ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2017, Vol. 43, No. 6, pp. 368–372. © Pleiades Publishing, Ltd., 2017.
Original Russian Text © L.I. Udalova, S.A. Adonin, P.A. Abramov, I.V. Korolkov, M.N. Sokolov, 2017, published in Koordinatsionnaya Khimiya, 2017, Vol. 43, No. 6, pp. 352–356.

Zn-Containing Double Complex Salts Formed by Keggin Type Polyoxotungstates: Synthesis and Crystal Structure

L. I. Udalova[a], **S. A. Adonin**[a, b, *], **P. A. Abramov**[a, b], **I. V. Korolkov**[a, b], **and M. N. Sokolov**[b, c]
[a] *Novosibirsk State University, Novosibirsk, 630090 Russia*
[b] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*
[c] *Butlerov Institute of Chemistry, Kazan (Volga Region) Federal University, Kazan, 420008 Russia*
**e-mail: adonin@niic.nsc.ru*

Received August 8, 2016

Abstract—Novel double complex salts, $[Zn(DMF)_6]_2[SiW_{12}O_{40}] \cdot 2H_2O$ (**I**) and $[Zn(H_2O)_2(DMF)_4][Zn(DMF)_6]_2[PW_{12}O_{40}]_2 \cdot 6DMF$ (**II**) (DMF = *N*,*N*-dimethylformamide), were prepared by the reaction of Zn^{2+} and heteropoly acids $H_x[EW_{12}O_{40}] \cdot xH_2O$ (E = P, X = 3, E = Si, X = 4) in DMF. Compounds **I** and **II** were studied by X-ray diffraction (CIF files CCDC nos. 1497570 (**I**) and 1497571 (**II**)) and IR spectroscopy.

Keywords: polyoxometalates, zinc, double complex salts, crystal structure

DOI: 10.1134/S1070328417050086

INTRODUCTION

Polyoxometalates (POMs) represent an extensive class of polynuclear coordination compounds consisting of transition metal atoms in a high (most often, the highest) oxidation state and the coordination environment composed of O atoms [1–3]. These complexes are of considerable interest for both fundamental inorganic chemistry and various related areas. Particular attention is paid to the catalytic activity of POMs [4–13], the possibility of using them as components of hybrid functional materials [14–22] and so on.

The classic Keggin type polyoxo anions $[XM_{12}O_{40}]^{n-}$ (M = Mo, W) belong to the most studied structural types of POMs [1]. These compounds tend to lose one or several $\{WO\}^{4+}$ groups (with increasing solution pH) to give lacunary POMs ($[PW_{11}O_{39}]^{7-}$, $[SiW_{11}O_{39}]^{8-}$, etc.), which are, in turn, able to coordinate heterometal atoms, while functioning as polydentate ligands [23]. Also, several complexes in which heterometal ions are coordinated to non-lacunary POM via terminal oxygen atoms have also been reported. This behavior is especially typical of the most oxophilic elements [24–26]. Complexes of this type are often synthesized using donor organic solvents that can complete the coordination sphere of the heteroatom. Previously [27], we demonstrated that an attempt to prepare a Cd-containing POM complex in DMF gives only a double complex salt with the $[Cd(DMF)_6]^{2+}$ cation; that is, Cd^{2+} is not coordinated to the polyoxo anion. Here we attempted the coordination of Zn^{2+} under similar conditions; this gave the complexes $[Zn(DMF)_6]_2[SiW_{12}O_{40}] \cdot 2H_2O$ (**I**) and $[Zn(H_2O)_2(DMF)_4][Zn(DMF)_6]_2[PW_{12}O_{40}]_2 \cdot 6DMF$ (**II**), which were studied by X-ray diffraction.

EXPERIMENTAL

The syntheses of **I** and **II** were performed in air. Reagent grade chemicals were received from commercial sources and used as received. The numbers of solvation water molecules for phospho- and silicotungstic acids were determined by elemental analysis (~11 and 15, respectively). Infrared spectra (KBr) were measured on a Scimitar FTS 2000 spectrometer. Powder X-ray diffraction analysis was performed on a Shimadzu XRD-7000 diffractometer at room temperature.

