equivalents. After formation of the agglomerated metal oxide, the second is a photocatalyzed reduction of the impurity, where the agglomerated metal oxide behaves as a photoexcited semiconductor. Unlike thermal activation where CH_4 evolution is limited to a stoichiometric reaction,[39,40] optical excitation of the resulting agglomerated metal oxide continues to photocatalyze the evolution of CH_4. A significant question arising from these experiments is the nature of the carbonaceous impurity and, since the agglomerated metal oxide is a photocatalyst, whether this impurity can be replenished by reaction with a simple carbon oxide.

Acknowledgment. Support of this research by the Research Foundation of the City University of New York, Dow Chemical Co.'s Technology Acquisition Program, the National Science Foundation (Grant CHE-8511727), and the New York State Science & Technology Foundation (Grant SSF (85)-5) is gratefully acknowledged. H.D.G. thanks Queens College for a Presidential Research Fellowship during 1987, Professor W. F. Berkowitz for many helpful discussions, and the Corning Glass Works for samples of porous Vycor glass.

Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; $Cr(CO)_5$, 26319-33-5; $Mo(CO)_5$, 32312-17-7; $W(CO)_5$, 30395-19-8; $Cr(CO)_4$, 56110-59-9; $Mo(CO)_4$, 44780-98-5; $W(CO)_4$, 114221-02-2; CO, 630-08-0; CH_4, 74-82-8; H_2, 1333-74-0; CO_2, 124-38-9; formaldehyde, 50-00-0; methanol, 67-56-1.

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Isolation and Crystal Structure of Manganese(II) Tetrafluoroborate: A Unique Example of Manganese(II) with Seven Unidentate Ligands

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Crystalline manganese(II) tetrafluoroborate has been isolated as the ansolvate from a solution in anhydrous hydrogen fluoride. Its crystal structure provides the first instance of Mn(II) in a seven-coordinate environment of unidentate ligand atoms, each of which is derived as a terminal fluorine atom from a BF_4 group; the MnF_7 coordination polyhedron is a monocapped trigonal prism. There are two types of tetrahedral BF_4 groups, one bridging four manganese atoms through each of its fluorine atoms and the other bridging only three manganese atoms, giving the formula $Mn(BF_4)_{4/4}(BF_4)_{3/3}$. Crystals of $Mn(BF_4)_2$ are orthorhombic with the space group *Pnma*, $Z = 4$, and unit cell dimensions $a = 8.6042$ (9) Å, $b = 5.4496$ (4) Å, and $c = 10.8673$ (9) Å. The structure was refined by a full-matrix least-squares method from 491 statistically significant reflections.

Introduction

Solubilities at room temperature of di- and trifluorides of d- and f-transition elements in "neutral" or natural anhydrous hydrogen fluoride (AHF) are very small, typically less than 5×10^{-3} *m* for d-transition-metal difluorides and much less again for trifluorides. Consequently, until relatively recently, it was not possible to use spectroscopy to gain information about the solvation environment of cations in AHF or to crystallize transition-metal compounds from AHF for structural determination. Deliberate enhancement of the acidity of AHF by use of fluorides that are Lewis acids of the solvent system led to greatly increased concentrations of transition-metal cations in AHF[1,2] and has overcome the two experimental problems outlined above.

UV–visible spectra in AHF have been recorded for a very wide range of d- and f-transition-metal cations,[1,3-5] and these and ESR spectra[6] indicate that coordination numbers and stereochemistries of cations in AHF are very similar—usually identical—to those in water or in fluoride environments in solids. Specifically the coordination numbers in AHF are generally 6 for first-row elements,[1,5] 8–9 for the trivalent lanthanides,[7] at least 9 for the divalent ions Sm^{2+}, Eu^{2+}, and Yb^{2+},[7] and 5 in the equatorial plane for UO_2^{2+}.[7] There is good evidence that coordination is by HF molecules, but the contribution made to the inner sphere by the counterions such as SbF_6^-, AsF_6^-, and BF_4^- is not easily determined at the present time, though it is expected to be negligible especially in diluted solutions.[4,7]

An extension of the studies of solvation of cations in AHF has been the attemped isolation from AHF of crystalline salts containing HF-solvated cations. Within this context solutions of manganese(II) tetrafluoroborate, produced by treating MnF_2 with BF_3 in AHF, readily gave colorless, well-formed crystals on cooling or on evaporating solvent from saturated solutions. These crystals were the subject of an X-ray crystallographic investigation, the results of which are reported in this paper.

