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A Double Complex Cd(II) Salt Containing the Keggin Polyoxoanion and the Supramolecular Cation of the [amide···H···amide]$^+$ Type

S. A. Adonin[a, b, *], L. I. Udalova[b], A. I. Smolentsev[a, b], M. N. Sokolov[a, b], and V. P. Fedin[a, b]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*

[b] *Novosibirsk State University, Novosibirsk, Russia*

**e-mail: adonin@niic.nsc.ru*

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Abstract—The complex $[H(DMFA)_2]_2[Cd(DMFA)_6][SiW_{12}O_{40}]$ (**I**) was obtained by a reaction between $H_4[SiW_{12}O_{40}]$, CdI_2, and $AgNO_3$ in *N*,*N*-dimethylformamide (DMF) and characterized by X-ray diffraction (CIF file CCDC No. 1041227). Structure **I** is made up of the complex cations $[Cd(DMF)_6]^{2+}$, the Keggin polyoxoanions $[SiW_{12}O_{40}]^{4-}$, and the dimeric cations $[DMF\cdots H\cdots DMF]^+$, in which two DMF molecules are linked by a short hydrogen bond (O···O, 2.39(2) Å). The cations of this type were compared with similar dimeric cations containing the fragment {amide···H···amide}.

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Polyoxometalates (POMs) are polynuclear oxo complexes containing transition metal atoms in their highest oxidation states. This class of compounds shows an exceptional variety of structural and chemical properties [1–4]. For this reason, POMs attract the attention of researchers in a number of fields related to inorganic chemistry. Many studies have been devoted to the catalytic activity of POMs [5–14] and to their use in materials science (including the preparation of magnetic materials) [15–20] and biotechnologies [21, 22].

The structural types of POMs are numerous, and the Keggin polyoxoanions $[XM_{12}O_{40}]^{n-}$ (M = Mo or W) are among the best studied ones [1, 2, 23]. One of the properties common in these anions is the tendency to eliminate one or more $\{WO\}^{4+}$ fragments with an increase in pH, yielding so-called lacunary polyoxoanions ($[PW_{11}O_{39}]^{7-}$, $[SiW_{11}O_{39}]^{8-}$, etc.). Such anions can act as polydentate ligands to a heterometal atom (complexes with more than 70 elements are currently known) [24]. In some cases, complete POMs can also function as ligands; e.g., they coordinate lanthanide ions [25–28] or dinuclear cluster fragments [29]. Such complexes have been obtained in nonaqueous media as well; solvent molecules are often involved in coordination, occupying the vacant sites of the heteroatom [25–28]. In this work, we tried to obtain cadmium-containing POM complexes using the above strategy. Only three Cd(II)-containing POMs have been structurally characterized to date [30–32]. Here we obtained and characterized the complex $[H(DMF)_2]_2[Cd(DMF)_6][SiW_{12}O_{40}]$ (**I**).

EXPERIMENTAL

The synthesis was carried out in air. Solvents were purified according to standard procedures. Commercial chemicals (reagent grade) were used as purchased. Elemental analysis was performed on a EuroEA 3000 CHN-analyzer at the Analytical laboratory of the Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences.

Synthesis of complex I. Cadmium diiodide (100 mg, 0.27 mmol) was dissolved in DMF (2 mL). Then $AgNO_3$ (92 mg, 0.54 mmol) was added with stirring. After 10 min, the precipitate of AgI was separated by filtration from the solution, to which a solution of $H_4[SiW_{12}O_{40}]$ (858 mg, 0.27 mmol) in DMF was added. Slow diffusion of the diethyl ether vapor resulted in the formation of colorless crystals of complex **I**. The yield was 89%.

For $C_{30}H_{72}CdN_{10}O_{50}SiW_{12}$			
anal. calcd. (%):	C, 9.69;	H, 1.95;	N, 3.77.
Found (%):	C, 9.71;	H, 2.01;	N, 3.81.

