Notes

Formation of Mono- and Multimanganese Cationic Species. Crystal Structure of $[\mathrm{Mn_4}(\mu\text{-Cl})_6(\mathrm{THF})_{12}][\mathrm{SnCl_5(THF)}]_2$

Zofia Janas, Tadeusz Lis, and Piotr Sobota*

Faculty of Chemistry, University of Wrocław,
14 F. Joliot-Curie St., 50-383 Wrocław, Poland

Received September 22, 1995

Introduction

Anhydrous dichlorides of the first transition series react readily with tetrahydrofuran (THF) to form compounds of composition $\mathrm{MCl_2{\cdot}1.5THF}$.[1] Until recently, the only well-documented structures of Fe and Co derivatives are the remarkable tetramers $[\mathrm{M_4}(\mu_3\text{-Cl})_3(\mu_2\text{-Cl})_4\mathrm{Cl_2(THF)_6}]$.[2,3] These species have limited solubilities in THF. However, we have found that they can be easily converted into well-soluble complex salts $[\mathrm{M_2}(\mu\text{-Cl})_3(\mathrm{THF})_6][\mathrm{SnCl_5(THF)}]$ (M = Fe, Co, Ni) by a reaction with $\mathrm{SnCl_4}$.[4,5]

$$2\mathrm{MCl_2} + \mathrm{SnCl_4} \xrightarrow[\mathrm{THF}]{} [\mathrm{M_2}(\mu\text{-Cl})_3(\mathrm{THF})_6][\mathrm{SnCl_5(THF)}] \quad (1)$$

$$\mathrm{M} = \mathrm{Fe, Co, Ni}$$

Non transition metal chlorides *e.g.* $\mathrm{MgCl_2}$ create similar cationic species.[6] The relationship between $\mathrm{Mg^{2+}}$ and $\mathrm{Mn^{2+}}$ chemistry is generally recognized. However, until now, manganese ionic species containing chloride and THF are not well documented. These have prompted us to study the reactivity of manganese dichloride toward $\mathrm{Cl^-}$ abstracting agents in THF. Herein, we report the synthesis and structural study of $[\mathrm{Mn(THF)_6}][\mathrm{SnCl_5(THF)}]_2$ (**1**) and $[\mathrm{Mn_4}(\mu\text{-Cl})_6(\mathrm{THF})_{12}][\mathrm{SnCl_5(THF)_2}]$ (**2**) complexes.

Experimental Section

All manipulations were carried out under an inert atmosphere by the use of a standard Schlenk system and a vacuum line. Tin tetrachloride was purchased from Aldrich Chemical Co. Ltd. The $\mathrm{MnCl_2{\cdot}1.5THF}$ was prepared by the reported procedure.[1] Solvents were dried by standard techniques. Magnetic susceptibilities were measured by the Faraday method within the temperatture range 81−293 K. Corrections for diamagnetism were made with Pascal's constants.[7] IR spectra were recorded on a Perkin-Elmer 180 spectrophotometer.

Preparation of 1. $\mathrm{SnCl_4}$ (2.81 g; 10.8 mmol) wad added dropwise to a stirred suspension of $\mathrm{MnCl_2{\cdot}1.5THF}$ (1.27 g; 5.4 mmol) in THF (50 cm^3). The reaction mixture was heated under reflux until the solution had cleared. The resulting colorless solution was left to crystallize at room temperature. After 24 h colorless needle-shaped crystals of **1** were formed. They were filtered off, washed with cool THF (3 × 5 cm^3), and vacuum dried. Yield: 4.95 g (75%). Anal. Calcd for $\mathrm{C_{32}H_{64}Cl_{10}MnO_8Sn_2}$: Cl, 28.97; Mn, 4.49; Sn, 19.40. Found: Cl, 28.41; Mn, 4.35; Sn, 19.50. IR (Nujol, cm^{-1}): ν(Sn−Cl) 300 m, 320 s. $\mu_{\mathrm{eff}} = 5.89\ \mu_{\mathrm{B}}$ at 293 K.

