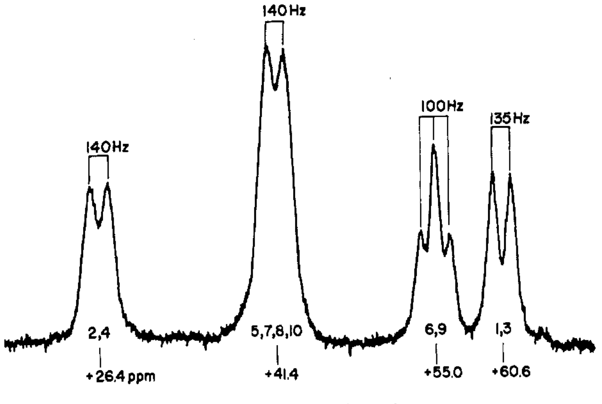

Figure 2.—The 80.5-MHz ^{11}B nmr spectrum of $Rb_2B_{10}H_{14}$ in H_2O.

cedure outlined in the literature.[3] The 80.5-MHz ^{11}B nmr spectra were obtained on an instrument designed by Professor F. A. L. Anet of the Department of Chemistry, University of California, Los Angeles, Calif. The ^{11}B nmr spectra of the rubidium, sodium, and tetra-*n*-butylphosphoniun salts of $B_{10}H_{14}^{2-}$ were obtained in water and methylene chloride, respectively. The spectra were identical indicating that any cation or solvent effects were negligible in determining the structure of $B_{10}H_{14}^{2-}$.

Discussion

The 80.5-MHz ^{11}B nmr spectrum of $Rb_2B_{10}H_{14}$ in H_2O clearly indicated (Figure 2) the presence of a BH_2 group at positions 6 and 9 in $B_{10}H_{14}^{2-}$ (Table I).

Table I

The 80.5-MHz ^{11}B Nmr Spectrum of $Rb_2B_{10}H_{14}$ in H_2O

Chemical shift[a] (J_{BH})	Signal (rel area)	Chemical shift[a] (J_{BH})	Signal (rel area)
+26.4 (140)	Doublet (2)	+55.0 (100)	Triplet (2)
+41.4 (140)	Doublet (4)	+60.6 (135)	Doublet (2)

[a] Chemical shift *vs.* an external capillary of methyl borate. The coupling constants are accurate to ±10 Hz.

We now compare the observed 2632 topology for $B_{10}H_{14}^{2-}$ based upon the $B_{10}H_{12}L_2$ structure with the 4450 topology based upon the hydrogen arrangement in $B_{10}H_{14}$. If for three-center bonds among boron atoms we retain only those of the central type,[4] there are 24 valence structures of the 2632 type: four each having single bonds 1-2, 3-8, 6-7; 1-2, 6-7, 8-9; 1-5, 3-7, 8-9; 1-5, 6-7, 8-9; 1-5, 6-7, 9-10; and two each having single bonds 1-3, 5-6, 8-9; 1-3, 5-6, 9-10. The 4450 topology has only one three-center valence structure, having single bonds 1-3, 2-6, 4-9, 5-10, 7-8. If we suppose that resonance confers stability, then the observed 2632 topology is favored.

On the other hand, the charge is much more evenly distributed in the 4450 topology, for which charges are 0.33− on B_1 and B_2, 0.17− on B_5, and 0.00 on B_6. By contrast, the equal weighting of charge distributions in the 2632 topology yields charges of 0.25− on B_1, 0.06− on B_2, 0.04− on B_5, and 0.61− on B_6. If the smoothing of the charge distribution is more important than resonance, we would therefore expect the 4450 topology to be favored contrary to these nmr results.

It has been noted that the formal replacement of a ligand, L, by H^- need not always yield the analogous structure. For example, this ambiguity was realized for $B_9H_{14}^-$ in the study[5] of the $B_9H_{13}(NCCH_3)$ structure. A recent X-ray diffraction study[6] has shown that $B_9H_{14}^-$ has a hydrogen arrangement not expected from analogy with $B_9H_{13}L$. The observed $B_9H_{14}^-$ structure is favored by both resonance and charge-smoothing arguments.[4] Thus $B_9H_{14}^-$ and $B_9H_{13}L$ make the structural ambiguity real; but only for the $B_{10}H_{14}^{2-}$ and $B_{10}H_{12}L_2$ pair do we have the first comparison of known structures which allows a choice of resonance stabilization, compared with an evened charge distribution, as a probable dominant factor in determining the hydrogen arrangement in the negative ion. Tests of the relative importance of these and other factors are to be expected in further studies of formally isoelectronic boron hydride ions and ligand derivatives.

