4 formula weights/unit cell; the lattice parameters are all close to 7.5 A. The only other dodecarborides known to be reported are three polymorphic forms of aluminum dodecarboride; α-AlB_{12} is tetragonal (a = 10.16 A and c = 14.28 A) and the β and γ forms are orthorhombic.[3]

In 1961, Chrétien and Lavéant reported the preparation of gallium dodecaboride (GaB_{12}).[4] They indexed the X-ray powder pattern on the basis of a tetragonal unit cell, with a = 12.93 A and c = 4.84 A. These results indicated the existence of a new type of metallic dodecaboride. An attempt was made to prepare single crystals of this compound for use in a three-dimensional crystal structure analysis.

Powder patterns of a number of samples prepared according to Chrétien and Lavéant's method of synthesis (heating pure gallium and boron in an evacuated quartz tube for about 24 hr at 1100–1300°) agreed with the pattern they reported. Small single crystals were found in three of the samples. A single-crystal X-ray diffraction investigation of one of these crystals showed it to be face-centered cubic with a lattice parameter of 5.43 A. It was subsequently identified as a single crystal of silicon. The powder pattern was reanalyzed after discarding those lines due to silicon, and the remaining lines were found to belong to a single-phase boron suboxide.[5] The apparent explanation for the formation of silicon is that the boron reduces the quartz.

Metallic gallium was undetected because the melting point of gallium (29°) is close to room temperature. Furthermore, the diffusivity of gallium into silicon dioxide at 1100–1300° is known to be large,[6] and a portion of the gallium can be assumed to have been adsorbed by the quartz crucible. However, X-ray diffraction rotation photographs taken of a few clusters of the polycrystalline material at −20° did show the presence of gallium.

Further attempts were made to synthesize gallium dodecaboride in a quartz-free environment. This included (1) prolonged heating (15 hr) of stoichiometric amounts of gallium and boron in a boron nitride crucible in an electron-beam zone refiner, at temperatures up to 1800°, and (2) heating the elements together in a boron nitride crucible inside an evacuated quartz tube at about 1100° for 1 month. The only product formed was boron suboxide. It was probably caused by the reaction of boron with oxygen adsorbed in the boron nitride crucibles.

On the basis of the present investigation, it seems rather certain that gallium dodecaboride has not been synthesized. This confirms Seybolt's observation that gallium and boron do not react.[7]

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Contribution from the Department of Chemistry,
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The Spectra of $[PtCl_4]^{2-}$ and $[PdCl_4]^{2-}$ in the LiCl–KCl Eutectic[1]

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In previous studies of the electronic absorption spectra of transition metal ions in fused-salt solvents, only octahedral or tetrahedral complexes (or distorted forms thereof) have been observed.[2] Since such studies can potentially yield information concerning the structure of fused salts, it seemed appropriate to investigate the effect of such a solvent on a square-planar complex. There has been considerable discussion of the assignments of the spectrum of the $[PtCl_4]^{2-}$ ion;[3–8] we have followed that of Chatt, Gamlen, and Orgel, which has been verified by Martin, Tucker, and Kassman. For the particular band of $[PdCl_4]^{2-}$ studied, we use the assignment of Day, *et al.*

Experimental Section

Spectra were recorded with a Unicam SP700 spectrophotometer; the furnace assembly and the method of preparation of solutions in the LiCl–KCl eutectic have been reported previously.[9]

Fused-quartz cells of 0.1-cm path length were used, sealed under vacuum. The LiCl and KCl used were Baker Analyzed reagent grade chemicals. The K_2PtCl_4 was Fisher "purified" material, while a sample of Cs_2PdCl_4 was prepared by precipitation with CsCl from a solution of Fisher $PdCl_2$ in 6 N HCl.

Results and Discussion

The spectra obtained are shown in Figures 1 and 2, with the band positions listed in Table I. The positions listed for the bands of K_2PtCl_4 in the LiCl–KCl eutectic have not been corrected for the effects of band overlap, as this is not necessary for the discussion which follows.

In discussing the changes observed in the spectra on changing the solvent and the temperature, three factors must be considered. These are (a) changes in the metal ion–ligand internuclear distance (and thus Dq) due to the thermal population of excited vibrational levels,[10] (b) a distortion toward tetrahedral symmetry, and (c) an orientation of solvent anions above and below the molecular plane to give a tetragonally distorted octahedral species.

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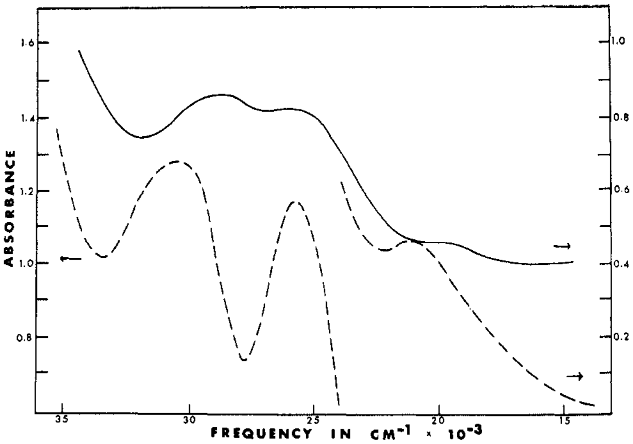

Figure 1.—Spectra of K_2PtCl_4: – – – –, 12 *N* HCl; ———, LiCl–KCl eutectic, 400°.

