A Cubane-Substituted Polyoxoanion: Structure and Magnetic Properties of $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 5H_2O$

Ulrich Kortz,*,[†] André Tézé, and Gilbert Hervé

Institut de Réactivité, Électrochimie et Microporosités, UMR C0173, Université de Versailles,
45 Avenue des États Unis, 78035 Versailles Cedex, France

Received September 22, 1998

The novel polyoxometalate $[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]^{2-}$ (**1**) has been synthesized and characterized by IR spectroscopy, polarography, elemental analysis, and magnetic measurements. An X-ray single-crystal analysis was carried out on $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 5H_2O$, which crystallizes in the orthorhombic system, space group *Pbcn*, with $a = 24.3131(3)$ Å, $b = 21.5400(1)$ Å, $c = 19.8936(3)$ Å, $V = 10418.4(2)$ Å^3, $Z = 8$, and $\rho_{calcd} = 3.767$ g/cm^3. Structural analysis based on 14 734 independent reflections leads to a solution, $R = 8.04\%$ ($I > 2\sigma(I)$). Anion **1** consists of a Ni_4O_4 cubane fragment which is inserted into a trivacant lacunary B-α-$[PW_9O_{34}]^{9-}$ Keggin unit. Magnetic measurements show that the Ni−Ni exchange interactions are ferromagnetic.

Introduction

Interest in polyoxometalates is increasing worldwide due to the enormous variety of structures leading to interesting and often unexpected properties in fields such as magnetochemistry, catalysis, and medicinal applications.[1−4] The mechanism of the formation of polyoxometalates, however, is still not well understood and often is described as self-assembly. This is especially true for synthetic techniques which do not allow one to monitor the reaction well, e.g., hydrothermal synthesis. Nevertheless, the synthesis of new compounds can often be based on a rational synthetic approach and careful observation of the reaction path. Polyoxometalates containing a certain number of transition metal ions (e.g., Ni^{2+}, Co^{2+}, Cu^{2+}) are of interest for their magnetic properties since the paramagnetic motifs are usually isolated from each other by the heteropolyanion frameworks. Therefore polyoxoanions incorporating paramagnetic metal ions may lead to exchange-coupled magnetic centers which are intermediate between molecular systems and extended solids.[5,6]

The challenge has been to synthesize polyoxoanions that contain a large number of transition metal ions, and the structural families of polyoxotungstates that have been investigated most are the sandwich-type Finke polyoxoanions, $[M_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[M_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ (M = Ni^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}).[7−10] In all of these structures the magnetically interesting fragment is the encapsulated rhomb-like tetrameric M_4O_{16} cluster. Another example of a Ni-substituted polyoxotungstate is $[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$, which is composed of three α-$[PW_9Ni_3]$ fragments being linked via two phosphate ions leading to a magnetic center of nine Ni atoms.[11]

Recently Coronado et al. reported the structure of the ion $[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]^{7-}$ which consists of a monocapped α-$[PW_9Ni_3]$ Keggin core, with the Ni triad being capped by a tungsten atom.[12]

In an attempt to maximize the number of Ni centers per polyoxoanion we investigated the interaction of the lacunary Keggin ion B-α-$[PW_9O_{34}]^{9-}$ with Ni^{2+} ions further.

Experimental Section

Synthesis. A 2.42 g sample of $Na_8H[B\text{-}PW_9O_{34}]$ (synthesized according to Domaille[13] and dried at 120 °C for 2 days) was added with stirring to a solution of 1.16 g of $NiSO_4\cdot 6H_2O$ in 50 mL of a 0.5 M sodium acetate buffer (pH 4.8). This solution was heated to 80 °C for 20 min and then cooled to room temperature. Addition of solid CsCl led to a greenish precipitate, which turned out to be a mixture of the light-green title compound and some not yet identified yellow material. The solid was collected in a sintered-glass frit and, because of the higher solubility of the yellow compound, purification was easily achieved by numerous washings with hot H_2O. The remaining light-green solid was air-dried (yield: 1.16 g; 35%), and some of it was redissolved in warm H_2O upon addition of solid $NaClO_4$. After filtration, the light-green filtrate was kept in an open container at room temperature. After a few days, green single-crystalline needles suitable

---

[†] Present address: Department of Chemistry, American University of Beirut, Bliss Street, P.O. Box 11-0236, Beirut, Lebanon. E-mail: ulrich.kortz@aub.edu.lb.

