stants for the complex species formed in 0.1 *M* Na_2CO_3 and in 0.1 *M* $Na_4P_2O_7$ are roughly equal, and that carbonate is bound much more tightly than sulfate, fluoride, bromide, and chloride.

U(VI) forms well defined $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$ species in solution with over-all stability constants, according to the work of Babko and Kodenskaya,[10] of 3.7×10^{15} and 5×10^{20}, respectively. The complexes of Am(VI) are similar to those of U(VI) in being readily precipitated by barium and calcium ions and absorbed by anion exchange resins in the carbonate form. The infrared spectra of solid sodium americyl(VI) carbonates establish the persistence of the O–Am(VI)–O group, and the presence of complexed carbonate or bicarbonate. However, under conditions which yield $Na_4UO_2(CO_3)_3$, an isostructural Am(VI) carbonate is not obtained. This result, together with the pronounced change in the Am(VI) spectrum in carbonate, suggests that Am(VI) exhibits a greater tendency toward hydrolysis or polymerization than does U(VI) in the presence of carbonate ion.

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Covalency of Metal–Ligand Bonds in Hexahaloselenates(IV) Studied by the Pure Quadrupole Resonance of Halogens

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The pure quadrupole resonance of halogens in some hexahaloselenates(IV) was observed at various temperatures. These complexes show a single resonance line, indicating that all halogen atoms in each compound are crystallographically equivalent except for potassium hexabromoselenate(IV) at temperatures below −33°. For this compound, three transition points are located between room and Dry Ice temperatures. The ionic character of selenium–halogen bonds and the net charge on a selenium atom were evaluated by means of the Townes–Dailey procedure. The covalent character plotted against the electronegativity difference between selenium and halogens practically coincides with the corresponding plot of hexahalotellurates(IV), yielding a single straight line. The net charge on the selenium atom is approximately equal to a unit positive charge, in agreement with the theoretical prediction based on the electronic configuration of a selenium atom.

Introduction

In discussing the nature of metal–ligand bonds in metal complexes, often use is made of rather vague terms such as covalent character, ionic character, and the hybrid of these in order to explain various properties of the complex compounds. However, in order to establish these concepts in a quantitative manner and to express the transition from ideal covalent bonds to pure ionic bonds, one must define the extent of covalent character by resorting to some experimental parameters that are characteristic of metal–ligand bonds and are measurable accurately. Pure quadrupole resonance frequencies can afford to give the necessary information. According to this definition, the covalent character of a metal–ligand bond is $1 - i$, where the ionic character i is given by the number of electrons belonging to the ligand atom in a metal complex minus the number of electrons in a free ligand atom.

We have observed the pure quadrupole resonance frequencies of halogens in a number of hexahalo complexes and discussed the covalent character of metal–ligand bonds in these complexes.[1–4] Conclusions were derived that for a given central atom the covalent character decreases with increasing electronegativity of halogens and that the electronic configuration of the central atom plays a major role in determining the covalent character of metal–ligand bonds and in varying the net charge on central atoms to a considerable extent. In order to gain some insight into this problem, it is of interest to study hexahaloselenates(IV) and compare the results with those of hexahalotellurates(IV) already studied, because selenium and tellurium have the same outer electronic configuration but differ in their electronegativities by as much as 0.3.[5]

Experimental

Apparatus.—Super-regenerative spectrometers already described[1] were used for the determination of the pure quadrupole resonance of halogens.

