very small variations with the change in outer cation. No unambiguous correlation could be observed between the isomer shift and the electronegativity of the cations.

Quadrupole Splitting.—All nitroprussides showed a symmetric doublet (except ferrous nitroprusside) with large quadrupole splittings (ΔE_Q = 1.50–2.00 mm/sec) which are comparable to those observed for high-spin Fe^{2+} compounds.[37] Quadrupole splitting in a series of compounds of similar geometry can be influenced by a number of factors, the most obvious of these being (i) electronegativity[38] of the cation, (ii) size of the cation,[26] and (iii) the lability of the electrons in the d orbitals of the cations. Since we are investigating the influence of an outer cation on an already existing large asymmetry, the variations due to the changes in the above parameters are, in general, not too large. We did not see any pronounced and systematic variation in the quadrupole splitting of any of the above factors.

Ferrous Nitroprusside.—The Mössbauer spectrum of ferrous nitroprusside consists of four well-resolved lines of almost equal intensity as shown in Figure 1. An analysis of this spectrum reveals that two of the lines correspond to the usual nitroprusside part of the compound and yield a quadrupole splitting, ΔE_Q, of 1.74 ± 0.03 mm/sec and an isomer shift, δ, of -0.01 ± 0.02 mm/sec. The remaining two lines would then give $\Delta E_Q = 2.75 \pm 0.05$ mm/sec and $\delta = 1.22 \pm 0.03$ mm/sec. These parameters correspond[37] to the high-spin state of Fe^{2+}. To confirm this we synthesized and studied $Fe[Mn(CN)_5NO]\cdot 2H_2O$ where the inner unit of nitroprusside anion is structurally the same but does not contain iron and the outer iron is present as such. This compound gave rise to only a two-line spectrum depicting the high-spin state of Fe^{2+}, with the Mössbauer parameters $\delta = 1.24 \pm 0.02$ mm/sec and $\Delta E_Q = 2.76 \pm 0.02$ mm/sec. These agree well with those assumed for the high-spin state in the case of ferrous nitroprusside. Therefore we can infer that there are two clearly defined states of iron, *i.e.*, (i) the inner iron in the usual low-spin state and covalently bonded with five CN^- and one NO^+ groups and (ii) the outer cationic iron in the high-spin state. This is a confirmation of the results of magnetic susceptibility measurements.[30]

Recently Fung and Drickamer[39] have also studied $Fe[Fe(CN)_5NO]$ and confirmed the presence of two types of irons by tagging them with ^{57}Fe separately. Our results are comparable with these within experimental error. These authors have also found that the percentage of high-spin iron increases with the increase in pressure.

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Electronic Spectra of Ruthenium(III) and Osmium(III) in Chloride Melts

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Ruthenium(III) adopts octahedral coordination in LiCl–KCl at 450° with the ligand field parameters Δ = 18.7, B = 0.49 and C = 2.3 kK. A preliminary study of osmium(III) chloride shows that it disproportionates to Os(IV) and Os metal in both LiCl–KCl and $BiCl_3$, the rate of decomposition rising markedly above 500°. However, the coordination of Os(III) appears to be distorted octahedral with a trigonal or tetragonal ligand field component of 4.0 kK and a spin-orbital coupling constant of 2.7 kK. Ruthenium(III), osmium(III), and osmium(IV) showed no electrochemical activity in LiCl–KCl.

The ligand field spectra of complexes of Ru(III) and Os(III) have not been studied in great detail. For example, Jørgensen[1,2] measured the spectrum of $RuCl_6^{3-}$ in hydrochloric acid but made no definite assignments, and Johnson and Dickinson[3] noted the presence of a weak band at 17.5 kK and a shoulder at 24.5 kK for $RuCl_3$ dissolved in LiCl–KCl eutectic melt. The spectrum of $Ru(ox)_3^{3-}$ (ox = oxalate) has been given and interpreted.[4] Again, Jørgensen[2] has reported the charge-transfer spectrum of $OsCl_6^{3-}$ in hydrochloric acid but no ligand field bands were observed. On the other hand, ligand field bands of the Os(III) complexes $Os(acac)_3$ and $OsCl_3(Sb(C_6H_5))_3$ have been assigned.[5,6]

In this paper we present further measurements of the spectrum of Ru(III) in LiCl–KCl and the first datum concerning Os(III) in both LiCl–KCl and $BiCl_3$. It transpires that Os(III) is in equilibrium with Os(IV) and Os metal in these melts but some useful information may be extracted from the spectra.

