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Synthesis, single-crystal structural determination and solution characterization of a new sandwich-type cadmium-containing heteropolytungstate

M.H. Alizadeh [a,*], Hossein Razavi [b], F. Mohammadi Zonoz [a], M.R. Mohammadi [a]

[a] *Department of Chemistry, Ferdowsi University, Mashhad, Iran*
[b] *Department of Chemistry, Georgetown University, Washington, DC, USA*

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Abstract

The novel dimeric phosphotungstate, $[P_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$, has been synthesized by an unusual reaction of A-β-$Na_8HPW_9O_{34}$ with cadmium nitrate under controlled pH conditions. This compound has also been synthesized by the reaction of B-α-$Na_8HPW_9O_{34}$ with cadmium nitrate. The unambiguous characterization of B-α-$[P_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ was accomplished by means of elemental analysis, IR, ^{31}P and ^{113}Cd NMR spectroscopy, and confirmed by a single crystal X-ray structural analysis of the NH_4^+ salt. The heteropolyanion consist of two lacunary B-α-$[PW_9O_{34}]^{9-}$ Keggin moieties linked via a rhomboid Cd_4O_{16} group leading to a sandwich-type structure. Acidification of this anion, like other $P_2W_{18}M_4O_{68}^{10-}$ (M = Co, Zn, ...) species, forms the $PW_{12}O_{40}^{3-}$ anions as the main product.

Keywords: Crystal structures; Polyoxometalate; Phosphotungstate; NMR; Heteropolyanion

1. Introduction

The chemistry of polyoxotungstates has been much developed. It holds great potential for catalytic and biomedical applications [1]. In 1973, Weakly et al. [2] established a novel structural class of heteropolyanions. They synthesized the $[P_2W_{18}Co_4(H_2O)_2O_{68}]^{10-}$ anion by the 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 [3] reported the synthesis of the same anion by the reaction of the lacunary trivacant B-$PW_9O_{34}^{9-}$ anion with Co^{2+} ions, obtaining better yields and without any by-products.

After 1981, this category of heteropolyanions, known as 'sandwich-type' or dimeric polytungstates, continued to attract much attention, particularly with respect to the trivacant heteropoly ligands derived from the Keggin structure. At present, several members of the sandwich-type heteropolyanion families, like $[P_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ and $[P_4W_{30}M_4(H_2O)_2O_{112}]^{16-}$ ($M^{2+} = Co^{2+}, Cu^{2+}, Zn^{2+}, \ldots$) have been synthesized [4]. Their chemistry is discussed [5] and, recently, the possibility of preparation of such compounds containing the $[SiW_9O_{34}]^{10-}$ unit were studied. Subsequently the anions $[Si_2W_{18}Zr_3O_{71}H_3]^{11-}$ and $[Si_2W_{18}Sn_3O_{68}]^{14-}$ have been synthesized [6,7].

The first report about cadmium-containing heteropolyanions, related to the mono lacunary anions of the Keggin and Dawson structures (XW_{11} and X_2W_{17}) were made by R. Contant [8]. In 1995, Kirby and Baker [9] reported the first sandwich-type heteropolyanions including Cd^{2+} ions based on the $[P_2W_{15}O_{56}]^{12-}$ defect structure, and later Bi et al. [10] prepared a series of dimeric polytungstates by reacting $[As_2W_{15}O_{56}]^{12-}$ with M^{2+} ions ($M = Cu^{II}, Mn^{II}, Co^{II}, Ni^{II}, Zn^{II}, Cd^{II}$). In this article, we describe the synthesis and crystal structure of a new cadmium-containing heteropolyanion, where two lacunary $PW_9O_{34}^{9-}$ units sandwich the four cadmiums. The chemical characterization of this

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* Corresponding author. Tel.: +98-5118-43-2023; fax: +98-5118-43-8032.
E-mail address: malizadeh@science1.um.ac.ir (M.H. Alizadeh).

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compound was accomplished by means of elemental analysis, IR, ^{31}P and ^{113}Cd NMR spectroscopy.

