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Synthesis, Structure, and Magnetic Properties of $(n\text{-Bu}_4\text{N})_2[\{\text{Ni(MeOH)}_2\}_2\{\text{Mo(NO)}\}_2(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{\text{Mo}_5\text{O}_{13}\text{(OMe)}_4\text{(NO)}\}_2]$, a New Type of Polyoxometalate Incorporating a Rhomb-like Cluster

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The oxo−nitrosyl compound $(n\text{-Bu}_4\text{N})_2[\{\text{Na(MeOH)}\}\text{Mo}_5\text{O}_{13}\text{(OMe)}_4\text{(NO)}]\cdot 3\text{MeOH}$ reacts with various nickel(II) salts in methanol to give $(n\text{-Bu}_4\text{N})_2[\{\text{Ni(MeOH)}_2\}_2\{\text{Mo(NO)}\}_2(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{\text{Mo}_5\text{O}_{13}\text{(OMe)}_4\text{(NO)}\}_2]$, which has been characterized by single-crystal X-ray diffraction analysis and magnetic susceptibility measurements. This reaction shows the dual behavior of the defect Lindqvist-type species $[\text{Mo}_5\text{O}_{13}\text{(OMe)}_4\text{(NO)}]^{3-}$, which can act both as a ligand and as a source of the $\{\text{Mo(NO)}\}^{3+}$ unit. Furthermore, the reaction is reminiscent of the dissolution−precipitation of oxide supports in the preparation of supported catalysts and provides a novel illustration of the potential of polyoxometalates for probing the reactivity of oxides. The new polyoxomolybdate is made of a central rhomb-like $\{\text{Ni}_2\text{Mo}_2\}$ cluster linked to two terminal $[\text{Mo}_5\text{O}_{13}\text{(OMe)}_4\text{(NO)}]^{3-}$ units, each terminal cluster being linked to a molybdenum center of the central unit through two oxo ligands. The two Ni(II) ions are coupled in a ferromagnetic way ($J = 13.1\ \text{cm}^{-1}$).

Introduction

Polyoxometalates are a large class of compounds which are of fundamental and practical interest.[1] In addition, their structural features and their extensive surface chemistry make them suitable as models for probing the properties of non molecular oxides.[2−4] This is especially apparent in the field of catalysis, where the potential of polyoxometalates has been demonstrated both by successful industrial applications and by promising laboratory results.[5] In particular, transition-metal derivatives of polyoxometalates have been documented to catalyze a considerable number of reactions.[5a] Besides, polyoxometalate-supported transition-metal complexes have been considered as analogues of solid oxide-supported catalysts.[6] Certainly the investigation of the chemistry of transition-metal-substituted polyoxometalates might contribute to the understanding at the molecular level of the different steps of the preparation of supported catalysts by impregnation of oxides with solutions of transition-metal ions. Indeed, it is now clear that the oxide surface may play the role of a counterion, a supramolecular ligand, or a reagent.[7] In particular, the support dissolution, followed by recombination with metal ions in the solution and eventually by deposition of a novel species or precipitation of a novel phase, is more frequent than it was previously thought.[8,9]

Transition-metal-substituted polyoxometalates are usually obtained from lacunary polyoxometalates.[1a] Those derived from monovacant species have been considered as inorganic analogues of metalloporphyrins.[10] Dimetallo[11a] and trimetallo[11b] derivatives have been obtained respectively from $\gamma\text{-[SiW}_{10}\text{O}_{36}]^{8-}$ and from α- and $\beta\text{-[SiW}_9\text{O}_{34}]^{10-}$. Furthermore, trinuclear sandwich complexes have been obtained from the lacunary anions $[\text{XW}_9\text{O}_{34}]^{n-}$,[12] and there are extensive series of tetranuclear complexes based on the lacunary anions B-$[\text{PW}_9\text{O}_{34}]^{9-}$,[13a−d] $[\text{P}_2\text{W}_{15}\text{O}_{56}]^{12-}$,[14] and B-$[\text{ZnW}_9\text{O}_{34}]^{12-}$.[15] A

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cubane-substituted polyoxoanion[13e] and larger species containing nonanuclear clusters[13d,16] have also been reported.