(1) Hill, C., Guest Ed. Special issue on Polyoxometalates. *Chem. Rev.* **1998**, January/February.
(2) *Polyoxometalates: from Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer: Dordrecht, The Netherlands, 1994.
(3) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34−48.
(4) Pope, M. T. *Heteropoly and Isopoly Oxometalates*; Springer-Verlag: Berlin, 1983.
(5) Gatteschi, D. *Adv. Mater.* **1994**, *6*, 635.
(6) *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer: Dordrecht, The Netherlands, 1991.
(7) Finke, R. G.; Droege, M. W.; Domaille, P. J. *Inorg. Chem.* **1987**, *26*, 3886.
(8) (a) Gómez-García, C. J.; Coronado, E.; Borrás-Almenar, J. J. *Inorg. Chem.* **1992**, *31*, 1667. (b) Casañ-Pastor, N.; Bas, J.; Coronado, E.; Pourroy, G.; Baker, L. C. W. *J. Am. Chem. Soc.* **1992**, *114*, 10380.
(9) Gómez-García, C. J.; Coronado, E.; Gómez-Romero, P.; Casañ-Pastor, N. *Inorg. Chem.* **1993**, *32*, 3378.
(10) (a) Gómez-García, C. J.; Borrás-Almenar, J. J.; Coronado, E.; Ouahab, L. *Inorg. Chem.* **1994**, *33*, 4016. b. Finke, R. G.; Weakley, T. J. R. *Inorg. Chem.* **1990**, *29*, 1235.
(11) Coronado, E.; Gómez-García, C. J. *Comments Inorg. Chem.* **1995**, *17*, 255.
(12) Gómez-García, C. J.; Coronado, E.; Ouahab, L. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 649.
(13) Domaille, P. J. *Inorganic Syntheses*; John Wiley & Sons: New York, 1990; Vol. 27, p 100.

10.1021/ic981138+ CCC: $18.00

Table 1. Crystal Data and Structure Refinement for $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 5H_2O$

empirical formula	$Cs_2PW_9Ni_4O_{48}H_{27}$
fw	2981.4
cryst syst	orthorhombic
space group	*Pbcn*
unit cell dimens	$a = 24.3131(3)$ Å $b = 21.5400(1)$ Å $c = 19.8936(3)$ Å
vol	10418.4(2) $Å^3$
Z	8
density (calcd)	3.767 Mg/m^3
abs coeff	22.699 mm^{-1}
$F(000)$	10 296
cryst size	$0.2 \times 0.02 \times 0.01$ mm^3
θ range for data collection	1.63−30.36°
limiting indices	$-33 \leq h \leq 34, -29 \leq k \leq 29, -27 \leq l \leq 20$
reflns collected	70 558
indep reflns	14 734 [R(int) = 0.2366]
abs correction	SADABS
refinement method	full-matrix least-squares on F^2
data/restraints/params	14703/0/342
goodness of fit on F^2	1.132
final R indices [$I > 2\sigma(I)$]	$R1^a = 0.0804$, $wR2^b = 0.1699$
R indices (all data)	R1 = 0.1319, wR2 = 0.2108
largest diff peak and hole	5.215 and −5.365 e $Å^{-3}$

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

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 5H_2O$

atom	x	y	z	$U(eq)^a$
W(1)	2419(1)	1802(1)	3399(1)	22(1)
W(2)	1016(1)	1837(1)	3635(1)	21(1)
W(3)	1852(1)	2766(1)	4632(1)	22(1)
W(4)	1243(1)	2048(1)	6171(1)	22(1)
W(5)	2728(1)	411(1)	6065(1)	21(1)
W(6)	3308(1)	1071(1)	4657(1)	23(1)
W(7)	2768(1)	2012(1)	5911(1)	23(1)
W(8)	409(1)	1140(1)	5134(1)	21(1)
W(9)	1234(1)	434(1)	6302(1)	20(1)
Cs(1)[b]	0	894(1)	2500	52(1)
Cs(2)	2938(1)	1373(1)	1422(1)	56(1)
Cs(3)[b]	1526(2)	3376(2)	2701(2)	75(1)
Ni(1)	1063(1)	−179(1)	8896(1)	20(1)
Ni(2)	1639(1)	1045(1)	857(1)	22(1)
Ni(3)	1836(1)	−458(1)	4962(1)	19(1)
Ni(4)	2362(1)	144(1)	3671(1)	21(1)
P(1)	1849(2)	1083(2)	4848(2)	14(1)

