such a condensation, presumably because the bond angle is greater, of the order of 109°.[16] To account for the absence or extreme weakness of the molecular ion in the mass spectrum of compounds of the type $RSn[Co(CO)_4]_3$, it has been suggested that a four-coordinate condensed species is formed under the conditions of the mass spectrometer.[4]

While the above reaction scheme accounts qualitatively for the main features, it should be noted that other more complex processes are undoubtedly occurring. Yields of the desired products are low, of the order of 10–15%, and considerable material is formed which is not soluble in *n*-pentane. The isolation of $ClSn[Co(CO)_4]_3$ implies that one process involves displacement of the acac ligands.

It was possible to isolate the monochloro derivative $(acac)_2SnClCo(CO)_4$ in very low yield by using a large excess of $(acac)_2SnCl_2$. This compound was characterized by analysis and infrared spectrum; the latter shows four bands in the terminal carbonyl stretching region, with positions and intensity distribution very similar to those of other mono-tetracarbonylcobalt derivatives of C_s symmetry.[2] The available evidence does not indicate whether the compound is *cis* or *trans*, but the *trans* isomer (V) is favored on the basis of the reaction scheme. Since $(acac)_2Sn(CH_3)_2$ has been reported to have the *trans* structure,[17] it is reasonable to expect that the electropositive $Co(CO)_4$ groups would occupy *trans* positions in II and that the mixed derivative V might also be *trans*.

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[16] It is perhaps appreciably greater than 109°, as has been suggested on the basis of an infrared investigation.[2] Moreover, recent X-ray structure determinations on bis(transition metal)tin and germanium have shown quite large angles: Fe–Sn–Fe = 128.6° in $Cl_2Sn[Fe(CO)_2C_5H_5]_2$ (J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, **6**, 968 (1967)); Mn–Sn–Mn = 117° in $(C_6H_5)_2Sn[Mn(CO)_5]_2$ (B. T. Kilbourne and H. M. Powell, *Chem. Ind.* (London), 1578 (1964)); Fe–Ge–Fe = 128° in $Cl_2Ge[Fe(CO)_2C_5H_5]_2$ (M. A. Bush and P. Woodward, *Chem. Commun.*, 166 (1967)).

[17] M. M. McGrady and R. S. Tobias, *J. Am. Chem. Soc.*, **87**, 1909 (1965).

CONTRIBUTION FROM NORTH AMERICAN AVIATION SCIENCE CENTER,
THOUSAND OAKS, CALIFORNIA 91360

Association Constants of Silver and Halide Ions in Molten Sulfates and Comparison with the Quasi-Lattice Theory

BY J. GUION[1]

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The association constants for the formation of AgX, AgX_2^-, and Ag_2X^+ have been evaluated from electromotive force measurements in Ag_2SO_4–Li_2SO_4–K_2SO_4 mixtures to which KBr or KI has been added. The temperature dependence for the association constants is not correctly described by the quasi-lattice theory, indicating a contribution to the entropy of association in addition to the configurational entropy of association.

Thermodynamic association constants for silver, cadmium, and lead ions with halide ions in molten alkali nitrates have been measured, and the dependence upon temperature has been shown to be consistent with theoretical calculations based upon the quasi-lattice model.[2–4] The temperature coefficients for the association constants of silver with polyatomic anions (sulfate and cyanide[5,6]) were not, however, correctly predicted by the theory, which should strictly be valid for mixtures containing only monovalent monatomic ions. This paper represents another test of the applicability of the theory to cases which do not conform to the model. We here describe our measurements of the association of silver ions with bromide or iodide in dilute solutions in the eutectic solvent Li_2SO_4–K_2SO_4 (71.5–28.5 mole %). These measurements will be compared with equations derived from the quasi-lattice theory[2] and the energies of associations which are deduced will be compared with a prediction based on the model of Flood, Førland, and Grjotheim.[7]