A few years ago, we reported the synthesis[17] of the lacunary species $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$, which turned to be a quite versatile ligand.[18] Indeed, this species is able to bind to transition-metal cations as well as to main group or organic cations and may be bidentate,[19] tetradentate,[17,20] or bisbidentdate.[19,21] In addition, it eventually transforms into new nitrosyl polyoxometalates.[17a,22,23] We report here on the reaction of $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ (for short $\{\text{Mo}_5\}$) with Ni^{2+}, which leads to a rhomb-like $\{\text{Mo}_2\text{Ni}_2\}$ cluster linked to two $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ ligands. A parallel is drawn between this reaction and the dissolution−precipitation of the oxide support in the preparation of supported catalysts.

Experimental Section

Materials and Methods. The oxo−nitrosyl precursor $(n\text{-Bu}_4\text{N})_2[\{\text{Na(MeOH)}\}\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]\cdot 3\text{MeOH}$ (**1**) was prepared as reported previously.[17] Reagent grade solvents (methanol, acetone, and diethyl ether) and nickel salts ($\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$, and $\text{NiBr}_2\cdot 4\text{H}_2\text{O}$) were purchased from Strem Chemicals or Aldrich and used as received. Absorption and diffuse reflectance IR spectra were recorded using KBr support on a Bio-Rad FT-IR 165 spectrophotometer; UV−visible and near-IR spectra were recorded respectively on a Shimadzu model UV-2101 spectrophotometer and on a Beckman model 5240 spectrophotometer. The magnetic susceptibility of compound **2a** was measured in the temperature range 6−278 K in a 3000 Oe applied magnetic field on a SQUID magnetometer. Elemental analyses were performed by the Service Central d'Analyse of the CNRS (Vernaison, France).

Preparation of $(n\text{-Bu}_4\text{N})_2[\{\text{Ni(MeOH)}_2\}_2\{\text{Mo(NO)}\}_2(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]$ (2a). A sample of $(n\text{-Bu}_4\text{N})_2[\{\text{Na(MeOH)}\}\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]\cdot 3\text{MeOH}$ (**1**)[17] (0.34 g, 0.25 mmol) was dissolved in 10 mL of methanol, and an equimolar amount of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.064 g, 0.25 mmol) was added. The resulting violet solution was stirred at room temperature for 2 h and then allowed to stand at room temperature. Dark green crystals of **2a** suitable for the X-ray analysis were collected after 3 weeks and washed with diethyl ether. Subsequent crops were contaminated by increasing amounts of $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{19}]$. Typical yield: 0.05 g (28% based on $\{\text{Mo}_5\}$). IR (KBr, cm^{-1}): 1644 (br), 1633 (sh), 1060 (sh), 1035 (s), 940 (s), 895 (s), 830 (s), 720 (br). UV (CH_3COCH_3): λ_{max}, nm (ϵ_{max}, L mol^{-1} cm^{-1}) 615 (287), 1100 (4). Anal. Calcd for $\text{C}_{48}\text{H}_{126}\text{Mo}_{12}\text{N}_6\text{Ni}_2\text{O}_{48}$: C, 20.41; H, 4.50; Mo, 40.76; N, 2.98; Ni, 4.16. Found: C, 19.30; H, 4.26; Mo, 39.56; N, 2.95; Ni, 4.16.

Table 1. Summary of X-ray Diffraction Data for (**2a**)

formula	$\text{C}_{48}\text{H}_{126}\text{N}_6\text{O}_{48}\text{Mo}_{12}\text{Ni}_2$	V, Å^3	9596(7)
fw, g mol^{-1}	2824.2	Z	4
cryst syst	monoclinic	T, °C	20
space group	$P\ 2_1/n$	λ, Å	0.710 69
a, Å	18.960(7)	μ(Mo Kα), cm^{-1}	19.53
b, Å	25.990(15)	ρ_{calc}, g cm^{-3}	1.905
c, Å	20.669(5)	R^a	0.087
β, deg	109.55(2)	$R_w{}^b$	0.094

