MnO₃Cl, Isolation and Crystal Structure

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Abstract. MnO₃Cl is prepared from KMnO₄ und ClSO₃H. The thermally very unstable compound is identified by its Raman spectrum and a single crystal structure determination: a = 715.4(5), b = 1008.3(7), c = 500.9(4) pm, space group Cmc2₁. Solid MnO₃Cl consists of molecules with only weak intermolecular interactions. The Mn-Cl bond length is 209.9(4) pm. The crystal structure is

Introduction

All manganese(VII) compounds except the salts of MnO_4^- are unstable. This is particularly true for the covalent derivatives Mn_2O_7 , MnO_3F , and especially MnO_3Cl . The latter two represent the only cases of Mn^{VII} -halogen bonds. MnO_3F has been prepared in quite large amounts from $KMnO_4$ and FSO_3H [1] (a warning against this preparation follows in the experimental part). It is therefore quite well characterized, including a structure determination by microwave spectroscopy in the gaseous state [2].

Our knowledge about MnO₃Cl is much less complete. This is certainly due to the high instability of the latter. It has been prepared at first by reacting KMnO₄ in H₂SO₄ with gaseous HCl [3]. Soon later the preparation from KMnO₄ and ClSO₃H was published, and all subsequent work with MnO₃Cl is based on this preparation [4]. The absorption spectrum of it has been discussed in some detail [5–8], also in combination with theoretical considerations [9–11]. An incomplete IR spectrum is known. The Raman bands have been derived from a Raman resonance spectrum [12]. Quite recently the reaction between MnO₃Cl and olefines has been studied by matrix isolation and density functional theory [13]. Modern techniques of low temperature isolation, crystallization, and spectroscopy allow now a much more detailed description of this elusive compound.

Results and Discussion

The preparation of MnO_3Cl from $KMnO_4$ and $ClSO_3H$ is certainly the method of choice [4]. In order to handle the

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Figure 1 Raman spectrum of MnO_3Cl , liquid, at -120 °C. Upper trace: parallel orientation, lower trace: perpendicular orientation. x = chlorine impurity.

extreme sensitive compound safely, solutions in CCl₄ have been used previously. We, however, isolated the compound and kept it at low temperatures all the time. MnO₃Cl can be handled at -100 °C without decomposition, if moisture and reducing materials are excluded. The Raman spectrum of the liquid is shown in Figure 1. Besides some inevitable amounts of Cl₂ the assignment of the six strong bands is very straightforward, see table 1. The assignment has been confirmed by a DFT calculation, values are also included in table 1. MnO₃Cl melts at about -130 °C. In a glass capil-

compared to those of MnO_3F , CrO_2Cl_2 , and ReO_3Cl , the X-ray crystal structure determinations of which are also submitted in this article.

Keywords: Manganese; Manganese trioxide chloride; Crystal structure



Figure 2 Structure of MnO_3Cl in the crystal, ORTEP representation, 50 % probability plot.

Table 1 Raman spectrum of MnO_3Cl , values in cm^{-1} , in brakkets: intensity

exp.	calcd.	assignment	
948 (20,dp)	1060 (15)	v MnO ₃ , E	
887 (100,p)	1013 (40)	$v \text{ MnO}_3, A_1$	
535, 544 (Cl ₂)		-, -	
457 (35,p)	471 (6)	v MnCl, A ₁	
365 (50,dp)	403(5)	δ MnO ₃ , E	
306 (25,p)	336(5)	δ MnO ₃ , A ₁	
217 (80,dp)	233(7)	δ MnO ₂ Cl, E	

lary we grew a single crystal and subjected it to a single crystal structure determination. As expected, the crystal structure shows monomeric units. Bond lengths, and angles, including calculated values, are collected in table 2.

We have prepared also MnO_3F [1], CrO_2Cl_2 [14, 15], and ReO_3Cl [16] by literature methods and subjected them to single crystal structure determinations. Crystals of CrO_2Cl_2 have been grown in a glass capillary at -110 °C, those of ReO_3Cl by recrystallizations from CFCl₃ at -80 °C, and those of MnO_3F by recrystallization from HF at -78 °C. The results are summarized in table 2 also.

