Table I

molality of solutes $\times 10^2$		initial atomic ratio of Hf/Zr	atomic ratio of Hf/Zr in product
Zr(IV)	Hf(IV)		
6	6	1	0.005
0.98	0.94	0.96	0.003
1.18	0.48	0.41	Hf not detectable

For a determination of the nature of the reduction product, the black precipitate observed at the electrode after electrolysis at <0 V vs. the Al(III)/Al reference electrode was treated with molten Al_2Cl_6 (to remove remaining NaCl) and filtered. The residual Al_2Cl_6 was removed by sublimation under vacuum; the shiny black precipitate was examined by powder X-ray diffraction. The powder pattern showed that the precipitate was either Al_3Hf[10] or a mixture of Al_3Hf and aluminum. Thus a simultaneous reduction of Hf(IV) and Al(III) is observed; depending on the ratio of Hf(IV) to $Al_2Cl_7^-$ and the potential of the electrode, the product is either Al_3Hf or a mixture of that compound with aluminum.

2. Electrochemical Separation of Zirconium from Hafnium. Since the difference between the reduction of Zr(IV) and $Al_2Cl_7^-$ increases slightly when the chloroaluminate melts become less acidic, melts containing ~50.5 mol % $AlCl_3$ were used for the separation experiments. The solubility of $HfCl_4$ in these melts at 175 °C is $\sim 8 \times 10^{-2}$ *m*. In a typical controlled-potential electrolysis experiment 50 g of an $AlCl_3$–NaCl (50.5 mol % $AlCl_3$) melt containing $\sim 10^{-2}$ *m* each of $ZrCl_4$ and $HfCl_4$ was used. The potential of a tungsten spiral cathode (area 3.5 cm^2) was controlled at 0.09 V vs. the Al(III)/Al reference electrode in the melt of the same composition. A reticulated vitreous carbon cylinder (4 cm long, 0.5 cm in diameter) was used as an anode; it was separated from the main compartment by a Pyrex frit of medium porosity. After 14 h of electrolysis at 175 °C voltammograms obtained at a tungsten microelectrode indicated that most of the Zr(IV) was reduced. The product was scraped from the electrode; residual $ZrCl_4$, $HfCl_4$, and Al_2Cl_6 were removed by sublimation at 205 °C. The product after sublimation was examined by X-ray fluorescence. This analysis showed that the atomic ratio of Hf/Zr decreased from 0.96 before the electrolysis to 0.003 in the product of the electrolysis. The Raman spectrum of the product showed a sharp line at 212 cm^{-1}, characteristic of $ZrCl_3$.[4] Results of three experiments are given in Table I. An excess of charge was involved in the reduction step; for example, in the experiment described above 164 coulombs were consumed compared to the expected value of 47 coulombs. It is likely that some of the chlorine produced at the anode reached the cathode to oxidize the $ZrCl_3$ product.

In preliminary experiments using platinum as the anode, the black cathodic deposit contained significant amounts of platinum. Clearly the use of platinum as an anodic counterelectrode in molten chloroaluminates should be avoided. In summary, we have demonstrated that hafnium-free zirconium can be produced by controlled-potential electrolysis using slightly acidic chloroaluminate melts. The separation factors achieved electrochemically are better than those achieved previously by chemical reduction.[6]

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Registry No. Zr, 7440-67-7; Hf, 7440-58-6.

