# Manganese(II) Hexafluoroarsenate: Unusually High Coordination of Manganese(II) in a Fluorine Environment[†]

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$Mn(AsF_6)_2$ was prepared from $MnF_2$ and $AsF_5$ in anhydrous hydrogen fluoride (aHF), and single crystals were grown from the respective solution. The compound crystallizes in the tetragonal space group $I\bar{4}2d$ with $a = 750.76(2)$ pm, $c = 1544.44(5)$ pm, and $Z = 4$ at 293 K. Due to combined sharing of edges and apexes with $AsF_6$ octahedra, coordination number 8 (Mn−F 4 × 213.0(2) pm and 4 × 241.9(3) pm) is observed for the first time with Mn(II) and fluorine ligands. A second crystalline modification is formed at about 243 K. From susceptibility measurements a magnetic moment of 5.42 $\mu_B$ is derived, but no magnetic ordering is observed above 4 K.

## Introduction

In course of our efforts to synthesize new binary fluorides of transition metals in high oxidation states (e.g. $AgF_3$, $CuF_3$, $NiF_4$, $MnF_4$) we were trying several different approaches. When we decided to use compounds $M(AsF_6)_2$ as starting materials, we found that their synthesis and characterization needed to be worked out more precisely than already described.[1,2] Depending on ratio and purity of starting materials ($MF_2 + AsF_5$ in aHF) and also on reaction conditions, a variety of phases are formed which makes the characterization of pure compounds by chemical analysis and spectroscopic methods almost impossible. Therefore we decided to prepare single crystals of the particular compounds in order to use the derived characteristic powder diagrams as the most powerful analytical tool for this kind of reaction product. Another question was to check in which reactions the +II oxidation state is conserved or under which conditions oxidation will occur.

## Experimental Section

**1. Apparatus and Reagents.** A nickel vacuum line with a mechanical pump, a mercury diffusion pump, and soda lime scrubbers for removal of volatile fluorides was used. The part of the vacuum line used for the transfer of aHF and $AsF_5$ was made entirely from Teflon or FEP in order to diminish corrosion and to avoid the formation of $H_2$. This part of the line was equipped with a Monel Helicoid pressure gauge (0−1500 Torr ± 0.3%, Bristol Babcock Inc.) connected to the line via a Teflon valve. FEP reaction vessels (18 mm o.d.) equipped with Teflon valves were used for all experiments. Manganese difluoride (Riedel-de-Haën) was used as supplied. Chemical analysis of $MnF_2$ is as follows. Found: Mn, 58.2; F, 39.7. Calcd: Mn, 59.11; F, 40.89. Arsenic pentafluoride was prepared by the reaction of $As_2O_3$ with elemental fluorine as described for the synthesis of $PF_5$;[3] aHF (Matheson) was purified as previously described[4] and finally treated with $K_2NiF_6$.

**2. Instrumentation.** The manipulation of the product and its crystals was done in a drybox (M Braun, Garching, Germany). The residual of water in the atmosphere within the drybox did never exceed 1 ppm. X-ray powder diffraction patterns were obtained by the Debye−Scherrer method with Straumanis loading using Cu Kα radiation. For experiments at lower temperatures the modified Guinier technique with Cu K$\alpha_1$ radiation was used.[5] Finely powdered samples were loaded into 0.5 mm thin-walled quartz glass capillaries. Single-crystal data were collected on an Enraf-Nonius CAD4 four-circle diffractometer applying Ag Kα radiation. Further details are given in Table 1. For magnetic susceptibility measurements powder samples were sealed in a self-compensating container prepared from 5 mm quartz glass tubing. The measurements were performed with a SQUID magnetometer (SHE. Corp.).

**3. Preparation of $Mn(AsF_6)_2$.** $MnF_2$ (6.38 mmol) was weight into an FEP reaction vessel equipped with a Teflon valve and a Teflon-coated stirring rod. After the reaction vessel was thoroughly evacuated, aHF (7 mL) was condensed onto $MnF_2$ and $AsF_5$ was slowly added at room temperature until all $MnF_2$ was dissolved and a colorless solution of $Mn(AsF_6)_2$ was obtained. The reaction is very quick and exothermic. After removal of all aHF a white solid was obtained (6.41 mmol of $Mn(AsF_6)_2$). Chemical analysis is as follows. Found: Mn, 12.0; $AsF_6$, 87.5. Calcd: Mn, 12.69; $AsF_6$, 87.31. During our preparations we never obtained a pink color of the solution as it was reported.[1]

**4. Preparation of Single Crystals.** The solubility of $Mn(AsF_6)_2$ in aHF is quite high, therefore, single crystals were grown from aHF solution. In the apparatus made from two FEP tubes (18 mm and 6 mm o.d.) a supersaturated solution of $Mn(AsF_6)_2$ in aHF was prepared in the wider tube and then poured into the narrower one. A temperature gradient of 6 K was maintained by cooling the wider tube with tap water (∼287 K) and keeping the narrower tube at 293 K. Single crystals of $Mn(AsF_6)_2$ were obtained on the walls of the tube.

