not strictly analogous to the $Zn(IDP)X_2$ type of compound we studied earlier. The failure to form $Zn(IDP)(C_6H_5PO_3)$ at room temperature would seem to indicate that phenylphosphonate is a stronger bridging group than cyanide, whereas the decomposition temperature of $Zn_2(IDP)(C_6H_5PO_3)_2$ would indicate that both cyanide and acetate are stronger bridging groups than phenylphosphonate. The apparent discrepancy in the strength of the bridging by phenylphosphonate groups can be resolved by the consideration that there are two kinds of bridges involved which have different strengths, one in which each oxygen is bonded to only one zinc atom and a second in which some oxygen atoms are shared by two zinc atoms. In the compounds reported in our earlier paper this is not the case, there being only one kind of bridge formed.

Even though both $Zn_2(IDP)(C_6H_5PO_3)_2$ and $Zn(py)(C_6H_5PO_3)$ are probably coördination polymers with inorganic backbones, their decomposition temperatures (275 and 185°, respectively) are not high enough to make them of practical interest. It appears that neutral coördinating groups are not bonded strongly enough to zinc for polymers containing such ligands to have substantial thermal stability.

Acknowledgments.—We are indebted to the Office of Naval Research for partial support of our studies and to our colleagues for assistance with parts of the experimental work, in particular Dr. J. R. Soulen for the TGA runs, Miss Ruth Kossatz for the infrared studies, and Mr. A. J. Hamilton. Our Analytical Department furnished the analytical results.

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Covalency of Metal–Ligand Bonds in Potassium Hexachloroiridate(IV) and Hexachloroösmate(IV) Studied by the Pure Quadrupole Resonance of Chlorine

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The pure quadrupole resonance of chlorine in paramagnetic complexes, K_2IrCl_6 and K_2OsCl_6, was observed at liquid nitrogen, Dry Ice, and room temperatures. Each of these complexes shows a single resonance line at all temperatures studied, indicating that all chlorine atoms in each complex are crystallographically equivalent, in agreement with the results of X-ray crystal analysis. With the greater π-bond character of metal–ligand bonds due to vacancies in the $d\epsilon$ orbitals of iridium and osmium ions, the σ-bond character decreases in the order of hexachloroplatinate(IV), hexachloroiridate(IV), and hexachloroösmate(IV), whereas the ionic character remains almost constant.

Introduction

We already have observed the pure quadrupole resonance of halogens in the hexahalo complexes of platinum, palladium, tellurium, selenium, and tin as well as the tetrabromo complexes of platinum and palladium and discussed the nature of metal–halogen bonds in these complexes.[2–6] Unlike these diamagnetic complexes having the $d\epsilon$ orbitals of the central atom completely filled with electrons, the hexahalo complexes of iridium and osmium are paramagnetic[7–9] owing to the presence of one and two holes, respectively, in the $d\epsilon$ orbitals. Accordingly, it is conceivable that partial π-bonds are formed between the $d\pi$ orbitals of the central atom and the $p\pi$ orbitals of ligand atoms. In fact, Griffiths, Owen, and others[10–13] have observed the electron spin resonance of some hexachloroiridates and concluded from the measurements of hyperfine structure and g-values that the π-bond character is involved in the metal–ligand bonds.

The present investigation of potassium hexachloroiridate(IV) and hexachloroösmate(IV) has been undertaken in order to examine the nature of metal–ligand bonds having a partial π-bond character.

Experimental

Apparatus.—The signals of pure quadrupole resonance were displayed on an oscilloscope of a super-regenerative spectrometer already described.[2]

Materials.—A commercial preparation of potassium hexachloroiridate(IV) was recrystallized from a hot aqueous solution to which a few drops of nitric acid were added in advance.[14] About 9 g. of the resulting black crystals was used. Commercial potassium hexachloroösmate(IV) was recrystallized from hot dilute hydrochloric acid solution to obtain dark red crystal grains (about 10 g.).