Table 1. Crystal Data for $[\mathrm{Mn_4}(\mu\text{-Cl})_6(\mathrm{THF})_{12}][\mathrm{SnCl_5(THF)}]_2$ (**2**)

formula	$[(\mathrm{C_4H_8O})_{12}\mathrm{Cl_6Mn_4}]^{2+}{\cdot}2[(\mathrm{C_4H_8O})\mathrm{Cl_5Sn}]^-$	
fw	1016.9	
space group	$P2_1/c$	
Z	2	
λ/Å	0.710 69	
T/K	170	290
μ/cm^{-1}	17.2	16.7
a/Å	10.354(12)	10.553(9)
b/Å	16.790(15)	16.967(21)
c/Å	24.35(3)	24.42(3)
β/deg	93.20(9)	93.38(9)
V/Å^3	4226(9)	4365(9)
ρ_{calc}/g cm^{-3}	1.598(4)	1.547(4)
$R(F)$		0.0277
$R_{\mathrm{W}}(F^2)$		0.0658

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$ $R_{\mathrm{W}} = \{\sum w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$

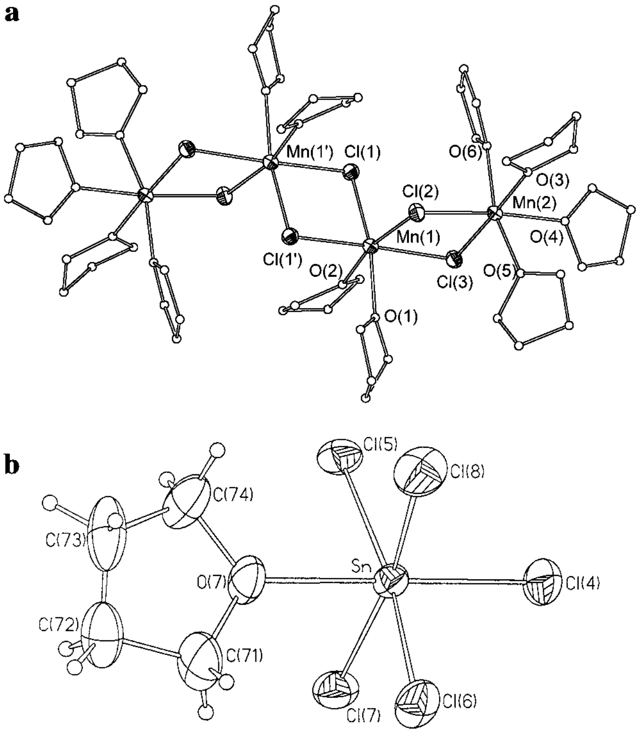

Figure 1. (a) Structure of the $[\mathrm{Mn_4}(\mu\text{-Cl})_6(\mathrm{THF})_{12}]^{2+}$ cation in $[\mathrm{Mn_4}(\mu\text{-Cl})_6(\mathrm{THF})_{12}][\mathrm{SnCl_5(THF)}]_2$ (**2**). (b) Structure of the $[\mathrm{SnCl_5(THF)}]^-$ anion in $[\mathrm{Mn_4}(\mu\text{-Cl})_6(\mathrm{THF})_{12}][\mathrm{SnCl_5(THF)}]_2$ **2**.

Preparation of 2. A suspension of $\mathrm{MnCl_2{\cdot}1.5THF}$ (1.32 g; 5.6 mmol) in THF (50 cm^3) after dropwise addition of $\mathrm{SnCl_4}$ (0.73 g; 2.8 mmol) was heated under reflux for 2 h. Next, the reaction mixture was filtered from unreacted $\mathrm{MnCl_2{\cdot}1.5THF}$ and the filtrate was left to crystallize at room temperature. After 24 h the colorless needle- and cubic-shaped crystals of **1** and **2** were formed, respectively. Crystals of **2** were separated by hand for X-ray analysis and IR spectra. IR (Nujol, cm^{-1}) for **2**: ν(Sn−Cl) 300 m, 320 s; ν(Mn−Cl) 212 s, 228 s.