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

Preparation of $(\text{PPN})_2[\{\text{Ni(MeOH)}_2\}_2\{\text{Mo(NO)}\}_2(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]$ (2b). Green thin plates of **2b** came out in 3 weeks after addition of $(\text{Ph}_3\text{PNPPh}_3)\text{Cl}$ (0.143 g, 0.25 mmol) to a solution of **1** and $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ prepared as above. Yield: 0.05 g (23% based on $\{\text{Mo}_5\}$). Anal. Calcd for $\text{C}_{88}\text{H}_{114}\text{Mo}_{12}\text{N}_6\text{Ni}_2\text{O}_{48}\text{P}_4$: C, 30.94; H, 3.36; Mo, 33.7; N, 2.46; Ni, 3.44; P, 3.63. Found: C, 29.63; H, 3.06; Mo, 33.72; N, 2.51; Ni, 3.59; P, 3.71.

X-ray Diffraction Study of $(n\text{-Bu}_4\text{N})_2[\{\text{Ni(MeOH)}_2\}_2\{\text{Mo(NO)}\}_2(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})\}_2]$ (2a). A dark green crystal of **2a** was mounted on an Enraf-Nonius CAD4-F diffractometer using graphite-monochromated Mo Kα radiation. The lattice parameters and the orientation matrix were obtained from a least-squares fit of the setting angles of 25 automatically centered reflections in the range $10.0° < \theta < 10.4°$. Crystal data and data collection parameters are listed in Table 1. Intensities were corrected for Lorentz-polarization effects. An empirical absorption correction was applied using DIFABS.[24] The structure was solved by direct methods (SHELXS-86)[25] and subsequent Fourier syntheses. Only the reflections with $I > 3\sigma(I)$ were used in calculations. Metal atoms were refined anisotropically, while light atoms were refined isotropically. Hydrogen atoms were not included in the refinements which were carried out using large-block matrix least-squares procedures. Neutral-atom scattering factors were used with anomalous dispersion corrections applied. All computations were performed using CRYSTALS.[26a] A view of the anion in **2a** is given in Figure 1.[26b] The numbering scheme for the $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ anion follows that previously adopted.[17] For one of the $\{\text{Mo}_5\}$ units, the Mo(II) center was labeled Mo(1), while the Mo(VI) centers were numbered from Mo(2) to (Mo(5). Terminal oxygen atoms (O_t) were labeled $\text{O}_{ii'}$, where i is the number of the molybdenum atom and $i' =$ 1 or 2 depending on whether the oxygen atom is axial or equatorial. Bridging oxygen atoms (O_b) were labeled $\text{O}_{ij,}$ where i and j are the indexes of the bridged molybdenum atoms. Finally, the central oxygen atom (O_c) was labeled O(10). The numbering scheme for the second $\{\text{Mo}_5\}$ unit was obtained by adding 100 to each basic index. The numbering scheme for the central tetranuclear cluster is given in Chart 1. Selected bond distances are given in Table 2.

Results

Syntheses. Compound **2a** was the only nickel complex obtained by reaction of $(n\text{-Bu}_4\text{N})_2[\{\text{Na(MeOH)}\}\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]\cdot 3\text{MeOH}$ (**1**) with either $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$, $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$, or $\text{NiBr}_2\cdot 4\text{H}_2\text{O}$ in methanol. Using the above procedure, the yield never exceeded 30%. The formation of **2a** from **1** requires the degradation of part of the latter with liberation of a $\{\text{Mo(NO)}\}^{3+}$ fragment, which then reacts with Ni(II) and the remaining cluster $[\text{Mo}_5\text{O}_{13}(\text{OMe})_4(\text{NO})]^{3-}$ to give $[\{\text{Ni(MeOH)}_2\}_2\{\text{Mo(NO)}\}_2$-

