Crystal Polarised Spectra, and Electronic Structures, of Some Pseudotetrahedral Cobalt(II) complexes with ' Soft ' Bonding Ligands

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The crystal polarised spectra of some pseudotetrahedral Co^{II} complexes having chromophores $[CoS_2Cl_2]$ and $[CoP_2X_2]$ ($X = Br^-, I^-$), have been recorded. The spectra may be assigned assuming an effective C_{2v} symmetry and spin–orbit coupling is found to be less important than the low-symmetry ligand field in modifying the electronic structure derived from T_d symmetry. The sequence of components derived from T_d symmetry is found to be: ${}^4T_1(F)$: $B_1 < A_2 < B_2$; ${}^4T_1(P)$: $B_2 < A_2 < B_1$. Crystal-field calculations fit the observed spectra only if parameters of the low symmetry components are treated as merely empirical parameters. Qualitative σ- and π-bonding parameters for the different donor ligands are derived and compared.

MUCH interest has been shown in the electronic structures of low-symmetry transition-metal complexes. The main aim is the assignment of electronic spectra followed by close correlation of these with ligand field or angular overlap calculations to establish the validity (or otherwise) of these bonding models.

For tetrahedral Co^{II} complexes the most detailed data is that on the $CoCl_4^{2-}$ ion [1] where it was found that the splitting of orbitally degenerate excited electronic states is dominated by low symmetry components (C_S) of the crystal field, rather than by spin–orbit coupling. There has been less success in assigning the spectra of pseudotetrahedral complexes. The splitting of the T-terms (derived from T_d symmetry) in $Co(py)_2Cl_2$ [2] could not be analysed closely because of unsuitable molecular alignment in the crystal unit cell. However, more recent work [3] on $Co(PPh_3)_2Cl_2$ led to a partial assignment with the A_2 terms in C_{2v} [derived from the ${}^4T_1(F)$ and ${}^4T_1(P)$ terms in T_d symmetry] being placed between the B terms derived from the same T_d terms. The precise ordering of the B terms was not determined, so correlations with crystal-field calculations were not possible.

Subsequently, the polarised spectra of $Co(etu)_2(OAc)_2$ (etu = imazolidine-2-thione) could not be interpreted assuming C_{2v} electric-dipole allowed electronic selection rules.[4] This was ascribed to significant interactions of further long-bonding oxygen atoms from the acetate groups.

In contrast to the above cases, preliminary crystal spectra data on some Co^{II} complexes of *ca.* C_{3v} symmetry [5] suggested that spin–orbit coupling is more important than low-symmetry components in modifying the T_d energy levels.

Substituted and unsubstituted thioureas also form pseudotetrahedral complexes, CoL_2X_2, with cobalt(II) halides.[6] The crystal structures of the *NN'*-diethylthiourea (dietu) complex and its zinc analogue have been determined,[7] and the latter is suitable for single-crystal spectra. This paper presents an analysis of this crystal spectra data, and the spectra of the $Co(PPh_3)_2X_2$ complexes (X = Br, I), together with a re-interpretation of the data on the chloride of this latter series. The intention is to compare splittings of the T_d energy levels between different chromophores. The results are compared with crystal-field calculations.

EXPERIMENTAL

$Co[(EtHN)_2CS]_2Cl_2$ $[Co(dietu)_2Cl_2]$ [6] and $Co(PPh_3)_2X_2$ (CoP_2X_2) [8] were prepared as in the literature. The cobalt compounds were diluted in the analogous zinc complexes by co-crystallisation. In all cases well-formed crystals were given on slow evaporation of butanol or ethanol solutions containing (nominal) concentrations of from 1—10% Co^{II}.

Crystal spectra, of three orthogonal faces, in the 12·5—35 kK range (1 kK = 1000 cm^{-1}) were obtained as described

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[1] J. Ferguson, *J. Chem. Phys.*, 1963, **39**, 116.

[2] J. Ferguson, *J. Chem. Phys.*, 1960, **32**, 528.

[3] C. Simo and S. L. Holt, *Inorg. Chem.*, 1968, **7**, 2655.

[4] S. L. Holt, E. Holt, and J. Watson, *J. Amer. Chem. Soc.*, 1970, **92**, 2721.

[5] B. B. Garrett, V. L. Goedken, and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1970, **92**, 489.

