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Structural Characterization and Magnetic Properties of Sandwich-Type Tungstoarsenate Complexes. Study of a Mixed-Valent V^{IV}_2/V^V Heteropolyanion

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Complexes $K_{11}Na_1[As_2W_{18}\{Mn(H_2O)\}_3O_{66}]\cdot 27H_2O$ **(1)** and $Na_{12}[As_2W_{18}\{Co(H_2O)\}_3O_{66}]\cdot 34H_2O$ **(2)** have been characterized. **1** crystallizes in the orthorhombic space group *Pnma*, with $a = 30.6484(4)$ Å, $b = 14.9946(2)$ Å, and $c = 19.17080(10)$ Å ($Z = 4$), while **2** crystallizes in the monoclinic space group *C*2/*c*, with $a = 14.124(2)$ Å, $b = 23.294(3)$ Å, $c = 32.247(3)$ Å, and $\beta = 98.935(10)°$ ($Z = 4$). Structures of the anions of **1** and **2** are similar, the divalent metals adopting a square pyramidal environment. $K_{11}[As_2W_{18}(VO)_3O_{66}]\cdot 23H_2O$ **(3)** crystallizes in the orthorhombic space group *Pnma*, with $a = 30.6240(5)$ Å, $b = 14.9861(2)$ Å, and $c = 19.2651(3)$ Å ($Z = 4$). The structure has revealed a disorder on two of the three metals linking the $[\alpha\text{-}AsW_9O_{33}]^{9-}$ parts. For these two vanadium atoms, the V═O bonds are directed alternatively toward the inside or the outside of the $[\alpha\text{-}AsW_9O_{33}]^{9-}$ cavity. The remaining vanadium shows a V═O bond always directed toward the outside of the cavity. Titration of V^{IV} by Ce^{IV} revealed that **3** is the mixed-valent $V^{IV}_2V^V$ species. Magnetic measurements are in agreement with this formulation. The high-temperature molar magnetic susceptibility of a powdered sample of **3** clearly confirms the presence of two d^1 centers. The two V^{IV} are antiferromagnetically coupled, with $J = -2.9$ cm^{-1} and $g = 1.93$. Crystallographic data do not permit the location of the two V^{IV} to be distinguished from the location of the V^V. As expected, the Mn^{II} are very weakly antiferromagnetically coupled in compound **1**. The complex $Na_8[Ni(H_2O)_6]_2[As_2W_{18}\{Ni(H_2O)\}_3O_{66}]\cdot 20H_2O$ **(4)** has been synthesized. The anion crystallized with two octahedral $[Ni(H_2O)_6]^{2+}$ as counterions. Magnetic data have been fitted assuming that the only exchange-coupled centers are the nickels of the polyanion. **4** exhibits an antiferromagnetic coupling with $J = -1.7$ cm^{-1}, $g = 2.27$, and $\theta = -1.5$ K.

Introduction

The chemistry of polyoxometalates leads to a large variety of structures and is of current interest due to the wide range of applications such as catalysis and medicine.[1] Polyoxometalates containing transition metal ions of the first row are also interesting for their magnetic properties.[2] Nuclearity and topology of these complexes can be controlled. For these compounds, the molecular entities are generally well-insulated from each other and quantum mechanical approaches are allowed.

New inorganic complexes with two $[\alpha\text{-}SbW_9O_{33}]^{9-}$ or $[\alpha\text{-}AsW_9O_{33}]^{9-}$ anions linked by four metals have been described recently.[3] Polyoxotungstates containing three paramagnetic centers can be obtained from these trivacant Keggin species, and inorganic complexes of $[\alpha\text{-}AsW_9O_{33}]^{9-}$ with divalent metal ions have been reported.[4] Nevertheless, only the Cu^{II} complex has been structurally characterized[5] and magnetically studied.[6] In $[As_2W_{18}\{Cu_3(H_2O)_2\}O_{66}]^{12-}$, a nearly equilateral triangle is formed by the d^1 centers, with an average Cu−Cu distance of 4.682 Å. The metals are antiferromagnetically coupled.

This work is devoted to the study of the $[As_2W_{18}\{M_3(H_2O)_3\}O_{66}]^{12-}$ series with various divalent metals. The related mixed-valence complex $V^{IV}_2V^V$ is also described. Structural characterizations (M = Mn^{II}, Co^{II}, V^{IV}/V^V) and magnetic properties (M = Mn^{II}, Ni^{II}, V^{IV}/V^V) are investigated.

Experimental Section

Preparation of Compounds. All chemicals were of reagent grade and used as received. $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$[7] and $Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$[3b] have been synthesized as previously described. For each complex, the total number of water molecules has been checked by TG studies.