[3] E. L. Muetterties, *Inorg. Chem.*, **2**, 647 (1963).

[4] I. R. Epstein and W. N. Lipscomb, *ibid.*, **10**, 1921 (1971).

[5] F. E. Wang, P. G. Simpson, and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1335 (1961), especially Figure 3.

[6] N. N. Greenwood, H. J. Gysling, and J. A. McGinnety, *Chem. Comm.*, 505 (1970).

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Synthesis and Characterization of Trichlorotetrahydrofuraniron(III)

By Linda S. Benner and Charles A. Root*

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Considerable work by Kern[1] and Fowles, Rice, and Walton[2] has been done to investigate the complexes formed by transition metal chlorides and tetrahydrofuran, THF. Contrary to the results of Kern,[1] we have been able to synthesize a monomeric, neutral complex by the reaction of anhydrous iron(III) chloride with THF. Interest in such complexes stems from the use of transition metal ions as catalysts in polymerization reactions of cyclic ethers. Cyclic ethers smaller than THF open readily in the presence of transition metal chlorides[3,4] and, under certain conditions, ring opening occurs in the THF–$FeCl_3$ system.[1,2]

In this paper we report the synthesis and characterization of the complex $FeCl_3 \cdot C_4H_8O$. The molecular weight data, obtained cryoscopically in benzene solution, indicate concentration-dependent association of the complex. Infrared data support coordination of THF to the metal and magnetic susceptibility data support assignment of a sextet ground state for iron(III). Electronic spectral data in benzene and in 1,2-dichloroethane are also reported.

Experimental Section

Reagents.—Anhydrous ferric chloride was prepared by passing chlorine gas over heated iron card teeth[5] and subliming the prod-

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[1] R. J. Kern, *J. Inorg. Nucl. Chem.*, **24**, 1105 (1962).

[2] G. W. A. Fowles, D. A. Rice, and R. A. Walton, *ibid.*, **31**, 3119 (1969).

[3] A. E. Gurgiolo, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **4** (2), 252 (1963).

[4] H. Uelzmann, U. S. Patent 3,240,722 (1966); *Chem. Abstr.*, **64**, 17736 (1966).

[5] H. F. Walton, "Inorganic Preparations," 8th ed, Prentice-Hall, Englewood Cliffs, N. J., 1962, p 113.

uct into tubes which were then evacuated and sealed. All other chemicals used were Baker Analyzed reagents, and all liquids used were dried and purified as described by Jolly.[6] Tetrahydrofuran was dried by treatment with sodium hydroxide pellets followed by sodium metal and finally distilled over lithium aluminum hydride. Benzene was dried over sodium and then distilled. 1,2-Dichloroethane was refluxed with phosphorus pentoxide and then distilled. The dried liquids, ferric chloride, and products were stored under nitrogen. *Anal.* Calcd for $FeCl_3$: Fe, 34.43; Cl, 65.57. Found: Fe, 34.22; Cl, 65.16.