[6] O. Piovesana and C. Furlani, *J. Inorg. Nuclear Chem.*, 1969, **30**, 1249.

[7] M. Bonamico and G. Dessy, personal communication.

[8] F. A. Cotton, D. M. L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 469.

previously.[9] Spectra of relatively large crystals in the near-i.r. region were recorded on a Beckman DK 1A instrument, polarisation being achieved using two matched Glan–Thompson prisms. Crystallographic axes were identified using Weissenberg techniques.

RESULTS

Crystal Structures.—Both crystal structures and spectra are referred to the axes of Figure 1.

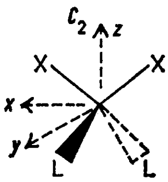

FIGURE 1 Axis notation for CoL_2X_2

$Zn(dietu)_2Cl_2$ crystallises from ethanol in space group $P2_1/c$, with $a = 10{\cdot}418$, $b = 14{\cdot}974$, $c = 24{\cdot}078$ Å, $\beta = 92°\ 16'$, and $Z = 8$. The (100) projection shows that there are two crystallographically independent molecules in the unit cell, but they are only very slightly misaligned (Figure 2). The *b*-axis corresponds to the molecular *y*-axis, and *c* is virtually aligned with the *x*-axis. Thus, spectra observed with the electric vector vibrating along *a*, *b*, and *c* should be (almost) purely *z*, *y*, and *x*, respectively.

Crystal structures of $M(PPh_3)_2X_2$ (X = Br or I; M = Co or Zn) are not known, although the analogous chloride is isomorphous with $Ni(PPh_3)_2Cl_2$.[10] Crystals of $(Zn,Co)(PPh_3)_2Br_2$ decompose quite rapidly in air and in the *X*-ray beam, and zero- and first-layer Weissenberg photographs were very poor in quality. Despite these difficulties, the bromide was found not to be isomorphous with the analogous nickel(II) complex.

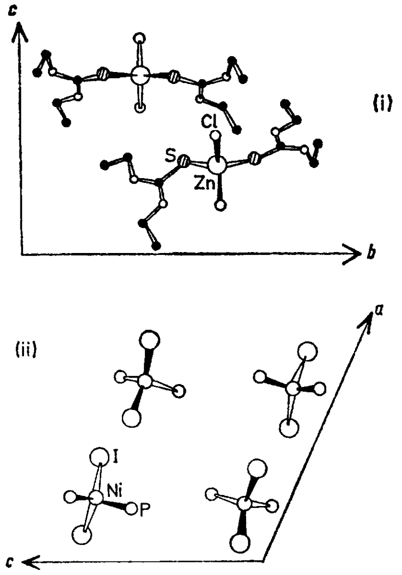

FIGURE 2 (i) (100) projection of $Zn(dietu)_2Cl_2$ (the two crystallographically independent Zn atoms only are shown). (ii) (010) projection of $Ni(PPh_3)_2I_2$ showing molecules approximately aligned along their molecular axes

Weissenberg photographs of $(Zn,Co)(PPh_3)_2I_2$ showed that the crystals are isomorphous with those of the analogous nickel(II) complex,[10] with: *a*, 19·6, $b = 10{\cdot}3$, $c = 18{\cdot}2$ Å, $\beta = 112°$, $Z = 4$, *P*2/*c* or *Pc*. Only a preliminary report of the crystal structure of $Ni(PPh_3)_2I_2$ has appeared,[10] but this is sufficient for the purposes of assignment of the spectra of the isomorphous Co^{II} complex. The molecular *x*-axes are roughly aligned along *a* (inclination to *a ca.* 9°) and the *y*-axes roughly along *c* (inclination *ca.* 10°), *z* being inclined by some 15—20° from the *ac* plane (Figure 2). Since the crystal structure of the bromide is not known, the interpretation of the spectrum has been extrapolated from that of the chloride and the iodide. This is unfortunate since the spectrum of the bromide is more clearly resolved than that of the other two halides.

Assignment.—Figures 3 and 4 show that band components are already well separated at room temperature provided alignment of molecules is suitable.

