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Synthesis, X-ray Crystal Structures, and Magnetic Properties of Ni_4 Complexes of a Macrocyclic Tetranucleating Ligand

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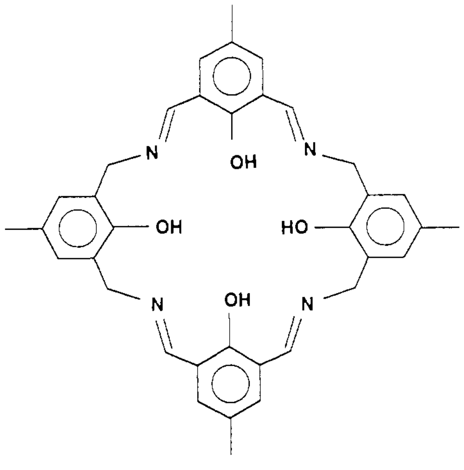
Replacement of the acetato ligands in the previously reported $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(CH_3CO_2)_2$ (where LH_4 is the macrocyclic tetra Schiff base formed by condensation of two molecules of 2,6-diformyl-4-methylphenol with two molecules of 2,6-bis(aminomethyl)-4-methylphenol) either by azide or by methoxide gives derivatives which, X-ray studies reveal, contain the intact $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)]^{2+}$ core present in the acetato complex. Crystal data: azido complex, $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2]$, monoclinic, $C2/c$ (No. 15), a = 24.121 (3) Å, b = 12.069 (3) Å, c = 14.234 (4) Å, β = 101.15 (1)°, Z = 4; methoxo complex, $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]{\cdot}3.36CH_3OH{\cdot}0.7H_2O$, monoclinic, $P2_1/a$ (No. 14), a = 13.243 (2) Å, b = 32.495 (6) Å, c = 14.431 (3) Å, β = 102.39 (2)°, Z = 4. The azido and methoxo complexes, like the parent acetato complex, contain a bowllike $[LNi_4(OH)]^{3+}$ unit with an unusual μ_4-OH group at the bottom of the bowl located below the center of an approximately rectangular Ni_4 arrangement. An unusual strongly hydrogen-bonded $(CH_3O{\cdot}H{\cdot}OCH_3)^-$ unit with a short O⋯O separation (2.492 (7) Å in the azido; 2.42 (1) Å in the methoxo) is located inside the bowl bridging the upper "face" of the Ni_4 group on the side opposite to the μ_4-OH group, each methoxo oxygen bridging two Ni's. Two μ_2-bridging sites on the lower convex side of the bowl which in the acetato complex are occupied by μ_2-acetates are occupied by H-bonded $(N_3^-{\cdot}HOH)$ combinations in the azido complex and by H-bonded $(CH_3O{\cdot}H{\cdot}OCH_3)^-$ combinations (O⋯O separation 2.53 (1) and 2.56 (1) Å) in the methoxo complex. The three complexes show very similar magnetic properties (300–4.2 K), the Ni_4 group behaving as an essentially noninteracting pair of Ni_2 units within which there is antiferromagnetic coupling with J values -33.3 cm^{-1} (acetato), -28.5 cm^{-1} (azido), and -30.0 cm^{-1} (methoxo); the coupled pairs are very probably those involving the dialdehyde-derived phenoxide bridges, which are essentially trigonal.

Introduction

Complexes of ligands which bind two or more metal centers in close proximity are important as potential catalysts,[3] as models for a number of metalloproteins,[4] and because of the opportunities they provide for the investigation of magnetic interactions. The study of macrocyclic ligands and their complexes has for many years been a very active area of research, interest in which continues to expand.[5] Described in this report are some complexes of the macrocyclic ligand I, represented LH_4, which is capable of binding four metal centers in close proximity. The synthesis and structure of the Ni_4 derivative $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(CH_3CO_2)_2$, hereinafter referred to as the acetato complex, were reported recently;[6] the form of the acetato complex most convenient for isolation and subsequent use is the monohydrate, while the material studied crystallographically was the tetramethanolate.[6] The synthesis and structure of two Ni_4 complexes related to the acetato complex are described below together with the magnetic properties of the three complexes.