2. Experimental

2.1. Chemicals and apparatus

All chemicals were reagent grade and used without further purification. The compounds A-β-$Na_8HPW_9O_{34}\cdot 24H_2O$ (abbreviated as A-PW_9) and B-α-$Na_8HPW_9O_{34}\cdot 19H_2O$ (abbreviated as B-PW_9) were prepared as previously described [4]. They were characterized by IR spectroscopy. Infrared spectra were recorded as KBr disks on a Buck 500 scientific spectrometer. All NMR spectra were recorded on a Bruker BRX 500 AVANCE spectrometer. The resonance frequency for the ^{31}P and ^{113}Cd nuclei are 202.46 and 110.92 MHz, respectively. Chemical shifts for ^{31}P and ^{113}Cd NMR spectra were externally referenced relative to 85% H_3PO_4 and 0.1 M cadmium perchlorate, respectively.

2.2. Preparation of the compound

$K_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 16H_2O$ was synthesized as follows: to a stirred solution of 1.08 g (3.5 mmol) of $Cd(NO_3)_2\cdot 4H_2O$ in 40 ml H_2O (pH adjusted to 6 by HOAc) was added 5.0 g (1.75 mmol) of A-PW_9 in small portions. The solution was refluxed for 1 h and then cooled to room temperature (r.t.). Potassium chloride (7.0 g) was added to the solution and the mixture was stirred for 15 min and filtered. This solid was recrystallized from 20 ml of hot water and dried under vacuum. (Yield: 1.9 g, 38%.) Elemental analysis for $K_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 16H_2O$: K, 6.95; P, 1.10; W, 58.84; Cd, 7.99; H_2O, 5.12. Found: K, 6.5; P, 1.02; W, 58.71; Cd, 7.79; H_2O, 4.93%.

In order to prepare crystals containing ammonium cations which are more suitable for crystallographic study, we prepared the ammonium salt of $[P_2W_{18}Cd_4(H_2O)_2O_{68}]^{10-}$ by substituting NH_4Cl for KCl.

2.3. Single-crystal X-ray diffraction analysis

A colorless prismatic single crystal of $(NH_4)_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]$ with dimensions 0.20 × 0.15 × 0.15 mm was used for the X-ray work. $(NH_4)_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 27H_2O$ crystallizes in the monoclinic system (space group $P2_1/n$) with $a = 13.113(2)$ Å, $b = 20.098(4)$ Å, $c = 16.278(3)$ Å, $\beta = 95.917(4)^\circ$ and $Z = 2$. 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). A total of 15 296 independent reflections ($2\theta_{max} = 65.2^\circ$ and $R_{int} = 0.0833$) were recorded, of which 11 355 reflections were considered $[I > 2\sigma(I)]$. The final cycle of refinement converged at $R = 0.0562$ and of $R_w = 0.1329$ $[I > 2\sigma(I)]$.

Crystallographic data and structure refinement parameters are listed in Table 1. The intensities were corrected for Lorentz-polarization effects, and the SADABS program [11] was applied for absorption correction. The structure was refined with SHELXL-97 [12] by full-matrix least-squares on F^2. The weighting scheme was $w = 1/[\sigma^2(F_0^2) + (0.0860P)^2]$ where $P = (F_0^2 + 2F_c^2)/3$. Bond lengths and bond angles of $(NH_4)_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]$ are given in Table 2.

3. Result and discussion

3.1. Synthesis

There are two main isomers for $PW_9O_{34}^{9-}$ anions. These isomers (A-PW_9 and B-PW_9) have been formed

Table 1
Crystal data and structure refinement of $(NH_4)_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 27H_2O$

Empirical formula	$H_{98}Cd_4N_{10}O_{97}P_2W_{18}$
Formula weight	5611.72
Temperature (K)	140(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	13.113(2)
b (Å)	20.098(4)
c (Å)	16.278(3)
α (°)	90
β (°)	95.917(4)
γ (°)	90
Volume (Å^3)	4267.3
Z	2
D_{calc} (Mg m^{-3})	4.367
Absorption coefficient (mm^{-1})	25.297
$F(000)$	4996
Crystal size (mm)	0.20 × 0.15 × 0.15
θ Range for data collection (°)	1.86–32.60
Index range	$-19 \le h \le 19$, $-30 \le k \le 29$, $-23 \le l \le 24$
Reflections collected	87 006
Independent reflections	15 296 ($R_{int} = 0.0833$)
Completeness to $\theta = 32.60^\circ$ (%)	98.3
Max/min transmission	0.789, 0.214
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	15 296/0/592
Goodness-of-fit on F^2	1.019
Final R indices for 11 355 reflections with $[I > 2\sigma(I)]$	$R_1 = 0.0562$, $wR_2 = 0.1329$
R indices (all data)	$R_1 = 0.0716$, $wR_2 = 0.1402$
Largest difference peak and hole (e Å^{-3})	5.221 and −5.330