Materials.—A commercial preparation of selenous acid, H_2SeO_3, was dissolved in concentrated hydrochloric acid. On passing hydrogen chloride through the solution, to which potassium chloride was added in advance, potassium hexachloroselenate(IV) precipitated.[6] The precipitates were washed with concentrated hydrochloric acid and dried in a stream of hydrogen

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

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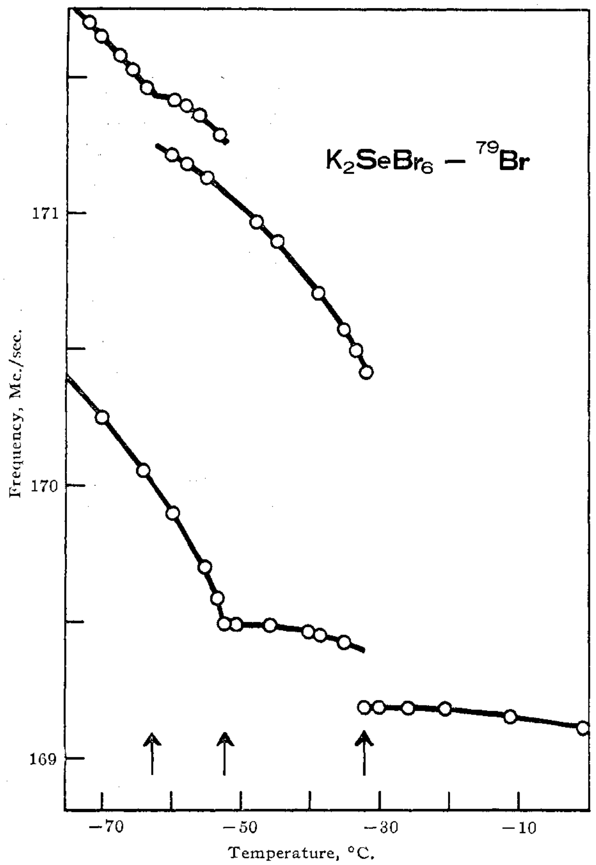

Fig. 1.—Transition points of potassium hexabromoselenate(IV) as revealed by the temperature dependence of pure quadrupole resonance frequencies.

chloride. Ammonium hexachloroselenate(IV) was prepared in a similar manner. The volumetric determination of chlorine in these compounds and of bromine in complexes described below was carried out after Volhard-Drechsel's method. *Anal.* Calcd. for K_2SeCl_6: Cl, 57.5. Found: Cl, 56.8. Calcd. for $(NH_4)_2SeCl_6$: Cl, 64.9. Found: Cl, 64.4.

Potassium, cesium, and ammonium hexabromoselenates(IV) were synthesized by adding potassium, cesium, and ammonium bromides, respectively, to a solution of selenium dioxide in concentrated hydrobromic acid.[7] The precipitates were washed with concentrated hydrobromic acid and dried over phosphorus pentoxide. *Anal.* Calcd. for K_2SeBr_6: Br, 75.3. Found: Br, 75.4. Calcd. for Cs_2SeBr_6: Br, 58.2. Found: Br, 57.8. Calcd. for $(NH_4)_2SeBr_6$: Br, 80.7. Found: Br, 80.5.

Results and Discussion

Measurements were made at liquid nitrogen, Dry Ice, and room temperatures. 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.

TABLE I

PURE QUADRUPOLE RESONANCE FREQUENCIES OF HALOGENS IN HEXAHALOSELENATES(IV)

Compound	Temp., °C	Frequency, Mc./sec.
K_2SeCl_6	21.5 ± 0.3	20.431 ± 0.001
	−70 ± 1	20.513 ± .001
	Liquid N_2	20.576 ± .003
$(NH_4)_2SeCl_6$	22.6 ± 0.3	20.693 ± .001
	−70 ± 1	20.770 ± .025
	Liquid N_2	20.877 ± .025
K_2SeBr_6	20.3 ± 0.3	169.036 ± .008
	−72 ± 1	171.69 ± .06 170.32 ± .06
	Liquid N_2	173.599 ± .015 173.285 ± .008 172.389 ± .015
Cs_2SeBr_6	19.0 ± 0.3	176.61 ± .05
	−76 ± 1	177.02 ± .05
	Liquid N_2	177.44 ± .05
$(NH_4)_2SeBr_6$	20.0 ± 0.3	171.357 ± .008
	−71 ± 1	171.957 ± .010
	Liquid N_2	172.623 ± .008