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Experimental Section

Synthesis. Analyses were performed by The Microanalytical Service, Department of Chemistry, University of Queensland, and The Australian Microanalytical Service, P.O. Box 211, Port Melbourne, Victoria 3207, Australia.

Azido Complex. A boiling solution of sodium azide (0.097 g, 1.5 mmol) in a mixture of water (2 mL) and methanol (8 mL) was added to the solid acetato complex monohydrate[6] (0.146 g, 0.14 mmol) whereupon the solid dissolved. The mixture was boiled down at atmospheric pressure until crystals started to separate and was then allowed to cool. The green crystalline product was collected, washed with methanol, and dried in air. Yield: 0.094 g, 66%. Anal. Calcd for $C_{38}H_{47}N_{10}O_{10}Ni_4$: C, 43.9; H, 4.6; N, 13.5. Found: C, 43.5; H, 4.3; N, 13.9.

Methoxo Complex. The acetato complex monohydrate[6] (0.200 g, 0.19 mmol) was dissolved in a boiling solution of potassium hydroxide (ca. 85%, 0.35 g, ca. 5.3 mmol) in methanol (18 mL). The hot mixture was filtered, and the filtrate was boiled down at atmospheric pressure to ca. 5 mL. Upon standing at 0 °C the solution deposited a green solid, which was recrystallized from methanol, collected, washed with methanol, and dried in air. Anal. Calcd for $C_{42}H_{62}N_4O_{15}Ni_4$: C, 45.9, H, 5.7; N, 5.1; Ni, 21.4. Found: C, 45.3; H, 5.8; N, 5.5; Ni, 22.1.

X-ray Crystallography. Crystals of the azido and methoxo complexes suitable for X-ray diffraction studies were obtained from methanol; both crystals were green in color. In both cases crystals were sealed with

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[1] University of Melbourne.
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[4] Fenton, D. E. In *Advances in Inorganic and Bioinorganic Mechanisms*; Sykes, A. G., Ed.; Academic Press Inc.: London, 1983; Vol. 2, p 187.
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Table I. Crystal Data Together with Details of the Data Collections and Structure Refinements for $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2$ and $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]{\cdot}3.36CH_3OH{\cdot}0.7H_2O$

	$[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2]$	$[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]{\cdot}3.36CH_3OH{\cdot}0.7H_2O$
formula	$C_{38}H_{44}N_{10}Ni_4O_9$	$C_{45.36}H_{68.84}N_4Ni_4O_{15.06}$
fw	1019.7	1146.0
cryst system	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	$P2_1/a$ (No. 14)
a, Å	24.121 (3)	13.243 (2)
b, Å	12.069 (3)	32.495 (6)
c, Å	14.234 (4)	14.431 (3)
β, deg	101.15 (1)	102.39 (2)
V, Å^3	4066 (3)	6065 (4)
Z	4	4
ρ(calcd), g cm^{-3}	1.666	1.25
temp, K	293 (2)	293 (2)
radiation (λ, Å)	Mo Kα, graphite monochromator (0.710 69)	Mo Kα, graphite monochromator (0.710 69)
no. of intensity control reflcns	3 measd every 3600 s; no significant variation	3 measd every 10 000 s; no significant variation
F(000)	2104	2388
cryst dimens (dist in mm from point within crystal)	$\pm(100)$, 0.09; $\pm(01\bar{1})$, 0.09; $\pm(11\bar{1})$, 0.09; $\pm(\bar{1}11)$, 0.11	$\pm(100)$, 0.27; $\pm(010)$, 0.14; $\pm(001)$, 0.07
μ, cm^{-1}	18.7	12.6
transm factors (SHELX-76)	max 0.749, min 0.719	max 0.843, min 0.697
2θ limits, deg	$2 \le 2\theta \le 50$	$2 \le 2\theta \le 50$
hkl limits		
h	$-2 \rightarrow 28$	$-1 \rightarrow 15$
k	$0 \rightarrow 14$	$0 \rightarrow 38$
l	$-16 \rightarrow 16$	$-17 \rightarrow 17$
scan mode	$\omega/2\theta$	$\omega/2\theta$
instrument	Enraf-Nonius CAD-4F diffractometer	
no. of reflcns collcd	4494	12297
no. of unique reflcns	3982	9805
R_{int}	0.051	0.022
no. of unique reflcns used $[I > n\sigma(I)]$	2470 ($n = 2.5$)	3922 ($n = 2$)
methods	refinement by least-squares; function minimized $\sum w\Delta^2$, where $\Delta = \|\|F_o\| - \|F_c\|\|$; SHELX-76	
weighting scheme	$w = k/[\sigma^2_{(F)} + gF^2]$	
g	0.001	0.001
k	1.521	1.0
final *R* $[=\sum\|\Delta\|/\sum\|F_o\|]$	0.060	0.081
final R_w $[=\sum w^{1/2}\|\Delta\|/\sum w^{1/2}\|F_o\|]$	0.060	0.080
max shift/esd for non-H atoms	0.002	0.05
goodness of fit	1.477	2.223
max resid electron density, e Å^{-3}	1.19	1.04

