

Figure 3.—Carbonyl stretching region of the infrared spectrum of $(\text{OC})_3\text{MnSn}(\text{C}_6\text{H}_5)_2\text{-Sn}(\text{C}_6\text{H}_5)_2\text{Mn}(\text{CO})_3$. Cyclohexane solution, about 1 mg/ml in 0.05-mm cells.

before in other bis-pentacarbonylmanganese and bis-tetracarbonylcobalt derivatives where the metal carbonyl moieties are separated by a single germanium or

tin atom.^{1,12} It has been attributed to a coupling of vibrations on the individual $\text{M}(\text{CO})_n$ groups across the intervening heteroatom, which is considered to occur by means of overlapping d orbitals on the three metal atoms.¹² The infrared spectrum of the MnSnSnMn compound is shown in Figure 3, and although the bands are not well resolved, it is possible to count at least seven medium or strong bands and shoulders.

If this is the result of coupling, as seems probable, then it would mark the first time coupling has been observed across *two* intervening metal atoms. Again, it would seem likely that an interaction over such a large distance takes place *via* π electrons of the metal-metal bonds. As a note of caution in attributing these extra bands to coupling, it should be remembered that an alternative explanation based on the presence of more than one conformational isomer of the molecule cannot be excluded; a conformational effect on metal carbonyl bands has recently been discovered.¹⁷

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(17) W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967).

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Organometallic Compounds with Metal-Metal Bonds. XI. Some Cobalt Carbonyl Derivatives of Six-Coordinate Tin¹

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Reaction of bis(2,4-pentanedionato)dichlorotin(IV) with tetracarbonylcobaltate(−I) anion yields under specified conditions the compounds $(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCo}_2(\text{CO})_7$, $(\text{C}_5\text{H}_7\text{O}_2)\text{Sn}[\text{Co}(\text{CO})_4]_2$, and $(\text{C}_5\text{H}_7\text{O}_2)_2\text{Sn}(\text{Cl})\text{Co}(\text{CO})_4$. The first has a bridging carbonyl group, and the suggested structure involves an SnCo_2 triangular cluster. The other two have only terminal carbonyl bands and are considered to be *trans*-octahedral derivatives. These are the first examples to be reported of metal-metal bonding by six-coordinate tin.

Introduction

Many tetracarbonylcobalt derivatives of tin(IV) have been reported in which tin is four-coordinate and presumably tetrahedral; examples are $(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$,² $\text{I}_2\text{Sn}[\text{Co}(\text{CO})_4]_2$,³ and $\text{ClSn}[\text{Co}(\text{CO})_4]_3$.⁴ In a preliminary communication⁵ we recently described the first metal-metal bonded derivative of six-coordinate tin, $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$,⁶ to which structure I was assigned. We now report full details of the preparation and properties of I and of the related compounds $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$ and $(\text{acac})_2\text{Sn}(\text{Cl})\text{Co}(\text{CO})_4$.

- (1) Part X: R. Kummer and W. A. G. Graham, *Inorg. Chem.*, in press.
- (2) Part IX: J. A. J. Thompson and W. A. G. Graham, *ibid.*, **6**, 1875 (1967).
- (3) D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967).
- (4) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1405 (1966).
- (5) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 2222 (1966).
- (6) D. J. Patmore and W. A. G. Graham, *Chem. Commun.*, **7** (1967).
- (7) We abbreviate the 2,4-pentanedionato ligand $(\text{C}_5\text{H}_7\text{O}_2)$ as acac.

Experimental Section

All reactions and crystallizations were carried out under an atmosphere of purified nitrogen. Tetrahydrofuran (THF) was freshly distilled from lithium aluminum hydride. Microanalyses were carried out by Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany. Molecular weights were determined using a Mechrolab osmometer at 37° in cyclohexane solution with benzil calibration. To prevent oxidation of these sensitive compounds, argon saturated with cyclohexane was passed into the chamber at $9 \text{ cm}^3 \text{ min}^{-1}$; under these conditions, the calibration curve was very nearly linear. Each reported value is the mean of determinations on six drops, with standard deviation as shown.

Infrared spectra were measured for cyclohexane solutions in 0.5-mm cells, using a Perkin-Elmer Model 337 grating spectrometer. Scale expansion and calibration were carried out as previously described.⁷ Mass spectra were obtained using an AEI

- (7) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, **5**, 2217 (1966).

