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Role of the Orbital Splitting in Electronic Spectra of Pseudotetrahedral Co^{II} Complexes

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Orbital splitting patterns for pseudotetrahedral ($Co^{II}A_2B_2$) and ($Co^{II}A_3B$) complexes, calculated by a weak-field model on quartet basis quantized along the C_2, respectively C_3 axes so as to allow correlation between the parent T_d, the mono- and the bisubstituted chromophores, are often in disagreement with the number and position of band components experimentally observed in the spectra of such complexes. Even when the major components evident in the ligand-field spectrum are in the same number as the predicted orbital sublevels, they do not always follow the expected orbital selection rules, and a rough parallelism holds between calculated and observed overall splittings within each tetrahedral T_1 band. A possible way to the rationalization of the observed patterns of band components and of their polarization behaviour is outlined in terms of different kinds of geometrie distortions, vibronic couplings and a more appropriate treatment of spin-orbit coupling effects, including those in the ligand atoms.

Introduction

The complex splitting patterns of the ligand field bands $^4A_2 \rightarrow a, b\ ^4T_1$ (T_d) in the spectra of tetrahedral and pseudotetrahedral Co^{II} complexes can be due to at least five different effects, namely (i) orbital splitting due to low (C_{3v} or C_{2v}) symmetry of the ligand field, which however can account only for a maximum of three components from each tetrahedral T term; (ii) spin-orbit coupling; (iii) vibronic couplings; (iv) Jahn-Teller distortions of the excited states (mainly from tetrahedral $e^3t_2^4+e^2t_2^5$ strong-field configurations; (v) mixing of ^2G states with the ^4P quartets. None of these factors alone can account satisfactorily for the experimental number and type of band components, and in fact there is until now no generally valid assignment scheme for such complexes. Each of the above mentioned factors has received more or less isolately attention in the literature; so *e.g.* Ferguson's[1] experimental work has presented evidence for vibronic couplings besides spin-orbit coupling in the spectra of $[CoX_4]^{2-}$, and the same author has discussed the possible assignment of the components of the tetrahedral bands of $[CoX_4]^{2-}$ to spin-orbit components, while being aware of the role of the Jahn-Teller distortions of the excited levels; the same problem was discussed by Weakliem.[2] Orbital splittings in pseudotetrahedral Co^{II} complexes of lower symmetry were reported and discussed by Carlin and Holt,[3] Ferguson,[4] Lever and Nelson,[5] and Cotton *et al.*[6] Simo and Holt[7] reported the most convincing example of assignement of the b$^4T_1$ level, split into three components, to pure orbital components in the spectrum of $CoCl_2(PPh_3)_2$, (which indeed are completely polarized along x or y or z, while other Co^{II} complexes of similar structures show less well defined polarization effects, *e.g.*[8] Recently Quagliano *et al.*[9] attempted an assignment of the components of the T bands of trigonal $[Co^{II}A_3B]$ complexes on the ground of crystal field calculations of the lower symmetry effects on the orbital energy levels, authough in all their spectra the number of experimental band components is, as is often the case, larger than that of predicted orbital sublevels.

Thus, literature reports present until now rather conflicting conclusions as to the possibility of assigning observed band components in terms of orbital splittings alone: while ref.[4,5,7-9] claim a satisfactory correlation of observed transitions to orbital sublevels, many other papers maintain more or less explicitly the contrary. The problem of the adequacy of orbital splitting alone to account for assignment of experimental spectra is therefore to be regarded as still open, and it deserves further investigation, at least for practical reasons, until more powerful and complete M.O. treatments will become easily applicable.

The present paper gives a unitary formulation of the ligand-field treatment of orbital splitting in pseudotetrahedral Co^{II} complexes of types $[CoA_2B_2]$ (C_{2v} symmetry) and $[CoA_3B]$ (C_{3v} symmetry), so as to facilitate comparison between both types of substituted Co^{II} chromophores, in a more general and systematic way than presented until now in single papers in the literature. Possible refinements with inclusion of spin-orbit effects will be also discussed, although they give little or no improvement over the orbital calculations,

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Table I. Definitions of radial integrals and of parameters of low-symmetry of pseudotetrahedral ligand fields

$$R_2 \equiv R_2(r) = \int_0^\infty [R_{3d}(r)]^2 \frac{r_<^2}{r_>^3} r^2 dr \qquad R_4 \equiv R_4(r) = \int_0^\infty [R_{3d}(r)]^2 \frac{r_<^4}{r_>^5} r^2 dr$$

