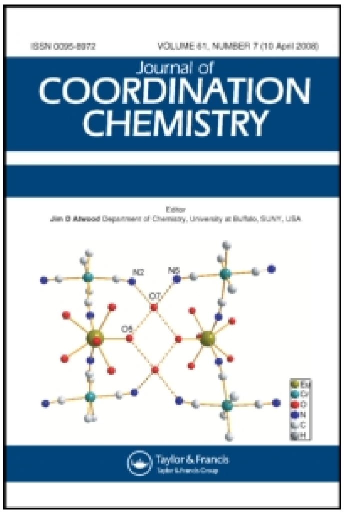

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Isomerically pure complexes of $[As_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ and $[As_2W_{18}Zn_2(CdOH_2)_2O_{68}]^{10-}$ were synthesized in high yield by self-assembly of WO_4^{2-} and $HAsO_4^{2-}$ (18 : 2) solution with the stoichiometric ratio of Cd^{2+} and Zn^{2+} ions. The complexes were characterized by elemental analysis, IR, Raman, ^{113}Cd NMR spectroscopy, and single crystal structure analysis. Single crystal structure analysis was carried out on $(NH_4)_{10}[As_2W_{18}Cd_4(H_2O)_2O_{68}] \cdot 23H_2O$ which crystallized in the monoclinic system, space group *C*2/*c* with $a = 23.512(3)$ Å, $b = 12.480(2)$ Å, $c = 30.583(4)$ Å, $\beta = 95.597(3)^\circ$, $Z = 4$, and $V = 8931(2)$ Å^3. The structure consists of two B-$AsW_9O_{34}^{9-}$ Keggin moieties linked via a rhomb-like Cd_4O_{14} group leading to a C_{2h} symmetry sandwich-type complex. Double- and single-line ^{113}Cd NMR spectra of $[As_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ and $[As_2W_{18}Zn_2(CdOH_2)_2O_{68}]^{10-}$, respectively, confirm C_{2h} symmetry for both anions in solution. Replacement of Cd^{2+} with Zn^{2+} in $[As_2W_{18}Zn_4(H_2O)_2O_{68}]^{10-}$ takes place only under vigorous conditions.

Keywords: Polytungstoarsenates; Sandwich-type complexes; Cadmium ion; Single crystal structure analysis; ^{113}Cd NMR spectroscopy

1. Introduction

Polyoxometalates have structural variety and interesting properties, and are used in catalysis, medicine, magnetism, and optics [1–6]. These compounds are divided into two subclasses, isopolyoxometalates, which consist of metal and oxygens, and heteropolyoxometalates, which consist of an additional heteroatom. The structural type most investigated is the Keggin anion, which is typically represented by the $[XM_{12}O_{40}]^{n-}$ formula, where X is Si^{IV}, P^V, As^V, etc. and M is W^{VI} or Mo^{VI}, composed of a XO_4 tetrahedron surrounded by twelve edge- and corner sharing metal-oxygen octahedra [7]. The lacunary or ''defect'' polyoxometalates, an important class of heteropolyoxometalates, are formed by addition of controlled amounts of alkali to preformed polyanions such as the Keggin anions. In these processes one, two or three WO_6

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octahedra are removed from the Keggin anions [8]. This category of heteropolyoxometalates forms most of the known transition metal ion derivatives of polyoxometalates. In 1973, Weakley *et al.* [9] synthesized $[P_2W_{18}Co_4(H_2O)_2O_{68}]^{10-}$ by reaction of a H^+_HPO_4^{2-}_Co^{2+}_WO_4^{2-} mixture of composition 11 : 2 : 4 : 18 at 100°C with a prolonged reaction time. In 1981, however, Finke and Droege [10] reported synthesis of $[P_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ anions by reaction of the trivacant lacunary B-$PW_9O_{34}^{9-}$ with $M = Co^{2+}$, Zn^{2+}, Cu^{2+}. Other isostructural complexes with $M = Ni^{2+}$, Mn^{2+}, Fe^{2+}, Fe^{3+}, $Mn^{2,3+}$, $Fe^{2+}Cu^{2+}$, and Cd^{2+} were synthesized in the same way [11]. This category is known as "sandwich-type" polyoxometalates. Trivacant lacunary $[AsW_9O_{34}]^{9-}$ analogs were reported by Wang *et al.* [12] with $[As_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ by reaction of B-$AsW_9O_{34}^{9-}$ with $M = Cd^{2+}$, Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}, but with little attention to Cd^{2+} derivatives. Sandwich-type polytungstoarsenates with two trivacant lacunary anions, A-$AsW_9O_{34}^{9-}$, are known [13]. In this article, the synthesis and characterization of two new cadmium containing sandwich-type complexes $[As_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ and $[As_2W_{18}Zn_2(CdOH_2)_2O_{68}]^{10-}$ are reported. The complexes were investigated by chemical analysis, FT-IR, Raman, and ^{113}Cd NMR spectra and single crystal analysis.

