration $t_2^5e^2$ (Figure). The energies of the excited states are parametrized relative to the ground state as zero, and these energy differences, together with the spin–orbit coupling parameter, ζ, are the variables for best-fit. In order to somewhat minimize the number of variables, ζ was set at a value slightly reduced from that of the free ion, *viz.* —500 cm^{-1}. Symmetry mixing of states was assumed to be negligible. Initially the principal susceptibilities of [Co(acacen)]·C_6H_6 and [Co(tacacen)] were calculated assuming that excited quartet-state interactions were negligible and this required diagonalization of an 18 × 18 matrix. However, in the light of our recent evaluation of published e.p.r. data for [Co(acacen)] and a large range of other low-spin cobalt(II) chelates,[15] in which quartet-state interactions were necessary in order to obtain a complete explanation of g and A values, we also calculated the K_i values by diagonalizing the complete 28 × 28 matrix.

The principal susceptibilities and moments of the two complexes could be well reproduced without taking into account any excited quartet-state interactions. We shall discuss this case first and then later the effect of including quartet states. The calculated values are given in Table 3

[13] K. S. Murray and R. M. Sheahan, *J.C.S. Chem. Comm.*, 1975, 475.

[14] K. S. Murray and R. M. Sheahan, *J.C.S. Dalton*, 1976, 999.

[15] K. S. Murray and R. M. Sheahan, in preparation.

together with the parameter values. It is to be noted that the states in parentheses in ${}^2T_2({}^1E)$ and ${}^2T_2({}^3A_2)$ are used to distinguish the e^2 component states. The ${}^2T_2({}^1A_1)$ state, which also obtains from $t_2{}^5e^2$, was excluded on account of its expected high energy and as its effect on the susceptibility is mimicked by ${}^2T_2({}^1E)$.

The effects on the principal susceptibilities of varying the energies of the various excited states have been discussed previously [14] and such effects become evident as one computes a set of best-fit parameters. Although there are a large number of variable parameters in the model, the final choice of the state energies is limited considerably in having to reproduce experimental susceptibilities in three directions and for a large temperature range. Small changes in the parameters would, however, not significantly affect the fit since a small change in one can often be absorbed by changes in another. In essence, the substantial temperature dependence of the principal moments in both complexes is due to a relatively large second-order Zeeman effect which arises from the close approach to the ground state of the various doublet- (and quartet-) state components, particularly those of ${}^2T_1({}^3A_2)$ and ${}^2T_1({}^1E)$. In the absence of any polarized crystal optical spectra there is no independent check on the exact magnitudes of the energy parameters. Those calculated do, however, fall into the range which has been observed in solution for chelates of the [Co(acacen)] type: [4,16] in such studies, bands of energy of less than 3 000 cm^{-1} have also been predicted. It is not possible to correlate the state energies derived here and the single-electron orbital energies which have been tentatively assigned in these absorption and circular-dichroism studies.[16] Except for one or two directions, the energies of the parameters deduced for [Co(acacen)] and [Co(tacacen)] are fairly similar. One significant difference is the need to reduce the orbital-reduction parameter, k, in the z direction for [Co(tacacen)] from 1 to 0.6. This is brought about by the very low μ_z value which was observed. The low value most likely results from a combination of inaccuracy in the measurement of such a small susceptibility, and the neglect of any ligand anisotropy, which, although likely to be small, would tend to decrease the observed K_z with respect to K_x and K_y. In order to fit the observed data it was necessary to assume a reduced k_z acting on the second-order term in the z direction, since the z component of ${}^2T_1({}^3A_2)$ which alone mixes into the ground state to give $K_z < K$ (spin only), also gives a large temperature-independent paramagnetism (t.i.p.) term which causes substantial non-Curie–Weiss behaviour in K_z.

As mentioned above, our recent refitting of published e.s.r. g and A tensors to closed-form expressions derived from our model have revealed the importance of, hitherto neglected, excited quartet states which lie close to the ground state.[15] In the case of [Co(acacen)] the results suggest that the quartet states are only of 1 000—2 000 cm^{-1} in energy. There are no comparable data on [Co(tacacen)], and it was assumed that quartet-state interactions were not quite so pronounced as in [Co(acacen)]. The calculated principal susceptibilities and moments, together with best-fit parameters, are given for this situation in Table 3(*c*). Again excellent fits are obtained, the only parameters other than those from ${}^4T_1$ which show any significant changes are those affecting μ_y, *i.e.* $\Delta^2T_2(xz)$ and $\Delta^2T_1({}^1E)y$; the variations do not affect the relative ordering of the excited states. At first sight it might seem surprising that the calculations of susceptibility for these complexes are apparently fairly insensitive to the inclusion of quartet states. It is because they contribute *via* spin–orbit coupling to second order only to the susceptibility, but they mix to first order into the hyperfine tensor, A, and hence their presence is much more readily detected. It is clear that, in future, any discussions concerning the detailed ordering of excited-state energy levels should, wherever possible, be based on data consistent with both magnetic-susceptibility and e.s.r. measurements.

