Inorg. Chem. **2001,** *40,* 5307−5310

Complexation of a Heptanuclear Polyoxotantalate Anion with K^+: Formation of a Supramolecular $[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]^{6+}$ Ring Structure[†]

Bernd Morgenstern, Jürgen Sander, Volker Huch, and Kaspar Hegetschweiler[*]

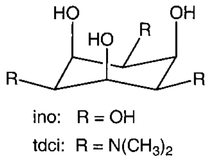
Anorganische Chemie, Universität des Saarlandes,
Postfach 15 11 50, D-66041 Saarbrücken, Germany

Received September 22, 2000

Introduction

Polyoxometalates (POMs) have attracted considerable attention over the past few years, as a consequence of their interesting structural properties[1] and their importance in catalysis and in medicine.[2,3] Interactions of POMs with proteins could play an important role in biological processes such as HIV-1 protease inhibition.[4] Host−guest interactions, and in particular the role of small ionic guests as templates, have been discussed intensively.[5] Recently the influence of univalent cations on formation and structure has been elucidated for a variety of POM complexes.[6] Additionally, it has been shown that facially coordinating polyalkoxides are particularly useful auxiliaries for the synthesis of POMs with novel structural properties.[6,7] As peripheral ligands, polyalkoxides are capable of shielding an oligonuclear M_xO_y core thereby preventing subsequent aggregation processes. They further stabilize the surface of the positive complex core by charge compensation. Tris(hydroxymethyl)ethane and related triols have successfully been utilized for the preparation of a variety of oxo-centered, oligonuclear complexes with Fe^{III}, Mn^{II} and Mn^{III}, V^{IV} and V^{V}, and Mo^{VI},[6,8−11] and we recently reported the preparation of a novel heptanuclear Ta^{V} complex using the cyclic 1,3,5-trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (tdci) as a surface complexing agent (Chart 1).[12] The resulting, neutral species $[H_{-11}Ta_7O_{12}(tdci)_6]$ (**1**) has a unique, rather porous $[Ta_7(\mu_2\text{-}O)_{12}]^{11+}$ double adamantane core. The open structure of this core obviously follows from the considerable steric demands of the six peripheral tdci ligands with their bulky dimethylamino groups. The complex is further stabilized by the overall zero charge. This is achieved by complete deprotonation of the coordinating hydroxy groups (−18) but only partial protonation (+7) of the weakly basic dimethylamino groups, and as a consequence, the resulting negative charge of −11 exactly compensates for the positive charge of the complex core. *cis*-Inositol (ino) is sterically considerably less demanding than tdci (Chart 1), and furthermore, there is no way to balance the negative charge of a corresponding complex $[Ta_7O_{12}(H_{-3}ino)_6]^{7-}$. However, both, the compensation of the negative charge and the stabilization of the porous architecture can be achieved by binding additional cations to the anionic complex. We have succeeded in crystallizing such an aggregate as a hydrated potassium salt, and here we report a convenient preparation method and the crystal structure of this compound.

Chart 1



Experimental Section

General. C,H analyses were performed by H. Feuerhake (Anorganische Chemie, Universität des Saarlandes; Ta and K analyses were performed by T. Allgayer/Prof. H. P. Beck (Analytische Chemie, Universität des Saarlandes) using ICPOES and AAS, respectively. ^1H and ^{13}C NMR spectra were measured on a Bruker DRX 500 spectrometer (with resonance frequencies of 500.13 and 125.9 MHz for ^1H and ^{13}C, respectively) with δ scale (ppm) and sodium (trimethylsilyl)propionate-d_4 (0 ppm) as internal standard. IR spectra were recorded on a Bruker Vector 22 FT IR spectrometer equipped with a Golden Gate ATR unit. Commercially available MeOH (absolute, Fluka), Et_3N (Fluka), D_2O (ARMAR), KOH (Fluka), and $Ta(OCH_3)_5$ and $TaCl_5$ (both from Aldrich) were used without further purification; *cis*-inositol was prepared according to the method of Angyal[13] and was obtained as a white solid (27% yield). ^1H NMR (ppm, D_2O): 3.66, 4.06 (broad signals). ^{13}C NMR (ppm, D_2O): 70.7, 76.3. Anal. Calcd for $C_6H_{12}O_6$: C, 40.00; H, 6.71. Found: C, 39.65; H, 6.50.