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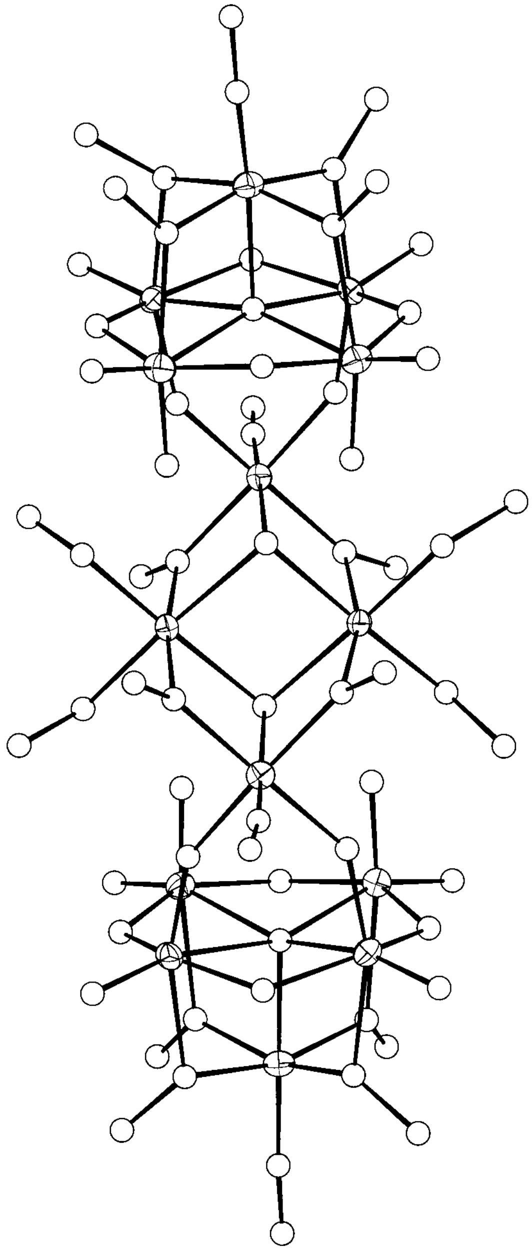

Figure 1. View[26b] of the anion of **2a**. Thermal ellipsoids are shown at the 20% probability level. See text for the atom-numbering scheme in the $[Mo_5O_{13}(OMe)_4(NO)]^{3+}$ units. The numbering scheme in the central unit is shown in Chart 1.

$(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{2-}$ and $(n\text{-}Bu_4N)_2[Mo_6O_{19}]$ as a byproduct. It was found that the yield in **2a** does not vary significantly upon either a moderate increase or decrease of the Ni(II)/$\{Mo_5\}$ ratio. The crystallization of **2a** slowed down and the yield decreased when the reactant mixture was heated or when dry methanol was used in place of wet methanol. While the unexpected effect of the temperature is still unexplained, the role of water in the decomposition of **1** has already been observed. Indeed, **1** transforms into $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$ upon pouring into water. On the other hand, the yield in **2a** may be increased up to >40% (based on $\{Mo_5\}$) by the addition of appropriate precursors for the $\{Mo(NO)\}^{3+}$ unit, such as the dinuclear complex $[Mo(NO)(Me_2CNO)_2(\mu\text{-OMe})]_2$.[27] This means that the liberation of $\{Mo(NO)\}^{3+}$ fragments from the latter effectively competes with the degradation of **1**.