The solid has been characterized as $Mn(BF_4)_2$. From the general viewpoint of inorganic chemistry the unique feature of this structure is the monocapped-trigonal-prismatic coordination of the manganese center, the seven-coordination being achieved by fluorine atoms derived from well-defined "monodentate" tetrafluoroborate anions.

In an extensive review of seven-coordinate compounds in 1979 Kepert[8] commented on the very small number of compounds containing seven identical unidentate ligands and he listed six known examples, including the structurally simple IF_7. The only example from the first row of the d transition metals was $V(CN)_7^{4-}$. In several compounds seven-coordination has been virtually forced on manganese(II) by the use of multidentate ligands with simple ligands occupying a small number of sites. An early example was that of H_2O bonded to the seventh site around Mn(II) when the other six were occupied by EDTA.[9] Other hexadentate ligands dictate similar stereochemistry.[10]

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There are examples of a combination of pentadentate macrocycles and two unidentate ligands providing seven-coordination[11,12] and of two H_2O molecules and one Cl atom with a tetradentate ligand.[13] In contrast to these structures $Mn(BF_4)_2$ contains no chelating groups but only monodentate anions that are formally quadruply and triply bridging to metal atoms. The two anion types are present in equal proportions within the infinite lattice.

The claim in the title of this paper that the structural type reported here is unique rests on two bases. First, manganese(II) in all earlier reported structural investigations is seven-coordinate only when at least one polydentate ligand is used. Second, the seven compounds listed by Kepert[8] as being the known examples of seven-coordination involving only unidentate ligands all involve discrete structural units e.g. uncharged IF_7 or monomeric cations or anions. $Mn(BF_4)_2$ is the first structure involving seven-coordination of Mn(II) by unidentate ligands within an infinite lattice.

Experimental Techniques and Procedures

Reagents. Anhydrous HF. Commercial HF was purified by three trap-to-trap distillations through a well-conditioned Kel-F vacuum line. The "heads and tails" of each distillation were discarded.

Boron Trifluoride. The commercial product (Matheson, 99.5%) was used as received.

Manganese Metal. Pure massive electrolytic manganese (Koch Light, 99.9%) as received was contaminated with some black surface oxide. This was removed by treatment with 10% aqueous hydrochloric acid until a uniform clean metallic surface was visible. The metal was washed with deionized water and acetone (AR grade) and then dried in an air stream.

Preparation of the $Mn(BF_4)_2$ Solution. All manipulations were carried out in passivated stainless steel, Kel-F, or synthetic sapphire (fused alumina) equipment by using standard vacuum line techniques for handling volatile fluorides.

In a typical reaction, 27.5 mg (0.5 mmol) of cleaned manganese was weighed into a well-conditioned Kel-F tube (volume 30 ml), which was then evacuated. A 5-mL portion of AHF was distilled onto the metal in vacuo, and gaseous BF_3 was applied at an overpressure of ca. 200 kPa with the precaution that the metal vacuum line was not exposed to the mixture of HF and BF_3 vapors; otherwise, rapid corrosion of the metal fittings can occur through dissolution of the passivating layer of fluoride.