$K_{11}Na_1[As_2W_{18}\{Mn(H_2O)\}_3O_{66}]\cdot 27H_2O$ (1). $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ (2.84 g) was dissolved in 5 mL of water. Then 0.255 g of $MnSO_4\cdot 1H_2O$ in 5 mL of water was added at room temperature and the mixture stirred for 15 min. Then, potassium chloride was added,

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(1) (a) *Polyoxometalates: From Platonic solid to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994. (b) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34−48. (c) Hill, C., Guest Ed. Special issue on Polyoxometalates. *Chem. Rev.* **1998**, January/February.

(2) (a) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer Academic Publishers: Dordrecht, The Nederlands, 1991. (b) Clemente-Juan, J. M.; Coronado, E. *Coord. Chem. Rev.* **1999**, *193*−*195*, 361−394.

(3) (a) Sazani, G.; Dickman, M. H.; Pope, M. T. *Inorg. Chem.* **2000**, *39*, 939−943. (b) Bösing, M.; Loose, I.; Pohlmann H.; Krebs, B. *Chem.*−*Eur. J.* **1997**, 1232−1237.

(4) Tourné, C.; Revel, A.; Tourné, G.; Vendrell, M. *C. R. Acad. Sc. Paris, Ser. C* **1973**, 277, 643.

(5) Robert, F.; Leyrie, M.; Hervé, G. *Acta Crystallogr.* **1982**, B38, 358−362.

(6) Kokozka, G. F.; Padula, F.; Goldstein, A. S.; Venturini, E. L.; Azevedo, L.; Siedle, A. R. *Inorg. Chem.* **1988**, *27*, 59.

(7) Tourné, C.; Tourné, G. *C. R. Acad. Sci. Paris, 281 C* **1975**, 933.

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Table 1. Crystallographic Data for $K_{11}Na_1[As_2W_{18}\{Mn(H_2O)\}_3O_{66}]\cdot 27H_2O$ (**1**), $Na_{12}[As_2W_{18}\{Co(H_2O)\}_3O_{66}]\cdot 34H_2O$ (**2**), $K_{11}[As_2W_{18}(VO)_3O_{66}]\cdot 23H_2O$ (**3**), and $K_{12}[Sb_2W_{18}\{Cu(H_2O)\}_3O_{66}]\cdot 41H_2O$ (**5**)

	(**1**)	(**2**)	(**3**)	(**5**)
empirical formula	$H_{60}As_2K_{10.94}Mn_3Na_{1.06}O_{96}W_{18}$	$H_{74}As_2Co_3Na_8O_{103}W_{18}$	$H_{46}As_2V_3K_{11}O_{92}W_{18}$	$H_{88}Sb_2Cu_3K_{12}O_{110}W_{18}$
fw	5672.56	5541.94	5560.43	6028
space group, Z	*Pnma* (No. 62), 4	*C*2/*c* (No. 15), 4	*Pnma* (No. 62), 4	*Pnma* (No. 62), 4
a, Å	30.6484(4)	14.124(2)	30.6240(5)	30.2359(3)
b, Å	14.9946(2)	23.294(3)	14.9861(2)	14.9889(2)
c, Å	19.17080(10)	32.247(3)	19.2651(3)	19.1354(3)
β, deg	90	98.935(10)	90	90
V, Å^3	8810.14(17)	10481(2)	8841.4(2)	8672.2(2)
ρ_{calc}, g cm^{-3}	4.277	3.512	4.177	4.329
μ, mm^{-1}	25.201	20.898	24.992	25.788
T, K	296(2)	296(2)	296(2)	296(2)
R (>2$\sigma(I)$)	$R1(F_o)^a = 0.0405$ $wR2(F_o^2)^b = 0.0805$	$R1(F_o)^a = 0.0732$ $wR2(F_o^2)^b = 0.1960$	$R1(F_o)^a = 0.0469$ $wR2(F_o^2)^b = 0.0993$	$R1(F_o)^a = 0.0525$ $wR2(F_o^2)^b = 0.1370$
R (all data)	$R1(F_o)^a = 0.0745$ $wR2(F_o^2)^b = 0.0926$	$R1(F_o)^a = 0.0904$ $wR2(F_o^2)^b = 0.2109$	$R1(F_o)^a = 0.0741$ $wR2(F_o^2)^b = 0.1097$	$R1(F_o)^a = 0.0798$ $wR2(F_o^2)^b = 0.1522$

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

until no further precipitation was observed. An orange powder was obtained by filtration and washed with water, ethanol, and ether (yield: 2.0 g, 72% based on manganese). The powder was allowed to crystallize after dissolution in water (200 mg/5 mL of H_2O) at room temperature. After 1 week, orange needle crystals suitable for X-ray diffraction were collected.