$$Dt = \frac{3}{7}\sum_{i=1}^{2}\left\{-\frac{2}{7}\left(\frac{3}{2}\cos^2\vartheta_i - \frac{1}{2}\right)R_2 + \left[\frac{1}{21}\left(\frac{35}{8}\cos^4\vartheta_i - \frac{15}{4}\cos^2\vartheta_i + \frac{121}{24}\right) - \frac{5}{24}\sin^4\vartheta_i\, e^{-4i\varphi_i}\right]R_4\right\} + \frac{3}{7}\sum_{i'=1}^{2}\left\{-\frac{2}{7}\left(\frac{3}{2}\cos^2\vartheta_{i'} - \frac{1}{2}\right)R'_2 + \right.$$
$$\left. + \left[\frac{1}{21}\left(\frac{35}{8}\cos^4\vartheta_{i'} - \frac{15}{4}\cos^2\vartheta_{i'} + \frac{3}{8}\right) - \frac{5}{24}\sin^4\vartheta_{i'}\, e^{-4i\varphi_{i'}}\right]R'_2\right\}$$

$$Ds = \frac{1}{7}\sum_{i=1}^{2}\left\{\left[\frac{11}{7}\left(\frac{3}{2}\cos^2\vartheta_i - \frac{1}{2}\right) - \frac{3}{2}e^{-2i\varphi_i}\sin^2\vartheta_i\right]R_2 + \left[-\frac{10}{7}\left(\frac{35}{8}\cos^4\vartheta_i - \frac{15}{4}\cos^2\vartheta_i + \frac{305}{216}\right) - \frac{5}{6}e^{-2i\varphi_i}\sin^2\vartheta_i\left(7\cos^2\vartheta_i - \frac{1}{2}\sin^2\vartheta_i\, e^{2i\varphi_i}1\right)\right]R_4\right\}$$
$$+ \frac{1}{7}\sum_{i'=1}^{2}\left\{\left[\frac{11}{7}\left(\frac{3}{2}\cos^2\vartheta_{i'} - \frac{1}{2}\right) - \frac{3}{2}e^{-2i\varphi_{i'}}\sin^2\vartheta_{i'}\right]R'_2 + \left[-\frac{10}{7}\left(\frac{35}{8}\cos^4\vartheta_{i'} - \frac{15}{4}\cos^2\vartheta_{i'} + \frac{3}{8}\right) - \frac{5}{6}\sin^2\vartheta_{i'}\, e^{-2i\varphi_{i'}}\left(7\cos^2\vartheta_{i'} - \frac{1}{2}\sin^2\vartheta_{i'}\, e^{-2i\varphi_{i'}}1\right)\right]R'_4\right\}$$

$$D\tau = -\frac{3}{7}\sum_{i=1}^{3}\left\{\left[\frac{1}{9}\left(\frac{35}{8}\cos^4\vartheta_i - \frac{15}{4}\cos^2\vartheta_i - \frac{23}{24}\right) + \frac{5\sqrt{2}}{18}\cos\vartheta_i\sin^3\vartheta_i\, e^{+3i\varphi_i}\right]R_4\right\} + \left[-\frac{1}{21}\left(\frac{35}{8}\cos^4\vartheta_{i'} - \frac{15}{4}\cos^2\vartheta_{i'} + \frac{3}{8}\right) + \frac{5\sqrt{2}}{42}\cos\vartheta_{i'}\sin^3\vartheta_{i'}\, e^{i3\varphi_{i'}}\right]R'_4$$

$$D\sigma = -\frac{1}{2}\left\{\sum_{i=1}^{3}\left[\frac{2}{7}\left(\frac{3}{2}\cos^2\vartheta_i - \frac{1}{2}\right)R_2 + \left(-\frac{5\sqrt{2}}{7}\cos\vartheta_i\sin^3\vartheta_i\, e^{i3\varphi_i} - \frac{160}{567}\right)R_4\right] + \frac{2}{7}\left(\frac{3}{2}\cos^2\vartheta_{i'} - \frac{1}{2}\right)R'_2 + \frac{5\sqrt{2}}{7}\cos\vartheta_{i'}\sin^3\vartheta_{i'}\, e^{3i\varphi_{i'}}R'_4\right\}$$

For tetrahedral angles

$$Dt = \frac{2}{21}(R_4 - R'_4) \qquad D\tau = \frac{1}{21}(R_4 - R'_4)$$

$$Ds = \frac{2}{7}(R_2 - R'_2) \qquad D\sigma = \frac{1}{7}(R_2 - R'_2)$$

Table II. Linear combinations of ${}^4L\psi(3/2,L,3/2,M_L)$ three-positron functions of the d^7 configuration spanning irr. representations of the C_{2v} and C_{3v} point groups.