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Results

Measurements were made at room, Dry Ice, and liquid nitrogen temperatures. The observed frequencies for chlorine isotopes gave a frequency ratio in agreement with the known value. Table I gives only the data on ^{35}Cl.

TABLE I

PURE QUADRUPOLE RESONANCE FREQUENCIES AND QUADRUPOLE COUPLING CONSTANTS OF CHLORINE IN POTASSIUM HEXACHLOROIRIDATE(IV) AND HEXACHLOROÖSMATE(IV)

Compound	Temp., °C.	Frequency, Mc./sec.	eQq, Mc./sec.
K_2IrCl_6	24.2	20.732 ± 0.003	
	−69	20.782 ± 0.002	
	Liquid N_2	20.841 ± 0.002	41.682
K_2OsCl_6	26.0	16.839 ± 0.002	
	−70	16.860 ± 0.002	
	Liquid N_2	16.897 ± 0.002	33.794

Potassium hexachloroiridate(IV) showed a signal-to-noise ratio of the ^{35}Cl resonance line equal to 3–4 at room temperature. The S/N ratio increased with decreasing temperature and was about 7 at liquid nitrogen temperature. The line was rather broad (*ca.* 10 kc.). The S/N ratio of the ^{35}Cl resonance line of potassium hexachloroösmate(IV) was about 10 throughout the temperature range of the present investigation. The line was sharp, the line width being less than 10 kc.

A single resonance line was observed at all temperatures at which the two complexes were studied, indicating that all chlorine atoms in each complex are crystallographically equivalent. This is in agreement with the results of X-ray crystal analysis carried out by McCullough,[15] who has shown that potassium hexachloroösmate(IV) forms cubic crystals of the potassium hexachloroplatinate(IV) structure. Since no data have been available on the crystal structure of potassium hexachloroiridate(IV) in the literature, we have taken the X-ray powder patterns by means of a Norelco X-ray diffractometer. The analysis of the patterns revealed that this compound also is isomorphous with potassium hexachloroplatinate(IV), the lattice constant being a = 9.745 Å. The isotropy of g values in the electron spin resonance of this complex[10–12] also may be noted.

Discussion

It has been believed for some time that the quadrupole resonance of halogens directly bonded to a paramagnetic atom or ion escapes detection owing to the Zeeman splitting of signals due to the magnetic field of unpaired electron spins. Only a few paramagnetic halides of iron group elements[16] are reported to show the pure quadrupole resonance of halogens. No reports ever have been published on the quadrupole resonance of paramagnetic complexes. The fact that the resonance lines were observed for paramagnetic complexes in the present investigation indicates that the magnetic field of unpaired electron spins is effectively averaged to zero at chlorine nuclei because of the rapid relaxation of unpaired electron spins in paramagnetic ions.

The observed quadrupole resonance frequencies of potassium hexachloroplatinate(IV),[2] hexachloroiridate(IV), and hexachloroösmate(IV), (26.0, 20.8, and 16.9 Mc./sec. at liquid nitrogen temperature) are quite different from one another, although the first one is very close to that of potassium hexachloropalladate(IV)[3] (26.7 Mc./sec.). These compounds show crystal structures of the same type,[15,17,18] the difference in lattice constants being at most 0.2%. Accordingly, the large difference in the observed quadrupole frequencies must be attributed to the difference in the electronic structure of complex ions rather than to the crystal effect.

Now, these complexes have the same formal charge (+4) on the central metal ion, the same coördination number (6), and practically the same electronegativity (2.0–2.1)[19–21] of the metal elements. Therefore the reason for the large difference between resonance frequencies of the platinum, iridium, and osmium complexes must be sought in the presence of a hole or holes in the dϵ (dπ) orbitals of iridium and osmium ions, respectively. The possibility of π-bond formation between the dπ orbital of the central ion and the pπ orbital of chlorine is supported by the results of electron spin resonance studies on ammonium, sodium, and potassium hexachloroiridates(IV) carried out by Griffiths, Owen, and others,[10–13,22] who have shown that the unpaired electron of an $[IrCl_6]^{-2}$ ion resides partly (about 30%) on six chlorine atoms, indicating the presence of π-bond character in Ir–Cl bonds to a considerable extent.

