π-bonding → metal d jumps, all allowed, in accord with the spectrum. If the system were flat, D_{3h} (Fig. 5b), we would have, for the ligand π-orbitals, $E' + E'' + A_2' + A_2''$; for the metal d-orbitals, $A' + E' + E''$. The spectrum then would be entirely different and one suspects the molecule would be less stabilized by π-bonding involving the highest d-orbital. We note as a detail that the distorted trigonal bipyramidal structure should show an additional slight Jahn–Teller distortion, but this, if it occurs, cannot be seen in our spectra.

Acknowledgments.—We are particularly indebted to Dr. P. S. Braterman for assistance in interpretation of spectra and access to the results of his ligand-field calculations prior to publication.[15] We wish to thank Dr. R. J. P. Williams, of Oxford, for helpful discussions and coöperation and acknowledge the assistance of the several agencies which have supported, in part, this investigation: The United Kingdom DSIR, NATO, and the United States Atomic Energy Commission under Contract AT(30-1)-905.

(15) P. S. Braterman, *Inorg. Chem.*, **2**, 448 (1963).

CONTRIBUTION FROM THE INORGANIC CHEMISTRY LABORATORY, OXFORD UNIVERSITY, OXFORD, ENGLAND

Copper(II) Bromide Complexes. II. A Discussion of the Tetrabromocuprate(II) Spectrum

BY P. S. BRATERMAN[1]

Received August 27, 1962

Selection rules are derived from symmetry arguments for the anticipated visible and near-ultraviolet spectrum of the $CuBr_4^{-2}$ anion, using both of the theoretically plausible models of the energy levels of this species. Comparison of results with the observed spectrum (given in part I), and with preliminary solid state spectra presented here, favors the model in which there is a hole in the d_{xy} orbital, as against the $d_{xz,yz}$. The bands in the visible then are assigned to forbidden or weakly allowed charge-transfer, and the ultraviolet bands to allowed charge-transfer. The energy gap between the two sets of bands is attributed to the effects of π-bonding.

Introduction

The species $CuBr_4^{-2}$ is familiar in the solid state, and the structure is known[2] to approximate closely to a tetrahedron distorted by shortening the *z*-axis (see Fig. 1). The same species recently has been identified in solution by Barnes and Hume,[3] and comparison of solid and solution spectra by these authors indicates that the anion does not differ materially in the two cases. We therefore take their purple $CuBr_4^{-2}$ in water and a variety of organic solvents to represent this anion.

Hypothetical tetrahedral Cu(II) possesses an orbital degeneracy and thus is expected to show a Jahn–Teller distortion. This is indeed found for $CuBr_4^{-2}$,[2] the symmetry being lowered from T_d to (very nearly) D_{2d}, with elements of symmetry S_4 around the *z*-axis, diagonal planes σ_d containing this axis, and twofold rotation around the *x*- and *y*-axes. This symmetry is not quite perfect in the crystal. The distortion described splits the $d_{xy,yz,zx}$, degenerate (T_2) in T_d, into d_{xy} (b_2) and $d_{yz,zx}$ (e) in D_{2d}.[4] Either the level b_2 lies highest, transitions being to this level, and the slight distortion from D_{2d} is fortuitous, or else the degenerate levels e lie highest, transitions being to these levels, and the irregularity of the structure might represent a further Jahn–Teller distortion which removes the twofold degeneracy. Both possibilities are explored here. Such levels as might reasonably be thought to be involved in the spectrum are assigned to their proper irreducible representations in T_d and D_{2d}, and arranged in rough order of energy on the basis of chemical intuition. It then is possible to make some predictions of relative intensity, which differ according to which model is taken, and to compare these predictions with the observed spectrum.