**5. X-ray Investigations.** Continuous X-ray powder investigations at varying temperatures showed a reversible phase transition at 238 K. Therefore a primary single-crystal investigation was performed at room temperature. A selected crystal contained in a quartz glass capillary was mounted on the diffractometer. After indexing of a first set of reflections, the unit cell dimensions and symmetry were checked by means of oscillation photographs around all three axis of the tetragonal unit cell. Later on accurate cell dimensions together with their esd's were refined from the $2\theta$ values of 24 reflections each centered at four different positions. Intensity data were collected in the $\omega/\theta$-scan mode. The intensities of two reference reflections monitored every two hours did not show any significant variation. The data were corrected in the usual way for Lorentz and polarization effects and for absorption on the basis of $\psi$-scans of eight reflections at different $2\theta$ values ($\Delta\psi = 9°$). The structure was solved in space group $I\bar{4}2d$ by locating the Mn and As atom, respectively, with the automatic Patterson method

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[†] Dedicated to Professor von Schnering on the occasion of his 65th birthday.

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**Table 1.** Crystal Data and Structure Refinement

| | |
|---|---|
| empirical formula | $Mn(AsF_6)_2$ |
| fw | 432.78 |
| temp (K) | 293 |
| wavelength (pm) | 56.087 |
| space group | $I\bar{4}2d$ (No. 122) |
| $a$ (pm) | 750.76(2) |
| $c$ (pm) | 1544.44(5) |
| $V$ (nm$^3$) | 0.87051(4) |
| formula units | 4 |
| $d$(calc) (g/cm$^3$) | 3.302 |
| abs coeff (mm$^{-1}$) | 4.844 |
| $F$(000) | 796 |
| $2\theta_{max}$ (deg) | 52 |
| reflcns collcd | 3738 |
| indepdt reflcns | 875 |
| $R_{int}$ | 0.0376 |
| refinement method | full-matrix least-squares on $F^2$ |
| params | 37 |
| goodness-of-fit on $F^2$ | 1.117 |
| $R$ indices $R_1$, w$R_2$ (all data)[a] | 0.0247, 0.0617 |
| extinction coeff | 0.0321(13) |
| absolute struct param $x$ | 0.00(3) |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where $n$ = number of reflections and $p$ = number of parameters refined.

**Table 2.** Final Positional and Displacement Parameters

| atom | $x$ | $y$ | $z$ | $U_{eq}$ (pm$^2$)[a] |
|---|---|---|---|---|
| As | 0 | 0.5 | 0.02631(2) | 261(1) |
| Mn | 0 | 0 | 0 | 258(1) |
| F1 | 0.1474(3) | 0.5324(3) | 0.1117(2) | 573(6) |
| F2 | 0.0519(3) | 0.2721(2) | 0.0297(1) | 398(4) |
| F3 | 0.1589(4) | 0.5357(3) | −0.0450(2) | 740(9) |

[a] $U_{eq}$ defined as $^1/_3$ of the trace of the $\mathbf{U}_{ij}$ tensors.

implemented in the program system SHELXTL-Plus.[6] A difference Fourier map after a first refinement based on $F^2$-values with SHELXL-93[7] revealed the positions of three fluorine atoms. After refinement of all five atoms including anisotropic displacement parameters an isotropic extinction correction was applied. The Flack parameter[8] refined to 0.00(3), which indicated the right set of parameters had been chosen and we were also not dealing with twinning by inversion. Further details on data collection and structure determination are given in Table 1; the final atomic coordinates are in Table 2. The numbering scheme is given in Figure 1. We also tried to cool several crystals to lower temperatures in order to reduce the thermal vibration in particular of the $AsF_6$ moiety. However, due to the phase transition all crystals shattered between 248 and 243 K. The difference in transition temperature, especially in comparison to the powder diffraction experiments, is most likely due to the quite different particle size of the samples. We are currently planning further experiments where we wish to grow crystals of the low-temperature phase and transfer them to the diffractometer without the intervening warm up.