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Synthesis of Substituted Octahedral Anions of Chromium(III), $[R_4N][cis\text{-}Cr(L\text{–}L)X_4]$, and the Nature of $Cr(L\text{–}L)_{1.5}X_3$ (L–L = Diphosphine or Diarsine; X = Cl, Br)

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Octahedral halo anions MX_6^{n-} are known for most transition metals, but substituted analogues containing neutral mono- (L) or bidentate (L–L) ligands are rare, especially in the 3d series.[2] The green $[Ph_4P][\textit{trans}\text{-}CrL_2Cl_4]$ (L = PEt_3, P-*n*-Bu_3) were obtained from $[CrL_2Cl_3]_2$ and Ph_4PCl in CH_2Cl_2.[3] During a study of chromium(III) complexes with soft donor ligands, as a prelude to examining small-molecule (O_2, NO, etc.) binding by chromium complexes, we isolated the *cis*-$[Cr(L\text{–}L)X_4]^-$ (X = Cl, Br) ions as R_4N^+ salts. Nyholm[4] obtained materials of empirical formula $Cr(das)_{1.5}X_3$ (das = *o*-$C_6H_4(AsMe_2)_2$) from chromium(III) halides and the ligand in moist acetone or alcohol, for which the three most likely formulations are $[Cr(das)_2X_2][Cr(das)X_4]$, $[Cr(das)_3][CrX_6]$, and $(das)X_3Cr(das)CrX_3(das)$. Since treatment with $HClO_4$ converted $Cr(das)_{1.5}X_3$ into $[Cr(das)_2X_2]ClO_4$, and attempts to prepare $[Cr(das)_3]^{3+}$ failed, Nyholm favored the first formulation. It should be noted however that a ligand-bridged dimeric structure was proposed for $Cr(Ph_2PCH_2CH_2PPh_2)_{1.5}X_3\cdot nH_2O$.[5] Our synthesis of $[Cr(L\text{–}L)X_4]^-$ led us to reinvestigate the $Cr(das)_{1.5}X_3$ complexes.

Results and Discussion

The reaction of $CrCl_3(THF)_3$, *n*-Pr_4NCl, and the appropriate bidentate ligand (L–L) in dry CH_2Cl_2 produced the tetrapropylammonium *cis*-tetrachloro(ligand)chromate(III), $[Pr_4N][\textit{cis}\text{-}CrCl_4(L\text{–}L)]$ (L–L = *o*-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(AsMe_2)_2$, $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, *cis*-$Ph_2AsCH{=}CHAsPh_2$), as blue powders. The $[Ph_3PCH_2Ph][Cr(\textit{o}\text{-}C_6H_4(AsMe_2)_2)Br_4]$ was obtained similarly (Table I). Attempts to isolate these anions using smaller cations were unsuccessful. It should be noted that reaction of $CrBr_3(THF)_3$ with R_4NBr in a 1:1 ratio in CH_2Cl_2 produces deep green solutions that may contain $[R_4N][Cr(THF)_2Br_4]$, although we have been unable to isolate these. The complexes are 1:1 electrolytes in 10^{-3} M nitromethane solutions and have magnetic moments ca. 3.88 μ_B as expected for d^3 Cr(III). The $[\textit{n}\text{-}Pr_4N][Cr(\textit{o}\text{-}C_6H_4(PMe_2)_2)Cl_4]$ complex is deliquescent, but the others are stable to moist air for short periods of time but are fairly readily decomposed by water or alcohols in solution. In spite of this, attempts to displace one halide from $[Cr(\textit{o}\text{-}C_6H_4(AsMe_2)_2)Cl_4]^-$ by stirring or heating CH_2Cl_2 or toluene solutions with monodentate ligands such as $PhMe_2P$, PPh_3, $AsMe_2Ph$, or MePhS (L), failed to give $[Cr(\textit{o}\text{-}C_6H_4(AsMe_2)_2)LCl_3]$, most of the starting complex being recovered unchanged.