DISCUSSION

The complex [Co(acacen)]$\cdot C_6H_6$ shows magnetic anisotropy which is typical of low-spin planar cobalt(II) complexes with an asymmetric ligand field within the plane ($K_x \gg K_y$ and K_z). However [Co(tacacen)] is much less anisotropic in the xy plane, tending towards the in-plane isotropy of a five-co-ordinate cobalt(II) Schiff-base complex. This suggests the presence of strong out-of-plane π bonding between the N_2S_2 donor atoms and the d_{xz} and d_{yz} orbitals of the cobalt(II) ion. In both chelates the anisotropy is dominated by the close approach of the d_{yz} orbital to the d_{z^2} orbital and is closest in [Co(acacen)]. The d_{xz}–d_{yz} orbital separation is much less in the N_2S_2 complex than in the N_2O_2 complex. In our study of [Co(salen)] systems [14] we showed that a correlation exists between the energies of the out-of-plane π orbitals and the relative abilities to bind molecules such as pyridine and dioxygen in the axial positions. The same arguments are relevant here. Structural studies have shown [17-21] that in the five-co-ordinate pyridine adducts, the pyridine molecule normally lies along the yz plane, and thus any influence of metal–ligand π bonding is restricted to the d_{xz} orbital which must be placed in an energetically favourable position to achieve good overlap. Using these arguments, the results predict that [Co(acacen)] should form a more stable pyridine adduct than [Co(tacacen)], and this appears to be the case in practice. In the six-co-ordinate dioxygen derivatives such as [Co(bacen)(py)(O_2)] [bacen = *NN'*-ethylenebis(benzoylacetoneiminato)] the oxygen molecule has been shown to lie in a plane at right angles to the pyridine molecule which is again in the yz plane.[18,19] This suggests that π bonding between O_2 and the d_{yz} orbital is important, and further that in the absence of any steric constraints the O_2 molecule lies along the xz plane because of the prior involvement of the d_{xz} metal orbital in π bonding with pyridine. Our conclusions are similar to those previously reached by Rodley and Robinson.[18] We feel that the influence of metal π orbitals, together with the presence of a d_{z^2}

---

[16] F. L. Urbach, R. D. Bereman, J. A. Topich, M. Hariharan, and B. J. Kalbacher, *J. Amer. Chem. Soc.*, 1974, **96**, 5063.

[17] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

[18] G. A. Rodley and W. T. Robinson, *Nature*, 1972, **235**, 438.

[19] M. Calligaris, G. Nardin, L. Randaccio, and G. Tauzher, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 419.

[20] M. Calligaris, G. Nardin, and L. Randaccio, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 477.

[21] M. Cesari, C. Neri, G. Perego, E. Perotti, and A. Zazzetta, *Chem. Comm.*, 1970, 276.

ground-state orbital, are important factors in the oxygenation of these cobalt(II) species, even though the dominant factor may, as Carter *et al.*[3] suggest, be the ability to oxidize from Co^{II} to Co^{III}, *i.e.* directly related to $E^{\ominus}(Co^{3+}–Co^{2+})$.

Finally we comment on recent e.s.r. studies of [Co(acacen)] made by Hoffman *et al.*[7] using nematic-glass oriented samples. In order to interpret their results they required g_y to be less than g_z.* This is clearly in conflict with the present single-crystal magnetic measurements and suggests to us that care is needed in deriving directional properties from nematic-phase work, particularly if such data are then related to the crystalline environment. Using $g_y < g_z$ they then had considerable difficulty in interpreting the g (and A) values by use of the treatment of Maki *et al.*,[22] which is now not surprising in view of the limitations of the treatment which we have stated.[13,15]

This work was supported by a grant from the Australian Research Grants Committee. We are grateful to Mr. A. van den Bergen for experimental assistance and to Drs. A. K. Gregson and J. E. Davies for help with computing.

[5/2200 *Received, 11th November,* 1975]

---

* *Note added at proof:* In a recent single-crystal e.s.r. study of [Co(bacen)] — [Ni(bacen)] (V. Malatesta and B. R. McGarvey, *Canad. J. Chem.*, 1975, **53**, 3791), g_y was found to be slightly less than g_z by analogy with the spectrum of [Cu(bacen)]; the crystal structure of none of these bacen chelates is known.

[22] A. H. Maki, N. Edelstein, A. Davidson, and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **84**, 4580.