Anal. Calcd for $K_{11}Na_1As_2W_{18}Mn_3O_{96}H_{60}$ (%): K 7.58; W 58.34; As 2.64; Mn 2.90. Found: K 7.29; W 57.50; As 2.64; Mn 3.03.

$Na_{12}[As_2W_{18}\{Co(H_2O)\}_3O_{66}]\cdot 34H_2O$ (2). $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ (2.84 g) was dissolved in 5 mL of water. After complete dissolution of the salt, 0.437 g of $Co(NO_3)_2\cdot 6H_2O$ in 5 mL of water was added. Then, the mixture was heated to 50 °C for 15 min. The solution was cooled to room temperature. After 1 h, a blue powder was obtained after filtration and washed with NaCl 2 M, ethanol, and ether (yield: 1.8 g, 65% based on cobalt). The powder was allowed to crystallize after dissolution in water (300 mg/5 mL of H_2O) at room temperature. After 3 days, blue parallelepipedic crystals suitable for X-ray diffraction were collected.

Anal. Calcd for $Na_{12}As_2W_{18}Co_3O_{103}H_{74}$ (%): Na 4.90; W 58.74; As 2.66; Co 3.14. Found: Na 5.30; W 61.22; As 2.97; Co 3.10.

$K_{11}[As_2W_{18}(VO)_3O_{66}]\cdot 23H_2O$ (3). $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ (2.84 g) was dissolved in 5 mL of water. Then 0.380 g of $(VO)SO_4\cdot 5H_2O$ in 5 mL of water was slowly added, simultaneously to a 1 M Na_2CO_3 solution, in order to keep the pH close to 8−8.5. The mixture was heated to 50 °C for 15 min. The solution was cooled to room temperature. Then solid potassium chloride (0.780 g) was added with stirring. After standing for 1 h at room temperature, a brown powder was obtained by filtration and washed with KCl 2 M, ethanol, and ether (yield: 1.65 g, 60% based on vanadium). The powder was allowed to crystallize after dissolution in water (300 mg/5 mL of H_2O) at 3 °C. After one night brown needle crystals suitable for X-ray diffraction were collected.

Anal. Calcd for $K_{11}As_2W_{18}V_3O_{92}H_{46}$ (%): K 7.73; W 59.51; As 2.70; V 2.75. Found: K 8.00; W 58.77; As 3.07; V 2.82.

$Na_8[Ni(H_2O)_6]_2[As_2W_{18}\{Ni(H_2O)\}_3O_{66}]\cdot 20H_2O$ (4). $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ (5.68 g) was dissolved in 5 mL of water. After complete dissolution of the salt, 1.40 g of $NiSO_4\cdot 7H_2O$ in 5 mL of water was added. Then, the mixture was heated to 50 °C for 15 min. The solution was cooled to room temperature. After 1 h, a yellow powder was obtained by filtration and washed with NaCl 2 M, ethanol, and ether (yield: 2.1 g, 65% based on nickel). The powder was allowed to crystallize after dissolution in water (400 mg/5 mL of H_2O) at 3 °C. After 2 days, yellow parallelepipedic crystals were collected.

Anal. Calcd for $Na_8As_2W_{18}Ni_5O_{101}H_{70}$ (%): Na 3.27; W 58.85; As 2.66; Ni 5.22. Found: Na 3.12; W 57.50; As 2.50; Ni 5.25.

$K_{12}[Sb_2W_{18}\{Cu(H_2O)\}_3O_{66}]\cdot 41H_2O$ (5). $Na_9[\alpha\text{-}SbW_9O_{33}]\cdot 19.5H_2O$ (4.0 g) was dissolved in 8 mL of water, and 0.507 g of $CuNO_3\cdot 3H_2O$ in 10 mL of water was added. The mixture was boiled for 30 min. Then, the solution was cooled to room temperature and potassium chloride was added until no further precipitation was observed. A green powder is obtained by filtration and washed with water, ethanol, and ether (yield: 4.0 g, 94% based on copper). The powder was allowed to crystallize after dissolution in water (300 mg/5 mL of H_2O) at room temperature. After one week, green parallelepipedic crystals suitable for X-ray diffraction were collected.

Anal. Calcd for $K_{12}Sb_2W_{18}Cu_3O_{110}H_{88}$ (%): K 7.75; W 54.70; Sb 4.02; Cu 3.15. Found: K 7.70; W 54.58; Sb 4.12; Cu 3.33.

