The Nature of the Metal-Ligand Bonds in Hexahalostannates(IV) and Ammonium Hexachloroplumbate(IV) Studied by the Pure Quadrupole Resonance of Halogens

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We have previously observed the pure quadrupole resonance of halogens in various metal halide complexes and discussed the nature of the metal-ligand bonds in these complexes.[1-6] From the investigations of hexahalo complexes, it has been brought to light that the covalent character of the metal-ligand bonds is linearly dependent only on the electronegativity difference between metal and ligand atoms in the case of central metal ions having the same outer electronic configuration. Both tin and lead have the same outer electronic configuration, different from those of selenium, tellurium, palladium and platinum, the hexahalo complexes of which have already been studied. The present investigation of hexahalostannates(IV) and ammonium hexachloroplumbate(IV) has been undertaken in order to confirm the above conclusion and to establish a linear relation between the ionic character of tin-halogen (or lead-halogen) bonds and the electronegativity difference between metal and halogen atoms.

Experimental

Materials. — Potassium hexachlorostannate(IV), ammonium hexachlorostannate(IV) and rubidium hexachlorostannate(IV) were prepared[7] by adding potassium chloride, ammonium chloride and rubidium chloride respectively to a solution of tin(IV) tetrachloride in hydrochloric acid containing a small amount of chlorine. All these compounds were separated as white crystals. Ammonium hexachloroplumbate(IV) was synthesized[8] by adding ammonium chloride to a solution of lead(IV) tetraacetate in concentrated hydrochloric acid. Yellow crystals were obtained. Rubidium hexabromostannate(IV) was prepared[9] from rubidium bromide and tin(IV) tetrabromide. Pale yellow crystals were separated and washed with concentrated hydrobromic acid containing a small quantity of bromine. Rubidium hexaiodostannate(IV) was obtained[10] by adding rubidium iodide to an alcoholic solution of hydrogen iodide. It formed black crytals. For identifying all these compounds, except for ammonium hexachloroplumbate(IV), quantitative analysis was made for halogens. All the samples were treated with an alkaline solution. Subsequently, the volumetric determination of the halogens was carried out by Volhard-Drechel's method. Ammonium hexachloroplumbate(IV) was identified by its X-ray powder patterns[11] as taken with a Norelco X-ray diffractometer.

Calcd. for K_2SnCl_6: Cl, 51.9. Found: Cl, 51.8. Calcd. for $(NH_4)_2SnCl_6$: Cl, 57.9. Found: Cl, 57.8. Calcd. for Rb_2SnCl_6: Cl, 42.3. Found: Cl, 42.0. Calcd. for Rb_2SnBr_6: Br, 62.3. Found: Br, 62.3. Calcd. for Rb_2SnI_6: I, 72.4. Found: I, 72.0.

Apparatus. — Self-quenching super-regenerative spectrometers which have already been described[1] were employed for the determination of the frequencies of the pure quadrupole resonance of halogens. A hexane thermometer was used in the range from −80 to 0°C.

Results and Discussion

Measurements were made at liquid nitrogen, dry ice and room temperatures. Additional measurements were carried out on potassium hexachlorostannate(IV) at 5~10°C intervals between dry ice and room temperatures for the determination of the transition points. The results are shown in Table I, from which data of less abundant isotopes ^{37}Cl and ^{81}Br are omitted because they give correct isotope frequency ratios.

Potassium hexachlorostannate(IV) yielded a single resonance line at room temperature, in

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

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

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

[4] K. Ito, K. Ito, D. Nakamura and M. Kubo, This Bulletin, **35**, 518 (1962).

[5] D. Nakamura, K. Ito and M. Kubo, *Inorg. Chem.*, **1**, 592 (1962).

[6] D. Nakamura, K. Ito and M. Kubo, ibid., **2**, 61 (1963).

[7] W. E. Henderson and W. C. Fernelius, "Inorganic Preparation," McGraw-Hill Book Co., Inc., New York (1935), p. 118.

[8] H. S. Booth, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York (1939), p. 49.

[9] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 7, Longmans, Green and Co., London (1940), p. 456.

[10] J. C. Bailar, Jr., "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., Inc., New York (1953), p. 121.

[11] ASTM Cards. 1-0163, American Society for Testing Materials.

TABLE I. PURE QUADRUPOLE RESONANCE FREQUENCIES OF HALOGENS IN HEXAHALOSTANNATES(IV) AND AMMONIUM HEXACHLOROPLUMBATE(IV)

