ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2020, Vol. 46, No. 12, pp. 812–816. © Pleiades Publishing, Ltd., 2020.
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The authors congratulate Academician of the Russian Academy of Sciences I.L. Eremenko on his 70th jubilee

Reversible Phase Transition in the MoO_2Cl_2(DME) Structure with the Retention of the Crystal System and Space Group

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Received April 24, 2020; revised April 29, 2020; accepted May 7, 2020

Abstract—A completely reversible phase transition in the MoO_2Cl_2(DME) compound with the retention of the crystal system and space group is discovered and studied. The transition is also accompanied by the doubling of the unit cell parameter and occurs without single crystal destruction. The crystal structure of the MoO_2Cl_2(DME) complex are determined at 160 (modification **I**) and 150 K (modification **II**) (CIF files CCDC nos. 1997752 and 1997751, respectively).

Keywords: phase transitions, diffraction pattern, systematic quenchings, weak intermolecular interactions

DOI: 10.1134/S1070328420110020

INTRODUCTION

In the recent time, physicochemical processes in the crystalline phases occurring without single crystal destruction, so called single-crystal-to-single-crystal transformations (SCSC), attract increased attention of researchers, since these processes provide opportunities for the development of basically novel devices, such as volume 3D modules for information recording [1] or photoswitches [2]. Among other processes, the photochemical reactions [3], spin transitions [4], and ligand isomerization [5] and ligand exchange in porous structures [6] are intensively studied. Second-order phase transitions in crystals induced by temperature or pressure changes also occur fairly frequently without crystallinity and habitus losses [7, 8]. One of the most popular methods for the determination of parameters of these transitions is the monitoring of the diffraction pattern of single crystals, although the changes in the diffraction pattern are not pronounced and need labor-consuming measurements of the dependences of the unit cell parameters on the temperature or pressure [9, 10]. We were interested in the cases where the changes in the diffraction patterns during phase transitions were distinctly pronounced and can easily be determined visually [11]. The latter takes place at such phase transitions where a change in the crystal symmetry is accompanied by the disappearance–appearance of glide symmetry elements or a multiplication of the unit cell dimensions, since this results in the disappearance–appearance of systematic absences [12].

The reverse phase transition in the single crystal of the MoO_2Cl_2(DME) complex in a range of 150–160 K was studied in this work. Two structures of the complex were determined at 160 (**I**) and 150 K (**II**).

EXPERIMENTAL

Anhydrous Na_2MoO_4 obtained by the calcination of $Na_2MoO_4 \cdot 2H_2O$ crystalline hydrate in a drying box at 120–140°C for 6 h was used. Commercially available Me_3SiCl (98% purity, Aldrich) was subjected to an additional dehydration by reflux over aluminum powder for 5 h followed by distillation in a dry argon flow. Anhydrous ethylene glycol dimethyl ether (DME) (99.5% purity, Merck) was used without additional dehydration.

^{1}H NMR and mass spectra were recorded on Varian VXR-400 and Varian CH-7aMAT spectrometers (USA), respectively.

Synthesis of MoO_2Cl_2(DME) was carried out using a previously described procedure [13]. The yield of the target product was 20.0 g (69%). The crystals suitable for X-ray diffraction analysis were prepared by the

Table 1. Crystallographic data and structure refinement parameters for modifications **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_4H_{10}O_4Cl_2Mo$	$C_4H_{10}O_4Cl_2Mo$
Fw	288.96	288.96
Crystal size, mm	0.40 × 0.30 × 0.20	0.35 × 0.20 × 0.10
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Temperature, K	160	150
a, Å	7.1866(1)	14.3460(3)
b, Å	11.0595(1)	11.1358(2)
c, Å	13.7604(3)	13.6587(2)
β, deg	117.653(1)	117.932(1)
V, Å^3	968.75(3)	1927.84(6)
Z	4	8
ρ_{calc}, g/cm^3	1.981	1.991
$\mu(MoK_\alpha)$, mm^{-1}	1.874	1.883
F(000)	568	1136
Range of θ, deg	2.49–27.49	1.61–27.47
Total number of reflections	6871	13 788
Independent reflections (R_{int})	2221 (0.0238)	4418 (0.0286)
Number of refined parameters	141	280
R_1 ($I > 2\sigma(I)$)	0.0230	0.0259
wR_2 (all data)	0.0609	0.0715
GoF	1.051	1.106
$\Delta\rho_{min}/\Delta\rho_{max}$, e/Å^3	–0.507/0.574	–0.457/0.777

recrystallization from a dry mixture of acetone with 20% DME.