Chart 1

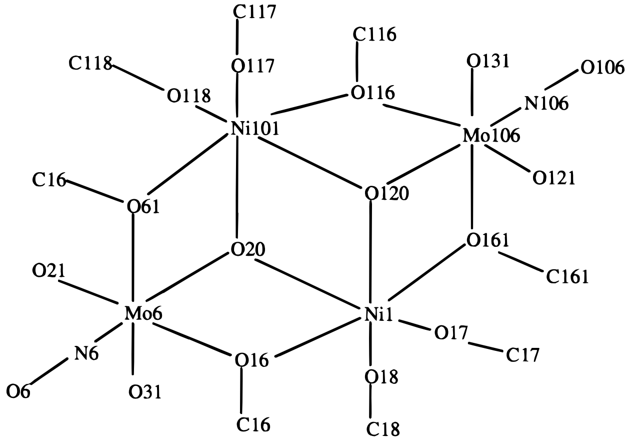

Table 2. Selected Bond Lengths (Å) for **2a**

Mo(6)−O(21)	2.03(3)	Mo(6)−O(31)	2.01(3)
Mo(6)−N(6)	1.73(4)	Mo(6)−O(16)	1.97(3)
Mo(6)−O(20)	2.12(3)	Mo(6)−O(61)	1.88(3)
Ni(1)−O(16)	2.04(3)	Ni(1)−O(17)	2.10(3)
Ni(1)−O(18)	2.00(3)	Ni(1)−O(20)	2.19(3)
Ni(1)−O(120)	2.11(3)	Ni(1)−O(161)	2.06(3)
Mo(106)−O(121)	2.01(2)	Mo(106)−O(131)	2.03(3)
Mo(106)−N(106)	1.70(4)	Mo(106)−O(116)	1.95(3)
Mo(106)−O(120)	2.17(3)	Mo(106)−O(161)	1.92(3)
Ni(101)−O(20)	2.06(3)	Ni(101)−O(61)	2.07(3)
Ni(101)−O(116)	2.10(3)	Ni(101)−O(117)	1.97(3)
Ni(101)−O(118)	2.05(3)	Ni(101)−O(120)	2.14(3)
C(12)−O(12)	1.36(6)	C(13)−O(13)	1.47(6)
C(14)−O(14)	1.52(6)	C(15)−O(15)	1.49(7)
N(1)−O(1)	1.29(5)	N(101)−O(101)	1.22(4)
C(112)−O(112)	1.40(6)	C(113)−O(113)	1.42(6)
C(114)−O(114)	1.40(5)	C(115)−O(115)	1.38(5)
N(6)−O(6)	1.18(4)	C(16)−O(16)	1.38(5)
C(17)−O(17)	1.50(6)	C(18)−O(18)	1.45(7)
C(61)−O(61)	1.44(5)	N(106)−O(106)	1.25(5)
C(116)−O(116)	1.49(6)	C(117)−O(117)	1.57(7)
C(118)−O(118)	1.57(6)	C(161)−O(161)	1.46(5)

Compound **2a** is insoluble in most solvents, notably methanol. However, it is slightly soluble and fairly stable in acetone, which allows its recrystallization in 1/1 methanol/acetone. It is slightly soluble in acetonitrile, where it transforms into $(n\text{-}Bu_4N)_3[Mo_6O_{18}(NO)]$. The PPN salt $(PPN)_2[\{Ni(MeOH)_2\}_2\{Mo(NO)\}_2(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ (**2b**) may be obtained as a green microcrystalline powder in a ca. 25% yield by addition of bis(triphenylphosphoranylidene)ammonium chloride to the initial solution of **1** and $NiCl_2{\cdot}6H_2O$. On the other hand, only the tetrabutylammonium salt **2a** was recovered after addition of $(Me_4N)Cl$ or $(Et_4N)Cl$ to the initial solution.

Crystal Structure of 2a. The crystal of **2a** consists of tetrabutylammonium cations and discrete anions $[\{Ni(MeOH)_2\}_2\{Mo(NO)\}_2(\mu_3\text{-OH})_2(\mu\text{-OMe})_4\{Mo_5O_{13}(OMe)_4(NO)\}_2]^{2-}$. The anion of **2a** may be viewed as a rhomb-like $\{Ni_2Mo_2\}$ cluster linked to two ligands $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$. Although this anion has no crystallographically imposed symmetry, its symmetry closely approaches C_{2h}. The central $\{Ni_2Mo_2\}$ unit is formed by four edge-sharing octahedra. Such a $\{M_4\}$ arrangement is found in the sandwich complexes $[M_4(H_2O)_2\{PW_9O_{34})_2\}]^{z-}$ [13a−d] and $[M_4(H_2O)_2\{P_2W_{15}O_{56})_2\}]^{z'-}$ [14] and in a number of tetramolybdates,[3] the prototype being $[Mo_4O_{10}(OMe)_6]^{2-}$.[28] According to the charge balance, six protons are associated with the $\{Mo_2Ni_2\}$ unit. These could be