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Experimental Section

Anhydrous $RuCl_3$ and K_2OsCl_6 (Alfa Inorganics) and $OsCl_3$ (Engelhard Industries Inc.) were used as supplied. LiCl–KCl eutectic, mixed from Baker Analyzed salts, was purified by the method of Maricle and Hume[7] and $BiCl_3$ was prepared as described by Yosim, *et al.*[8] Concentrated solutions of $RuCl_3$, $OsCl_3$, and K_2OsCl_6 were made by melting finely ground mixtures of the salts and filtering through a sintered-glass disk. Samples containing Ru(III) were analyzed for ruthenium by colorimetry as described by Ayres and Young[9] with a Beckman DK-2A spectrophotometer.

Molten salt spectra were obtained with a Cary 14H spectrophotometer using a furnace described elsewhere.[10] Samples were contained in 1-cm^2 silica cells (Pyrocell) and sealed under dry nitrogen and the spectra of each solvent and solution were measured *vs.* air. Concentrations were calculated on the assumption that the density of a dilute solution was the same as that of the solvent.[11] All manipulations were carried out in a drybox.

In an attempt, futile in fact, to throw further light on the changes taking place in the osmium system, current–voltage curves of solutions were measured; the experimental arrangement was similar to that of Johnson and Mackenzie.[12] The instrumentation included a Sargent Model IV coulometric current source to generate Pt(II) for a Pt(II)–Pt(0) reference electrode and a Sargent Model XVI polarograph. Microelectrodes were of platinum (area 1.26×10^{-3} cm^2) and tungsten (area 1.32×10^{-3} cm^2).

Results and Discussion

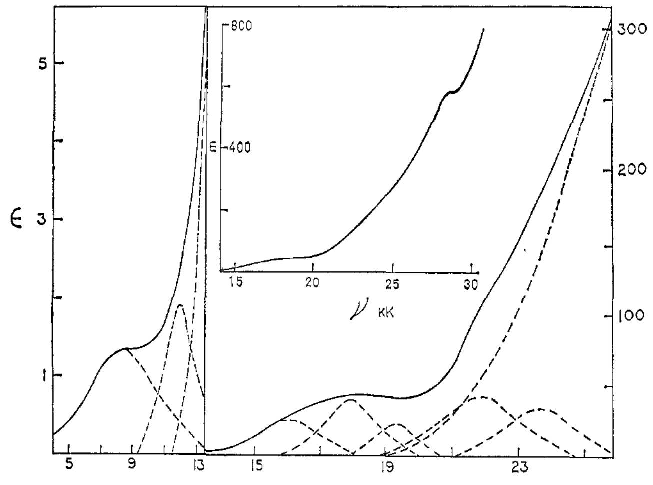

Figure 1.—Spectrum of $RuCl_3$ in LiCl–KCl eutectic melt at 450°. Main figure covers the region from 4 to 26 kK; inset covers that from 14 to 30 kK.

Ruthenium(III) Spectrum.—Figure 1 shows the spectrum of $RuCl_3$ in LiCl–KCl eutectic melt at 450°. It has been broken down into Gaussian components by the method of Chatt, *et al.*,[13] and Table I summarizes the band positions, intensities, and assignments. In octahedral symmetry the ground state of Ru(III), $4d^5$, is $^2T_{2g}$ according to magnetic susceptibility data.[14,15] With a spin–orbital coupling constant, ζ, of about 1500 cm^{-1} it is possible to describe the energy levels in a Russell–Saunders coupling scheme. Thus the first two observed transitions are assigned as spin-forbidden d–d, the next five as spin-allowed d–d, and the last two as charge-transfer transitions. The assignment $\gamma_5 \leftarrow \pi$ of the 28.50-kK band was given by Jørgensen.[2]

Table I

ν_{found}, kK	ϵ^a	$10^4 f$	δ	Assignment	ν_{calcd}, kK
8.42	1.39	0.27	4.75	$^4T_{1g} \leftarrow {}^2T_{2g}$	8.23
				$^6A_{1g} \leftarrow$	8.64
12.02	1.89	0.22	2.54	$^4T_{2g} \leftarrow$	11.66
16.00	26.1	2.47	2.06	$^2A_{2g} \leftarrow$	16.11
				$^2T_{1g} \leftarrow$	16.27
17.87	37.9	3.56	2.04	$^2T_{2g} \leftarrow$	17.48
19.23	22.7	1.54	1.48	$^2E_g \leftarrow$	18.68
21.73	43.9	5.77	2.86	$^2T_{1g} \leftarrow$	21.90
23.56	34.0	4.06	2.60	$^2A_{1g} \leftarrow$	24.02
28.50	580	230	7.60	$\gamma_5 \leftarrow \pi$	
33.00	$\sim$1150			$\gamma_5 \leftarrow$	

[a] Standard error of 0.15 (5%) from 4 to 14.5 kK and 2.8 (6%) from 14.5 to 26 kK.