The far-IR spectra of a *cis*-$[CrCl_4(L\text{–}L)]^-$ ion should show four chromium–chlorine stretching vibrations ($2A_1 + B_1 + B_2$), and despite the complications produced by absorptions of L-L in the same region, three or four bands were generally

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Table I. Chromium(III) Physical and Spectroscopic Data

complex	% C[a]	% H	% X	% N	% Cr	color	ν(Cr–X), cm^{-1} [b]
$[NPr_4][Cr(o\text{-}C_6H_4(PMe_2)_2)Cl_4]$	45.3 (45.6)	7.9 (7.6)	24.3 (24.6)	2.2 (2.4)	...	purple	375 sh, 355 m, 330 s, 305 sh
$[NPr_4][Cr(o\text{-}C_6H_4(AsMe_2)_2)Cl_4]$	39.4 (39.6)	6.1 (6.6)	21.8 (21.3)	2.0 (2.1)	7.2 (7.8)	blue	358 sh, 333 m, 325 s, 312 sh
$[NPr_4][Cr(Ph_2PCH_2CH_2PPh_2)Cl_4]$	58.5 (58.6)	6.1 (6.7)	17.0 (18.2)	1.9 (1.8)	5.9 (6.7)	purple	366 sh, 340 m, 315 sh, 300 s
$[NPr_4][Cr(Ph_2PCH{=}CHPPh_2)Cl_4]$	58.4 (58.7)	6.7 (6.4)	17.9 (18.3)	1.9 (1.8)	6.3 (6.7)	purple	340 s, 315 s
$[NPr_4][Cr(Ph_2AsCH{=}CHAsPh_2)Cl_4]$	52.2 (52.8)	5.4 (5.6)	16.2 (16.8)	1.7 (1.6)	6.0 (6.0)	purple	346 m, 335 s, 302 s
$[PPh_3CH_2Ph][Cr(o\text{-}C_6H_4(AsMe_2)_2)Br_4]$	41.8 (41.5)	3.6 (3.8)	30.9 (31.7)	... ...	... ...	blue	312 m, 285 s, 258 s
$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Cl_3$	30.5 (30.7)	4.0 (4.1)	18.0 (18.1)	... ...	9.3 (8.8)	green	380 m, 333 sh, 321 s, 307 sh
$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Br_3$	25.4 (25.0)	3.8 (3.3)	32.6 (33.3)	... ...	... ...	green	320, 285, 258 sh
$[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]ClO_4$	30.3 (30.2)	4.3 (4.0)	...	...	...	bright green	380 m
$[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2Br_2]ClO_4$	27.2 (27.2)	3.6 (3.6)				bright green	320 m

[a] Found values are given, with calculated values in parentheses. [b] Nujol mulls. All complexes have magnetic moments close to μ_{eff} = 3.88 μ_B/Cr as expected for Cr(III).

identified (Table I). The characterization of these $[CrX_4(das)]^-$ complexes enabled us to definitely identify the structure present in $Cr(das)_{1.5}X_3$ (X = Cl, Br), by far-IR spectroscopy. (Attempts to grow crystals of $Cr(das)_{1.5}X_3$ for X-ray crystallographic examination were frustrated by the poor solubility, and only powders were produced from in situ syntheses.) The $[Cr(das)_2X_2]ClO_4$ were readily obtained by treatment of $Cr(das)_{1.5}X_3$ with $HClO_4$, and as can be seen from Table I, the bands in the IR spectrum of $Cr(das)_{1.5}Cl_3$ in the range 400–200 cm^{-1} are all accounted for by superimposition of the spectra of $[Cr(das)Cl_4]^-$ and $[Cr(das)_2Cl_2]^+$. Similar conclusions are drawn for $Cr(das)_{1.5}Br_3$, although here the overlapping of Cr–Br and ligand bands makes the spectral assignments more difficult. Thus the far-IR spectra demonstrate that the $Cr(das)_{1.5}X_3$ complexes are indeed [*trans*-$Cr(das)_2X_2]^+$ [*cis*-$Cr(das)X_4]^-$.

Experimental Section

All reactions were carried out under dry dinitrogen by using standard Schlenk tube and dry box techniques. $CrCl_3(THF)_3$ was prepared from anhydrous $CrCl_3$, zinc dust, and dry tetrahydrofuran,[6] and $CrBr_3(THF)_3$ analogously from anhydrous $CrBr_3$. Physical measurements were made as described previously.[7]

$Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}X_3$ (X = Cl, Br). $CrX_3(THF)_3$ (1 mmol) was dissolved in dry dichloromethane (20 cm^3), the solution filtered, and *o*-phenylenebis(dimethylarsine) (0.57 g, 2 mmol) added. When the mixture was stirred at room temperature, green solids separated, which were filtered off, rinsed thoroughly with diethyl ether, and dried in vacuo; yield ca. 70%.