2. Experimental

2.1. *Chemicals and apparatus*

All chemicals were reagent grade and used without purification. Infrared spectra were recorded as KBr discs on a Buck 500 scientific spectrometer and Raman spectra on a Bomen MB-154 Fourier transfer Raman spectrometer in a capillary tube. NMR spectra were recorded on a Bruker BRX 500 AVANCE spectrometer. The resonance frequency for the ^{113}Cd nuclei is 110.92 MHz and chemical shifts for ^{113}Cd NMR spectra were externally referenced relative to 0.1 M cadmium perchlorate. The compound $K_{10}[As_2W_{18}Zn_4(H_2O)_2O_{68}] \cdot xH_2O$ was prepared according to the procedure of $K_{10}[As_2W_{18}Cd_4(H_2O)_2O_{68}] \cdot 17H_2O$, but instead of $Cd(NO_3)_2 \cdot 4H_2O$, the stoichiometric amount of $Zn(NO_3)_2 \cdot 6H_2O$ was added.

2.2. *Preparation of the compounds*

2.2.1. $K_{10}[As_2W_{18}Cd_4(H_2O)_2O_{68}] \cdot 17H_2O$ (1). Glacial acetic acid (3.5 mL) was added to a solution of $Na_2WO_4 \cdot 2H_2O$ (14.85 g, 45 mmol) and $Na_2HAsO_4 \cdot 7H_2O$ (1.58 g, 55 mmol) in 75 mL H_2O; the resulting solution was added in small portions to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (3.25 g, 10.5 mmol) in 75 mL H_2O and refluxed for 1 h. Addition of solid KCl (20 g) to the filtrate led to white crystalline powder, which was recrystallized at least twice in hot water (Yield: 12.5 g, 86%). Anal. Calcd for $K_{10}[As_2W_{18}Cd_4(H_2O)_2O_{68}] \cdot 17H_2O$ (%): K, 6.82; As, 2.62; W, 57.76; Cd, 7.85; H_2O, 5.34. Found: K, 6.10; As, 2.31; W, 56.60; Cd, 7.30; H_2O, 5.15.

2.2.2. $(NH_4)_{10}[As_2W_{18}Cd_4(H_2O)_2O_{68}] \cdot 23H_2O$ (2). The compound $(NH_4)_{10}[As_2W_{18}Cd_4(H_2O)_2O_{68}] \cdot 17H_2O$ was prepared according to the above procedure, but instead of potassium chloride, ammonium chloride was added. Yield 12.0 g (85.7%).

Crystals suitable for crystallographic study were obtained by recrystallization of white crystalline powder. Anal. Calcd for $(NH_4)_{10}[As_2W_{18}Cd_4(H_2O)_2O_{68}] \cdot 23H_2O$ (%): As, 2.66; W, 58.80; Cd, 7.99; $(H_2O + NH_3)$, 10.56. Found: As, 2.37; W, 57.20; Cd, 7.83; $(H_2O + NH_3)$, 10.25.

2.2.3. $K_{10}[As_2W_{18}Zn_2(CdOH_2)_2O_{68}] \cdot 13H_2O$ (3). Glacial acetic acid (3.5 mL) was added to a solution of $Na_2WO_4 \cdot 2H_2O$ (14.85 g, 45 mmol) and $Na_2HAsO_4 \cdot 7H_2O$ (1.58 g, 55 mmol) in 75 mL H_2O, and the resulting solution was added in small portions to a solution of $Cd(NO_3)_2 \cdot 4H_2O$ (1.625 g, 5.25 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (1.72 g, 5.78 mmol) in 75 mL H_2O and refluxed for 1 h. Addition of solid KCl (20 g) to the filtrate led to a white crystalline powder, recrystallized at least twice in hot water (Yield: 12.0 g, 86%). Anal. Calcd for $K_{10}[As_2W_{18}Zn_2(CdOH_2)_2O_{68}] \cdot 13H_2O$ (%): K, 7.03; As, 2.69; W, 59.11; Cd, 4.04; Zn, 2.43; H_2O, 4.21. Found: K, 6.68; As, 2.31; W, 58.48; Cd, 3.71; Zn, 2.38; H_2O, 4.20.