Compound	Temp., °C	Frequency Mc./sec.
K_2SnCl_6	25.5	15.065±0.002
	−76	15.379±0.003
		15.507±0.003
		15.548±0.003
	Liquid N_2	15.73 ±0.05
$(NH_4)_2SnCl_6$	23.0	15.474±0.002
	−76	15.539±0.003
	Liquid N_2	15.61 ±0.03
		15.65 ±0.03
Rb_2SnCl_6	23.0	15.60 ±0.02
	−77	15.61 ±0.02
	Liquid N_2	15.63 ±0.03
$(NH_4)_2PbCl_6$	20.6	17.061±0.002
	−76	17.142±0.003
	Liquid N_2	17.26 ±0.05
Rb_2SnBr_6	23.5	128.34 ±0.03
	−77	128.62 ±0.05
	Liquid N_2	128.91 ±0.05
Rb_2SnI_6	20.1	130.48 ±0.10
	Liquid N_2	132.57 ±0.10

agreement with its cubic structure of the potassium hexachloroplatinate(IV) type as established by X-ray analysis.[12,13] As the temperature was lowered, the single resonance line was observed to disappear at about −9.5°C. The resonance frequency measured at −6.6°C was 15.068 Mc./sec. The temperature coefficient of the resonance line was about zero in the range from 5 to −8°C. As the temperature was raised, the resonance line appeared abruptly at about −8.5°C. These observations prove the existance of a transition point in the vicinity of −8.5°C. Below this transition point, at least two resonance lines were barely observed. Accordingly, the crystal structure of this compound is less symmetric below the transition point. At the dry ice temperature, three resonance lines were clearly observed. Therefore, another transition point might be expected to exist between the first transition point and the dry ice temperature, as has already been observed in the case of potassium hexabromoselenate(IV). However, above −70°C the intensity of the resonance lines was too weak to permit the determination of another transition point definitely. At the liquid nitrogen temperature, two weak resonance lines were observed, revealing the presence of at least one transition point between dry ice and liquid nitrogen temperatures. In their study of heat capacity,[17] Morfee et al. have reported no transition except for a λ-point, which is in agreement with the first transition point mentioned above.

Ammonim hexachlorostannate(IV) showed a single absorption line at room and dry ice temperatures. This indicates that all the chlorine atoms in the crystal are crystallographically equivalent, a fiinding which is in agreement with the results of X-ray structural analysis.[12] At the liquid nitrogen temperature, two very weak resonance lines were observed. Although Morfee et al. have obtained a normal heat capacity curve[14] between dry ice and liquid nitrogen temperatures, at least one transition point is likely to exist in this temperature range, because doublet absorption lines were observed at the liquid nitrogen temperature.

Rubidium hexachlorostannate(IV), ammonium hexachloroplumbate(IV) and rubidium hexabromostannate(IV) yielded a single absorption line at all the temperatures studied, as was expected from the potassium hexachloroplatinate(IV)-type structure established by X-ray analysis.[15]

Rubidium hexaiodostannate(IV) showed a very weak single resonance line, ν_1, at room and liquid nitrogen temperatures, in agreement with the results of X-ray crystal analysis.[16] At the dry ice temperature, no resonance line could be observed. As the nuclear spin of ^{127}I is 5/2, two resonance lines, ν_1 and ν_2, are expected to be observed. Our attempt to find the ν_2 resonance frequency was, however, unsuccessful, probably because the sensitivity of our spectrometer was low in this frequency range.

Since the crystals of hexahalostannates(IV) and hexachloroplumbates(IV) are known to consist of cations and complex anions with the O_h symmetry,[17] the asymmetry parameter of the electric field gradient about the halogen nucleus vanishes. Therefore, the quadrupole coupling constant, eQq (in Mc./sec.), is equal to twice the resonance frequency for the case of a 3/2 nuclear spin and to 20/3 times the ν_1 resonance frequency for a 5/2 nuclear spin.[18]

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12) G. Engel, *Z. Krist.*, **90**, 341 (1935).

13) H. E. Swanson, N. T. Gilfrich and M. I. Cook, "Standard X-ray Diffraction Powder Patterns," NBS Circular 539, Vol. 6 (1956), p. 38.

14) R. G. S. Morfee, L. A. K. Staveley, S. T. Walters and D. L. Wigley, *J. Phys. Chem. Solids*, **13**, 132 (1960).

15) See Ref. 12 for Rb_2SnCl_6 and $(NH_4)_2PbCl_6$. For Rb_2SnBr_6: J. A. A. Ketelaar, A. A. Rietdijk and C. H. Staveren, *Rec. trav. chim.*, **56**, 907 (1937).

16) W. Werker, ibid., **58**, 257 (1939).

17) R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York (1948).

18) See for instance, T. P. Das and E. L. Hahn, "Solid State Physics," Supplement 1. Academic Press, Inc., New York (1958).

From the calculated quadrupole coupling constants (data at liquid nitrogen temperature were used, and the frequencies of the doublet components were averaged), the ionic character, *i*, of the metal-halogen bonds was evaluated by Townes and Dailey's procedure.[19,20] Fifteen per cent *s*-hybridization of the halogen σ bond orbitals was assumed in accordance with the data of Dailey and Townes.[20] From the evaluated ionic character, *i*, of the metal-halogen bonds, the net charge, ρ, on a central metal atom was calculated by

$$\rho = 4 - 6(1 - i)$$

The results are given in Table II, in which the corresponding data for hexahalotellurates(IV)[4] and hexabromostannates(IV)[5] are included for purposes of comparison.