We utilized the concentration cell

$$\mathrm{Ag}\left|\begin{array}{l}\left.\begin{array}{l}\mathrm{Li_2SO_4}\\ \mathrm{K_2SO_4}\end{array}\right\}\text{eutectic}\\ \quad\mathrm{Ag_2SO_4}\end{array}\right\|\begin{array}{l}\left.\begin{array}{l}\mathrm{Li_2SO_4}\\ \mathrm{K_2SO_4}\end{array}\right\}\text{eutectic}\\ \mathrm{Ag_2SO_4}\quad + \mathrm{KX}\end{array}\left|\mathrm{Ag}\right.$$

where X is either Br or I. The association of silver with chloride ions in this solvent has been measured by Woolner and Hill.[8]

From the change of emf of the cell with the addition of KX one can determine the activity coefficients of Ag_2SO_4. From these activity coefficients, which are less than unity, one can calculate the association con-

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[1] Laboratoire d'Electrochimie et de Chimie Physique, University of Strasbourg, Strasbourg, France.

[2] M. Blander in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, Inc., New York, N. Y., 1967, p 127.

[3] M. Blander, *J. Phys. Chem.*, **63**, 1262 (1959).

[4] J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960).

[5] W. J. Watt and M. Blander, *ibid.*, **64**, 729 (1960).

[6] D. L. Manning, J. Braunstein, and M. Blander, *ibid.*, **66**, 2069 (1962).

[7] H. Flood, T. Førland, and K. Grjotheim, *Z. Anorg. Allgem. Chem.*, **276**, 289 (1954).

[8] E. S. Woolner and D. G. Hill, *J. Phys. Chem.*, **67**, 1571 (1963).

stants for the silver and halide ions by procedures described previously.[9]

Experimental Section

The method of measurement has been described in detail elsewhere.[10] The reference electrode consisted of a silica tube 10 mm in o.d. × 100 mm, with a side tube 3 mm in o.d. × 20 mm connected to the lower end. Pure asbestos fiber was packed in the side tube and acted as a salt bridge between the half-cells. The salt mixture of the right-hand half-cell was contained in a silica beaker 60 mm in o.d. × 120 mm. The two silver electrodes were made of pure 16-gauge (B & S) silver wires fitted snugly into silica tubes, 1.5 mm in o.d. The lower end of each wire was melted to a bead so as to present a large surface and to avoid mass transfer of silver along the electrode due to the influence of unavoidable temperature gradients in the cell. This procedure resulted in potentials which were stable to less than ±0.2 mv during the whole run. The exposed portions of the electrodes were thus easily adjustable to the same horizontal level as the calibrated Pt—Pt-10% Rh thermocouple used for temperature measurements. The whole cell was located in a flat-bottomed silica tube, with an Asbestolite cork cover with holes for the introduction of the electrodes, tubes, and thermocouple. Stirring of the solutions was achieved by bubbling argon through the melts. Because of the dimensions of the cell this method of stirring proved to be very efficient. The furnace was a Marshall multitap furnace; the temperature control achieved by a manual adjustment of an autotransformer allowed a constancy of ±2°. A Leeds and Northrup K-3 precision potentiometer was used for the emf readings.

Procedure

Anhydrous Li_2SO_4 was prepared from pure monohydrate, $Li_2SO_4 \cdot H_2O$ (Baker Analyzed reagent grade), heated for 24 hr at 85°, and finally dried at 130°. KBr, KI, K_2SO_4, and Ag_2SO_4, all Baker Analyzed reagents, were dried at 130°. Proper amounts of Ag_2SO_4 were added to a molten mixture K_2SO_4–Li_2SO_4 of eutectic composition (71.5 mole % Li_2SO_4). The reference half-cell was then partially filled, with care being exercised to avoid formation of trapped bubbles of gas between the asbestos and the melt. This was done by heating this section on a gas burner until the adsorbed gas in the asbestos was removed. When the two half-cells are of the same concentration in Ag_2SO_4, a zero potential should be expected. This was not usually the case, but a constant potential, in the range −2.5 to +2.5 mv, was obtained within several hours. We have no completely satisfactory explanation of this phenomenon, which can be related to the response of the electrode in these dilute solutions, for at first the potential decreases constantly and finally reaches an apparent equilibrium state value. This latter quantity varying from one experiment to another may be linked with the nature of the junction between the half-cells, different in each experiment, and/or with the existence of a temperature gradient resulting in a thermal emf developed. The important fact is that for a given concentration of Ag_2SO_4, at a given temperature the different experiments are highly reproducible. Our experimental emf's were corrected for the difference between the initial value and zero when the concentrations of Ag_2SO_4 were the same in both half-cells.