MS9 spectrometer, samples being introduced by direct evaporation at low temperature.

Bis(2,4-pentanedionato)heptacarbonyldicobalttin(IV), $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$.—A solution of $\text{NaCo}(\text{CO})_4$ was prepared in THF by the sodium amalgam reduction of 3.8 g (11.1 mmoles) of dicobalt octacarbonyl. This was added rapidly to a vigorously stirred solution of $(\text{acac})_2\text{SnCl}_2$ (7.8 g, 20.2 mmoles) in 50 ml of THF at room temperature. After 5 min of stirring, THF was evaporated *in vacuo* and the residue was extracted with *n*-pentane. After concentrating to 50 ml, the extract was cooled to -20° giving a deposit of dark oily crystals of impure product. The mother liquor from this crystallization was evaporated to 20 ml and again cooled to -20° , this time affording 0.4 g of $\text{ClSn}[\text{Co}(\text{CO})_4]_2$.⁴ Further evaporation of the mother liquor to 10 ml, followed by cooling to -80° , afforded a mixture of oil and crystals, which on recrystallization from *n*-pentane gave a further yield of impure product. Two recrystallizations of the combined products from *n*-pentane afforded 0.85 g of pure product as red crystals, mp $86\text{--}88^\circ$ dec, with a yield of 12% based on $\text{Co}_2(\text{CO})_8$.

Anal. Calcd for $(\text{C}_5\text{H}_7\text{O}_2)_2\text{SnCo}_2(\text{CO})_7$: C, 32.36; H, 2.24; O, 27.89; mol wt, 630.9. Found: C, 32.92; H, 2.22; O, 27.27; mol wt (concentration, 17.3 mg/ml), 648 ± 4 .

Carbonyl stretching bands were observed at 2076 (m), 2036 (s), 2013 (s), 2004 (m), 1994 (m), and 1836 (m) cm^{-1} .

Bis(2,4-pentanedionato)bis(tetracarbonylcobalt)tin(IV), $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.—A solution of 3.6 g (10.5 mmoles) of $\text{Co}_2(\text{CO})_8$ in 50 ml of THF was reduced with sodium amalgam and added dropwise *very slowly* (about 1 drop every 2 sec) to a well-stirred solution of 7.8 g (20.2 mmoles) of $(\text{acac})_2\text{SnCl}_2$ in 50 ml of THF at room temperature. When all of the $\text{Co}(\text{CO})_4^-$ solution had been added (1.5–2 hr), the THF was removed at reduced pressure and the residue was extracted with 100 ml of *n*-pentane. This was cooled to -80° and deposited impure product as a dark red oily solid. After several recrystallizations from *n*-pentane at -20° , red-brown crystals of product were obtained. Evaporation of the mother liquor to 10 ml and cooling to -20° gave additional product. Recrystallization of combined products from *n*-pentane at -20° afforded 0.5 g of crystals, mp 88° dec.

Anal. Calcd for $(\text{C}_5\text{H}_7\text{O}_2)_2\text{Sn}[\text{Co}(\text{CO})_4]_2$: C, 32.81; H, 2.14; O, 29.14; mol wt, 658.9. Found: C, 32.82; H, 2.21; O, 28.79; mol wt, 670 ± 51 (1.07 mg/ml), 686 ± 20 (3.16 mg/ml), 720 ± 7 (13.88 mg/ml), 741 ± 4 (27.2 mg/ml).

Carbonyl stretching bands were observed at 2101 (w), 2091 (m), 2088 (m), 2069 (s), 2023 (s), 2020 (m, sh), 2013 (s), and 2003 (s) cm^{-1} .

Effect of Rate of Addition of $\text{Co}(\text{CO})_4^-$ to $(\text{acac})_2\text{SnCl}_2$.—Solutions of 20 mmoles of $\text{NaCo}(\text{CO})_4$ in 50 ml of THF and 20 mmoles of $(\text{acac})_2\text{SnCl}_2$ in 50 ml of THF were prepared. (a) To half of the $(\text{acac})_2\text{SnCl}_2$ solution half of the $\text{Co}(\text{CO})_4^-$ solution was added rapidly (in less than 2 sec) and worked up as above affording 0.3 g of $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$. (b) To the remaining half of the $(\text{acac})_2\text{SnCl}_2$ solution the remainder of the $\text{Co}(\text{CO})_4^-$ solution was added dropwise over a period of 2 hr. Work-up in the usual way afforded 0.3 g of $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.

