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

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The pure quadrupole resonances of halogens in eight hexahalotellurates(IV) were determined at liquid nitrogen, Dry Ice and room temperatures. Some of these complexes show a single resonance line in agreement with the results of X-ray analysis. Others give rise to a triplet, suggesting less symmetric crystal structures. From the observed quadrupole coupling constants, the covalent character of Te-X bonds was calculated by means of Towns-Dailey procedure. The covalent character 0.3-0.5 is smaller than that of the corresponding bonds in hexahaloplatinates(IV) and hexahalopalladates(IV) by as much as about 0.20, in spite of practically the same electronegativity of tellurium, platinum and palladium. The net charge on a tellurium atom amounts to a unit charge or more in contradiction to the electroneutrality principle. This was explained in terms of the electronic configuration of a tellurium ion.

Introduction

The nature of metal-ligand bonds in metal complexes has been discussed both theoretically¹ and experimentally,² but the quantitative estimation of the covalent character of these bonds still leaves much to be desired. In a series of papers,³ the present authors have reported the results of measurements on the nuclear quadrupole resonances of halogens in a variety of platinum and palladium complexes. An analysis of the data by means of Towns-Dailey's procedure⁴ has led, among other things, to the conclusion that the covalent character of a metal-ligand bond was affected by the oxidation number (formal charge) and the coordination number of the central metal ion, besides being dependent on the difference between the electronegativities of atoms involved in the bond.

The present investigation on hexahalotellurates(IV) has been undertaken because tellurium has an electronic structure quite different from that of platinum or palladium. Accordingly, comparison of the present results with those on platinum and palladium complexes already reported will give valuable information on the effect of the electronic configuration of the central ion on the metal-ligand bonds.

Experimental

Apparatus.—Self-quenching super-regenerative spectrometers and an externally quenched super-regenerative spectrometer already described³ were employed for the determination of the frequencies of pure quadrupole resonance. For strong lines of bromine and iodine appearing in the frequency range 100-250 Mc., a new externally quenched spectrometer⁵ was preferable to the self-quenching type, because the resonance frequencies could be determined more accurately at the expense of sensitivity.

Materials.—Ammonium hexachlorotellurate(IV), potassium hexabromotellurate(IV), ammonium hexabromotellurate(IV), cesium hexabromotellurate(IV) and tetramethylammonium hexabromotellurate(IV) were synthesized by

methods found in the literature.⁶ Potassium, ammonium and cesium hexaiodotellurates(IV) were prepared in a similar manner as black crystals. Since no data were available in the literature for identifying these new compounds, quantitative analysis was made for iodine and tellurium. For this purpose, the samples of these compounds were treated with an alkali. Subsequently, the volumetric determination of iodine was carried out after Volhard-Drechsel's method. For the gravimetric determination of tellurium the complexes were reduced with sulfurous acid and hydrazine hydrochloride and the resulting precipitate of tellurium was weighed.

Anal. Calcd. for K_2TeI_6 : I, 78.7; Te, 13.2. Found: I, 78.9; Te, 13.1. Calcd. for $(NH_4)_2TeI_6$: I, 82.3; Te, 13.8. Found: I, 82.2; Te, 14.2. Calcd. for Cs_2TeI_6 : I, 65.9; Te, 11.1. Found: I, 66.2; Te, 11.7.

Results

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 (Cl^{37} and Br^{81}) are omitted, because they give correct isotope frequency ratios. The resonance frequencies plotted against temperature are not strictly linear; the curves are slightly convex upwards as confirmed by additional measurements carried out on some of the complexes at 5-15° intervals between Dry Ice and room temperatures. Based on this temperature dependence, along with the relation $2\nu_1 \geq \nu_2$, the designation of multiplet components can be made as shown in the last column of Table I.

Ammonium hexachlorotellurate(IV) showed a single resonance line at all temperatures studied, indicating that all chlorine atoms are crystallographically equivalent. This agrees with the results of X-ray analysis,⁷ which has shown that the compound forms potassium hexachloroplatinate(IV) type crystals.

Potassium hexabromotellurate(IV) gave rise to a triplet revealing the presence of at least three kinds of nonequivalent bromine atoms. The multiplet components of the triplet changed the order of frequency values with temperature: the frequencies of multiplet components II and III coincide with each other at a temperature (*ca.* -40°) between room and Dry Ice temperatures. The powder pattern of this compound taken with a Norelco X-ray diffractometer resembled that of potassium hexachloroplatinate(IV) but showed a greater number of diffraction lines. The pattern could be interpreted

(6) W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 189

(7) G. Engel, *Z. Krist.*, **A90**, 341 (1935).