After a given concentration cell had reached such equilibrium, small crystals of KBr or KI of known weight were added, and the corresponding emf was determined. Equilibrium was attained within 30 min or less after each addition. Since the solubilities of the silver halides are fairly low, each addition of KX was of the order of 0.5×10^{-4} mole/mole of mixture. The experiments were carried out at several different concentrations and temperatures.

The activity coefficient was calculated from eq 1 where the validity of the Nernst law for dilute solutions of Ag_2SO_4 has been assumed.[11] E is the emf change, F

$$RT \ln \gamma_{\mathrm{Ag_2SO_4}} = 2FE + 2N_{\mathrm{X}}\text{-}RT \qquad (1)$$

the Faraday constant, T the temperature in °K, and N_{X}- the ion fraction of X^-.

In the present measurements[12] the last term is negligible. The standard states are chosen such that the activity coefficients are unity at infinite dilution of all solutes in the solvent M_2SO_4.

The values of log $\gamma_{\mathrm{Ag_2SO_4}}$ as a function of R_{KX} are shown in Figures 1 and 2. The variable R_{KX} is related to the mole fraction of KX as

$$\frac{n_{\mathrm{KX}}}{n_{\mathrm{M_2SO_4}} + n_{\mathrm{Ag_2SO_4}} + n_{\mathrm{KX}}} \simeq \frac{n_{\mathrm{KX}}}{n_{\mathrm{M_2SO_4}}} = R_{\mathrm{KX}}$$

Similarly $R_{\mathrm{Ag_2SO_4}}$ is defined by $n_{\mathrm{Ag_2SO_4}}/n_{\mathrm{M_2SO_4}} = R_{\mathrm{Ag_2SO_4}}$, n_{KX} and $n_{\mathrm{M_2SO_4}}$ being the number of moles of KX and eutectic mixture of sulfates, respectively.

From our results it is seen that the temperature has a negligible effect upon the slope of log γ *vs.* R_{KI} and R_{KBr}. In contrast to the KBr case, the slope of log γ *vs.* R_{KI} is a strong function of the concentration of Ag_2SO_4.

Calculation of Association Constants

By utilizing the treatment of several authors[3,9] in designating as K_1, K_{12}, and K_2 the association constants corresponding to the associations

$$\mathrm{Ag^+} + \mathrm{X^-} \rightleftarrows \mathrm{AgX} \qquad (K_1) \qquad \text{(I)}$$

$$\mathrm{Ag^+} + \mathrm{AgX} \rightleftarrows \mathrm{Ag_2X^+} \qquad (K_{12}) \qquad \text{(II)}$$

$$\mathrm{AgX} + \mathrm{X^-} \rightleftarrows \mathrm{AgX_2^-} \qquad (K_2) \qquad \text{(III)}$$

the following partially unexpanded equation may be written (for extensive details of calculation see ref 9, for instance)

$$-{}^1/_2 \ln \gamma_{\mathrm{Ag_2SO_4}} = \frac{K_1}{1 + K_1 R_{\mathrm{Ag_2SO_4}} + \ldots} R_{\mathrm{KX}} + \frac{(K_1K_2 - {}^1/_2K_1^2)}{(1 + K_1R_{\mathrm{Ag_2SO_4}} + \ldots)^2} R_{\mathrm{KX}}^2 + \frac{2K_1K_{12}}{(1 + K_1R_{\mathrm{Ag_2SO_4}} + \ldots)} R_{\mathrm{Ag_2SO_4}} R_{\mathrm{KX}} \qquad (2)$$

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[9] J. Braunstein, M. Blander, and R. M. Lindgren, *J. Am. Chem. Soc.*, **84**, 1529 (1962).

[10] M. Blander, F. F. Blankenship, and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959).

[11] C. H. Liu, *ibid.*, **66**, 164 (1962).

