Polyoxometalate−Diphosphate Complexes. 4.[1] Structure of $Na_4[(O_3PCHN(CH_3)_2PO_3)W_2O_6]\cdot 11H_2O$

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Introduction

We are currently investigating heteropolyanion complexes with diphosphate species as hetero groups in order to understand the reactivity of biological oligophosphates and esters (*e.g.* $P_2O_7^{4-}$, ADP) with polyoxomolybdates and polyoxotungstates. Since it is known that molybdate promotes the hydrolysis of biological oligophosphates and esters,[2] complexes of the hydrolytically-stable pyrophosphate analog methylenediphosphonate ($O_3PCH_2PO_3^{4-}$), are also of interest. We have already characterized three structural families of diphosphate complexes of polyoxotungstates and polyoxomolybdates. The metal:heterogroup ratios are 3:1 in $[(O_3PXPO_3)_4W_{12}O_{36}]^{16-}$,[3] 6:1 in $[(O_3PXPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ (X = O, CH_2),[4] and 18:1 in $[(O_3POPO_3)Mo_{18}O_{54}]^{4-}$.[5]

In the course of exploring possible analogues of these complexes, we have isolated a novel linear polymeric anion $([(O_3PCHN(CH_3)_2PO_3)W_2O_6]^{4-})_\infty$ which incorporates the hetero group (dimethylamino)methylenediphosphonate.

Experimental Section

(Dimethylamino)methylenediphosphonic acid ($H_2O_3PCHN(CH_3)_2PO_3H_2$) was synthesized using a published procedure.[6] The purity was checked by ^{31}P and ^1H NMR spectroscopy. An aqueous solution, which was 0.07 *M* in $H_2O_3PCHN(CH_3)_2PO_3H_2$ and 0.42 *M* in Na_2WO_4 at pH 6, after standing at room temperature for *ca.* 2 months, yielded colorless crystals of the title compound. Upon stirring and heating, the crystals redissolved in water.

Crystal data and structure refinement data for $Na_4[(O_3PCHN(CH_3)_2PO_3)W_2O_6]\cdot 11H_2O$ are summarized in Tables 1 and S1 (supporting information), respectively. The X-ray structure determination was performed using a Siemens P4/RA diffractometer with graphite-monochromated Mo Kα radiation. Three check reflections measured every 100 scans indicated that the chosen crystal did not decompose during data collection. The structure was solved by direct methods and refined by full-matrix least-squares analysis with the SHELX-93 package (G. M. Sheldrick), the minimized function being $\sum w(|F_o| - |F_c|)^2$. The weighting scheme employed was $w = 1/[\sigma^2(F_o^2) + (0.1088P)^2 + 26.88P]$ where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$. An absorption correction (SHELXA) was applied. Thermal vibrations were treated anisotropically for the W atoms only. The atomic coordinates are reported in Table 2, and ranges of bond lengths and angles, in Table 3. A complete tabulation of bond lengths and angles is available as supporting information (Table S3).

Discussion

The structure of $([(O_3PCHN(CH_3)_2PO_3)W_2O_6]^{4-})_\infty$ represents a novel polymeric heteropolyanion of tungsten. It is composed of negatively-charged chains where $[(O_3PCHN(CH_3)_2PO_3)W_2O_6]^{4-}$ (**I**) is the repeat unit. **I** comprises two corner-shared WO_6 octahedra and one (dimethylamino)methylenediphosphonate (MAMDP) hetero group (see Figure 1). Since the two W−O bonds which are trans to terminal oxygens are

Table 1. Crystallographic Data for $Na_4[(O_3PCHN(CH_3)_2PO_3)W_2O_6]\cdot 11H_2O$

$Na_4P_2NC_3W_2O_{23}H_{29}$	fw 968.8
$a = 10.113(2)$ Å	space group $P2_1/c$ (No.14)
$b = 18.136(7)$ Å	$T = 173$ K
$c = 13.739(1)$ Å	$\lambda = 0.710\,73$ Å
$\beta = 92.47(1)°$	$\varrho_{calcd} = 2.479$ g cm^{-3}
$V = 2517.5(11)$ Å^3	$\mu = 9.420$ mm^{-1}
$Z = 4$	R1 = 0.0664, wR2 = 0.1677[a]