Table 2
Selected bond distances (Å) and angles (°) in $(NH_4)_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 27H_2O$

Bond lengths			
W(1)–O(1)	1.704(7)	W(6)–O(6)	1.723(8)
W(1)–O(15)	1.872(4)	W(6)–O(6C)	1.782(7)
W(1)–O(12)	1.881(7)	W(6)–O(56)	1.918(8)
W(1)–O(14)	1.894(7)	W(6)–O(67)	1.954(7)
W(1)–O(13)	1.901(8)	W(6)–O(26)	2.022(8)
W(2)–O(2)	1.711(8)	W(6)–O(2P)	2.393(7)
W(2)–O(26)	1.840(8)	W(7)–O(7)	1.725(8)
W(2)–O(27)	1.848(7)	W(7)–O(7C)	1.767(8)
W(2)–O(12)	1.932(7)	W(7)–O(67)	1.903(7)
W(2)–O(23)	1.939(8)	W(7)–O(78)	1.949(7)
W(3)–O(3)	1.704(9)	W(7)–O(27)	2.044(7)
W(3)–O(38)	1.880(7)	W(7)–O(2P)	2.439(7)
W(3)–O(23)	1.892(8)	W(8)–O(8)	1.719(7)
W(3)–O(39)	1.893(7)	W(8)–O(8C)	1.773(7)
W(3)–O(13)	1.928(7)	W(8)–O(78)	1.874(7)
W(4)–O(4)	1.712(8)	W(8)–O(89)	1.967(7)
W(4)–O(4C)	1.814(7)	W(8)–O(38)	2.016(7)
W(4)–O(49)	1.900(7)	W(8)–O(3P)	2.433(7)
W(4)–O(45)	1.921(7)	W(9)–O(9)	1.718(8)
W(4)–O(14)	1.986(7)	W(9)–O(9C)	1.824(7)
W(4)–O(1P)	2.409(7)	W(9)–O(89)	1.905(7)
W(5)–O(5)	1.719(8)	W(9)–O(49)	1.930(7)
W(5)–O(2C)#1	1.768(7)	W(9)–O(39)	2.012(7)
W(5)–O(56)	1.905(8)	W(9)–O(3P)	2.435(7)
W(5)–O(45)	1.936(7)	Cd(1)–O(6C)	2.209(7)
W(5)–O(15)	2.024(7)	Cd(1)–O(7C)	2.210(8)
W(5)–O(1P)	2.467(7)	Cd(1)–O(9C)#1	2.269(8)
Cd(1)–O(4C)#1	2.270(7)	Cd(2)–Cd(1)#1	3.4665(11)
Cd(1)–O(1C)	2.309(8)	P(1)–O(3P)	1.524(7)
Cd(1)–O(4P)	2.489(7)	P(1)–O(1P)	1.532(7)
Cd(1)–Cd(2)#1	3.4665(11)	P(1)–O(2P)	1.546(7)
Cd(2)–O(8C)	2.191(8)	P(1)–O(4P)	1.550(7)
Cd(2)–O(2C)	2.205(8)	O(2C)–W(5)#1	1.768(7)
Cd(2)–O(9C)	2.220(8)	O(4P)–Cd(2)#1	2.341(7)
Cd(2)–O(4C)#1	2.262(7)	O(4C)–Cd(2)#1	2.262(7)
Cd(2)–O(4P)#1	2.341(7)	O(4C)–Cd(1)#1	2.270(7)
Cd(2)–O(4P)	2.414(6)	O(9C)–Cd(1)#1	2.269(8)
Bond angles			
O(6C)–Cd(1)–O(7C)	94.6(3)	O(9C)#1–Cd(1)–Cd(2)#1	38.93(19)
O(6C)–Cd(1)–O(9C)#1	88.3(3)	O(4C)#1–Cd(1)–Cd(2)#1	84.04(18)
O(7C)–Cd(1)–O(9C)#1	164.4(3)	O(1C)–Cd(1)–Cd(2)#1	142.5(2)
O(6C)–Cd(1)–O(4C)#1	162.5(3)	O(4P)–Cd(1)–Cd(2)#1	42.47(15)
O(7C)–Cd(1)–O(4C)#1	91.5(3)	O(8C)–Cd(2)–O(2C)	98.4(3)
O(9C)#1–Cd(1)–O(4C)#1	81.6(3)	O(8C)–Cd(2)–O(9C)	96.8(3)
O(6C)–Cd(1)–O(1C)	92.5(3)	O(2C)–Cd(2)–O(9C)	95.7(3)
O(7C)–Cd(1)–O(1C)	90.1(3)	O(8C)–Cd(2)–O(4C)#1	90.2(3)
O(9C)#1–Cd(1)–O(1C)	105.1(3)	O(2C)–Cd(2)–O(4C)#1	94.9(3)
O(4C)#1–Cd(1)–O(1C)	103.9(3)	O(9C)–Cd(2)–O(4C)#1	166.3(3)
O(6C)–Cd(1)–O(4P)	81.4(3)	O(8C)–Cd(2)–O(4P)#1	169.1(3)
O(7C)–Cd(1)–O(4P)	84.2(3)	O(2C)–Cd(2)–O(4P)#1	91.9(3)
O(9C)#1–Cd(1)–O(4P)	81.0(2)	O(9C)–Cd(2)–O(4P)#1	85.4(3)
O(4C)#1–Cd(1)–O(4P)	82.9(2)	O(4C)–Cd(2)–O(4P)#1	85.6(3)
O(1C)–Cd(1)–O(4P)	171.3(3)	O(8C)–Cd(2)–O(4P)	84.3(2)
O(6C)–Cd(1)–Cd(2)#1	79.2(2)	O(2C)–Cd(2)–O(4P)	177.3(3)
O(7C)–Cd(1)–Cd(2)#1	126.7(2)	O(9C)–Cd(2)–O(4P)	84.2(3)
O(4C)#1–Cd(2)–O(4P)	84.8(2)	P(1)–O(4P)–Cd(1)	123.8(4)
O(4P)#1–Cd(2)–O(4P)	85.3(2)	Cd(2)#1–O(4P)–Cd(1)	91.7(2)
O(8C)–Cd(2)–Cd(1)#1	136.69(19)	Cd(2)–O(4P)–Cd(1)	90.8(2)
O(2C)–Cd(2)–Cd(1)#1	90.7(2)	W(4)–O(4C)–Cd(2)#1	132.3(4)
O(9C)–Cd(2)–Cd(1)#1	40.0(2)	W(4)–O(4C)–Cd(1)#1	123.9(4)
O(4C)#1–Cd(2)–Cd(1)#1	131.30(18)	Cd(2)#1–O(4C)–Cd(1)#1	100.8(4)
O(4P)#1–Cd(2)–Cd(1)#1	45.87(17)	W(6)–O(6C)–Cd(1)	136.1(4)