Synthesis of I. Dimethylformamide (3.5 mL) was added to a mixture of $ZnCl_2$ (43 mg, 0.32 mmol) and $AgNO_3$ (108 mg, 0.64 mmol). After vigorous stirring, the AgCl precipitate that formed was filtered off, and $H_4[SiW_{12}O_{40}] \cdot 15H_2O$ (500 mg, 0.16 mmol) in 3 mL of DMF was added to the resulting solution. Slow diffusion of diethyl ether vapor into the mixture gave crystals suitable for X-ray diffraction in 78% yield.

IR (4000–400 cm^{-1}): 3483 w, 2934 w, 2814 w, 1645 s, 1494 w, 1433 m, 1375 m, 1253 w, 1116 m, 1060 w, 1014 m, 968 s, 918 s, 885 m, 793 s, 681 w, 534 m, 384m.

Synthesis of II. Dimethylformamide (3.5 mL) was added to a mixture of $ZnCl_2$ (24 mg, 0.17 mmol) and

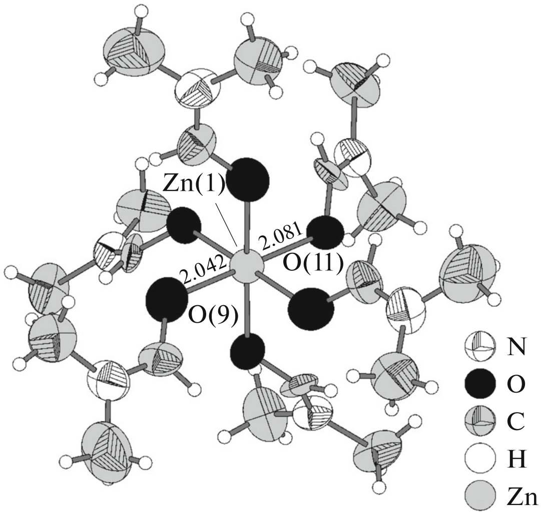

Fig. 1. Structure of the $[Zn(DMF)_6]^{2+}$ cation in the crystal of complex **I**. Thermal ellipsoids are shown at 50% probability.

$AgNO_3$ (59 mg, 0.35 mmol). After vigorous stirring for 30 min, the AgCl precipitate that formed was filtered off, and $H_3[PW_{12}O_{40}] \cdot 11H_2O$ (520 mg, 0.17 mmol) in 3 mL of DMF was added to the resulting solution. Slow diffusion of diethyl ether vapor into the mixture gave crystals of **II** suitable for X-ray diffraction in 83% yield (in relation to Zn).

IR (4000–400 cm^{-1}): 3466 w, 2931 w, 2891 w, 2809 w, 1651 s, 1495 w, 1436 m, 1418 w, 1377 m, 1254 w, 1114 w, 1080 s, 981 s, 896 s, 809 s, 685 w, 595 w, 511 m.

X-ray diffraction. The structure of **I** was determined on an XCalibur (Agilent Technologies) diffractometer by a standard procedure (MoK_α, λ = 0.71073 Å, graphite monochromator). The reflection intensities were measured in the φ-scan mode for narrow (0.5°) frames. The absorption corrections were applied empirically by the SCALE3 ABSPACK algorithm [28]. The structure was solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms using the SHELX2014\7 algorithm and the ShelXle program [29]. The crystal of **I** was a merohedral twin with 0.3/0.7 component ratio; the twin law was (–1.0, 0; 0, –1, 0; 0, 0, –1). The crystal structure had large voids with a volume of 384 Å^3. Analysis of the residual electron density (PLATON [30], SQUEEZE function [31]) gave a value of 16*e* per formula unit. According to DTA, the structure contained approximately two water molecules per formula unit.