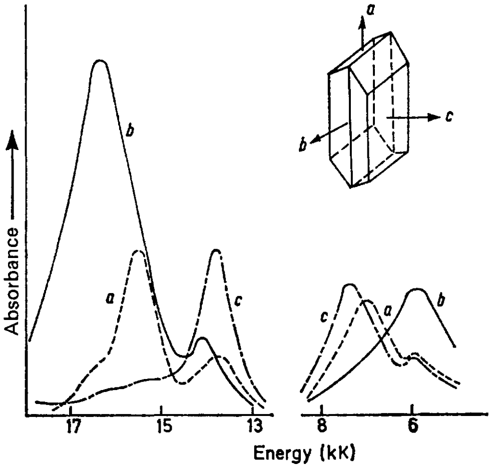

FIGURE 3 Crystal spectra of $(Zn,Co)(dietu)_2Cl_2$ along *a*, *b*, and *c*. Insets show crystal morphology and unit cell directions. The two halves of the spectra are not on the same intensity scale

It is sometimes necessary to cool to liquid helium temperature, in cases similar to the present ones, to separate spin–orbit components, vibrational structure, and further low-symmetry crystal-field components. The presence of the strongly asymmetric crystal field in the present complexes makes it unlikely that room-temperature spectra are misleading.

Crystal spectra of $(Zn,Co)(dietu)_2Cl_2$ are shown in Figure 3. The spectrum of this substituted thiourea shows three main absorptions in the near-i.r. and three in the visible region: 5·9 and 16·6 kK (*b*); 7·1 and 15·6 (*a*); 7·4 and 14·2 kK (*c*). There is residual intensity of each of the bands in the other directions due presumably both to small misalignment of the crystals and to the slightly differing crystallographic environments of the zinc atoms. The latter is also observed as slight differences in energy; for example, the residual of the 14·0 kK band in *E* parallel to *a* shows some splitting, giving low-intensity bands at 14·1 and 13·9 kK. Although the energy differences between the two bands at *ca.* 7 kK is small (300 cm^{-1}), it is reproducible.

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[9] A. A. G. Tomlinson, *J. Chem. Soc.* (*A*), 1971, 1409.

[10] G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625.

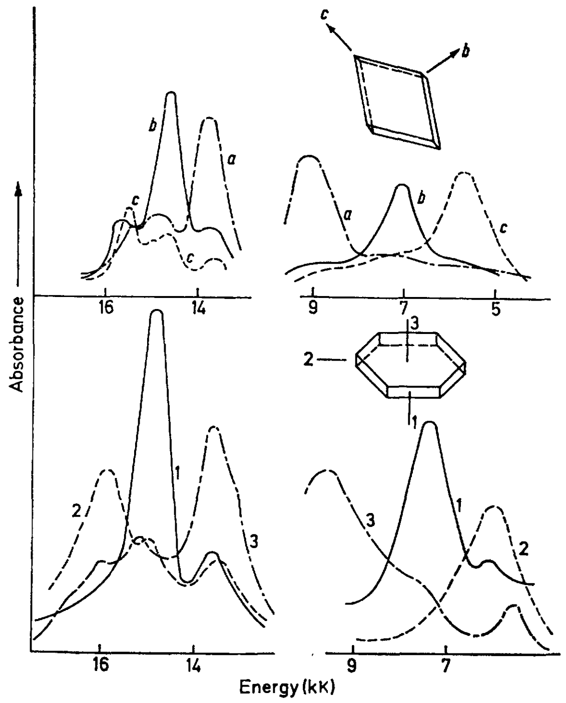

FIGURE 4 Crystal spectra of (i) (Zn,Co)(PPh$_3$)$_2$I$_2$ and (ii) (Zn,Co)(PPh$_3$)$_2$Br$_2$, the first recorded along *a*, *b*, and ~*c*, the second along the extinction directions. Intensity scales are different for the two halves of the spectra

Figure 4 shows the spectra of (Zn,Co)P$_2$Br$_2$ and (Zn,Co)-P$_2$I$_2$. These latter spectra were taken along the extinction directions of more than one face and show obvious similarities to those of the chloride,[3] those of the bromide being particularly indicative of near alignment of molecules in the unit cell. The bromide also shows a series of bands with an interval of *ca.* 900 cm^{-1} centred at *ca.* 16·0 kK (see Table). Gross colour changes (orange-brown $\vec{E}$ parallel to *b*, yellow-green $\vec{E}$ parallel to *c*) in the case of the iodide are due to strongly polarised charge-transfer bands in the visible and near-u.v. at 19·9, 23·9, and 26·7 kK, the first two of which are most intense when *E* is parallel to *b*.