For $C_4H_{10}O_4Cl_2Mo$

Anal. calcd., %	C, 16.40	H, 3.34	Cl, 24.42
Found, %	C, 16.63	H, 3.49	Cl, 24.54

^{1}H NMR ($CDCl_3$), δ, ppm: 3.95 s (4H, CH_2O–), 4.00 s (6H, $-OCH_3$).

Mass spectrum (EI, 70 eV): 200 (MH^+-DME), 165 (MH^+-DME-Cl), 90 (DME).

X-ray diffraction analyses of modifications **I** and **II** were carried out on a Siemens 1K automated diffractometer (Germany). The phase transition was monitored on a Bruker SMART APEX II automated diffractometer (Germany) using MoK_α radiation (λ = 0.71073 Å, graphite monochromator) in the ω scan mode. An absorption correction was applied by measurements of equivalent reflection intensities [14]. The structures of modifications **I** and **II** were solved by a direct method and refined by full-matrix anisotropic least squares on F^2 for all non-hydrogen atoms [15]. All hydrogen atoms were found from the difference Fourier synthesis and refined isotropically. The crystallographic data and structure refinement results for modifications **I** and **II** are presented in Table 1. Selected bond lengths and bond angles are given in Table 2.

The structures of modifications **I** and **II** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1997752 and 1997751, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

We searched for polymorphous modifications characterized by the doubling of one of the presented unit cell parameters (taking into account possible transpositions of axes) in the Cambridge Structural Database [16]. The structures of polymorphs of the tungsten complex WO_2Cl_2(DME) attracted our attention: KUDGIZ (monoclinic **I**) and KUDGIZ01

Table 2. Selected bond lengths (Å) and angles (deg) for modifications **I** and **II**

Bonds and angles	**II** (150 K)		**I** (160 K)
	molecule 1	molecule 2	Z' = 1
Mo=O	1.688(2), 1.692(2)	1.687(2), 1.691(2)	1.686(2), 1.689(2)
Mo–Cl	2.3501(7), 2.3692(7)	2.3641(7), 2.3688(8)	2.3580(8), 2.3621(7)
Mo–O	2.297(2), 2.311(2)	2.278(2), 2.304(2)	2.2806(15), 2.303(2)
O=Mo=O	104.75(10)	104.84(12)	104.77(10)
ClMoCl	157.22(3)	158.82(3)	158.08(3)
OMoO	70.61(6)	70.71(6)	70.94(6)

(monoclinic **II**). The first of these structures was studied at room temperature [17], and the second structure was studied at 120 K [18]. The authors [18] noticed that the lattice parameters were similar for both polymorphs, but they did not consider the possibility of a phase transition. We revealed during preliminary experiments that the operation with WO_2Cl_2(DME) was very inconvenient because it was not resistant to hydrolysis. We decided to study the molybdenum analog, the more so the both compounds are isostructural at room temperature [19].

The crystal structures of the MoO_2Cl_2(DME) complex were determined at 160 (**I**) and 150 K (**II**). It turned out that the structures of modifications **I** and **II** had the same crystal system and the same space group no. 14 but differed twice by the cell parameter *a* (Table 1), cell volume, and number of crystallographically independent molecules Z' (Figs. 1 and 2, respectively). It turned out that the completely reversible phase transition occurred between these temperatures without any appreciable degradation of the single crystal quality. The intensities of a series of reflections forbidden for the high-temperature phase (doubling reflections with the odd index *h* for the low-temperature modification, Fig. 3) was monitored to determine the exact position of the transition point. As can be seen, the transition is situated in a narrow range less than 1 K and accompanied by a sharp change in the intensities of systematic absences.

The molecules of the complex in both modifications are localized in general positions and represent distorted octahedra with the *cis* arrangement of doubly bound terminal oxygen atoms (O=Mo) and *trans* arrangement of the chlorine atoms. As can be seen from the data in Table 2, the geometric parameters of the complex change very slightly during the phase transition.

This phase transition results in a significant mutual shift of the molecules. The shortest intermolecular Mo···Mo distances in the structure of modification **I** are 5.59 and 6.00 Å, whereas in modification **II** they are appreciably longer: 5.71 and 6.06 Å.

The structure of modification **I** exhibits the shortened intermolecular contact of the methylene group and terminal oxygen atom (O=Mo) with the H···O distance equal to 2.50 Å, which can be considered as a C–H···O hydrogen bond of the medium strength [20]. In the structure of modification **II**, this contact is significantly weakened (2.60 Å) on cooling, but several shortened C–H···Cl contacts (2.74–2.86 Å) are formed. It is most likely that this phase transition occurs due to the weakening of some contacts with the simultaneous enhancement of other weak intermolecular interactions C–H···X, which are structure forming for this compound due to cooperativity.

