

[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, NAGOYA UNIVERSITY, CHIKUSA, NAGOYA, JAPAN]

Covalency of Metal-Ligand Bonds in K_2PdCl_6 , K_2PdBr_6 , K_2PdBr_4 and K_2PtBr_4 Studied by the Pure Quadrupole Resonance of Halogens

BY KAZUO ITO, DAIYU NAKAMURA, YUKIO KURITA, KOJI ITO AND MASAJI KUBO

RECEIVED MAY 11, 1961

The pure quadrupole resonances of halogens in potassium hexachloropalladate(IV), hexabromopalladate(IV), tetrabromopalladate(II) and tetrabromoplatinate(II) were determined at liquid nitrogen, Dry Ice and room temperatures. Each of these complexes showed a single resonance line, indicating that all halogen atoms are crystallographically equivalent in agreement with the results of X-ray analysis. The covalent character of metal-halogen bonds calculated from the quadrupole coupling constant by means of the Townes-Dailey procedure varied from 0.40 to 0.63 depending on the formal charge on the central atom. However, the net charge on the central atom was always a fraction of an electronic charge.

Introduction

In a preceding paper,¹ we reported the results of study on the pure quadrupole resonances of halogens in potassium hexahaloplatinates(IV). It was shown that the nuclear quadrupole resonance frequencies afforded valuable information on the covalent character of metal-ligand bonds in these complexes. The results obtained by an analysis through Townes-Dailey's procedure² were in agreement with the conclusion derived by Collet,³ who studied the X-ray absorption spectra of bivalent and quadrivalent platinum complexes and showed that the net charge on the central atom was almost zero for these complexes. Besides, the results have given support to presumptions on the nature of metal-ligand bonds in complexes obtained from the observation of electron spin resonances of some paramagnetic complexes^{4,5} and other sources of information.^{6,7}

Similar observations were made on a few potassium hexahalopalladates(IV) as well as on potassium tetrabromopalladate(II) and tetrabromoplatinate(II). The results of analysis are presented in this paper.

Experimental

Apparatus.—A self-quenching super-regenerative spectrometer already described¹ was employed for the determination of the frequencies of pure quadrupole resonance of halogens.

Materials.—A commercial preparation of potassium tetrachloropalladate(II) was oxidized with chlorine. Potassium hexachloropalladate(IV) was obtained as brick red crystals.⁸ Commercially available palladium(II) bromide was dissolved in hydrobromic acid. The equivalent amount of potassium bromide was added to the solution. On evaporating the solution over a water bath, potassium tetrabromopalladate(II) separated as dark red brown crystals.⁹ Potassium hexabromopalladate(IV) was prepared by the reaction of potassium tetrabromopalladate(II) with bromine vapor.⁹ It formed black crystals. A commercial sample of potassium hexabromoplatinate(IV) was reduced with potassium oxalate.¹⁰ The resulting black crystals of potassium tetra-

bromoplatinate(II) were separated. These samples were washed with water and dried over phosphorus pentoxide in a desiccator. On drying, potassium tetrabromoplatinate(II) turned brown purple in color.

Results and Discussion

Measurements were made at liquid nitrogen, Dry Ice and room temperatures. The results are shown in Table I. The absorptions of both Br^{79} and Br^{81} were observed, the isotopic ratio of the resonance frequencies $\nu(Br^{79})/\nu(Br^{81})$ being 1.197 in agreement with values found in the literature within experimental errors. On the other hand, a single line attributable to the more abundant isotope Cl^{35} (abundance, 75.4 %) was observed for potassium hexachloropalladate(IV). Only the data of the more abundant isotopes, Cl^{35} and Br^{79} , are listed in Table I.

TABLE I

PURE QUADRUPOLE RESONANCE FREQUENCIES OF Cl^{35} AND Br^{79} IN SOME PALLADIUM AND PLATINUM COMPLEXES

Compound	Temp., °C.	Frequency, ^a Mc./sec.	Approximate S/N ratio
K_2PdCl_6	27	26.55	1.5-2
	-73	26.65	1.5-2
	Liq. N_2	26.75	1.5-2
K_2PdBr_6	27	201.81	7-8
	-73	202.43	7-8
	Liq. N_2	205.34	7-8
$K_2PdBr_4^b$	27	129.34	1.5-2
	-73	129.77	1.5-2
K_2PtBr_4	27	138.70	3-4
	-73	139.26	3-4
	Liq. N_2	139.84	2-3

^a The estimated error of the frequencies was within ± 0.05 Mc./sec. ^b No resonance line was observed at liquid nitrogen temperature.

The absorption of the less abundant isotope Cl^{37} (abundance, 24.6%) escaped detection, presumably for the following three reasons. In the first place, the signal-to-noise ratio of palladium complexes is approximately one half as great as that of the corresponding platinum complexes regardless of the coordination number and the kind of ligands, as shown in Table I and also in Table I of the preceding paper.¹ Secondly, the ratio decreases to about one fifth on substituting bromine in palladium and platinum complexes with chlorine. In addition, the S/N ratio of a tetracoordinated palladium or platinum complex is about one fifth as great as that of the corresponding hexacoordinated complex. In fact, it was not feasible to observe the absorption even of the more abundant isotope Cl^{35}

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in potassium tetrachloroplatinate(II) and potassium tetrachloropalladate(II).