$\{[Ta_7O_{12}(H_{-3}ino)_6]\subset[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]\}K\cdot19H_2O$ (2K·19H₂O). To a solution of *cis*-inositol (250 mg, 1.39 mmol) in boiling MeOH was added dropwise a solution of $Ta(OCH_3)_5$ (544 mg, 1.62 mmol, dissolved in 10 mL of MeOH). A white, microcrystalline solid precipitated. Aqueous 1 mol dm^{-3} KOH (9.7 mL) was then added. The mixture was refluxed for 1 h and was allowed to stand at room temperature for another 1 h. The resulting solid was filtered off and dried over P_4O_{10} under reduced pressure. Yield: 388 mg (50%) of **2**K·19H_2O. Anal. Calcd for $C_{36}H_{120}K_7O_{81}Ta_7$: C, 12.76; H, 3.57; K, 8.07; Ta, 37.37. Found: C, 12.85; H, 2.71; K, 7.94; Ta, 37.23. IR (cm^{-1}): 2864, 1652, 1400, 1369, 1288, 1150, 1095, 1037, 953, 878, 770, 656, 506. ^1H NMR (D_2O): 4.31 (1H), 4.28 (2H), 3.48 (1 H), 3.47 (2H). ^{13}C NMR: 78.45, 78.15, 70.79, 70.53. Single crystals of composition **2**K·

[†] Metal Binding of Polyalcohols. 6. Part 5: ref 12.

[*] Author to whom correspondence should be addressed.

(1) (a) Baker, L. C. W.; Glick, D. C. *Chem. Rev.* **1998**, *98*, 3. (b) Jeannin, Y. P. *Chem. Rev.* **1998**, *98*, 51. (c) Müller, A.; Peters, F.; Pope, M. T.; Gatteschi, D. *Chem. Rev.* **1998**, *98*, 239. (d) Coronado, E.; Gomez-Garcia, C. J. *Chem. Rev.* **1998**, *98*, 273. (e) Klemperer, W. G.; Wall, C. G. *Chem. Rev.* **1998**, *98*, 297.

(2) (a) Kozhevnikov, I. V. *Chem. Rev.* **1998**, *98*, 171. (b) Mizuno, N.; Misono, M. *Chem. Rev.* **1998**, *98*, 199. (c) Sadakane, M.; Steckhan, E. *Chem. Rev.* **1998**, *98*, 219.

(3) Rhule, J. T.; Hill, C. L.; Judd, D. A.; Schinazi, R. F. *Chem. Rev.* **1998**, *98*, 327.

(4) Judd, D. A.; Nettles, J. H.; Nevins, N.; Snyder, J. P.; Liotta, D. C.; Tang, J.; Ermolieff, J.; Schinazi, R. F.; Hill, C. L. *J. Am. Chem. Soc.* **2001**, *123*, 886.

(5) (a) Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2328. (b) Rohmer, M.-M.; Benard, M.; Blaudeau, J.-P.; Maestre, J.-M.; Poblet, J.-M. *Coord. Chem. Rev.* **1998**, *178−180*, 1019.

(6) Khan, M. I.; Chen, Q.; Salta, J.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1996**, *35*, 1880.

(7) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77.

(8) (a) Hegetschweiler, K.; Schmalle, H.; Streit, H. M.; Schneider, W. *Inorg. Chem.* **1990**, *29*, 3625. (b) Cornia, A.; Gatteschi, D.; Hegetschweiler, K.; Hausherr-Primo, L.; Gramlich, V. *Inorg. Chem.* **1996**, *35*, 4414.

(9) Cavaluzzo, M.; Chen, Q.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1993**, 131.

(10) (a) Khan, M. I.; Chen, Q.; Höpe, H.; Parkin, S.; O'Connor, C. J.; Zubieta, J. *Inorg. Chem.* **1993**, *32*, 2929. (b) Chen, Q.; Goshorn, D. P.; Scholes, C. P.; Tan, X.; Zubieta, J. *J. Am. Chem. Soc.* **1992**, *114*, 4667.

(11) Liu, S.; Ma, L.; McGowty, D.; Zubieta, J. *Polyhedron* **1990**, *9*, 1541.

(12) Hegetschweiler, K.; Raber, T.; Reiss, G. J.; Frank, W.; Wörle, M.; Currao, A.; Nesper, R.; Kradolfer, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1964.

(13) Angyal, S. J.; Odier, L.; Tate, M. E. *Carbohydr. Res.* **1995**, *266*, 143.