The metal reacted rapidly with the evolution of hydrogen, which was periodically removed by freezing the reaction mixture in liquid N_2 and pumping:

$$\mathrm{Mn} + 2\mathrm{HF} + 2\mathrm{BF}_3 \xrightarrow{\mathrm{AHF}} \mathrm{Mn}^{2+}(\mathrm{solv}) + 2\mathrm{BF}_4^- + \mathrm{H}_2$$

At the completion of the reaction, the metal had dissolved to produce a clear colorless solution containing manganese(II) tetrafluoroborate, which was identified spectroscopically.[7]

Isolation of Crystals. This process was carried out in a fused-alumina tube because of the superior optical transparency of the material over that of conventional Kel-F equipment, thus enabling the crystals to be easily seen. The AHF solution prepared above was carefully poured in vacuo into an evacuated fused-alumina tube, and the solution was concentrated by the careful evaporation of solvent (and BF_3) until the first signs of crystallization became evident. The BF_3 content in the solution was maintained by periodic addition as outlined above in order to maintain the acidity of the solution. The slightly supersaturated solution was allowed to stand at room temperature for several hours during which time crystal growth occurred on the walls of the tube. After some time the solution was poured away into a slightly cooled storage container. Residual traces of solvent were then removed by "flash pumping".

The container and crystals were then examined under the microscope and the positions of suitable crystals noted.

Preliminary tests revealed that the crystals were extremely hygroscopic, liquefying within seconds in the atmosphere, and therefore their complete isolation from moisture was essential. In view of the method of preparation and the anticipated presence of HF, it was considered that conventional glass capillaries might not be suitable and therefore specially prepared FEP and Kel-F capillaries were investigated for this purpose. However, none was found to be suitable, as decomposition of test crystals rapidly occurred in the laboratory atmosphere, probably due to porosity of the extremely thin capillary walls and resultant diffusion of moisture. The possibility of encasing the plastic capillary within a larger glass capillary was not followed up because of the excessive attenuation of the X-ray beam through these materials. It was then found to be quite satisfactory to use conventional Lindemann glass capillaries.

Table I. Crystal Data and Details of Crystal Structure Determination of $Mn(BF_4)_2$

formula	$Mn(BF_4)_2$
fw	228.55
cryst syst	orthorhombic
space group	*Pnma* (D_{2h}^{16}, No. 62)
a, Å	8.6042 (9)
b, Å	5.4496 (4)
c, Å	10.8673 (9)
vol, Å^3	509.6 (1)
Z	4
ρ(calcd), g cm^{-3}	2.98
cryst dimens (dist from centroid), mm	±(011), 0.120; ±(001), 0.175; $(1\bar{1}\bar{1})$, 0.130; $(\bar{1}\bar{1}\bar{1})$, 0.130; $\pm(\bar{4}30)$, 0.158; $(0\bar{1}2)$, 0.130; $(0\bar{1}\bar{2})$, 0.130; $(2\bar{2}1)$, 0.140; $\pm(20\bar{1})$, 0.170; $(\bar{2}\bar{2}1)$, 0.140
temp, K	295 (1)
radiation (λ, Å)	Cu Kα, Ni filtered (1.5418)
F(000)	428
μ, cm^{-1}	224.8
min, max transmission factors	0.0193, 0.1171
2θ range, deg	$3 \le 2\theta \le 140$
range of *hkl*	$0 \le h \le 10$; $-6 \le k \le 6$; $-13 \le l \le 13$
no. of rflns measd	2295
no. of rflns used ($I \ge 3\sigma(I)$)	1827
no. of unique rflns	491
R_{amal}	0.089
no. of variables	62
refinement	full-matrix least-squares; function minimized $\sum w\Delta^2$
weighting scheme	$w = [k/(\sigma^2_F + g\lvert F\rvert^2)]$; $k = 19.60$, $g = 0.000\,34$
isotropic extinction param, *x*	7.7 (7) × 10^{-6}
final R_1 ($\sum\lvert\Delta F\rvert/\sum\lvert F_o\rvert$)	0.051
final R_w ($\sum w^{1/2}\lvert\Delta F\rvert/\sum w^{1/2}\lvert F_o\rvert$)	0.061
max shift/esd	0.001
max residual electron density, e Å^{-3}	1.2

Transfer of the crystals into capillaries was undertaken in a glovebox by using a funnel arrangement, which minimized contact of the crystals (which are potentially unstable due to loss of BF_3) with the atmosphere of the glovebox. The open ends of the capillaries were sealed temporarily with Kel-F grease and then permanently outside the box over a small hot flame.