[a] R indices [$I > 2\sigma(I)$]: $\sum w(|F_o| - |F_c|)^2$, where $w = 1/[\sigma^2(F_o2) + (0.1088P)^2 + 26.88P]$ and $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for $Na_4[(O_3PCHN(CH_3)_2PO_3)W_2O_6]\cdot 11H_2O$

atom	*x*	*y*	*z*	*U*(eq)[a]
W1	144(1)	1820(1)	8964(1)	4(1)
W2	71(1)	2002(1)	6222(1)	5(1)
P1	−1600(4)	3157(2)	7700(3)	6(1)
P2	1440(4)	3267(2)	7785(3)	7(1)
O1A	−11(11)	2325(6)	10157(7)	9(2)
O1B	1431(11)	2738(6)	8659(7)	8(2)
O1C	−1412(11)	2635(6)	8562(7)	6(2)
O1D	1617(11)	1312(6)	9250(7)	7(2)
O1E	121(10)	1691(6)	7576(6)	1(2)
O1F	−1054(11)	1153(6)	9148(7)	8(2)
O1P	−2840(11)	3614(6)	7740(7)	9(2)
O2A	1370(11)	2852(6)	6808(7)	7(2)
O2B	1467(12)	1495(6)	5914(8)	13(2)
O2C	−1228(12)	1409(6)	5846(7)	11(2)
O2D	−1473(11)	2773(6)	6730(7)	5(2)
O2P	2525(12)	3813(6)	7853(8)	12(2)
N1	−164(17)	4473(10)	7457(11)	29(4)
C1	−154(22)	3769(12)	7934(15)	30(5)
C2	−406(23)	4398(12)	6320(15)	30(5)
C3	−1176(20)	5016(11)	7758(13)	23(4)
Na1[b]	5000	5000	5000	13(2)
Na2	3617(7)	4788(4)	7057(4)	13(1)
Na3[b]	5000	5000	1000	11(2)
Na4	5013(7)	7012(4)	9996(5)	14(1)
Na5	6755(13)	6313(7)	7404(8)	68(3)
O1W	4926(13)	5363(7)	8317(8)	17(3)
O2W	7338(13)	5142(7)	4594(8)	18(3)
O3W	4570(13)	5960(7)	6112(8)	15(3)
O4W	4108(13)	6862(7)	8327(9)	20(3)
O5W	3244(12)	7861(6)	10092(8)	14(2)
O6W	5100(13)	7165(7)	11801(8)	17(3)
O7W	3422(12)	5982(6)	10314(8)	13(2)
O8W	6472(12)	7956(7)	9476(8)	15(3)
O9W	6540(12)	5989(6)	10229(8)	12(2)
O10W	5257(12)	4087(7)	6296(8)	14(3)
O11W	1882(13)	5508(7)	7605(8)	16(3)

[a] Isotropic displacement parameters. The tungsten atoms were refined anisotropically (see Table S2, supporting information). [b] Occupancy 0.5.

Table 3. Ranges of Bond Lengths (Å) and Angles (deg) in $Na_4[(O_3PCHN(CH_3)_2PO_3)W_2O_6]\cdot 11H_2O$

$W-O_{terminal}$	1.742−1.780(13[a])
$W-O_{doubly\ bridging}$(cis to terminal O)	1.886−1.943(10)
$W-O_{doubly\ bridging}$(trans to terminal O)	2.159−2.230(12)
$P-O_{terminal}$	1.482−1.509(13)
$P-O_{doubly\ bridging}$	1.514−1.539(11)
P−C	1.852−1.859(25)
N−CH	1.434(29)
$N-CH_3$	1.508−1.580(28)
W−O−W	156.0−167.0(7)
P−C−P	111.9(12)

[a] Averages of the individual esd's.

(1) Part 1: see ref 3. Part 2: see ref 5. Part 3: see ref 4.
(2) Weil-Malherbe, H.; Green, R. H. *Biochem. J.* **1951**, *49*, 286.
(3) Kortz, U.; Jameson, G. B.; Pope, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 2659.
(4) Kortz, U.; Pope, M. T. *Inorg. Chem.* **1995**, *34*, 2160.
(5) Kortz, U.; Pope, M. T. *Inorg. Chem.* **1994**, *33*, 5643.
(6) Bollinger, J. E.; Roundhill, D. M. *Inorg. Chem.* **1993**, *32*, 2821.