	C_{2v}	Γ	C_{3v}	Γ
${}^4P$	$\sqrt{\frac{1}{2}}\left[-\sqrt{\frac{3}{5}}(21\text{-}2) + \sqrt{\frac{2}{5}}(20\text{-}1) - \sqrt{\frac{2}{5}}(10\text{-}2) + \sqrt{\frac{3}{5}}(2\text{-}1\text{-}2)\right]$	B_1	$\sqrt{\frac{1}{2}}\left[-\sqrt{\frac{3}{5}}(21\text{-}2) + \sqrt{\frac{2}{5}}(20\text{-}1) - \sqrt{\frac{2}{5}}(10\text{-}2) + \sqrt{\frac{3}{5}}(2\text{-}1\text{-}2)\right]$	E
	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[-\sqrt{\frac{3}{5}}(21\text{-}2) - \sqrt{\frac{2}{5}}(20\text{-}1) + \sqrt{\frac{2}{5}}(10\text{-}2) - \sqrt{\frac{3}{5}}(2\text{-}1\text{-}2)\right]$	B_2	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[-\sqrt{\frac{3}{5}}(21\text{-}2) + \sqrt{\frac{2}{5}}(20\text{-}1) + \sqrt{\frac{2}{5}}(10\text{-}2) - \sqrt{\frac{3}{5}}(2\text{-}1\text{-}2)\right]$	
	$\sqrt{\frac{1}{5}}(20\text{-}2) - \sqrt{\frac{4}{5}}(10\text{-}1)$	A_1	$\sqrt{\frac{1}{5}}(20\text{-}2) - \sqrt{\frac{4}{5}}(10\text{-}1)$	A_1
${}^4F$	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[\sqrt{\frac{3}{5}}(20\text{-}1) + \sqrt{\frac{2}{5}}(21\text{-}2) - \sqrt{\frac{2}{5}}(2\text{-}1\text{-}2) - \sqrt{\frac{3}{5}}(10\text{-}2)\right]$	B_1	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[\sqrt{\frac{3}{5}}(20\text{-}1) + \sqrt{\frac{2}{5}}(21\text{-}2) - \sqrt{\frac{2}{5}}(2\text{-}1\text{-}2) - \sqrt{\frac{3}{5}}(10\text{-}2)\right]$	E
	$\sqrt{\frac{1}{2}}\left[\sqrt{\frac{3}{5}}(20\text{-}1) + \sqrt{\frac{2}{5}}(21\text{-}2) + \sqrt{\frac{2}{5}}(2\text{-}1\text{-}2) + \sqrt{\frac{3}{5}}(10\text{-}2)\right]$	B_2	$\sqrt{\frac{1}{2}}\left[\sqrt{\frac{3}{5}}(20\text{-}1) + \sqrt{\frac{2}{5}}(21\text{-}2) + \sqrt{\frac{2}{5}}(2\text{-}1\text{-}2) + \sqrt{\frac{3}{5}}(10\text{-}2)\right]$	
	$\sqrt{\frac{4}{5}}(20\text{-}2) + \sqrt{\frac{1}{5}}(10\text{-}1)$	A_1	$\sqrt{\frac{4}{5}}(20\text{-}2) + \sqrt{\frac{1}{5}}(10\text{-}1)$	A_1
	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[(210) + (0\text{-}1\text{-}2)\right]$	B_2	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[(210) + (0\text{-}1\text{-}2)\right]$	B_2
	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[(210) - (0\text{-}1\text{-}2)\right]$	B_1	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[(210) - (0\text{-}1\text{-}2)\right]$	A_1
	$\sqrt{\frac{1}{2}}\left[(21\text{-}1) + (1\text{-}1\text{-}2)\right]$	A_1	$\sqrt{\frac{1}{2}}\left[(21\text{-}1) + (1\text{-}1\text{-}2)\right]$	E
	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[(21\text{-}1) - (1\text{-}1\text{-}2)\right]$	A_2	$\frac{1}{i}\sqrt{\frac{1}{2}}\left[(21\text{-}1) - (1\text{-}1\text{-}2)\right]$	

Table III. Weak-field matrices of the d^7 quartets in low symmetries (C_{2v} and C_{3v})

$-\frac{14}{3}Dq+7D\tau$	$-\sqrt{5}\ \frac{4}{3}Dq$	$\sqrt{30}\ \frac{2}{3}Dq$	$a^4E(^4F)$
	$\frac{2}{3}Dq-D\tau+\frac{3}{5}D\sigma$	$\sqrt{6}(\frac{2}{3}Dq-6D\tau-\frac{4}{5}D\sigma)$	$b^4E(^4F)$
		$15B+\frac{7}{5}D\sigma$	$^4E(T_1,P)$

$a^4A_2(^4F)$	$2Dq-3D\tau-D\sigma$		
$b^4A_2(^4F)$	$4\sqrt{5}\ Dq$	$4Dq-6D\tau+\frac{4}{5}D\sigma$	
$^4A_2(T_1,P)$	$-\sqrt{5}\ \frac{4}{3}Dq$	$\frac{8}{3}Dq-4D\tau+\frac{12}{5}D\sigma$	$15B-\frac{14}{5}D\sigma$

$$\langle ^4A_1|V|^4A_1\rangle = 2Dq-3D\tau-D\sigma$$

$-3Dq+\frac{7}{6}Dt$	$\sqrt{\frac{3}{5}}(5Dq-\frac{95}{18}Dt-\frac{1}{3}Ds)$	$\sqrt{\frac{2}{5}}(5Dq-\frac{5}{2}Dt-2Ds)$	$a^4B_2(^4F)$
	$-Dq-\frac{11}{6}Dt+\frac{2}{5}Ds$	$\sqrt{6}(-Dq-\frac{1}{6}Dt-\frac{2}{15}Ds)$	$b^4B_2(^4F)$
		$15B+\frac{7}{5}Ds$	$^4B_2(T_1,P)$