$[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2X_2]ClO_4$. $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}X_3$ (1 mmol) was added to 40% aqueous perchloric acid and the mixture stirred for 4–5 h. The bright green solids were separated by filtration and washed with distilled water, until the washings were colorless. The solids were rinsed with diethyl ether and dried; yield ca. 65%.

$[N\text{-}n\text{-}Pr_4][Cr(L\text{-}L)Cl_4]$ (L-L = $o\text{-}C_6H_4(AsMe_2)_2$, $Ph_2PCH_2CH_2PPh_2$, *cis*-$Ph_2PCH{=}CHPPh_2$, $Ph_2AsCH{=}CHAsPh_2$. *n*-Pr_4NCl was dried by heating at 80–90 °C in vacuo for 2 days. The appropriate ligand (2 mmol), $CrCl_3(THF)_3$ (2 mmol), and *n*-Pr_4NCl (2 mmol) were dissolved in CH_2Cl_2 and the solutions combined and stirred for several hours. The solutions were filtered and concentrated in vacuo. The oils produced were stirred with petroleum ether until they were converted to fine powders, which were filtered off and dried in vacuo. $[N\text{-}n\text{-}Pr_4][Cr(o\text{-}C_6H_4(PMe_2)_2)Cl_4]$ was prepared similarly in acetone and $[Ph_3PCH_2Ph][Cr(o\text{-}C_6H_4(AsMe_2)_2)Br_4]$ from the ligand, $CrBr_3(THF)_3$, and Ph_3PCH_2PhBr.

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Registry No. $[NPr_4][Cr(o\text{-}C_6H_4(PMe_2)_2)Cl_4]$, 82456-75-5; $[NPr_4][Cr(o\text{-}C_6H_4(AsMe_2)_2)Cl_4]$, 82456-77-7; $[NPr_4][Cr(Ph_2PCH_2CH_2PPh_2)Cl_4]$, 82456-79-9; $[NPr_4][Cr(Ph_2PCH{=}CHPPh_2)Cl_4]$, 82469-03-2; $[NPr_4][Cr(Ph_2AsCH{=}CHAsPh_2)Cl_4]$, 82456-81-3; $[PPh_3CH_2Ph][Cr(o\text{-}C_6H_4(AsMe_2)_2)Br_4]$, 82456-83-5; $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Cl_3$, 82456-84-6; $Cr[o\text{-}C_6H_4(AsMe_2)_2]_{1.5}Br_3$, 82456-85-7; $[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2Cl_2]ClO_4$, 14127-30-1; $[Cr(o\text{-}C_6H_4(AsMe_2)_2)_2Br_2]ClO_4$, 60536-77-8; $CrCl_3(THF)_3$, 10170-68-0; $CrBr_3(THF)_3$, 82456-86-8.

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Electrochemical Oxidation and Reduction of Methylcobalamin and Coenzyme B_{12}

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Although the electrochemical reduction of alkylcobalamins has been reported, the number of electrons involved and the reaction products were in doubt.[1-3] The oxidation of these compounds has not previously been studied. We report here the spectroelectrochemical and product analysis of both the electrochemical oxidation and reduction of methylcobalamin and coenzyme B_{12}. The electrochemical reactions of the alkylcobalamins are completely different from those of vitamin B_{12}, cyano[Co(III)]cobalamin, and other cobalamins.[1,4,5]

Experimental Section

The cyclic voltammetric and coulometric studies of coenzyme B_{12} and methylcobalamin were carried out in 0.5 M Na_2SO_4. In both cases, Britton–Robinson buffer was used.

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