In (a) and (b), all conditions other than the rate of mixing were identical.

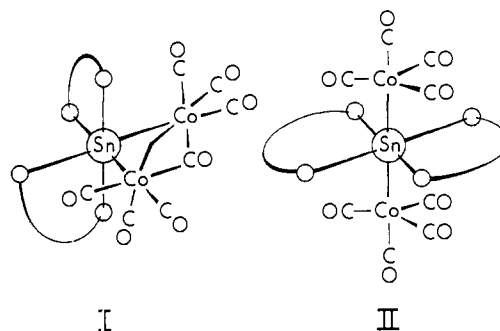
Bis(2,4-pentanedionato)chloro(tetracarbonylcobalt)tin(IV), $(\text{acac})_2\text{ClSnCo}(\text{CO})_4$.—A solution of 9.3 mmoles of $\text{NaCo}(\text{CO})_4$ in THF was added to 6.1 g (15.8 mmoles) of $(\text{acac})_2\text{SnCl}_2$ in the same solvent at room temperature with stirring. After 10 min THF was removed *in vacuo* and the residue extracted with *n*-pentane. Cooling the extract to -20° produced a mixture of dark red needles of $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ and light orange crystals of product. The crystals were hand separated and the crystals of product recrystallized twice from *n*-pentane at -20° affording 0.05 g of yellow crystals, mp $109\text{--}110^\circ$.

Anal. Calcd for $(\text{C}_5\text{H}_7\text{O}_2)\text{ClSnCo}(\text{CO})_4$: C, 32.1; H, 2.7; O, 24.5; Cl, 6.8. Found: C, 31.4; H, 2.9; O, 25.7; Cl, 5.0.

Carbonyl stretching bands were observed at 2096 (s), 2034 (s), 2022 (s), and 2009 (s) cm^{-1} .

Discussion

As previously noted, the compound $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$ is most reasonably assigned structure I. The composition is established by elemental analysis and



by an exact mass determination on the m/e 632 peak of the mass spectrum. Neither of these methods absolutely excludes the possibility that the compound is an octacarbonyl; analytical differences are slight, and other tin derivatives of cobalt carbonyl are known in which the highest observed m/e is one CO group less than the molecular ion.⁴ However, the single strong infrared band at 1836 cm^{-1} , clearly due to a bridging carbonyl group, and five medium to strong bands in the terminal region (Figure 1a) support the heptacarbonyl structure I.

The structure proposed preserves approximately octahedral geometry for both tin and cobalt. The cobalt–cobalt bond, pictured as bent, results in an inert gas configuration for the cobalt atoms in this diamagnetic compound. Structure I can be regarded as derived from the dicobalt octacarbonyl structure by replacing one of the bridging carbonyl groups with the $(\text{acac})_2\text{Sn}$ moiety. From this viewpoint, it is related to

the structure of $\text{HC}=\text{CHC}(\text{O})\text{OCCo}_2(\text{CO})_7$, in which two cobalt atoms are bridged by a carbon atom of a lactone ring.⁹

The nmr spectrum of I, while not inconsistent with the proposed structure, does not establish it unambiguously. In benzene solution only two signals were observed, at τ 5.62 and 8.99 in an intensity ratio of 1:5.8 clearly due to the CH and CH_3 protons of the 2,4-pentanedionato ligands. However, for a *cis* configuration of acac rings, there are two pairs of nonequivalent methyl groups, and a splitting of the methyl signal might be expected, as is the case with $(\text{acac})_2\text{SnCl}_2$.¹⁰ No indication of splitting was observed, however. Since the splitting is not expected to be large (it was only 0.02 ppm for benzene solutions of the $(\text{acac})_2\text{Sn}$ dihalides), it may have been obscured by quadrupole broadening of the signal caused by the cobalt atoms. Also, it has been reported that splitting in the *cis* dihalides is not observed at higher temperatures, and

(8) G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 372 (1924).

(9) O. S. Mills and G. Robinson, *Proc. Chem. Soc.*, 156 (1958).

(10) J. A. S. Smith and E. J. Wilkins, *Chem. Commun.*, 381 (1965).

