$$t_{2g}(xy) = a(xy) + \frac{b}{2}(x_1 + y_2 + y_4 + x_5)$$

Consider the $K(t_{2g}(xz), t_{2g}(xy))$ integral for CrF_6^{3-}. In the notation of the previous paper,[1] this integral is $(t_{2g}(xz),\ t_{2g}(xy)|t_{2g}(xy),\ t_{2g}(xz))$. Consequently, evaluation involves the fourth power of the coefficients a and b. If one neglects all three- and four-center integrals such as $(xz,\ y_1|y_3,\ x_3)$ but evaluates all one- and two-center integrals using the +2 wave function for the metal d orbital and the fluoride 2p orbital for the ligands, one obtains

$$K \text{ (in au)} = a^4(0.03099) + a^3b(0.00558) + a^2b^2(0.00178) + ab^3(0.00119) + b^4(0.00971)$$

It is apparent from this calculation that, when $|a|$ is significantly larger than $|b|$, K is dominated by the first term in the expression. From Table II, $a = 0.970$ and $b = -0.454$, so K(complete) = 0.0260 au. Since $a^4(0.03099) = 0.0274$, to a fair degree of approximation the value of K depends only upon the corresponding value of the metal interaction multiplied by the fourth power of the coefficient of the d orbital in the molecular orbital. Analogously, interactions involving the t_{2g} and e_g orbitals, whose metal orbital coefficients are a and c, respectively, can be approximated by a^2c^2 times the corresponding metal interaction integral.

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The Spectrum of Potassium Hexachlororhenate(IV) in Fused Salts[1]

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The visible spectrum of K_2ReCl_6 has been investigated in molten dimethyl sulfone, diethylamine hydrochloride, and LiCl–KCl mixtures, at temperatures up to 600°. A splitting of some of the bands has been observed which is dependent on the solvent.

Introduction

The literature reports a number of studies of the electronic spectra of transition metal ions in fused-salt solvents which have given considerable information about complexes and their structures in such media. However, this work has been limited to first-row transition metals.[2] This communication deals with a study of potassium hexachlororhenate(IV) in various fused systems, and the effects of the melt on this octahedral species. We are not concerned with formation of the complex in the melt, as is generally the case when a simple compound is added to the fused salt. Owing to the very large octahedral site stabilization energy of Re(IV) (approximately 84 kcal/mole), the octahedral–tetrahedral equilibrium which has been observed for many of the first-row transition metal ions[3] is not expected. However, interesting information on the nature of ionic interactions with the complex species in the melt can be obtained.

Eisenstein has performed a theoretical analysis of the $ReCl_6^{2-}$ ion, including the spin–orbit interactions.[4] He assigned the energy levels as follows (cm^{-1}, the listed energies are quoted from his paper)

$^4A_2$	(Γ_8)	0	$^2T_1$	(Γ_6)	9,574
$^2T_1$	(Γ_8)	<7700	$^2T_2$	(Γ_7)	14,180
^2E	(Γ_8)	9105	$^2T_2$	(Γ_8)	15,385

The Γ's are representations in the cubic double group. He also tentatively assigned bands at 35,900 and 39,000 cm^{-1} to transitions to the $^4T_2$ and $^4T_1$ levels, respectively, recognizing the possibility that these could be charge-transfer bands masking the ligand field bands.

The detail observed for the transitions $^4A_2\ (\Gamma_8) \rightarrow {}^2E\ (\Gamma_8),\ {}^2T_1\ (\Gamma_6),\ {}^2T_2\ (\Gamma_7)$ is vibrational fine structure.[5]

Experimental Section

The furnace assembly for the Unicam SP700 spectrophotometer with which all spectra were obtained and the method for the preparation of solutions of air-sensitive samples in the LiCl–KCl eutectic have been described previously.[6]

The K_2ReCl_6 was prepared by the method of Rulfs and Meyer,[7] using potassium perrhenate obtained from the S. W. Shattuck Co.

The dimethyl sulfone was Eastman Practical grade, recrystallized from methanol. Diethylamine hydrochloride was prepared by passing HCl gas into a solution of freshly distilled Eastman diethylamine in Fisher Reagent grade benzene.

Stoppered fused-quartz cells of 1-cm light path were used for the spectra of solutions of K_2ReCl_6 in dimethyl sulfone and diethylamine hydrochloride. These and the reference solutions were prepared and maintained under a dry nitrogen atmosphere. The LiCl–KCl studies were done in similar cells which were sealed under vacuum.

The analyses were performed on a Beckman Model DU spec-

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(1) Based on part of a thesis to be submitted by J. A. McIntyre to the Graduate School of Rensselaer Polytechnic Institute as partial fulfillment of the requirements for the degree of Doctor of Philosophy. Supported by National Science Foundation Grant NSF-GP-1942.