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located from bond valence sum (BVS) calculations where BVS $= \sum BV_i = \sum \exp[(r_0 - r_i)/B]$, $r_0 = 1.390$ Å for $C^{2-}-O^{2-}$, $r_0 = 1.907$ Å for $Mo^{6+}-O^{2-}$, $r_0 = 1.835$ Å for $Mo^{2+}-O^{2-}$, $r_0 = 1.654$ Å for $Ni^{2+}-O^{2-}$, and $B = 0.37$.[29] The BVS values fall in the range 1.796−2.084, except for the two oxo ligands O(20) and O(120) and the four terminal methoxo ligands O(17), O(18), O(117), and O(118), which have BVS values in the range 0.958−1.242 and are therefore presumed to be protonated. Thus, the Mo sites of the $\{Ni_2Mo_2\}$ cluster display MoO_5N coordination to one nitrosyl group, two terminal oxo ligands of the $\{Mo_5\}$ units, two doubly bridging methoxo ligands, and one triply bridging hydroxo ligand. The Ni(II) centers display NiO_6 coordination to two terminal methanol ligands, two doubly bridging methoxo ligands, and two triply bridging hydroxo ligands (Chart 1).

Each terminal $\{Mo_5\}$ cluster is linked to a molybdenum center of the central unit through two terminal oxo ligands. Such a bidentate coordination mode of the $\{Mo_5\}$ cluster is precedented.[19] The geometry of the chelated $\{Mo_5\}$ cluster is only slightly altered with respect to the free (in fact sodium complex) $\{Mo_5\}$ unit.[17] However, the Mo−O bond lengths involving the oxygen atoms linked to the central unit are in the range 1.78−1.83 Å and thus are significantly lengthened in relation to those involving "free" terminal oxygen atoms (1.69−1.74 Å). Although a thorough discussion of hydrogen bonds is precluded because the hydrogen atoms could not be located, weak hydrogen bonding likely occurs between the μ_3-OH ligands of the central unit and the "free" terminal oxo ligands of the $\{Mo_5\}$ ligands owing to O···O distances of ca. 2.9 Å.

Infrared Spectra. The IR spectrum of **2a** is dominated by the characteristic features of the $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ unit. However, the central $\{Ni_2Mo_2\}$ cluster shows itself in the splitting of the band assigned to ν(NO) at ca. 1640 cm^{-1} and in the enhancement of the bands assigned to ν(O−C) of methoxo and methanol ligands around 1035 cm^{-1}. The three-band pattern in the region 830−940 cm^{-1} is characteristic of a bidentate $\{Mo_5\}$ unit, and the broad band at 720 cm^{-1} is attributed to ν(Mo−O−Mo).[18] The latter is masked by absorption features characteristic of the PPN cation in the spectrum of **2b**. Additional features at 3468 and 3306 cm^{-1} in the spectra of **2a** and **2b** arise from the OH stretching vibration of the μ_3-OH and terminal CH_3OH ligands.

Electronic Spectroscopy. The electronic spectrum of **2a** in acetone displays a very broad shoulder at 615 nm ($\epsilon = 287$ L mol^{-1} cm^{-1}) on the tail of a more intense charge-transfer band, instead of the well-defined band observed for **1** as well as for a number of other derivatives including the $\{Mo_5\}$ unit, and assigned to a $d_{xz},d_{yz} \rightarrow d_{xy}$ transition within the $\{Mo^{II}(NO)\}^{3+}$ unit (ϵ ca. 70 L mol^{-1} cm^{-1}).[17] It is noteworthy that the intensity of this feature accounts fairly well for the presence of four $\{Mo^{II}(NO)\}^{3+}$ chromophores in **2a**. In addition, the spectrum of **2a** displays a weak band at ca. 1100 nm ($\epsilon = 4$ L mol^{-1} cm^{-1}) which may be attributed to a $^3A_{2g} \rightarrow {}^3T_{2g}$ transition within the $Ni^{II}O_6$ chromophores, assuming octahedral symmetry. The two other spin-allowed d−d transitions for the Ni(II) ions are masked by the absorption of the $\{Mo^{II}(NO)\}^{3+}$ chromophore and by ligand-to-metal charge-transfer absorption.