$^4B_1(T_1,P)$	$15B-\frac{7}{5}Ds$		
$a^4B_1(^4F)$	$\sqrt{6}(-Dq+\frac{17}{18}Dt+\frac{2}{15}Ds)$	$-Dq+\frac{47}{18}Dt-\frac{2}{5}Ds$	
$b^4B_1(^4F)$	$\sqrt{\frac{2}{5}}(-5Dq+\frac{25}{18}Dt+2Ds)$	$\sqrt{\frac{3}{5}}(-5Dq-\frac{25}{18}Dt-\frac{1}{3}Ds)$	$-3Dq+\frac{7}{6}Dt$

$b^4A_1(^4F)$	$-6Dq+\frac{7}{3}Dt$		
$a^4A_1(^4F)$	$\sqrt{\frac{12}{5}}(\frac{5}{9}Dt-\frac{1}{3}Ds)$	$12Dq-\frac{14}{3}Dt$	
$b^4A_1(T_1,P)$	$-4Dq+\frac{14}{9}Dt$	$\sqrt{\frac{3}{5}}(-\frac{20}{9}Dt+\frac{4}{3}Ds)$	$15B$

$$\langle ^4A_2|V|^4A_2\rangle = 2Dq-\frac{7}{9}Dt$$

at least for lower-symmetrical complexes. Comparisons are made with selected experimental data, including some of the most recent spectroscopic results.

In the following, basis functions and matrix elements are given for orbital calculations on [$Co^{II}A_2B_2$] (C_{2v}) and [$Co^{II}A_3B$] (C_{3v}) complexes to be carried out in the weak field scheme on the quartet three-positron ψ (3/2 L 3/2 M_L) functions of ^{4}F and ^{4}P quantized along the C_2 axis of C_{2v}, respectively C_3 of C_{3v}.

Departures from the true tetrahedral symmetry of [CoA_4] species regarded as the parent undistorted chromophores are described unitarily by defining the weak field parameters Ds, Dt (C_{2v}) and D_σ, D_τ (C_{3v}) in terms of the common radial parameters R_2(L) and R_4(L) (Table I).

The tetragonal weak field parameters Ds and Dt can completely describe also a rhombic field of C_{2v} symmetry. Table II gives the assignment of the basis functions to the irreducible representations of both groups, and Table III the matrices of the ligand field potentials in both groups with the basis of Table II. The definitions and matrices collected in Table I, II, and III allow numerical calculations for any kind of pseudotetrahedral Co^{II} chromophore of effective symmetry C_{3v} or C_{2v}, also if bond angles are distorted from tetrahedral values. The unitary definition of the low-symmetry D parameters allows comparison between magnitudes of splitting in both symmetries; thus, the threefold spliting of tetrahedral T terms in CoA_2B_2 complexes of C_{2v} symmetry is nearly symmetrical (first order spacing 7/5 D_s = 2/5 (R_2–R_2') for b^T1 (^{4}P), and unsymmetrical (total splitting 1/9 (R_4+R'_4)) for a^4T_1 (^{4}F) in C_{2v} complexes, while in C_{3v} complexes the splitting is 2/5 D_σ = 3/5 (R_2–R_2') for b^4T_1 (^{4}P) hence larger than the single interval in C_{2v}, and the orbital E terms lie, as a rule, higher than the A terms. The overall splitting of b^4T_1 is expected in C_{2v} to be larger by some 40% than in C_{3v} complexes, with the same ligands A and B. Our matrices are different from those given by Quagliano *et al.* for a different basis,[9] but yield coincident numerical results, after allowing for a few misprints in the matrices of ref.[9]

As an example, we report the results of one such calculation intended for comparison with the experimental behaviour of mixed cobalt(II)-halide-phosphine complexes, whose spectra have been recently investigated in more detail[10] than in earlier studies.[11] For want of structural data on all complexes, we assumed tetrahedral angles; numerical results obtained with the parameter values listed in Table IV, are reported in Figure 1 and compared with the experimental data for complexes in the systems Co^{II}–X^-–PPh_3 given in Table V and Figures 1, 2, and 3.

In these systems the number of experimental band components of $\rightarrow b^4T_1$ is three, as expected from orbital calculations for $CoX_2(PR_3)_2$ species (although with largely asymmetric spacing), while it is larger than expected (four instead of two) for [$CoX_3(PR_3)$]$^-$ spe-

(10) L. Sestili and C. Furlani, to be published.