The crystal structures of MnO₃Cl, MnO₃F, CrO₂Cl₂, and ReO₃Cl are based on molecules that have only weak intermolecular interactions. Bond distances and angles within the MnO₃ group in MnO₃Cl agree well with those observed in gaseous MnO₃F [2] and crystalline Mn₂O₇ [17]. The Mn-Cl bond length in MnO₃Cl of 209.9(4) pm is the first determined Mn^{VII}-Cl bond length, and agrees well with the expectation, e.g. if compared to the Cr-Cl bond lengths of 211.4 – 211.8 pm in CrO₂Cl₂. The instability of the compound is therefore not a result of a particularly weak Mn-Cl bond, but rather a result of the energy gain by the internal redox process. Intermolecular O…Cl and Cl…Cl

Table 2 Bond lengths/pm and angles/° of oxide halides.

MnO ₃ Cl			
Mn-O1	158.4(12)	O1-Mn-O1'	110.2(7)
Mn-O2	158.8(8)	O1-Mn-O2	110.3(5)
Mn-Cl	209.9(4)		
MnO ₃ F			
Mn - (O,F)1	162.0(2)	(O,F)1-Mn-(O,F)1'	109.5(1)
Mn - (O,F)2	162,2(2)	(O,F)1 - Mn - (O,F)2	109.5(1)
		(O,F)2-Mn-(O,F)2	109.3(1)
MnO ₃ F			
(microwave, gas [2])			
Mn-O	158.6(5)	O-Mn-F	108.5(10)
Mn-F	172.4(10)		
CrO ₂ Cl ₂			
Cr-O1	157.3(7)	O1-Cr-O2	108.5(2)
Cr-O2	157.5(4)	O-Cr-Cl	109.5, 108.5
Cr-Cl1	211.8(2)		108.1, 109.0(2)
Cr-Cl2	211.4(2)	Cl1-Cr-Cl2	113.1(1)
ReO ₃ Cl			
Re-O1	169.9(6)	O1-Re-O2	108.4(3)
Re-O2	169.9(7)	O1-Re-O3	107.5(3)
Re-O3	170.7(5)	O2-Re-O3	108.3(3)
Re-Cl	221.9(2)	Cl-Re-O	111.5, 112.1, 108.9(2)

Table 3 Crystallographic data

MnO ₃ Cl	MnO ₃ F	CrO_2Cl_2	ReO ₃ Cl
138.4	121.8	154.2	69.7
-150	-120	-150	-100
$Cmc2_1$	C2/c	P2 ₁	$P2_1/n$
715.4(5)	916.3(10)	644.5(3)	562.3(2)
1008.3(7)	434.9(4)	497.1(3)	896.4(4)
500.9(4)	841.7(11)	717.5(4)	764.4(2)
	116.78(3)	106.58(1)	94.68(2)
361.3	299.5	220.4	383.9
4	4	2	4
2.544	2.705	2.334	4.665
4.20	4.23	3.63	32.17
26.4	30.5	35.5	30.5
730	2364	895	4675
352	457	841	1163
29	25	48	47
0.142	0.064	0.154	0.1054
0.0415	0.024	0.049	0.047
	$\begin{array}{c} MnO_{3}Cl\\ 138.4\\ -150\\ Cmc2_{1}\\ 715.4(5)\\ 1008.3(7)\\ 500.9(4)\\ \end{array}\\ \begin{array}{c} 361.3\\ 4\\ 2.544\\ 4.20\\ 26.4\\ 730\\ 352\\ 29\\ 0.142\\ 0.0415\\ \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

contacts are in the vicinity of the sum of the van der Waals radii of these atomic combinations. Nevertheless the packing seems to be governed by the zig zag chain chlorinechlorine interactions of 360.4 pm lengths, as indicated by dotted lines in figure 2. 350 pm is considered a typical distance for Cl···Cl contacts [18]. Possibly the shortest Cl···Cl contact of 307.0 pm is observed in crystalline ClF [19]. As in ClF the chlorine atom in MnO₃Cl bears a positive charge of 0.2 according to the Mullikan charge analysis.