Potassium hexachloropalladate(IV), which is red at room temperature, assumes an orange color at Dry Ice temperature, suggesting a phase transition taking place between these temperatures. However, this transition was not disclosed by the mean temperature coefficient of the absorption frequency, which was of the same order of magnitude as observed for potassium hexachloroplatinate(IV) undergoing no phase transition. The frequencies 26.6 and 201.8 Mc./sec. observed for potassium hexachloropalladate(IV) and potassium hexabromopalladate(IV) are very close to 25.8 and 200.2 Mc./sec. for the corresponding platinum complexes,¹ respectively. This indicates a striking similarity in electronic structures between these two pairs of complexes.

All the compounds studied showed a single resonance line, indicating that chlorine or bromine atoms are equivalent in a crystal in agreement with the results of X-ray crystal analysis. It has been reported¹¹ that both potassium hexachloropalladate(IV) and potassium hexabromopalladate(IV) have a crystal structure similar to that of potassium hexachloroplatinate(IV), in which all chlorine atoms are crystallographically equivalent. No reports are available in the literature on the crystal structures of potassium tetrabromopalladate(II) and potassium tetrabromoplatinate(II). Therefore, the X-ray powder patterns of these complexes were taken by means of a Norelco X-ray diffractometer. It was found that these compounds formed tetragonal crystals of the potassium tetrachloroplatinate(II) type,¹² in which all halogen atoms are mutually equivalent. The observed lattice constants were $a = 7.39$, $c = 4.28$ and $a = 7.36$, $c = 4.32$ Å. for these two compounds, respectively.

The pure quadrupole resonance frequency of a nucleus having a spin $I = 3/2$ is given by

$$\nu = \frac{1}{2} eQq (1 + \frac{1}{3}\eta^2)^{1/2}$$

where eQq and η denote the quadrupole coupling constant and the asymmetry parameter, respectively. In potassium hexachloroplatinate(IV) type crystals, the electric field gradient at a halogen atom has four-fold axial symmetry about the metal-halogen bond, leading to a vanishing asymmetry parameter. No such *ad hoc* reason exists for potassium tetrabromopalladate(II) and tetrabromoplatinate(II). However, since a finite asymmetry parameter often is attributed¹³ to the π -character of a bond between the halogen atom in question and the central metal atom, the asymmetry parameters of potassium tetrabromopalladate(II) and tetrabromoplatinate(II) are presumed for the following reasons to be much less than 0.06–0.13^{14–18} usually observed for chlorine

bonded with carbon. First, bromine has a small tendency to form a bond having a double bond character compared with chlorine.^{19,20} Secondly, the electronegativity of palladium or platinum, 1.9–2.2, is smaller than that of carbon, 2.5.^{1,21} Lastly, the $5p$ or $6p$ orbital of the central metal atom available for the formation of double bonds with ligands is much less stable than the $2p\pi$ orbital of carbon^{22,23} and is involved in conjugation, depending on its orientation, with the π -orbitals of two or four bromine atoms. Accordingly, the asymmetry parameter was assumed to be zero for these tetrabromo complexes. The quadrupole coupling constants of halogens calculated with $\eta = 0$ are shown in Table II.

TABLE II

QUADRUPOLE COUPLING CONSTANTS OF Cl^{35} AND Br^{79} IN SOME PALLADIUM AND PLATINUM COMPLEXES

Compound	Temp.	eQq , Mc./sec.
K_2PdCl_6	Liq. N_2	53.50
K_2PdBr_6	Liq. N_2	410.68
K_2PdBr_4	-73°	259.54
K_2PtBr_4	Liq. N_2	279.68

Townes and Dailey² have shown that the quadrupole coupling constant of halogen can be related to the ionic character i of the bond involving the halogen atom, the effect of π -character of the bond being disregarded.

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

where $(eQq)_{\text{atm}}$ denotes the atomic quadrupole coupling constant; s is the extent of s -character in the bonding orbital of the halogen. Gordy²⁴ has assumed that $s = 0$, while Dailey and Townes²⁵ have presumed 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. Since the latter authors' assumption seems to be more adequate, the covalent character, $1 - i$, of metal-halogen bonds in question was evaluated assuming $s = 0.15$. The net charge ρ on the central metal ion was calculated by $\rho = 4 - 6(1 - i)$ for hexacoordinated metal ions and by $\rho = 2 - 4(1 - i)$ for tetracoordinated ones. The results are shown in Table III, in which the data of potassium hexahaloplatinate(IV)¹ are included for comparison.