## Discussion

$Mn(AsF_6)_2$ crystallizes in the noncentrosymmetric space group $I\bar{4}2d$ with four formula units in the tetragonal unit cell. The manganese atom is located on a position (4a) with point symmetry $\bar{4}$ and is coordinated by two different sets of fluorine atoms each set containing four equivalent atoms (Figure 1). To our knowledge this is the first compound where Mn(II) shows the unusually high coordination number 8 in a pure fluorine environment. So far this type of coordination has only been found in a small number of compounds where Mn(II) is bonded by oxygen ligands. The Mn−F2 distance (213.0 pm) is identical to the values found e.g. in $MnF_2$.[9] In comparison the Mn−F1 distance (241.9 pm) is considerably longer but without any doubt has to be interpreted as a bonding interaction. As expected the shorter Mn−F bonds are involved in an apex-sharing interaction between the $AsF_6$ octahedron and the polyhedron around the manganese atom while the longer Mn−F bonds are observed for the edge-sharing arrangement which is less favorable from an electrostatic point of view. Interestingly in the structure of the closely related compound $Mn(BF_4)_2$[10] only apex-sharing and coordination number 7 is observed for manganese, although $BF_4^-$ is considerably smaller than $AsF_6^-$. The $AsF_6$ octahedron in $Mn(AsF_6)_2$ shows point symmetry 2, and accordingly three different kinds of fluorine atoms are connected to the arsenic atom. F3 is not interacting with Mn and therefore shows a typical distance of 164.6 pm as observed in many structures for nonbridging fluorine atoms in $AsF_6$ units. Pronounced thermal vibration of the fluorine atoms results in considerable shortening of the As−F distances. Correction for rigid body motion leads to As−F1 177.3 pm, As−F2 176.9 pm, and As−F3 168.0 pm, respectively. The rather large difference between the Mn−F bonds is not resembled with the small difference between the corresponding As−F distances. As each $AsF_6$ octahedron is sharing one edge and two corners each with a different manganese atom and each manganese polyhedron is sharing two edges and four corners with six different $AsF_6$ octahedra, a three-dimensional network is formed. A different picture is developing if we are considering the structure as a close packing of $AsF_6$ spheres with Mn atoms in octahedral holes. The evolving arrangement is nicely resembling the structure of anatase, a modification of $TiO_2$.

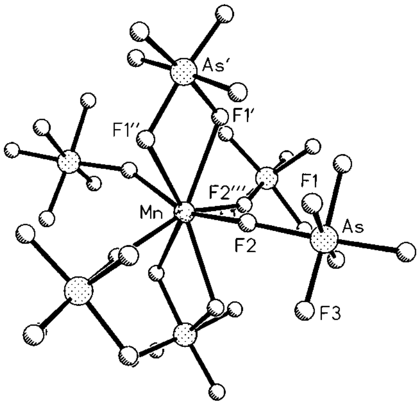

**Figure 1.** Basic structural unit in $Mn(AsF_6)_2$. Selected distances (pm) and angles (deg): As−F1 173.8(2), As−F2 175.5(1), As−F3 164.6(2), Mn−F1′ 241.9(3), Mn−F2 213.0(2); As−F2−Mn 152.6(1), As′−F1′−Mn 111.4(1), F1′−Mn−F1″ 55.9(1), F2−Mn−F2‴ 92.66(2), F1′−As′−F1″ 81.4(2), F3−As−F3‴ 96.0(2).

Magnetic susceptibility data for $Mn(AsF_6)_2$ very closely obey the Curie−Weiss law. From the slope a magnetic moment of 5.42 $\mu_B$ is derived which corresponds to the spin-only value of Mn(II). Down to 4 K no magnetic ordering is observed, which is interesting as manganese(II) fluorine compounds are well-known for antiferromagnetic ordering at rather high temperatures between 50 and 100 K. Obviously, in $Mn(AsF_6)_2$ the Mn ions are well separated so that no interaction occurs. However, in

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a closely related Co compound we recently observed magnetic ordering at low temperatures.[11]

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**Supporting Information Available:** A figure showing the reciprocal magnetic susceptibility vs temperature for a powder sample of $Mn(AsF_6)_2$ (1 page). An X-ray crystallographic file, in CIF format, is available. Access and ordering information is given on any current masthead page.

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