Potassium hexachloroselenate(IV) and ammonium hexachloroselenate(IV) showed a single resonance line at all temperatures studied, indicating that all chlorine atoms are crystallographically equivalent in each compound. This agrees with the results of X-ray analysis of the latter compound,[8] which has been found to crystallize in a face-centered cubic lattice of the potassium hexachloroplatinate(IV) type. Since no X-ray data have been available for the former compound, we have taken its powder patterns by means of a Norelco X-ray diffractometer. This compound is very hygroscopic, but is stable in a sealed tube. Therefore, the sample was coated with a Mylar film and investigated. The results of X-ray diffraction indicated that this compound forms a face-centered cubic lattice with its lattice constant $a = 9.861$ Å. Table II gives the comparison of calculated with observed $\sin^2 \theta$ values (θ = the Bragg angle) for various reflection planes characterized by the Miller indices, *hkl*, the Kα line of copper being used throughout.

Potassium hexabromoselenate(IV) gives rise to a single resonance line at room temperature and two lines at Dry Ice temperature, suggesting the presence of a transition point between these two temperatures. Therefore, frequency measurements were made at intermediate temperatures. The results were much more complicated than expected: three transition points were located at −33, −52, and −64°, as shown in Fig. 1. A single frequency was observed at temperatures above the first transition point, below which two resonance lines appeared, the signal-to-noise ratio of one line at a lower frequency being about twice as great as that of the other. Below the second transition point, another line was observable. The resulting three resonance lines showed almost equal intensity. One of them disappeared below the third transition point. At liquid nitrogen temperature, three resonance lines were observed. Accordingly, at least one transition point exists between Dry Ice and liquid nitrogen temperatures. The X-ray crystal analysis has shown that this compound forms cubic crystals at room temperature.[9] Evidently, the crystal lattice is less symmetric below the first transition point.

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TABLE II

COMPARISON OF CALCULATED WITH OBSERVED $\sin^2 \theta$ VALUES FOR POTASSIUM HEXACHLOROSELENATE(IV)[a]

hkl	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$	Intensity
111	0.0184	0.0183	Strong
200	.0244	.0244	Weak
220	.0489	.0488	Medium
311	.0672	.0671	Medium
222	.0734	.0732	Very strong
400	.0978	.0978	Strong
331	.1161	.1159	Very weak
420	.1219	.1220	Very weak
422	.1463	.1464	Weak
333, 511	.1648	.1648	Weak
440	.1952	.1952	Strong
531	.2134	.2135	Weak
442, 600	.2195	.2196	Very weak
533	.2625	.2623	Very weak
622	.2682	.2684	Very weak
444	.2928	.2928	Medium

[a] Calibration was made by means of the standard reflection angle of silicon. It was confirmed that the Mylar film yielded a broad line centered at $\theta = 12.9°$ and that potassium chloride formed by the partial decomposition of the sample gave rise to weak reflections. These lines are not listed in this table.

TABLE III

COMPARISON OF CALCULATED WITH OBSERVED $\sin^2 \theta$ VALUES FOR CESIUM HEXABROMOSELENATE(IV)

hkl	$\sin^2 \theta_{obs}$	$\sin^2 \theta_{calc}$	Intensity
111	0.0155	0.0156	Weak
220	.0415	.0415	Weak
311	.0569	.0570	Very weak
222	.0623	.0622	Very strong
400	.0829	.0829	Strong
422	.1244	.1244	Very weak
333, 511	.1399	.1399	Very weak
440	.1661	.1658	Medium
531	.1811	.1814	Very weak
620	.2069	.2073	Very weak
622	.2280	.2280	Weak
444	.2485	.2487	Very weak
551, 711	.2644	.2643	Very weak
642	.2902	.2902	Very weak
800	.3314	.3316	Very weak

Both cesium hexabromoselenate(IV) and ammonium hexabromoselenate(IV) yielded a single resonance line at all temperatures of the present investigation. Therefore, it is concluded that all bromine atoms in each compound are crystallographically equivalent, in agreement with the results of X-ray crystal analysis of the latter compound.[10] Since no X-ray crystal data were available for the former compound, powder patterns were recorded by means of a Norelco X-ray diffractometer. They could be interpreted as arising from a face-centered cubic lattice having $a = 10.7_0$ A. Table III shows the adequacy of the present analysis.