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Table IV. Adopted sets of parameters values.

Set	R_4	R_2	R_4'	R_2'	D_q	D_t	D_s	D_τ	D_σ
A	-5.00	-8.00	-6.50	-10.40	-0.37	0.14_3	0.68_6	0.07	0.34
B	-4.20	-8.40	-5.88	-11.76	-0.31	0.16	0.96	0.08	0.48
C	-4.20	-8.40	-5.46	-10.92	-0.31	0.12	0.72	0.06	0.36

B = 0.70

Table V. Selected values of ligand-field band components of pseudotetrahedral Co^{II} complexes; absorptions in kK and (log ε); shoulders in parenthesis.

Formula	Medium	$^4A_2 \rightarrow a^4T_1(T_d)$			$^4A_2 \rightarrow b^4T_1(^4P)(T_d)$			Ref.
$Co(EPTCH)_2Cl_2$ [a]	CH_2Cl_2	5.55(2.18)	(6.66)(1.98)	7.85(1.88)	13.70(2.67)	15.27(2.78)	16.53(2.78)	10
$Co(EPTCH)_2Br_2$ [a]	CH_2Cl_2	5.35(2.08)	(6.37)(1.93)	7.54(1.85)	13.60(2.75)	14.59(2.75)	15.87(2.73)	10
$Co(EPTCH)_2I_2$ [a]	CH_2Cl_2	5.17(2.07)	6.09(2.04)	7.40(2.08)	12.93(2.99)	13.85(2.90)	14.97(2.83)	11
$Co(tu)_2Cl_2$ [b]	$(CH_3)_2CO$	5.55(2.04)	6.17(1.93)	7.60(1.81)	14.40(2.63)	15.50(2.69)	16.70(2.64)	11
$Co(tu)_2Br_2$ [b]	$(CH_3)_2CO$	5.45(2.03)	6.15(1.96)	7.57(1.88)	14.00(2.72)	15.00(2.71)	16.20(2.64)	10
$Co(tu)_2I_2$ [b]	$(CH_3)_2CO$	5.30(1.96)	6.25(2.00)	7.31(2.01)	13.30(2.86)	14.20(2.87)	15.30(268)	11
$Co[(C_6H_5)_3AsO]_2Cl_2$	CH_2Cl_2	5.24(1.78)	5.78(1.81)	6.56(1.83)	14.81(2.73)	(15.50)	(16.60)	12
$Co[(C_6H_5)_3As]_2I_2$	$CHCl_3$	(5.32)	5.83(1.67)	7.14(1.84)	14.18(2.52)	15.20(2.63)	(16.30)	12
$Co(C_7H_6N_2)_2Cl_2$	$(CH_3)_2CO$	6.17(1.84)	6.99(1.86)	9.26(1.71)	15.82(2.79)	16.26(2.80)	17.24(2.60)	13
$Co(C_7H_6N_2)_2Br_2$	$(CH_3)_2CO$	(6.06)	6.83(1.92)	8.95(1.83)	15.38(2.87)	15.87(2.85)	16.86(2.65)	13
$Co(C_7H_6N_2)_2I_2$	$(CH_3)_2CO$	(5.85)	6.67(1.74)	8.58(1.72)	14.51(2.86)	15.24(2.92)	16.26(2.77)	13
$CoCl_2L_2$ [c]	CH_3CN				14.90(2.62)	16.53(2.45)	17.86(2.43)	14
$[CoCl_3L]^-$ [c]	CH_3CN				14.88(2.74)	(15.38)(2.65)	17.25(2.66)	14
$CoBr_2L_2$ [c]	CH_3CN				14.77(2.78)	16.35(2.48)	17.12(2.30)	14
$[CoBr_3L]^-$ [c]	CH_3CN				14.61(2.86)	15.97(2.65)	16.40(2.69)	14
$Co(tu)_4(ClO_4)_2$ [b]	$(CH_3)_2CO$			7.22(2.23)	13.89(2.80)	14.58(2.84)	(15.60)	15
$Co[(C_6H_5)_3P]_2Cl_2$	CH_2Cl_2	6.33	7.84	10.50	13.78(2.62)	16.00(2.83)	16.76(2.82)	16
$Co[(C_6H_5)_3P]_2Br_2$	CH_2Cl_2	6.13	7.55	10.00	13.44(2.67)	15.25(2.87)	15.75(2.80)	16
$Co[(C_6H_5)_3P]_2I_2$	CH_2Cl_2	5.70	7.00	8.90	12.88(2.88)	14.00(3.07)	14.72(2.92)	16
$Co(L_N^+)Br_3$ [e]	Polarized crystal spectra		7.27		14.62; 14.81; 15.38; 15.70; 16.10			8
$[(C_6H_5)_3P]_2Zn(Co)Cl_2$	Polarized crystal spectra	6.40	8.00	10.70	13.55; 15.75; 16.555; 16.778; 16.863; 17.065; 17.153; 17.405; 17.645; 18.315.			6
$Co(etu)_2(OAc)_2$	Polarized crystal spectra				14.15; 14.40; (14.55); (14.85); 17.10; (17.5); 18.7; 18.75.			7
$[CoCl_4]^{2-}$	CH_2Cl_2				14.55(2.84)	15.14(2.77)	15.94(2.62) 16.35(2.33)	16
$[CoBr_4]^{2-}$	CH_2Cl_2				14.04(3.01)	14.54(2.95)	15.31(2.76) 15.82(2.42)	16
$[CoI_4]^{2-}$	CH_2Cl_2				12.90(3.14)	13.24(3.04)	13.80(2.87) 14.40(2.73)	16
$[CoCl_3P(C_6H_5)_3]^-$	CH_2Cl_2				14.56(2.76)	15.20(2.71)	15.68(2.48) 16.86(2.82)	16
$[CoBr_3P(C_6H_5)_3]^-$	CH_2Cl_2				14.08(2.86)	14.68(2.77)	15.08(2.69) 15.94(2.83)	16
$[CoI_3P(C_6H_5)_3]^-$	CH_2Cl_2				12.93(3.08)	13.38(2.98)	14.17(2.83) 14.48(2.81)	16