As already has been found for potassium hexahaloplatinate(IV), the covalent character of metal-ligand bonds in potassium hexahalopalladate(IV) also increases with decreasing electronegativity of halogens or with decreasing difference between the electronegativities of atoms forming the bond. Almost perfect agreement exists between the numerical magnitudes of the covalent character

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TABLE III
THE COVALENT CHARACTER OF METAL-HALOGEN BONDS
AND THE NET CHARGE ON THE CENTRAL METAL ATOM^a

Compound	Covalent character	Net charge
K ₂ PdCl ₆	0.57	0.58
K ₂ PdBr ₆	.63	.22
K ₂ PtCl ₆ ^b	.56	.64
K ₂ PtBr ₆ ^b	.62	.28
K ₂ PtI ₆ ^b	.70	-.20
K ₂ PdBr ₄	.40	.40
K ₂ PtBr ₄	.43	.28

^a Data at liquid nitrogen temperature were used except for K₂PdBr₄, for which those at Dry Ice temperature were employed. See ref. ^b to Table I. ^b See ref. 1.

of the metal-ligand bonds in potassium hexahalo-palladates(IV) and the corresponding hexahalo-platinates(IV). The same is true with potassium tetrabromopalladate(II) and tetrabromoplatinate(II). This is quite understandable, because palladium and platinum have electronic configurations similar to each other and almost the same electronegativity.²¹

The covalent character, $1 - i$, amounting to as much as about 60% in potassium hexahalopalladates(IV) and hexahaloplatinates(IV) is considerably greater than about 40% found for potassium tetrabromopalladate(II) and tetrabromoplatinate-

(II). It is interesting to note that charges migrating toward the central metal ion in accordance to the covalent character, $1 - i$, of metal-ligand bonds partially neutralize the formal charge on the central ion so as to reduce it to a fraction of an electronic charge, whether the formal charge is four or two. This conclusion suggests a simple and useful method for the estimation of the covalent character of metal-ligand bonds in complexes involving transition metals.

$$\text{Covalent character} = \frac{\text{Formal charge} - \text{Net charge}}{\text{Coordination number}}$$

where the net charge = $0 - 0.6e$. Collet³ has studied the X-ray absorption spectra of bivalent and quadrivalent platinum complexes and found almost vanishing net charges on these platinum ions.

As mentioned above, the difference between the electronegativities of the central atom and the ligand is an important factor affecting the covalent character of the metal-ligand bonds and in consequence the net charge of the central metal atom. However, for a central metal atom having a number of ligands, also the formal charge, *i.e.*, the charge on the central atom for a hypothetical 100% ionic structure, is an important factor in determining the extent of covalent character.

[CONTRIBUTION OF THE JEPSON LABORATORY OF CHEMISTRY, CLARK UNIVERSITY, WORCESTER, MASSACHUSETTS]

Infrared Spectra of Aqueous Solutions. I. Metal Chelate Compounds of Amino Acids¹

BY KAZUO NAKAMOTO,* YUKIYOSHI MORIMOTO* AND ARTHUR E. MARTELL*

RECEIVED MARCH 10, 1961

Thirty metal chelate compounds have been prepared from eight amino acids, and their infrared spectra have been measured in aqueous solution as well as in the crystalline state. The nature of the metal-carboxylate coordinate linkages, as well as the relative bond strengths, are deduced from the variation in the antisymmetric and symmetric carboxyl stretching frequencies. It is concluded that the frequency order of the carboxyl stretching vibration in a series of metal chelate compounds of the same ligand can be used as a measure of relative strengths of the metal-oxygen bonds if the comparison is made from data obtained from pure samples in the same physical state.

Introduction

Aqueous infrared spectra were first measured by Gore, *et al.*,² and the application of this technique to the determination of complexes in solution was reported recently.³

This paper is the first of a series of reports on infrared spectra of aqueous solutions of metal chelate compounds. The general purpose of this investigation is to obtain microscopic information on the nature of the bonds between metal ions and organic ligands in aqueous solution. In this study the carboxylate stretching frequencies are studied as a guide to the nature and extent of metal-

oxygen binding of alpha amino acid chelate compounds in aqueous solution.

The antisymmetric carboxyl stretching frequencies of the metal chelate compounds of amino acids have been interpreted in a variety of ways in recent years. For example, Sen, *et al.*,⁴ and Saraceno, *et al.*,⁵ claimed that the metal-oxygen bonds in Cu(II), Ni(II) and Zn(II) glycinate are essentially ionic since their frequencies are almost the same as those of potassium glycinate and sodium acetate. They also concluded that these metals use sp hybrid orbitals in forming linear bonds with the nitrogen atoms of the ligands. On the other hand, Rosenberg⁶ concluded that the shift of the carboxyl band to higher frequencies in the order Ni(II) < Cu(II) < Pt(II) is an indication of in-

(1) This work was supported by a research grant, A-3095, from the National Institute of Arthritis and Metabolic Diseases, Public Health Service.

* Department of Chemistry, Illinois Institute of Technology, Technology Center, Chicago 16, Ill.

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