Calculation of Spectrum.—First, we reduce the representations of T_d in the lowered symmetry D_{2d} by taking the characters of the former set under the operations of D_{2d} and expressing the numbers so obtained as a linear combination of characters of irreducible representations of D_{2d}. The results are given in eq. 1. Attention is drawn to the fact that while

$$T_d \rightarrow D_{2d}:\quad A_1 \rightarrow a_1 \qquad T_1 \rightarrow e + a_2 \qquad (1)$$
$$A_2 \rightarrow b_1 \qquad T_2 \rightarrow e + b_2$$
$$E \rightarrow a_1 + b_1$$

x,y,z belong to T_2 in T_d, which reduces to e (x,y) + b_2 (z) in D_{2d}, e also can originate in T_1.

Next we reduce ligand and metal orbitals to obtain Table I. The order of ligand orbitals is derived as follows: the most stable outer shell electrons of the Br^- ion will be derived from 4s atomic orbitals and be σ-bonding. The next most stable will be the p(σ) orbitals, which are stabilized electrostatically by

(1) William Ramsay and Ralph Forster Laboratories, University College, London.

(2) F. C. Lingafelter and B. Morosin, *Acta Cryst.*, **13**, 807 (1960).

(3) J. C. Barnes and D. N. Hume, *Inorg. Chem.*, **2**, 444 (1963).

(4) We use capitals for representations of T_d, lower case symbols for those of D_{2d}.

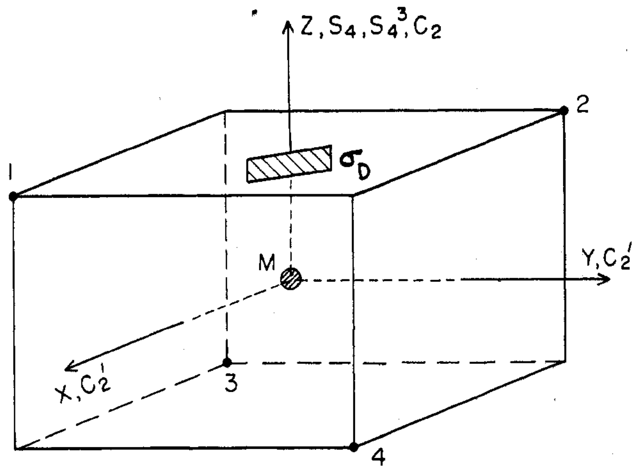

Fig. 1.—The structure of $CuBr_4^{-2}$ in Cs_2CuBr_4 (idealized): M = Cu; bromides at 1, 2, 3, and 4; ∠ 1M2 = 130°, ∠ 1M3 = 102°, ∠ 2M3 = 100°, ∠ 3M4 = 126°.

TABLE I

THE ORBITALS OF $CuBr_4^{-2}$

No.	Nature	Symmetry	Label[a]	Notes
1e	Cu 3d	T_2e	yz,zx	Transform in this problem as x,y
$1b_2$	Cu 3d	T_2b_2	xy	Transforms like z
$2a_1$	Cu 3d	E a_1	z^2	
$2b_1$	Cu 3d	E b_1	$x^2 - y^2$	
3e	Ligand p non-bonding	T_1e	$\bar{x}_3,\bar{y}_3$	Transformation related to x,y by eq. 2
$3a_2$	Ligand p non-bonding	T_1a_2	$\bar{z}_3$	
4e	Ligand p π-bonding	T_2e	x_4,y_4	Order of occurrence of 4,5 uncertain, see Appendix for labeling
$4b_2$	Ligand p π-bonding	T_2b_2	z_4	
$5a_1$	Ligand p π-bonding	E a_1	a_5	
$5b_1$	Ligand p π-bonding	E b_1	b_5	
6e	Ligand p σ-bonding	T_2e	x_6,y_6	In fact 6 and 8 mix, as do 7 and 9
$6b_2$	Ligand p σ-bonding	T_2b_2	z_6	
$7a_1$	Ligand p σ-bonding	A_1a_1	a_7	
8e	Ligand s σ-bonding	T_2e	x_8,y_8	
$8b_2$	Ligand s σ-bonding	T_2b_2	z_8	
$9a_1$	Ligand s σ-bonding	A_1a_1	a_9	

[a] Strictly speaking, these columns ignore covalent bonding, but remain useful for purposes of classification in real problems.