mother liquor in Lindemann glass tubes although in the azido case this was subsequently found to have been unnecessary. Photographic studies showed that the crystals of both compounds were monoclinic with that of the azido complex being *C*-centered. The remaining X-ray diffraction measurements were made using an Enraf-Nonius CAD-4F diffractometer. Accurate values of the unit cell parameters and the orientation matrix for each crystal were determined from a least-squares treatment of the angular settings of 25 carefully centered reflections. The experimental details of the data collections together with details of absorption corrections[7a,8] and the least-squares refinement procedures[8] are given in Table I. Absorption corrections were numerically evaluated by Gaussian integration to a precision of 0.5%; no corrections were made for extinction. Both structures were solved using the automatic Patterson interpretation routine of the SHELXS system.[9] Parameters for the scattering curve of atomic nickel together with the corrections for anomalous dispersion effects were taken from ref 7b,c whereas for the remaining atoms values incorporated in the SHELX-76 system were used. Anisotropic thermal parameters were applied to all the non-hydrogen atoms except those of the solvent molecules of the $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]{\cdot}3.36CH_3OH{\cdot}0.7H_2O$ crystals for which individual isotropic thermal parameters were used. In the final stages of the refinement for each compound evidence of all the hydrogen atoms of the macrocyclic ligand and the methyl groups of the methoxide ligands was observed in difference maps, and these were included in the model at their calculated positions with a common isotropic thermal parameter being refined for each H-type. For the azido complex the hydrogen atoms of the coordinated water molecule were not observed whereas those associated with the hydroxide and the H-bonded methoxide groups were identified and included in the refinement. The corresponding atoms in the $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]$ complex were not located and were not included in the model. For the crystal of this complex several molecules of solvent of crystallization were evident and on the basis of electron density values it was clear that not all sites were fully occupied; this aspect was taken into account in the refinement. The analysis of variance for each structure determination showed no unusual features. Crystallographic diagrams were prepared using the ORTEP program.[10]

Magnetic Measurements. Magnetic susceptibility measurements were made using an Oxford Instruments Faraday balance.

Results

Synthesis. Reaction of the acetato complex with azide ion was studied with the possibility in mind that the rodlike azide unit might be incorporated at the central Ni_4 site in some unusual fashion. The result observed was substitution of the acetate ligands by azide and water to give $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2$, hereafter referred to as the azido complex, whose structure and magnetic properties are discussed below. Reaction between the acetato complex and KOH or NR_4OH in methanol gave solvated $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]$, hereafter called the methoxo complex, whose structure and magnetic properties are described below.

Crystallography. Structures of the azido and methoxo complexes were determined using single-crystal X-ray diffraction,

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(8) Sheldrick, G. M. *SHELX-76, A Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.

(9) Sheldrick, G. M. *SHELXS-86, A Program for Crystal Structure Determination*; Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; *Crystallographic Computing 3*; Oxford University Press: Oxford, U.K., 1985; p 175.