Crystal Structure Determination of $Mn(BF_4)_2$. A preliminary photographic study indicated that the colorless crystals were orthorhombic, possessing the space group *Pnma* or *Pn*2_1*a* because of the systematic absences $0kl$ ($k + l = 2n + 1$) and $hk0$ ($h = 2n + 1$); a satisfactory solution was found in the centrosymmetric space group *Pnma*. An approximately hexagonal tabletlike crystal contained in a Lindemann glass tube was mounted with its *a* axis coincident with the ϕ axis of a Siemens AED automatic three-circle single-crystal diffractometer. Accurate cell dimensions together with their esd values were obtained by a least-squares method[14] with the 2θ values measured for 12 carefully centered, well-resolved, near-axial reflections; λ(Cu Kα_1) = 1.540 51 Å. Crystal data are given in Table I.

Intensity data were collected by means of a "five-value" $\theta/2\theta$ scan method[15] with Cu Kα (nickel-filtered) radiation. Because of the relatively high linear absorption coefficient of the crystal and its irregular morphology, intensity data were collected for the complete copper hemisphere to a maximum Bragg angle of 70° together with some repeated measurements. The net intensity of a reference reflection, monitored

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Table II. Fractional Atomic Coordinates for $Mn(BF_4)_2$

atom	x	y	z
Mn	0.2527	$^1/_4$	0.3978 (1)
F(1)	0.2469 (5)	$^1/_4$	0.1884 (4)
F(2)	0.4246 (8)	$^1/_4$	0.5456 (6)
F(3)	0.0051 (5)	$^1/_4$	0.3605 (3)
F(4)	0.3998 (5)	0.5429 (6)	0.3415 (3)
F(5)	0.1663 (4)	0.5414 (6)	0.5209 (3)
F(6)	0.4088 (7)	$^1/_4$	0.7544 (6)
B(1)	0.5036 (10)	$^1/_4$	0.6565 (7)
B(2)	0.3524 (11)	$^1/_4$	0.0929 (6)

after every 20 intensity measurements, showed no significant variation during the data collection. Other details of the data collection are given in Table I. The intensity values were corrected for Lorentz, polarization, and absorption effects; absorption corrections were numerically evaluated by Gaussian integration to a precision of 0.5%.[16a,17] Averaging of equivalent reflections yielded 491 independent reflections with an R_{amal} value of 0.089.[17] The relatively high R_{amal} value, together with the 10 reflections that showed significant inconsistencies between equivalent terms, was attributed to the high absorption coefficient and the problems of adequate description of the crystal morphology. Several attempts were made to improve the description of the crystal shape, and that reported in Table I was the best obtained.

Coordinates of the manganese atom were derived from a Patterson synthesis with the remaining atoms being located in the subsequent difference map. A full-matrix least-squares refinement of positional and isotropic thermal parameters converged with $R = 0.11$. The refinement was continued with anisotropic temperature factors and a weighting scheme of the form $w = [k/(\sigma_F^2 + g|F|^2)]$ where values of k and g were redetermined after each refinement cycle. An isotropic extinction parameter, x, was also included in the refinement so that F_c was modified according to $F_c(\text{cor}) = F_c(1 - xF_c^2/\sin\theta)$. The values of R, R_w, k, G, and x at convergence, together with the maximum value of shift/esd, are given in Table I. The analysis of variance showed no special features, indicating that an appropriate weighting scheme had been used. The maximum residual electron density of 1.2 e Å^{-3} was 1.20 Å from the Mn atom.

Calculations were performed by using the SHELX-76 system[17] on a VAX 11/780 computer. Scattering curves used for B and F were those collected by Sheldrick[17] while that for the neutral Mn atom, which was corrected for anomalous dispersion,[16b] was taken from ref 16c.

The final atomic coordinates are given in Table II; the numbering scheme is shown in Figure 1.

Discussion

Description of the Structure. The unit cell of $Mn(BF_4)_2$ contains four formula units of composition $Mn(BF_4)_2$. There is no AHF of crystallization, which is a surprising outcome when it is considered that the solution from which the crystals were obtained contained $Mn(FH)_6^{2+}$ cations according to the UV-visible and ESR spectroscopic evidence.[6] This unsolvated species is in stark contrast to the nature of similar transition-metal salts when isolated from other polar solvents such as water or alcohols, where crystalline materials containing a high proportion of combined solvent are commonly encountered.

