TABLE III

LATTICE CONSTANTS OBSERVED AND CALCULATED, Å.

Compound	Observed	Calcd. from Pauling[a]	Calcd. from Wyckoff[b]
Zn_3PI_3	5.945	5.88	5.96
Zn_3AsI_3	6.006	5.92	6.01

[a] Calculated from Pauling's tetrahedral covalent radii [L. Pauling, "The Nature of the Chemical Bond," Third Edition, Cornell University Press, Ithaca, N. Y., 1960, p. 246]. [b] Calculated from Wyckoff's neutral atomic radii from tetrahedral crystals [R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1960, Table III, 13, Chapter III, Table p. 33].

The density calculated for Zn_3PI_3 from the lattice constants and the structure (with one formula weight per unit cell) is 4.81, while the value determined by displacement of benzene in a specific gravity bottle is 4.87 g./ml. It may be of interest to note that this value is higher than the reported density of either of the reactants, Zn_3P_2 (4.55) and ZnI_2 (4.666).

Physical and Chemical Properties.—Both new compounds are dark gray. They do not melt but rather decompose into the compounds from which they were formed starting at about 600° when sealed under vacuum. Under "open" vacuum they begin to lose ZnI_2 at about 300°. Alcohol dissolves out ZnI_2, leaving Zn_3P_2 (or Zn_3As_2) behind. These chemical properties are very similar to those of Ag_2HgI_4. On exposure to moist air, deliquescence occurs.

No tendency for the new compounds to form single crystals was observed. Crystals could not be grown from solution in excess molten ZnI_2 or from the vapor phase. Attempts were made to measure electrical conductivity of pressed pellets of the powder as a function of temperature, but only erratic behavior was observed. This may have been due to changes in composition resulting from absorption of water even though the pellet was kept in a stream of nitrogen dried with Drierite and from loss of ZnI_2 as the pellet was heated. At room temperature, the conductivity of the compounds is of the order of 10^{-10} ohm^{-1} cm.$^{-1}$.

Discussion

The synthesis of compounds with an antichalcopyrite structure remains unattained. However the new compounds reported here represent a closely related new modification of the zincblende structure. They are chemically related to antichalcopyrite in that the cation sublattice consists entirely of zinc and the anion sublattice is shared by elements from groups V and VII of the periodic table. They are structurally related to an anti-$MgGeP_2$ (or anti-α'-$ZnSnAs_2$) structure in that their anions are disordered in one of the zincblende sublattices. They are structurally related to γ-Ga_2Se_3[14] in that cations and vacancies are disordered in the other sublattice of the zincblende structure. Finally, they are related to the zincblende type "Phase I" which extends from 10 to 20 mole % Ag_2S in the Ag_2S–HgI_2 system[15] in that disordered anions of two different valence states and disordered cations and vacancies are present; these differ however in the number of unlike cations present and the valence states of some of the elements involved.

Acknowledgments.—The authors wish to thank Mr. John J. Minchak for having prepared some of the samples described herein, and Dr. Y. Okaya for writing the least-squares refinement program and providing many helpful comments on the quantitative aspects of the structure determination.

(14) H. Hahn and W. Klingler, *Z. anorg. allgem. Chem.*, **259**, 135 (1949).

(15) L. Suchow and G. R. Pond, *J. Phys. Chem.*, **58**, 240 (1954).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY FOR NUCLEAR SCIENCE,
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Copper(II) Bromide Complexes. I. A Spectrophotometric Study

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Spectrophotometric studies on copper(II) bromide–lithium bromide mixtures in aqueous and organic solvents and on solid bromocuprates of known structure have shown that the highest bromide complex formed is the $CuBr_4^{-2}$ ion. This species is purple. The green color observed at lower bromide concentrations in various solvents is felt to be $CuBr_3^-\cdot 2$ solvent.