Preparation of $FeCl_3 \cdot C_4H_8O$.—All reactions and manipulations were carried out in a moisture-free, nitrogen-filled glove bag. An open dish of phosphorus pentoxide was kept in the bag as a desiccant. Ferric chloride was slowly added with constant stirring to an excess of tetrahydrofuran. A $FeCl_3$:THF mole ratio of approximately 1:11 was necessary to ensure complete dissolution. The resulting solution was filtered into evaporating dishes and allowed to evaporate to dryness. More THF was removed by placing the product under low pressure of <2 Torr for 2–3 hr at room temperature. Then, with constant stirring, the solid was slowly dissolved in a minimal amount of benzene. Dissolution was incomplete due to formation of a tarry substance. The resulting yellow solution was filtered and frozen in an isopropyl alcohol–Dry Ice bath, and the benzene was sublimed under a low pressure of <2 Torr. When the product appeared to be dry, the tube was warmed to 50° to ensure complete removal of benzene. Unless the solvent was completely removed, further purification was unsuccessful and decomposition occurred. The pure compound was obtained by subliming the yellow powder at 80–85° at a pressure of <2 Torr. The compound remained stable at a pressure of 0.45 mm and at 90°. The final product was gold-colored crystals, and the residue was a red-brown powder. The yield for the yellow powder was 79% and the recovery after sublimation was 93%, giving an overall yield of 73%. *Anal.* Calcd for $FeCl_3 \cdot C_4H_8O$: Fe, 23.84; Cl, 45.37. Found: Fe, 23.72; Cl, 45.06. Iron analyses were performed by the EDTA[7] and dichromate[8] methods. Chloride analyses were done potentiometrically[9] using a silver-saturated $Hg-Hg_2SO_4$ electrode pair.

Spectral Measurements.—Infrared studies of the 4000–400-cm^{-1} region were carried out using a Perkin-Elmer Model 337 grating infrared spectrophotometer. Nujol mulls, hexachlorobutadiene mulls, and benzene solutions of the complex were studied using potassium bromide windows. Near-infrared, visible, and ultraviolet absorption spectra of benzene and of 1,2-dichloroethane solutions were obtained using a Cary Model 14 spectrophotometer equipped with 5-cm quartz cells. All samples were prepared under a dry nitrogen atmosphere and protected from moisture while the spectra were recorded.

Molecular Weight Determination.—Molecular weights were determined by a molal freezing point depression study of benzene solutions of the complex.

Magnetic Measurements.—Magnetic susceptibilities were measured by the method of Evans[10] as modified by Fritz and Schwarzhans.[11] A Varian A-60A spectrometer was used to measure the shifts in the cyclohexane resonance of 92:8 benzene–cyclohexane solutions. The temperature was maintained at 40 ± 1°. Magnetic moments were calculated from susceptibilities corrected using Pascal's constants for ligand diamagnetism and assuming Curie law behavior. Tris(acetylacetonato)iron(III) was used as the calibrant assuming $\mu_{eff} = 5.95$ BM.[12]

Results and Discussion

Trichlorotetrahydrofuraniron(III), $FeCl_3 \cdot C_4H_8O$, is synthesized by direct reaction of iron(III) chloride with tetrahydrofuran. The crude olive green product is purified by first freeze-drying a benzene solution of the complex. The yellow powder thus obtained is then sublimed at 80–85° (<2 Torr). Ring opening as described by Kern[1] may account for the observation of tarry material when the crude product is dissolved in benzene.

In order to find a solvent to effect purification and to study various properties of the complex, the solubilities of the complex were investigated. Kern[1] reported that, in general, the tetrahydrofuranates of transition metal halides are insoluble in noncoordinating solvents, soluble in THF, and soluble in alcohols, esters, ketones, and other solvents which will replace THF in the coordination sphere. $FeCl_3 \cdot C_4H_8O$ is moderately soluble in THF, benzene, and 1,2-dichloroethane, slightly soluble in nitrobenzene, mesitylene, and chloroform, and insoluble in carbon tetrachloride, cyclohexane, and *n*-hexane. THF cannot be used for purification because the tarry side products of the reaction are somewhat soluble in THF, whereas they are insoluble in benzene. In the presence of any moisture the complex rapidly decomposes.

The infrared spectra of $FeCl_3 \cdot C_4H_8O$ in Nujol mulls and benzene solution show a shift of the C–O–C asymmetric and symmetric stretching frequencies to lower energies as observed in other THF complexes of transition metal halides.[1,2] The shift is attributed to O-coordination of the THF to the metal. These data are summarized in Table I. The spectra in benzene solution are superimposable with those studied in Nujol with the exception of the small shifts noted in Table I.