To date only one other structural characterization of a salt containing a transition-metal cation and that has been isolated from AHF has been reported. This is $UO_2F_2 \cdot 3SbF_5$,[18] which is also nonsolvated although the AHF solution from which the solid is obtained contains UO_2^{2+}(solv) and fluoroantimonate anions.[3,7] It appears, on the basis of the limited structural data available from that structural determination and the present work, that the HF molecule is a weakly solvating ligand for ionic species even though bulk AHF is an excellent solvent for ionic compounds.

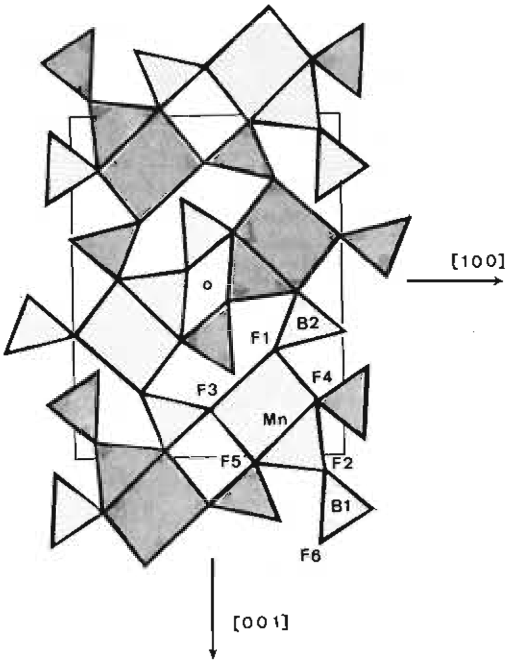

Figure 1. View of the $Mn(BF_4)_2$ crystal structure down [010]. The numbering scheme employed is also shown. The origin of the unit cell is indicated by O. The coordination polyhedra situated about the mirror plane at $y = {}^3/_4$ are indicated by the darker shading.

Table III. Important Interatomic Distances (Å) and Angles (deg) for $Mn(BF_4)_2$[a]

(a) Distances			
Mn–F(1)	2.276 (4)	B(1)–F(2)	1.384 (10)
Mn–F(2)	2.183 (7)	B(1)–F($4^{II},4^{III}$)	1.402 (6)
Mn–F(3)	2.169 (4)	B(1)–F(6)	1.341 (10)
Mn–F($4,4^{I}$)	2.127 (4)	B(2)–F(1)	1.378 (9)
Mn–F($5,5^{I}$)	2.205 (3)	B(2)–F(3^{IV})	1.408 (10)
Mn···F($6^{VII},6^{VIII}$)	3.433 (4)	B(2)–F($5^{V},5^{VI}$)	1.390 (5)

(b) Angles			
F(1)–Mn–F(2)	138.6 (2)	F(4)–Mn–F(5)	80.5 (2)
F(1)–Mn–F(3)	78.0 (2)	F(4)–Mn–F(5^{I})	156.3 (2)
F(1)–Mn–F($4,4^{I}$)	74.1 (2)	F(5)–Mn–F(5^{I})	92.1 (2)
F(1)–Mn–F($5,5^{I}$)	126.8 (2)	F(2)–B(1)–F($4^{II},4^{III}$)	107.7 (4)
F(2)–Mn–F(3)	143.4 (2)	F(2)–B(1)–F(6)	113.1 (4)
F(2)–Mn–F($4,4^{I}$)	79.0 (2)	F(4^{II})–B(1)–F(4^{III})	107.2 (4)
F(2)–Mn–F($5,5^{I}$)	77.4 (2)	F($4^{II},4^{III}$)–B(1)–F(6)	110.4 (4)
F(3)–Mn–F($4,4^{I}$)	122.1 (2)	F(1)–B(2)–F(3^{IV})	110.2 (4)
F(3)–Mn–F($5,5^{I}$)	77.4 (2)	F(1)–B(2)–F($5^{V},5^{VI}$)	110.4 (4)
F(4)–Mn–F(4^{I})	97.3 (2)	F(3^{IV})–B(2)–F($5^{V},5^{VI}$)	108.1 (4)
		F(5^{V})–B(2)–F(5^{VI})	109.7 (4)