X-ray diffraction analysis. Structure **I** was determined by X-ray diffraction on a Bruker-NoniusX8 Apex 4KCCD single-crystal diffractometer (MoK_α radiation, graphite monochromator, $\lambda = 0.71073$ Å). Reflection intensities were measured using standard techniques. An absorption correction was applied empirically with the SADABS program [33]. The structure was solved by direct methods and refined by the full-matrix least-squares method with the

Table 1. Crystallographic parameters and the data collection and refinement statistics for structure **I**

Parameter	Value
M	3719.67
Temperature, K	296
Crystal dimensions, mm	0.25 × 0.20 × 0.10
Crystal system	Orthorhombic
Space group	*Pbca*
a, Å	19.6490(4)
b, Å	18.2385(4)
c, Å	20.9993(6)
V, Å^3	7525.5(3)
Z	4
ρ_{calcd}, g/cm^{-3}	3.283
$\mu(MoK_\alpha)$, mm^{-1}	18.651
θ scan range, deg	2.20–26.37
Ranges of h, k, and l indices	$-24 \le h \le 23$ $-19 \le k \le 22$ $-18 \le l \le 26$
$F(000)$	6688
Number of measured reflections	41843
Number of unique reflections (R_{int})	7693 (0.0438)
Number of reflections with $I > 2\sigma(I)$	6191
Number of parameters refined	529
R ($F^2 > 2\sigma(F^2)$)	$R_1 = 0.0433$, $wR_2 = 0.0857$
$R(F^2)$ (for all reflections)	$R_1 = 0.0600$, $wR_2 = 0.0903$
GOOF	1.053
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	2.573/–1.748

SHELXTL program package [34]. The positions of the non-hydrogen atoms were refined anisotropically. The hydrogen atoms of DMF were located geometrically and refined using a riding model. The positions of the protons localized between DMF molecules (in the cations $[H(DMF)_2]^+$) were not determined directly; they were included in the molecular formula of the complex for compensation of the negative charge of the polyoxoanion. The crystallographic parameters and the data collection and refinement statistics for structure **I** are given in Table 1. Selected bond lengths and bond angles are listed in Table 2. The crystallographic data for structure **I** have been deposited with the Cambridge Structural Database (CCDC No. 1041227; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

According to the X-ray diffraction data, the Cd(II) atom is not coordinated by the polyoxoanion $[SiW_{12}O_{40}]^{4-}$, regardless of its relatively high negative charge. The Cd^{2+} ion forms the octahedral cationic complex $[Cd(DMF)_6]^{2+}$ (Fig. 1); two coordinated DMF molecules are each disordered over two positions. The average Cd–O bond length is 2.262 Å; the OCdO and CdOC angles are 86.5(5)°–93.5(5)° and 127.7°, respectively (Table 2). The formation of octahedral complexes with solvent molecules as the only ligands is uncommon in the chemistry of Cd(II), although a number of structures containing the cation $[Cd(DMF)_6]^{2+}$ have been described in [35–37].

The structure of the anion $[SiW_{12}O_{40}]^{4-}$ is typical of the Keggin polyoxoanions; the bond lengths (Table 2) and other geometrical parameters agree with the literature data for the compounds of this type.

Structure **I** contains one cation $[Cd(DMF)_6]^{2+}$ and one anion $[SiW_{12}O_{40}]^{4-}$. Since four more DMF molecules are also present in the complex, it is advisable to assume their protonation leading to the supramolecular cationic dimers $[DMF\cdots H\cdots DMF]^+$ (Fig. 2). Indeed, the short O···O distance (2.39(2) Å) suggests strong symmetric hydrogen bonding between two DMF molecules. The resulting dimer is nonplanar because of steric hindrances; the dihedral angle between the planes is ~70°. This type of protonation of the amide group, though reported earlier, is still uncommon. At present, the Cambridge Structural Database includes 12 identified complexes containing the fragments {(N–C)O···H$^+$···}. The hydrogen bond length ranges from 2.39(2) to 2.47(1) Å (Table 3).