atom	x	y	z	U(iso)
O(1)	2404(6)	1122(6)	5210(7)	21(3)
O(2)	1387(6)	1141(6)	5389(7)	21(3)
O(3)	1798(5)	1630(6)	4354(6)	18(3)
O(4)	1798(5)	466(6)	4472(6)	19(3)
O(5)	562(6)	1866(7)	5789(7)	27(3)
O(6)	1070(7)	2613(7)	6755(8)	31(3)
O(7)	1206(6)	1321(6)	6691(7)	20(3)
O(8)	1651(6)	144(6)	8251(7)	21(3)
O(9)	1205(6)	−649(6)	4326(7)	19(3)
O(10)	612(6)	1738(7)	4467(7)	27(3)
O(11)	934(6)	1267(7)	8003(7)	25(3)
O(12)	2017(6)	559(7)	6451(7)	23(3)
O(13)	3980(7)	1068(7)	4419(8)	34(4)
O(14)	1253(6)	2659(6)	4073(7)	21(3)
O(15)	1010(5)	1031(6)	3474(6)	17(3)
O(16)	516(6)	645(7)	5954(7)	24(3)
O(17)	1673(6)	1986(7)	3098(7)	25(3)
O(18)	2885(6)	1289(7)	6411(7)	23(3)
O(19)	3070(6)	3(7)	6695(7)	29(3)
O(20)	3000(6)	1661(7)	4058(8)	29(3)
O(21)	2026(6)	2021(7)	6266(7)	26(3)
O(22)	1860(7)	3568(7)	4712(7)	28(3)
O(23)	393(7)	189(7)	8374(8)	30(3)
O(24)	−296(7)	1221(7)	5129(8)	30(3)
O(25)	1633(8)	1922(9)	8990(10)	48(5)
O(26)	2138(7)	1408(8)	7775(8)	38(4)
O(27)	2297(6)	−693(6)	4142(7)	23(3)
O(28)	2374(6)	993(7)	3226(7)	26(3)
O(29)	3018(6)	443(7)	4205(8)	30(3)
O(30)	3358(6)	581(6)	5493(7)	22(3)
O(31)	1048(7)	34(7)	7020(8)	30(3)
O(32)	1839(7)	−1337(7)	5405(8)	30(3)
O(33)	3084(6)	2560(7)	6402(7)	28(3)
O(34)	553(6)	503(7)	4601(7)	25(3)
O(35)	1401(6)	2540(6)	5387(7)	22(3)
O(36)	3328(6)	1798(6)	5311(7)	21(3)
O(37)	2492(6)	−186(7)	5533(7)	27(3)
O(38)	2454(6)	2532(7)	5208(7)	26(3)
O(39)	1354(6)	−161(6)	5710(7)	23(3)
O(40)	2324(6)	2621(7)	3900(7)	25(3)
O(41)	518(7)	2126(7)	3103(8)	32(3)
O(42)	2896(7)	−276(8)	3002(9)	39(4)
O(43)	2801(7)	2106(7)	2745(8)	31(3)
O(1W)	1645(10)	1169(11)	1885(12)	66(6)
O(2W)	624(10)	2729(11)	1647(12)	66(6)
O(3W)	−205(12)	2186(13)	6782(14)	87(8)
O(4W)	226(7)	3131(8)	4939(8)	36(4)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] Occupancy 0.5.

for X-ray crystallography were obtained. Anal. Calcd for $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 24H_2O$: Cs, 8.00; W, 49.79; Ni, 7.06; P, 0.93. Found: Cs, 8.18; W, 49.37; Ni, 7.05; P, 0.93. Elemental analysis was performed by the Service Central d'Analyse of CNRS at 69390 Vernaison, France.