Data Collection and Processing. Intensities were collected with a KUMA KM4 four-circle diffractometer with Oxford Cryosystem-Cryostream Cooler in the ω−2θ mode (with crystal of dimensions 0.3 × 0.3 × 0.3 mm) and Mo Kα radiation up to 2θ = 56°. Intensities of

---

(1) Fowles, G. W. A.; Rice, D. A.; Walton, R. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 3119.
(2) Bel'skii, V. K.; Ishchenko, V. M.; Bulychev, B. M.; Protskii, A. N.; Soloveichik, G. L.; Ellert, O. G.; Seifulina, Z. M.; Rakitin, Yu. V.; Novotortsev, V. M. *Inorg. Chim. Acta* **1985**, *96*, 123. Cotton, F. A.; Luck, R. L.; Son, K.-A. *Inorg. Chim. Acta* **1991**, *179*, 11.
(3) Sobota, P.; Olejnik, Z.; Utko, J.; Lis, T. *Polyhedron* **1993**, *12*, 613.
(4) Janas, Z.; Sobota, P.; Lis, T. *J. Chem. Soc., Dalton Trans.* **1991**, 2429.
(5) Janas, Z.; Lis, T.; Sobota, P. *Polyhedron* **1992**, *11*, 3019.
(6) Sobota, P.; Płuziński, T.; Lis, T. *Z. Anorg. Allg. Chem.* **1986**, *533*, 215.
(7) Earnshaw, A. *Introduction of Magnetochemistry*; Academic Press: London, 1968, p 5.

S0020-1669(95)01236-5 CCC: $12.00

Table 2. Selected Interatomic Distances (Å) and Bond Angles (deg) for $[Mn_4(\mu\text{-}Cl)_6(THF)_{12}][SnCl_5(THF)]_2$ (**2**)[a]