Table 2 (*Continued*)

Bond lengths			
O(4P)–Cd(2)–Cd(1)#1	87.44(17)	W(7)–O(7C)–Cd(1)	134.1(4)
W(5)#1–O(2C)–Cd(2)	131.9(4)	W(8)–O(8C)–Cd(2)	135.1(4)
P(1)–O(4P)–Cd(2)#1	123.0(4)	W(9)–O(9C)–Cd(2)	131.2(4)
P(1)–O(4P)–Cd(2)	123.8(4)	W(9)–O(9C)–Cd(1)#1	125.7(4)
Cd(2)#1–O(4P)–Cd(2)	94.7(2)	Cd(2)–O(9C)–Cd(1)#1	101.1(3)

Symmetry transformations used to generate equivalent atoms: #1 $-X+1$, $-Y$, $-Z+2$.

from the Keggin structure [4]. The A-PW_9 ligand reacts with divalent Mn, Fe, Ni, Co, Cu, Zn and Pd to give the series of anions $[P_2W_{18}M_3(H_2O)_3O_{68}]^{12-}$ (abbreviated as $P_2W_{18}M_3$), while the reaction of these cations with B-PW_9, produced $[P_2W_{18}M_4(H_2O)_2O_{68}]^{10-}$ (abbreviated as $P_2W_{18}M_4$) species [13].

The chemistry of A-PW_9 and B-PW_9 isomers has been investigated [4,14]. It has been established that the B-PW_9 isomer is formed from the deformation of A-PW_9 by a thermal process. This anion (B-PW_9) is unstable in aqueous solution and converts to the thermodynamically more stable A-PW_9, unless it is reacted with a transition metal cation. There are large numbers of equilibria among several different species in the solutions of polyoxometalates. The factors that affect these equilibria are mainly pH, temperature and the concentration of reagents. The solution pH is a very important factor, since at lower pH the predominant polyoxometalates species is the $[PW_{11}O_{39}]^{7-}$ anion, while at higher pH the polyoxometalates hydrolyzes. The common method for preparation of $P_2W_{18}M_4$ species are based on the reaction of the M^{2+} cation with the B-PW_9 isomer in aqueous solution (pH 7.0–8.0). Due to the hydrolysis of Cd^{2+} ions in this pH, this procedure seems not to be suitable for the preparation of the $P_2W_{18}Cd_4$ compound. The problem above can be solved by adjusting the pH using some sort of buffer solution (pH 6.0).