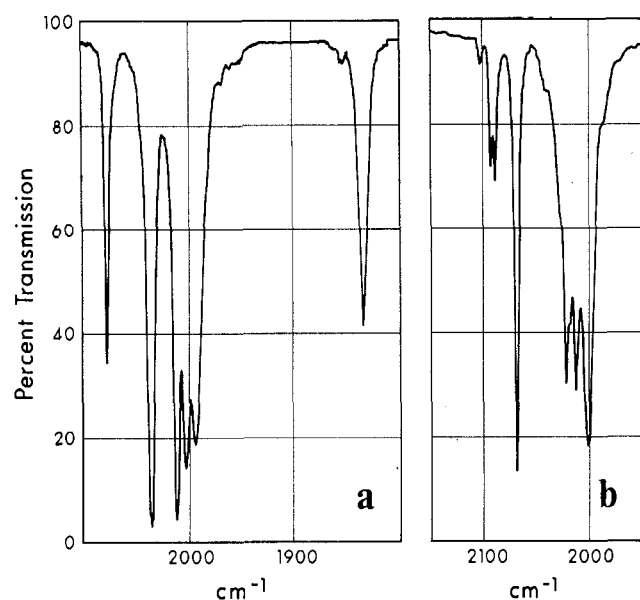


Figure 1.—Carbonyl stretching region of the infrared spectrum in cyclohexane solutions: (a) $(\text{acac})_2\text{SnCo}_2(\text{CO})_7$; (b) $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$.

either of the averaging mechanisms suggested in that case may operate here at lower temperatures.¹¹

Further investigation of the reaction has shown that I is formed as the main product isolable by pentane extraction only where the $\text{NaCo}(\text{CO})_4$ solution is mixed rapidly with $(\text{acac})_2\text{SnCl}_2$. By very slow addition of the carbonylate solution to the tin compound, a different product is obtained. Elemental analysis suggests the formula $(\text{acac})_2\text{Sn}[\text{Co}(\text{CO})_4]_2$, while only terminal carbonyl bands are present in the infrared spectrum. The highest fragment observed in the mass spectrum corresponds to $[(\text{acac})_2\text{SnCo}_2(\text{CO})_7]^+$, which we consider to be one CO group less than the molecular ion. The fragmentation pattern is rather similar to that of I, but has in addition a peak at 489 due to $[(\text{acac})_2\text{SnCo}(\text{CO})_4]^+$. There is also one at 377 due to $[(\text{acac})_2\text{SnCo}]^+$ which is relatively weak in I.

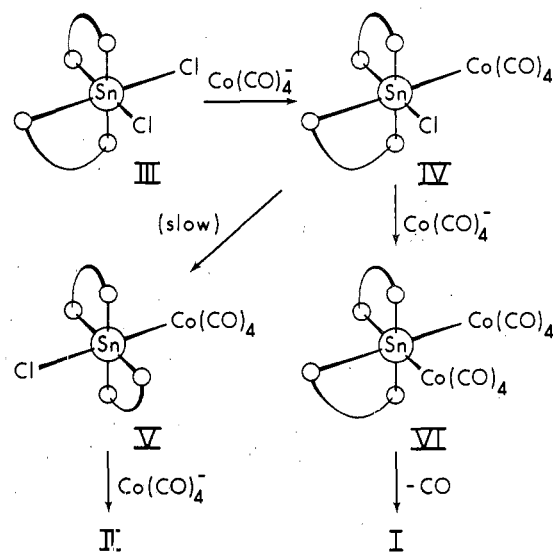
These facts are consistent with the *trans* structure II for the second product. In II, the individual Sn-Co bonds can break more easily than in the triangular SnCo_2 grouping of I, giving rise to a more abundant $[(\text{acac})_2\text{SnCo}]^+$ peak. Also, the fragment $[(\text{acac})_2\text{SnCo}(\text{CO})_4]^+$ would not be expected to result easily from I, since it would involve breaking of Sn-Co, Co-Co, and Co-CO bonds.