Since chlorine has a spin $I = 3/2$, the pure quadrupole resonance frequency is given by

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

where eQq denotes the quadrupole coupling constant and η is the asymmetry parameter, which vanishes for $[IrCl_6]^{-2}$ and $[OsCl_6]^{-2}$ having O_h symmetry. The quadrupole coupling constants calculated for the lowest temperature studied are listed in the last column of Table I.

According to Townes and Dailey[23,24] the quadrupole coupling constant eQq of halogens can be expressed as

$$eQq = U_p(eQq)_{\text{atom}} \qquad (2)$$

where $(eQq)_{\text{atom}}$ stands for the atomic quadrupole coupling constant and U_p is the number of unbalanced p electrons defined by[25] eq. 3.

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$$U_p = \frac{N_x + N_y}{2} - N_z \qquad (3)$$

Here, N_x, N_y, and N_z are the numbers of electrons in $3p_x$, $3p_y$, and $3p_z$ orbitals of chlorine, respectively, the z axis being taken along the direction from the central metal ion to a chlorine atom in question.

Let the ionic character of metal–ligand bonds in a hexachloroiridate(IV) or hexachloroösmate(IV) ion be denoted by i. A covalent σ-bond can be formed between a central metal atom and a chlorine atom, when one of the $5d\gamma^2 6s6p^3$ hybridized orbitals of the metal atom overlaps with one of the sp_z hybridized orbitals of chlorine. In the light of the valence bond method, the resulting covalent σ-bond character of the metal–ligand bond is expressed by σ. Since there is a vacancy in the $d\epsilon$ orbitals of an iridium or osmium ion, π-bonds also can be formed between the two atoms in question. Depending on whether the $3p_x$ or $3p_y$ orbital of chlorine ($2p\pi$ makes a negligible contribution compared with $3p\pi$[13]) is involved in bond formation with the corresponding $5d\epsilon$ orbital (d_{xz} or d_{yz}) of the central metal atom, one has covalent π-bond character, π_x or π_y, for the metal–ligand bond. The O_h symmetry of the complex ions requires that

$$\pi_x = \pi_y = \frac{1}{2}\pi \qquad (4)$$

where π stands for the over-all covalent π-character of the bond. In other words, $\pi/2$ is the extent of contribution of the resonance structure, in which only a π-bond is involved in the bond formation, to the normal state. Accordingly

$$i + \sigma + \pi = 1 \qquad (5)$$

For this electronic structure

$$\left.\begin{aligned} N_x &= 2i + 2\sigma + \pi_x + 2\pi_y \\ N_y &= 2i + 2\sigma + 2\pi_x + \pi_y \end{aligned}\right\} \qquad (6a)$$

since each of the bonding orbitals contributes a single electron to N_x, N_y, or N_z. On the other hand

$$N_z = 2i + [(1 - s) + 2s]\sigma + 2\pi_x + 2\pi_y \qquad (6b)$$

where s denotes the s character of the sp_z hybridized orbitals of chlorine. The coefficient in brackets takes into account the sp_z hybridization, by which the bonding orbital having s character to some extent contributes one electron while the pair of electrons not participating in the bond formation acquires the corresponding p_z character. From eq. 5 and 6, one has

$$\left.\begin{aligned} N_x &= 2 - \pi_x \\ N_y &= 2 - \pi_y \\ N_z &= 2 - (1 - s)\sigma \end{aligned}\right\} \qquad (7)$$