[a] Symmetry operations: (I) $x, {}^1/_2 - y, z$; (II) $1 - x, y - {}^1/_2, 1 - z$; (III) $1 - x, 1 - y, 1 - z$; (IV) ${}^1/_2 + x, y, {}^1/_2 - z$; (V) ${}^1/_2 - x, 1 - y, z - {}^1/_2$; (VI) ${}^1/_2 - x, y - {}^1/_2, z - {}^1/_2$; (VII) ${}^1/_2 - x, {}^1/_2 + y, z - {}^1/_2$; (VIII) ${}^1/_2 - x, y - {}^1/_2, z - {}^1/_2$.

$Mn(BF_4)_2$ forms a condensed structure. If the structure is considered in terms of only its fluorine atoms, each fluorine atom has an average volume of 15.9 Å^3, a value typical of close-packed structures. However, the structure does not conform to any of the common structure types and we believe it to be unique. The three-dimensional arrangement comprises an articulation, involving corner linking only, of two crystallographically independent BF_4 tetrahedral units and a MnF_7 monocapped-trigonal-prismatic unit. The BF_4 units bridge the MnF_7 polyhedra in a complex fashion, which is shown in Figure 1. With the exception of F(6) all the F atoms participate in both types of coordination polyhedra. Each BF_4 and MnF_7 unit is located about a crystallographic mirror plane. Important interatomic distances and angles are given in Table III.

Manganese Environment. A most interesting feature of the $Mn(BF_4)_2$ structure is the monocapped-trigonal-prismatic environment of the manganese atom; this is shown in Figure 2. As has already been noted, the coordination number of 7 is very rare for first-row transition metals. As can be seen from Table III, the Mn–F bond distances show the substantial range of 2.127 (4) – 2.276 (4) Å. These distances may be compared with the two

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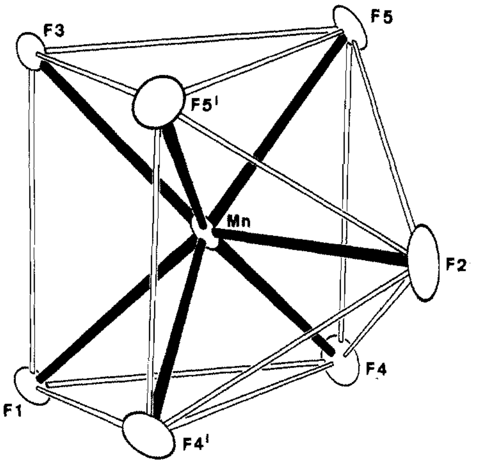

Figure 2. Seven-coordinate monocapped-trigonal-prismatic environment of the manganese atom in $Mn(BF_4)_2$. The Mn, F(1), F(2), and F(3) atoms all lie on a mirror plane.

independent Mn–F distances of 2.10 (1) and 2.13 (1) Å found in MnF_2, where the metal atom adopts a slightly distorted octahedral environment.[19] The distances in $Mn(BF_4)_2$ are clearly longer, presumably the result of the higher coordination number.