The structure of compound **II** was determined on a Bruker-Apex Duo diffractometer by a standard procedure (MoK_α, λ = 0.71073 Å, graphite monochromator). The reflection intensities were measured in the φ- and ω-scan modes for narrow (0.5°) frames. The absorption corrections were applied empirically using the SADABS program [32]. The structure was solved by direct methods and refined by full-matrix least squares in the anisotropic approximation for non-hydrogen atoms using the SHELX2014\7 algorithm and the ShelXle program [29]. The hydrogen atoms of the DMF molecule were placed into geometrically calculated positions and refined in the rigid-body approximation. The hydrogen atoms of the coordinated water molecules were refined from X-ray diffraction experiment. The crystal data and refinement details for **I** and **II** are summarized in Table 1. The geometric parameters of hydrogen bonds are presented in Table 2.

The atom coordinates and other parameters of the structure are deposited with the Cambridge Crystallographic Data Centre (nos. 1497570 (**I**), 1497571 (**II**); http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

As noted above, the primary objective of this study was to attempt the coordination of Zn^{2+} to non-lacunary polyoxo anions in a solvent with a high donor number. Previously, it was shown that this type of coordination is possible for some metals if the POM charge is relatively high, in particular, for the reduced $[PMo_{12}O_{40}]^{n-}$ species [33] and for some polyoxoniobates and -tantalates [34–36]. Nevertheless, according to obtained results, double complex salts are formed in the Zn^{2+}–$[EW_{12}O_{40}]^{n-}$–DMF systems, where E = P, Si, without binding of zinc to POM oxygen atoms. Compound **I** contains $[Zn(DMF)_6]^{2+}$ cations (Fig. 1) with Zn–O bond lengths of 2.042–2.081 Å, which is comparable with published data [37, 38]. A distinctive feature of structure **II** is that apart from four DMF molecules, the Zn^{2+} coordination sphere contains two aqua ligands, which come from

Table 1. Crystallographic parameters and X-ray diffraction experiment details for **I** and **II**

Parameter	Value	
	I	**II**
Molecular formula	$C_{36}H_{84}N_{12}O_{52}SiZn_2W_{12}$	$C_{66}H_{158}N_{22}O_{104}P_2Zn_3W_{24}$
M	3882.18	7594.58
System, space group	Trigonal; $P\bar{3}$	Triclinic; $P\bar{1}$
Temperature, K	130	150
a, Å	15.9959(3)	12.9441(9)
b, Å	15.9959(3)	13.6751(10)
c, Å	32.4526(7)	23.0847(17)
α, deg	90	90.901(2)
β, deg	90	98.296(2)
γ, deg	120	97.7080(19)
V, Å^3	7191.1(3)	4004.4(5)
Z	3	1
μ, mm^{-1}	14.92	17.72
Crystal size, mm	0.25 × 0.20 × 0.12	0.40 × 0.30 × 0.20
Absorption correction	Empirical, based on spherical harmonics, using the SCALE3 ABSPACK algorithm (CrysAlisPRO 1.171.38.41; Rigaku Oxford Diffraction, 2015)	Empirical, using the SADABS program (Bruker-AXS, 2004)
$T_{\min}, T_{\max}$	0.214, 1.000	0.053, 0.126
Numbers of measured and unique reflections and reflections with $I > 2\sigma(I)$	12834, 6546, 5814	83126, 19257, 17866
R_{int}	0.035	0.036
$(\sin\theta/\lambda)_{\max}$, Å^{-1}	0.625	0.661
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.044, 0.110, 1.06	0.026, 0.069, 1.20
Number of refined parameters, restraints	345, 13	1003, 30
Refinement of hydrogen atom positions	Geometrically calculated positions	Independent geometrically calculated positions
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0477P)^2 + 102.0764P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.021P)^2 + 29.7557P]$, where $P = (F_o^2 + 2F_c^2)/3$
Residual electron density (max/min), e/Å^3	2.84/–1.75	2.31/–2.38
Absolute configuration	Refined as an inversion twin	
Absolute configuration parameter	0.34(3)	