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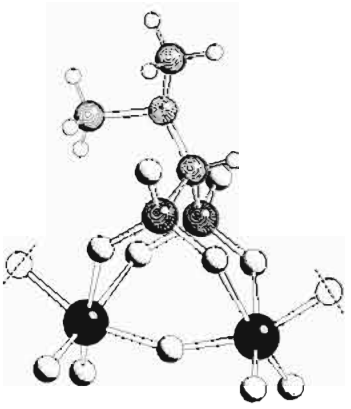

Figure 1. Ball and stick representation of the structure of $[(O_3PCHN(CH_3)_2PO_3)W_2O_6]^{4-}$ (**I**). The two oxygen atoms which are shared with W atoms of the adjacent repeat units are shown as open circles split by broken lines. The positions of the H atoms were calculated.

long (2.159−2.230(12) Å), **I** may be viewed as two corner-linked WO_4 tetrahedra[7] which are bridged by MAMDP. In the polymer, the monomeric units are linked to give an undulating chain in which the hetero groups alternate up and down (see Figure 2). Interestingly the dimethylamino groups of all MAMDP's in a chain point in the same direction (in neighboring chains they point the other way). In each chain, the tungsten atoms and their bridging oxygens can be viewed as the planar backbone describing a sine wave.

The anionic chains are parallel to each other, and they are separated by a network of Na^+ ions and water molecules. The sodium cations are bound to oxygens of the anion and to water molecules (see Figure 3). All Na^+ ions except Na5 are coordinated to six oxygens quasi-octahedrally ($Na_{six\text{-}coord}$···O, 2.340−2.692(14) Å). All of them belong to water molecules except the terminal phosphonate oxygen O2P, which belongs to the anion. The $NaO_x(H_2O)_{6-x}$ ($x = 0, 1$) octahedra are linked by sharing corners, edges, and faces. Na5 is only four-coordinated (distorted planar) to two water molecules and two oxygens (O1D, O2B) which are terminal oxygens of the two tungsten atoms in **I** ($Na_{four\text{-}coord}$···O, 2.851−2.880(19) Å).

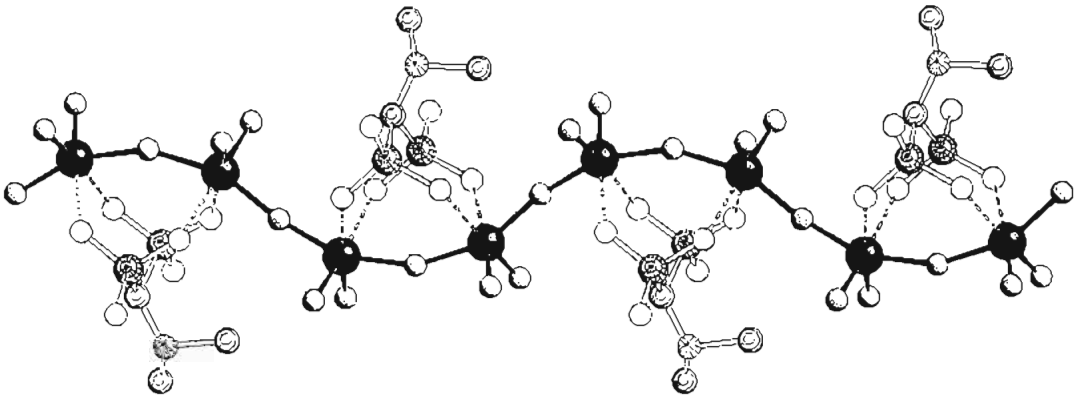

Figure 2. Structure of the polymeric anion $([(O_3PCHN(CH_3)_2PO_3)W_2O_6]^{4-})_\infty$ represented as an adduct of chains of corner-linked WO_4 tetrahedra. The four shortest bonds of each metal atom are emphasized, and the two long bonds are indicated by broken lines. Oxygen atoms of the hetero groups are not shaded, and the H atoms are omitted for clarity.