The completely reversible phase transition in the MoO_2Cl_2(DME) structure with the retention of the crystal system and space group was found. The transition is accompanied by the doubling of the unit cell parameters and occurs without single crystal destruction. It is shown that the transition is situated in a narrow temperature range less than 1 K and is accompanied by a sharp change in the intensities of systematic absences easily observed visually. This makes this

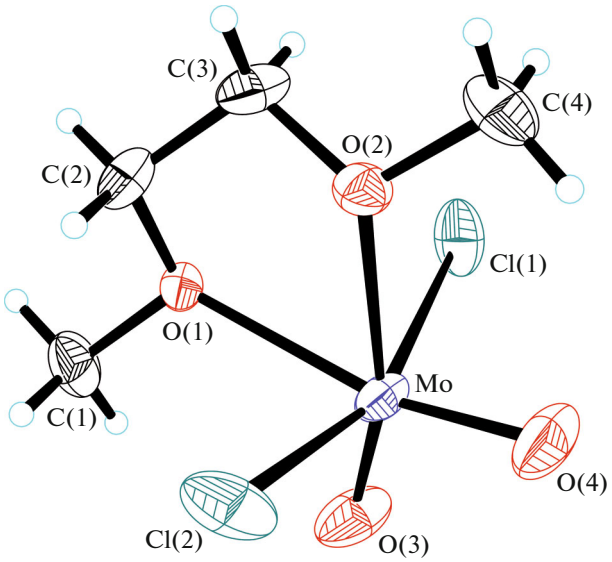

Fig. 1. Crystallographically independent molecule in the structure of modification **I**. Thermal ellipsoids are presented with 50% probability.

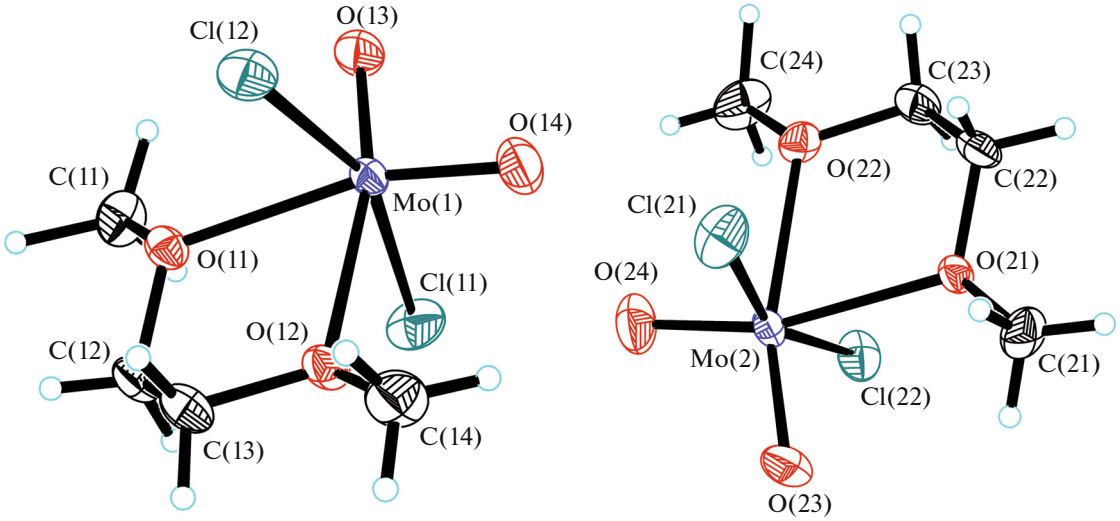

Fig. 2. Both crystallographically independent molecules of the structure of modification **II**. Thermal ellipsoids are presented with 50% probability.

compound very convenient for the fast calibration of low-temperatures accessories to diffractometers, the more so the transition point (156 K) lies almost at middle of a temperature range of 100–200 K in which, according to the CSD data, more than 50% single-crystal experiments are presently carried out.

ACKNOWLEDGMENTS

The authors are grateful to Prof. J.A.K. Howard (Durham University, Great Britain) for the kindly presented opportunity to use the diffractometric equipment and O.V. Dolomanov (Moscow State University, Russia) for fruitful discussion.

FUNDING

The phase transition was studied in terms of state assignment of the Center for Collective Use of the Kurnakov Institute of General and Inorganic Chemistry (Russian Academy of Sciences).