The crystals of hexahaloselenates(IV) are known[11] to consist of cations and complex anions $[SeX_6]^{2-}$ having O_h symmetry. In fact, various hexahaloselenates(IV) having the same halogen atoms as ligands and differing in cations show quadrupole resonance frequencies that are independent of the kind of cations in the complex compounds and are characteristic of the complex anion in question within an accuracy of 3% or less. This suggests that the effect of neighboring ions on a complex anion in question is negligibly small. One may discuss the electronic structure of a single complex anion disregarding the effect of its surroundings, as already has been pointed out in our previous paper.[12] Since the asymmetry parameter $\eta = 0$ for O_h symmetry, the nuclear quadrupole coupling constant eQq (in Mc./sec.) is given by twice the observed frequency[13] (data at liquid nitrogen temperature being used). The covalent character, $1 - i$, of metal–halogen bonds is defined by Townes and Dailey[14] as

$$eQq = (1 - i)(1 - s)(eQq)_{atom}$$

where $(eQq)_{atom}$ denotes the atomic quadrupole coupling constant and s is the extent of s-character in the bonding orbital of the halogen. Gordy[15] has assumed that $s = 0$, while Dailey and Townes[16] have assumed that the atomic orbital of halogen has 15% s-character when the halogen atom is bonded to an atom more electropositive than the halogen by as much as 0.25 unit. In the following calculations, it is assumed tentatively that $s = 15\%$. The net charge ρ on a selenium atom is given by

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

because the tetrapositive formal charge on a selenium atom is partially neutralized by negative charges migrating from halogen ions through coördination bonds. The results are shown in Table IV, in which the corresponding data for hexahalotellurates(IV) are included for comparison.

TABLE IV

THE QUADRUPOLE COUPLING CONSTANTS OF ^{35}Cl AND ^{79}Br AT LIQUID NITROGEN TEMPERATURE, THE COVALENT CHARACTER, $1 - i$, OF Se–X BONDS, AND THE NET CHARGE, ρ, ON A SELENIUM ATOM IN HEXAHALOSELENATES(IV)

Compound	eQq, Mc./sec.	$1 - i$	ρ
K_2SeCl_6	41.15	0.44	1.36
$(NH_4)_2SeCl_6$	41.75	.45	1.30
K_2SeBr_6	346.2	.53	0.82
Cs_2SeBr_6	354.9	.54	.76
$(NH_4)_2SeBr_6$	345.2	.53	.82
$(NH_4)_2TeCl_6$	30.27	.32	2.08
M_2TeBr_6	273.50[a]	.42	1.48

[a] Average over M = K, Cs, NH_4, and $N(CH_3)_4$.

In accordance with the increase in the electronegativity of selenium (2.4) over that of tellurium (2.1),[5] the covalent character of Se–X bonds is greater than that of Te–X bonds in the corresponding complexes. The difference in the extents of covalent character is