An assignment of the *d–d* bands may be arrived at after reassignment of that of Co(PPh$_3$)$_2$Cl$_2$ [3] using the co-ordinates of Figure 1 and the molecular alignment already known for Ni(PPh$_3$)$_2$Cl$_2$.[10,11]

From the electronic selection rules for C_{2v} symmetry (assuming a $^4A_2$ ground state, and the co-ordinates of Figure 1):

$$^4A_2 \longrightarrow {}^4B_1(y);\ {}^4B_2(x);\ {}^4A_2(z),$$

this spectrum is assigned as:

$$\begin{array}{lll} ^4A_2 \longrightarrow & ^4B_2 & 10\cdot7 \text{ and } 13\cdot55 \text{ kK} \\ \longrightarrow & ^4A_2 & 8\cdot0 \text{ and } 15\cdot75 \text{ kK} \\ \longrightarrow & ^4B_1 & 6\cdot4 \text{ and } ca.\ 17 \text{ kK.} \end{array}$$

This gives the energy level ordering: $a^4T_1(F)$ in T_d: $^4B_1 < {}^4A_2 < {}^4B_2$; $b^4T_1(P)$ in T_d: $^4B_2 < {}^4A_2 < {}^4B^1$. Transitions to the components of $^4T_2(F)$ are not observed, as is usually the case. The very similar polarisation behaviour of the bromide and iodide suggest an analogous assignment.

Turning to chromophore [CoS$_2$Cl$_2$], inspection of Figure 3 shows that the spectrum may be assigned as:

$$\begin{array}{lll} ^4A_2 \longrightarrow & ^4B_1 & 5\cdot9 \text{ and } 16\cdot6 \text{ kK} \\ \longrightarrow & ^4A_2 & 7\cdot1 \text{ and } 15\cdot6 \text{ kK} \\ \longrightarrow & ^4B_2 & 7\cdot4 \text{ and } 14\cdot2 \text{ kK} \end{array}$$

This assignment gives the same energy level ordering as that of Co(PPh$_3$)$_2$Cl$_2$.

The above assignments appear to fit the experimental behaviour well, and residual intensities in all cases are not marked. Other, possible, assignments appear less likely for the following reasons. (i) The effective molecular symmetry cannot be higher (*e.g.* D_{2d}) than C_{2v} since there are clear differences in *x*, *y*, and *z* directions. A higher symmetry would give selection rules predicting degeneracy in two molecular directions. (ii) The possibility of a ground state different from $^4A_2$ [caused possibly by splitting of the $^4T_2(F)$ term in T_d symmetry such that one of the components becomes lower in energy than $^4A_2$] is discounted since this cannot reproduce the observed sequence. (iii) Spin–orbit selection rules would predict the existence of more components than are actually observed (see Table)

Electronic spectra and crystal-field parameters (kK)

	Co(dietu)$_2$Cl$_2$	Co(PPh$_3$)$_2$Cl$_2$ *	Co(PPh$_3$)$_2$Br$_2$	Co(PPh$_3$)$_2$I$_2$	Assignments
	5·6 *b* *y*	6·4 *a* *y*	6·0	5·80 *c* *y*	$^4B_1[^4T_1(^4F)] \longleftarrow {}^4A_2[^4T_1(^4F)]$
	7·1 *a* *z*	8·0 *b* *z*	7·6	7·10 *b* *z*	$A_2[^4T_1(^4F)] \longleftarrow$
	7·4 *c* *x*	10·7 *c* *x*	9·7	9·2 *a* *x*	$B_2[^4T_1(^4F)] \longleftarrow$
	14·0 *c* *x*	13·6 *c* *x*	13·5	12·8 *a* *x*	$B_1[^4T_1(P)] \longleftarrow {}^4A_2[^4T_1(F)]$
	15·4 *a* *z*	15·8 *b* *z*	14·9	13·8 *b* *z*	$A_2[^4T_1(P)] \longleftarrow$
	16·4 *b* *y*	16·7 *a* *y*	15·9	14·7 *c* *y*	$B_2[^4T_1(P)] \longleftarrow$
			15·25 16·0 16·7		Spin–orbit components?
	19·70 20·20		21·60 22·20 24·1		Spin–forbidden transitions
Ds	+0·64	+0·83	+0·64	+0·51	
Dt	−0·29	−0·67	−0·57$_5$	−0·52$_5$	
d_σ	+0·41	−0·02	−0·12	−0·22	
d_π	+1·68	+2·91	+2·40	+2·07	
B	0·69	0·67	0·63	0·58	

* Ref. 3.