Mn(1)···Mn(1′)	3.715(4)	Mn(1)···Mn(2)	3.692(4)
Mn(1)−Cl(1)	2.521(2)	Mn(2)−Cl(2)	2.504(3)
Mn(1)−Cl(1′)	2.526(3)	Mn(2)−Cl(3)	2.475(2)
Mn(1)−Cl(2)	2.527(2)	Mn(2)−O(3)	2.200(4)
Mn(1)−Cl(3)	2.579(3)	Mn(2)−O(4)	2.241(4)
Mn(1)−O(1)	2.225(4)	Mn(2)−O(5)	2.205(3)
Mn(1)−O(2)	2.199(3)	Mn(2)−O(6)	2.199(4)
Sn−Cl(4)	2.380(2)	Sn−Cl(7)	2.399(3)
Sn−Cl(5)	2.401(2)	Sn−Cl(8)	2.383(3)
Sn−Cl(6)	2.396(3)	Sn−O(7)	2.247(4)
Cl(1)−Mn(1)−Cl(1′)	85.2(1)	Cl(2)−Mn(2)−Cl(3)	86.4(1)
Cl(1)−Mn(1)−Cl(2)	99.3(1)	Cl(2)−Mn(2)−O(3)	90.5(2)
Cl(1)−Mn(1)−Cl(3)	97.8(1)	Cl(2)−Mn(2)−O(4)	174.5(2)
Cl(2)−Mn(1)−Cl(1′)	94.8(1)	Cl(2)−Mn(2)−O(5)	92.5(2)
Cl(2)−Mn(1)−Cl(3)	83.7(1)	Cl(2)−Mn(2)−O(6)	97.2(2)
Cl(3)−Mn(1)−Cl(1′)	176.8(1)	Cl(3)−Mn(2)−O(3)	176.9(2)
O(1)−Mn(1)−Cl(1)	168.6(2)	Cl(3)−Mn(2)−O(4)	90.7(2)
O(1)−Mn(1)−Cl(1′)	89.5(2)	Cl(3)−Mn(2)−O(5)	95.8(2)
O(1)−Mn(1)−Cl(2)	91.2(2)	Cl(3)−Mn(2)−O(6)	95.3(2)
O(1)−Mn(1)−Cl(3)	87.6(2)	O(3)−Mn(2)−O(4)	92.4(2)
O(2)−Mn(1)−Cl(1)	87.9(2)	O(3)−Mn(2)−O(5)	84.2(2)
O(2)−Mn(1)−Cl(1′)	94.5(2)	O(3)−Mn(2)−O(6)	85.2(2)
O(2)−Mn(1)−Cl(2)	168.7(2)	O(4)−Mn(2)−O(5)	83.1(2)
O(2)−Mn(1)−Cl(3)	86.7(2)	O(4)−Mn(2)−O(6)	87.8(2)
O(2)−Mn(1)−O(1)	82.4(2)	O(5)−Mn(2)−O(6)	165.7(2)
Mn(1)−Cl(1)−Mn(1′)	94.8(1)	Mn(1)−Cl(2)−Mn(2)	94.4(1)
Mn(1)−Cl(3)−Mn(2)	93.8(1)	Cl(6)−Sn−Cl(7)	89.6(1)
Cl(4)−Sn−Cl(5)	94.8(1)	Cl(6)−Sn−Cl(8)	89.7(1)
Cl(4)−Sn−Cl(6)	94.4(1)	Cl(7)−Sn−Cl(8)	170.5(1)
Cl(4)−Sn−Cl(7)	94.3(1)	Cl(4)−Sn−O(7)	178.7(2)
Cl(4)−Sn−Cl(8)	95.2(1)	Cl(5)−Sn−O(7)	84.5(2)
Cl(5)−Sn−Cl(6)	170.8(1)	Cl(6)−Sn−O(7)	86.3(2)
Cl(5)−Sn−Cl(7)	89.6(1)	Cl(7)−Sn−O(7)	84.7(2)
Cl(5)−Sn−Cl(8)	89.8(1)	Cl(8)−Sn−O(7)	85.8(2)

[a] Primed atoms related to unprimed atoms by $1 - x$, $1 - y$, $1 - z$.

three standard reflections monitored after every 100 intensity scan decreased approximately 10%. A total of 9503 recorded data were rescaled according to the intensities of the control reflections and were corrected for Lorentz and polarization factors.

The structure was solved by direct methods and refined by full-matrix least-squares methods using the program SHELXL.[8] All H atoms were included in geometry calculated positions with $d(C-H) = 0.99$ Å. An absorption correction following the DIFABS[9] procedure was applied; minimal and maximal absorption corrections were 0.93 and 1.048; $R_{merg} = 0.0227$. Least-squares converged with $R = 0.0277$ and $R_w(F^2) = 0.0658$ for 4584 reflections with $I > 3\sigma(I)$ and 415 refined parameters. Table 1 gives the crystal data for $[Mn_4(\mu\text{-}Cl)_6(THF)_{12}][SnCl_5(THF)]_2$ (**2**).