10.1021/ic0010858 CCC: $20.00

Table 1. Crystallographic Data for $\{[Ta_7O_{12}(H_{-3}ino)_6]\subset[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]\}K\cdot 19H_2O$

empirical formula	$C_{36}H_{120}K_7O_{81}Ta_7$
fw	3389.7
cryst syst	orthorhombic
space group	*Pnnm* (No. 58)
a, *b*, *c*, Å	12.539(3), 17.010(3), 21.027(4)
Z	2
T, K	293
λ(Mo Kα), Å	0.71073
ρ_{calcd}, g cm^{-3}	2.510
μ, mm^{-1}	8.958
R1 [$I > 2\sigma(I)$][a]	0.029
wR2 (all data)[b]	0.078

[a] $R1 = \sum|F_o - F_c|/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$.

$19H_2O$ suitable for X-ray analysis were grown from aqueous solution (colorless needles).

X-ray Diffraction Analysis. Diffraction data for **2**$K\cdot 19H_2O$ were collected on a STOE IPDS diffractometer using monochromated Mo Kα radiation and a crystal of approximate dimensions 0.2 × 0.3 × 0.5 mm (Table 1); 25098 reflections were collected in the range $2.02° < \theta < 24.15°$ without significant loss of intensity. The data were corrected for Lorentz and polarization effects. An absorption correction was not performed. The structure was solved using direct methods (SHELXS-97)[14] and refined using full-matrix least-squares calculations (SHELXL-97)[15] on F^2. C(21) appeared to have a nonpositive definite displacement ellipsoid and was refined isotropically. All other non-hydrogen atoms were refined with anisotropic displacement parameters. The remaining K^+ counterion was found to be distributed over four symmetry-equivalent sites sharing these sites with three water molecules. This position (O7w) was therefore refined as an oxygen atom with an occupancy of 120%. Some of the water molecules (O1w, O5w, O7) proved to be disordered and were refined with two positions (labeled as A and B) with site occupancies of 50%. All H(−C) hydrogen atoms were placed at calculated positions using a riding model and isotropic displacement parameters which were fixed at $1.2U_{eq}$ of the corresponding heavy atom prior to the final refinement. The hydrogen atoms of the bridging water ligands, the nondisordered terminal water ligand, and the equatorial hydroxy groups (except O16) were located in a difference Fourier map and were refined freely with variable isotropic displacement parameters. U_{iso} of H(8O1) appeared to be unusually small and was fixed at $1.2U_{eq}$ of O(8). Further hydrogen atoms were not considered. A total of 3558 unique data were used for the final refinement of 370 parameters. The minimum and maximum in the final residual electron density map were −1.3 and +1.6 e Å^{-3}.

Results and Discussion

The direct reaction of *cis*-inositol and $TaCl_5$ in MeOH in the presence of a noncoordinating weak base (NEt_3) resulted in the precipitation of a white solid. The ^1H and ^{13}C NMR spectra (D_2O) showed that this product represented a mixture of various species. In the presence of excess KOH, this mixture reacted slowly to give the heterometallic aggregate $[Ta_7O_{12}(H_{-3}ino)_6]\subset[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]^-$ (**2**$^-$), which crystallized as the hydrated potassium salt **2**$K\cdot 19H_2O$ in the form of colorless needles after a period of several weeks. Since this reaction produces a waste amount of $HNEt_3Cl$ as a coprecipitate, the isolation of the compound as a pure substance in a reasonable yield proved difficult. We therefore developed a straightforward synthetic route, using $Ta(OCH_3)_5$, *cis*-inositol, and KOH as starting material. The complex could then be isolated as a pure substance with reasonable yield (50%), and single crystals could be grown from aqueous solution within a few days. The primary reaction product and the single crystals have the same elemental composition and showed virtually identical IR spectra, indicating thus direct formation of this complex upon reaction of $Ta(OCH_3)_5$, inositol, and KOH. Moreover, NMR spectroscopic measurements in D_2O confirmed that only one species is present in aqueous solution. Both the ^1H and ^{13}C spectra exclusively exhibited 4 signals with a 1:2:2:1 ratio, indicative of local C_s symmetry for the six symmetry-equivalent inositol moieties.