X-ray Crystallography. A light-green needle with dimensions $0.2 \times 0.02 \times 0.01$ mm^3 was mounted on a glass fiber for indexing and intensity data collection at room temperature on a Siemens Smart-CCD diffractometer equipped with a normal focus 2.4 kW sealed-tube X-ray source ($\lambda = 0.710\ 73$ Å). Intensity data were collected in 1271 frames with increasing ω (width of 0.3° per frame). Unit cell dimensions were refined by a least-squares fit on $I \geq 10\sigma(I)$ reflections. Of the 70 558 reflections ($2\theta_{max} = 60.72°$), 14 734 unique reflections ($R_{int} = 0.23$) were considered observed ($I > 2\sigma(I)$) after *Lp* and absorption corrections. An absorption correction was performed using the *SADABS* program.[14] On the basis of systematic absences and statistics of intensity distribution, the space group was determined to be *Pbcn*. Direct methods were used to locate the metal atoms, and then the oxygen atoms were found from successive difference maps. The final cycle of refinement, including the atomic coordinates, anisotropic thermal parameters (all metal atoms and phosphorus), and isotropic thermal parameters (all oxygen atoms) converged at $R = 0.0804$ and $R_w = 0.1699$ ($I > 2\sigma(I)$). In the final difference map the deepest hole was −5.365 e $Å^{-3}$ and the highest peak 5.215 e $Å^{-3}$. Corrections for secondary extinction and anomalous dispersion were applied. Neutral-atom scattering factors were used. Structure solution and least-squares refinements were performed on a Silicon-Graphics Indy R5000 workstation using the *SHELXTL-Plus* programs. Crystallographic data are summarized in Table 1, and the positional parameters are shown in Table 2.

Spectral and Magnetic Measurements. The IR spectrum was recorded on a Nicolet 550 FTIR spectrophotometer in a KBr pellet. The polarogram was obtained in a sodium acetate buffer solution (1 M, pH 4.8). The magnetic measurements were carried out with a SQUID magnetometer in the temperature range 2−290 K up to 50 kG.

Results and Discussion

Structure of $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 5H_2O$. The novel polyoxoanion **1** can be described as a lacunary *B*-α-$[PW_9O_{34}]^{9-}$ unit which accommodates three edge-shared NiO_6 octahedra leading to a complete Keggin structure.[15] Since the Ni triad is capped by a fourth Ni atom, the structure of **1** can also be viewed as a trivacant Keggin ion which has incorporated a Ni_4O_4 cubane unit (see Figures 1 and 2). This is

---

(14) Sheldrick, G. M. *SADABS*; Siemens Analytical X-ray Instrument Division: Madison, WI, 1995.

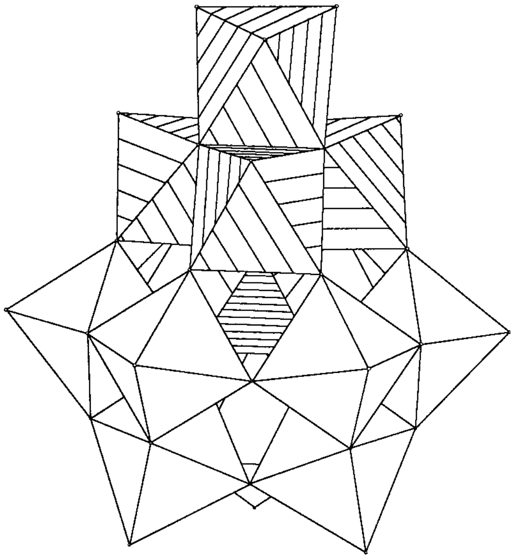

Figure 1. Polyhedral representation of $[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]^{2-}$ (**1**).

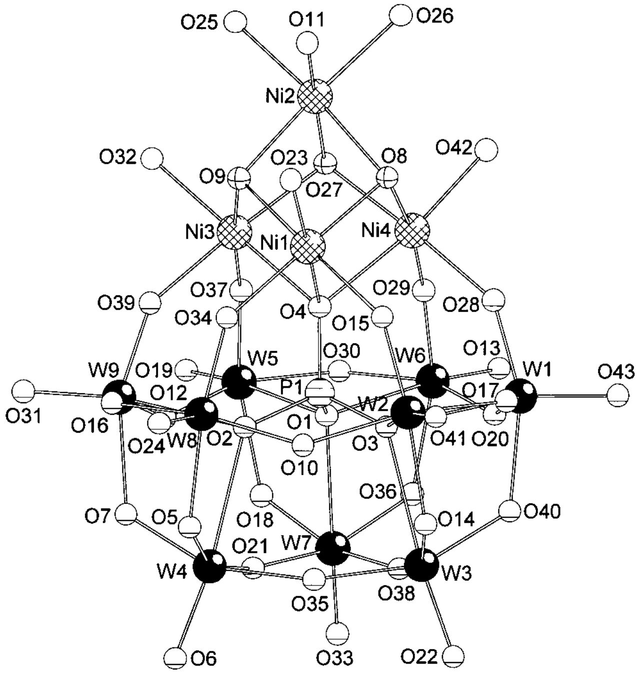

Figure 2. Ball and stick representation of $[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]^{2-}$ (**1**) showing the labeling scheme. The six water molecules are represented by the small empty spheres, and the three OH groups are shown as small crosshatched spheres. The two additional protons are not represented (see text).