Table 2. Some geometric parameters of hydrogen bonds in **II**

D–H···A	Distance, Å			DHA angle, deg
	D–H	H···A	D···A	
O(47)—(1)···O(51)	0.94	1.81	2.722	162
O(47)—(2)···O(52)	0.81	1.86	2.674	175

the initial hydrated acid, $H_3[PW_{12}O_{40}] \cdot 11H_2O$. The $Zn{-}O_{DMF}$ distances (2.112 Å) are somewhat longer than $Zn{-}O_{H2O}$ (2.093 Å). The structure of the $[Zn(DMF)_4(H_2O)_2]^{2+}$ cation was characterized here for the first time, although structurally related fragments containing four amine ligands and two other O-donor ligands were reported previously [39–41]. It is of interest that in structure **II**, the $[Zn(DMF)_4(H_2O)_2]^{2+}$ cations form supramolecular associates with two additional DMF molecules via hydrogen bonding (O(47)···O(52), 2.674; O(47)···O(52), 2.722Å) (Fig. 2).

The crystal packings of **I** and **II** are shown in Fig. 3. Powder X-ray diffraction data confirm that the samples of **I** and **II** are single phases. The IR spectra of the compounds exhibit strong characteristic bands (1645 and 1651 cm^{-1}) corresponding to C=O vibrations of coordinated DMF (cf. [42, 43]).

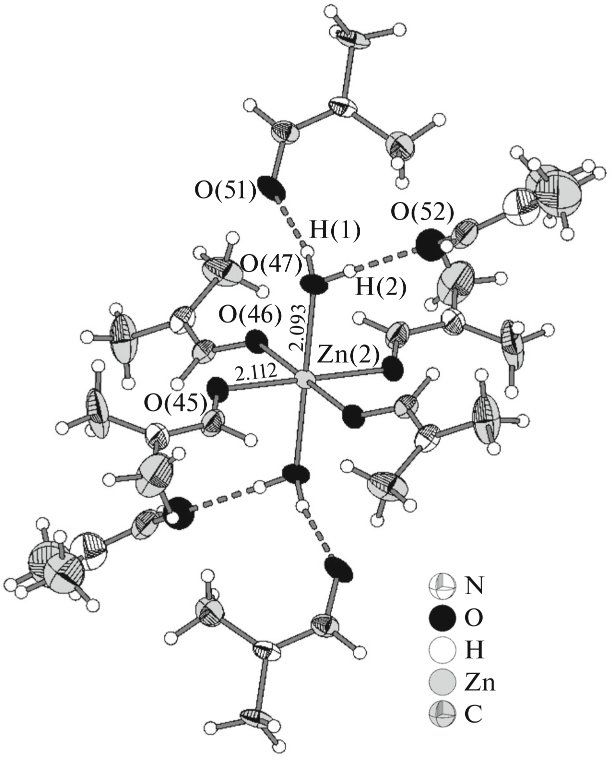

Fig. 2. Structure of the $\{[Zn(H_2O)_2(DMF)_4] \cdot 2DMF\}^{2+}$ cation in the crystal of complex **II**. Thermal ellipsoids are shown at 50% probability.