The striking color changes when solutions of copper(II) bromide, particularly in non-aqueous media, are treated with hydrogen or alkali bromide have attracted the interest of a number of investigators. Kosower, Martin, and Meloche[3] interpreted the spectral changes observed in an alcoholic copper(II) bromide solution on addition of hydrogen bromide in terms of a series of six mononuclear copper(II) bromide complexes. The low stability in aqueous solution of the $CuBr^+$ ion,[4] which we have found not to be changed significantly in going to alcoholic medium,[5] suggests that an alternative interpretation might better explain the observed

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(3) E. M. Kosower, R. L. Martin, and V. W. Meloche, *J. Am. Chem. Soc.*, **79**, 1509 (1957).

(4) P. S. Farrington, *ibid.*, **74**, 966 (1952).

(5) J. C. Barnes and D. N. Hume, *J. Phys. Chem.*, **67**, 526 (1963).

facts. Matsuo[6] recently has confirmed the low formation constant of the first complex in aqueous medium and estimated correspondingly smaller formation constants for the succeeding steps. Yatsimirskii and Mal'kova[7] studied the absorption spectra of copper acetate–lithium bromide mixtures in anhydrous acetic acid, assuming the highest complex formed to be hexabromocuprate(II). Our results, however, indicate this assumption to be unjustifiable. The present paper describes a spectrophotometric study and interpretation of the copper(II) bromide system in various solvents, particularly acetonitrile, and in the solid state.

Experimental

Materials.—Copper(II) bromide and oxide, hydrobromic acid, lithium bromide and carbonates, and perchloric acid were utilized directly as Analytical Reagent grade chemicals. Lithium bromide was dried *in vacuo* at 130° for several hours before use. Alcohols, diethyl ether, and dimethylformamide were of Analytical Reagent grade. Acetonitrile was especially purified and dried by treatment with strong alkali and distillation over phosphorus pentoxide. Other solvents used were of commercial grade, appropriately dried, if necessary.

Apparatus and Technique.—Most spectra were run in 5-mm. or 1-mm. silica cells, Teflon-stoppered, using a Cary Model 14 recording spectrophotometer. For exact quantitative measurements, a Beckman DU spectrophotometer was employed. A Unicam S.P. 500 spectrophotometer was utilized for some of the reflectance measurements.

Autoxidation–Reduction of Copper(II) Bromide.—The principal experimental complication in the study of copper(II) bromide complexation in solution is autodecomposition into copper(I) bromide, or its complexes, and bromine. The reaction is observed to take place slowly in the solid at room temperature.[8] In solution, the decomposition is more rapid. Doehlemann and Fromherz[9] reported that as much as 19% of the copper was present in the monovalent state in aqueous solutions with a high lithium bromide concentration. We have found that with cupric bromide in acetonitrile at room temperature, about half the copper is reduced in 24 hr. If the solution is boiled, a mixture of bromine and acetonitrile is distilled off and the reaction proceeds to completion. On addition of water to the solution remaining undistilled, cuprous bromide is precipitated.

At room temperature, the concentration of free bromine remains minute, being detectable spectrophotometrically only immediately after mixing. This suggests bromination of the solvent, as was found with cupric bromide in acetone and methyl isobutyl ketone by Denaro and Occleshaw.[10] The absorption maxima of the copper(I) bromide complexes lie below 250 mμ and are hidden by the bromide band in this region. If any mixed copper(I)–copper(II) bromide complexes form, they do not absorb in the visible region, unlike the chlorides.[11]

Spectra

Purple Solutions.—A very characteristic, intense purple color is obtained when copper(II) bromide is treated with a large excess of hydrogen bromide or alkali bromide in any of a number of solvents. Table I summarizes the spectra of the purple solutions obtained in several solvents when cupric bromide and an excess of lithium bromide were dissolved, and also the spectra of the solid compounds Cs_2CuBr_4 and $(R_4N)_2CuBr_4$, where R is *n*-butyl. The spectra of the solids were measured by reflectance and that of $(R_4N)_2CuBr_4$ also by transmission through a thin layer of crystals on a glass plate and as a mull in hexachlorobutadiene. All these methods gave very similar spectra.