the first example of a regular homometallic cubane fragment being associated with a lacunary polyoxoanion. The IR spectrum of the cesium salt of **1** (see Figure 3) is a good indicator of the purity of the compound in the solid state. The anion is considered to have a dinegative charge based on charge balance considerations, leading to an unusually low charge density. Two protons are assumed to be bound directly to surface oxygen atoms of the lacunary Keggin fragment. However, bond valence sum calculations did not allow the assignment of specific binding sites for the protons; most likely they are distributed over various oxygen atoms.[16] Bond lengths and angles of the *B*-α-$[PW_9O_{34}]$ fragment are not unusual.

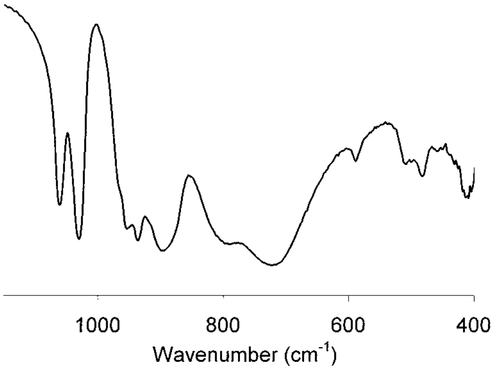

Figure 3. Infrared spectrum of $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot24H_2O$ recorded in a KBr pellet.

It is of interest to examine the coordination of Ni (see Figure 2). There are two types of Ni ions, the three of the triad (Ni1, Ni3, and Ni4) and the one capping them (Ni2). All of them are octahedrally coordinated by oxygen atoms, and the Ni atoms of the triad have one terminal ligand each (Ni1−O23, Ni3−O32, and Ni4−O42) whereas Ni2 has three terminal ligands (O11, O25, and O26). All terminal ligands are water molecules as indicated by bond valence sum calculations.[16] The bond valences for oxygens O23, O32, O42, O11, O25, and O26 are 0.31, 0.31, 0.32, 0.29, 0.34, and 0.26, respectively, strongly suggesting diprotonation for all of them. Using the same method allows the identification of the three μ_3-bridging oxygens of the cubane unit as OH groups. Summation of the bond valences for oxygens O8, O9, and O27 leads to values of 1.08, 1.10, and 1.01, respectively, indicating monoprotonation. Bond lengths and angles of the cubane fragment are shown in Table 3. From the distances of O11, O25, and O26 from each other (O11···O25, 2.96 Å; O11···O26, 2.98 Å; and O25···O26, 2.94 Å) it can be inferred that H-bonding is present between the three terminal H_2O molecules. Additional intermolecular H-bonding interaction is indicated by the distances of O11 and O25 from doubly bridging O atoms (W−O−W) of a neighboring polyoxoanion (O11···O7*, 2.70 Å; O25···O40*, 2.73 Å). There are three cesium counterions in the lattice, but two of them (Cs1 and Cs3) are in half-occupancy positions. The Cs^+ ions have coordination numbers 9, 10, and 11, respectively (Cs···O, 3.026−3.737(21) Å), and they are coordinated to oxygens of different polyoxoanions as well as to water molecules of hydration.

An interesting aspect of the novel polyanion **1** is that the Ni atom capping the triangular Ni_3 unit has three terminal water molecules, which is a rare feature in transition metal substituted polyoxometalates.[17] This unusual $Ni(OH_2)_3$ site may give rise to interesting catalytic properties of **1**; it might also be a good center for further structural derivatization of the PW_9Ni_4 complex.

Polarography studies of **1** in acetate buffer indicated a first reduction wave at −0.85 V and a not well resolved second wave at −0.97 V (vs SCE). This second wave is affected by reduction of the aqueous solvent which takes place at −1.1 V, i.e., at a potential about 200 mV more positive than the reduction potential of the pure buffer solution.

Magnetic Properties. The results of magnetic measurements for $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot5H_2O$ are displayed in

---

(15) Keggin, J. F. *Nature* **1933**, *131*, 908.

(16) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244.