Owing to the bond formation, the number of electrons in each of the 3p orbitals of chlorine is decreased from 2 for a chlorine ion by half an amount allotted to the bonding electron pairs. Equations 2–7 yield

$$eQq = \{(1 - s)(1 - i - \pi) - \pi/2\}(eQq)_{\text{atom}} \qquad (8)$$

The atomic quadrupole coupling constant of ^{35}Cl has been determined[26] as $|(eQq)_{\text{atom}}| = 109.74$ Mc./sec. Townes and Dailey[24,25] have estimated the extent of s character in the sp hybridized bonding orbital of chlorine as $s = 15\%$. From electron spin resonance experiments carried out by Griffiths, *et al.*,[10,11,13] the π-bond character of metal–ligand bonds in hexachloroiridates(IV) is estimated to be 5.3% or $\pi/2 = 2.7\%$. Similar experiments have not yet been performed on hexachloroösmates(IV). However, since an Os^{+4} ion has two vacancies in its $d\epsilon$ orbitals rather than one vacancy as in an Ir^{+4} ion, it is reasonable to assume that the number of electrons migrating from a chlorine ion to osmium through π-bonding is twice as large as that from chlorine to iridium. In other words, π is assumed to be equal to 10.8% for a hexachloroösmate(IV) ion.[27] Using these data, the ionic character i and the σ-bond character σ were calculated along with the net charge ρ (in electronic charge units) on the central metal ion.

$$\rho = 4 - 6\sigma - 6\pi = 4 - 6(1 - i) \qquad (9)$$

The results are shown in Table II, in which data for a hexachloroplatinate(IV) ion[2] are included for comparison.

TABLE II

THE BOND CHARACTER OF METAL–LIGAND BONDS AND THE NET CHARGE ON THE CENTRAL METAL ATOM IN POTASSIUM HEXACHLOROIRIDATE(IV) AND HEXACHLOROÖSMATE(IV)

Compound	Ionic character, i	σ-Bond character, σ	π-Bond character, π	Net charge, ρ
K_2PtCl_6	0.44	0.56	0	0.64
K_2IrCl_6	.47	.48	.054	.80
K_2OsCl_6	.47	.43	.108	.80

It is seen that with increasing π-bond character of metal–ligand bonds, the σ-bond character decreases in the order of hexachloroplatinate(IV), hexachloroiridate(IV), and hexachloroösmate(IV). On the other hand, the ionic character remains almost constant as expected from nearly the same electronegativities of platinum, iridium, and osmium. As a result, the net charge is a positive fraction of the electronic charge throughout this series of complexes in conformity with Pauling's electroneutrality principle, the increase of the net charge on the central atom due to the decrease in the σ-bond character being compensated by the decrease of the charge due to the π-bond formation. In a previous paper,[6] we have shown that the covalent character, $1 - i$, of metal–halogen bonds M–X in hexahaloplatinate(IV) and hexahalopalladate(IV) plotted against the difference, $\Delta\chi_X - \Delta\chi_M$, between the electronegativities of atoms involved in the bonds gives a straight line within the reliability of the electronegativity values. The present data on hexachloroiridate(IV) and hexachloroösmate(IV) also conform to this linear relation, whereas if the π-bond character is disregarded they deviate from the straight line to a considerable extent and the net charges on iridium and

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[27] If it is assumed that $\pi = 9$–13% instead of 10.8%, one has $i = 0.50$–0.43, $\sigma = 0.42$–0.44, and $\rho = 1.00$–0.58 for a hexachloroösmate(IV) ion, conclusions subsequently derived being thereby unaltered.

osmium are increased in contradiction to Pauling's principle. This indicates unequivocally the importance of the π-character of Ir–Cl and Os–Cl bonds.

Although the present discussion is open to criticism as to the adequacy of the assumed extent of s character of sp hybridized orbitals, the extent of π-character of Os–Cl bonds in a hexachloroösmate(IV) ion, etc., the present authors believe that at least an interpretation is presented which is consistent with the experimental data obtained and assumptions made and can throw light upon some phases of the problem of the nature of metal–halogen bonds in complexes.