[a] EPTCH = $C_6H_5NH(CS)OC_2H_5$; [b] tu = thiourea; [c] L = CH_3CN; [d] Absorptions of the band $^4A_2 \rightarrow a^4T_1(T_d)$ from ref. 12; [e] L_{N^+} = N—ethyl—1.4—diazobicyclo[2.2.2]octonium cation.

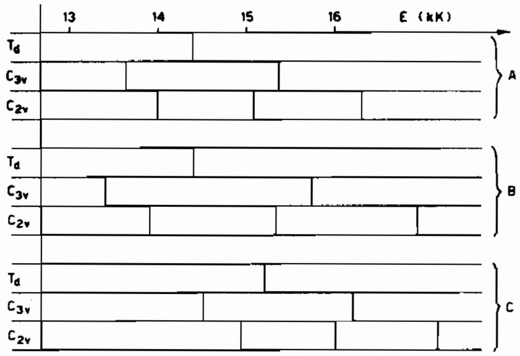

Figure 1. Calculated orbital splitting of the ^4P level in pseudotetrahedral cobalt(II) complexes; adopted sets of parameters values as in table 4; sets A, B, C correspond grossly to mixed chloro-, bromo- and iodo-complexes of Co^{II} with phosphines (compare fig. 2).

cies. This is another example of conflicting evidence, suggesting the possibility of one-to-one assignment of band components to orbital sublevels (like *e.g.* in ref.[5] and[7]) in some pseudotetrahedral Co^{II} complexes, and ruling it out in some others. In any case however, a correlation seems to hold between centers of gravity of component groups and orbital sublevels; a rough correspondence is found indeed in the total splitting of the b^4T_1 terms, which, in agreement with the present calculations, is somewhat larger in C_{2v} than in C_{3v} complexes. At constant B (constant nephelauxetic effect),

(12) A. A. G. Tomlinson and O. Piovesana, private communication.

(13) P. Porta, T. Tarantelli, and C. Furlani, *J. Chem. Soc.* (*A*), (1971).

(14) O. Piovesana and C. Furlani, *J. Inorg. Nucl. Chem.*, *30*, 1249 (1968).

(15) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *Inorg. Chem.*, *1*, 239 (1962).

(16) M. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, *84*, 1543 (1962).

a blue shift is predicted in our model on going from $[CoA_4]^=$ to $[CoA_3B]^-$ to $[CoA_2B_2]$, *i.e.* on replacing halides through phosphine ligands. In the Co^{II} halide-phosphine systems the center of gravity of b^4T_1 does not show such blue shift, but this is easily justified as an effect of larger nephelauxetic decrease with phosphine ligands, while in our model calculations we assumed B to be constant.

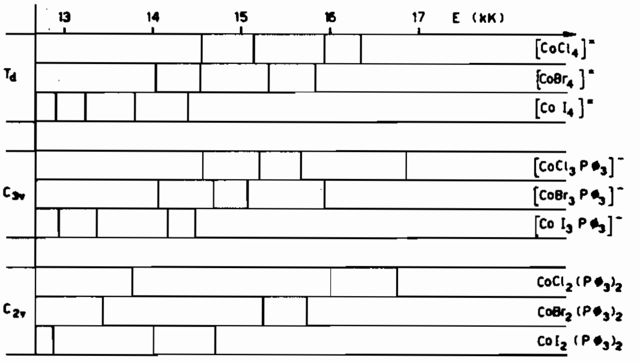

Figure 2. Experimental ligand-field spectrum in the visible region ($^4A_2 \rightarrow b^4T_1(^4P), T_d$) of mixed cobalt-halide-phosphine complexes.