virtue of pointing toward the cation (as found by Shulman and Sugano[5] in K_3NiF_6). Next come two sets of π-bonding orbitals, whose relative energies we are unable to assess, and above them the π-non-bonding orbitals, of which there are in this problem only one set. Finally we have the metal d-orbitals, placed at highest energy because the longest wave length band in the spectrum of $CuBr_4^{-2}$ as at present known seems an obvious candidate for the classification d → d (E → T_2). There is only one hole in the set of orbitals so far listed, to which visible and near-ultraviolet transitions will occur. This hole will be either in T_2e (xz,yz) or in T_2b_2 (xy); we cannot at this stage of the argument say which.

As the third stage of the argument we classify all transitions to d T_2 (e + b_2) in T_d and D_{2d}. We use the fact that the symmetry of a transition is given by the direct product of the symmetries of ground and excited states, and correlate the assignments in the two groups by direct inspection, formally replacing T_2 by x,y (e) + z (b_2), and reducing the resulting expressions both in T_d and in D_{2d}. For $T_1 \rightarrow T_2$, no such easy procedure is available, but since T_1 and T_2 differ only in the signs of their characters under σ_d and S_4, we can construct a true statement about $T_1 \rightarrow T_2$ from the corresponding statement about $T_2 \rightarrow T_2$ by systematically replacing A_1, A_2, T_1, T_2, a, and b with A_2, A_1, T_2, T_1, b, and a. Using the fact that a transition is symmetry-allowed (for electric dipole radiation) if and only if it belongs to the same irreducible representation of the group of the problem as does at least one of x,y,z, we classify transitions as T_d-allowed, D_{2d}-allowed, and "forbidden" (vibronically allowed). We expect, however, that "forbidden" charge-transfer will be more intense than "allowed" d–d transitions. Transitions allowed in T_d should be more intense than transitions of the same general nature which are "semi-allowed" only by virtue of the distortion to D_{2d}. "Allowed" transitions should be polarized either in the x,y plane (e), or at right angles to it (b_2), while those "forbidden" need not be, since they can be activated by more than one vibration.

We soon find that for many of the transitions involved an unambiguous assignment is not possible. To see how this contingency arises, consider a hypothetical transition from a full to an empty p subshell in the symmetry of our problem. The ground state will be A_1, and for the symmetry of the several terms of the excited singlet state (and of the associated transitions) we have

$$T_2\ (e + b_2) \times T_2\ (e + b_2) = T_1 + T_2 + A_1 + E\ (2e + 2a_1 + a_2 + b_1 + b_2)$$

The configurations of symmetry e must arise from the transitions (x,y) → z′,z → (x′,y′), but there is no reason for assigning different amounts of T_1 or T_2 character to either of these pure states. In fact, for a vanishingly small distortion, the excited states are

$$T_2e\text{: } (x \rightarrow z') + (z \rightarrow x');\quad (y \rightarrow z') + (z \rightarrow y')$$

$$T_1e\text{: } (x \rightarrow z') - (z \rightarrow x');\quad (y \rightarrow z') - (z \rightarrow y') \qquad (2)$$

where (x → z′) represents the pure configuration in which an electron has been excited from p (x) to p′ (z). The representations of T_d and D_{2d} are related by configuration interaction, as shown in Fig. 2. If the perturbation is small (as at (1) in Fig. 2), the excited state will be closely related to a state of the undistorted molecule, and one of the transitions will be much more intense than the other, while if the excited state can be described as a pure configuration of D_{2d}, as at (2) in Fig. 2, then the distinction between T_1e and T_2e can no longer be maintained, and both transitions will be of comparable intensity. However, if we do not know the order of T_1 and T_2 in the undistorted molecule, then even if the parentage of these e states in T_d is defined, we do not know its value. We therefore label transitions of e symmetry and doubtful parentage "?e," and describe them as "at least semi-allowed."

(5) R. G. Shulman and S. Sugano, *J. Chem. Phys.*, **36**, 3496 (1962).