TABLE I

SPECTRA OF PURPLE BROMOCUPRATE(II) COMPLEXES

Solutions	Positions of band maxima, mμ					
Water, 6 *M* LiBr or HBr	270	340	425sh	525	590	1100
Alcohols, 3 *M* LiBr	270	340	425sh	525	590	1100
Dimethylformamide	270	350	430	540	600	1100
Acetonitrile	270	350	425sh	528	610	1100
Log extinction coeff.	3.8	3.8	(3.1)	3.3	3.1	2.2
Solids						
Cs_2CuBr_4 (R)	^{a}	^{a}	430	525	600sh	^{b}
$(R_4N)_2CuBr_4$ (R)	^{a}	^{a}	430	530	625	^{b}
$(R_4N)_2CuBr_4$ (T)	^{a}	340	425	525	590	1100
$(R_4N)_2CuBr_4$ (M)	^{a}	^{a}	^{a}	525	610	1100

(R), reflectance; (T) transmittance; (M), mull in HCBD; sh, shoulder.

[a] Out of range of technique. [b] Limit of instrument 1000 mμ, band maximum just beyond this.

It is clear that all these spectra must originate in the same complex. The crystal structure of cesium tetrabromocuprate(II) was determined by Morosin and Lingafelter,[12] who found that the ion $CuBr_4^{-2}$ exists in the solid as a discrete tetrahedron, which is tetragonally distorted, presumably because of the Jahn–Teller effect. Thus the spectrum in Table I must be that of the $CuBr_4^{-2}$ anion.

This is the species obtained in solution at the highest concentrations of lithium bromide or hydrobromic acid, and thus we must reject the assignment of bands to the species $CuBr_5^{-3}$ and $CuBr_6^{-4}$ by Kosower, Martin, and Meloche, who assumed that each species in solution would give rise to only one band.

For the same reason, the claim by Yatsimirskii and Mal'kova to have obtained complexes with more than four bromides per copper in glacial acetic acid cannot be sustained. Their work will be discussed later in this paper.

The species extracted from a cupric bromide solution onto a strong anion exchange resin in the bromide form colors the resin intensely purple. When the diffuse transmission spectrum of the resin lightly loaded with copper was obtained, it was found to resemble markedly the spectra in Table I in the region 400 to 800 mμ, the range being limited by the technique used. Thus we can say that $CuBr_4^{-2}$ is the principal species adsorbed on the resin.

Green Solutions.—In some organic solvents a green solution is obtained at bromide concentrations lower than those needed to form the purple species. Figure 1 shows the spectrum of a 10 m*M* solution of cupric

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(6) S. Matsuo, *J. Chem. Soc. Japan*, **82**, 1330, 1334 (1961).

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

(8) S. Carter and N. Megson, *J. Chem. Soc.*, 2954 (1928).

(9) E. Doehlemann and H. Fromherz, *Z. physik. Chem.*, **A171**, 353 (1934).

(10) A. R. Denaro and V. J. Occleshaw, *Anal. Chim. Acta*, **13**, 239 (1955).

(11) H. McConnell and N. Davidson, *J. Am. Chem. Soc.*, **72**, 3168 (1950).

(12) B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **13**, 807 (1960).

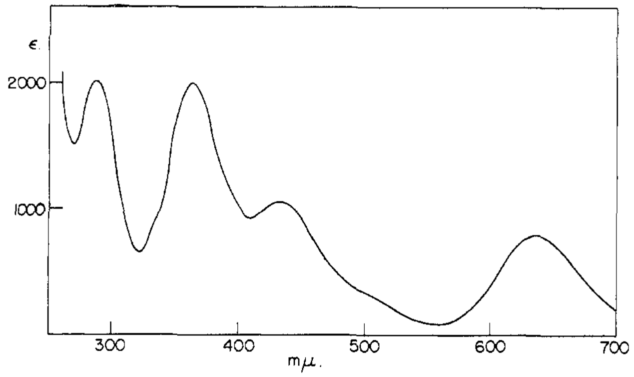

Fig. 1.—Absorption spectrum of cupric bromide, approximately 0.01 *M*, in acetonitrile (green solution).