The metal atom is situated within the trigonal prism component of its coordination polyhedron [defined by F(1), F(3), F(4$^{\text{I}}$), F(5), and F(5$^{\text{I}}$)] and lies 0.442 Å from the plane through the atoms defining the capped face [F(4), F(4$^{\text{I}}$), F(5), and F(5$^{\text{I}}$)]. This face is precisely planar, a consequence of the crystallographic symmetry, and the other two rectangular faces are essentially planar, the maximum deviation from planarity being 0.018 Å; the distance of the Mn atom from these faces is 1.020 Å. The capping atom is F(2) with the Mn–F(2) bond almost exactly normal to the face, the angle between the normal and the bond being 1.5°. The two independent distances between F(2) and the atoms of the capped face are 2.741 (6) and 2.745 (7) Å. The closest approach to the two uncapped rectangular faces is made by F(6$^{\text{VII}}$) and F(6$^{\text{VIII}}$), but the very long distance of 3.433 (4) Å formed by these atoms to the manganese atom indicates that there is no significant bonding between them and that the Mn atom is truly seven-coordinate. This is supported by a comparison of the F···F distances around the coordination polyhedra. Those between the symmetry-related atoms of the capped face are 3.192 (5) and 3.176 (5) Å. These are very much larger than the remaining F···F distances, which all lie in the range 2.655 (5) – 2.800 (5) Å, indicating that neither of the two remaining rectangular faces is capped. These distances also indicate that the introduction of the seventh ligand expands the capped face by folding the other two rectangular faces about the hinge formed by F(1) and F(3).

BF_4 Tetrahedral Units. The relationship of the two crystallographically independent BF_4 tetrahedral with respect to the MnF_7 unit is shown in Figure 1. The BF_4 groups adopt different bridging arrangements. Each of the fluorine atoms of that group which has B(2) as its central atom also participates in the coordination polyhedron of a different Mn atom and hence may be considered in a formal sense to be quadruply bridging and described as $(BF_4)_{4/4}$. Only three of the fluorine atoms of the tetrahedral unit that has B(1) as its central atom coordinate a Mn atom; the fourth fluorine atom F(6), as has already been noted, does not. This BF_4 unit is therefore triply bridging and can be described as $(BF_4)_{3/3}$. Thus, the overall structure can be written as $Mn(BF_4)_{4/4}(BF_4)_{3/3}$.

As can be seen from Table III, the B–F bond lengths, which lie between 1.341 (10) and 1.408 (10) Å, are comparable with those found, for example, for $Ca(BF_4)_2$[20] [1.384 (3)–1.393 (3) Å] and KBF_4[21] [1.378 (5)–1.391 (3) Å]. As expected, the shortest bond is B1–F(6) since F(6) does not participate in any further bonding. The bond angles around the B atoms are close to the ideal tetrahedral value.

Acknowledgment. We wish to acknowledge continued and substantial financial assistance from the Australian Research Grants Scheme.

Registry No. $Mn(BF_4)_2$, 30744-82-2; BF_3, 7637-07-2; HF, 7664-39-3; Mn, 7439-96-5.

Supplementary Material Available: Listings of thermal parameters and deviations from least-squares mean planes and a figure that depicts the atomic arrangement in the unit cell (3 pages); a listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Notes

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Estimation of the Rh–Rh Bond Dissociation Energy in the (Octaethylporphyrinato)rhodium(II) Dimer by ^1H NMR Line Broadening

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The octaethylporphyrin rhodium dimer $[(OEP)Rh]_2$ has an interesting range of organometallic reactivity that includes reaction with H_2, reaction with C–H bonds in alkylaromatics[1,2] and aldehydes and ketones,[3] and addition to C–C[4] and CO[5] multiple bonds. The reactivity patterns of $[(OEP)Rh]_2$ in hydrocarbon media suggest the importance of the metallo radical, $(OEP)Rh^{II\bullet}$, and Halpern has demonstrated that the kinetics for addition of $[(OEP)Rh]_2$ to styrene can be described by a metallo radical chain mechanism.[4] Thermodynamic and reactivity studies for the (OEP)Rh system have suggested that the (OEP)Rh–C bonds must be relatively strong (~50–60 kcal/mol) and that the Rh–H bond energy is in the expected range (~60 kcal/mol).[6] Evaluation of absolute Rh–H and Rh–C bond energies for the (OEP)Rh system depends upon having a reliable value for the Rh–Rh bond energy in the dimer $[(OEP)Rh]_2$. This paper reports on an estimation of the Rh–Rh bond dissociation energy in $[(OEP)Rh]_2$ from ^1H NMR line broadening studies and the use of this value in deriving the (Rh–H)BDE in (OEP)Rh–H and the (Rh–C)BDE in (OEP)Rh–CHO.

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