Table 2. Summary of Bond Distances in the Heptanuclear Complex **2**$^-$ Together with Corresponding Values of the tdci Complex **1** for Comparison

	2$^-$			**1**
	min	max	av	av
$O_{alkoxo}-K$	2.716(4)	2.783(4)	2.759	
$O_{oxo}-K$	2.869(4)	3.028(5)	2.955	
$\mu_2\text{-}H_2O-K$	2.950(7)	3.012(6)	2.974	
$O_{hydroxy}-K$	2.938(7)	3.058(5)	2.991	
$H_2O_{(term)}-K$	2.892(8)	2.92(2)	2.911	
$O_{oxo}-Ta_{centr}$	1.987(6)	1.988(6)	1.987	1.982
$O_{oxo}-Ta_{periph}$	1.932(6)	1.959(4)	1.951	1.919
$O_{alkoxo}-Ta$	2.007(4)	2.026(4)	2.014	2.044
O−C	1.407(9)	1.445(8)	1.431	
C−C	1.509(10)	1.538(10)	1.527	

The structure of this complex was established by single-crystal X-ray analysis. It can be described as an anionic, heptanuclear $[Ta_7O_{12}(H_{-3}ino)_6]^{7-}$ moiety which is surrounded by a hexanuclear $[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]^{6+}$ ring (Figure 1). The $[Ta_7O_{12}(H_{-3}ino)_6]^{7-}$ moiety and the previously described tdci complex **1** have closely related structures (Table 2) with a $[Ta_7(\mu_2\text{-}O)_{12}]^{11+}$ core consisting of two corner-sharing Ta_4O_6-adamantane cages. The two adamantane cages define a total of eight fused $\overline{Ta-O-Ta-O-Ta\text{-}O}$ six-membered rings. Six of these rings have the central Ta(1) atom in common. All the rings are slightly puckered and have an almost ideal chair conformation.[16] The central Ta(1) atom is placed on a center of inversion and has a regular octahedral TaO_6 coordination environment consisting entirely of inorganic O^{-II} ligands. The remaining six Ta atoms also have an approximately octahedral TaO_6 geometry with coordination spheres consisting of three facially oriented inorganic O^{-II} ligands and the three axial alkoxo oxygens of an inositol ligand. The entire resulting Ta_7O_{30} skeleton can be described as an aggregate of seven TaO_6 octahedra which are fused exclusively by common vertexes. Although structures with *exclusive* corner sharing of MO_6 octahedra are well established in solid state materials such as ReO_3,[17] this structure type is extremely rare in POM chemistry.[18]

The central $[Ta_7O_{12}]^{11+}$ double adamantane core has a rodlike shape, and this rod is surrounded by the six inositol moieties, arranged in such a way that the midpoints of the corresponding C_6-rings define a regular trigonal antiprism (Figure 1b). This antiprism deviates only slightly from regular octahedral symmetry (the two equilateral triangular bases have lengths of 8.49−8.53 Å whereas the legs of the isosceles triangles have lengths of 9.12−9.19 Å), and the $[Ta_7O_{12}(H_{-3}ino)_6]^{7-}$ unit of **2**$^-$ has approximate D_{3d} symmetry (the crystallographic symmetry is C_{2h}). As shown in Figure 2, the $[Ta_7O_{12}]^{11+}$ rod of **1** is almost

---

(14) Sheldrick, G. M. *SHELXS97, a program for the solution of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

(15) Sheldrick, G. M. *SHELXL97, a program for the refinement of crystal structures*; University of Göttingen: Göttingen, Germany, 1997.

(16) Puckering parameters for the various $\overline{Ta-O-Ta-O-Ta\text{-}O}$ rings according to Cremer and Pople (Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354−1358): $Q = 0.47$ Å, $\theta = 0.9-1.7°$.

(17) Wells, A. F. *Structural inorganic chemistry*, 5th ed.; Clarendon Press: Oxford, U.K., 1984.

(18) (a) Arimondo, P. B.; Calderazzo, F.; Hiemeyer, R.; Maichle-Mössmer, C.; Marchetti, F.; Pampaloni, G.; Strähle, J. *Inorg. Chem.* **1998**, *37*, 5507. (b) Johansson, A.; Kessler, V. G. *Polyhedron* **2000**, *19*, 1791.