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[11] R. J. Fereday, B. J. Hathaway, and R. J. Dudley, *J. Chem. Soc.* (*A*), 1970, 571.

DISCUSSION

The assignment is ' minimal ' in that it is confined to determining the gross effect of the C_{2v} ligand field on the energy levels. However, the spectra show several other points of interest. Apart from the fact that the components of b^4T_1 are more intense that those of a^4T_1, presumably due to successively greater ' borrowing ' of intensity from charge-transfer states, one transition occurs with greater intensity than the other two for the b^4T_1 components. In (Co,Zn)(dietu)$_2$Cl$_2$, as in (Co,Zn)P$_2$Cl$_2$, it is the highest energy band, at 16·6 kK, that is more intense. The broadness of this band in both spectra indicate that it probably contains both spin–orbit components and vibrational structure. By contrast, in (Zn,Co)P$_2$Br$_2$ and (Zn,Co)P$_2$I$_2$ the most intense band is the centre one, assigned as $^4A_2 \longleftarrow {}^4A_2$, and it is narrow suggesting that it contains little, if any, contribution from spin–orbit components and vibrational structure. Presumably this indicates that x, y, and z transition moments are not equal, and that mixing of odd character into the otherwise even d-electron wavefunctions has taken place anisotropically, as expected. It would be difficult to assign different vibronic ' powers ' to different vibrations.

Both (Zn,Co)(dietu)$_2$Cl$_2$ and (Zn,Co)P$_2$Br$_2$, in relatively high concentrations of cobalt ion, showed the presence of several spin-forbidden transitions in the region 20—25 kK. Since not all the doublet transitions are seen [in (Zn,Co)P$_2$I$_2$ none are observed due to the charge-transfer bands in the visible region] it is not possible to assign them with any certainty.[12]

Correlations of the spectra with crystal-field calculations must take account of the following results. (i) The energy sequence of the $^4B_1$ and $^4B_2$ components changes on going from a^4T_1 to b^4T_1. (ii) Splitting of a^4T_1 in the chromophore [CoS$_2$Cl] is smaller than that of b^4T_1, while in [CoP$_2$X$_2$] the opposite is true. (iii) The splitting of both $^4T_1(P)$ and (F) terms is greater for the [CoP$_2$X$_2$] chromophores than for the [CoS$_2$Cl$_2$] one, and the splitting of b^4T_1 becomes larger in the chromophore [CoP$_2$X$_2$] in the order: $\mathrm{I}^- < \mathrm{Br}^- < \mathrm{Cl}^-$.

A calculation based on a simple crystal-field model,[13] whether using point dipoles or point charges, is unable to reproduce all the above characteristics. Thus, if the spectrochemical strength of the ligands is represented by a scaling of the parameters $G_{2\mathrm{L}} = \langle r^2/R_\mathrm{L}{}^3\rangle$ and $G_{4\mathrm{L}} = \langle r^4/R_\mathrm{L}{}^5\rangle$,[13] the calculation gives the one-electron orbital sequence shown in Figure 5 (a). The one-electron orbital splitting produced predicts a large difference between $E(d_{xz})$ and $E(d_{yz})$, which are destabilised by ligands X and L, respectively. The many-electron scheme predicted by this calculation [Figure 5 (b)] gives an ordering of the terms in which the components of both a^4T_1 and b^4T_1 follow the same sequence, and a much smaller splitting for a $^4T_1$ than for b^4T_1. Thus orbital splitting, *i.e.* the number and type of components, can be correctly predicted, but sequence and energy intervals are more difficult to predict.[13]

The three B_1 components of the tetrahedral orbital triplets a, b^4T_1, and $^4T_2$ are linear combinations of the strong field products:

$$(z^2\,.\,xy\,.\,yz)^{-1},\ [xy\,.\,(x^2-y^2)\,.\,yz]^{-1},\ [z^2\,.\,(x^2-y^2)\,.\,xz]^{-1}$$

of which the first two (in the crystal-field point-charge model) are shifted to higher energy, and the third to lower energy, by the rhombic component of the crystal field. By contrast, of the three parent products of the B_2 terms:

$$[z^2\,.\,(x^2-y^2)\,.\,yz]^{-1},\ (z^2\,.\,xy\,.\,yz)^{-1},\ [xy\,.\,(x^2-y^2)\,.\,xz]^{-1},$$

the first is shifted to higher energy, and the other two to lower energy, by the C_{2v} field in the same model.