2.3. *Single-crystal X-ray diffraction analysis*

A colorless prismatic single crystal of $(NH_4)_{10}[As_2W_{18}Cd_4(H_2O)_2O_{68}] \cdot 23H_2O$ with dimensions of $0.1 \times 0.1 \times 0.1\ \text{mm}^3$ which crystallizes in monoclinic system [space group $C2/c$ with $a = 23.512(3)$ Å, $b = 12.480(2)$ Å, $c = 30.583(4)$ Å, $\beta = 95.597(3)^\circ$, and $Z = 4$] was used for the X-ray work. The unit cell of **2** is shown in figure 1. Intensity measurements were made at 140 K on a Bruker SMART 1000 CCD single crystal diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Total 13,043 independent reflections ($\theta_{\max} = 60.08^\circ$ and $R(\text{int}) = 0.0551$) were recorded, of which 9471 reflections were considered [$I > 2\sigma(I)$]. Data collection, indexing and initial cell refinements were done with APEX2 software [14]. Absorption correction was performed with SADABS [15]. The structure was solved by direct methods and difference maps (SHELXTL, *v* 5.10) [15]. All atoms were refined anisotropically. Scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-ray Crystallography* [16]. Structure solution, refinement, and generation of publication materials were performed using SHELXTL, *v* 5.10 software. Crystal data collection, refinement parameters, and selected bond lengths are given in tables 1 and 2, respectively.

3. Results and discussion

3.1. *IR and Raman spectroscopy*

Infrared spectra of three complexes which have very similar patterns confirm that these complexes have the same structures. Infrared spectra of these complexes are also similar to that of $AsW_{12}O_{40}^{3-}$ so these complexes are Keggin-like, sandwich-type polyoxometalates. The IR summary: (i) all of the characteristic vibrational frequencies decrease in comparison with those of $[AsW_{12}O_{40}]^{3-}$, attributed to increase in the negative charge of the anions, (ii) the asymmetric stretching vibration of W–Oc–W in $[AsW_{12}O_{40}]^{3-}$ is split into two peaks, (iii) IR and Raman spectra of **1** (Supplementary

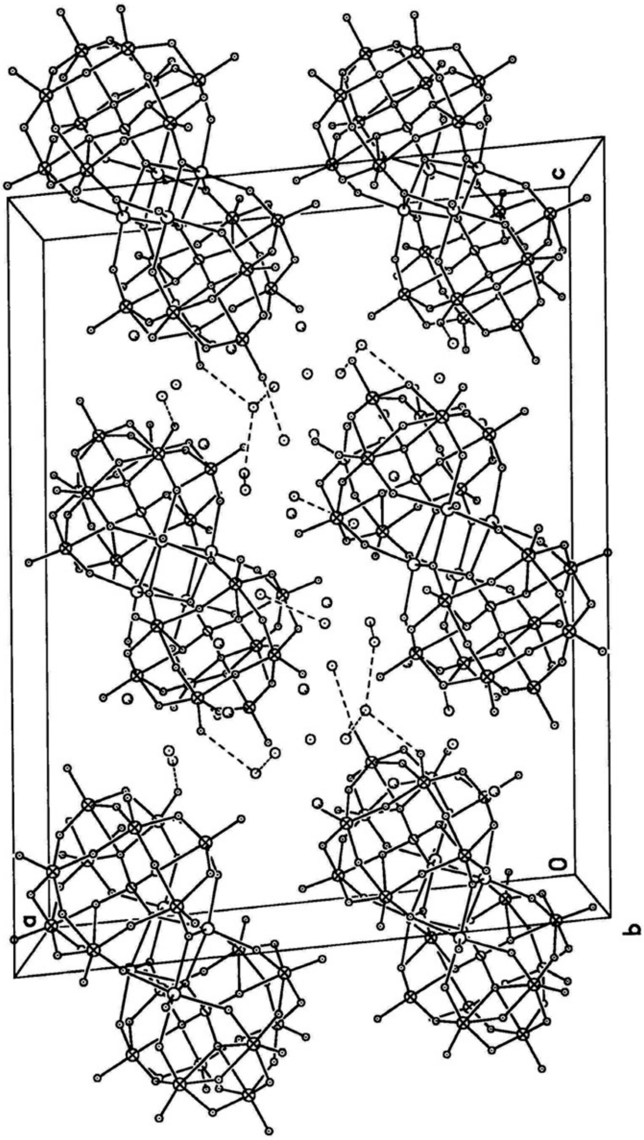

Figure 1. The unit cell of **2**.

material) are not similar, confirming that **1** has a centrosymmetric structure, and (iv) in the range 1000–700 cm^{-1}, characteristic bands were assigned to the asymmetric stretching vibrations of the terminal bonds W–Od (950–960 cm^{-1}), bridging W–Ob–W (830–840 cm^{-1}), As–O (870–880 cm^{-1}) and bridging W–Oc–W (800–700 cm^{-1}) [17].