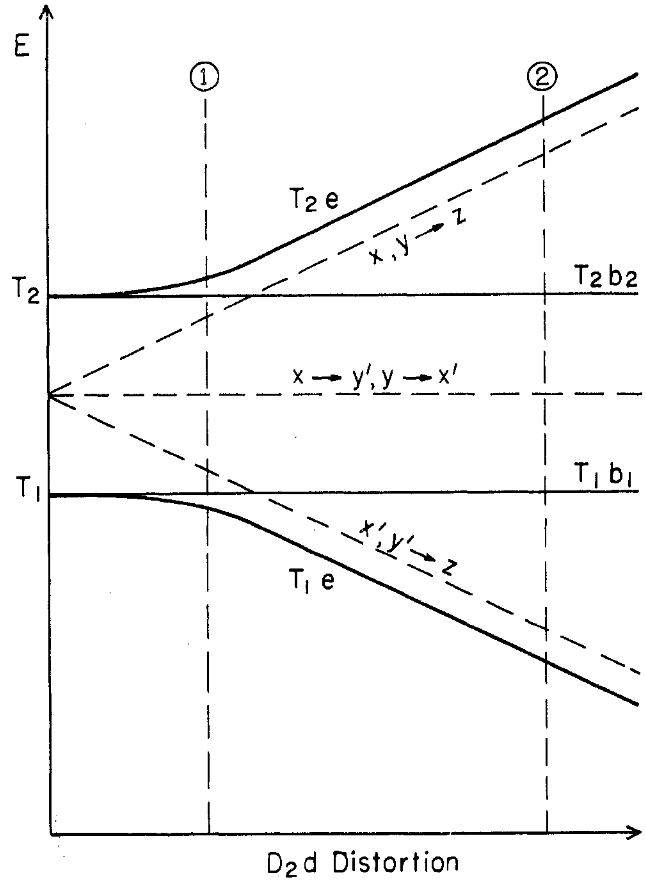

Fig. 2.—A possible effect of configuration interaction on a p → p′ transition in T_d (D_{2d}) symmetry.

Experimental

Polarized spectra (Fig. 4) were obtained by melting tetra-*n*-butylammonium tetrabromocuprate(II) on a microscopic slide, covering with a second slide, and allowing the thin film to cool. The solid film contains purple, non-crystalline material and small brown areas of crystal. These areas are strongly dichroic and a selected area gave the spectra shown on a Beckman DK 2 spectrophotometer. These spectra show the 525 mμ band at angles of maximum and minimum absorption: the two other visible bands appear to be unpolarized. The spectra cannot be related to the crystal axes because of the nature of the specimen.

Results and Discussion

The results of the theoretical analysis are listed in Tables II and III and shown graphically in Fig. 3, together with the observed spectrum, the energy intervals in the predicted spectra (A and B) of Fig. 3, which play no part in the argument, being arbitrarily drawn so as to be close to the observed spectrum (C). The results favor Table III (spectrum A), and the preliminary polarized spectra support this conclusion.

On either model, there will be a first d → d band in the far-infrared which has not yet been found, either because it is at too low energy to have been observed to date, or, perhaps, because it might well be of far lower intensity than the near-infrared band. This should consist of two components, but these are expected, on either model, to differ markedly in intensity, and only one is observed.[5a] The visible bands are charge-transfer bands of the form T_1 (non-bonding)