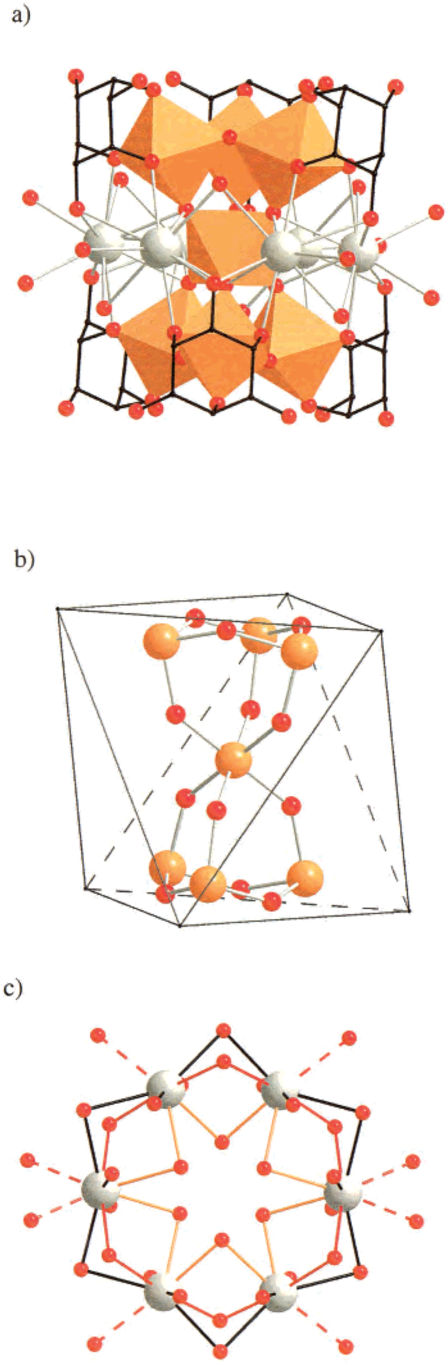


Figure 1. Molecular architecture of the complex anion ($\mathbf{2}^-$): (a) The entire $\{[Ta_7O_{12}(H_{-3}ino)_6]\subset[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]\}^-$ aggregate. The seven Ta centers are represented as orange octahedra, the K^+ cations as gray spheres, the oxygen atoms as red spheres, and the carbon atoms of the cyclohexane residues by a black stick model. Hydrogen atoms are omitted for clarity. (b) Ball and stick model of the rod-shaped $[Ta_7\text{-}(\mu_2\text{-}O)_{12}]^{11+}$ core together with the positions of the six inositolato ligands, indicated by the trigonal antiprism defined by the midpoints of the six cyclohexane rings. (c) Ball and stick model of the surrounding $[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]^{6+}$ ring together with some oxygen atoms of the anion, showing the different types of oxygen atoms bonded to the K^+ centers: six inorganic O^{-II} anions (orange bonds), six μ_2-H_2O molecules (solid red bonds), 6 bridging hydroxy and 12 terminal alkoxo groups of the inositol ligands (black bonds), and eight terminally coordinating water molecules (broken red bonds).

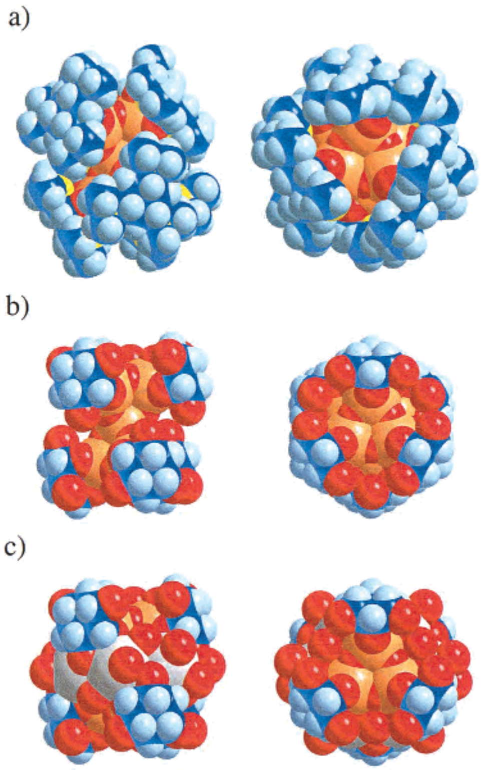


Figure 2. Space-filling models of (a) $[H_{-11}Ta_7O_{12}(tdci)_6]$ (**1**), (b) $[Ta_7O_{12}(H_{-3}ino)_6]^{7-}$, and (c) $\{[Ta_7O_{12}(H_{-3}ino)_6]\subset[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]\}^-$ ($\mathbf{2}^-$) showing the lipophilic (C, H: blue color) and hydrophilic (O: red color) regions of the molecular surface. Hydrogen atoms bonded to oxygen atoms are omitted. The partially protonated nitrogen atoms of **1** and the K^+ cations of $\mathbf{2}^-$ are represented by yellow and gray spheres, respectively.