[12] The experimental data have been deposited as Document No. 9559 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and by remitting $1.25 for photoprints, or $1.25 for 35-mm microfilm. Advance payment is required. Make checks or money orders payable to: Chief. Photoduplication Service, Library of Congress.

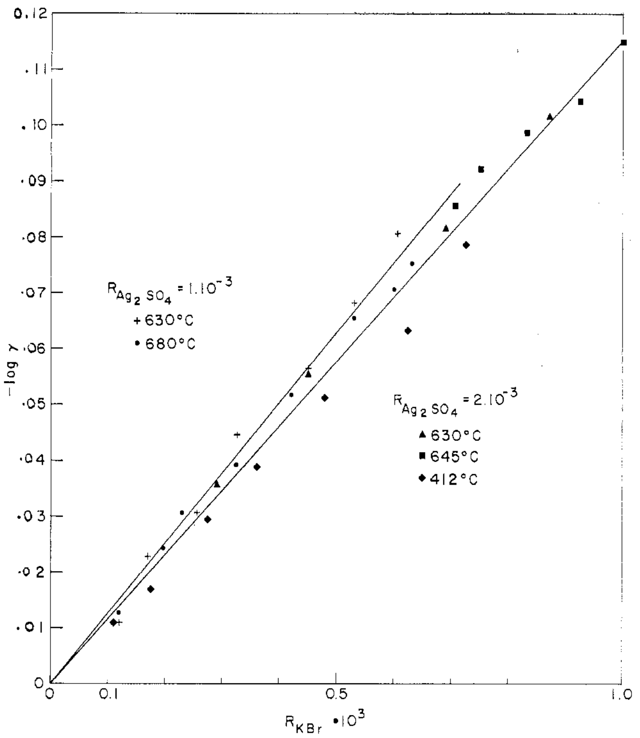

Figure 1.—Experimental values of log $\gamma_{Ag_2SO_4}$ *vs.* R_{KBr} for different concentrations of Ag_2SO_4 and different temperatures.

from which one obtains

$$\frac{-2}{\left(\frac{\partial \ln \gamma_{Ag_2SO_4}}{\partial R_{KX}}\right)_{R_{KX}=0}} = \left[\frac{1}{K_1} + R_{Ag_2SO_4} + \ldots\right] \times \left[\frac{1}{1 + 2K_{12}R_{Ag_2SO_4}}\right] \quad (3)$$

The plot of Figure 3 represents this function *vs.* $R_{Ag_2SO_4}$ and shows the necessity of going to low concentrations for the case of Ag–I associations. Notice also that the slope of this straight line is about 1 which indicates that K_{12} is close to zero for Ag–I associations. For Ag–Br associations a plot as in Figure 3 has a zero slope indicating that $K_{12} \simeq {}^1/_2K_1$, where $K_1 = 160 \pm 20$. The values of K_1 are given in Table I.

Furthermore, one has to be very careful when using the expanded form of eq 2

$$-{}^1/_2 \ln \gamma_{Ag_2SO_4} = K_1R_{KX} + (K_1K_2 - {}^1/_2K_1^2)R_{KX}^2 + (2K_1K_{12} - K_1^2)R_{Ag_2SO_4}R_{KX} \quad (4)$$

The evaluation of K_1 from experimental data utilizing eq 4 will be valid only for $1 \gg K_1R_{Ag_2SO_4}$. This criterion is not stated in the commonly used methods of Fronnaeus, Leden, and Deford and Hume, as pointed out in ref 9. If this condition holds from eq 4, one gets the association constant K_1; for instance

$$-{}^1/_2\left(\frac{\partial \ln \gamma_{Ag_2SO_4}}{\partial R_{KX}}\right)_{\substack{R_{KX}=0\\R_{Ag_2SO_4}=0}} = K_1 \quad (5)$$

K_2 and K_{12} may be also derived easily from eq 4. According to quasi-lattice theory, the association constant K_1 is related to the parameters Z, which is the coordi-