Table 2. Selected bond lengths *d* (Å) and bond angles ω (deg) in structure **I***

Bond	*d*, Å	Bond	*d*, Å
Cd(1)–O(23)	2.287(14)	W(4)–O(12)	2.498(14)
Cd(1)–O(24)	2.276(9)	W(4)–O(13)	1.662(9)
Cd(1) –O(25)	2.223(14)	W(4)–O(14)	1.879(13)
W(1)–O(1)	1.679(10)	W(4)–O(15)	1.881(12)
W(1)–O(2)	1.894(9)	W(4)–O(16)	1.902(11)
W(1)–O(3)	1.891(9)	W(4)–O(8)^{ii}	2.365(13)
W(1)–O(4)	2.373(12)	W(5)–O(11)	1.894(11)
W(1)–O(18)^{ii}	1.902(10)	W(5)–O(12)	2.376(13)
W(1)–O(20)^{ii}	2.377(13)	W(5)–O(16)	1.876(10)
W(1)–O(22)^{ii}	1.888(10)	W(5)–O(17)	1.670(9)
W(2)–O(2)	1.876(10)	W(5)–O(18)	1.885(10)
W(2)–O(4)	2.501(12)	W(5)–O(19)	1.915(10)
W(2)–O(5)	1.665(9)	W(5)–O(20)	2.390(13)
W(2)–O(6)	1.906(10)	W(6)–O(7)	1.876(13)
W(2)–O(7)	1.908(14)	W(6)–O(8)	2.322(13)
W(2)–O(8)	2.370(13)	W(6)–O(19)	1.872(11)
W(2)–O(15)^{ii}	1.888(13)	W(6)–O(20)	2.461(15)
W(3)–O(3)	1.903(9)	W(6)–O(21)	1.675(9)
W(3)–O(4)	2.391(12)	W(6)–O(22)	1.884(11)
W(3)–O(6)	1.862(9)	W(6)–O(14)^{ii}	1.910(13)
W(3)–O(9)	1.673(9)	Si(1)–O(4)	1.573(13)
W(3)–O(10)	1.908(9)	Si(1)–O(8)	1.700(13)
W(3)–O(11)	1.876(10)	Si(1)–O(12)	1.590(13)
W(3)–O(12)	2.374(14)	Si(1)–O(20)	1.593(13)
W(4)–O(10)	1.900(11)		
Angle	ω, deg	Angle	ω, deg
O(23)Cd(1)O(24)	91.4(4)	Cd(1)O25C(7*A*)	120.7(18)
O(23)Cd(1)O(25)	87.6(6)	O(4)Si(1)O(20)	112.9(7)
O(23)Cd(1)O(24)^{i}	88.6(4)	O(4)Si(1)O(8)^{ii}	105.4(6)
O(23)Cd(1)O(25)^{i}	92.4(6)	O(4)Si(1)O(12)^{ii}	112.5(7)
O(24)Cd(1)O(25)	93.5(5)	O(8)Si(1)O(12)	106.0(7)
O(24)Cd1O(25)^{i}	86.5(5)	O(8)Si(1)O(20)^{ii}	107.9(7)
Cd(1)O(23)C(1)	137.4(18)	O(12)Si(1)O(20)^{ii}	111.7(7)
Cd(1)O(24)C(4)	125.0(9)		

* The symmetry operation codes are ^{i} 1 – *x*, –*y*, –*z*; ^{ii} –*x*, –*y*, –*z*.

