Pure Quadrupole Resonance of Halogens in Potassium Hexahalorhenates(IV)

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Studies on the pure quadrupole resonance of chlorine in paramagnetic potassium hexachloroiridate(IV) and hexachloroosmate(IV)(1) have shown that metal-ligand bonds in these complexes involve π bond character, because the $d\varepsilon$ orbitals of iridium and osmium ions have one and two holes, respectively. This paper presents some preliminary results obtained for potassium hexachlororhenate(IV), hexabromorhenate(IV) and hexaiodorhenate(IV), rhenium ions in which have three electrons in their degenerate $d\varepsilon$ orbitals leaving three vacancies.

Resonance lines were observed by means of super-regenerative spectrometers described elsewhere(2). At room temperature, potassium hexachlororhenate(IV) and hexabromorhenate(IV) show a single resonance line for each isotope of halogens. This is in conformity with the cubic structure of these crystals as determined by X-ray analysis(3,4). On the other hand, the ν_1 as well as ν_2 signal of iodine in potassium hexaiodorhenate(IV) consists of three lines of equal intensity. This indicates the presence of at least three kinds of crystallographically nonequivalent iodine atoms in crystals. Orthorhombic symmetry has already been verified for the crystal structure(5), although detailed structural analysis has not been performed as yet. The observed resonance frequencies are shown in Table I.

Frequency measurements carried out between room and dry ice temperatures have revealed the existence of three transition points at about −4, −16 and −27°C for potassium hexabromorhenate(IV), whereas two transition points are reported to exist at −28 and −48°C from heat capacity(6).

TABLE I. PURE QUADRUPOLE RESONANCE FREQUENCIES OF ^{35}Cl, ^{79}Br AND ^{127}I IN POTASSIUM HEXAHALORHENATES(IV)

Compound		Temp., °C	Frequency, Mc./sec.
K_2ReCl_6		23.0	13.887±0.001
K_2ReBr_6		18.0	112.70±0.03
K_2ReI_6	ν_1	21.0	121.91±0.03 122.99±0.03 123.13±0.03
	ν_2	20.6	243.68±0.07 245.16±0.07 245.34±0.07

It is quite remarkable that the temperature coefficient of resonance frequencies of potassium hexachlororhenate(IV) and hexabromorhenate(IV) is positive (+0.13 and +2.8 kc. sec^{-1} deg^{-1} for K_2ReCl_6 and K_2ReBr_6, respectively, near room temperature), whereas in the majority of cases, the temperature coefficient of pure quadrupole resonance frequencies is negative. Only a few exceptions have ever been reported to this rule (WCl_6(7), $TiBr_4$(8) and $ThCl_4$(9)). No metal complexes have been known to show a negative temperature coefficient of the resonance frequencies. However, the rather abnormal value is not surprising, because the temperature coefficient (−1.0, −0.54, −0.22 and +0.13 kc. sec^{-1} deg^{-1} for K_2PtCl_6(2), K_2IrCl_6, K_2OsCl_6(1) and K_2ReCl_6, respectively) increases progressively with increasing electron defficiency in the $d\varepsilon$ orbitals of the central metal ions. It appears that some close parallelism exists between the temperature coefficient of the quadrupole resonance frequencies and the extent of π bond character of metal-ligand bonds. The detailed analysis of experimental results is now in progress and will be published shortly.

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