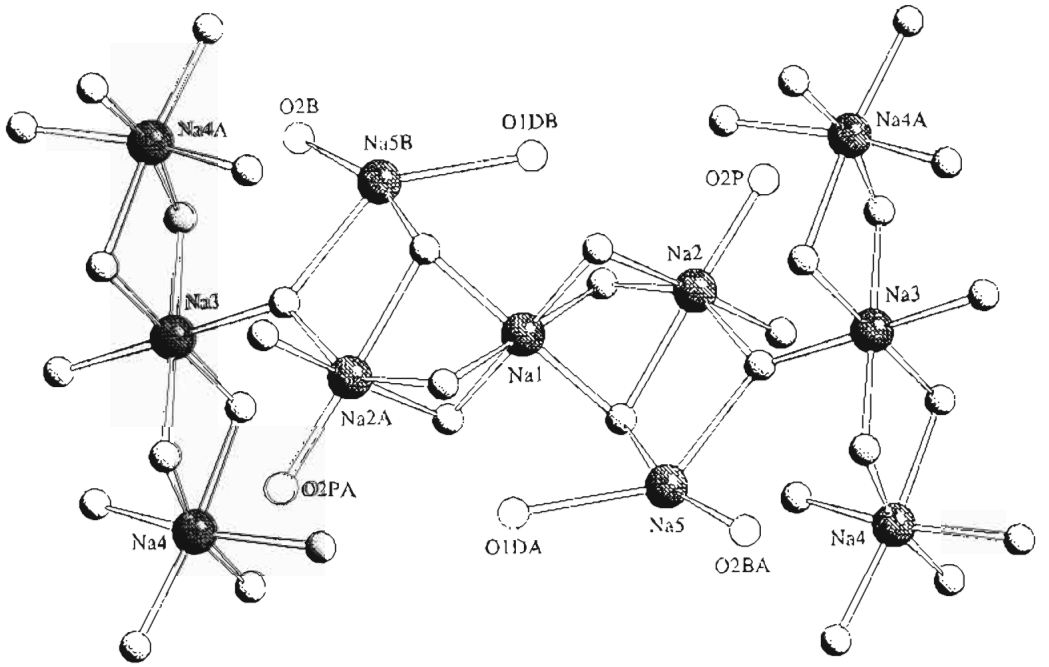

Figure 3. Network of Na^+ ions and water molecules in $Na_4[(O_3PCHN(CH_3)_2PO_3)W_2O_6]\cdot 11H_2O$. The small shaded circles represent water molecules, and the open circles represent oxygen atoms of the anion. O2B and O1DB are the terminal oxygens of two W atoms in a repeat unit, and O2P is a terminal oxygen of the hetero group in the adjacent repeat unit in the same anionic chain. The same applies for O1DA, O2BA, and O2PA, but they belong to a different chain. The positions of Na1 and Na3 have occupancy 0.5.

Therefore the anionic polymeric chain is linked to the cationic framework only through Na5 and Na2.

Acknowledgment. We thank the NSF for support of this work through Grants CHE-9115394 (assistance in purchase of diffractometer) and CHE-9215228. Figures 1−3 were generated by Schakal 92 (copyright Egbert Keller, University of Freiburg).

(7) Day, V. W.; Fredrich, M. F.; Klemperer, W. G.; Shum, W. *J. Am. Chem. Soc.* **1977**, *99*, 952.

Supporting Information Available: Tables of crystal and structural refinement data, anisotropic displacement parameters, and bond lengths and angles (5 pages). Ordering information is given on any current masthead page.

IC9501071

Additions and Corrections

1995, Volume 34

Weiping Shao, Hongzhe Sun, Yiming Yao, and Wenxia Tang*: ^{1}H NMR Studies of the Imidazole Complex of Cytochrome *c*: Resonance Assignment and Structural Characterization of the Heme Cavity.

Page 685. In Table 2, the minus signs of chemical shifts for some δ_2H_3 and δ_1H_3 values were inadvertently omitted and should be added as follows: Leu35 δ_2H_3 −0.30 ppm, Leu64 δ_2H_3 −0.43 ppm, Leu68 δ_2H_3 −1.30 ppm, Leu98 δ_2H_3 −0.32 ppm, Leu64 δ_1H_3 −0.36 ppm, Leu68 δ_1H_3 −0.35 ppm. The value given for Leu94 δ_2H_3 (0.70 ppm) was erroneous and should be corrected to 0.07 ppm.

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