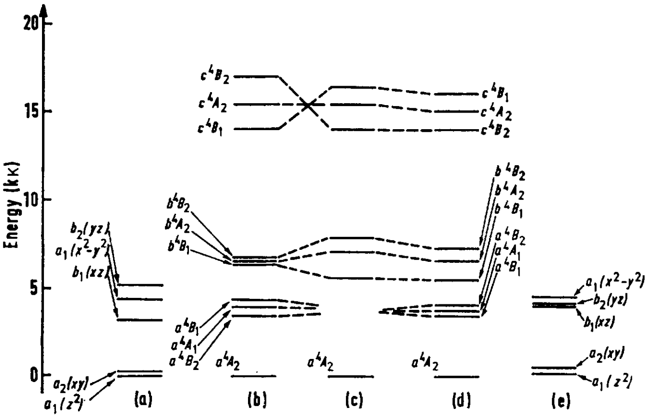

FIGURE 5 One-election orbitals and system of quartet energy levels for chromophore [CoS$_2$Cl$_2$]: (a) and (b) calculated with point charge electrostatic model; $G_{4\mathrm{Cl}} = 4{\cdot}2$; $G_{4\mathrm{S}} = 6{\cdot}20$; $G_{2\mathrm{L}} = 2G_{4\mathrm{L}}$, corresponding to $Dq = 0{\cdot}38$; $Dt = -0{\cdot}29$; $Ds = -1{\cdot}14$: (d) and (e) calculated with empirical values of tetragonality parameters; $Dq = -0{\cdot}36$; $Dt = +0{\cdot}64$, corresponding to $G_{4\mathrm{Cl}} = 3{\cdot}40$; $G_{4\mathrm{S}} = 6{\cdot}40$; $G_{2\mathrm{Cl}} - G_{2\mathrm{S}} = +2{\cdot}24$; and (c) experimental for (Zn,Co)(dietu)$_2$Cl$_2$ in crystal. All parameters expressed in kK. $B = 0{\cdot}69$ kK, axes as in Figure 1

The poor quantitative agreement may then be due to inability of the point charge model to predict the correct eigenvectors of the excited states, rather than to incorrect prediction of energies.

The experimental results may be rationalised better if the parameters of the low-symmetry components are treated as purely empirical parameters. Thus, the splittings are given by:

$$b^4T_1\colon\ E(^4B_1) - E(^4B_2) = +\frac{14}{5}Ds$$

$$a^4T_1\colon\ E(^4B_1) - E(^4B_2) = +\frac{20}{3}Dt + \frac{1}{5}Ds$$

that of b^4T_1 depending only on Ds, while that of a^4T_1 depends mainly on Dt. Choosing Ds and Dt parameters of opposite sign gives the one-electron orbital sequence, and term system, of figures 5(c) and (d), respectively, which agree with experiments. A close fit was obtained for (Zn,Co)(dietu)$_2$Cl$_2$ with $B = 0{\cdot}69$, Dq(av.) $= -0{\cdot}36$,

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[12] A. D. Liehr, *J. Phys. Chem.*, 1963, **67**, 1314.

[13] A. Flamini, L. Sestili, and C. Furlani, *Inorg. Chim. Acta*, **1971**, **5**, 241.

$Ds = +0{\cdot}64$, and $Dt = -0{\cdot}29$ kK for *a*, b^4T_1, values implying very large low-symmetry effects.

The parameters obtained are ' unconventional ' and probably not transferable to octahedral chromophores since, on passing from halide to S- or P-containing ligand, $\langle r^4/R_L{}^5\rangle$ increases, while $\langle r^2/R_L{}^3\rangle$ decreases substantially, which is not easy to explain.