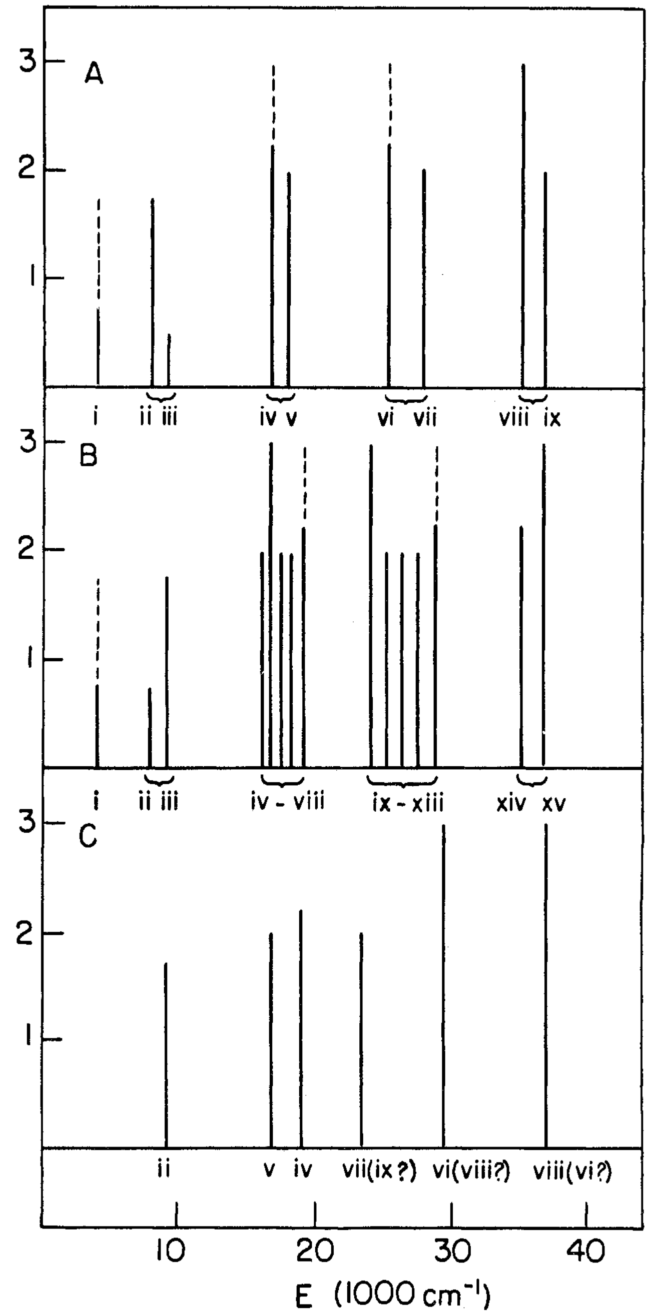

Fig. 3.—Spectrum of $CuBr_4^{-2}$: A, after Table III; B, after Table II; C, observed,[2] transitions numbered as in A.

→ T_2. Of the two, one is more intense and appreciably polarized, while the other is weaker and apparently unpolarized. If e lies above b_2 (Table II, Fig. 3B), we expect this group of transitions to contain one allowed component and one at least semi-allowed, polarized in the opposite sense, of nature 3e → 1e and $3a_2$ → 1e, respectively (transitions iv and viii of Table II). On the other hand, if b_2 lies above e (Fig. 3A, Table III), there will be two transitions (iv and v of Table III), one forbidden and the other at least semi-allowed. The latter transition will be polarized; the former, to a first approximation, will not be, if activated by a vibration of symmetry T_1 (a_2 + e).

(5a) NOTE ADDED IN PROOF.—A. G. Karipides and T. S. Piper, *Inorg. Chem.*, **1**, 970 (1962), have observed both components, and discuss their results in terms of the same model as is favored by this work.