3.2. *Structures*

Single crystal analysis was carried out on **2**, which is isostructural with **1** and **3**. The complex crystallizes in the monoclinic space group *C2/c*, with a total number of 47

Table 1. Crystallographic data for $(NH_4)_{10}As_2W_{18}Cd_4(H_2O)_2O_{68} \cdot 23H_2O$ (**2**).

Empirical formula	$H_{90}As_2Cd_4N_{10}O_{93}W_{18}$
Formula weight	5627.56
Temperature (K)	140(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	*C2/c*
Unit cell dimensions (Å, °)	
a	23.512(3)
b	12.480(2)
c	30.583(4)
α	90°
β	95.597(3)°
γ	90°
Volume (Å^3), *Z*	8931(2), 4
Calculated density ($mg\,m^{-3}$)	4.185
Absorption coefficient (mm^{-1})	24.868
F(000)	9976
Crystal size (mm^3)	0.1 × 0.1 × 0.1
θ range for data collection (°)	1.85–30.04
Limiting indices	$-33 \leq h \leq 32$, $-17 \leq k \leq 17$, $-43 \leq l \leq 43$
Reflections collected	52,622
Independent reflection	13,043 [*R*(int) = 0.0551]
Completeness to $\theta = 30.04$ (%)	99.6
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.801 and 0.226
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	13043/0/582
Goodness-of-fit on F^2	0.995
Final *R* indices [for 9471 rflns. with $I > 2\sigma(I)$]	$R_1 = 0.0496$, $wR_2 = 0.1078$
R indices (all data)	$R_1 = 0.0676$, $wR_2 = 0.1128$
Largest difference peak and hole (e Å^{-3})	7.531 and –2.366

The weighting used is $w = 1/[\sigma^2(F_o^2) + (0.0572P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

(one half) atoms in the anion which contains 9W, 1As, 2Cd, and 35O atoms in the asymmetric unit. The structure of **2** is shown in figure 2. The anion contains a structure with two trivacant lacunary anions, B-$AsW_9O_{34}^{9-}$, linked via a rhomb-like Cd_4O_{14} group leading to a C_{2h} symmetry, sandwich-type complex. The rhomb-like Cd_4O_{14} group is formed by four edge-sharing CdO_6 octahedra. Similar to Keggin-like, sandwich-type polyoxometalates, coordination spheres of cadmiums in the asymmetric unit are different, one fully coordinated with oxygens of B-$AsW_9O_{34}^{9-}$ units and the other one, in addition to oxygen, has H_2O as ligand. The relevant distances and angles for the Cd_4O_{16} unit are summarized in figure 3.

Ammonium cations and lattice waters fill gaps of the polyoxometalates in **1**. Hydrogen-bonding interactions between ammonium cations and oxygens of the polyoxometalates or lattice waters bind the polyoxometalate complexes together in the unit cell. Hydrogen-bond N···O and O···O distances vary from 2.54 to 2.89 Å.

3.3. ^{113}*Cd NMR spectra*

The ^{113}Cd NMR spectrum of **1** in D_2O shows peaks of equal intensity at 60.97 and 17.57 ppm (Supplementary material) corresponding to the two symmetry-equivalent Cd

Table 2. Selected bond lengths and heavy metal distances for **2**.