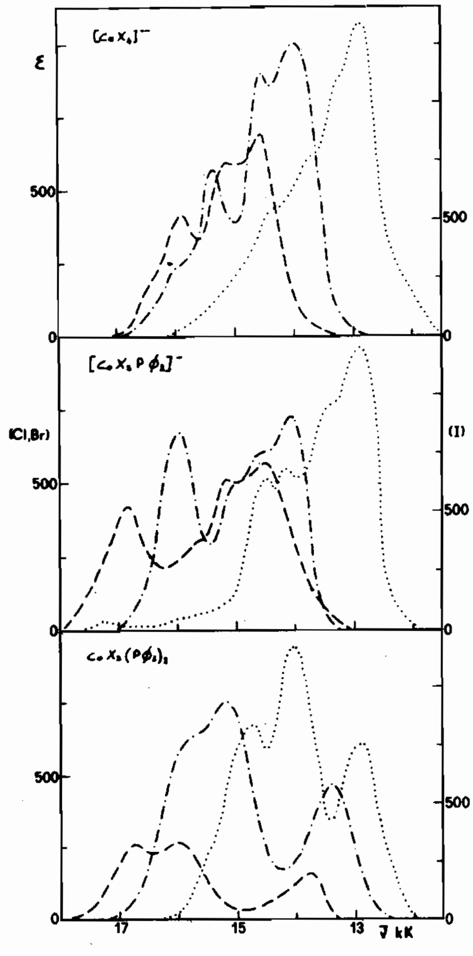

Figure 3. Absorption spectra of mixed cobalt-halide-phosphine complex ($[CoX_4]^{2-}$,$[CoX_3P\emptyset_3]^-$,$CoX_2(P\emptyset_3)_2$) in CH_2Cl_2 (from ref. (16))

——— X = Cl —·—·— X = Br X = I ......

Turning now to a more general discussion, we remark that the experimental situations are only in part encouraging to the interpretive potentialities of purely orbial calculations, since besides examples of spectra neatly and completely assignable in terms of orbital components alone such as $CoCl_2(PPh_3)_2$,[7] there are cases where the polarizations predicted by orbital selection rules are less well fulfilled, *e.g.* $Co(etu)_2(Oac)_2$*[8] where the b^4T_1 group of levels shows one component polarised along x and one along z, but *two* along y, then cases such as $Co(tu)_2Cl_2$ and $Co(diettu)_2Cl_2$* where polarization effects are large but incomplete,[12] to finish with $Co(EPTCH)_2Br_2$[13] and similar species where, despite the favourable alignment of molecular chromophores in the crystal, the ligand field spectra exhibit little or no polarization, as if ony spin-orbit selection rules, or other selection rules else than the purely orbital ones of C_{2v}, where followed. Some apparent one-to-one correspondences cannot be interpreted very simply, and require some words of caution; thus, all CoL_2X_2 complexes (L = thiourea or substitute thiourea, X = Cl, Br, I) show in their solution spectra three distinct components of nearly equal intensity and nearly equal frequency spacing in each T_1 term,[14] which it would be tempting to assign to the three orbital C_{2v} components, but care has to be exerted before definitely accepting such an identification, because preliminary measurements of polarized crystal spectra of $Co(diettu)_2Cl_2$[12] show that the order in the sequence of orbital components may be different from the predictions of simple point ligand models such as the present one.

Table VI. Spin-orbit matrix of $^4P(d^7)$ in units of $\zeta(3d)$

$P_z(-1/2)$	$P_x(1/2)$	$P_y(1/2)$	$P_x(-3/2)$	$P_y(-3/2)$	$P_z(3/2)$
0	1/3	−1/3	$-\sqrt{3}/6$	$-\sqrt{3}/6$	0
	0	1/6	0	0	$-\sqrt{3}/6$
		0	0	0	$-\sqrt{3}/6$
			0	−½	0
				0	0
					0

Inclusion of spin-orbit coupling does not improve in general the possibility of one-to-one assignments of band components; while namely spin-orbit splitting is considerable in $[CoA_4]$ complexes (total spread of the multiplet is to first order 4ζ (^4L) for a,b^4T_1, hence ~0.7 kK) although still smaller than the experimental energy distances, the spin-orbit splitting is calculated to be smaller on the levels of C_{3v} complexes (reaching a few tenths of kK only within the orbital E states, which are therefore the only ones to be split sufficiently as to give rise to more observed band components),

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* etu = ethylenethiourea; diettu = N,N'—diethylthiourea.

and still smaller or even practically negligible with C_{2v} complexes. This situation had already been observed for a^4T_1 (^4F) of some C_{2v} complexes,[5] and we report a similar result calculated for b^4T_1 (^4P): the matrix elements are given (only for b^4T_1, *i.e.* neglecting interactions with other orbital levels) in Table VI, for the basis of Table I, and the results of a numerical calculation are reported in Figure 4.

