Angular-overlap Parameters for Tetrahalogeno-complexes of Copper(II) and Cobalt(II) †

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Single-crystal magnetic susceptibilities and electronic spectra of $Cs_2[CuCl_4]$, $Cs_2[CuBr_4]$, $Cs_3[CoCl_4]Cl$, $Cs_3[CoBr_4]Br$, and $[NEt_4]_2[NiCl_4]$ are interpreted within the angular-overlap model for ligand fields. Unambiguous values for σ- and π-bonding parameters are determined by the spectra of the copper complexes. Ranges for these parameter values are obtained from the magnetic moments and zero-field-splitting values of the cobalt complexes.

WE have recently developed[1] a system of interpreting the paramagnetic susceptibilities and electronic spectra of low-symmetry transition-metal complexes, in which the ligand field is represented by the angular overlap model (a.o.m.).[2] Several applications[3] have revealed chemically sensible trends in the angular-overlap parameters and as part of our efforts to establish series of these parameters, 'inner spectrochemical series,' we have re-examined some tetrahalogeno-complexes of copper(II), nickel(II), and cobalt(II) ions. The copper and cobalt systems provide rather severe tests for the present model. The magnetic anisotropy of these nearly perfect tetrahedral cobalt molecules is very small and the principal magnetic moments vary little with temperature, as is also the case for the moments of the tetrahalogenocopper systems. We are therefore concerned to discover how much bonding information can be obtained from these near-high-symmetry species in what might reasonably be regarded as limiting cases for the a.o.m.

Low-temperature principal susceptibilities (χ/c.g.s. units × 10^{-6}) and moments (μ/B.M.) * of $Cs_3[CoCl_4]Cl$. A molar diamagnetic correction, 3.02×10^{-4} c.g.s. units, has been applied

T/K	$\chi_{\parallel}$	$\chi_{\perp}$	$\bar{\chi}$	$\mu_{\parallel}$	$\mu_{\perp}$	$\bar{\mu}$
105	26 600	23 900	24 800	4.72	4.48	4.57
95	29 500	26 400	27 500	4.74	4.48	4.57
85	33 200	29 300	30 600	4.75	4.47	4.56
75	37 500	33 100	34 500	4.74	4.45	4.55
65	42 700	37 700	39 400	4.77	4.43	4.52
55	57 500	44 400	46 800	4.76	4.42	4.53
45	64 000	53 000	56 700	4.80	4.37	4.52
35	86 000	67 400	73 600	4.91	4.34	4.54
25	126 100	92 200	103 800	5.04	4.29	4.55
20	158 580	109 500	125 900	5.04	4.19	4.49

* 1 B.M. $\simeq 9.27 \times 10^{-24}$ A m^2.

RESULTS

The complexes studied are $Cs_2[CuCl_4]$, $Cs_2[CuBr_4]$, $Cs_3[CoCl_4]Cl$, $Cs_3[CoBr_4]Br$, and $[NEt_4]_2[NiCl_4]$. Except for the magnetic susceptibilities of $Cs_3[CoCl_4]Cl$, all the data discussed below are drawn from the literature. In the case of $Cs_3[CoCl_4]Cl$ we extended measurements of susceptibilities parallel and perpendicular to the unique axis of these tetragonal crystals from 80 down to 20 K. These measurements were made as part of the calibration checks on our new Faraday balance.[4] They confirm earlier magnetic-susceptibility measurements[5,6] in the range 80—300 K and, for the sake of completeness, we report the unexceptional new results from 80 down to 20 K in the Table.

Crystals of $Cs_3[CoCl_4]Cl$ were prepared and recrystallised as described earlier.[5,6]

DISCUSSION

$Cs_2[CuCl_4]$ *and* $Cs_2[CuBr_4]$.—Calculations were made within the complete ^2D free-ion term as basis using the model described earlier.[1] In addition to ζ, the spin–

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† No reprints available.