Physical Measurements. TGA. Thermogravimetry was carried out under nitrogen flow (60 mL/min) with a Perkin-Elmer electrobalance TGA-7 at a heating rate of 1 °C/min up to 600 °C.

Elemental analysis was performed by the Service Central d'Analyse of CNRS at 69390 Vernaison, France.

X-ray Crystallography. Intensity data collection was carried out with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using Mo Kα monochromatized radiation ($\lambda = 0.71073$ Å). The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program[8] based on the method of Blessing.[9] The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package.[10] Crystallographic data are given in Table 1. As crystal structures for all these complexes show disorder in the range of water molecules and counterions, the exact formula and molecular weight given in the table have been established considering elemental analysis and TG studies. Selected bond distances are listed in Table 2. Additional crystallographic information is given in the Supporting Information.

Magnetic measurements were performed with a MPMS SQUID magnetometer (Quantum Design Inc.).

Results and Discussion

Synthesis. Compounds **1**, **2**, **4**, and **5** were synthesized without controlling the pH. The pH of the solution was found to be crucial in the synthesis of **3**. During the addition of the $(VO)SO_4\cdot 5H_2O$ solution on $Na_9[\alpha\text{-}AsW_9O_{33}]\cdot 19.5H_2O$ in water, sodium carbonate was added in order to keep the pH between 8 and 8.5. The resulting solution was titrated by Ce^{IV}. The equivalence was obtained for 2 molar equiv of oxidant. Titration of the isolated complex **3** gave the same result. It follows from this result, elemental analysis, and X-ray study that this compound must be formulated as the mixed-valent $V^{IV}{}_2V^V$ species. This has been clearly verified by magnetic measurements (see below). If no base is added during the synthesis, the final pH of the reaction is 5.5, and titration by Ce^{IV} indicates

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(8) Sheldrick, G. M. *SADABS; program for scaling and correction of area detector data*; University of Göttingen: Göttingen, Germany, 1997.

(9) Blessing, R. *Acta Crystallogr.* **1995**, *A51*, 33.

(10) Sheldrick, G. M. *SHELX-TL version 5.03*, *Software Package for the Crystal Structure Determination*; Siemens Analytical X-ray Instrument Division: Madison, WI, 1994.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $K_{11}Na_1[As_2W_{18}\{Mn(H_2O)\}_3O_{66}]\cdot 27H_2O$ (**1**), $Na_{12}[As_2W_{18}\{Co(H_2O)\}_3O_{66}]\cdot 34H_2O$ (**2**), $K_{11}[As_2W_{18}(VO)_3O_{66}]\cdot 23H_2O$ (**3**), and $K_{12}[Sb_2W_{18}\{Cu(H_2O)\}_3O_{66}]\cdot 41H_2O$ (**5**) with Standard Deviations

	(**1**)	(**2**)	(**3**)	(**5**)
$W-O_t{}^a$	1.706(7)−1.748(8)	1.714(12)−1.763(14)	1.710(8)−1.738(10)	1.717(15)−1.750(11)
$W-O_{w2}{}^b$	1.774(8)−2.062(7)	1.775(12)−2.028(12)	1.795(9)−2.051(8)	1.785(10)−2.031(10)
$W-O_{w3x}{}^{b,c}$	2.328(7)−2.407(10)	2.333(11)−2.364(11)	2.336(7)−2.372(11)	2.251(10)−2.356(12)
$X-O^c$	1.788(7)−1.797(7)	1.790(11)−1.801(11)	1.781(11)−1.808(8)	1.941(12)−1.995(9)
$M-O_w{}^{b,d}$	2.057(8)−2.082(7)	2.008(13)−2.032(11)	1.978(9)−2.087(13)	1.922(10)−1.995(9)
$M{=}O^d$			V(1)−O39: 1.735(19) V(2A)-O50: 1.760(13) V(2B)-O51: 1.58(5)	
$M-O_{H2}{}^{b,d}$	2.157(14) 2.162(10)	2.08(2) 2.046(17)		2.352(19) 2.304(14)
$O-W-O_{cis}$	72.0(3)−104.8(4)	71.5(5)−104.8(6)	72.0(3)−103.8(4)	72.2(4)−104.8(5)
$O-W-O_{trans}$	156.9(3)−172.7(3)	156.9(5)−173.5(6)	157.8(3)−172.6(4)	157.8(4)−170.7(4)
$O-X-O^{c,}$	96.9(4)−97.8(3)	96.5(5)−97.0(5)	97.3(5)−98.3(3)	90.8(4)−92.1(6)
$O-M-O_{cis}{}^d$	84.6(3)−103.5(4)	88.6(5)−101.5(3)	81.9(5)−108(3)	87.4(6)−99.3(5)
$O-M-O_{trans}{}^d$	160.2(3)−164.2(4)	157.0(7)−166.7(7)	159.0(5)−165.8(6)	167.9(4)−170.3(5)
$M-M^d$	5.110−5.180	5.048−5.088	4.298−5.100	4.838−4.859