The ligand field parameters for a d^n system in O_h may be calculated from the Tanabe–Sugano determinants;[16] these do, however, neglect spin–orbital coupling. At first sight this is a serious objection since ζ_{4d} may be as high as 1500 K but the effect of spin–orbital coupling of this magnitude is merely to add a splitting of each band by 2000 or 2250 K (quartet *vs.* doublet). As with the spectra of many $4d^n$ ion complexes this splitting is not observed. If it were, up to 16 ligand field transitions would be expected instead of the 8 resolved by gaussian analysis.

For the mode of calculation, several options are open, as pointed out by Stevenson,[17] but it is possible to write the first few transitions as linear equations in Δ, B, and C and then to find the best values of Δ, B, and C which fit the experimental data. Full instructions for carrying out this procedure will be published elsewhere.[18] Applying it to the data of Table I, we find the parameters $\Delta = 18.7$ kK, $B = 0.49$ kK, and $C = 2.3$ kK with the calculated transition energies listed in the last column. The standard deviation in the calculated energies is 0.35 kK or 2.26%.

For $Ru(ox)_3{}^{3-}$, Olliff and Odell[4] reported $\Delta = 28.7$ kK and $B = 0.56$ kK with the assumption of $C = 4B$; for Rh(III) in the LiCl–KCl melt and the tris-oxalate complex a similar divergence is apparent[19,20] (*cf.* Table II). A limited number of results is available but if we take into account the usual trends for both Δ and B, *viz.*, $\Delta_{Rh(III)} \sim \Delta_{Ru(III)}$, $\Delta_{Cl^-} < \Delta_{ox^{2-}} \sim \Delta_{H_2O}$ and $B_{Cl^-} < B_{ox^{2-}} \sim B_{H_2O}$, we see that the results for Ru(III) in LiCl–KCl are quite reasonable and support the idea of an octahedral coordination of Ru(III) in the melt.

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TABLE II

SPECTRAL PARAMETERS FOR Ru(III), Rh(III), AND Co(III)

System	Δ, kK	*B*, kK	*C*, kK	Ref
Ru(III) in LiCl–KCl	18.7	0.49	2.29	
$Ru(ox)_3{}^{3-}$	28.7	0.56	$=4B$	4
Rh(III) in LiCl–KCl	19.3	0.37		19
$Rh(ox)_3{}^{3-}$	26.4			20
Rh(III) in H_2O	27.0	0.51		20
Co(III) in H_2O	18.2	0.67		20
$Co(ox)_3{}^{3-}$	18.0	0.54		20

Osmium(III) Spectra.—The spectra of $OsCl_3$ in LiCl–KCl eutectic at 450° and $BiCl_3$ at 270° are presented in Figure 2. In Figure 3 the temperature dependence of the low-energy electronic spectrum for the eutectic is illustrated.

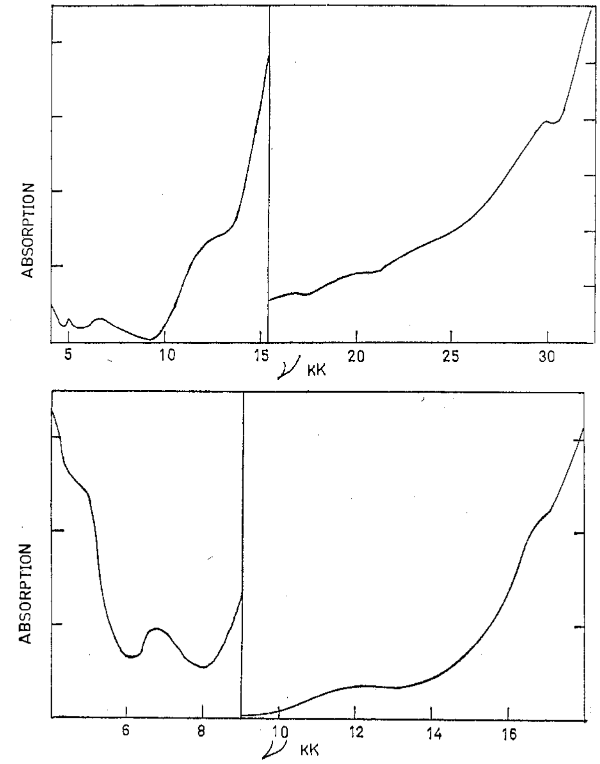

Figure 2.—Spectra of $OsCl_3$ solutions: top, in LiCl–KCl eutectic at 450°; bottom, in $BiCl_3$ at 270°.