(1) J. C. Bailar, Jr., and D. H. Busch, "The Chemistry of the Coordination Compounds," Reinhold Publ. Corp., New York, N. Y., 1956; F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958; J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge Univ. Press, New York, N. Y., 1961.

(2) J. Owen, *Discussions Faraday Soc.*, **19**, 127 (1955); K. D. Bowers and J. Owen, *Repts. Progr. in Phys.*, **18**, 304 (1955).

(3) D. Nakamura, Y. Kurita, K. Ito and M. Kubo, *J. Am. Chem. Soc.*, **82**, 5783 (1960); K. Ito, D. Nakamura, Y. Kurita, K. Ito and M. Kubo, *ibid.*, **83**, 4526 (1961).

(4) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949); B. P. Dailey and C. H. Townes, *ibid.*, **23**, 118 (1955); B. P. Dailey, *Discussions Faraday Soc.*, **19**, 255 (1955).

(5) S. Kojima, K. Tsukada, A. Shimauchi and Y. Hinaga, *J. Phys. Soc. Japan*, **9**, 795 (1954).

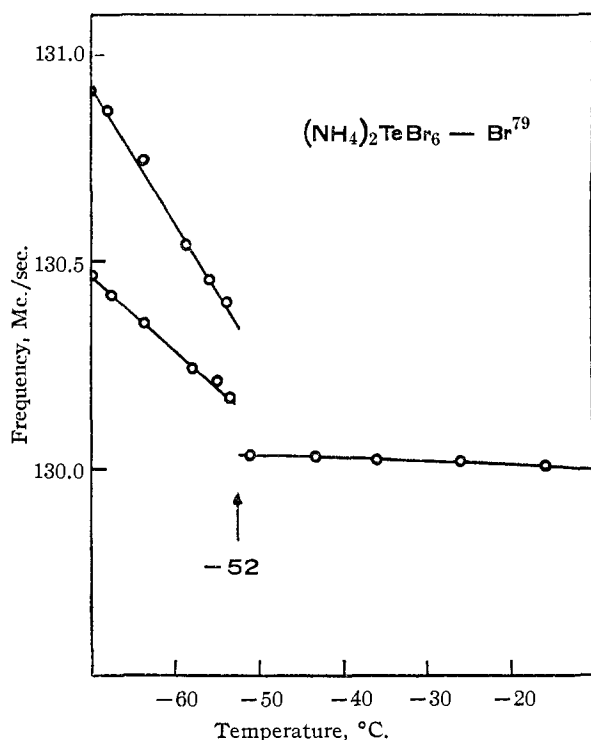


Fig. 1.—The temperature dependence of the pure quadrupole resonance frequencies of Br^{79} in ammonium hexabromotellurate(IV).

fairly well with a tetragonal lattice having $a = 10.6_1 \text{ \AA}$. and $c/a = 0.97_5$ resulting from the contraction of a potassium hexachloroplatinate(IV) type cubic lattice along one of its crystal axes. The appearance of triplet lines, however, suggests a quasi-tetragonal structure of still lower symmetry.

Ammonium hexabromotellurate(IV) yielded a single absorption line at room temperature in agreement with its cubic structure of the potassium hexachloroplatinate(IV) type as found by X-ray analysis.⁸ At the lower temperatures studied, it showed a triplet, two lines of which were barely resolvable at Dry Ice temperature. One line on the high-frequency side was weaker than the other, the separation between them being less than 10 kc. The observed frequencies are plotted against temperature in Fig. 1. A transition point at -52° is obvious. Another transition point is likely to exist between Dry Ice and liquid nitrogen temperatures, because otherwise the frequencies of the multiplet components plotted against temperature would show an abnormal behavior. This compound changed its color from red to orange on cooling at about -20° . At liquid nitrogen temperature, the color was pale yellow. Color change was noticed also for other hexabromotellurates (IV) regardless of whether or not a transition point was indicated by the temperature dependence of the observed resonance frequencies.

Cesium hexabromotellurate(IV) showed a single absorption line at all temperatures studied, as expected from the potassium hexachloroplatinate(IV) type structure found by X-ray analysis.⁹ Tetra-

(8) L. M. Manojlovic, *Bull. Inst. Nuclear Sci. "Boris Kidrich" (Belgrade)*, **7**, 79 (1957).

methylammonium hexabromotellurate(IV) also gave rise to a single line although the observed X-ray powder pattern indicated a crystal structure quite different from that of potassium hexachloroplatinate(IV).