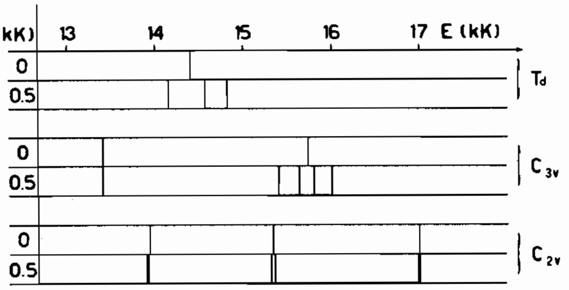

Figure 4. Effect of first-order spin-orbit coupling on the orbital sublevels of ^4P in pseudotetrahedral Co^{II} complexes of different symmetries (parameter set B).

This confirms and generalizes the conclusion, previously reached for some isolated cases,[4,5] that spin-orbit effects, at least as they are calculated in the present scheme by the assumption of a single value of ζ for all levels, add little or nothing to the possibility of assignment of all observed band components in pseudotetrahedral Co^{II} complexes, and suggests that vibronic effects and possibly Jahn-Teller distortions should be taken into account as well. Nevertheless, we feel that spin-orbit coupling, if more properly treated in the course of a complete M.O. calculation including selective interaction of metal orbitals with ligand orbitals of different Γ (for which no simple reckoning scheme is available until now), could account for most basic features of the structure of d–d bands in pseudotetrahedral Co^{II} complexes. Thus, the prediction that spin-orbit splitting effects are smallest in the presence of large orbital splittings, compares favourably with the experimental fact that orbital selection rules are better obeyed (*i.e.* Γ's of orbital sublevels are good quantum numbers) with complexes such as $CoCl_2(PPh_3)_2$, which have C_{2v} symmetry (maximum orbital splitting), and contain ligands with small spin-orbit couplings and large spectrochemical difference. On the other hand, failure to observe sharp polarization effects occurs mainly with Co^{II} complexes containing heavy donor atoms and having small spectrochemical differences between A and B, as if the higher spin-orbit coupling of, say, Br and I, helped by smaller distances between orbital sublevels, could bring a more effective scrambling of different orbital states in the actual levels. Present scarce knowledge of the relativistic nephelauxetic effect does not allow more precise statements to this regard; until now, only values of ζ lower than in the free metal ion have been reported for tetrahedral cobalt(II) complexes, the decrease being generally explained as a delocalization effect, but there is a tendence to relatively higher ζ values with heavier halogen ligands,[14] and mixing of ligand ζ in the actual orbitals of the partly filled shell could conceivably raise ζ (complex) above the value ζ (3d) $= 538$ cm^{-1} of the free metal ion.[19] An additional difficulty arises from possible geometric distortions of the coordination tetrahedra, as is suggested by the fact that the overall splitting of b^4T_1 decreases in the order $CoCl_2(PPh_3)_2 > CoBr_2(PPh_3)_2 > CoI_2(PPh_3)_2$, while the spectrochemical differences Cl–P, Br–P, and I–P would suggest the opposite trend; such deviations may be caused by interference between different ligands or by distortions of the tetrahedral angles, especially plausible with bulky and polarizable ligands, (a point-charge calculation whose results are shown in Figure 5 predicts that even small deviations from tetrahedral angles can cause considerable shifts of the one-electron energy levels) and both factors imply that in such cases also an accurate knowledge of bond angles and distances will be required from X-ray crystallographic data before a really meaningful ligand-field treatment of lower symmetry effects can be attempted.

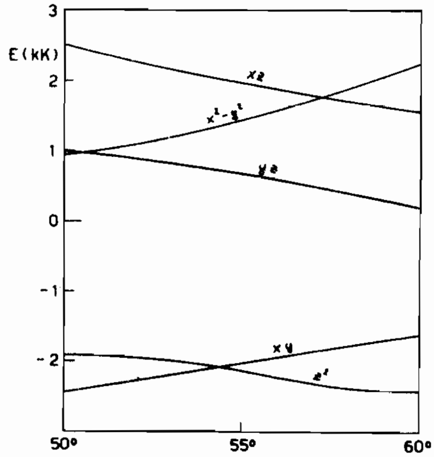

Figure 5. Effect of angular distortion on the calculated one-electron energy levels of d-orbitals in a pseudotetrahedral $M(II)A_2B_2$ complex; $R_2(A) = 8.0$ kK, $R_4(A) = 4.2$, $R_2(B) = 11.8$, $R_4(B) = 5.9$; δ_A variable, $\delta_B = \pi - 54°44'$.

(17) L. Sestili and C. Furlani, *J. Inorg. Nucl. Chem.*, *32*, 1997 (1970).

(18) F. A. Cotton, O. D. Faut, and J. T. Mague, *Inorg. Chem.*, *3*, 17 (1964).

(19) Griffith, The Theory of Transition Metal Ions, Cambridge at the University Press, 1964.