TABLE II

SPECTRUM OF $CuBr_4^{-2}$ IF 1e LIES ABOVE $1b_2$

No.	Transition	Symm.	Label	Notes
i	$1b_2 \rightarrow 1e$	?e	$xy \rightarrow xz,yz$	d–d, at least semi-allowed
ii	$2a_1 \rightarrow 1e$	T_1e	$z^2 \rightarrow xz,yz$	d–d, semi-allowed only
iii	$2b_1 \rightarrow 1e$	T_2e	$x^2 - y^2 \rightarrow xz,yz$	d–d, allowed
iv[a]	$3e \rightarrow 1e$	T_1a_2	$\bar{x}_3,\bar{y}_3 \rightarrow xz,yz$	Forbidden
v	$3e \rightarrow 1e$	T_2b_2		Allowed
vi	$3e \rightarrow 1e$	E a_1		Forbidden
vii	$3e \rightarrow 1e$	E b_1		Forbidden
viii	$3a_2 \rightarrow 1e$	?e	$\bar{z}_3 \rightarrow xz,yz$	At least semi-allowed
ix	$4e \rightarrow 1e$	T_1b_2	$x_4,y_4 \rightarrow xz,yz$	Allowed
x	$4e \rightarrow 1e$	T_2a_2	$x_4,y_4 \rightarrow xz,yz$	Forbidden
xi	$4e \rightarrow 1e$	E b_1	$x_4,y_4 \rightarrow xz,yz$	Forbidden
xii	$4e \rightarrow 1e$	E a_1	$x_4,y_4 \rightarrow xz,yz$	Forbidden
xiii	$4b_2 \rightarrow 1e$	?e	$z_4 \rightarrow xz,yz$	At least semi-allowed
xiv	$5a_1 \rightarrow 1e$	T_1e	$a_5 \rightarrow xz,yz$	Semi-allowed
xv	$5b_1 \rightarrow 1e$	T_2e	$b_5 \rightarrow xz,yz$	Allowed

[a] This and all subsequent transitions are "charge transfer."

TABLE III

SPECTRUM OF $CuBr_4^{-2}$ IF $1b_2$ LIES ABOVE 1e

No.	Transition	Symm.	Label	Notes
i	$1e \rightarrow 1b_2$	?e	$xz,yz \rightarrow xy$	d–d, at least semi-allowed
ii	$2a_1 \rightarrow 1b_2$	T_2b_2	$z^2 \rightarrow xy$	d–d, allowed
iii	$2b_1 \rightarrow 1b_2$	T_1a_2	$x^2 - y^2 \rightarrow xy$	d–d, forbidden
iv[a]	$3e \rightarrow 1b_2$	?e	$\bar{x}_3,\bar{y}_3 \rightarrow xy$	At least semi-allowed
v	$3a_2 \rightarrow 1b_2$	A_2b_1	$\bar{z}_3 \rightarrow xy$	Forbidden
vi	$4e \rightarrow 1b_2$	?e	$x_4,y_4 \rightarrow xy$	At least semi-allowed
vii	$4b_2 \rightarrow 1b_2$	A_1a_1	$z_4 \rightarrow xy$	Forbidden
viii	$5a_1 \rightarrow 1b_2$	T_2b_2	$a_5 \rightarrow xy$	Allowed
ix	$5b_1 \rightarrow 1b_2$	T_1a_2	$b_5 \rightarrow xy$	Forbidden

[a] This and all subsequent transitions are "charge transfer."

The lowest of the next group of bands is a weak, unpolarized charge-transfer (v or vii of Table III), followed by two permitted bands (vi and vii). Of these, vi must be classified as T_2e, being strongly allowed; this fact may not, however, be related to the description of iv as T_1e, as we are dealing with different first-order transitions. Earlier workers,[6] in analyzing the spectrum of $CuBr_4^{-2}$ (misassigned by them to $CuBr_6^{4-}$; see ref. 2), claim to have found a band (ix or vii?) underneath the allowed transitions, but this may be a case of overbold use of gaussian analysis.

It is difficult to reconcile the data with the alternative assumption that e lies above b_2. For in that case, the transitions $3e \rightarrow 1e$, $3a_2 \rightarrow 1e$, $4e \rightarrow 1e$, $4b_2 \rightarrow 1e$, $5a_1 \rightarrow 1e$, and $5b_2 \rightarrow 1e$ each contain one and only one transition allowed in D_{2d} and therefore polarized. For the lowest-energy charge-transfer to be unpolarized, on this model (since all transitions of type $3e \rightarrow 1e$, for example, are degenerate), the transitions $3e \rightarrow 1e$ and $3a_2 \rightarrow 1e$ would have to be superposed. Then the second charge-transfer would have to be of type $4 \rightarrow 1e$, implying an energy gap of less than 2000 cm.$^{-1}$ between π-bonding and π-non-bonding levels, and it is not then clear why this second charge-transfer band should be polarized, or what has happened to the missing component of the transitions $4 \rightarrow 1e$.