(10) Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

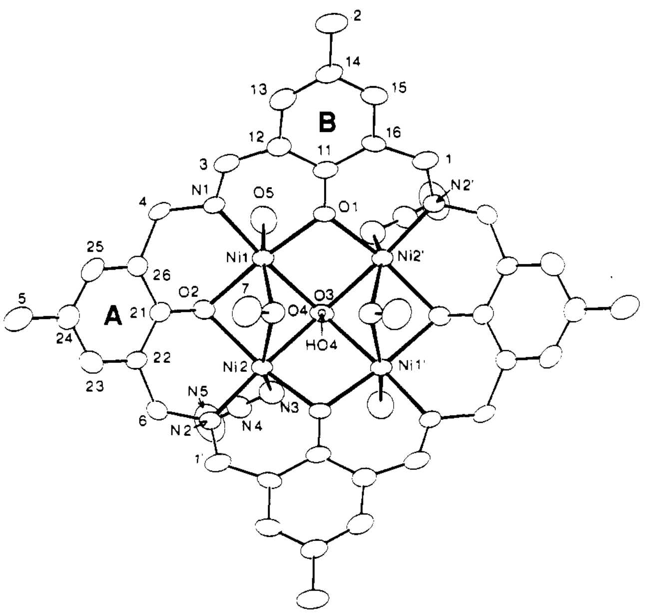

Figure 1. ORTEP plot of the $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2$ molecule, showing a view down the 2-fold axis looking into the molecular bowl. Atoms designated by a number only are carbon atoms. A and B denote the diamine and dialdehyde components, respectively.

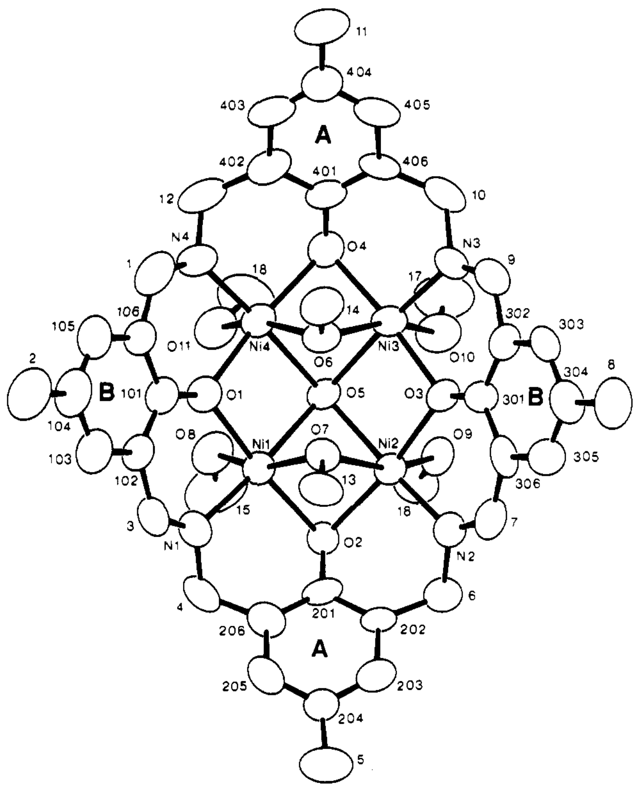

Figure 2. ORTEP plot of the $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3$ molecule in the 3.36 CH_3OH–0.7 H_2O solvated crystals, showing a view down the pseudo-2 fold axis looking in the molecular bowl. Atoms designated by a number only are carbon atoms. A and B denote the diamine and dialdehyde components, respectively.

details of which, together with crystal data, are given in Table I. Atom-numbering schemes for the azido complex and the methoxo complex are given in the ORTEPs presented in Figures 1and 2, respectively. Views of the two molecules from a different angle are presented in Figure 3 (the azido complex) and Figure 4 (the methoxo complex). Fractional atomic coordinates for the nonhydrogen atoms in the azido complex are given in Table II and for the methoxo complex in Table III. Selected bond lengths and angles for the azido complex are given in Table IV and for the methoxo complex in Table V.

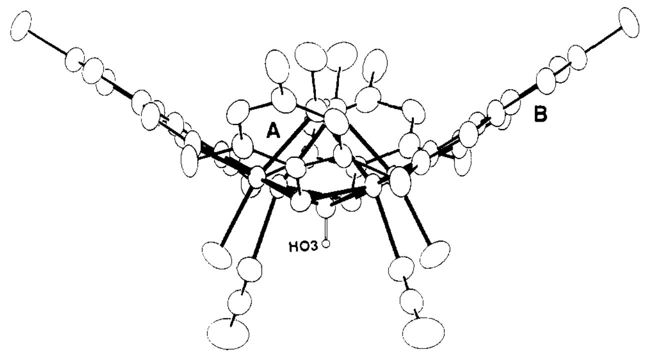

Figure 3. $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2$ viewed perpendicular to the 2-fold axis with the diamine and dialdehyde components designated as in Figure 1.