Results and Discussion

The reaction of $MnCl_2{\cdot}1.5THF$ with $SnCl_4$ in a 1:2 molar ratio in THF gives colorless needle-shaped crystals of composition $MnCl_2{\cdot}2SnCl_4{\cdot}8THF$ (**1**) in 75% yield. The elemental analysis, IR spectroscopy and magnetic measurements of compound **1** (see Experimental Section) suggested it to be the stannate salt of the monomeric manganese $[Mn(THF)_6]^{2+}$ cation.

$$MnCl_2{\cdot}1.5THF + 2SnCl_4 \xrightarrow[THF]{} \underset{\mathbf{1}}{[Mn(THF)_6][SnCl_5(THF)]_2} \qquad (2)$$

Crystallographic data of **1** proved it to be composed of already well documented $[Mn(THF)_6]^{2+}$ cations[10] and $[SnCl_5(THF)]^-$ anions[4,5,11] in a 1:2 molar ratio. However, a THF solution of $SnCl_4$ and an excess of $MnCl_2$ yielded a mixture of air-sensitive colorless needle- and cubic-shaped crystals of **1** and $[Mn_4(\mu\text{-}Cl)_6(THF)_{12}][SnCl_5(THF)]_2$ (**2**), respectively. Compounds **1** and

$$5MnCl_2{\cdot}1.5THF + 4SnCl_4 \xrightarrow[THF]{} \underset{\mathbf{1}}{[Mn(THF)_6][SnCl_5(THF)]_2} + \underset{\mathbf{2}}{[Mn_4(\mu\text{-}Cl)_6(THF)_{12}][SnCl_5(THF)]_2} \qquad (3)$$

2 can be stored under an inert atmosphere. They are quite soluble in THF and in other solvents such as CH_2Cl_2 rapidly decompose to initial substrates. Crystals of **2** were separated by hand for IR spectroscopy and crystallographic study. The molecular structure of **2** is shown in Figure 1a,b and selected bond lengths and angles are summarized in Table 2. Crystals of **2** consist of $[Mn_4(\mu\text{-}Cl)_6(THF)_{12}]^{2+}$ cations and $[SnCl_5(THF)]^-$ anions in a 1:2 ratio. The structure of the cation includes four six-coordinate Mn(II) centers linked by double chloride bridges to form tetrameric chains with a symmetry center. Two THF molecules complete the octahedral coordination sphere of the internal Mn atoms and are in a *cis* orientation. A similar THF orientation is observed for the Mg^{2+} ions in the $[(Cp_2Ti)_2Mg_2(\mu\text{-}Cl)_6(THF)_4]$ complex.[12] On the periphery of the cation, the Mn(2) atoms are coordinated by four THF molecules. The Mn(1)···Mn(1′) and Mn(1)···Mn(2) distances of 3.715(4) and 3.692(4) Å, respectively, are well outside metal−metal bonding distances and are close to those found in β-$RbMnCl_3$ with μ-Cl bridges (3.774 Å)[13] and in $[(CH_3)_2CHNH_3]_2[Mn_2(\mu\text{-}Cl)_2Cl_4(H_2O)_4]$ (3.828 Å).[14] The Mn−Cl distances in the cation of **2** range from 2.475(2) to 2.579(3) Å and are generally near the bond lengths for bridging Cl found in the $[MnCl_6]^{4-}$ octahedra.[15] The differences in Mn−Cl bond lengths in **2** are consistent with the relative *trans* influences of chloride and THF. A similar *trans* effect is seen in Mn−O distances. The bond angles about the manganese atoms are as expected. The major distortion from idealized octahedral geometry is in the O(2)−Mn(1)−Cl(2) and O(5)−Mn(2)−O(4) angles, which are 168.7(2) and 83.1(2)°, respectively. The average bridging Mn−Cl−Mn angle is 94.3(2)° and is comparable to those in the $[A]_2[Mn_2(\mu\text{-}Cl)_2Cl_4(H_2O)_4]$ compound family [94.8(2) and 94.6(6)° for A = $[(CH_3)_3NH]^+$ and $[(CH_3)_2CHNH_3]^+$, respectively].[14,16]

The structure of the octahedral $[SnCl_5(THF)]^-$ anion of **2** is similar to those observed in crystals of *trans*-$[MCl_2(THF)_4][SnCl_5(THF)]$ (M = Ti, Cr)[4,11] and $[M_2(\mu\text{-}Cl)_3(THF)_6][SnCl_5(THF)]$ (M = Fe, Ni).[4,5] In all these cases, the bond lengths and angles are comparable. However, in the case of **2**, considerably lower thermal parameters were obtained.