B-PW_9 was added to a Cd^{2+} solution and stirred for 15 min at r.t. A mixture of heteropoly anions was formed including $P_2W_{18}Cd_4$ at a very low yield. By increasing the reaction time, the yield of $P_2W_{18}Cd_4$ was improved. Raising the temperature and refluxing the mixture further enhanced the yield, even at shorter reaction times. The report by Knoth et al. [15] that $P_2W_{18}M_3$ was converted to $P_2W_{18}M_4$ in solution at temperatures above 100 °C led us to examine the possibility of synthesizing $P_2W_{18}Cd_4$ using the A-PW_9 anion. When the reaction of A-PW_9 and Cd^{2+} was carried out at room temperature, the main product was $[PW_{11}Cd(H_2O)O_{39}]^{5-}$, established by IR and elemental analysis. This compound was the main product after increasing the temperature to 75 °C. However, after the reaction mixture was refluxed for 1 h, $P_2W_{18}Cd_4$ was obtained. No appreciable change in yield was observed by refluxing for a longer time. The $P_2W_{18}Cd_4$ anion is unstable in acidic media. The behavior of this compound is similar to the other $P_2W_{18}M_4$ anions. When $P_2W_{18}M_4$ salts are passed through a strongly acidic ion-exchange column, the PW_{12} anion forms as the main product [13]. We observed that when solutions of $P_2W_{18}Cd_4$ were passed through a strongly acidic ion-exchange column (or were kept under acidic conditions with $pH < 1$), the main product was the PW_{12} anion. This similarity was an indirect indication that a Keggin-like structure is the skeletal framework of the tetra cadmium dimer ($P_2W_{18}Cd_4$).

3.2. X-ray single-crystal structure analysis of the NH_4^+ salt

The structure of $P_2W_{18}Cd_4(H_2O)_2O_{68}^{10-}$ is shown in Fig. 1. The anion contains two B-α-PW_9O_{34} ligands linked via a Cd_4O_{16} unit, formed by four edge-sharing CdO_6 octahedra. The structure of this compound is similar to that of $P_2W_{18}M_4$ which has already been reported for M = Mn, Co, Ni, Cu and Zn [16]. The relevant distances and angles for the Cd_4O_{16} unit are summarized in Fig. 2.

The comparison of the average bond lengths for some isostructural compounds are listed in Table 3. The X–O and M–O distances increase, as the size of the M atom increases. Other bond lengths do not show any significant differences.

3.3. Vibration spectroscopy

The vibrational spectra of the polyanions are relatively sensitive to structural modifications. The infrared spectrum of $P_2W_{18}Cd_4$ (Fig. 3) is very similar to $P_2W_{18}M_4$ and PW_{12} anions. The PW_{12} anion, having tetrahedral symmetry, gives four prominent bands: P–O, W–O (terminal), W–O–W (corner-sharing octahedra), and W–O–W (edge-sharing octahedra) at 1080, 985, 887 and 807(br) cm^{-1}, respectively [17]. The asymmetric phosphate stretch in PW_{12} is triply degenerate, so that lowering the symmetry moves the degeneracy and results in band splitting [13]. However, as shown in Fig. 3, the IR spectrum of $P_2W_{18}Cd_4$ shows a single band at about 1030 cm^{-1} which is near the position of the P–O band in the IR spectrum of PW_{12}. This similarity indicates that the tetrahedral symmetry