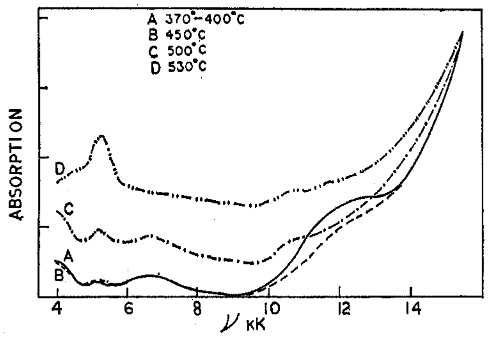

Figure 3.—Temperature dependence of the spectrum of $OsCl_3$ in LiCl–KCl eutectic melt.

Below 400°, the melts were clear and light brown and the spectrum remained constant for 12 hr (Figure 3A). As the temperature increased, the band at ~5 kK increased in intensity relative to the rest and at 500° a new band appeared at ~11 kK while dark particles were discernible in the solution. Nevertheless, up to 500°, the spectrum for a given temperature was stable for at least 5 hr. At 530°, this stability was lost. The spectral changes were accompanied by the increased deposition of dark particles in the cell and the formation of a brown deposit on the cooler walls above the melt until the actual melt became colorless and finally the dark particles completely disappeared. Examination of the cell later showed the rough surfaces to have been etched and an odor like that of OsO_4 was noticed.

In a separate experiment a concentrated solution of $OsCl_3$ in LiCl–KCl was heated to 550° in a Pyrex tube. The same dark brown deposit condensed on the upper sides of the tube but instead of particles a metallic mirror was formed. The brown deposit gave no flame reaction for Li or K. In another instance some of the particles were filtered off and found to be insoluble in acid but readily oxidized in air at 250° to a vapor. The brown solid dissolved in 6 *N* HCl to give a solution with a spectrum characteristic of Os(IV).[3,21 22]

The set of peaks which develop with time is the same as the spectrum of Na_2OsCl_6[21] and K_2OsCl_6 in LiCl–KCl but the species is longer lived in the presence of Os(III). We conclude that (i) Os(III), like Re(III)[23] and Zr(III),[24] disproportionates in LiCl–KCl, (ii) Os(IV) is volatilized as the tetrachloride, and (iii) Os metal reduces the silica of the cell.

If the Os(IV) spectrum is subtracted from the composite spectra of the melt solutions, the Os(III) bands listed in Table III are identified. In addition we have included the band with a clear maximum at 3.3 kK found for a $CHCl_3$ solution of $OsCl_3$. Since in neither $BiCl_3$ nor LiCl–KCl is Os(III) or Os(IV) obtained at a known concentration (Os(III) disproportionating and Os(IV) volatizing), it is not possible to assign absorptivities to the bands. We estimate by comparing the 5- and 11-kK bands in LiCl–KCl and noting from the absorptivity of the 11-kK band in HCl[22] that the 5-kK band of Os(IV) has $\epsilon_{\max}$ ~150.

TABLE III[a]

ν, kK	Intens	Assignment in D_{3h}	Solvent
3.3	Medium	$\Gamma_5 \leftarrow \Gamma_4$	$CHCl_3$
<4	Medium	$\Gamma_5 \leftarrow \Gamma_4$	LiCl–KCl
6.6	Weak	$\Gamma_4 \leftarrow \Gamma_4$	
12.0	Medium		
16.0	Strong		
19.5	Strong		
23.5	Strong		
30.0	Strong	Charge transfer	

[a] $\delta = -4.0$ kK; $\zeta = 2.7$ kK.

Os(III) has the configuration $5d^5$. In a pure octahedral field the ground state is $^2T_{2g}$ but this is split by strong spin–orbital coupling into Γ_7 at $-\zeta$ and Γ_8 at $\zeta/2$ where ζ is the one-electron 5d spin–orbital coupling constant; thus a near-ir band of energy $^3/_2\zeta$ would be anticipated. However, the axial distortion of octahedral d^5 complexes is predicted on theoretical grounds[1] and found in practice. The energy levels in rhombic (D_{3h}) and tetragonal symmetry (D_{4h}) then become[25] $\Gamma_4(D_{3h})$ or $\Gamma_7(D_{4h})$ at $^1/_2\cdot$