[a] t indicates a terminal oxygen. [b]The subscript letters indicate symbol and numbers of bonded neighbor atoms of oxygen. [c]X refers to As^{III} in **1**, **2**, and **3** and Sb^{III} in **5**. [d]M refers to the paramagnetic centers of the complexes (Mn^{II} in **1**, Co^{II} in **2**, $V^{IV/V}$ in **3**, and Cu^{II} in **5**).

that all the vanadium in solution is in the V^{IV} oxidation state, showing that oxidation occurs only under basic conditions. Attempts to crystallize the pure homovalent $V^{IV}{}_3$ complex have failed. $[As_2W_{18}\{Ni(H_2O)\}_3O_{66}]^{12-}$ crystallized with two $[Ni(H_2O)_6]^{2+}$ as counterions even when the Ni^{II} salt was added in stoichiometric amount. This is due to the instability of the nickel complex. In fact, while compounds **1**, **2**, and **3** are relatively stable in solution, **4** decomposes quickly at room temperature.

Structures. **1**, **2**, and **3** are constituted by two $[\alpha\text{-}AsW_9O_{33}]^{9-}$, in which the arrangement of the WO_6 octahedra around the AsO_3 pyramid are identical to that found for similar compounds containing As^{III} as a central atom.[11] The two subunits are linked by three transition metals of the first row (respectively Mn^{II}, Co^{II}, and $(V^{IV}{}_2V^V)$) through four oxygen atoms of different W_3O_{13} groups, as previously observed for $H_2Rb_4[As_2W_{21}O_{69}(H_2O)]\cdot 34H_2O$.[12] A fifth coordination site is occupied by an exogenous ligand, leading to a square pyramidal environment for these metals. The belt formed by the three transition metals is completed by three alkaline cations, which fill the holes between the paramagnetic metals. The same considerations can be made for complex **5**, where $[\alpha\text{-}SbW_9O_{33}]^{9-}$ replaces the $[\alpha\text{-}AsW_9O_{33}]^{9-}$ moiety. Crystallographic data for **1**, **2**, **3**, and **5** are given in Table 1. Selected bond distances are listed in Table 2.

$K_{11}Na_1[As_2W_{18}\{Mn(H_2O)\}_3O_{66}]\cdot 27H_2O$ (Figure 1) crystallizes in the orthorhombic space group *Pnma*. The cell is similar to that found previously by Robert et al. for the analogous compound $K_{12}[As_2W_{18}\{Cu_3(H_2O)_2\}O_{66}]\cdot 11H_2O$.[5] Nevertheless, two main differences are observed between these two complexes. First, a major difference is the relative position of the two $[\alpha\text{-}AsW_9O_{33}]^{9-}$. For $K_{12}[As_2W_{18}\{Cu_3(H_2O)_2\}O_{66}]\cdot 11H_2O$, it has been shown that an AsW_9 subunit has undergone a glide with respect to the other in a direction parallel to the Cu_3 plane. On the contrary, the AsW_9 groups in **1** face each other exactly. This observation is against the assumption that the repulsion of the lone pairs of the As atoms is the cause of this gliding.[5] Second, it has been found that for $K_{12}[As_2W_{18}\{Cu_3(H_2O)_2\}O_{66}]\cdot 11H_2O$, two Cu^{II} are in a square pyramidal environment, while the third one is four coordinated, adopting a local D_{4h} symmetry. This contrasts with complex **1**, where the three Mn^{II} are in a square pyramidal environment, a water molecule completing the coordination sphere of the manganese, with an average $Mn-O_w$ bond length of 2.070 Å and $Mn-O_{H2}$[13] bond length of 2.159 Å. This environment for the Mn^{II} cations and the relative positions of the two AsW_9 subunits are similar to those found recently for $Na_{11}(NH_4)[Sb_2W_{18}\{Mn(H_2O)\}_3O_{66}]\cdot 45H_2O$ by Bösing et al.,[14] suggesting that the conformation of the anion is at least as much influenced by the transition metal coordination mode as by the repulsion of the lone pairs of the heteroatoms.