Both ν_1 and ν_2 of potassium and ammonium hexaiodotellurates(IV) consisted of triplet lines. The X-ray powder patterns of these compounds were similar to that of potassium hexabromotellurate(IV): they could be interpreted fairly well with tetragonal lattices having $a = 11.5_0 \text{ \AA}$, $c/a = 0.98_0$ and $a = 11.5_4 \text{ \AA}$, $c/a = 0.98_4$, respectively. However, the triplets suggest less symmetric crystal structure of these two compounds.

Cesium hexaiodotellurate(IV) crystals showed a single line in agreement with the results of experiments on the X-ray powder pattern, which showed that this compound was isomorphous with potassium hexachloroplatinate(IV) and that $a = 11.6_4 \text{ \AA}$.

Potassium hexachlorotellurate(IV) showed a resonance signal at about 15 Mc./sec., which was too weak to be determined accurately. Cesium, tetramethylammonium, tetraethylammonium, tetrapropylammonium and trimethyl-benzylammonium hexachlorotellurates(IV), tetraethylammonium, tetrapropylammonium and trimethyl-benzylammonium hexabromotellurates(IV) and tetramethylammonium, tetraethylammonium, tetrapropylammonium and trimethyl-benzylammonium hexaiodotellurates(IV) also were synthesized and tested, but no absorption signals were observed.

Discussion

The data of ν_1 and ν_2 of hexaiodotellurates(IV) can be used with the tabulated values of Livingston and Zeldes¹⁰ to yield the values of quadrupole coupling constants and asymmetry parameters. The asymmetry parameter of cesium hexaiodotellurate(IV) showing a singlet resonance line was practically zero, whereas those of other hexaiodotellurates(IV) giving rise to a triplet were finite. The small asymmetry parameters are attributable to the effect of neighboring ions in a crystal¹¹ and also to thermal motion, because no finite asymmetry parameter is expected for an isolated $[\text{TeX}_6]^{--}$ ion having a perfect octahedral structure. In calculating the quadrupole coupling constants from the single observed frequencies of the hexachlorotellurate(IV) and hexabromotellurates(IV), η was assumed to be zero, because it was presumed to be small. The temperature coefficient of the observed frequencies was of the correct order of magnitude. The results are shown in Table II.

The quadrupole coupling constants of compounds having the same complex anion are close to one another regardless of the difference of cations eventually accompanied by the difference in crystal structure. This suggests that the coupling constant is characteristic of a complex anion $[\text{TeX}_6]^{--}$ rather than of a complex compound $\text{M}_2\text{-}$

(9) K. W. Bagnall, R. W. M. D'Eye and J. H. Freeman, *J. Chem. Soc.*, 3963 (1955).

(10) R. Livingston and H. Zeldes, "Table of Eigenvalues for Pure Quadrupole Spectra, Spin 5/2," Oak Ridge Natl. Lab.

(11) C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **20**, 35 (1952).

TABLE I
PURE QUADRUPOLE RESONANCE FREQUENCIES OF HALOGENS
IN HEXAHALOTELLURATES(IV)

Compound	Temp., °C.	Frequency, Mc./sec.	Designation of multiplet components
(NH ₄) ₂ TeCl ₆ ³⁵	26.0 ± 0.3	14.993 ± 0.015	
	-68 ± 1	15.041 ± .020	
	Liquid N ₂	15.137 ± .020	
K ₂ TeBr ₆ ⁷⁹	17.9 ± 0.3	133.477 ± .035	I
		133.001 ± .020	II
		132.520 ± .035	III
	-69 ± 1	134.719 ± .035	I
		134.084 ± .050	III
		133.817 ± .025	II
Liquid N ₂	135.946 ± .020	I	
	135.670 ± .015	III	
	134.496 ± .015	II	
(NH ₄) ₂ TeBr ₆ ⁷⁹	18.0 ± 0.3	129.943 ± .013	
	-70 ± 1	130.900 ± .060 ^a	
	Liquid N ₂	130.474 ± .035	
		135.062 ± .015	
		134.258 ± .015	
Cs ₂ TeBr ₆ ⁷⁹	16.8 ± 0.3	135.601 ± .010	
	-71.5 ± 1	135.782 ± .010	
	Liquid N ₂	135.962 ± .010	
(NMe ₄) ₂ TeBr ₆ ⁷⁹	16.5 ± 0.3	141.10 ± .05	
	-70 ± 1	141.89 ± .05	
	Liquid N ₂	142.58 ± .05	
K ₂ TeI ₆	17.5 ± 0.3	151.991 ± .015	I
		151.579 ± .020	II
		150.571 ± .008	III
	-69 ± 1	153.001 ± .020	I
		152.880 ± .025	II
		151.206 ± .008	III
	Liquid N ₂	154.250 ± .015	II
		154.095 ± .015	I
		151.878 ± .008	III
	K ₂ TeI ₆	20.4 ± 0.3	302.915 ± .025
302.502 ± .030			II
300.753 ± .015			III
-69 ± 1		304.952 ± .045	II
		304.780 ± .035	I
		301.964 ± .015	III
Liquid N ₂		307.353 ± .025	II
		300.603 ± .025	I
		303.230 ± .015	III
(NH ₄) ₂ TeI ₆		18.2 ± 0.3	150.331 ± .015
	149.552 ± .008		II
	148.154 ± .015		III
	-69 ± 1	151.721 ± .015	I
		150.218 ± .008	II
		149.206 ± .008	III
	Liquid N ₂	153.831 ± .008	
		152.165 ± .008	
		148.173 ± .015	
	20.5 ± 0.3	300.198 ± .025	I
298.858 ± .015		II	
296.080 ± .025		III	
303.230 ± .030		I	
300.286 ± .015		II	
297.873 ± .015		III	
Liquid N ₂	306.192 ± .015		
	302.335 ± .015		
	295.123 ± .025		