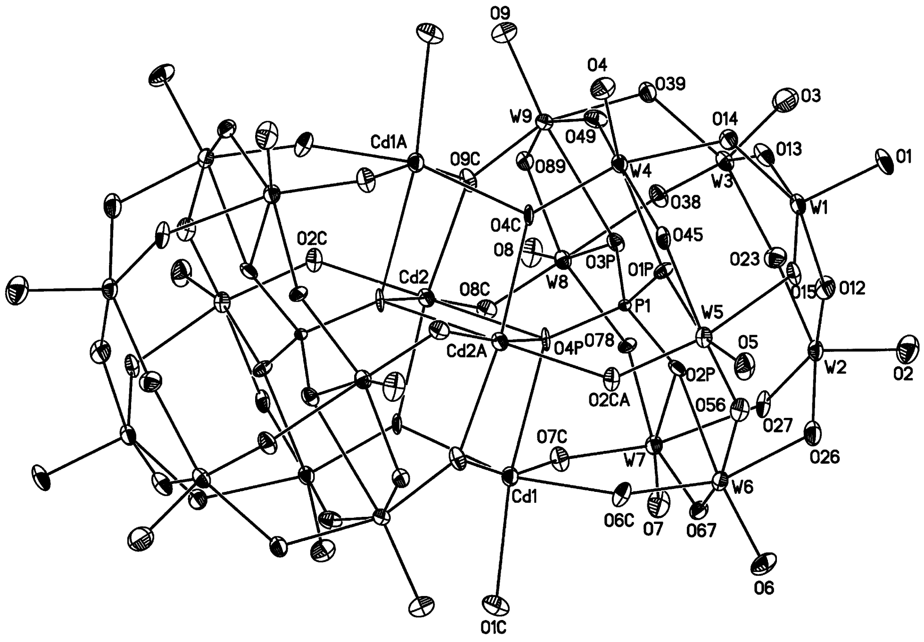

Fig. 1. Structure of $(NH_4)_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 27H_2O$.

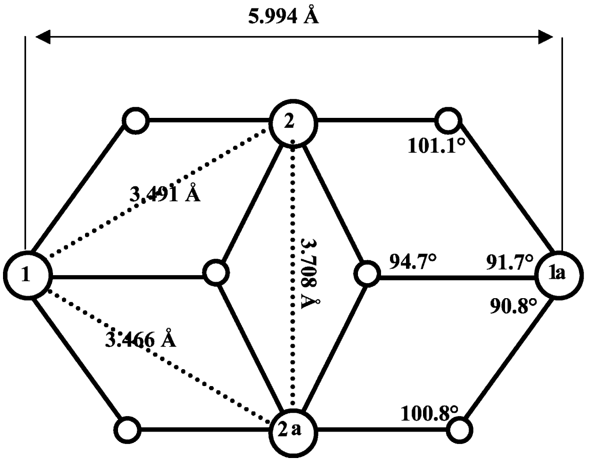

Fig. 2. Relevant distances (Å) and angles (°) for the Cd_4O_{16} unit of $(NH_4)_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 27H_2O$.

Table 3
Mean bond lengths (Å) in $[P_2W_{18}M_4(H_2O)_2O_{68}]^{10}$

X, M	P, Cd	P, Co [a]
X–O	1.85	1.58
M–O	2.28	2.09
W(1)–O	1.85	1.98
W(2,3)–O	1.86	1.96
W(4,5)–O	1.96	1.97
W(6,7)–O	1.97	1.96
W(8,9)–O	1.97	1.97
All W–O	1.935	1.968

[a] Ref. [19].

or pseudo tetrahedral symmetry of the phosphate group is retained. The IR spectrum also indicates that the $P_2W_{18}Cd_4$ is structurally similar to $P_2W_{18}M_4$ compounds [4].

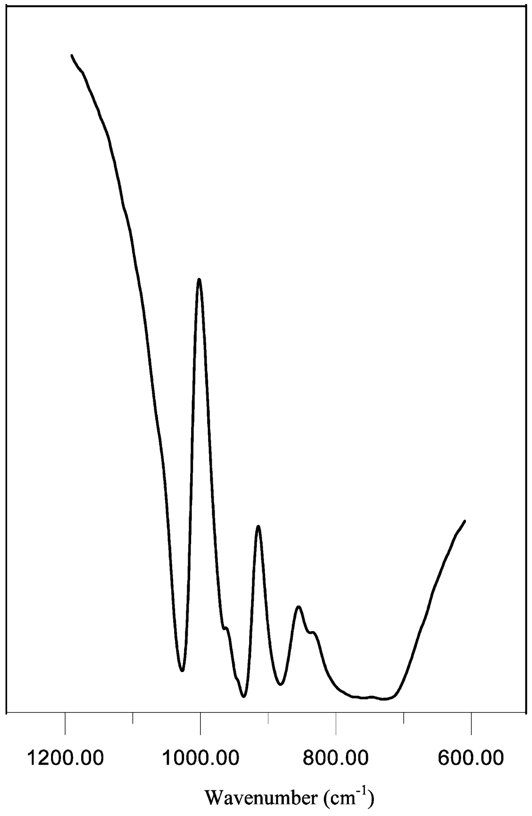

Fig. 3. IR spectrum of $K_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 16H_2O$.