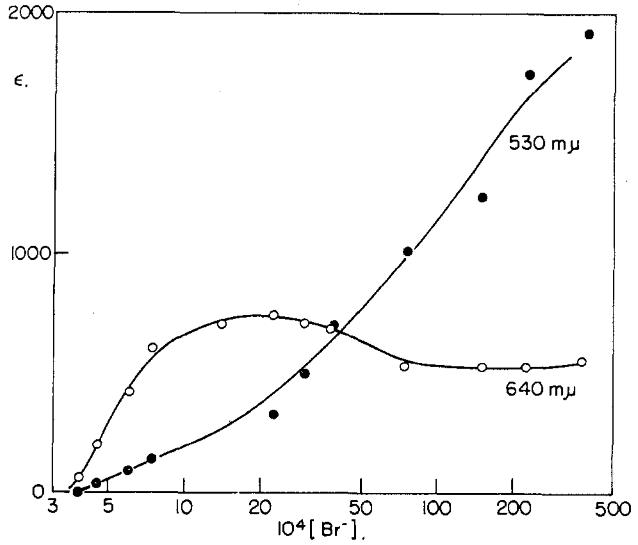

Fig. 2.—Effect of addition of lithium bromide to approximately 5 m*M* cupric perchlorate in acetonitrile.

bromide in acetonitrile in which about half of the copper(II) is present as species A, some 10% as CuBr$_4^{-2}$, and the remainder as solvated Cu^{+2}. The last does not contribute significantly to the observed spectrum in the region shown in the figure. The extinction coefficients quoted are based on total copper(II). The spectra in glacial acetic acid, acetone, ethyl acetate, and amyl acetate are qualitatively identical. This spectrum never appears in water or alcoholic solvents.

Figure 2 shows the effect of adding lithium bromide to a fixed concentration of cupric perchlorate in acetonitrile, measured by the absorbance at 525 and 640 mμ. These wave lengths are characteristic of the purple and green species, respectively. No bands ever appear in these solutions other than those associated with these two species, except the transient bromine band mentioned earlier. Thus it may be assumed that only these two bromocuprate(II) complexes are formed in this solvent. We will denote the green species by (A).

Table II

Spectrum of Species A in Various Solvents

Solvent	Positions of band maxima, mμ				
Acetonitrile	265	360	425	640	900
Ethyl acetate	. . .	335	425	640	880
Amyl acetate	290	330sh	420sh	640	880
Glacial acetic acid	280	370	435	640	880
Acetone	. . .	. . .	440	650	880
Log extinction coeff.	3.5	3.5	3.2	3.2	2.2

The concentration of (A) rises steeply at low bromide concentrations, reaches a maximum, and then diminishes as tetrabromocuprate(II) ion becomes the dominant species. The absorbance at 640 mμ never falls to zero because of a contribution from the band of the purple complex at 610 mμ.

The formation of the CuBr$_4^{-2}$ ion requires a higher bromide concentration when the ionic strength of the solution is increased by the addition of lithium perchlorate. When the indifferent salt concentration was 1 *M*, species A approached closer to full formation than in the example shown (no added salt) because of the suppression of the higher species.

Cupric bromide is almost insoluble in ethyl acetate or glacial acetic acid unless lithium bromide is added, resulting in the formation of species A. This suggests that this species involves more than two bromides per copper.

Attempts were made to interpret quantitatively changes in the absorption spectra of copper(II) solutions in various solvents as a function of added bromide at constant ionic strength. The rapid fading of the solutions as the copper was reduced to copper(I) made it very difficult to relate observed absorbances to accurately known copper concentrations. Even though the samples were analyzed for copper(II) immediately after the spectra had been run, the experimental error of around 10% prevented identification of the number of bromides involved in the change from green to purple.