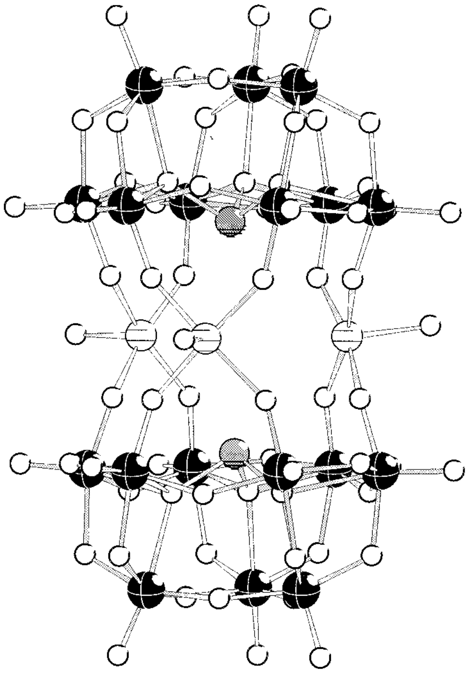

Figure 1. Ball-and-stick structural representation of the anions $[X_2W_{18}(M(H_2O))_3O_{66}]^{9-}$ ($X = As^{III}$, $M = Mn^{2+}$ (**1**), Co^{2+} (**2**); $X = Sb^{III}$, $M = Cu^{II}$ (**5**)): black crosshatched circles, W; white circles, O; gray shaded circles, X; white hatched circles, M.

In order to verify this hypothesis, the crystal structure of $K_{12}[Sb_2W_{18}\{Cu(H_2O)\}_3O_{66}]\cdot 41H_2O$ has been resolved. Each copper is bonded to a water molecule with an average Cu−

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(11) Leyrie, M.; Hervé, G.; Tézé, A.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1980**, *19*, 1746.

(12) Jeannin, Y.; Martin-Frère, J. *J. Am. Chem. Soc.* **1981**, *103*, 1664−1667.

(13) The subscript letters indicate symbol and numbers of bonded neighbor atoms of oxygen.

(14) Bösing, M.; Nöh, A.; Loose, I.; Krebs, B. *J. Am. Chem. Soc.* **1998**, *7252*, 2−7259.

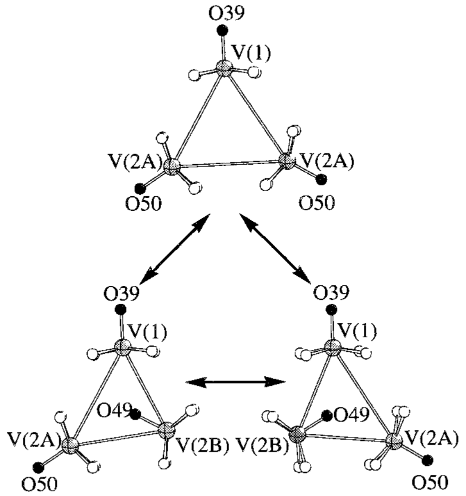

Figure 2. Representation of the disorder scheme of the vanadium atoms in compound $[As_2W_{18}(V(O))_3O_{66}]^{9-}$ (**3**) and their first coordination shell: gray crosshatched circles, V; white circles, O; black circles, OH_2.

O_{H2} bond length of 2.328 Å. Thus, the three Cu^{II} adopt a square pyramidal geometry. As for complex **1**, we observed that the two AsW_9 subunits face each other exactly. This led us to propose that the gliding observed for $K_{12}[As_2W_{18}\{Cu_3(H_2O)_2\}O_{66}]\cdot 11H_2O$ is due to its unique observed difference in the local symmetries of the cuprous centers.

$Na_{12}[As_2W_{18}\{Co(H_2O)\}_3O_{66}]\cdot 3_2O$ (Figure 1) crystallizes in the monoclinic space group *C*2/*c*. As usual for polyoxometalates containing sodium as counterions, only eight of the 12 sodium ions have been found due to disorder on these ions (see for example ref 14). Structure of $[As_2W_{18}\{Co(H_2O)\}_3O_{66}]^{9-}$ is strictly similar to that found for **1**, with an average $Co-O_w$ bond length of 2.020 Å and $Co-O_{H2}$ bond length of 2.063 Å. As for compounds **1** and **5**, the paramagnetic metals form a nearly equilateral triangle with Co−Co distances of 5.048 and 5.088 Å.