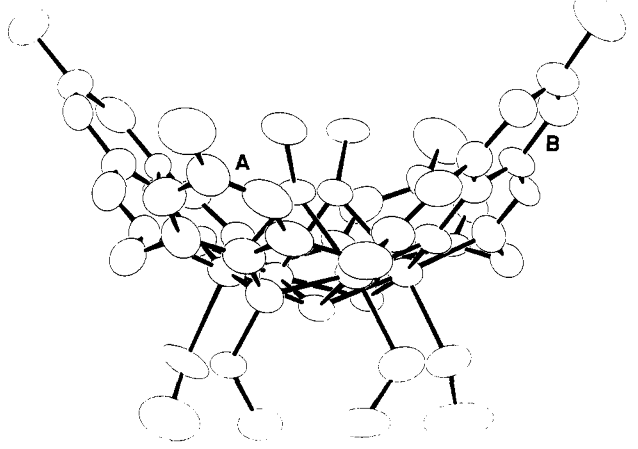

Figure 4. $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3$ viewed perpendicular to the pseudo-2 fold axis with the diamine and dialdehyde components designated as in Figure 2.

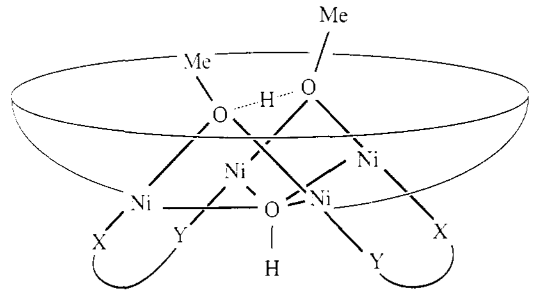

Figure 5. Representation of the bowllike $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(XY)_2$ structure common to the acetato complex ($XY = CH_3CO_2^-$), the azido complex (XY = H bonded $(N_3{\cdot}H\text{–}OH)^-$), and the methoxo complex (XY = H-bonded $(CH_3O{\cdot}H{\cdot}OCH_3)^-$).

Magnetic Properties. The magnetic susceptibilities of the acetato monohydrate, azido, and methoxo complexes were measured on a Faraday balance over the temperature range 300–4.2 K with an applied field of 10 000 G. The susceptibility versus temperature plots are all very similar in shape, and only the azido example, together with the corresponding μ (per Ni) vs T plot, is shown in Figure 6. Antiferromagnetic exchange interactions are responsible for a maximum in the χ/T plots, and there are small differences in the T_{max} values for the three complexes, viz. acetato, ca. 99 K; azido, ca. 85 K; and methoxo, ca. 85 K, indicative of slightly stronger coupling in the acetato case. Small quantities of monomer impurity and/or second-order Zeeman (TIP) effects are responsible for the leveling off at small nonzero χ values below 10 K. The magnetic moment values (per Ni) for all three complexes decrease gradually from ca. 2.92 μ_B at 295 K to ca. 0.1 μ_B at 4.2 K.

In approaching the theoretical interpretation of the susceptibility data, it was decided to use the binuclear expression given

Table II. Fractional Atomic Coordinates for $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2$ (Esd Values in Parentheses)