TABLE I

INFRARED SPECTRA OF $FeCl_3 \cdot C_4H_8O$

Sample	Asym C–O–C str $\bar{\nu}$, cm^{-1}	Asym C–O–C str $\Delta\bar{\nu}$,[a] cm^{-1}	Sym C–O–C str $\bar{\nu}$, cm^{-1}	Sym C–O–C str $\Delta\bar{\nu}$,[a] cm^{-1}
THF, neat	1070		909	
$FeCl_3 \cdot C_4H_8O$, Nujol	988	82	833	76
$FeCl_3 \cdot C_4H_8O$, benzene	993	77	843	66

[a] $\Delta\bar{\nu}$ is the shift in frequency relative to uncoordinated THF.

Cryoscopic molecular weight data obtained in benzene over a concentration range of 0.0197–0.126 *m* show that the complex $FeCl_3 \cdot C_4H_8O$ is monomeric at low concentration but that association increases with increasing concentration. A plot of the data, including calculated error limits, is shown in Figure 1.

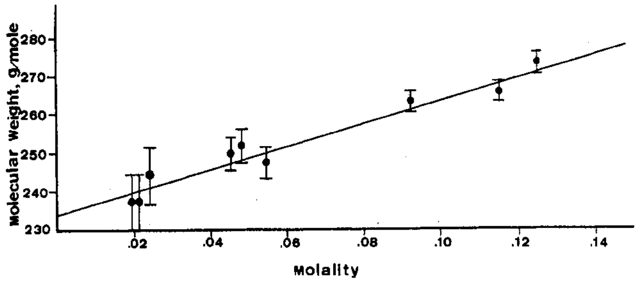

Figure 1.—Cryoscopically determined molecular weight of $FeCl_3 \cdot C_4H_8O$ in benzene.

These data and the infrared shifts show conclusively that the THF is coordinated to iron(III) without ring cleavage.

The complex is further characterized by its elec-

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(6) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds," Prentice-Hall, Englewood Cliffs, N. J., 1970, pp 116–121.

(7) R. B. Fischer and D. G. Peters, "Quantitative Chemical Analysis," 3rd ed, W. B. Saunders, Co., Philadelphia, Pa., 1968, p 436.

(8) J. S. Fritz and G. H. Schenk, "Quantitative Analytical Chemistry," Allyn and Bacon, Boston, Mass., 1968, p 415.

(9) Reference 7, p 743.

(10) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(11) H. P. Fritz and K. E. Schwarzhans, *J. Organometal. Chem.*, **1**, 208 (1964).

(12) L. Cambi and L. Szego, *Chem. Ber.*, **64**, 2591 (1931).

tronic absorption spectrum which was measured from 9090 to 37,800 cm^{-1}. Benzene was used in the visible region since this solvent was used for all other solution measurements. 1,2-Dichloroethane was used to record the entire spectrum. Table II summarizes these data. All bands found between 9090 and 21,000 cm^{-1} are believed to be La Porte and spin-forbidden transitions from the sextet ground state of the spin-free d^5 configuration to excited quartet states. Assignments on the basis of a four-coordinate structure of C_{3v} symmetry are not made in more detail due to the fact that the complex is involved in concentration-dependent association. If it is assumed that only monomers and dimers are present in solution, the molecular weight data indicate that at 5.95×10^{-2} *m*, the mole fraction of monomer is 0.92. This would give a ratio of $[\mathrm{Fe}]_{\mathrm{mon}}/[\mathrm{Fe}]_{\mathrm{dim}} = 6.0$, where $[\mathrm{Fe}]_{\mathrm{mon}}$ is the formal concentration of Fe in monomer and $[\mathrm{Fe}]_{\mathrm{dim}}$ is the formal concentration of Fe in dimer. Thus, assuming equimolar absorptivities for Fe in each form, the ratio of absorbances $A_{\mathrm{mon}}/A_{\mathrm{dim}}$ is ~6.0. Therefore, some of the observed shoulders in the absorption spectrum could be due to dimer absorption. It should be noted that there are no data which rule out association beyond the dimeric form. Calculation assuming the presence of only monomers and trimers gives an absorbance ratio of ~7.4 monomers to 1 trimer, assuming equal molar absorptivities. Thus, the greater the degree of association in solution, the more likely it is that the bands are due to monomer. An intense charge-transfer band is observed at 28,900 cm^{-1} in 1,2-dichloroethane. The benzene solution shows the beginning of a charge-transfer band at considerably lower energy than the 1,2-dichloroethane solution, thus making observation of the ligand field bands difficult. The coincidence of the bands at 14,900, 16,700, and 17,100 cm^{-1} may indicate that the same solute structure exists in both solvents. A sketch of the 1,2-dichloroethane spectrum is shown in Figure 2.