The above results showed that chloride transfer between $MnCl_2$ and $SnCl_4$ in THF results in the formation of $[Mn(THF)_6]^{2+}$ and $[Mn_4(\mu\text{-}Cl)_6(THF)_{12}]^{2+}$ cations. Although, the formation of poly- and oligomeric Mn(II) compounds is not uncommon,[15] to our knowledge the tetrameric $[Mn_4(\mu\text{-}Cl)_6(THF)_{12}]^{2+}$ cation is the first crystallographically characterized. Attempts to isolate other Mn(II) ionic species, *e.g.* $[M_2(\mu\text{-}Cl)_3(THF)_6]^+$, which have been well documented for Mg(II),[6]

---

(8) Sheldrick, G. SHELXL-93. Program for the refinement of crystal structures. Univ. of Gottingen, Germany, 1994.

(9) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.

(10) Stolz, P.; Pohl, S. *Z. Naturforsch.* **1988**, *43B*, 175. Kong, G.; Harakas, G. N.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1995**, *117*, 3502.

(11) Janas, Z.; Sobota, P.; Lis, T. *Polyhedron* **1988**, *7*, 2655.

(12) Stephan, D. W. *Organometallics* **1992**, *11*, 996.

(13) Jensen, S. J. *Acta Chem. Scand.* **1967**, *21*, 889.

(14) Willett, R. D. *Acta Crystallogr.* **1979**, *B35*, 178.

(15) Chiswell, B.; McKenzie, D.; Lindoy, L. F. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, England, 1987; Vol. 4, p 58.

(16) Caputo, R. E.; Willett, R. D.; Muir, J. A. *Acta Crystallogr.* **1976**, *B32*, 2639.

V(II),[17] Fe(II),[4] Ni(II)[5] dichlorides, failed. Equally, $MgCl_2$ shows the ability to give a family of ions: $[MgCl(THF)_5]^+$, $[Mg(THF)_6]^{2+}$, $[MgCl_4]^{2-}$ depending on the nature of Lewis reactants *e.g.* MCl_3 (M = Al, Fe) or MCl_4 (M = Ti, Zr) and the actual condition used.[18] Additionally it is well-known that in a presence of abstracting agents $FeCl_2$ is able to create in THF anionic species incorporating chloride bridges *e.g.* $[Fe_2(\mu\text{-}Cl)_2Cl_4]^{2-}$ and $[Fe_3(\mu\text{-}Cl)_4Cl_4]^{2-}$.[19]

The results presented here and previously indicate that evidently a facile equilibrium exists:

$$5[MnCl_2(THF)_{1.5}] \rightleftharpoons [Mn(THF)_6]^{2+} + [Mn_4(\mu\text{-}Cl)_6(THF)_{12}]^{2+} + 4Cl^- \quad (4)$$

The Cl^- anion can react with $SnCl_4$ to form the $[SnCl_5(THF)]^-$ anion. To date, it follows that the $[SnCl_5(THF)]^-$ ion forms the least soluble salts with cations which precipitate as compounds **1** and **2** and influences the reaction equilibrium.

Acknowledgment. We thank the State Committee Scientific Research for financial support of this work Grant No. 3T09A 016 08.

Supporting Information Available: Tables giving crystallographic data final hydrogen atom coordinates of all atoms, anisotropic thermal parameters for non-H atoms, and distances and angles for **2** (10 pages). Ordering information is given on any current masthead page.

IC951236K

---

(17) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377. Bouma, R. J.; Teuben, J. H.; Beukema, W. R.; Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 2715.

(18) Sobota, P. *Polyhedron* **1992**, *11*, 715.

(19) Solari, C.; Corazza, F.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1990**, 1245.