(17) (a) Bosing, M.; Loose, I.; Pohlmann, H.; Krebs, B. *Chem.—Eur. J.* **1997**, *3*, 1232. (b) Rodewald, D.; Jeannin, Y. *C. R. Acad. Sci., Ser. IIc: Chim.* **1998**, *1*, 175.

Table 3. Bond Distances (Å) and Angles (deg) for the Ni_4 Cubane Fragment of $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 5H_2O$

Ni(1)−O(34)	2.00(2)	Ni(3)−O(39)	1.997(14)
Ni(1)−O(9)	2.009(13)	Ni(3)−O(9)	2.032(14)
Ni(1)−O(15)	2.023(13)	Ni(3)−O(37)	2.04(2)
Ni(1)−O(8)	2.043(14)	Ni(3)−O(27)	2.045(14)
Ni(1)−O(23)	2.09(2)	Ni(3)−O(32)	2.09(2)
Ni(1)−O(4)	2.212(13)	Ni(3)−O(4)	2.218(13)
Ni(2)−O(9)	2.021(13)	Ni(4)−O(8)	2.020(14)
Ni(2)−O(8)	2.043(14)	Ni(4)−O(29)	2.02(2)
Ni(2)−O(25)	2.06(2)	Ni(4)−O(28)	2.03(2)
Ni(2)−O(27)	2.102(14)	Ni(4)−O(27)	2.037(14)
Ni(2)−O(11)	2.11(2)	Ni(4)−O(42)	2.07(2)
Ni(2)−O(26)	2.14(2)	Ni(4)−O(4)	2.214(13)

O(34)−Ni(1)−O(9)	96.8(6)	O(9)−Ni(3)−O(4)	83.0(5)
O(34)−Ni(1)−O(15)	86.3(6)	O(37)−Ni(3)−O(4)	91.1(5)
O(9)−Ni(1)−O(15)	173.8(6)	O(27)−Ni(3)−O(4)	83.9(5)
O(34)−Ni(1)−O(8)	173.8(6)	O(32)−Ni(3)−O(4)	177.6(6)
O(9)−Ni(1)−O(8)	81.0(5)	O(8)−Ni(4)−O(29)	172.5(6)
O(15)−Ni(1)−O(8)	95.3(5)	O(8)−Ni(4)−O(28)	96.2(6)
O(34)−Ni(1)−O(23)	89.9(6)	O(29)−Ni(4)−O(28)	86.1(6)
O(9)−Ni(1)−O(23)	90.4(6)	O(8)−Ni(4)−O(27)	81.5(6)
O(15)−Ni(1)−O(23)	95.0(6)	O(29)−Ni(4)−O(27)	95.8(6)
O(8)−Ni(1)−O(23)	95.9(6)	O(28)−Ni(4)−O(27)	176.0(6)
O(34)−Ni(1)−O(4)	92.3(5)	O(8)−Ni(4)−O(42)	97.9(6)
O(9)−Ni(1)−O(4)	83.7(5)	O(29)−Ni(4)−O(42)	89.0(7)
O(15)−Ni(1)−O(4)	90.8(5)	O(28)−Ni(4)−O(42)	96.0(7)
O(8)−Ni(1)−O(4)	81.7(5)	O(27)−Ni(4)−O(42)	87.5(6)
O(23)−Ni(1)−O(4)	173.9(6)	O(8)−Ni(4)−O(4)	82.2(5)
O(9)−Ni(2)−O(8)	80.8(5)	O(29)−Ni(4)−O(4)	90.6(6)
O(9)−Ni(2)−O(25)	94.8(7)	O(28)−Ni(4)−O(4)	92.3(5)
O(8)−Ni(2)−O(25)	174.5(7)	O(27)−Ni(4)−O(4)	84.2(5)
O(9)−Ni(2)−O(27)	81.2(5)	O(42)−Ni(4)−O(4)	171.6(6)
O(8)−Ni(2)−O(27)	79.4(5)	P(1)−O(4)−Ni(1)	124.1(8)
O(25)−Ni(2)−O(27)	96.8(7)	P(1)−O(4)−Ni(4)	125.1(8)
O(9)−Ni(2)−O(11)	93.9(6)	Ni(1)−O(4)−Ni(4)	92.3(5)
O(8)−Ni(2)−O(11)	93.4(6)	P(1)−O(4)−Ni(3)	124.1(7)
O(25)−Ni(2)−O(11)	90.1(7)	Ni(1)−O(4)−Ni(3)	90.6(5)
O(27)−Ni(2)−O(11)	171.8(6)	Ni(4)−O(4)−Ni(3)	90.6(5)
O(9)−Ni(2)−O(26)	176.0(6)	Ni(4)−O(8)−Ni(1)	103.5(6)
O(8)−Ni(2)−O(26)	96.1(6)	Ni(4)−O(8)−Ni(2)	100.0(6)
O(25)−Ni(2)−O(26)	88.1(7)	Ni(1)−O(8)−Ni(2)	96.8(6)
O(27)−Ni(2)−O(26)	95.7(6)	Ni(1)−O(9)−Ni(2)	98.5(6)
O(11)−Ni(2)−O(26)	88.8(6)	Ni(1)−O(9)−Ni(3)	102.3(6)
O(39)−Ni(3)−O(9)	95.0(6)	Ni(2)−O(9)−Ni(3)	98.8(6)
O(39)−Ni(3)−O(37)	87.3(6)	W(2)−O(15)−Ni(1)	144.7(7)
O(9)−Ni(3)−O(37)	173.7(6)	Ni(4)−O(27)−Ni(3)	101.0(6)
O(39)−Ni(3)−O(27)	174.4(6)	Ni(4)−O(27)−Ni(2)	97.5(6)
O(9)−Ni(3)−O(27)	82.3(6)	Ni(3)−O(27)−Ni(2)	95.8(6)
O(37)−Ni(3)−O(27)	94.9(6)		
O(39)−Ni(3)−O(32)	88.7(6)		
O(9)−Ni(3)−O(32)	94.6(6)		
O(37)−Ni(3)−O(32)	91.3(6)		
O(27)−Ni(3)−O(32)	96.3(6)		
O(39)−Ni(3)−O(4)	91.0(5)		