Cs ₂ TeI ₆	ν ₁	18.5 ± 0.3	153.219 ± .006
		-70 ± 1	153.648 ± .006
	ν ₂	Liquid N ₂	154.140 ± .006
		21.0 ± 0.3	306.402 ± .015
-70 ± 1		307.296 ± .015	
	Liquid N ₂	308.288 ± .015	

^a A closely spaced doublet. ^b The correspondence between the sets of triplet lines necessary for the designation is not clear owing to the existence of transition points.

TABLE II
QUADRUPOLE COUPLING CONSTANTS AND ASYMMETRY PARAMETERS OF Cl³⁵, Br⁷⁹ AND I¹²⁷ IN HEXAHALOTELLURATES(IV)

Compound	Temp., °C.	Multiplet component	eQq, Mc./sec.	η
(NH ₄) ₂ TeCl ₆	Liq. N ₂		30.27	0
K ₂ TeBr ₆	Liq. N ₂		270.74	0
(NH ₄) ₂ TeBr ₆	Liq. N ₂		266.18	0
Cs ₂ TeBr ₆	Liq. N ₂		271.92	0
(NMe ₄) ₂ TeBr ₆	Liq. N ₂		285.16	0
[TeBr ₆] ²⁻	Liq. N ₂		273.50 (average)	
K ₂ TeI ₆	20	I	1010.27 ± 0.06	0.050 ± 0.002
		II	1008.68 ± .07	.038 ± .003
		III	1002.71 ± .04	.030 ± .002
	-70	II	1017.00 ± .10	.045 ± .003
		I	1016.63 ± .08	.056 ± .002
		III	1006.82 ± .04	.034 ± .002
Liq. N ₂	II	1025.11 ± .05	.054 ± .002	
	I	1022.85 ± .06	.063 ± .002	
	III	1011.04 ± .04	.037 ± .001	
(NH ₄) ₂ TeI ₆	20	I	1000.92 ± .05	.031 ± .002
		II	996.33 ± .03	.023 ± .002
		III	987.06 ± .06	.020 ± .003
	-70	I	1010.98 ± .08	.023 ± .004
		II	1001.07 ± .04	.020 ± .002
		III	993.22 ± .04	.038 ± .001
Liq. N ₂		1021.41 ± .04	.061 ± .001	
		1008.82 ± .04	.071 ± .001	
		984.39 ± .06	.057 ± .002	
Cs ₂ TeI ₆	20	1021.39 ± .04	.004 ± .005	
	-70	1024.32 ± .03	.000 ± .008	
	Liq. N ₂	1027.60 ± .03	.000 ± .007	
[TeI ₆] ²⁻	Liq. N ₂	1017.38 (average)		

TeX₆, the chemical effect¹² being predominant over the crystal effects due to neighboring ions.

Townes and Dailey⁴ have shown that the quadrupole coupling constant of halogen can be related to the covalent character (1 - i) of the bond involving the halogen atom.

$$eQq = (1 - i)(1 - s)(eQq)_{\text{atm}}$$

where i denotes the ionic character of the bond; s = 0.15⁴ is the extent of s-character in the bonding orbital of the halogen; (eQq)_{atm}¹³ stands for the atomic quadrupole coupling constant. The net charge ρ on the central ion can be calculated by³

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

From the observed quadrupole coupling constants, the covalent character of Te-X bonds and the net charge on a tellurium atom were calculated as shown in Table III, in which potassium hexahalo-platinates(IV) and hexahalopalladates(IV) also are listed for comparison.