(2) Recent surveys are given by D. M. Gruen in "Fused Salts," B. R. Sundheim, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1964, Chapter 5, and G. P. Smith in "Molten Salt Chemistry," M. Blander, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 427.

(3) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963).

(4) J. C. Eisenstein, *J. Chem. Phys.*, **34**, 1628 (1961).

(5) C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 710 (1955).

(6) R. A. Bailey and J. A. McIntyre, *Rev. Sci. Instr.*, **36**, 968 (1965).

(7) C. L. Rulfs and R. J. Meyer, *J. Am. Chem. Soc.*, **77**, 4505 (1955).

TABLE I

SPECTRA OF $ReCl_6^{2-}$ IN VARIOUS SOLVENTS

	1.2 *N* HCl		Dimethyl sulfone		Diethylamine hydrochloride[b]		LiCl–KCl eutectic				90 mole % LiCl–KCl	
			135–200°		260°	285°	450°		600°		600°	
Transition, $^4A_2$ (Γ_8) →	cm^{-1}	ϵ[a]	cm^{-1}	ϵ	cm^{-1}	cm^{-1}	cm^{-1}	ϵ	cm^{-1}	ϵ	cm^{-1}	ϵ
$^2T_1$ (Γ_8)	7,650	5	7,600	5	7,600	7,600	7,000	14	7,000	14	7,000	14
	7,900 sh		7,850 sh		7,900 sh	7,950 sh	7,950		7,950		7,950	
^2E (Γ_8)	9,200		9,150		9,050	9,100						
	9,400	8	9,400	8	9,200		9,300	46	9,200	46	9,200	46
$^2T_1$ (Γ_6)	9,550		9,600		9,400	9,500						
	9,700		9,700		9,550							
$^2T_2$ (Γ_7)	14,100		14,150		14,150	14,150	14,100	9	14,100	9	14,100	9
	14,300	6	14,250	6	14,300	14,300						
$^2T_2$ (Γ_8)	15,400	5	15,400	5	15,200	15,200	15,100	5	15,100	5	15,050	5
	15,700 sh		15,750 sh		15,800 sh	15,800 sh	16,150	4	16,150	4	16,150	4
	32,000 sh		32,000 sh									
	34,500 sh		34,500 sh									
	35,500	12,875	35,200	13,000			35,200		35,200			
	39,000		37,500									

[a] Molar absorptivity M^{-1} cm^{-1}. [b] ϵ not determined; density unknown.

trophotometer, using the absorption band at 281.5 mμ, which has been shown[8,9] to be suitable for analysis. The samples were dissolved from the high-temperature cells with aqueous HCl. Calibrations were done with solutions having about as much excess salt as the samples.

Results and Discussion

The peak positions of the various spectra obtained in this study are listed in Table I. The values for aqueous HCl, included for comparison, are our values, but these are in excellent agreement with those quoted by Eisenstein.[4] The spectra are illustrated in Figures 1–5.

It is evident that the most obvious changes are the increased splittings of the $^2T_1$ (Γ_8) and $^2T_2$ (Γ_8) levels in the LiCl–KCl eutectic. The high-energy spectrum in dimethyl sulfone is similar to that in aqueous solution with only small shifts in the position of two bands, whereas in the LiCl–KCl eutectic only one band is observed. Since there is some question as to whether these are ligand field or charge-transfer bands, interpretation of this change is difficult.

The spectra in aqueous HCl solution and in molten dimethyl sulfone are essentially identical. A small change due to the increased temperature is observed in molten diethylamine hydrochloride. There is some loss of the vibrational fine structure, as well as a slight increase in intensity of the low-energy side of the band relative to the high-energy side, observed in the transitions $^4A_2$ (Γ_8) → ^2E (Γ_8), $^2T_1$ (Γ_6), $^2T_2$ (Γ_7). This can be ascribed to the increased population of higher vibrational levels at elevated temperatures.[10]

Because the 5d transition metal ions have very large values of the ligand field splitting energy Δ, the spectrum should be insensitive to temperature changes. The shifts normally observed are due to changes in the metal ion–ligand internuclear distance, which changes the strength of the field about the central metal ion. However, the change in magnitude of Δ caused by this is also small relative to the already very large Δ of $ReCl_6^{2-}$ (33,500 cm^{-1}).[4] In addition, the energy levels of interest here are not particularly sensitive to changes in Δ.