In contrast to this the fluorine atom in MnO_3F bears a negative charge (-0.2) The lack of such weak interactions in solid MnO_3F may be the reason for the complete disorder of the oxygen and fluorine atoms, so that no individual bond lengths and angles can be given. Only the averaged bond lengths of 160.0 - 160.2(2) pm lie in the expected region, when they are compared to the weighed average of three Mn=O bonds with 158.6 and one Mn-F of 172.4 pm lengths from the microwave structure.

In the second publication on MnO_3Cl also MnO_2Cl_2 and $MnOCl_3$ have been reported [4]. We have also tried to ob-

tain these elusive compounds, but they turned out to be so unstable that attempts to grow single crystals remained futile.

Experimental Part

All manipulations were carried out under vacuum or in an Argon atmosphere with standard Schlenk techniques.

Raman spectra were measured on Bruker RFS 100 spectrometer (with 1064 nm line of Nd:YAG laser) at -120 °C. Single crystals were obtained by annealing samples in a glass capillary (MnO₃Cl, CrO₂Cl₂) directly on the diffractometer.

Single crystals grown from solution (MnO₃F, ReO₃Cl) were handled in a special device [20], cut to an appropriate size, and mounted on a Bruker SMART CCD 1000 TU diffractometer. This works with MoK α irradiation, a graphite monochromator, a scan width of 0.3° in ω , and a measuring time of 20 s per frame. After semi empirical absorption corrections (SADABS) by equalizing symmetry-equivalent reflections, the SHELX programs were used for solution and refinement [21]. Experimental details are laid down in table 3, results in table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftliche technische Zusammenarbeit mbH, D-76344 Eggenstein-Leopoldshafen, under the CSD numbers 416749 (MnO₃Cl), 416748 (MnO₃F), 416750 (CrO₂Cl₂), and 416751 (Re-O₃Cl). Details can be obtained on quoting the depository numbers, names of authors and the journal citation.

MnO₃Cl: 15 ml chlorosulphuric acid are placed in a two-necked Schlenk flask and cooled down to -75 °C. To the rapidly stirred HSO₃Cl small portions (~0.1 g) of 0.75 g fine powdered KMnO₄ are added. The HSO₃Cl becomes green as the KMnO₄ dissolves. In order to dissolve the KMnO₄ completely the reaction mixture has to be warmed to -30 °C, and the solution becomes dark brown.MnO₃Cl is now separated quickly on a vacuum line with a -30 °C trap and a -80 °C trap. Traces of Mn₂O₇ are collected in the -30 °C trap, and MnO₃Cl in the -80 °C trap. Yield: ~0,4 g (60 %) of a dark brown oil. After isolation the sample should be stored in liquid nitrogen to prevent decomposition. Solid MnO₃Cl is dark green.

For X-ray structure analysis MnO₃Cl is transferred under dynamic vacuum into a small trap. Then a small amount of MnO₃Cl is condensed under static vacuum into a 0.5 mm Lindemann capillary at -196 °C, which is directly connected to the trap. All further manipulations with the capillary (fixing it on the sample holder for X-ray diffraction) are carried out in liquid nitrogen.

MnO₃F: *Warning:* Preparation from KMnO₄ and HSO₃F, according to [1]: Reaction of 2 g KMnO₄ with 15 g HSO₃F and distillation of the volatiles into a -78 °C trap produced a large amount of a green FMnO₃/HSO₃F mixture. This resulted in a severe explosion if warmed to -30 °C.

Preparation from KMnO₄ and HF: 1 g KMnO₄ is weighed into a PFA tube (tetrafluoroethylen-perfluorovinylether-copolymer). 15 ml anhydrous HF is condensed on it with the help of a metal vacuum line, resulting in a green solution. The bulk of the liquid is distilled at 0 °C into a PFA U-trap held at -77 °C. At -50 °C

HF is slowly pumped off, and green crystals of MnO_3F are formed. These were immediately transferred to the diffractometer. The yield of MnO_3F is very low, estimated to be 1-3 %.

CrO₂Cl₂ is prepared from K₂Cr₂O₇, NaCl, and H₂SO₄ [5].