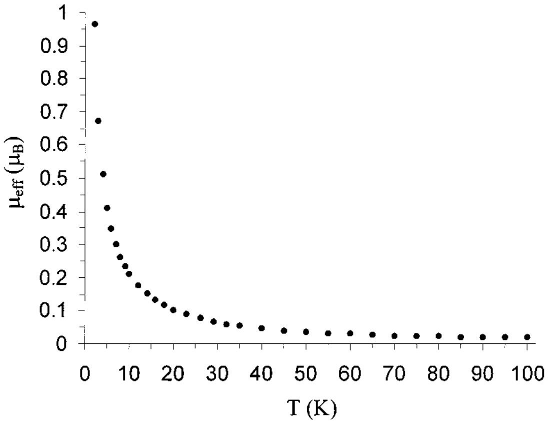

Figure 4. Plot of the effective magnetic moment as a function of temperature for $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 24H_2O$ in a constant magnetic field of 1 kG.

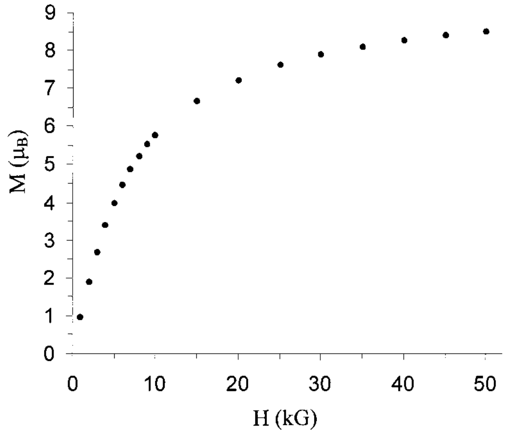

Figure 5. Plot of magnetization of $Cs_2[H_2PW_9Ni_4O_{34}(OH)_3(H_2O)_6]\cdot 24H_2O$ at 2 K.

Figures 4 and 5. Magnetization as a function of temperature at a constant magnetic field of 1 kG exponentially decreases with increasing temperature from 0.97 μ_B at 2 K to 0.1 μ_B at 20 K and then levels out to 0.011 μ_B at higher temperatures (Figure 4). Such behavior indicates ferromagnetic interactions of the nickel atoms in the Ni_4O_4 cubane fragment. This observation is in accordance with the dependence of magnetization on the magnetic field as shown in Figure 5. The measurements were done at $T = 2$ K and at magnetic fields from 1 to 50 kG. A Brillouin curve is observed with a saturation value of 8.51 μ_B at 50 kG, which is very close to the expected value for a $S = 4$ spin state and indicates that intercluster interaction is negligible.