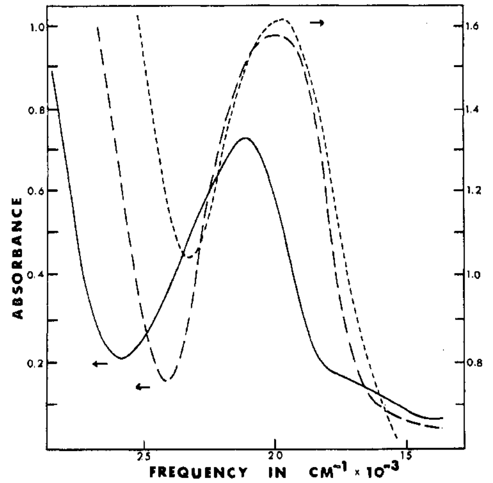

Figure 2.—Spectra of Cs_2PdCl_4: ———, 6 *N* HCl; – – – –, LiCl–KCl eutectic, 400°; --------, LiCl–KCl eutectic, 600°.

TABLE I

SPECTRA OF K_2PtCl_4 AND Cs_2PdCl_4 IN VARIOUS SOLVENTS

Solution	Band maxima, cm^{-1} (ϵ_{max}) $^1A_{1g}$ → ^3E_g	$^1A_{1g}$ → $^1A_{2g}$	$^1A_{1g}$ → ^1E_g
K_2PtCl_4 in 12 *N* HCl	21,200 (22)	25,700 (57)	30,400 (65)
K_2PtCl_4 in H_2O	21,100 (18)	25,600 (60)	30,500 (69)
K_2PtCl_4 in LiCl–KCl eutectic, 400°	19,500 (~8)	25,600 (~15)	28,800 (~15)
K_2PtCl_4 in LiCl–KCl eutectic, 450°	19,000 (~8)	25,600 (~15)	28,400 (~15)
Cs_2PdCl_4 in 6 *N* HCl		21,200 (150)	
Cs_2PdCl_4 in LiCl–KCl eutectic, 400°		20,300 (~240)	
Cs_2PdCl_4 in LiCl–KCl eutectic, 500°		20,100 (~260)	
Cs_2PdCl_4 in LiCl–KCl eutectic, 600°		19,900 (~270)	

The first possibility can be eliminated as the primary cause of the spectral changes in this example by a consideration of the shifts of the bands as observed by Martin, *et al.*,[7] in their investigation of the polarized crystal spectra of K_2PtCl_4 at 15 and 298°K. These workers found that the shifts of the three bands ($^1A_{1g} \rightarrow {}^3E_g$, $^1A_{2g}$, ^1E_g) were all of about the same magnitude. It is obvious from Figure 1 that this is not the case here, so that some other effect must also be considered.

Distortion to a tetrahedral structure is unlikely since the changes in the spectrum are comparatively slight. Gruen and McBeth,[11] in their study of Ni(II) in chloride melts, found a tetrahedral configuration in CsCl, but a tetragonal structure in LiCl. The larger size of Pt(II) would tend to favor the latter, while the chemical properties of this species make a tetrahedral form unexpected. Possibility c is more attractive from the latter point of view and can be justified from the nature of the spectral changes.

The orientation of solvent anions above and below the molecular plane will destabilize the d_{z^2} and d_{xz}, d_{yz} orbitals relative to the $d_{x^2-y^2}$ and d_{xy} orbitals, while not affecting the energy separation between the latter pair. Thus the $^1A_{1g} \rightarrow {}^1A_{2g}$ band should not shift, while the $^1A_{1g} \rightarrow {}^3E_g$, ^1E_g bands should shift toward the red, as is observed. A similar shift was observed and interpreted in the same way by Chatt, *et al.*,[3] for $[\{(n\text{-}C_5H_{11})_2NH\}_2PtCl_2]$ in hexane and ethanol. The fact that the bands shift further toward the red on increasing the temperature follows from the observation by Hafner and Nachtrieb in their nmr studies of molten salts[12] that cations and anions associate in molten salts with a positive temperature coefficient. If this holds for the melt chloride ion–platinum interactions here, the d_{z^2} and d_{xz}, d_{yz} orbitals would be further raised relative to the d_{xy} and $d_{x^2-y^2}$ orbitals.

Although the same arguments will hold for $[PdCl_4]^{2-}$, the situation is not so well defined since the observed band is actually a composite of the bands due to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$, ^1E_g. However, it is observed that on going to the LiCl–KCl eutectic the band becomes more symmetrical, indicating that the $^1A_{1g} \rightarrow {}^1E_g$ is shifting toward the red.

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Nickel(II) Complexes of Aromatic Amine Oximes

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Complexes utilizing *s*-triazines as ligands have not been extensively investigated. It would be of interest to see how such compounds compare with analogous pyridine ligands. For this reason we have prepared

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