Solutions in Diethyl Ether.—Figure 3 compares the spectrum of CuBr$_4^{-2}$ in acetonitrile with that of a solution of cupric bromide and lithium bromide in diethyl ether. It can be seen that the spectra are qualitatively similar, but that the bands in the ethereal solution are displaced toward the ultraviolet. The only band not so displaced is the (d–d) transition which stays at 1100 mμ. Monnier[13] analyzed ethereal solutions of this type and decided that the complex present was Li$_2$CuBr$_4$. If the tetrabromocuprate(II) ion was present as ion-pairs, it would be expected to displace the charge transfer spectrum more than the (d–d).

Anomalous Solid Spectra.—The reflectance spectrum of tetraethylammonium tetrabromocuprate(II), and the spectra of this compound as mulls in carbon tetrachloride and hexachlorobutadiene differ from the usual CuBr$_4^{-2}$ spectrum. The (d–d) transition has moved further into the infrared, to 1350 mμ, and the doublet at 525 and 600 mμ becomes three ill-resolved peaks.

The tetra-*n*-butylammonium salt gives the usual CuBr$_4^{-2}$ spectrum by reflectance, transmission, and as a mull in hexachlorobutadiene (Table I). However,

(13) G. Monnier, *Ann. Chim.* (Paris), [13] **2**, 14 (1957).

when mulled in carbon tetrachloride, benzene, or toluene, the spectrum obtained resembles that of the tetraethyl salt. The purple solid becomes green when moistened with these solvents, returning to its original appearance as the solvent evaporates.

Cupric Bromide Tetrahydrate.—The hydrate is unstable at room temperature and must be prepared and handled below 18°. It was prepared as described by Carter and Megson[8] and the reflectance spectrum of the solid was measured (Fig. 4). The difference from the other spectra is evident.

Discussion

Species A.—The species we have called A was investigated by Yatsimirskii and Mal'kova[7] in glacial acetic acid solutions. They analyzed spectrophotometric data by Job's method and the Bjerrum corresponding solution technique and concluded that "A" was $CuBr_4^{-2}$. At higher lithium bromide concentrations they obtained a spectrum identical with those in Table I and concluded that this must be $CuBr_6^{-4}$. Our identification of these spectra with $CuBr_4^{-2}$ leads us to conclude that (A) contains less than four bromides per copper.

The "corresponding solutions" plot should be horizontal at $\bar{n} = 4$ if $CuBr_4^{-2}$ is the only species present. The curve reported by the Russian workers at 640 mμ approached $\bar{n} = 4$ at high bromide concentrations, but the increase from 3 to 4 occupies a wide range of ligand concentration. They comment that this behavior indicates the formation of one or more species with less than four bromides per copper. In the Job method it is difficult to decide between $\bar{n} = 3$ and $\bar{n} = 4$ since these represent peaks at bromide fractions of 0.75 and 0.80 in the solutions. Several of the Job plots in the Russian paper peak at bromide fractions below 0.80, but none below 0.75. It is well known that Job's method of continuous variation is susceptible to misinterpretation, particularly when a mixture of species is involved[14] as is true here where some of the tetrabromide complex certainly is present.

Combining the observations of Yatsimirskii and Mal'kova with our own work in acetonitrile, we feel confident that species A is $CuBr_3^-$. The presence of the (d–d) band at 900 mμ, compared with 1100 in $CuBr_4^{-2}$ and 800 in $Cu(H_2O)_6^{+2}$ and $Cu(CH_3CN)_6^{+2}$ suggests that this species is solvated, the ligand field being somewhat reduced by replacing some of the water molecules in hexaaquocopper(II) by bromide.

The permitted charge transfer bands at 265 and 360 mμ do not shift very far from those in $CuBr_4^{-2}$, suggesting that the ligand π-bonding is not altered greatly. The band at 425 mμ which is only vibronically allowed in $CuBr_4^{-2}$ is enhanced in species A. This could only happen if the S_4 symmetry were destroyed.