In terms of a semi-empirical M.O. description,[14] the $d\sigma$ and $d\pi$ bonding parameters for (Zn,Co)(dietu)$_2$Cl$_2$ are given by: $d_\sigma = \frac{4}{3}\,(e_{\sigma\mathrm{Cl}} - e_{\sigma\mathrm{S}}) = +0{\cdot}41$ and $d\pi = (e_{\pi\mathrm{Cl}} - e_{\pi\mathrm{S}}) = +1{\cdot}68$ kK. This suggests that chlorine and sulphur ligands do not greatly differ in σ-antibonding ability (Cl appears to be only slightly more σ-antibonding than S) while Cl appears much more π-antibonding than S (*i.e.* S appears a much stronger π-acceptor than Cl). These parameters appear reasonable and in line with intuition, although the fact that the values found cannot be transferred to octahedral chromophores makes them less secure quantitatively. Keeping in mind these limitations, the other data of the Table also appear reasonable. For example, comparison between [CoS$_2$Cl$_2$] and [CoP$_2$Cl$_2$] chromophores shows P to be slightly more σ-antibonding, but much more π-bonding (or π-accepting), than S. In the series [CoP$_2$X$_2$], σ-antibonding ability decreases in the order: $\mathrm{Cl}^- > \mathrm{Br}^- > \mathrm{I}^-$ (I^- being a weaker σ-donor than is P while Cl^- is equally strong) as expected. $d\pi$ decreases in the same order, *i.e.* I^- is a weaker π-donor (or better π-acceptor) than Cl^-, although still a far weaker π-acceptor than P, as expected.

CONCLUSIONS

Although quantitative parameter values deduced from the bonding models used are only rough approximations, the data show the inadequacy of a ' one-dimensional ' spectrochemical series. It is particularly inadequate when ligands of very different π-bonding and π-antibonding character are present together. We conclude that ligand π-character plays an important role in the electronic structures of pseudotetrahedral Co$^{\mathrm{II}}$ complexes. It is also possible that lack of spectrochemical transferability between approximate T_d and O_h is due to ' co-operative electronic ' effects between different ligands in the same complex.

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APPENDIX

The weak-field matrices of d^3, d^7 in pseudotetrahedral MA$_2$B$_2$ (C_{2v})

$$\begin{array}{lllll}
 & {}^4T_1,{}^4P & 15B + \frac{7}{5}Ds & & \\
{}^4B_1: & {}^4T_1,{}^4F & 4Dq + \frac{5}{9}Dt - \frac{4}{5}Ds & -6Dq + \frac{10}{3}Dt + \frac{1}{10}Ds & \\
 & {}^4T_2,{}^4F & \frac{3}{5}Dt + \frac{16}{15}Ds & \frac{4}{3}\cdot\frac{5}{3}Dt - \frac{1}{60}Ds & 2Dq - \frac{10}{9}Dt - \frac{1}{2}Ds
\end{array}$$

$$\begin{array}{lllll}
15B - \frac{7}{5}Ds & 4Dq - \frac{5}{9}Dt + \frac{4}{5}Ds & -\frac{5}{3}Dt - \frac{16}{15}Ds & {}^4T_1,{}^4P & \\
 & -6Dq - \frac{10}{3}Dt - \frac{1}{10}Ds & -\frac{4}{3}\cdot\frac{5}{3}Dt + \frac{1}{60}Ds & {}^4T_1,{}^4F & :{}^4B_2 \\
 & & 2Dq + \frac{10}{9}Dt + \frac{1}{2}Ds & {}^4T_2,{}^4F &
\end{array}$$

$$\begin{array}{lllll}
 & {}^4T_1,{}^4P & 15B & & \\
{}^4A_2: & {}^4T_1,{}^4F & 4Dq & -6Dq & \\
 & {}^4A_2,{}^4F & -\frac{4}{3}\cdot\frac{5}{3}Dt + \frac{16}{15}Ds & \frac{2}{3}\cdot\frac{5}{3}Dt - \frac{4}{15}Ds & 12\,Dq
\end{array}$$

$${}^4A_1({}^4T_2,{}^4F) = 2Dq$$

$$Dq = -\frac{1}{27}(G_{4\mathrm{S,P}} + G_{4\mathrm{X}}).\quad Dt = \frac{2}{21}(G_{4\mathrm{X}} - G_{4\mathrm{S,P}}).\quad Ds = \frac{2}{7}(G_{2\mathrm{X}} - G_{2\mathrm{S,P}}).$$

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[14] D. McClure in ' Advances in the Chemistry of the Co-ordination Compounds,' ed. S. Kirschner, Macmillan, New York, 1961, p. 498; A. B. P. Lever, *Co-ordination Chem. Rev.*, 1968, **3**, 119.