ReO₃Cl [16]: 3 g (8.25 mmol) freshly sublimed ReCl₅ is suspended in 10 ml CFCl₃. The temperature is kept at 10 °C during the entire reaction time. Cl₂O is prepared in situ from Cl₂ and HgO dried by passage through P₂O₅ and slowly added to the reaction mixture. After about 6 hrs. the green solution turns red (ReOCl₄), finally colorless. The solvent is pumped away at -60 °C and 10^{-3} mbar, yield 90 %, based on ReCl₅. Mp 4.5 °C, bp 128 °C. Raman spectrum: 1001, 435, 344, 335, 303, 196 cm⁻¹. Also ReOCl₄ can be reacted with Cl₂O. This reaction is finished within 2 hrs, the yield is similarly high.

DFT-calculations are done with the GAUSSIAN package [22], the Becke 3 parameter hybrid functional [23], and the correlation functional of *Lee, Yang, and Parr* [24]. Basis sets used throughout: 6-311+G(d,p).

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References

- [1] A. Engelbrecht, A. Grosse, J. Am. Chem. Soc. 1954, 76, 2042.
- [2] A. Javan, A. Engelbrecht, Phys. Rev. 1954, 96, 649-658.
- [3] D. Michel, D. Doiwa, Naturwissenschaften 1966, 53, 129-130.
- [4] T. S. Briggs, J. Inorg. Nucl. Chem. 1968, 30, 2866-2869.
- [5] P. J. Aymonino, H. Schulze, A. Mueller, Z. Naturforsch. 1969, 24b, 1508-1510.
- [6] J. Jasminski, S. C. Holt, J. Chem. Soc., Chem. Commun. 1972, 1046–1047.
- [7] E. Varetti, A. Müller, Z. Anorg. Allg. Chem. 1978, 442, 230–234.
- [8] M. Cieslak-Golonka, Bull. Acad. Polon. Sc., Ser. Sciences Chim. 1980, 28, 643–649.
- [9] P. Decleva, G. Fronzoni, A. Lisini, M. Stener, Chem. Phys. 1994, 186, 1-16.
- [10] I. Bytheway, M. W. Wong, Chem. Phys. Lett. 1998, 282, 219-226.
- [11] G. Fronzoni, M. Coreno, M. de Simone, P. Franceschi, C. Furlani, K. C. Prince, P. Decleva, *PhysChemChemPhys.* 2003, 5, 2758–2769.
- [12] E. L. Varetti, J. Raman Spectrosc. 1991, 22, 307-309.
- [13] T. Wistuba, C. Limberg, Chem. Europ. J. 2001, 7, 4674-4685.
- [14] G. Brauer, Handbuch der präparativen Anorganischen Chemie, III, Ferdinand Encke Verlag, Stuttgart 1981, p. 1322–1523.
- [15] W. Geilmann, F. W. Wigge, W. Biltz, Z. Anorg. Allg. Chem. 1933, 214, 244-247.
- [16] K. Dehnicke, W. Liese, Chem. Ber. 1977, 110, 3959-3960.
- [17] A. Simon, R. Dromskowska, B. Krebs, B. Hettig, Angew. Chem. 1987, 99, 150–161; Angew. Chem. Int. Ed. Engl. 1987, 26, 139–140.
- [18] R. S. Rowland, R. Taylor, J. Phys. Chem. 1996, 100, 7384-7391.
- [19] R. Boese, A. D. Boese, D. Bläser, M. Y. Antipin, A. Ellern, K. Seppelt, Angew. Chem. 1997, 109, 1538–1541; Angew. Chem. Int. Ed. Engl. 1997, 36, 1489–1492.

- [20] H. Schumann, W. Genthe, E. Hahn, M.-B. Hossein, D. v. d. Helm, J. Organomet. Chem. 1986, 28, 2561–2567.
- [21] G. M. Sheldrick, Program for Crystal Structure Solution, Universität Göttingen: Göttingen, Germany, 1986; *SHELXS*, Universität Göttingen: Göttingen, Germany, 1997.
- [22] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gom-

perts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003. Gaussian *03*, revision B.04, Gaussian, Inc.: Pittsburgh, PA, 2003.

- [23] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [24] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785.