As observed for platinum and palladium complexes,³ the covalent character of metal ligand bonds in hexahalotellurates(IV) increases with decreasing difference between the electronegativities

(12) C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957); **30**, 1265 (1959).

(13) V. Jaccarino and J. G. King, *Phys. Rev.*, **83**, 471 (1951); J. G. King and V. Jaccarino, *ibid.*, **91**, 209 (1953); V. Jaccarino, J. G. King, R. A. Satten and H. H. Stroke, *ibid.*, **94**, 1798 (1954).

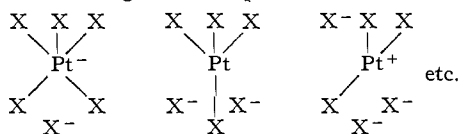
TABLE III
THE COVALENT CHARACTER OF Te-X BONDS AND THE NET
CHARGE ON A TELLURIUM ATOM^a

Compound	Covalent character	Net charge
(NH ₄) ₂ TeCl ₆	0.32	2.08
M ₂ TeBr ₆	.42	1.48
M ₂ TeI ₆	.52	0.88
K ₂ PtCl ₆	.56	.64
K ₂ PtBr ₆	.62	.28
K ₂ PtI ₆	.70	-.20
K ₂ PdCl ₆	.57	.58
K ₂ PdBr ₆	.63	.22

^a Data at liquid nitrogen temperature were used throughout.

of atoms forming the bond. In general, the covalent character of the Te-X bonds are smaller than those of the corresponding bonds in platinum and palladium complexes by as much as about 0.20. The net charge on a tellurium atom amounts almost to a unit charge or more, whereas that on a platinum or palladium atom is only a fraction of an electronic charge. The reason for this must be looked for in the electronic configuration of the central ion, because the electronegativity 2.1-2.2 of tellurium^{14,15} is practically identical with those of platinum and palladium and also because the oxidation number and the coordination number of the central tellurium atom are the same as those of a platinum or palladium atom in the complexes.

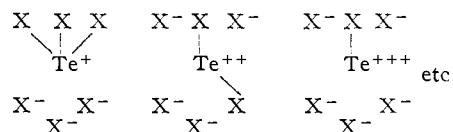
Platinum(IV) can form as much as six equivalent bonding orbitals from six atomic orbitals 5d²6s6p³. Accordingly, resonance among various electronic structures is possible of which the second one is presumed to be the most important in view of the observed net charge on the platinum atom. On the



(14) M. Hałssinsky, *J. phys. radium*, **7**, 7 (1946); H. O. Pritchard and H. A. Skinner, *Chem. Revs.*, **55**, 745 (1955); W. Gordy and W. J. O. Thomas, *J. Chem. Phys.*, **24**, 439 (1956).

(15) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1960, p. 93.

other hand, tellurium(IV) having an outer electronic configuration 4d¹⁰5s² can avail itself of only three 5p orbitals for forming bonds with halogen in a [TeX₆]⁻⁻ ion, because 5d and 6s orbitals are less stable than 5p orbitals by 6-7 e.v. in a neutral tellurium atom. Therefore, the nature of the Te-X bonds can be represented by a resonance hybrid among



It should be noted that no resonance structure having a vanishing formal charge on the central atom is conceivable. The observed formal charge on tellurium is greater by about a unit charge than that on platinum or palladium in the corresponding complex in agreement with this conclusion. Discussions given above do not exclude possible contribution of 5d and 6s orbitals to the bonding. The net charge less than unity allotted to a tellurium atom in hexaiodotellurates(IV) may be explained in terms of this contribution.

Another evidence in favor of the aforementioned resonance structures is afforded by consideration of Te-X bond lengths. Pauling¹⁵ pointed out that the Te-X distance¹⁶ in [TeCl₆]⁻⁻ and [TeBr₆]⁻⁻ is greater than the sum of covalent radii by 0.17-0.23 and 0.16 Å.; respectively. Later, he proposed¹⁷ an empirical formula for interatomic distances of fractional bonds.

$$D(n) - D(1) = -0.60 \log n$$

Here $D(n)$ is the bond length for bond number n (less than 1) and $D(1)$ is the bond length for a single bond of similar type (using similar bond orbitals). The equation gives $D(1/2) - D(1) = 0.18$ Å. and $D(1/3) - D(1) = 0.29$ Å. for hexachloro- and hexabromotellurate(IV) ions in agreement with the observed values.

(16) J. M. Bowen, *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London, 1958.

(17) Ref 15, p. 255.