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[6] M. Gerloch and R. Richards, *J.C.S. Dalton*, 1972, 980.

orbit coupling coefficient, and k, the orbital-reduction factor, there are only two ligand-field parameters: e_σ and e_π describing σ and π interactions. Fitting this model to the published[7] magnetic susceptibilities is unsatisfactory in that fair agreement is possible for a wide range of parameter values. Similar situations obtain for both $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ ions, proper allowance for the exact molecular geometries[8,9] having been made in both cases, although a.o.m. parameters have been averaged over the somewhat unequal Cu–X (X = Cl or Br) bond lengths in each complex ion. The best defined parameter is k, being *ca.* 0.6 for the chloro- and *ca.* 0.3 for the bromo-complex. The spin–orbit ζ parameter is virtually completely undefined by the magnetic susceptibilities in this treatment. Similarly, wide variations in e_σ with correlated e_π values are possible for fitting to the magnetic properties. These poor results are dramatically improved, however, by consideration of the electronic spectra. Single-crystal polarised spectra have been reported and assigned[10] for all the *d–d* transitions in $Cs_2[CuCl_4]$ and for the two highest bands[11] in $Cs_2[CuBr_4]$. Fitting these transitions to our model gave unique values for the angular-overlap parameters, for both complexes, *viz.*:

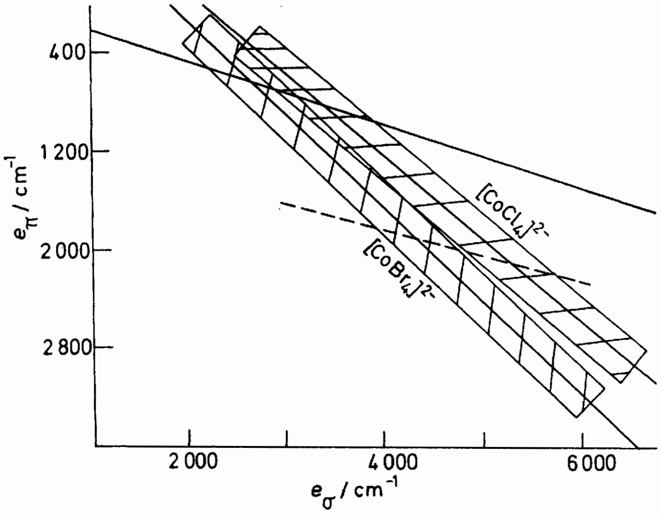
Complex	e_σ/cm^{-1}	e_π/cm^{-1}	e_π/e_σ
$Cs_2[CuCl_4]$	6 800	1 800	0.26
$Cs_2[CuBr_4]$	5 500	850	0.15

In the chloro-case the quotient e_π/e_σ is close to 0.25, a value suggested by overlap considerations[12] in idealised circumstances. Despite the presumably greater size of bromine orbitals relative to those of chlorine, it seems that their greater diffuseness and the longer Cu–Br bonds determine the lower e values for the bromo-complex. Insofar as the relation (1)[13] holds in these

$$\Delta_{\text{tet}} = \tfrac{4}{9}(3e_\sigma - 4e_\pi) \qquad (1)$$

distorted tetrahedra, we note that the corresponding Δ_{tet} values for these ions are essentially equal (*ca.* 5 880 cm^{-1}). Interpretations of this equality within a point-charge electrostatic model are clearly less satisfactory than that revealed by the angular-overlap parameters.

$Cs_3[CoCl_4]Cl$ *and* $Cs_3[CoBr_4]Br$.—Here calculations were made within the complete spin-quartet basis, $^4F + {}^4P$, using the same parameters as for the copper complexes plus the interelectron-repulsion parameter, B. The complexes have both been the subject of much study.[5,6,14,15] The criteria for good fit include the agreement with the zero-field splitting factor δ determined from e.s.r.[13] and spectral studies[14] as well as the reproduction of the principal molecular and crystal susceptibilities (over the range 20—300 K for the chloro-complex, 80—300 K for the bromo-complex[6]). Excellent agreement for all these quantities (better than 2%) was possible for both complexes. (Calculations were made for the $[CoBr_4]^{2-}$ ion assuming identical geometry as that determined[16] for $[CoCl_4]^{2-}$.) However, these fits were obtained for wide ranges of the parameters. Spin–orbit coupling parameters were again ill defined but best fits occur for ζ close to the free-ion value ζ_0. The orbital-reduction factors are close to unity but are not well established for either complex. Fitting values for the angular-overlap parameters are shown in the Figure.