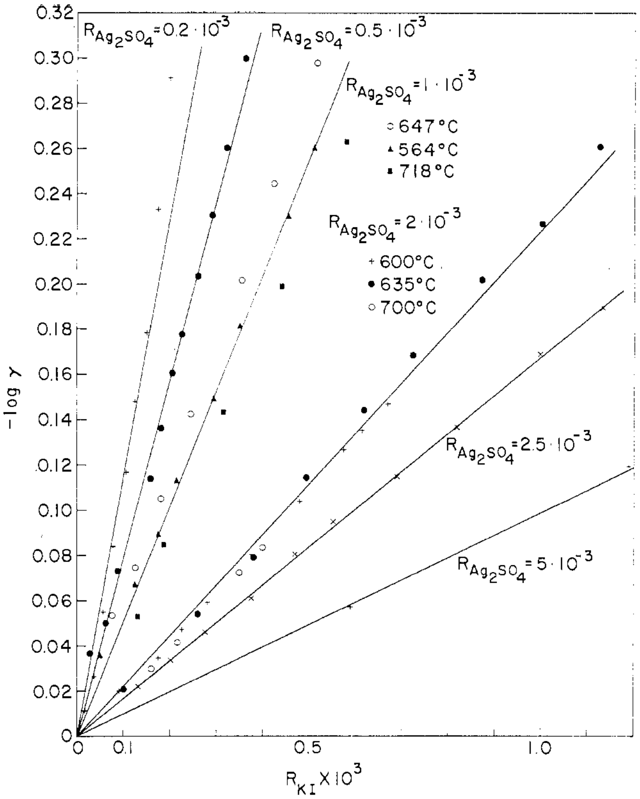

Figure 2.—Experimental results for log $\gamma_{Ag_2SO_4}$ *vs.* R_{KI} for different concentrations of Ag_2SO_4 and different temperatures.

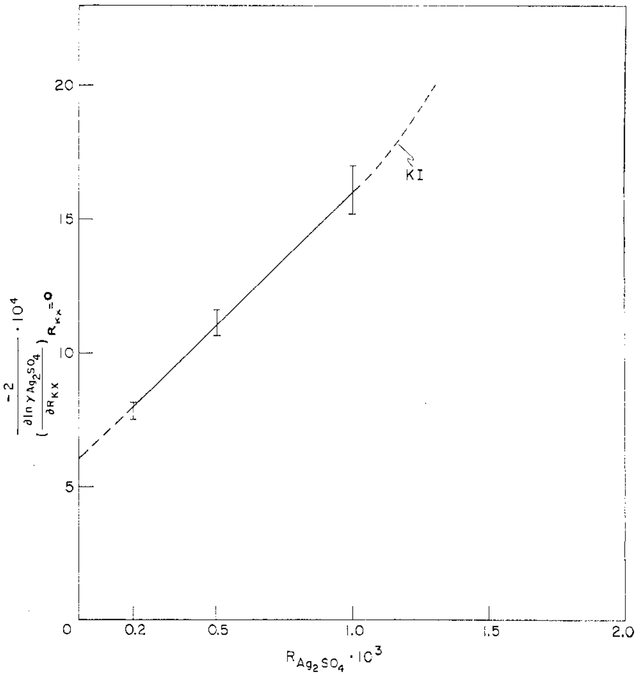

Figure 3.—Extrapolation process used to get the association constant K_1 according to eq 3 for I^- with Ag^+.

TABLE I

CALCULATED VALUES OF ASSOCIATION CONSTANTS[a]

	AgCl[8]	AgBr	AgI
K_1	28[8]	160 ± 20	1700 ± 150
K_2	. . .	80 ± 40	850 ± 150
K_{12}	. . .	80 ± 40	0
$-\Delta A_{\text{exptl}}$, kcal/mole	3.8	6.8	9.1
$-\Delta A_{\text{calcd}}$, kcal/mole	3.2	4.6	6.1

[a] Solvent M_2SO_4.

nation number, and $\beta = \exp(-\Delta A/RT)$, where ΔA defines the energy of ion pair-formation, by

$$K_1 = Z(\beta - 1) \qquad (6)$$

As the plot of log γ *vs.* R_{KX} shows no dependence on $(R_{\text{KX}})^2$, we may deduce that $K_2 \simeq K_1/2$. The deviations from a straight line which could be observed in each case at high values of R_{KX} were related to the appearance of AgX liquid and a slight evaporation of this compound which was much more pronounced for AgI than for AgBr. Thus, these deviations from a straight line are artifacts not related to association in solution. The values of K_2 and K_{12} are also shown in Table I.