CONTRIBUTION FROM THE AEROSPACE RESEARCH LABORATORIES,
OFFICE OF AEROSPACE RESEARCH, WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Gas Phase Chromatography of Metal Chelates of Acetylacetone, Trifluoroacetylacetone, and Hexafluoroacetylacetone[1]

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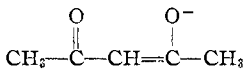
The gas phase chromatography of metal chelates of acetylacetone, trifluoroacetylacetone, and hexafluoroacetylacetone was investigated. Chelates of the fluorine-containing β-diketones are more volatile and can be eluted at much lower column temperatures than corresponding complexes of acetylacetone. Trifluoroacetylacetonato complexes of beryllium(II), aluminum(III), indium(III), chromium(III), iron(III), copper(II), rhodium(III), zirconium(IV), and hafnium(IV) were successfully eluted in the gas phase. Separations of multi-component mixtures of chelates were rapid and efficient. Geometrical isomers of chromium(III) trifluoroacetylacetonate were separated by gas–liquid chromatography. The separation of optical iosmers by gas–liquid and gas–solid chromatography is discussed.

Introduction

Gas chromatography has enjoyed remarkable success in the separation and analysis of countless organic compounds. Extraordinary speed, power of resolution, and sensitivity are characteristics which render the technique attractive for separative and analytical purposes.

Several investigations have been concerned with the separation of anhydrous metal halides[4–7] by gas chromatography. With a few exceptions, high column temperatures are required to elute the halides and reactivity of the compounds presents a problem in sample handling and in choice of materials with which to pack the column.[5] A more serious problem arises from the polymeric, non-volatile characteristics of many metal halides. Recent studies[8,9] have indicated that beryllium(II), aluminum(III), and chromium(III) acetylacetonates are sufficiently volatile and thermally stable to be subjected to gas chromatography. Brandt and Heveran[9] have recently reported that gas chromatography can be used for trace analysis of chromium.

This study was initiated to explore the applicability of gas phase chromatography to the separation of volatile metal chelates. Gas phase chromatographic separations of mixtures of metal chelates, of *cis* and *trans* isomers, and of optical isomers were studied. Metal chelates containing anions of the following β-diketones were investigated: 2,4-pentanedione (acac), 1,1,1-trifluoro-2,4-pentanedione (tfa), and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa).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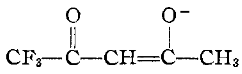
acac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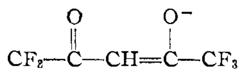
tfa


$$\mathrm{CF_3{-}\overset{\overset{O}{\|}}{C}{-}CH{=}\overset{\overset{O^-}{|}}{C}{-}CF_3}$$
hfa

Experimental

Reagents.—2,4-Pentanedione was purchased from Matheson, Coleman and Bell and was used without further purification. 1,1,1-Trifluoro-2,4-pentanedione and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione were purchased from Columbia Organic Chemical Co. and redistilled prior to use.

Synthesis of Chelates.—The acetylacetonates were prepared by conventional methods and purified by recrystallization and, in some cases, by sublimation at reduced pressure.

The trifluoroacetylacetonates were prepared by methods similar to previously reported procedures.[10,11] In most instances this involved the addition of an aqueous solution of trifluoroacetylacetone, neutralized with ammonium hydroxide, to an aqueous solution of the metal ion. The product was separated by filtration or extraction and purified by recrystallization and, in some instances, by sublimation at reduced pressure. The zirconium(IV) and hafnium(IV) complexes of trifluoroacetylacetone were

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[1] Presented in part by R. E. Sievers, R. W. Moshier, and B. W. Ponder, 141st National Meeting, American Chemical Society, Washington, D. C., March, 1962.

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