Bond	Bond length (Å)
W–Oa (av)	2.409
W–Ob(av)	1.917
W–Oc (av)	1.947
W–Od (av)	1.721
W–O(Cd) (av)	1.782
As–O (av)	1.689
As–O(Cd)	1.671
Cd(1)–O(1C)	2.278
Cd(1)–O(4A)	2.438
Cd(1)–O(4C)#1	2.312
Cd(1)–O(6C)	2.248
Cd(1)–O(7C)	2.235
Cd(1)#1–O(9C)	2.286
Cd(2)–O(4A)	2.372
Cd(2)–O(4A)#1	2.377
Cd(2)–O(4C)	2.278
Cd(2)–O(5C)	2.205
Cd(2)–O(8C)#1	2.174
Cd(2)#1–O(9C)	2.263
Cd(1) ··· Cd(1)#1	6.053
Cd(2) ··· Cd(2)#1	3.653
Cd(1) ··· Cd(2)	3.512
Cd(1) ··· Cd(2)#1	3.558

Symmetry transformations used to generate equivalent atoms: #1: $-0.5-x$, $1.5-y$, $-z$.

atoms in the complex. This pattern confirms the structure of the anion in solution is in agreement with the solid state structure. The ^{113}Cd NMR spectrum of **3** shows a peak at 27.1 ppm corresponding to the two symmetry-equivalent Cd atoms. In **1** and **2**, two B-AsW_9O_{27} units are joined by $M_4O_{14}(H_2O)_2$ bridges and there are two types of M^{2+} ions in the $M_4O_{14}(H_2O)_2$ fragment. One type, which consists of two Cd ions, is fully coordinated with oxygen atoms and the other, which also consists of two Cd ions, in addition to oxygen, each has a H_2O coordinated. The ^{113}Cd NMR spectrum of $[P_2W_{20}Cd(H_2O)O_{71}]^{14-}$ [18] which has one H_2O coordinated to Cd^{2+} shows one peak at 14.4 ppm; we assign the peak at 17.57 ppm for **1** to the Cd^{2+} which have H_2O and the peak at 27.1 ppm in the ^{113}Cd NMR spectrum of **3** to H_2O coordinated to Cd^{2+}. Therefore, in **3** the structural H_2O are coordinated to Cd^{2+}. Single crystal structural analysis of $[P_4W_{30}Fe^{III}{}_2Na_2(H_2O)_2O_{112}]^{16-}$ [19] confirms that structural H_2O are coordinated to the larger ions (Na^+).

3.4. *Replacement reaction*

Potassium salt of $[As_2W_{18}Zn_4(H_2O)_2O_{68}]^{10-}$ was examined for replacement of Zn^{2+} ions with Cd^{2+} ions under various conditions. The results show that the complete replacement takes place only under vigorous heating with a ten-fold molar excess of Cd^{2+}. This behavior is similar to metal substitution reactions for the $[WZn_3(H_2O)_3(ZnW_9O_{34}]^{12-}$ and $[WCo_3(H_2O)_3(CoW_9O_{34}]^{12-}$ [20] but is opposite to

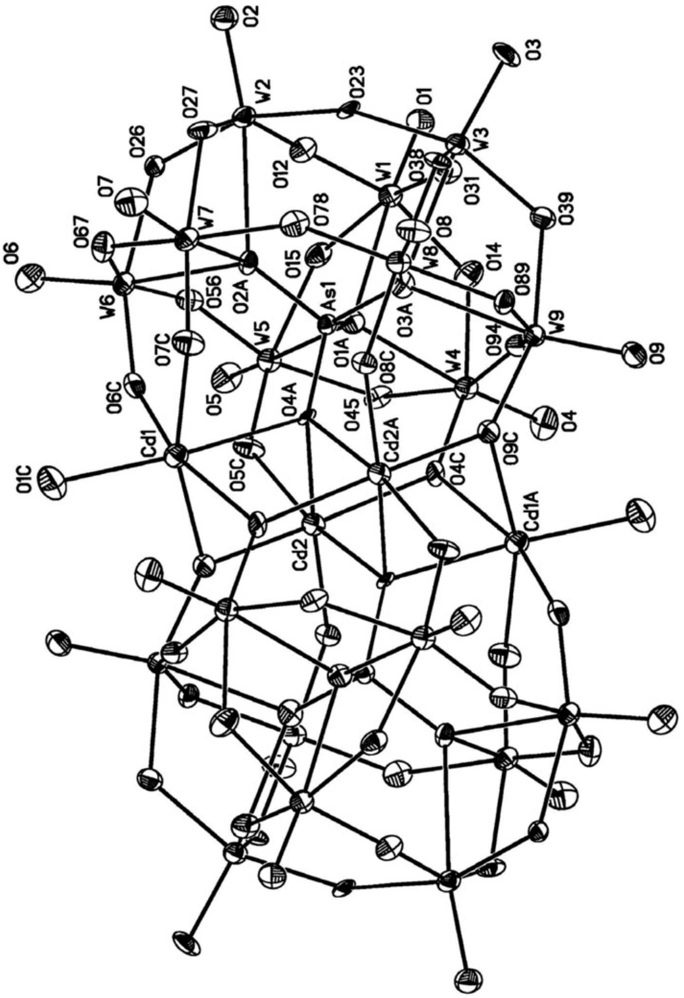

Figure 2. Structure of $[As_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ (**2**) showing 50% probability thermal ellipsoids.