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$(-\delta/3 - \zeta/2 - Q)$, $\Gamma_5(D_{3h})$ or $\Gamma_6(D_{4h})$ at $\delta/3 + \zeta/2$, and $\Gamma_4(D_{3h})$ or $\Gamma_7(D_{4h})$ at $^1/_2(-\delta/3 - \zeta/2 + Q)$, where $Q^2 = \delta^2 + \delta\zeta + (^3/_2\zeta)^2$ and δ is the axial ligand field strength. Applying these expressions to the data of Table III we find $\delta = -4.0$ kK and $\zeta = 2.7$ kK which are quite reasonable values when we consider $\delta = -3.15$ kK and $\zeta = 3.15$ kK for $Os^{III}(acac)_3$[5] and ζ_{5d} is usually 2.5–3.5 kK.[21,26,27]

The origin of the four visible bands is less clear. By comparison with Ir(III) in LiCl–KCl[19] we might anticipate $\Delta = 25$ kK and $B = 0.3$ kK and taking $C = 4.5B$ for pure octahedral symmetry would expect transitions to the states $^4T_1$, $^4T_2$, and $^6A_1$ at 18.5, 21.0, and 32.5, respectively. If spin–orbital coupling is considered instead of interelectronic repulsion, then bands are predicted at 5, 22.5, 27.5, and 32.5 kK.[27] The addition of the axial distortion to a mixture of these sets could conceivably yield a series of bands starting at 16 kK but not obviously one at 12 kK nor, in particular, bands of high intensity relative to those found in the near-ir spectrum. It is tempting to speculate that Os(III), like Re(III), is polymeric in compounds with chloride. Further work on this system is in progress.

Voltammetry.—No reduction waves were obtained for $RuCl_3$, $OsCl_3$, or K_2OsCl_6 in LiCl–KCl eutectic melt. A similar situation was noted for K_2RuCl_6, $K_2RuCl_5 \cdot H_2O$, and $K_4Os(CN)_6$ in several aqueous media[28] and it appears[29-31] that reduction waves of Ru and Os compounds are only observed when oxygen is involved in one of the complexing ligands.

Acknowledgment.—This work was supported by the National Research Council of Canada. We are also indebted to L. G. Boxall for programming assistance.

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Microwave Spectrum, Molecular Structure, and Quadrupole Coupling in 2-Chloro-1,6-dicarbahexaborane(6)[1a]

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The microwave spectrum of 2-chloro-1,6-dicarbahexaborane(6) has been observed and rotational constants have been assigned for nine isotopic species. The boron–boron and boron–chlorine bond lengths were determined and the molecule was shown to exist as a distorted octahedron. The ^{35}Cl quadrupole coupling constant is 49.7 ± 2 MHz and the asymmetry parameter is zero within experimental error.

Introduction

The class of carbon–boron–hydrogen compounds commonly known as carboranes has received considerable attention in recent years. The unusual bonding arrangements in these molecules have made the determination of their molecular structures and properties particularly significant and intriguing. Though the nmr and ir spectra of some of the carboranes that have been studied in the past were insufficient to determine their gross structures, there was little doubt of the atomic arrangement and shape of the symmetric $C_2B_4H_6$ carborane. In spite of this, the determination of the accurate molecular structure of this octahedral framework is important in order to compare its bond lengths to those in other systems and to understand better the chemical bonding in carboranes. Since *sym*-$C_2B_4H_6$ has no dipole moment, we had to await the synthesis of a substituted derivative before the structure could be determined by microwave spectroscopy. In this study we report the microwave spectrum and partial molecular structure of 2-chloro-1,6-dicarbahexaborane(6). Unfortunately at this time the synthesis of the compound is not efficient enough to allow an economical preparation of enriched ^{13}C isotopic species, and the structure determination is incomplete.

Experimental Section

A sample of the title compound (*ca.* 50 mmol) was obtained from J. Spielman and was used without further purification. The compound is stable at room temperature, and despite repeated reusage of the same sample for a period of nearly 2 years, no serious decomposition was noted. The microwave spectrum was observed in the range 8–38 GHz using a conventional 100-kHz Stark-modulated spectrometer and 10–12-ft wave guide sample cells which were cooled below room temperature. Phase-locking techniques were employed for study of the quadrupole splittings of some low *J* transitions.

Observed Spectrum and Assignment

The microwave spectrum shows a multitude of weak- to medium-intensity lines owing both to the presence of several observable isotopic species and to the effects of the quadrupolar nuclei. Some difficulty was experienced at first in assigning the spectrum since Stark effects were not readily apparent and R-branch series for some isotopic species overlapped. The spectra of the nine major isotopic species were eventually assigned with the help of a good initial rigid-rotor approximation and by making approximate relative intensity measurements.

(1) (a) Supported by the United States Air Force Office of Scientific Research, under Grant AFOSR 849-67. (b) Alfred P. Sloan Foundation Research Fellow.