TABLE II, THE QUADRUPOLE COUPLING CONSTANT OF ^{35}Cl, ^{79}Br AND ^{127}I AT LIQUID NITROGEN TEMPERATURE, THE IONIC CHARACTER, *i*, OF METAL-LIGAND BONDS, AND THE NET CHARGE, ρ, ON A CENTRAL METAL ATOM IN HEXAHALO COMPLEXES

Compound	*eQq* Mc./sec.	*i*	ρ
K_2SnCl_6	31.46	0.66	1.96
$(NH_4)_2SnCl_6$	31.26	0.66	1.96
Rb_2SnCl_6	31.26	0.66	1.96
$(NH_4)_2PbCl_6$	34.52	0.63	1.78
K_2SnBr_6[a]	261.1	0.60	1.60
$(NH_4)_2SnBr_6$[a]	253.7	0.61	1.66
Rb_2SnBr_6	257.8	0.61	1.66
Rb_2SnI_6	883.8	0.55	1.30
$(NH_4)_2TeCl_6$[b]	30.27	0.68	2.08
R_2TeBr_6[b,c]	273.5	0.58	1.48
R_2TeI_6[b,d]	1017.6	0.48	0.88

a) See Ref. 5.
b) See Ref. 4.
c) Average over R=K, NH_4, Cs and NMe_4.
d) Average over R=K, NH_4, Rb and Cs. Data of Rb_2TeI_6 to be published.

The ionic character of the tin-halogen bonds in hexahalostannates(IV) decreases with the decreasing electronegativity difference between tin(IV) and halogens, as has already been observed for various complexes.[1-6] Judging from the same electronegativity values of the central metal atoms, it is reasonable to assume that the extent of the ionic character of hexachlorostannates(IV) is very close to that of ammonium hexachloroplumbate(IV). The electronegativity values selected by Gordy were used in this paper.[21]

Although tin(IV) and lead(IV) are more electropositive than tellurium (as much as 0.3 in electronegativity units), the extent of the ionic character for hexachlorostannates(IV) and ammonium hexachloroplumbate(IV) is almost equal to that of ammonium hexachlorotellurate(IV). This fact must be attributed to the difference in the electronic structure of the central metal atoms. We have already pointed out, from the results for hexabromostannates(IV),[5] that a tin(IV) atom has one 5s orbital, as well as three 5p orbitals, available for forming bonds with halogen atoms in a $[SnX_6]^{2-}$ ion. On the other hand, tellurium(IV) can use only three 5p orbitals for bond formation.[4] Therefore, tin(IV)-halogen bonds are more covalent in character than tellurium(IV)-halogen bonds, if the electronegativity differences between metal and ligand atoms are the same. This interpretation is also valid for ammonium hexachloroplumbate(IV), because the outer electronic configuration of a lead(IV) atom is equivalent to that of a tin(IV) atom provided that all the principal quantum numbers are increased by one.

In a preceding paper[6] we reported, on the basis of a study of various hexahalo complexes, that the covalent character of the bonds between a central metal atom, M, and ligands, X, is in linear relation to the electronegativity difference $\Delta\chi = \chi_X - \chi_M$. The present investigation adds another series of linear relations, as is illustrated in Fig. 1. The three straight lines in Fig. 1 indicate that the only factor

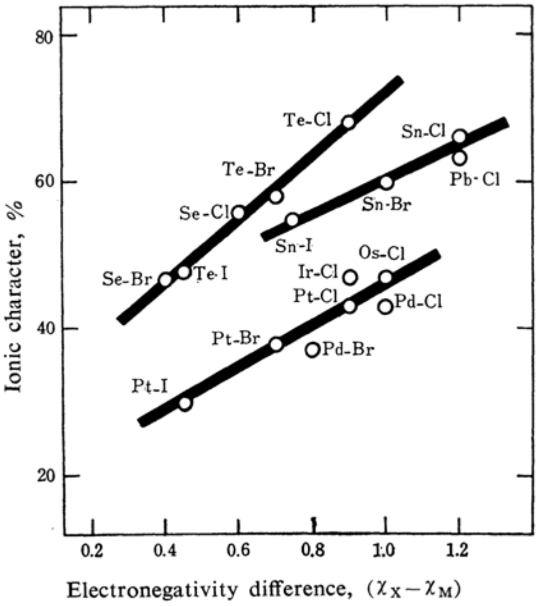

Fig. 1. Dependence of the ionic character of metal-ligand bonds in hexahalo complexes on the difference between the electronegativities of ligands and the central atom.

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[19] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).
[20] B. P. Dailey and C. H. Townes, ibid., **23**, 118 (1955).
[21] W. Gordy and W. J. O. Thomas, ibid., **24**, 439 (1956).

determining the ionic character of the metal-ligand bonds in a hexahalo complex is the electronegativity difference between ligands and the central metal atom if the central metal atoms belong to the same family of the periodic table. This linear relation offers useful information, because with it one can estimate the extent of ionic character of metal-ligand bonds whenever necessary data are avaialable for hexahalo complexes.

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