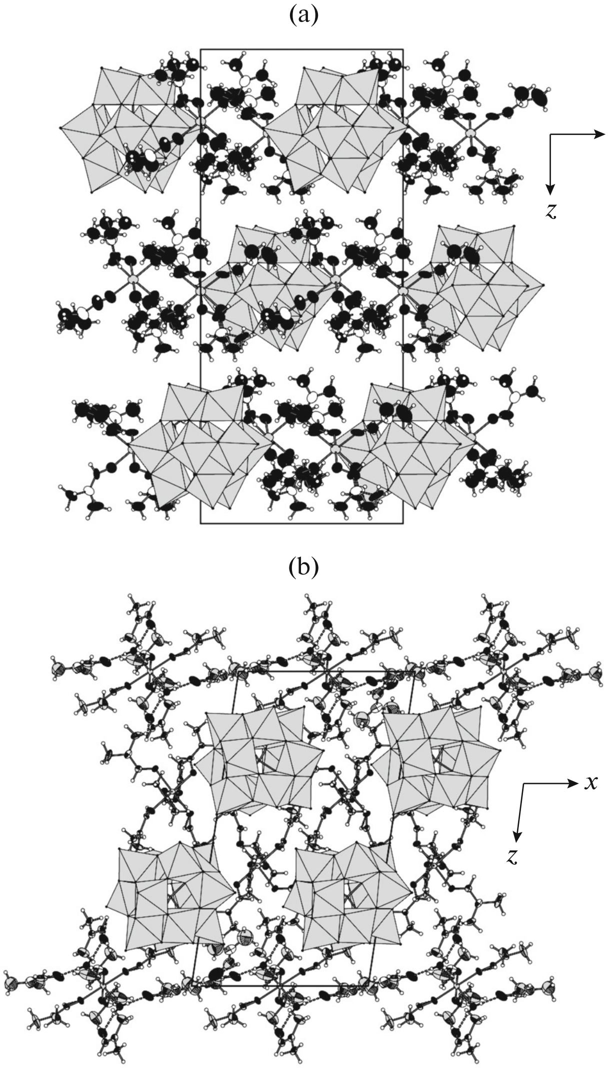

Fig. 3. Crystal packing of complexes (a) **I** and (b) **II**. The polyoxo anions are presented as coordination polyhedra. Thermal ellipsoids are shown at 50% probability.

ACKNOWLEDGMENTS

The authors are grateful to the Russian Foundation for Basic Research for the support (project no. 16-03-00309).

