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Covalency of Metal-Ligand Bonds in Hexabromostannates(IV) Studied by the Pure Quadrupole Resonance of Bromine

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The pure quadrupole resonance of bromine was observed in potassium hexabromostannate(IV) and ammonium hexabromostannate(IV). The potassium complex showed a triplet, indicating the presence of at least three kinds of non-equivalent bromine atoms in the crystals. The ammonium complex gave rise to a single resonance line in agreement with the results of X-ray analysis. The covalent character of Sn–Br bonds calculated from the observed quadrupole coupling constants is smaller and the net charge on the central metal atom is greater than those of the corresponding platinum or palladium complexes. This is explained in terms of the smaller electronegativity of tin and the difference between the electronic structures of Sn^{IV} and Pt^{IV} (or Pd^{IV}).

Introduction

In a series of papers,[2–4] we have reported the results of study on the pure quadrupole resonance of halogens in hexahaloplatinates(IV), hexahalopalladates(IV), and hexahalotellurates(IV). By means of an analysis through the Townes-Dailey procedure,[5] the covalent character of metal-ligand bonds was evaluated and discussed in relation to the electronic structure of these complexes. Whereas the inner d orbitals of palladium(IV) and platinum(IV) ions (4d for Pd, 5d for Pt) are partially filled with electrons, leaving vacant orbitals available for the d^2sp^3 hybridization, the 4d orbitals of both tin and tellurium ions are completely occupied. Unlike a tellurium(IV) ion, in which the 5s orbital is filled, a tin(IV) ion has a vacant 5s orbital. The present investigation has been undertaken in order to discuss the nature of Sn–Br bonds in potassium hexabromostannate(IV) and ammonium hexabromostannate(IV).

Experimental

Apparatus.—A self-quenching super-regenerative spectrometer already described[2] was employed for the determination of the frequencies of the pure quadrupole resonance of bromine.

Materials.—Potassium hexabromostannate(IV)[6] was prepared by adding potassium bromide to the solution of tin(IV) tetrabromide in hydrobromic acid containing a small amount of bromine. Pale yellow crystals were separated and recrystallized from the mixture of dilute hydrobromic acid and a small quantity of bromine. *Anal.* Calcd. for K_2SnBr_6: Br, 70.9. Found: Br, 70.6. Ammonium hexabromostannate(IV)[6] was prepared from ammonium bromide and tin(IV) tetrabromide and was recrystallized in a similar manner. It formed pale yellow crystals. *Anal.* Calcd. for $(NH_4)_2SnBr_6$: Br, 75.6. Found: Br, 75.3.

Results and Discussion

Measurements were made at liquid nitrogen, Dry Ice, and room temperatures. The known ratio of quadrupole moments of bromine isotopes, ^{79}Br and ^{81}Br, was used to identify the bromine resonance lines. The observed resonance frequencies of ^{79}Br at these temperatures are listed in Table I. Additional measurements were made at intermediate temperatures in order to follow the temperature dependence of the frequency of each multiplet component correctly. The curves of multiplet frequencies plotted against temperature are gently sloping downward with increasing

TABLE I

PURE QUADRUPOLE RESONANCE FREQUENCIES AND QUADRUPOLE COUPLING CONSTANTS OF BROMINE IN HEXABROMOSTANNATES(IV)

Compound	Multiplet components	Frequency, Mc./sec.[a]			*eQq*, Mc./sec.
		23.0°	−72°	Liquid N_2 temp.	
K_2SnBr_6	I	128.71	129.83	130.53	261.14
	II	128.02	128.73	129.17	
	III	127.12	129.52	132.00	
$(NH_4)_2SnBr_6$		126.53	126.87	...[b]	253.74

[a] Experimental errors are estimated at ±0.05 or less.
[b] No resonance line was observed.

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[2] D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5783 (1960).

[3] K. Ito, D. Nakamura, Y. Kurita, K. Ito, and M. Kubo, *ibid.*, **83**, 4526 (1961).

[4] D. Nakamura, K. Ito, and M. Kubo, *ibid.*, **84**, 163 (1962).