Magnetic Properties. The magnetic behavior of **2a** is displayed in Figure 2. The product $\chi_M T$ increases continuously as T is decreased, which indicates the presence of ferromagnetic exchange interactions within the anion of **2a**. The terminal $\{Mo_5\}$ units are composed of linear diamagnetic d^4-$\{Mo^{II}(NO)\}^{3+}$ and d^0-Mo^{VI} units and, thus, are diamagnetic. The central $\{Ni_2Mo_2\}$ unit is made of two diamagnetic d^4-$\{Mo^{II}(NO)\}^{3+}$ units and two octahedral d^8-Ni^{II} centers. Thus the only exchange interactions are those between the Ni^{II} ions through the OH bridges.

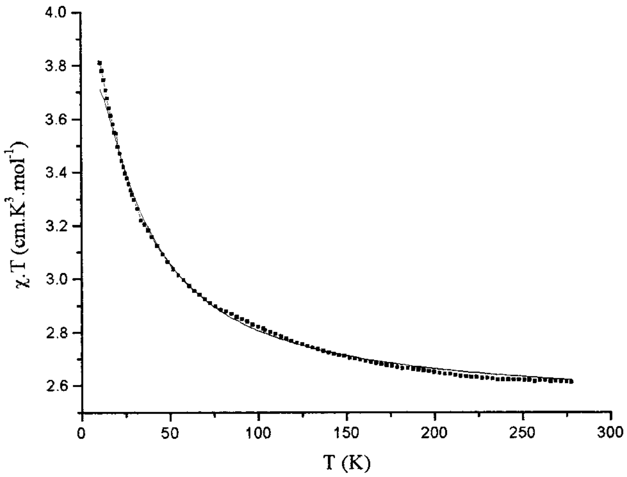

Figure 2. Plot of $\chi_M T$ vs T for **2a**. The solid line represents the best fit to eq 1.

At first, both an isotropic exchange interaction, written as $J\hat{S}_1\hat{S}_2$, and an axial anisotropy were considered, and the susceptibility was calculated from the expressions given by Ginsberg et al.[30] As the fitting of the magnetic data led to a quite small, hardly significant, value of the zero-field splitting parameter, the local anisotropy was then neglected and the experimental data were fitted using the following expression of the susceptibility:

$$\chi_M = \frac{2N(g\beta)^2}{kT} \frac{5 + \exp\frac{-2J}{kT}}{5 + 3\exp\frac{-2J}{kT} + \exp\frac{-3J}{kT}} \qquad (1)$$

where g, β, and k have their usual meanings. The best fit of this equation was obtained with $g = 2.24$ and $J = +13.1$ cm^{-1} (Figure 2). There is no evidence of intermolecular interaction, which is consistent with the crystal structure.

Discussion

Complexes of the type $(n\text{-}Bu_4N)_2[M^{II}(H_2O)_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ (M^{II} = Mn, Co, or Cu) have been obtained by reaction of $M(NO_3)_2 \cdot xH_2O$ (M = Mn, $x = 4$; M = Co, $x = 6$; M = Cu, $x = 3$) with **1** in methanol.[18] According to their IR spectra, these compounds are clearly similar. The Mn and Co compounds have been characterized by single-crystal X-ray crystallography.[18] Although they are not isomorphous, their anions are indeed isostructural. The M^{II} ion achieves octahedral MO_6 coordination to two trans H_2O ligands and two bidentate $\{Mo_5\}$ ligands. We could not obtain evidence for the formation of the similar product $(n\text{-}Bu_4N)_2[Ni^{II}(H_2O)_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ by reaction of hydrated Ni(II) salts with **1** in methanol. Instead, only compound **2a** was obtained. The anion of **2a** contains two intact $\{Mo_5\}$ units linked in the same way as in the complexes $(n\text{-}Bu_4N)_2[M^{II}(H_2O)_2\{Mo_5O_{13}(OMe)_4(NO)\}_2]$ (M^{II} = Mn or Co). However, part of the ligand has been decomposed, and