REFERENCES

1. Pope, M.T., *Heteropoly and Isopoly Oxometalates*, Berlin: Springer, 1983.
2. Nyman, M. and Burns, P.C., *Chem. Soc. Rev.*, 2012, vol. 41, p. 7354.
3. Oms, O., Dolbecq, A., and Mialane, P., *Chem. Soc. Rev.*, 2012, vol. 41, p. 7497.
4. Long, Z., Liu, Y., Zhao, P., et al., *Catal. Commun.*, 2015, vol. 59, p. 1.
5. Choi, A.E.S., Roces, S., Dugos, N., et al., *Fuel*, 2016, vol. 180, p. 127.
6. Dai, J., Zhong, W., Yi, W., et al., *Appl. Catal.*, 2016, vol. 192, p. 325.
7. Zhai, Q., Zhang, L., Zhao, X., et al., *Appl. Surf. Sci.*, 2016, vol. 377, p. 17.
8. Ye, J.-X., Wang, J.-Y., Wang, X., et al., *Catal. Commun.*, 2016, vol. 81, p. 1.
9. Wang, T., Lu, Y., Wu, H., et al., *Inorg. Chim. Acta*, 2016, vol. 446, p. 13.
10. Zonoz, F.M. and Aliabadi, F., *Inorg. Chim. Acta*, 2016, vol. 444, p. 87.
11. Ma, H., Li, C., Yin, J., et al., *Mater. Lett.*, 2016, vol. 168, p. 103.
12. Wang, R.-Q., Suo, L., Zheng, D.-M., et al., *Inorg. Chim. Acta*, 2016, vol. 443, p. 218.
13. Song, X., Zhu, W., Yan, Y., et al., *J. Mol. Catal. A: Chem.,* 2016, vol. 413, p. 32.
14. Sun, Y.-H., Li, G.-D., Cui, X.-B., et al., *Inorg. Chem. Commun.*, 2016, vol. 66, p. 24.
15. Bertan, B., Eren, T., Ermis, I., et al., *J. Colloid Interface Sci.*, 2016, vol. 470, p. 14.
16. Wan, R., Wang, Y., Han, M., et al., *Inorg. Chem. Commun.*, 2016, vol. 68, p. 72.
17. Lombana, A., Rinfray, C., Volatron, F., et al., *J. Phys. Chem.*, 2016, vol. 120, p. 2837.
18. Duan, Y., Clemente-Juan, J.M., Gimenez-Saiz, C., et al., *Inorg. Chem.*, 2016, vol. 55, p. 925.
19. Tang, J., Li, X.-Y., Wu, H., et al., *Langmuir*, 2016, vol. 32, p. 460.
20. Li, H., Yang, W., Wang, X., et al., *Gryst. Growth Des.*, 2016, vol. 16, p. 108.
21. Kim, M., Weinstock, I.A., Geletii, Y.V., et al., *ACS Catal.*, 2015, vol. 5, p. 7048.
22. Meninno, S., Parrella, A., Brancatelli, G. et al., *Org. Lett.*, 2015, vol. 17, p. 5100.
23. Cavaleiro, A.M.V., Pedrosa, De., Jesus, J.D., and Nogueira, H.I.S., *Metal Clusters in Chemistry*, Braunstein, P., Oro, L.A., and Raithby, P.R., Eds., Weinheim: Wiley, 2008.
24. Liu, D.-D. and Chen, Y.-G., *Inorg. Chim. Acta*, 2013, vol. 401, p. 70.
25. Mang, B.-F., You, W.-S., Sung, X.-F., et al., *Inorg. Chem. Commun.*, 2011, vol. 14, p. 35.
26. Zhang, L.-Z., Gu, W., Dong, Z., et al., *J. Solid State Chem.*, 2009, vol. 182, p. 1040.
27. Adonin, S.A., Udalova, L.I., Smolentsev, A.I., et al., *Russ. J. Coord. Chem.*, 2015, vol. 41, p. 633.
28. *CrysAlisPro. Agilent Technologies. Version 1.171.37.35 (release 13-08-2014 CrysAlis171 .NET).*
29. Hübschle, C.B., Sheldrick, G.M., and Dittrich, B., *J. Appl. Crystallogr.*, 2011, vol. 44, p. 1281.
30. Spek, A.L., *Acta Crystallogr., Sect. D: Struct. Biol.*, 2009, vol. 65, p. 148.
31. Vandersluis, P. and Spek, A.L., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, vol. 46, p. 194.
32. Sheldrick, G.M., *SADABS*, Göttingen: Univ. of Göttingen, 1996.
33. Bakri, R., Booth, A., Harle, G., et al., *Chem. Commun.*, 2012, vol. 48, p. 2779.
34. Son, J.-H. and Casey, W.H., *Chem. Commun.*, 2015, vol. 51, p. 1436.
35. Abramov, P.A., Vicent, C., Kompankov, N.B., et al., *Eur. J. Inorg. Chem.*, 2016, p. 154.
36. Abramov, P.A., Kompankov, N.B., and Sokolov, M.N., *Russ. J. Coord. Chem.*, 2016, vol. 42, p. 311.
37. Kaplan, P.T., Xu, L., Chen, B., et al., *Organometallics*, 2013, vol. 32, p. 7552.
38. Wang, J.-P., Wu, Q., and Niu, J.-Y., *Chin. J. Inorg. Chem.*, 2002, vol. 18, p. 957.
39. Muesmann, T.W.T., Zitzer, C., Mietrach, A., et al., *Dalton Trans.*, 2011, vol. 40, p. 3128.
40. Muesmann, T.W.T., Sitzer, C., Wickleder, M.S., et al., *Inorg. Chim. Acta*, 2011, vol. 369, p. 45.
41. Saffon-Merceron, N., Barthelemy, M.-C., Laurent, C., et al., *Inorg. Chim. Acta*, 2015, vol. 426, p. 15.
42. Boyarskaya, I.A. and Akopyan, S.Kh., *Russ. J. Gen. Chem.*, 2008, vol. 78, p. 2317.
43. Kharitonov, Yu.Ya. and Tsintsadze, G.V., *Russ. J. Inorg. Chem.*, 1965, vol. 18, p. 22.

Translated by Z. Svitanko