Table 3. Hydrogen bond lengths in the dimeric cations [amide···H···amide]$^+$ (in structure **I** and other complexes)

CCDC code	Dimerized molecule	Counterion	O···O distance	References
	DMF	$[SiW_{12}O_{40}]^{4-}$	2.39(2)	This study
BADCIS10				
BADCIS20	Urea	$[SiF_6]^{2-}$	2.424(1), 2.442(1)	[38–40]
BADCIS30				
DEGBOH	*N*,*N*-Dimethylacetamide	ClO_4^-	2.39(8)	[41]
FAMXIA	Acetamide	NO_3^-	2.43(1)	[42]
GICDAX	1,1,3,3-Tetramethylurea	$[PW_{12}O_{40}]^{3-}$	2.47(1)	[43]
JIJRUP	*N*-(*o*-Tolyl)acetamide	NO_3^-	2.424(2)	[44]
QADPAO	[(η^6-*p*-cym)Ru(N-2,4-dimethoxy-Ph-picolinamide)Cl]	PF_6^-	2.428(4)	[45]
QADPES	[(η^6-*p*-cym)Ru(N-2-fluoro-Ph-picolinamide)Cl]	PF_6^-	2.462(4)	[45]
QECCUY	*N*,*N*-Dimethylpropionamide	$[PMo_{12}O_{40}]^{3-}$	2.43(1), 2.45(1), 2.43(1), 2.44(1)	[46]
ROPRUJ	DMF	*	2.413(5)	[47]
SEGMOG	*N*,*N*-Dimethylacetamide	Br^-	2.448(9)	[48]
XAYGOV	Paracetamol	Cl^-	2.426(2), 2.427(2)	[49]

* Catecholatobis(tetrachlorocatecholato)phosphorus.

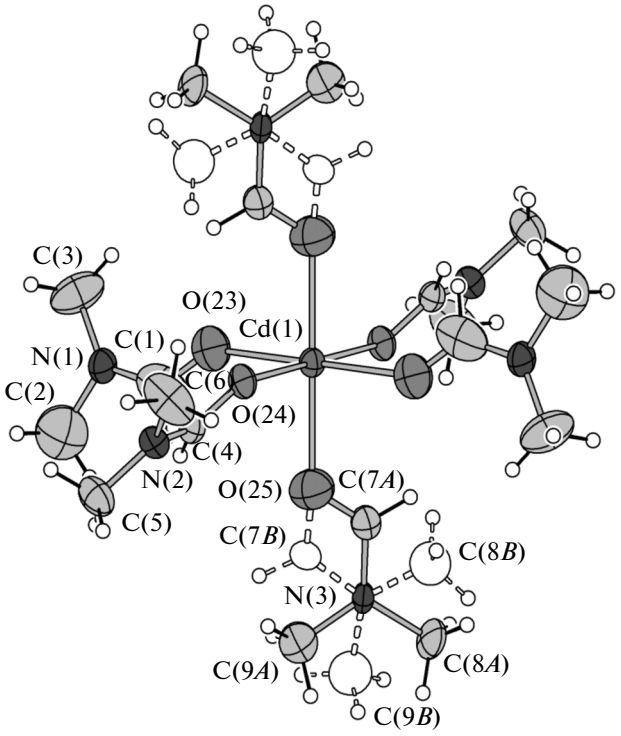

Fig. 1. The cation $[Cd(DMF)_6]^{2+}$ with the marked asymmetric fragment. The atoms are represented as thermal displacement ellipsoids (30% probability). The white ellipsoids and the dashed bonds refer to the alternative positions of the disordered DMF molecules.

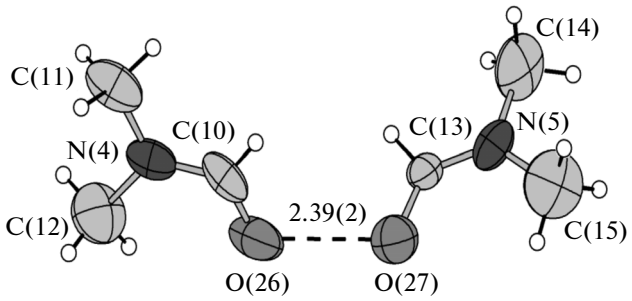

Fig. 2. The dimeric cation $[H(DMF)_2]^+$ with atomic displacement ellipsoids (30% probability). The hydrogen bond O···H···O is indicated with a dashed line.

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