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

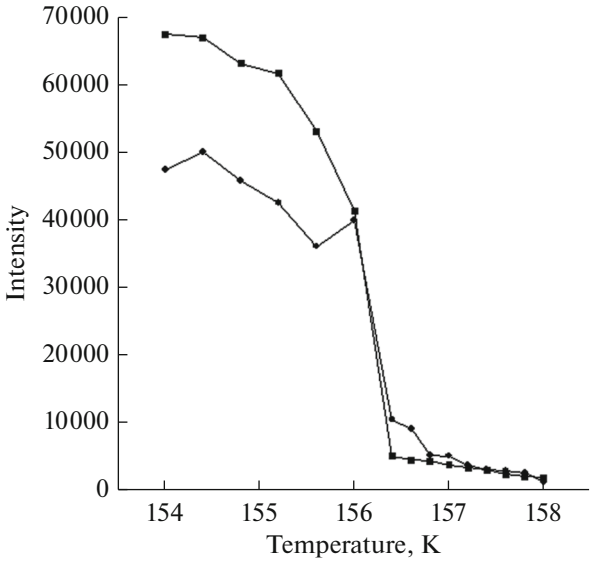

Fig. 3. Temperature dependences of the intensity of two reflections forbidden for the phase of modification **I**.

REFERENCES

1. Kuz'mina, L.G., Vedernikov, A.I., Gromov, S.P., and Alfimov, M.V., *Crystallogr. Rep.*, 2019, vol. 64, no. 5, p. 691. https://doi.org/10.1134/S1063774519050122
2. Marchivie, M., Guionneau, P., Howard, J.A.K., et al., *J. Am. Chem. Soc.*, 2002, vol. 124, no. 2, p. 194. https://doi.org/10.1021/ja016980k
3. Huang, S.-L., Andy-Hor, T.S., and Jin, G.-X., *Coord. Chem. Rev.*, 2016, vol. 346, p. 112. https://doi.org/10.1016/j.ccr.2016.06.009
4. Money, V.A., Radosavljevic-Evans, I., Halcrow, M.A., et al., *Chem. Commun.*, 2003, p. 158. https://doi.org/10.1039/B210146G
5. Mikhailov, A., Vukovic, V., and Kijatkin, C., et al., *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2019, vol. 75, no. 6, p. 1152. https://doi.org/10.1107/S205252061901357X
6. Manna, B., Desai, A.V., and Kumar, N., et al., *Cryst. Eng. Commun.*, 2015, vol. 17, no. 46, p. 8796. https://doi.org/10.1039/c5ce00139k

7. Yufit, D.S., Chetina, O.V., and Howard, J.A.K., *J. Mol. Struct.*, 2006, vol. 784, nos. 1–3, p. 214. https://doi.org/10.1016/j.molstruc.2005.09.007
8. Spencer, E.C., Angel, R.J., and Ross, N.L., et al., *J. Am. Chem. Soc.*, 2009, vol. 131, no. 11, p. 4022. https://doi.org/10.1021/ja808531m
9. Vatsadze, S.Z., Gavrilova, G.V., and Zyuz'kevich, F.S., et al., *Russ. Chem. Bull.*, 2016, vol. 65, no. 7, p. 1761. https://doi.org/10.1007/s11172-016-1508-7
10. Zaitsev, K.V., Lam, K., and Poleshchuk, O.Kh., et al., *Eur. J. Inorg. Chem.,* 2019, no. 22, p. 2750. https://doi.org/10.1002/ejic.201900316
11. Leech, M.A., Howard, J.A.K., Dahaoui, S., et al., *Chem. Commun.*, 1999, no. 22, p. 2245. https://doi.org/10.1039/a906876g
12. *International Tables for Crystallography. Space-Group Symmetry*, Hahn, Th., Ed., Dordrecht: Springer, 2005.
13. Rufanov, K.A., Zarubin, D.N., and Ustynyuk, N.A., et al., *Polyhedron*, 2001, vol. 20, no. 5, p. 379.
14. Sheldrick, G.M., *SADABS. Program for Scaling and Correction of Area Detector Data*, Göttingen: Univ. of Göttingen, 1997.
15. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112. https://doi.org/10.1107/S0108767307043930
16. Groom, C.R., Bruno, I.J., Lightfoot, M.P., and Ward, S.C., *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.*, 2016, vol. 72, no. 2, p. 171. https://doi.org/10.1107/S2052520616003954
17. Dreisch, K., Andersson, C., and Stålhandske, C., *Polyhedron*, 1991, vol. 10, nos. 20–21, p. 2417. https://doi.org/10.1016/S0277-5387(00)86203-8
18. Davis, M.F., Levason, W., Light, M., et al., *Eur. J. Inorg. Chem.,* 2007, no. 13, p. 1903. https://doi.org/10.1002/ejic.200700043
19. Kamenar, B., Penavić, M., Korpar-Čolig, B., and Marković, B., *Inorg. Chim. Acta*, 1982, vol. 65, p. L245. https://doi.org/10.1016/S0020-1693(00)93562-X
20. Steiner, T., *Crystallogr. Rev.*, 2003, vol. 9, nos. 2–3, p. 177. https://doi.org/10.1080/0889311031000162177

Translated by E. Yablonskaya