Assuming a value of $Z = 4$, *i.e.*, the coordination number for sulfates in the solid state, we calculated the corresponding association energies. A crude comparison with the values derived from the model proposed by Flood and co-workers may also be made. Considering the equilibrium

$$^1/_2\text{Ag}_2\text{SO}_4 + \text{KX} \rightleftharpoons \text{AgX} + {^1/_2}\text{K}_2\text{SO}_4$$

and using the data of Table II,[13] we calculated the value of $\Delta A \cong \Delta H/2$, where ΔH designates the enthalpy change for the above reaction, assuming that the sums of the heat capacities of the reactants and products are the same. The two sets of values are also shown in Table I, and, considering the assumptions made, the agreement is satisfactory.

TABLE II

THERMODYNAMIC DATA FOR CALCULATION OF ΔH^{13}

Compd	Heat of formation of solid, ΔH_{298}, kcal/mole	Heat of fusion, ΔH_f, kcal/mole
K_2SO_4	−342.66	10.7
Ag_2SO_4	−170.50	5.9
AgBr	−23.78	2.18
AgCl	−30.36	3.16
AgI	−14.91	3.72
KBr	−93.73	7
KCl	−104.17	6.1
KI	−78.31	(8)[a]

[a] Estimated value.

Conclusions

The association constants for silver with bromide and iodide ions in sulfate melts have been calculated. Including the results of Woolner and Hill for the chloride, the values of K_1 follow the general trend $K_{1\text{AgI}} > K_{1\text{AgBr}} > K_{1\text{AgCl}}$ observed for these salts with other solvents.

However, the temperature dependence for these association constants is not correctly described by the quasi-lattice model, which is strictly valid for mixtures containing only monovalent monatomic ions. This indicates that the entropy of association in the sulfate melt contains contributions in addition to the configurational entropy of association calculated from the quasi-lattice theory.

Acknowledgments.—We express appreciation to Dr. Milton Blander of North American Aviation for many fruitful discussions and for suggesting this work and to NATO for a postdoctoral fellowship.

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(13) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," U. S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WASHINGTON STATE UNIVERSITY, PULLMAN, WASHINGTON 99163

The Electronic Absorption Spectra of Monomeric Copper(II) Chloride Species and the Electron Spin Resonance Spectrum of the Square-Planar $CuCl_4^{2-}$ Ion

BY ROGER D. WILLETT, O. L. LILES, JR.,[1] AND CHRISTIAN MICHELSON[2]

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The electronic absorption spectra of several monomeric copper(II) chloride species have been measured in the solid state. In both the square-planar and tetrahedral species, the positions of the charge-transfer bands are quite similar. It is found that the position of the absorption band for the d–d transitions is critical in distinguishing between these two possible geometries. This band occurs at 12,800 cm^{-1} in the square-planar species while it is located in the 5500–9000-cm^{-1} range in the tetrahedral species, the exact value of the maximum depending on the amount of distortion in the latter. At the low temperature, a phase transition occurs in the square-planar complexes, changing from a light yellow to a pale green. This involves a change in surroundings of the square-planar ion so that the symmetry of the complex changes from D_{4h} to C_{4v}. Spectral studies indicate only slight changes (<500 cm^{-1}) in the positions of the major absorption bands. The esr spectra of single crystals of the square-planar ions were investigated. Analysis of these data indicates that approximately 50% of the unpaired electron is delocalized onto the ligand.

Introduction

Recently the study of the structure and spectra of copper(II) halide complexes has received considerable attention again. The existence of the distorted tetrahedral $CuCl_4^{2-}$ ion has been known for some time in solids such as Cs_2CuCl_4.[3] The spectra of this com-

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[1] Taken in part from the M.S. thesis of O. L. Liles, Jr., Washington State University, Pullman, Wash., Aug 1966.

[2] Undergraduate NSF recipient.

[3] L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).