Correspondence

Crystal Spectrum of Cs_2CuBr_4

Sir:

Solution spectra[1] of $CuBr_4^{-2}$ ion exhibit a d–d band at about 11,500 cm.$^{-1}$; this seems unusually high for a $T_2 \rightarrow E$ transition since Δ for $NiBr_4^{-2}$ is reported[2] to be 3380 cm.$^{-1}$. The availability of crystal structures for Cs_2CuBr_4[3] and Cs_2ZnBr_4[4] prompted us to investigate the crystal spectra.

To a fair approximation the complex ion in Cs_2CuBr_4 has D_{2d} symmetry.[3] The bond distances are all nearly equal. In the flattened tetrahedron the two obtuse angles are 130.4 and 126.4°, from which the average polar angle α is 64°; in a tetrahedron α is 54.7°; in Cs_2ZnBr_4[4] α is 56.° In the crystal only a plane of symmetry is retained at the copper ion site (point group C_s).

We have measured the spectrum at 77°K. in mixed crystals and as a plate of Cs_2CuBr_4 on the zinc crystal. No appreciable difference was observed; therefore we assume α is 64° in the dilute crystal. Light was incident on the (001) face and polarized $\parallel$ or $\perp$ to the plane of symmetry σ. Splitting was apparent even in unpolarized light. The band maxima occur at 8000 cm.$^{-1}$ ($\parallel$) and 7570 cm.$^{-1}$ ($\perp$). The ratio of dipole strengths is $4.6(\parallel)/1(\perp)$. We do not consider Cs_2CuCl_4 in this note because the distortion is smaller.

In D_{2d} symmetry the ionic model predicts the following splitting energies of the 3d levels.

$$\begin{aligned}
A_1&: E(d_0) = 2Ds + 6Dt\\
B_1&: E(d_{x^2-y^2}) = -2Ds + Dt - Dr\\
B_2&: E(d_{xy}) = -2Ds + Dt + Dr\\
E&: E(d_{\pm1}) = Ds - 4Dt
\end{aligned}$$

where

$$\begin{aligned}
Ds &= 2/7(3\cos^2\alpha - 1)\rho_2\\
Dt &= 1/14(35/3\cos^4\alpha - 10\cos^2\alpha + 1)\rho_4\\
Dr &= 5/6(\sin^4\alpha)\rho_4
\end{aligned}$$

The radial parameters ρ_n will be determined empirically since it is well known that the ionic model fails to give reasonable values. We proceed with the hope that the angular parameters of the ionic model are adequate. It also is necessary to take spin-orbit coupling into account since the free ion λ of Cu^{+2} is quite large. The required matrices of $\mathbf{l}\cdot\mathbf{s}$ in units of $\lambda\hbar^2$ are

$$\begin{array}{l} d_{xy}\\ d_{x^2-y^2}\\ d_{\pm1} \end{array}\begin{bmatrix} 0 & -i & i\sqrt{\frac{1}{2}}\\ & 0 & \sqrt{\frac{1}{2}}\\ & & \frac{1}{2} \end{bmatrix} \qquad \begin{array}{l} d_0\\ d_{\pm1} \end{array}\begin{bmatrix} 0 & \sqrt{\frac{3}{2}}\\ & -\frac{1}{2} \end{bmatrix}$$

Qualitatively, for z axis compression this model predicts a B_2 ground state and that the observed bands are transitions to B_1 and A_1, the latter being higher in energy (see Fig. 1). In the lower symmetry C_s the correlation is B_2 and A_1 to A' and B_1 to A''. The selection rules $A' \xleftrightarrow{\parallel\sigma} A'$ and $A' \xleftrightarrow{\perp\sigma} A''$ confirm these assignments since the high energy band is polarized $\parallel$ to σ. Furthermore, it is clear that the D_{2d} part of the field plays a large part in determining the intensity since the forbidden transition $B_2 \rightarrow B_1$ is considerably weaker than the allowed $B_2 \rightarrow A_1$. We have not taken into account the partial breakdown of C_s selection rules due to spin-orbit coupling.

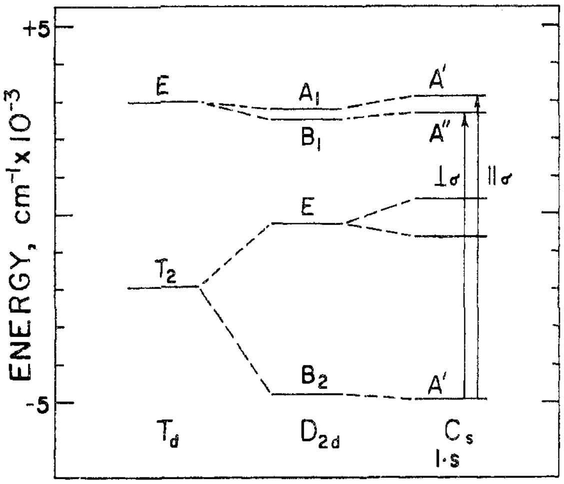

Fig. 1.—Approximate energy level diagram for Cs_2CuBr_4.