completely shielded by the bulky, lipophilic dimethylamino groups, whereas the $[Ta_7O_{12}(H_{-3}ino)_6]^{7-}$ anion of $\mathbf{2}^-$ has a bipolar structure with lipophilic and hydrophilic zones. The lipophilic region is represented by the six cyclohexane residues; it is located around the two poles of the rod. The poles themselves, together with the equator, represent the hydrophilic parts of the anion. In particular, the equatorial region may be regarded as a torus-like hydrophilic pocket. This pocket is filled by the $[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]^{6+}$ ring (Figure 2). The obvious function of this ring is (by analogy with the partially protonated dimethylamino groups of **1**) filling of empty space and charge compensation.

The six K^+ cations of the ring structure are generated by two crystallographically independent positions (K1 and K2). The ring is exactly planar (Figure 1c). It is an almost regular hexagon with K⋯K distances of 4.02 Å (K1⋯K2) and 3.86 Å (K2⋯K2). These rather short K⋯K distances[19] are due to exclusive face sharing of the six fused coordination polyhedra. Five different types of oxygen atoms are involved in the binding of these K^+ cations (Figure 1c): (i) Each of the six inorganic O_{oxo}^{-II} anions bonded to the Ta1 center additionally binds two K^+ cations and has thus a $\mu_4\text{-}O{-}K_2Ta_2$ geometry with a coordination number of 4. (ii) Two of the three axial alkoxo groups of each inositol ligand which are coordinated to a peripheral Ta atom undergo further binding of a K^+ center giving rise to a $Ta{-}\mu_2\text{-}O(C){-}K$ bridge with trigonal pyramidal geometry for the oxygen atom. (iii) One of the three equatorial hydroxy groups of each inositol ligand bridges two K^+ cations and has (together with the proton and the carbon atom) a coordination number of 4 (Figure 3a). The coordination environment of the K^+ cations is completed by (iv) six bridging

---

(19) Walba, D. M.; Richards, R. M.; Hermsmeier, M.; Haltiwanger, R. C. *J. Am. Chem. Soc.* **1987**, *109*, 7081.

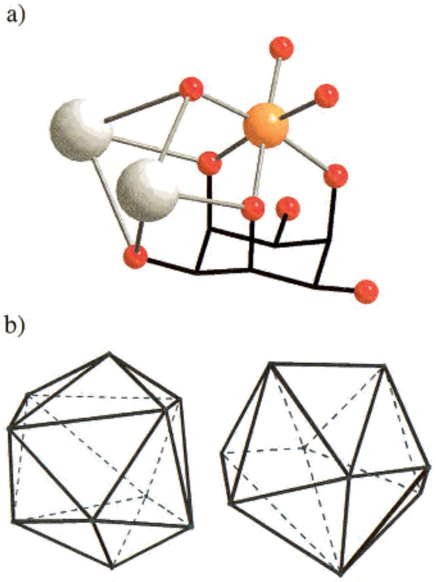


Figure 3. Selected structural properties of $\mathbf{2}^-$: (a) the $(H_{-3}ino)K_2TaO_3$ fragment (with hydrogen atoms omitted); (b) the coordination polyhedra of the two types of K^+ cations.

μ_2-H_2O ligands and (v) eight terminally coordinating H_2O ligands (Figure 3b). Bridging of K^+ cations by water ligands is well-established both in finite complexes and also in solid state structures.[20,21] A remarkable property of the μ_2-H_2O bridges is, however, the arrangement of the four ligated atoms (2H, 2K) around the water oxygen. These form a distorted square pyramid rather than the expected tetrahedral geometry. This peculiar feature is obviously due to hydrogen bonding between the bridging water ligands and the alkoxo groups of the inositolato moieties bonded to K^+ (average O···O distance, 2.82 Å; average O···H distance, 2.09 Å; average O−H···O angle, 153°). K(1) and K(2) differ with respect to their coordination numbers (Figure 3b). K1 is bonded to two terminal water ligands and has a coordination number of 10. Its coordination polyhedron can be described as a distorted bicapped square antiprism. K2 binds only one terminal water ligand and has a coordination number of 9 with an irregular coordination polyhedron. The rather long K−O distances (K1, 2.783(4)−3.028(5) Å, average 2.933 Å; K2, 2.716(4)−3.058(5) Å, average 2.901 Å) are obviously a consequence of these high coordination numbers.