Relations between e_σ and e_π values in $Cs_3[CoCl_4]Cl$ and $Cs_3[CoBr_4]Br$ reproducing the observed magnetism and spectral and e.s.r. properties (see text). For the solid line, $e_\pi/e_\sigma = 0.25$

The molecular geometry of these ions very closely approximates to T_d symmetry so that relation (1) should hold quite well. The values of e_σ and e_π lying on the lines in the Figure correspond, within fitting margins, to this relation. The lines of fit are bounded to some extent, fits beyond the end points being less good. Attempts to restrict the fitting regions by recourse to spectra are, not surprisingly, ineffective. Any values of e_σ and e_π on the line for the chloro-complex, but not elsewhere, reproduce the $^4A_2(T_d) \rightarrow {}^4T_1(F, T_d)$ spectral bands satisfactorily. Transitions to $^4T_1(P)$ may be accommodated by variations in B which does not assist the determination of e values. The criterion for ' satisfactory ' fit here is that the average energy and spread of transitions within the $^4T_1(F)$ band are reproduced. It does not appear possible to improve the agreement beyond what has been attempted by Jesson:[14] in any case, the general pattern of energies within this band is reasonably well reproduced. The spectral fitting does suggest a ζ value for the chloro-ion close to the free-ion

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value and slightly larger than ζ_0 for the bromo-complex. From relation (1) we find $\Delta_{\text{tet}} = 3\,100$ cm^{-1} for $Cs_3[CoCl_4]Cl$ and 2 750 cm^{-1} for $Cs_3[CoBr_4]Br$. Little more may be deduced, beyond the observation that equal values for e_σ in the chloro- and bromo-ions require $e_\pi(\text{Br}) > e_\pi(\text{Cl})$: alternatively, by moving parallel to the broken line in the Figure, a larger decrease in e_σ on replacing Cl by Br is accompanied by a smaller decrease in e_π. Whatever the actual values for e_σ and e_π in these systems it seems clear that rather different behaviour obtains for the cobalt(II) and copper(II) complexes. The quotient e_π/e_σ varies along the lines of fit in the Figure from the limiting case of zero for very low e_σ values to *ca.* 0.5 when $e_\sigma \sim 7\,000$ cm^{-1}. For comparison with the tetrachlorocopper complex, if we assume that e_π/e_σ for $[CoCl_4]^{2-}$ is 0.25, we have $e_\sigma = 3\,600$ cm^{-1} and $e_\pi = 900$ cm^{-1}.

$[NEt_4]_2[NiCl_4]$.—The susceptibilities of this complex undergo an abrupt change [17] at *ca.* 220 K so we attempted to fit the magnetic properties only in the restricted range 230—300 K. Calculations were made within the basis $^3F + {}^3P$ using the same parameter set as for the cobalt complexes. A qualitatively similar situation emerges in that a ' diagonal ' correlation between the e_σ and e_π values is apparent. However, the fitting region is so flat, because of the restricted temperature range, that further analysis is impossible.

Conclusions.—At the outset of this work we had hoped to find straightforward relations between e_σ and e_π values and as functions of the electron configuration of the metal atom. The rather different degrees of distortion from T_d symmetry observed in $[CuCl_4]^{2-}$, $[CuBr_4]^{2-}$, $[CoCl_4]^{2-}$, and $[NiCl_4]^{2-}$ (ref. 17) should not be too important a factor here, for the a.o.m. explicitly takes all the ligand positions and orientations into account. Our failure to analyse the data for $[NiCl_4]^{2-}$ is disappointing but hardly surprising. Similarly the lack of separation between e_σ and e_π values for the cobalt complexes is almost certainly determined by the very small amount of distortion from tetrahedral symmetry in these ions, together with the orbital-singlet nature of their ground terms, giving rise to very small magnetic anisotropy. It is perhaps more surprising that so little could be deduced from the magnetism alone in the case of the copper complexes and we presume from this and other, unpublished, experience with copper complexes that the essential lack of temperature dependence of the moments is largely responsible for this. We sense that a useful rule of thumb may be that magnetic studies on mononuclear copper(II) systems may be unrewarding. On the positive side, e_σ and e_π values for $[CuCl_4]^{2-}$ and $[CuBr_4]^{2-}$ ions seem well established from the spectra.

We thank the S.R.C. for support in building the Faraday balance and for the award of a research studentship (to D. A. C.).

[6/1997 *Received, 27th October,* 1976]

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