[5] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

[6] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 7, Longmans, Green and Co., London, 1940, p. 456; B. Rayman and K. Preis, *Ann. Chem.*, **223**, 326 (1884).

temperature and are slightly convex upward as in the case of hexahalotellurates(IV).[4]

Potassium hexabromostannate(IV) showed a triplet at all temperatures studied, revealing the presence of at least three kinds of non-equivalent bromine atoms in the crystals of this compound. The multiplet components, I, II, and III, of the triplet changed the order of frequency values with temperature. The frequencies of II and III coincide with each other at a temperature (*ca.* −25°) between room and Dry Ice temperatures, while those of I and II coincide at a temperature (*ca.* −100°) between Dry Ice and liquid nitrogen temperatures. Although potassium hexabromostannate(IV) was found to crystallize in a slightly distorted potassium hexachloroplatinate(IV) structure,[7] complete crystal analysis has not been performed as yet. The observed X-ray powder patterns of this compound are similar to those of potassium hexaiodoplatinate(IV), potassium hexabromotellurate(IV), potassium hexaiodotellurate(IV), and ammonium hexaiodotellurate(IV), all of which show triplet resonance lines of halogens.[2,4] Accordingly, it is suggested that these compounds are isomorphic with one another.

Ammonium hexabromostannate(IV) showed a single resonance line at all temperatures studied between room and Dry Ice temperatures. This agrees with the results of X-ray analysis,[7,8] which have shown that this compound forms potassium hexachloroplatinate(IV) type crystals. A search for the corresponding resonance line at liquid nitrogen temperature was unsuccessful.

From the observed quadrupole resonance frequencies (data available at the lowest temperature of observation were used and the frequencies of the triplet components were averaged) the quadrupole coupling constants were evaluated as shown in Table I. The covalent character, $1 - i$, of Sn–Br bonds and the net charge ρ on a tin atom were calculated by[5]

$$eQq = (1 - i)(1 - s)(eQq)_{\text{atom}}$$
$$\rho = 4 - 6(1 - i)$$

where $(eQq)_{\text{atom}}$ denotes the atomic quadrupole coupling constant, i is the extent of ionic character, and s is the extent of s-character in the bonding orbital of the halogen. In accordance with Dailey and Townes' assumption,[9] $s = 15\%$ was used throughout. The results are shown in Table II, in which potassium hexabromoplatinate(IV) and potassium hexabromopalladate(IV)[3] are included for comparison.

TABLE II

THE COVALENT CHARACTER OF METAL–LIGAND BONDS, THE NET CHARGE, AND THE ELECTRONEGATIVITY OF THE CENTRAL METAL ATOM

Compound	Covalent character	Net charge	Electronegativity
K_2SnBr_6	0.40	1.60	1.7
$(NH_4)_2SnBr_6$	.39	1.66	1.7
K_2PtBr_6	.62	0.28	2.1
K_2PdBr_6	.63	.22	2.0

The covalent character of Sn–Br bonds is smaller than those of the corresponding bonds in platinum and palladium complexes by as much as about 0.2. Conceivable reason for this is twofold. In the first place, the electronegativity (1.7) of a tin atom[10] is smaller than that of platinum and palladium atoms by about 0.4. The small electronegativity of the central atom decreases the covalent character of metal–ligand bonds. We already have found[2,3] from the results for potassium hexahaloplatinates(IV) and hexahalopalladates(IV) that the change of covalent character with the difference between electronegativities of the central metal atom and the ligand atom is $d(1 - i)/d(\chi_M - \chi_X) = 0.30$ to a good approximation. Since the electronegativity difference $\chi_{Pt} - \chi_{Sn}$ is 0.4, one may expect a decrease in the covalent character of Sn–Br bonds below that of Pt–Br bonds by only 0.12 rather than by 0.22 as was actually found. Secondly, bond orbitals involved in the Sn–Br bonds are different from those of Pt–Br and Pd–Br bonds, because the 4d orbitals of a tin(IV) ion are filled, whereas the 4d and 5d orbitals of palladium(IV) and platinum(IV) ions, respectively, are partially occupied. Accordingly, whereas platinum(IV) can avail itself of six bonding orbitals resulting from the $5d^26s6p^3$ hybridization, tin(IV) uses one 5s and three 5p orbitals for bond formation, 5d orbitals being less important. Conceivable resonance structures are I, II (IIa and IIb), and III (IIIa and IIIb) having zero, one, and two positive charges on the tin atom, respectively, contribution from those having three or more charges being disregarded.