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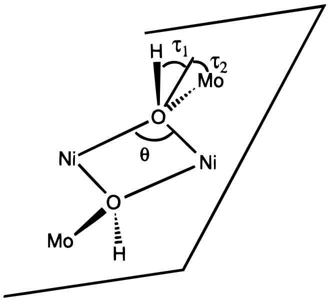
subsequent reaggregation led to the formation of a new $\{Ni_2Mo_2\}$ cluster. Although various ligands are known to transform upon reaction with metal ions, the above reaction is especially reminiscent of the reactions of the dissolution−reprecipitation of oxides by reaction with metal ions in solution. The latter mechanism has been demonstrated by the formation of nickel(II) phyllosilicates[8a] and hydrotalcite-like mixed phases[8b] upon contact of nickel precursors in solution respectively with silica and γ-alumina, and by the formation of the Anderson-type heteropolyoxomolybdate $[Al(OH)_6Mo_6O_{18}]^{3-}$ upon deposition of ammonium molybdate on γ-alumina.[8c,9] It can be expected that related studies on polyoxometalates will provide synthetic, spectroscopic, and structural models for the understanding at the molecular level of the various steps in the preparation of supported catalysts.

Chart 2



The Ni(II) ions in **2a** are coupled in a ferromagnetic way. Other ferromagnetic nickel(II) clusters encapsulated in Keggin or Dawson trivacant polyoxotungstates have been reported.[13,14] Ferromagnetic exchange interactions through oxo or hydroxo bridges occur in both rhomb-like[13,14] and cubane-type[13e,31−33] tetranuclear clusters which consist of edge-sharing octahedra. The exchange interaction is composed of two terms which represent respectively a ferromagnetic contribution and an antiferromagnetic contribution.[34] It is known that in a bis (μ-hydroxo) dinuclear complex, the J value depends on the bridging Ni−O−Ni angle (θ), the dihedral angle between the O−Ni−O planes (δ), and the out-of-plane deviations of the groups attached to the bridging atom (τ). Thus the exchange interaction between the two nickel(II) ions in the anion of **2a** can be analyzed using Chart 2. The deviation of the dinuclear unit from centrosymmetry is quite small so that δ is very close to 180° and only one set of (averaged) parameters θ, τ_1 (for H), and τ_2 (for Mo) is required: $\theta \cong 95.5°$, $\tau_1 \cong 50°$, and $\tau_2 \cong 10°$.

Ferromagnetic exchange pathways should be dominant for θ in the range 90−95°, a situation close to ensuring orthogonality between the Ni(II) magnetic orbitals. This appears to be the case for **2a**. On the contrary, antiferromagnetic exchange interactions have been observed in phenoxy-bridged dinuclear nickel complexes with Ni−O−Ni angles from 99.5° to 105.7°.[35] A linear dependence of the exchange coupling constant on the Ni−O−Ni angle has been found in these complexes.[35b] The crossover angle of 97° from ferromagnetic to antiferromagnetic interaction is nearly the same as for dihydroxy-bridged dinuclear copper complexes.[36] Although the extrapolation at a bridge angle of 95.5° properly predicts ferromagnetic coupling for **2a**, the extrapolated value, $J = +24$ cm^{-1}, is nearly twice the experimental value. Clearly the nature (here H and a Mo(II) center) and the geometrical arrangement (i.e., the values of τ_1 and τ_2) of the groups attached to the bridging oxygen atom have a strong influence on the orbitals of the oxygen bridge involved in the exchange and therefore on the antiferromagnetic part of the interaction. Our result provides a new experimental point for better understanding of the detailed mechanism of the exchange as analyzed by quantum calculations.[37]

Concluding Remarks

This work provides a novel representative of the ubiquitous class of rhomb-like tetranuclear clusters and a further illustration of the dual behavior of the oxo−nitrosyl complex $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$, which has proved a versatile ligand and a convenient source of the $\{Mo(NO)\}^{3+}$ unit. More generally, it illustrates the potential of polyoxometalates for probing the reactivity of oxides.

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Supporting Information Available: Listings of the atom coordinates, isotropic and anisotropic thermal parameters, and selected bond lengths and angles for **2a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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