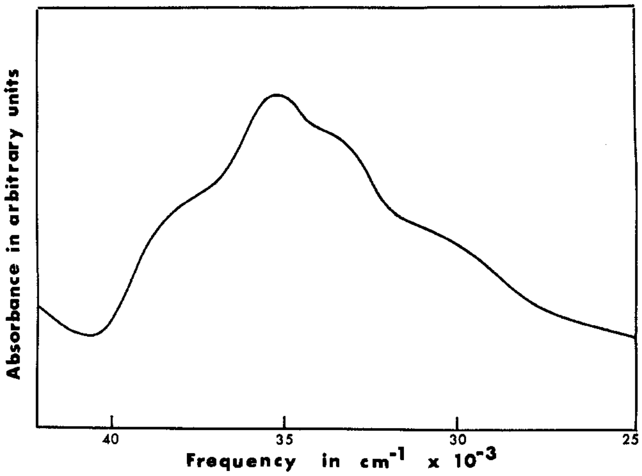

Figure 1.—Ultraviolet spectrum of $ReCl_6^{2-}$ in molten dimethyl sulfone at 135°.

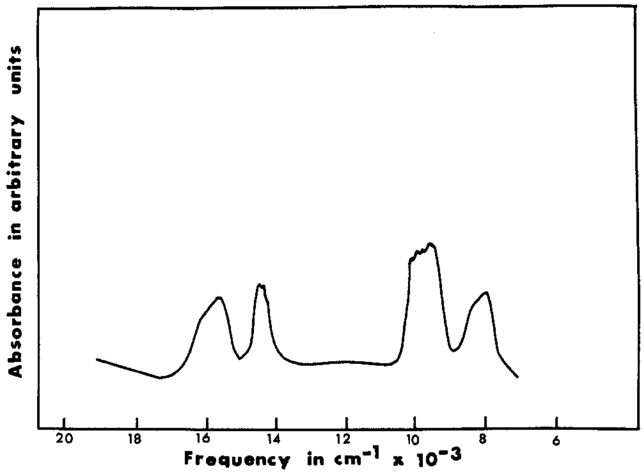

Figure 2.—Visible spectrum of $ReCl_6^{2-}$ in molten dimethyl sulfone at 135°.

In the LiCl–KCl melts a splitting of the $^2T_1$ (Γ_8)

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[8] C. L. Rulfs and R. J. Meyer, *Anal. Chem.*, **27**, 1387 (1955).

[9] V. W. Meloche and R. L. Martin, *ibid.*, **28**, 1671 (1956).

[10] T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, Chapter 4.

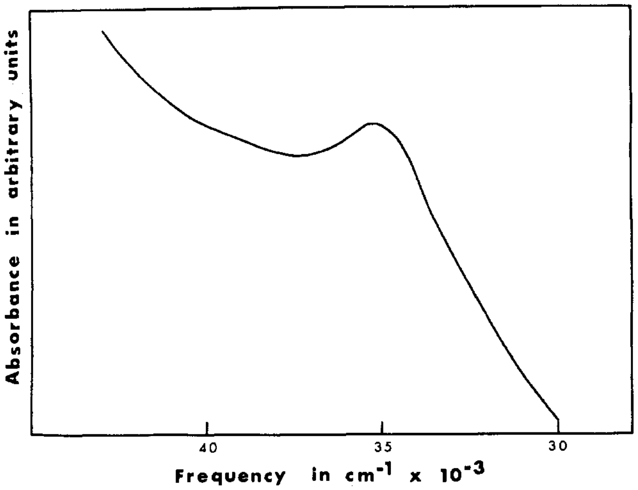

Figure 3.—Ultraviolet spectrum of $ReCl_6^{2-}$ in molten LiCl–KCl cutectic at 450°.

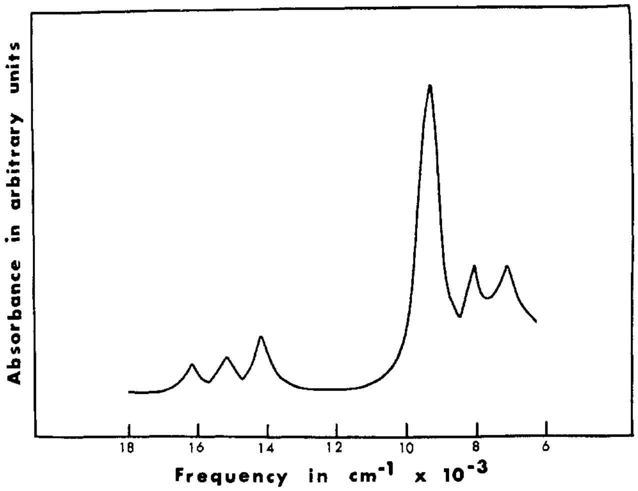

Figure 4.—Visible spectrum of $ReCl_6^{2-}$ in molten LiCl–KCl eutectic at 450°.