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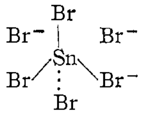
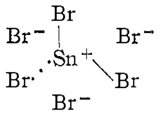
[7] G. Markstein and H. Nowotny, *Z. Krist.*, **100**, 265 (1938).

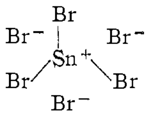
[8] R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948.

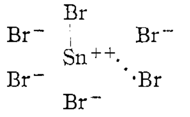
[9] B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).

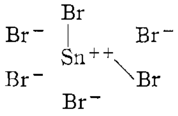
[10] For instance, W. Gordy and W. J. O. Thomas, *ibid.*, **24**, 439 (1956).


I (24)


IIa (48)


IIb (8)


IIIa (30)


IIIb (12)

Here, full lines and broken lines indicate bonds involving the p orbital and the s orbital, respectively. There are 24 equivalent structures for type I, while the II and III types have 56 and 42 structures, respectively. The predominance of types II and III over I is contrasted with the case of hexabromoplatinates(IV), in which structures having a vanishing charge on the platinum atom are the most important, as has been discussed already.[4] The increase in the positive charge on the central atom implies increase in the ionic character or decrease in the covalent character of metal–ligand bonds.

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Association Constants of Silver(I) and Cyanide Ions in Molten Equimolar Sodium Nitrate–Potassium Nitrate Mixtures

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Electromotive force measurements were used to evaluate the association constants K_1, K_2, and $K_{1,2}$ for the formation of AgCN, $Ag(CN)_2^-$, and Ag_2CN^+, respectively, in dilute solutions of Ag^+ and CN^- in molten equimolar $NaNO_3$–KNO_3 mixtures at 246, 286, and 326°. The very strong associations necessitated measurements at extremely low concentrations in order to evaluate the association constants. Values of K_1, K_2, and $K_{1,2}$ in mole fraction units are 230,000, 140,000, and 80,000 at 246°; 220,000, 105,000, and 60,000 at 286°; and 190,000, (50,000), and (36,000) at 326°. The entropies of association of the ion pair involving the diatomic CN^- (and the polyatomic SO_4^{-2} previously measured) are much more positive than for the association of Ag^+ with the monatomic ions Cl^- and Br^- and are larger than the "configurational" contribution to the entropy of association calculated from the quasi-lattice model.

Introduction

In previous papers[2] it has been shown that the temperature coefficients of some of the association constants for the monatomic ions Ag^+ with Cl^-, or Br^-, in molten nitrates are correctly predicted by the quasi-lattice theory.[3] It is of interest to test the theory for associations involving polyatomic ions to see what influence changes of the internal (including rotational) degrees of freedom of ions involved in the association process will have on the temperature coefficients of the association constants. In this report measurements are presented on solutions of Ag^+ and CN^- ions in molten equimolar mixtures of $NaNO_3$ and KNO_3. The only prior measurements in molten salts involving a polyatomic ligand were for the association of Ag^+ and SO_4^{-2} in molten KNO_3.[4] It also may be noted that values of K_1 do not appear to have been measured in water for the association of Ag^+ and CN^-.

Electromotive force measurements in the cell

Ag	$AgNO_3$ NaCN $NaNO_3$–KNO_3 (50–50) mole %	$AgNO_3$ NaCN $NaNO_3$–KNO_3 (50–50) mole %	Ag

were made and used to calculate the association constants K_1, K_2, and $K_{1,2}$ for the formation of AgCN, $Ag(CN)_2^-$, and Ag_2CN^+, respectively. The association constants are very high and measurements at extremely low concentrations of Ag^+ and CN^- were required to evaluate them.

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(1) Operated for the United States Atomic Energy Commission by Union Carbide Corporation.

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(2) See, for example, M. Blander, F. F. Blankenship, and R. F. Newton, *J. Phys. Chem.*, **63**, 1259 (1959); J. Braunstein and M. Blander, *ibid.*, **64**, 10 (1960); A. Alvarez-Funes, J. Braunstein, and M. Blander, *J. Am. Chem. Soc.*, **84**, 1538 (1962).

(3) M. Blander, *J. Chem. Phys.*, **34**, 432 (1961); M. Blander, *J. Phys. Chem.*, **63**, 1262 (1959).

(4) W. J. Watt and M. Blander, *ibid.*, **64**, 729 (1960).