The infrared spectrum of II in the carbonyl stretching region (Figure 1b) shows that only terminal carbonyl groups are present.¹² This compound provides a striking example of the effect of conformational changes on the symmetry-predicted infrared spectra of metal carbonyls, to which attention has previously been drawn.^{13,14} The conformation shown in II has C_{2v}

symmetry, for which seven infrared-active carbonyl stretching bands are expected ($3 A_1 + 3 B_1 + B_2$). Rotation of one $\text{Co}(\text{CO})_4$ group by 60° about the tin-cobalt bond leads to C_i symmetry, with only four bands expected in the infrared. Other conformations may give rise to a full eight bands. We count seven or eight bands in Figure 1b and attribute the shoulders to ^{13}C effects. This is well above the "local symmetry" value of four, indicative of appreciable coupling of CO groups across the three intervening metal atoms. Such coupling is also observed in four-coordinate tin derivatives.²

An examination of the molecular weight of II in cyclohexane solution showed that association occurs at higher concentrations. The compound was essentially monomeric at 1 mg/ml and about 12% associated at 27 mg/ml, the highest concentration studied. Association has been observed in other 2,4-pentanedionato complexes,¹⁵ and may result in this case from a change of chelating acac groups to bridging bidentate ligands.

The decisive influence of rate of addition on the products of the reaction can be plausibly accounted for. Previous work has indicated that $(\text{acac})_2\text{SnCl}_2$ has a *cis* configuration as shown in III.^{10,11} Displacement of chloride ion by an initial $\text{Co}(\text{CO})_4^-$ anion would produce the intermediate *cis*- $(\text{acac})_2\text{SnClCo}(\text{CO})_4$, IV. It is postulated that IV isomerizes to the *trans* configuration V relatively slowly. Rapid addition of a second mole of $\text{Co}(\text{CO})_4^-$ would result in displacement of chloride from IV before isomerization could occur; this would produce the *cis*-bis(tetracarbonylcobalt) intermediate, VI, which is assumed to eliminate carbon monoxide in an intramolecular condensation, yielding I, in which the cobalt-cobalt bond holds the molecule in the *cis* arrangement. Slow addition of $\text{Co}(\text{CO})_4^-$ anion permits IV to isomerize to V, and the product is then II.



Facile condensation of the intermediate IV seems reasonable because the Co-Sn-Co bond angle must approximate 90° . Bis-tetracarbonylcobalt derivatives of four-coordinate tin do not spontaneously undergo

(11) J. W. Faller and A. Davison, *Inorg. Chem.*, **6**, 182 (1967).
 (12) At higher concentrations, the relative intensities of the 2091- and 2088- cm^{-1} bands are reversed. The age of the cyclohexane solution also influences the relative intensities of these bands in an irreproducible way.
 (13) J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1365 (1967).
 (14) W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967).

(15) J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 370 (1966).

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 $\text{RSn}[\text{Co}(\text{CO})_4]_3$, 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 $\text{ClSn}[\text{Co}(\text{CO})_4]_3$ implies that one process involves displacement of the acac ligands.

(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: $\text{Fe-Sn-Fe} = 128.6^\circ$ in $\text{Cl}_2\text{Sn}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ (J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, **6**, 968 (1967)); $\text{Mn-Sn-Mn} = 117^\circ$ in $(\text{C}_5\text{H}_5)_2\text{Sn}[\text{Mn}(\text{CO})_2]_2$ (B. T. Kilbourne and H. M. Powell, *Chem. Ind. (London)*, 1578 (1964)); $\text{Fe-Ge-Fe} = 128^\circ$ in $\text{Cl}_2\text{Ge}[\text{Fe}(\text{CO})_2\text{C}_5\text{H}_5]_2$ (M. A. Bush and P. Woodward, *Chem. Commun.*, 166 (1967)).

It was possible to isolate the monochloro derivative $(\text{acac})_2\text{SnClCo}(\text{CO})_4$ in very low yield by using a large excess of $(\text{acac})_2\text{SnCl}_2$. 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 $(\text{acac})_2\text{Sn}(\text{CH}_3)_2$ has been reported to have the *trans* structure,¹⁷ it is reasonable to expect that the electropositive $\text{Co}(\text{CO})_4$ groups would occupy *trans* positions in II and that the mixed derivative V might also be *trans*.

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

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

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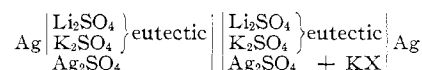
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The association constants for the formation of AgX , AgX_2^- , and Ag_2X^+ have been evaluated from electromotive force measurements in Ag_2SO_4 – Li_2SO_4 – K_2SO_4 mixtures to which KBr or KI has been added. The temperature dependence for the association 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 theory² 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



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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(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).