3.4. ^{31}P NMR spectroscopy

The ^{31}P NMR spectrum of the $P_2W_{18}Cd_4$ anion exhibits a single line at −2.37 ppm upfield from the

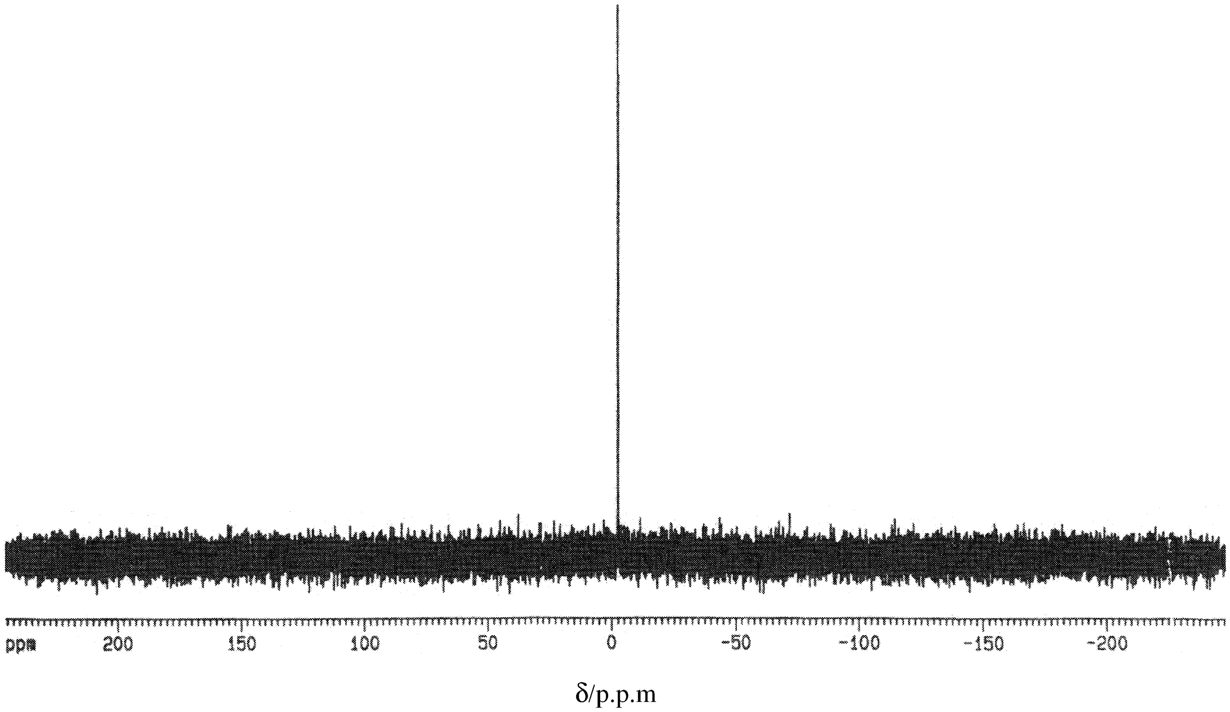

Fig. 4. ^{31}P NMR spectrum of $K_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 16H_2O$.

external standard, i.e. 85% H_3PO_4 (Fig. 4), indicating that the dimeric complex contains only one type of phosphorus. Also, this pattern indicates that a single product with high purity is obtained under the reaction conditions. This band is assigned to the central PO_4 unit of the polyoxotungstate [18]. The nuclei of ^{111}Cd and ^{113}Cd are NMR-active and it might be expected that $^2J_{Cd\text{-}p}$ would be observed, but Kirby and Baker [9] explained that this expectation is not correct and only a small broadening can be observed. The ^{31}P NMR spectrum of $P_2W_{18}Cd_4$ also indicates small broadening near the baseline.