A large number of coordination complexes containing the Ni_4O_4 cubane unit have been synthesized, and for many of them magnetic properties have been reported.[18] However, only a few Ni-containing polyoxometalates have been synthesized and investigated for their magnetic properties. Coronado's anion, $[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]^{7-}$, is structurally the one most similar to **1**, but it contains only three Ni atoms per anion.[12] Coronado reported a $S = 3$ ground state with intramolecular ferromagnetic interaction of the three Ni atoms per polyoxoanion and intermolecular antiferromagnetic interaction between polyoxoanions. The dimeric polyoxoanions, $[Ni_4(H_2O)_2(PW_9O_{34})_2]^{10-}$ and $[Ni_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$, respectively, contain four Ni atoms like **1**, but they have a rhomb-like Ni_4O_{16} structural motif.[7−10] However, because of edge-sharing of the NiO_6 octahedra in both cases the Ni−O−Ni angles are between 90 and 100°, i.e., a range in which ferromagnetic Ni−Ni exchange pathways are dominant.[19]

---

(18) (a) Salah El Fallah, M.; Rentschler, E.; Caneschi, A.; Gatteschi, D. *Inorg. Chim. Acta* **1996**, *247*, 231. (b) Halcrow, M. A.; Sun, J.-S.; Huffman, J. C.; Christou, G. *Inorg. Chem.* **1995**, *34*, 4167. (c) Blake, A. J.; Brechin, E. K.; Codron, A.; Gould, R. O.; Grant, C. M.; Parsons, S.; Rawson, J. M.; Winpenny, R. E. P. *J. Chem. Soc., Chem. Commun.* **1995**, 1983. (d) Ballester, L.; Coronado, E.; Gutiérrez, A.; Monge, A.; Perpiñán, M. F.; Pinilla, E.; Rico, T. *Inorg. Chem.* **1992**, *31*, 2053. (e) Paap, F.; Bouwman, E.; Driessen, W. L.; de Graaff, R. A. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1985**, 737. (f) Gladfelter, W. L.; Lynch, M. W.; Schaefer, W. P.; Hendrickson, D. N.; Gray, H. B. *Inorg. Chem.* **1981**, *20*, 2390. (g) Bertrand, J. A.; Marabella, C.; Vanderveer, D. G. *Inorg. Chim. Acta* **1978**, *26*, 113. (h) Barnes, J. A.; Hatfield, W. E. *Inorg. Chem.* **1971**, *10*, 2355. (i) Bertrand, J. A.; Ginsberg, A. P.; Kaplan, R. I.; Kirkwood, C. E.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1971**, *10*, 1971. (j) Andrew, J. E.; Blake, A. B. *J. Chem. Soc. A* **1969**, 1456.

(19) Ginsberg, A. P. *Inorg. Chim. Acta, Rev.* **1971**, *5*, 45.

Conclusions

We have reported a new heteropolyanion which is the first example of a cubane fragment incorporated in a lacunary polyoxoanion. The title compound is of interest for its structural and magnetic features. From a structural viewpoint the combination of the two families of cubane and polyoxometalate compounds in one single species is clearly unique. Another view of the structure allows identification of one of the Ni atoms as being part of a $[Ni(OH_2)_3]^{2+}$ cap which is attached to an overall complete Keggin structure, $[H_2PW_9Ni_3O_{34}(OH)_3(H_2O)_3]^{4-}$, at its most basic site to the bridging oxygens of the Ni_3 triad. The capping Ni has three terminal water molecules which can be of interest for structural derivatization and potential catalytic activity of the novel anion. The magnetic properties of the title compound are dominated by well-isolated Ni_4O_4 fragments in a polyoxometalate matrix which allows direct measurement of the exchange interaction of the paramagnetic cluster without any interference from intercluster interaction. It might be possible to synthesize analogues of the title compound containing other first-row transition metals leading to other, analogous compounds with interesting magnetic properties.

Acknowledgment. U.K. thanks the French Ministry of Education for an Alfred Kastler fellowship. We thank Dr. Didier Riou for help with X-ray crystallography and Mr. M. Nogues for doing the magnetic measurements. This manuscript was completed during a visit of U.K. in the laboratory of Prof. M. T. Pope at Georgetown University. We thank Prof. Pope for helpful discussions. Figures 1 and 2 were generated by Diamond Version 2.0B (copyright Crystal Impact GbR).

Supporting Information Available: Complete tables of bond lengths and angles and a table of anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

IC981138+