Conclusions

The spectrum of the $CuBr_4^{-2}$ anion can best be interpreted on the assumption that the Cu $3d_{xy}$ is the

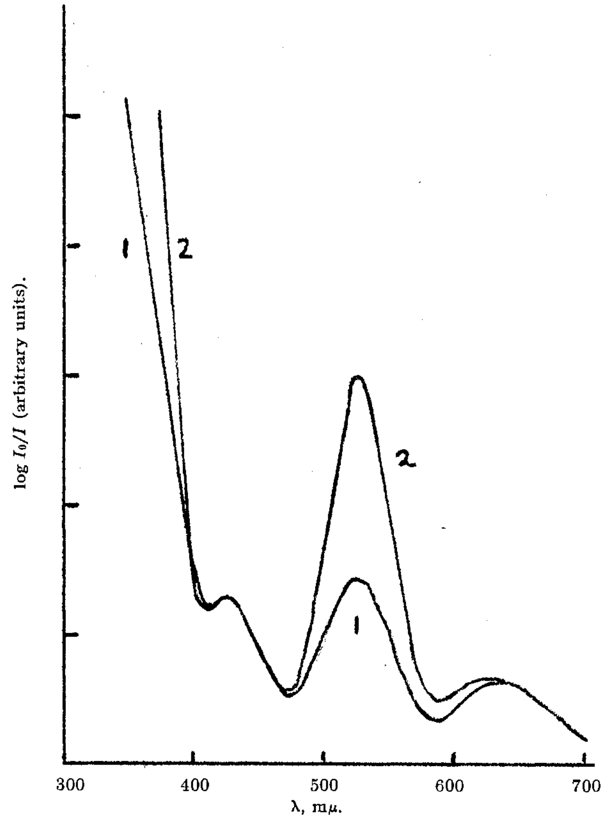

Fig. 4.—Spectra of tetra-*n*-butylammonium tetrabromocuprate (II) polarized in two directions at right angles.

highest-lying level used and is partly empty, the observed transitions being to this level. Then the bands in the visible are due to charge-transfer from non-bonding (T_1) p-orbitals on the bromides to copper, and the higher-energy bands to charge-transfer from π-bonding orbitals to the copper. The energy gap between the two sets of bands is further evidence of the importance of π-bonding in complexes.

Appendix

The Orbitals of Table I.—Label ligands as shown in Fig. 1. Take $p_n = e^{i\theta_n}$, where θ_n is measured round the nM axis. Clearly p_n and p_n^* are σ-non-bonding. Take

$$p_1 + p_2 - p_3 - p_4 = p_z\sqrt{8}$$

and likewise for p_x and p_y. Then

$$p_z - p_z^* = \bar{z}_3$$

$$p_z + p_z^* = z_4$$

Take

$$p_1 + p_2 + p_3 + p_4 = P\sqrt{8}$$

Then

$$P + P^* = a_5$$

$$P - P^* = b_5$$

Each ligand gives rise to two σ-bonding orbitals, approximately 4p (σ) and 4s, respectively, though these will mix to some extent. Then for p (σ)'s

$$1 + 2 - 3 - 4 = z_6\sqrt{4}$$

(6) K. B. Yatsimirskii and T. V. Mal'kova, *Russian J. Inorg. Chem.*, **6**, 426 (1961).

$$1 + 2 + 3 + 4 = a_7\sqrt{4}$$

and for s's

$$1 + 2 + 3 + 4 = a_9\sqrt{4}$$

$$1 + 2 - 3 - 4 = z_8\sqrt{4}$$

Acknowledgments.—The author wishes to thank Dr. J. C. Barnes and Professor D. N. Hume for valuable discussions, access to material before publication, and (J. C. B.) for the data of Fig. 4, and to thank the DSIR for a grant.