TABLE II

ELECTRONIC ABSORPTION SPECTRA OF $FeCl_3 \cdot C_4H_8O$

Solvent	Concn,[a] *M*	$\bar{\nu}_{\mathrm{max}}$, cm^{-1}	ϵ_{max},[b] M^{-1} cm^{-1}
Benzene	7.21×10^{-2}	14,900	2.38
		16,700 sh	
		17,100	2.74
1,2-Dichloroethane	5.95×10^{-2}	14,900	1.64
		16,700 sh	
		17,100	
		18,300 sh	
		19,400	1.83
		21,000 sh[c]	
1,2-Dichloroethane	3.22×10^{-5}	28,900	6880

[a] These are formal concentrations of iron(III). [b] The ϵ values were calculated without consideration of the increasing absorption due to a charge-transfer band on which all the d–d transitions are superimposed. [c] The 21,000-cm^{-1} shoulder was observed for a solution qualitatively diluted to a concentration between 4×10^{-3} and 1×10^{-2} *M*.

Magnetic susceptibility measurements made in a benzene–cyclohexane solution show that at low concentrations the iron(III) has a spin-free d^5 ground state. Seven measurements over a concentration range of 1.90×10^{-2}–4.81×10^{-2} *M* give an average value for μ_{eff} of 5.79 ± 0.03 BM.

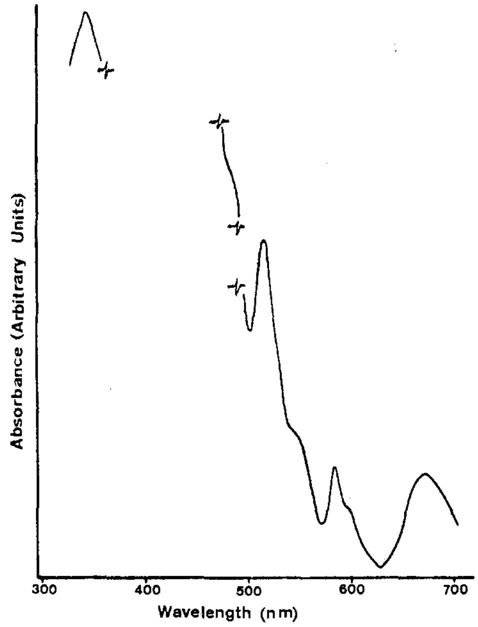

Figure 2.—Electronic spectrum of $FeCl_3 \cdot C_4H_8O$ in 1,2-dichloroethane showing six d–d transitions and one charge-transfer transition.

In summary, the complex $FeCl_3 \cdot C_4H_8O$ has been prepared and shown to contain O-coordinated THF. The complex is monomeric in benzene at low concentrations but associates as the concentration increases. The structure appears to be the same in benzene and 1,2-dichloroethane solutions, and all measurements are consistent with a four-coordinate, high-spin iron(III) complex.

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An Adduct of Tetracyanoethylene and Triphenylphosphine

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Tetracyanoethylene (TCNE) is a well-known electron acceptor and triphenylphosphine (TPP) is a well-known donor. It would appear reasonable that adduct formation should occur between them. However, as Shine and Gordon[1] have pointed out, "in studies of complexes between TCNE and heteroatomic donors by spectral methods most workers report other reactions which make complex detection difficult." Our experience with the TCNE–TPP system has been no different. Reported here is the preparation and characterization of a solid TCNE–TPP adduct and also a brief account of the solution behavior of these substances and other bases related to TPP.

A 2:1 TCNE–TPP adduct has been prepared by Reddy and Weis[2] for which they propose the structure

[1] H. J. Shine and R. J. Gordon, *J. Org. Chem.*, **35**, 949 (1970).

[2] G. S. Reddy and C. D. Weis, *ibid.*, **28**, 1822 (1963).