With (1) the two experimental band maxima, (2) λ of -800 cm.$^{-1}$, and (3) $\alpha = 64°$ we have solved the equations by trial and obtained the results: $Ds = -700$ cm.$^{-1}$; $Dt = -230$ cm.$^{-1}$; $Dr = 3610$ cm.$^{-1}$; $\rho_2 = 5800$ cm.$^{-1}$; $\rho_4 = 6600$ cm.$^{-1}$. The $d_{\pm1}$ level should occur at about 4600 cm.$^{-1}$ and be split by about 1000 cm.$^{-1}$.

Although these calculations should not be taken to be much more than illustrative, the results are

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(1) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(2) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 4161 (1961).

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

(4) B. Morosin and E. C. Lingafelter, *ibid.*, **12**, 744 (1959).

quite reasonable. The value of ρ_4 is closer to that for $NiBr_4^{-2}$, 4560 cm.$^{-1}$, than would have been expected if the distortion were neglected. However, it is still rather high, a fact that we must ascribe to the larger covalency of the more electronegative copper ion. The ratio ρ_2/ρ_4 is 0.9, in consonance with previous experimental determinations which suggest this ratio is considerably smaller than the value of 2 or 3 predicted by Hartree-Fock metal ion functions.[5]

The predicted splitting of the T_2 state is very large and the ground state is non-degenerate as required by the Jahn-Teller theorem. Ballhausen and Liehr[6] have correctly pointed out that even tetrahedral $CuBr_4^{-2}$ is strictly not a case to which this theorem applies since the spin-orbit splitting alone (*ca.* 1000 cm.$^{-1}$) provides a non-degenerate ground state. Comparison with the but slightly distorted $ZnBr_4^{-2}$ ion suggests that spin-orbit coupling is insufficient to stabilize the $CuBr_4^{-2}$ ion against further distortion than already is provided by the lattice.

Acknowledgment.—This research was supported by the National Science Foundation.

(5) H. A. Weakliem, *J. Chem. Phys.*, **36**, 2117 (1962).

(6) C. J. Ballhausen and A. D. Liehr, *J. Mol. Spectry.*, **4**, 190 (1960).

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The Preparation of a Series of Compounds Containing the Pentachloroalkoxoniobate (IV) Anion

Sir:

We wish to report the preparation of a new class of niobium(IV) compounds. In particular, pyridinium pentachloromethoxoniobate(IV), $(py)_2[Nb(OCH_3)Cl_5]$, has been prepared by the electrolytic reduction of $NbCl_5$ dissolved in anhydrous methanol (saturated with anhydrous HCl), followed by the addition of a hot methanol solution of pyridinium chloride. The compound, which results after cooling for several hours, is obtained as a red-brown, spiny, crystalline agglomerate.

Anal. Calcd. for $(pyH)_2Nb(OCH_3)Cl_5$: C, 28.61; H, 3.27; Cl, 38.45; Nb, 20.13. Found: C, 28.67; H, 3.30; Cl, 38.21; Nb, 20.21.

In agreement with the formulation $Nb(OCH_3)Cl_5^{-2}$, the infrared spectrum reveals no absorption characteristic of the OH group, but does show an intense band at 1095 cm.$^{-1}$ which is not due to pyridinium ion, but is typical of the C–O stretching mode in alkoxides. Furthermore, the spectrum indicates the presence of pyridinium ion and not ligand pyridine.[1]

Magnetic studies indicate Curie–Weiss paramagnetism (Table I) and verify the presence of the niobium(IV) ion, with $4d^1$ configuration.

TABLE I

Temp., °K.	$\chi'_M \times 10^6$	θ	μ_{eff}
299	1020	61°	1.72
196	1425		
77	2700		

The compound is extremely sensitive to air, turning blue and then white. It is soluble in water and gives an immediate brown coloration and then slowly deposits a brown hydrous oxide. It is soluble with decomposition in alcohols. In dimethylformamide, solution is accompanied by a violet color which changes quickly to blue. It is insoluble in dimethyl sulfoxide and common organic solvents, such as benzene, ethers, and ketones.

By varying the organic base and the solvent, a series of methoxy, ethoxy, and isopropoxy compounds has been obtained. They are similar, except in color, to $(py)_2[Nb(OCH_3)Cl_5]$, and will be described in detail in a later publication. Further work will include an investigation of the distinct color differences in these compounds and the preparation of the analogous bromides, iodides, and thiocyanates.

(1) N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp *J. Inorg. Nucl. Chem.*, **18**, 79 (1961).

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Mechanism of Alkylborane Isomerization[1]

Sir:

I wish to present evidence which suggests that an intramolecular bridge hydrogen tautomerism

(1) Presented at the American Chemical Society Regional Meeting, Los Angeles, Calif., December, 1960.