3.5. ^{113}Cd NMR spectroscopy

The ^{113}Cd NMR spectrum of $P_2W_{18}Cd_4$ shows two broad peaks with about equal intensities at 26.25 and 52.76 ppm downfield from the external standard, i.e. 0.1 M cadmium perchlorate (Fig. 5). This pattern confirms that the sandwich complex contains two type of cadmium, which is in agreement with the structural analysis. In the $P_2W_{18}M_4$ anions, two B-PW_9O_{27} units are joined by $M_4O_{14}(H_2O)_2$ bridges and there are two types of M^{2+} ion in the $M_4O_{14}(H_2O)_2$ fragment. One type, that consists of two Cd ions, is fully coordinated

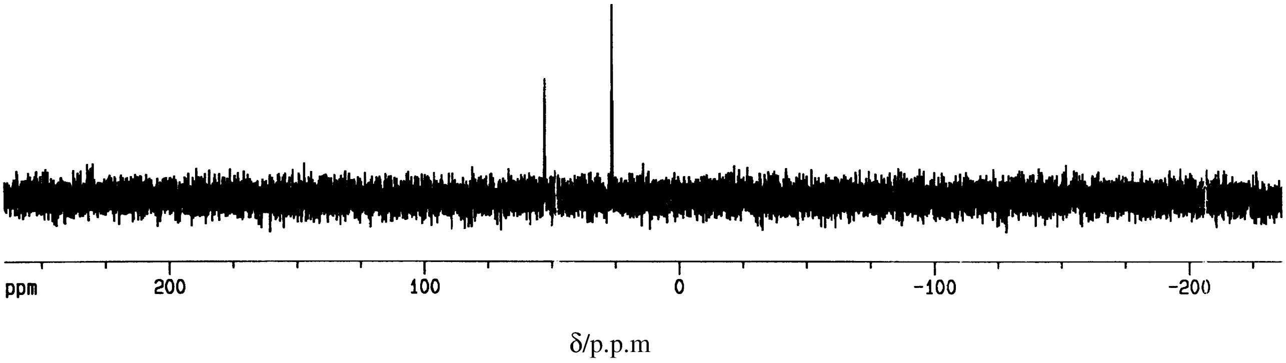

Fig. 5. ^{113}Cd NMR spectrum of $K_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 16H_2O$.

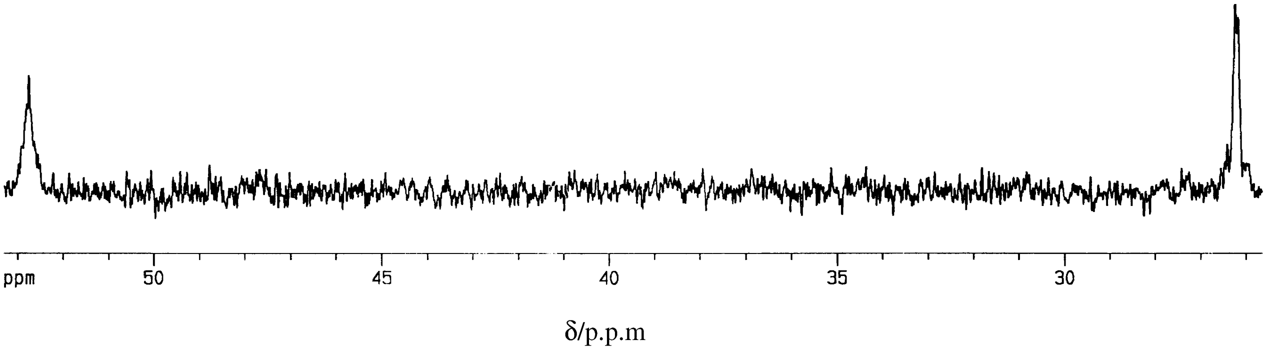

Fig. 6. Expanded ^{113}Cd NMR spectrum of $K_{10}[P_2W_{18}Cd_4(H_2O)_2O_{68}]\cdot 16H_2O$.

by oxygen atoms and the other, in addition to oxygen, has H_2O molecules as ligands. The peak broadening and its multiplicity (Fig. 6) can be explained by the effect of indirect spin–spin coupling of Cd species with ^{31}P and ^{113}Cd nuclei through Cd–O–P and Cd–O–Cd bonds.

4. Conclusion

A new type of polyoxometalate anion that sandwiches four Cd^{2+} ions between two trivacant lacunary derivatives of the Keggin tungstophosphate anion has been prepared in approximately 38% yield from A-PW_9 in buffered solution. The anion is stable in aqueous solution confirmed by ^{31}P and ^{113}Cd NMR, and incorporates a novel Cd_4 heteroatom cluster of C_{2h} symmetry. Preliminary experiments suggest that other heteroatoms like Si^{4+} can form analogous complexes.

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, CCDC No. 412580. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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