CONTRIBUTION FROM CYANAMID EUROPEAN RESEARCH INSTITUTE, COLOGNY, GENEVA, SWITZERLAND

Spectra and Constitution of Antimony(III), Antimony(V) Hexahalide Salts and Related Compounds

BY PETER DAY[1]

Received October 22, 1962

Reflection spectra of Sb(III), Sb(V); Bi(III), Sb(V); In(III), Sb(V); and Tl(III), Sb(V) hexahalide complexes diluted in hexahalostannate(IV) crystals are reported for a number of cations. The pure compounds $Cs_2Bi_{0.5}Sb_{0.5}Cl_6$, $Cs_2In_{0.5}Sb_{0.5}Cl_6$, and $Cs_2Tl_{0.5}Sb_{0.5}Cl_6$ also have been prepared and characterized from their X-ray powder photographs. The Bi and In compounds show evidence of superlattice formation which is assumed to exist, undetected, in the Sb(III), Sb(V) compounds. On this evidence the solid spectra have been assigned to electron transfer transitions from the ns^2 or $(n + 1)s^2$ shell of the trivalent ion to the ns_0 shell of the pentavalent ion. The abnormally deep colors of the In and Tl compounds also are discussed.

The "interaction color" of Sb(III), Sb(V) in HCl solution was studied some time ago,[2] but the spectra of the corresponding solids have not been reported, although the appearance of the crystals suggests that they must be quite different. The cesium salt Cs_2SbCl_6 was first prepared by Wells,[3] who showed that it was isomorphous with Cs_2PbCl_6, and the ammonium compound also forms mixed crystals with $(NH_4)_2SnCl_6$ and $(NH_4)_2PtCl_6$.[4] Early authors thought that these compounds were derivatives of $SbCl_4$, but Elliot showed that $(NH_4)_2SbBr_6$ was diamagnetic,[5a] and therefore presumably contained equal amounts of Sb(III) and Sb(V). Sb(IV) remains a possibility if the compounds were antiferromagnetic, with a very high Néel temperature. There is a simple theory[5b] for antiferromagnetism in the isostructural K_2IrCl_6 which invokes electron transfer from chlorine to iridium, but when it is applied to the antimony case, one finds that the maximum amount of charge transfer could not give a Néel temperature above 50°K., so the compounds would be strongly paramagnetic at room temperature. This is further strong evidence against Sb(IV).

However, the X-ray powder diagrams[6] can be indexed quite accurately in terms of a pure K_2PtCl_6 lattice, *i.e.*, the $Sb(III)Cl_6$ and $Sb(V)Cl_6$ units are either indistinguishable or randomly distributed. Since these units carry different charges if there really are two different valences present, a random distribution is perhaps not likely. The X-ray scattering powers of Sb(III) and Sb(V) must be so similar that a superlattice could not be detected.

The intense colors of mixed valence solids make it very difficult to measure their transmission spectra, and only a few are recorded in the literature.[7] Their diffuse reflection spectra also are broadened and distorted. Because the antimony(III),(V) solids can be homogeneously diluted with Sn(IV), this problem is avoided. Only diffuse reflection spectra are reported here, but we hope later to obtain oscillator strengths as a function of concentration from single crystal spectra using a microscope.

If this class of compounds contains Sb(III) and Sb(V), we would expect analogous Bi(III), Sb(V) salts, and the cesium compound has been prepared. In an effort to discover whether there is a superlattice of trivalent and pentavalent ions, we also prepared In(III), Sb(V), and Tl(III), Sb(V), salts.

Experimental

Preparations.—All the preparations were carried out in 12 *M* HCl solution. For the Sb(III), Sb(V) compounds Weinland and Schmidt's method[4] is convenient. A solution of Sb_2O_3 is divided into two equal portions, one of which is saturated with chlorine, and then warmed to remove the excess. Recombining the two solutions produces the characteristic yellow "interaction color." When anhydrous $SnCl_4$ is added, followed by an alkali metal halide solution, mixed Sb(III), Sb(V), Sn(IV) compounds crystallize on cooling.

For equal ratios of Sb to Sn, more concentrated solutions deposit chlorostannate crystals containing more Sb (*i.e.*, darker color). Thus, because the chlorostannates become more soluble in 12 *M* HCl with decreasing size of the alkali metal cation,

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