The remaining charge of −1 of the entire aggregate $\mathbf{2}^-$ is compensated by an additional K^+ cation. It was, however, difficult to locate this cation unambiguously. Seven additional peaks were located in a difference Fourier map, and these corresponded mainly to the water of crystallization. The most intense of these peaks (O7w) exhibited a sensible environment for a K^+ cation. Since this peak lies on a general position, and only one countercation is required for charge balance, the cation must therefore be distributed over the four symmetry-equivalent sites.[22] A refinement of electron density of this site revealed a peak height corresponding to 1.2 oxygen atoms. This amount corresponds closely to the average of one K^+ cation and three oxygen atoms. It appears though that the countercation and three water molecules occupy the four symmetry-equivalent positions at random. Such a model is not unreasonable, because K−O bond distances correspond approximately to water−water distances in a hydrogen-bonded structure. The random distribution of these atoms leads to a characteristic disordering of some of the water molecules with partially occupied positions indicated as A and B. This disorder also affects one of the terminally coordinating water molecules of $\mathbf{2}^-$ which exhibited a significantly different K−O bond distance depending on the presence or absence of the countercation in its neighborhood.

Conclusions

This paper reports the second example of a POM with a double adamantane structure. Our results clearly confirmed that the use of polyalcohols as peripheral ligands is a promising strategy for obtaining POMs of unusual structure. The formation of the $[Ta_7O_{12}]^{11+}$ core in the presence of both tdci and *cis*-inositol is a strong indication that ligands with a *cis*-1,3,5-cyclohexanetriol structure are especially suited to generate this particular geometry. As noted in the previously described tdci complex **1**,[12] the heptanuclear species is not the direct product in the reaction of $TaCl_5$ with the polyol ligand and NEt_3, but forms in a slow aggregation process in aqueous solution. The present investigation also confirms our previously reported assertions that additional shielding and charge compensation are necessary to stabilize the open $[Ta_7O_{12}]^{11+}$ core. In the tdci complex **1**, this is achieved by the bulky, partially protonated dimethylamino groups. However, in the *cis*-inositol complex the required stabilization is only possible by an additional binding of six K^+ cations to the equatorial area of the anion, and the formation of the $[Ta_7O_{12}(H_{-3}ino)_6]^{7-}$ core and of the $[K_6\text{-}(\mu\text{-}OH_2)_6\text{-}(OH_2)_8]^{6+}$ ring are obviously mutually conditional.

Acknowledgment. We thank Prof. M. Veith for providing the X-ray facility and Dr. P. Osvath (Melbourne, Australia) for helpful advice and suggestions. Financial support by the Fonds der Chemischen Industrie (Frankfurt/M) and by the Project Biologically Composed Materials and Systems (BKMS) of the Saarland is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic files including the structural data for $\mathbf{2}K\cdot 19H_2O$ in CIF format and an ORTEP representation of the complex anion $\mathbf{2}^-$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0010858

---

(20) (a) Sellmann, D.; Allmann, C.; Heinemann, F.; Knoch, F.; Sutter, J. *J. Organomet. Chem.* **1997**, *541*, 291. (b) Kilic, Z.; Yildiz, M.; Hökelek, T.; Erdogan, B. *J. Chem. Soc., Dalton Trans.* **1998**, 3635.

(21) (a) Anderson, T. H.; Lingafelter, E. C. *Acta Crystallogr.* **1951**, *4*, 181. (b) Beurskens, G.; Jeffrey, G. A. *J. Chem. Phys.* **1964**, *41*, 917.

(22) Attempts were made to resolve this disorder by refining the data in a space group of lower symmetry. In the monoclinic space group $P2_1/n$ ($\beta = 90.16(3)°$, 6851 unique data, 630 parameters, R1 = 0.033, wR2 (all data) = 0.087), the four symmetry-equivalent positions of O7w split into two pairs of crystallographically independent sites due to the lack of a mirror plane. However, a refinement of the electron density of the two independent sites did not reveal any difference within significance.