metal substitution reactions for the A-type $[P_2W_{18}M_3(H_2O)_3O_{68}]^{12-}$, M = Co^{2+}, Cu^{2+}, Fe^{2+}, Mn^{2+}, Ni^{2+}, Pd^{2+}, and Zn^{2+} [21], where metal substitution reactions are carried out in moderate (room temperature) conditions. This differentiation in behavior may be attributed to relatively tight and closed arrangement of the sandwich filling metal ions in the former sandwich-type polyoxometalates.

3.5. *Electronic spectroscopy*

The UV-electronic spectra of **1** and **3** exhibit two bands at 195 and 250 nm assigned to W–Od and W–Ob–W transitions, respectively (Od is a terminal oxygen and Ob is a bridging oxygen) [22].

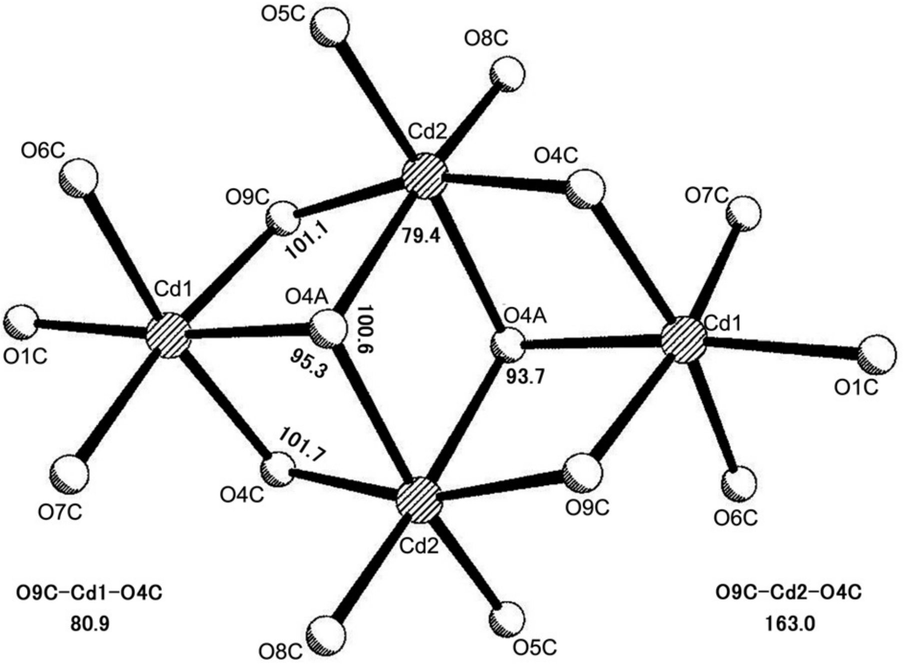

Figure 3. The coordination sphere of the cadmiums in **2**.

4. Conclusion

The complexes $[As_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ and $[As_2W_{18}Zn_2(CdOH_2)_2O_{68}]^{10-}$ were synthesized by the self-assembly reaction and characterized by elemental analysis, IR, Raman, ^{113}Cd NMR spectroscopy, and single crystal structure analysis. The structures consist of two B-$AsW_9O_{34}^{9-}$ trivacant lacunary anions linked via a rhomb-like Cd_4O_{14} group leading to a C_{2h} symmetry, sandwich-type complex. Two or one resonances in ^{113}Cd NMR spectra of $[As_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ and $[As_2W_{18}Zn_2(CdOH_2)_2O_{68}]^{10-}$, respectively, confirm C_{2h} symmetry for both anions in the solution. Replacement of the Cd^{2+} ion with the Zn^{2+} ion in the $[As_2W_{18}Zn_4(H_2O)_2O_{68}]^{10-}$ takes place only under vigorous conditions.

Supplementary material

Crystallographic data (CIF file) for the structural analysis have been deposited with the Fachinformationszentium Karlsruhe (FIZ), CSD-number 420260 ($H_{90}As_2Cd_4N_{10}O_{93}W_{18}$). These data can be obtained free of charge via Email: crysdata@FIZ-Karsruhe.de; Tel.: +49 7247 808 310; Fax: +49 7247 808 136.

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