$K_{11}[As_2W_{18}(VO)_3O_{66}]\cdot 23H_2O$ (Figure 2) crystallizes in the orthorhombic space group *Pnma*. As for compound $H_2Rb_4[As_2W_{21}O_{69}(H_2O)]\cdot 34H_2O$, a disorder has been found on the metals linking the two AsW_9 parts. It appears that if V(1) exhibits no significant disorder, with a V(1)═O bond directed toward the outside of the cavity, the two remaining vanadium ions occupy the sites V(2A) and V(2B) with a ratio $^2/_3$:$^1/_3$. V(2A) shows a V═O bond directed toward the outside of the cavity, while V(2B) shows the vanadyl bond directed toward the inside of the cavity (see Figure 2). As no water molecules have been found at a distance less than 2.4 Å, the environment of V(1), V(2A), and V(2B) can be all considered as square pyramidal. V(1) and V(2A) are distinguished from V(2B) by V═O distances. If the vanadyl bonds are longer than expected when the oxo group is directed outside the cavity (1.735(19) and 1.760(13) Å, respectively), the V(2B)═O bond is short (1.58(5) Å). Crystallographic data does not permit the two V^{IV} sites to be distinguished from the V^V one.

Magnetic Properties. SQUID measurements on the Cobalt cluster **2** have not been performed. For Co^{II} in square pyramidal environment, INS measurements are needed for the determination of the exchange pattern splitting of the ground state due to its large anisotropy.[15] The molar magnetic susceptibility χ_M of powder samples of **1**, **3**, and **4** have been measured as a function of the temperature. The results are shown in Figures 3 and 4 in the form of a $\chi_M T$ versus T plot. The isotropic exchange Hamiltonian $\hat{H} = -J(\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3 + \hat{S}_1\hat{S}_3)$ has been used, assuming that the magnetic cluster is formed by an equilateral triangle (see Table 2 for metal−metal distances).

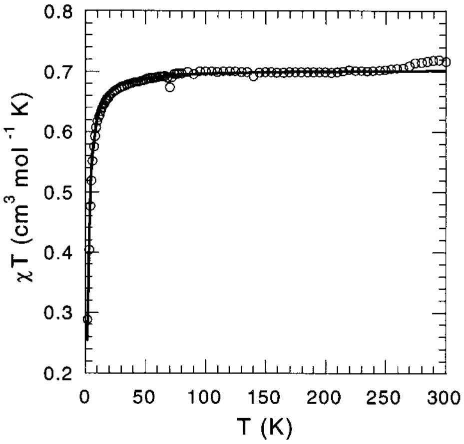

Figure 3. Temperature times magnetic susceptibility per mole of $K_{11}[As_2W_{18}(VO)_3O_{66}]\cdot 23H_2O$ **(3)** as a function of temperature. The solid line was generated from the best fit parameters given in the text.

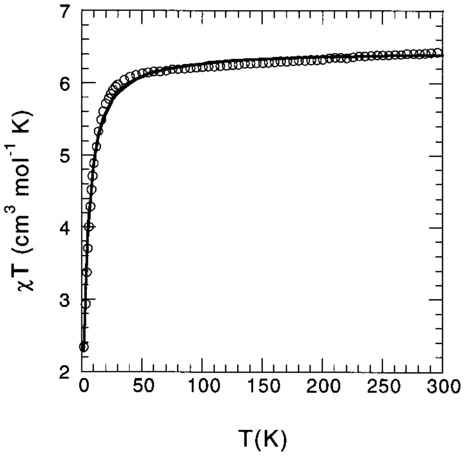

Figure 4. Temperature times magnetic susceptibility per mole of $Na_8[Ni(H_2O)_6)]_2[As_2W_{18}\{Ni(H_2O)\}_3O_{66}]\cdot 20H_2O$ **(4)** as a function of temperature. The solid line was generated from the best fit parameters given in the text.

The product $\chi_M T$ is nearly constant with T from 10 K ($\chi_M T = 13.28$ cm^3 mol^{-1} K) to room temperature ($\chi_M T = 13.22$ cm^3 mol^{-1} K) for the manganese trimer **1** (not shown). The $\chi_M T$ value is in agreement with three noncoupled high-spin Mn(II), and the temperature dependence can be mainly described by a Curie−Weiss law. Nevertheless, attempts to fit the data to a HDVV law have been done with

$$\chi_M T = (N\beta^2 g^2/4k)(1 + 20x^{3/2} + 105x^4 + 210x^{15/2} + 330x^{12} + 429x^{35/2} + 455x^{24} + 340x^{63/2})/(1 + 4x^{3/2} + 9x^4 + 10x^{15/2} + 10x^{12} + 9x^{35/2} + 7x^{24} + 4x^{63/2})$$

with

$$x = \exp(J/kT)$$

The best fit is obtained with $J = -0.03$ cm^{-1} and $g = 2.01$ with a value of $R = 3 \times 10^{-5}$,[16] showing a very weak antiferromagnetic coupling. Attempts to fit the data to a model

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[15] Clemente, J. M.; Andres, H.; Aebersold, M.; Borras-Almenar, J. J.; Coronado, E.; Güdel, H. U.; Büttner, H.; Kearly, G. *Inorg. Chem.* **1997**, *36*, 2244.