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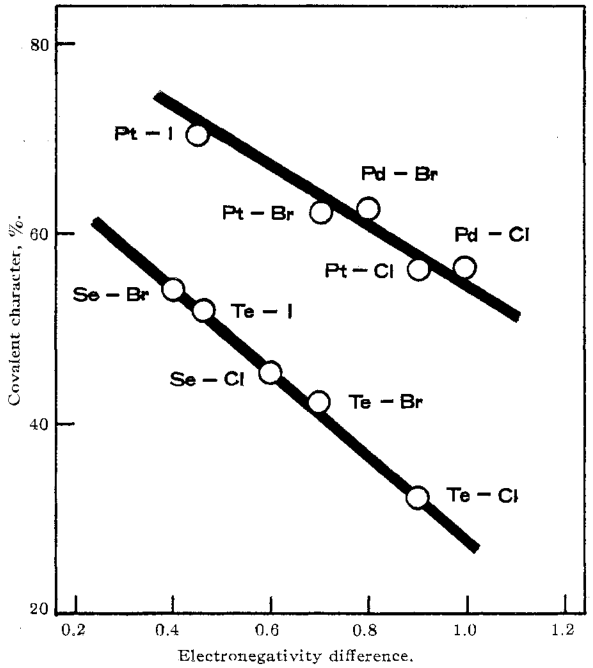

Fig. 2.—Dependence of the covalent character of metal–ligand bonds in hexahalo complexes on the difference between the electronegativities of ligands and the central atom.

0.12 for hexachloro complexes and 0.11 for hexabromo complexes. The close agreement of the two values with each other suggests that the covalent character of bonds between the central atom M and ligands X is in linear relation to the electronegativity difference $\Delta\chi = \chi_X - \chi_M$. The relation between the covalent character and $\Delta\chi$ is shown in Fig. 2. It will be seen that hexahaloselenates(IV) and hexahalotellurates(IV), having the same outer electronic configuration of the central atoms, yield a single straight line, while the data for hexahaloplatinates(IV) and hexahalopalladates(IV) lie approximately on another straight line. This simple rule of linearity is useful, because it permits one to estimate the extent of covalent character of M–X bonds whenever necessary data are available for complexes of analogous structure.

The net charge on a selenium atom in these complexes is close to a unit charge rather than to zero, as might be expected from Pauling's electroneutrality principle.[17] We already have pointed out that tellurium(IV), having an outer electronic configuration $4d^{10}5s^2$, can avail itself of only three 5p orbitals for forming bonds with halogen in a $[TeX_6]^{2-}$ ion, because 5d and 6s orbitals are less stable than 5p orbitals and accordingly no significant resonance structures carrying no formal charge on the central atom are conceivable. The same reasoning applies to hexahaloselenates(IV) provided that all principal quantum numbers are reduced by one. The observed net charge on a selenium atom ranging over 0.8–1.3*e* is consistent with this theoretical conclusion.

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The Chelate Effect Studied by Calorimetry, Potentiometry, and Electron Spin Resonance

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The thermodynamics of chelation of complexes of 2,2′-bipyridine and pyridine with Mn(II), Ni(II), Cu(II), and Zn(II) were studied by calorimetry and potentiometry. The chelate stabilization for pyridine is of the same order as that for ethylenediamine complexes. The enthalpy and entropy contributions to the chelate effect are analyzed, the former being significant for the Cu(II) and Ni(II) ions. The chelate effect is further divided into cratic and unitary portions. Possibilities of using electron spin resonance as a tool in studying complex stabilities are illustrated. Good agreement is obtained between e.s.r. and traditional measurements.

Introduction

The pyridine and bipyridine systems of transition metal complexes provide an excellent pair for studying the bonding of chelates. Previous work on the thermodynamics of bipyridine complexes[2] has developed methods for the systematic investigation of a variety of ligands with transition metal ions employing both calorimetry and potentiometry. The chelate effect was defined by Schwarzenbach[3] as the added stability conferred upon a complex containing bidentate or higher order ligands as compared with that from unidentate ligands. The effect can be studied if a suitable coördinating ligand and its corresponding dimer can be found. Spike and Parry[4] studied the chelate effect with primary amines and discussed enthalpy effects with Cu(II). Schwarzenbach[2] studied ethylenedi-

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(1) Department of Chemistry, University of Missouri, Columbia, Mo. Abstracted in part from Ph.D. Thesis of J. E. Bauman, University of Michigan, 1961. This work was supported by the National Institutes of Health (CF-12,177).

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