We suggest that the species is $CuBr_3^- \cdot 2$ solvent, having the distorted trigonal bypyramidal structure shown in Fig. 5a. The microsymmetry of the Cu–Br bonds is largely preserved, while the S_4 symmetry is replaced by C_{3v}. In C_{3v}, the ligand π-orbitals become $2E + A_1 + A_2$, the metal d-orbitals become $A_1 + E + E$, and if (as seems reasonable) $A_1(z^2)$ is not the highest lying, we have one π-non-bonding → metal d and three

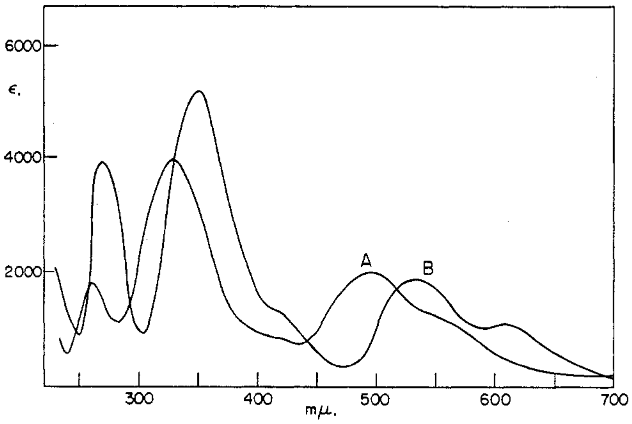

Fig. 3.—Spectra of cupric bromide with large excess of lithium bromide: A, in diethyl ether; B, in acetonitrile.

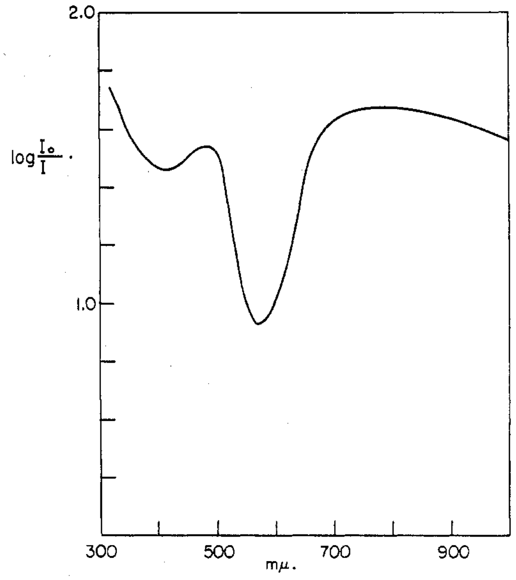

Fig. 4.—Reflection spectrum of solid cupric bromide tetrahydrate.

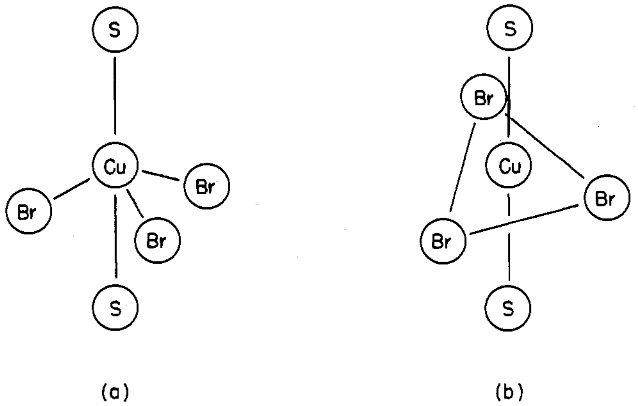

Fig. 5.—Possible structures for the species $CuBr_3^- \cdot 2$ solvent.

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(14) F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955).

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

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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

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

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 $p(\sigma)$ orbitals, which are stabilized electrostatically by

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[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}.