[16] $R = [\Sigma(\chi_M T_{calc} - \chi_M T_{obs})^2/\Sigma(\chi_M T_{obs})^2]$.

that considers an axial single ion anisotropy term and $J = 0$ cm^{-1} have not been successful, suggesting that the $\chi_M T$ dependence versus T at low temperature cannot be interpreted without considering the antiferromagnetic exchange.

The thermal variation of the $\chi_M T$ product of the mixed-valence $V^{IV}{}_2V^{V}$ compound **3** exhibits a strong decrease below 20 K (Figure 3). This clearly shows an antiferromagnetic nature of the interactions, leading to a singlet ground state. The $\chi_M T$ value at high temperature is consistent with the number of unpaired electrons per formula ($\chi_M T = 0.70$ cm^3 mol^{-1} K), indicating a real agreement between titration of the V^{IV} by Ce^{IV} and magnetic data. $\chi_M T$ could be expressed as follows:

$$\chi_M T = (2N\beta^2 g^2/k)/(3 + x^{-1})$$

with

$$x = \exp(J/kT)$$

The best fit parameters are $J = -2.9$ cm^{-1} and $g = 1.93$ ($R = 1 \times 10^{-4}$). This value of J is the smallest ever observed for polyoxovanadates, but can be compared with coupling constants previously determined for complexes containing μ_2-(PO_4) ($J = -9$ cm^{-1})[17] and μ_2-(AsO_4) ($J = -10$ cm^{-1})[18] bridges. This result seems reasonable considering the long O−W−O−W−O bridge connecting the two V^{IV} ions in **3**.

Complex **4** contains two different types of Ni^{II}. It has been postulated that only the exchange-coupled metals are those encapsulated by the $[\alpha\text{-}AsW_9O_{33}]^{9-}$ parts[19] (Figure 4). Thus $\chi_M T$ could be expressed[20]

$$\chi_M T = T/(T - \theta)[(2N\beta^2 g^2/k)(3x + 10x^3 + 14x^6)/(1 + 9x + 10x^3 + 7x^6) + g^2/2]$$

with

$$x = \exp(J/kT)$$

The best fit is obtained for $J = -1.7$ cm^{-1}, $g = 2.27$, and $\theta = -1.5$ K ($R = 3 \times 10^{-5}$), showing that the Ni−Ni exchange interactions are antiferromagnetic.

Conclusion

The synthesis and the single-crystal X-ray structural characterization of three novel arsenatopolytungstates $[As_2W_{18}M_3O_{66}]^{12-}$ ($M = Mn^{II}$, Co^{II}, and V^{IV}/V^{V}) are reported. In each case, the metals are in a square pyramidal environment. Except for the cobalt complex, the magnetic behavior of these complexes has been studied and interpreted. They all exhibit antiferromagnetic exchange interactions. Titration of V^{IV} by Ce^{IV} in compound **3** has been done. Surprisingly, it revealed that the complex is the mixed-valent $V^{IV}{}_2V^{V}$ species. This result is in agreement with the magnetic measurements. The analogous nickel complex has also been synthesized. It crystallizes with two $[Ni(H_2O)_6]^{2+}$ as counterions. This is mainly due to the instability of nickel complexes with $[\alpha\text{-}AsW_9O_{33}]^{9-}$ derivative, which can lead to a mixture of compounds in solution. Isolation and X-ray characterization of these different Ni^{II} complexes are under study.

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Supporting Information Available: Four X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) Castro, S. L.; Cass, M. E.; Hollander, F. J.; Bartley, S. L. *Inorg. Chem.* **1995**, *34*, 466.

(18) Gatteschi, D.; Tsukerblatt, B.; Barra, A. L.; Brunel, L. C.; Müller, A.; Döring, J. *Inorg. Chem.* **1993**, *32*, 2114.

(19) This assumption is supported by X-ray single-crystal analysis of this complex. Compound **4** crystallizes in the monoclinic system, space group $C2/c$, with $a = 13.885(9)$ Å, $b = 22.896(8)$ Å, $c = 31.788(2)$ Å, and $\beta = 98.386(30)°$. Comparison with complex **2** strongly suggests that **2** and **4** are isostructural. It appears that distances between the three Ni(II) of the polyoxoanion and the two counterions $[Ni(H_2O)_6]^{2+}$ are in the range 8−10 Å. Complete crystallographic data are not given due to poor refinement caused by the unstability of the crystal (R ($>2\sigma(I)$): R1 = 0.186).

(20) Gomez-Garcia, C. J.; Coronado, E.; Ouahab, L., *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 649.