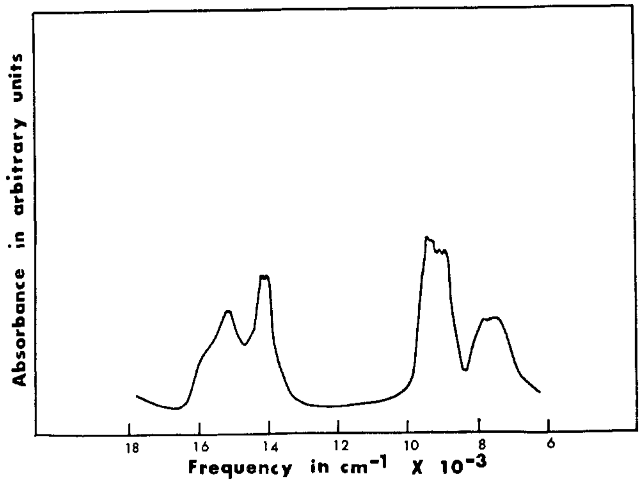

Figure 5.—Visible spectrum of $ReCl_6^{2-}$ in molten diethylamine hydrochloride at 245°.

and $^2T_2$ (Γ_8) energy levels of 1050 and 950 cm^{-1}, respectively, is observed. Such splitting has been observed by Gruen,[11] also. Eisenstein's calculations[4] showed that, of the six levels considered here, the $^2T_1$ (Γ_8) and $^2T_2$ (Γ_8) would split, in a tetragonally distorted field, and attributed the shoulder in the $^2T_2$ (Γ_8) peak to a small distortion of this sort. (It appears to us that this shoulder represents a transition at very nearly 16,000 cm^{-1}.) Broadening of the $^2T_1$ (Γ_8) peak was further evidence for a distortion; our aqueous spectra confirm the presence of a shoulder in this peak. An alternative interpretation, that the shoulder arose from vibrational states, was originally unlikely because of the shapes of these bands[4] and seems definitely ruled out by the behavior at high temperatures.

The splitting in the LiCl–KCl melt is not simply a temperature effect since in the organic melts, even at 285°, the two bands show essentially no change from those in aqueous solution at room temperature, whereas in the LiCl–KCl melt at 450° they are split considerably. In addition, there is no significant change in the degree of splitting on increasing the temperature from 450 to 600° in the LiCl–KCl melt. (Spectra taken in this melt below 450° were unsatisfactory owing to limited solubility of K_2ReCl_6.) It is apparently due to melt–complex ion interactions.

The ability of cations in a melt to affect the energy levels of an anion has been demonstrated by Boston and Smith,[12] who showed that the magnitude of the shift of the $n \rightarrow \pi^*$ band of the nitrate ion was a function of the ratio of the charge to radius of the cation. Similar observations of the effects of melt cations on the spectrum of $NiCl_4^{2-}$ have been reported by Boston and Smith[13] and Gruen and McBeth.[14] However, it is only in melts with a strongly polarizing cation that the interactions are great enough to cause the observed splitting of the $ReCl_6^{2-}$ ion levels, as can be seen from the spectrum in diethylamine hydrochloride, where the $(C_2H_5)_2NH_2^+$ cation does not cause the level to split very much. Moreover, in a melt of 90 mole % LiCl–10 mole % KCl at 600° there is a 50 cm^{-1} greater split of the $^2T_2$ (Γ_8) level than in the eutectic at the same temperature. This must be interpreted as being due to the smaller (average) cation–anion distance which results from the increased proportion of the smaller Li^+ ions.[14]

Stephens and Drickamer[15] have reported that the $^2T_2$ (Γ_8) level became a doublet when the solid was subjected to pressures up to 50,000 atm. In their report, no mention was made of the effects on other levels. However, the two peaks reported at about 15,000 and 16,000 cm^{-1} were pressure invariant in position; only their relative intensities changed. This is not expected if they are due to a pressure-induced distortion. It does not seem possible to account for these two peaks with perfect O_h symmetry. It is possible that the $ReCl_6^{2-}$ ion exhibits some tetragonal distortion,[4] and the change in the spectrum with pressure is due to a change in transition probabilities. The effect of the molten salt solvent may also involve an increased distortion since the energies of the transitions change.

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[11] D. M. Gruen, private communication.

[12] C. R. Boston and G. P. Smith, *J. Chem. Phys.*, **34**, 1396 (1961).

[13] C. R. Boston and G. P. Smith, *J. Phys. Chem.*, **62**, 409 (1958).

[14] D. M. Gruen and R. L. McBeth, *ibid.*, **63**, 393 (1959).

[15] D. R. Stephens and H. G. Drickamer, *J. Chem. Phys.*, **30**, 1364 (1959).