atom	*x*	*y*	*z*
Ni(1)	0.47744 (4)	0.31671 (8)	0.10359 (7)
Ni(2)	0.58161 (4)	0.33490 (8)	0.22531 (7)
O(1)	0.4056 (2)	0.2714 (4)	0.1423 (4)
O(2)	0.5556 (2)	0.3640 (4)	0.0776 (3)
O(3)	0.5000	0.3774 (7)	0.2500
O(4)	0.5238 (2)	0.1880 (4)	0.1797 (4)
O(5)	0.4415 (3)	0.4692 (5)	0.0622 (5)
N(1)	0.4520 (3)	0.2528 (6)	−0.0250 (4)
N(2)	0.6585 (3)	0.2880 (5)	0.2116 (4)
N(3)	0.6005 (3)	0.4970 (6)	0.2675 (5)
N(4)	0.6312 (3)	0.5607 (6)	0.2382 (5)
N(5)	0.6608 (4)	0.6222 (8)	0.2136 (7)
C(1)	0.6948 (3)	0.2343 (7)	0.2731 (6)
C(2)	0.2208 (4)	0.0210 (8)	−0.0618 (6)
C(3)	0.4057 (3)	0.1987 (7)	−0.0532 (6)
C(4)	0.4850 (3)	0.2840 (8)	−0.0960 (5)
C(5)	0.6565 (4)	0.1037 (9)	−0.1776 (7)
C(6)	0.6748 (3)	0.3263 (8)	0.1235 (5)
C(7)	0.5359 (5)	0.0854 (8)	0.1415 (7)
C(11)	0.3627 (3)	0.2137 (7)	0.0950 (5)
C(12)	0.3633 (3)	0.1727 (6)	0.0025 (5)
C(13)	0.3168 (4)	0.1106 (7)	−0.0448 (6)
C(14)	0.2700 (3)	0.0884 (7)	−0.0068 (6)
C(15)	0.2686 (3)	0.1330 (7)	0.0828 (6)
C(16)	0.3136 (3)	0.1937 (7)	0.1343 (5)
C(21)	0.5795 (3)	0.2983 (6)	0.0177 (5)
C(22)	0.6371 (3)	0.2759 (7)	0.0377 (5)
C(23)	0.6611 (3)	0.2108 (7)	−0.0249 (6)
C(24)	0.6295 (4)	0.1683 (7)	−0.1085 (6)
C(25)	0.5725 (4)	0.1908 (7)	−0.1269 (5)
C(26)	0.5472 (3)	0.2550 (7)	−0.0665 (5)
H(03)	0.5000	0.45 (1)	0.2500
H(04)	0.5000	0.18 (1)	0.2500

in eq 1 (modified to include a Curie-like monomer fraction)

$$\chi/\mathrm{Ni} = \frac{N\beta^2 g^2}{2kT}\left[\frac{10 + 2\exp(-4J/kT)}{5 + 3\exp(-4J/kT) + \exp(-6J/kT)}\right] + \chi_{\mathrm{TIP}} \quad (1)$$

appropriate to the Heisenberg–Dirac–Van Vleck isotropic exchange Hamiltonian $H = -2JS_1{\cdot}S_2$, where $S_1 = S_2 = 1$ and the *g* values are assumed equal for each Ni center. In other words, it was assumed that the four Ni atoms in these rectangular arrays interacted as isolated coupled pairs.

A least-squares fitting to eq 1 yielded excellent fits in all three cases as shown for the azido case in Figure 6. The shape of the χ plot, particularly in the $\chi_{\max}$ region is primarily determined by the exchange coupling constant, *J*. At other temperatures the *g* value in particular and the values of χ_{TIP} and monomer fraction significantly affect the size of χ. These interdependencies were evident in the fitting of the nonzero χ values observed below 10 K in which incorporation of a χ_{TIP} (at all temperatures) value of ca. 400×10^{-6} cgs/Ni led to a calculated *g* value, viz. 2.17, smaller than that obtained when χ_{TIP} was set at zero, viz. 2.34. Inclusion of a 0.3% fraction of monomer, with $\chi_{\mathrm{TIP}} = 0$, also reproduced the <10 K data quite well and with a less marked influence on the size of the *g* parameter. The key parameter, *J*, not significantly influenced by any of the above nuances, was found to be −33.3 cm^{-1} for the acetato, −28.5 cm^{-1} for the azido, and −30.0 cm^{-1} for the methoxo complexes.

Discussion

Common Structural Features. The component $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)]^{2+}$, represented schematically in Figure 5, is common to the acetato, the azido, and the methoxo complexes. In all three cases the overall molecular arrangement resembles a bowl. In the azido and acetato complexes there is a 2-fold axis of rotation passing through the bowl. Although a crystallographic 2-fold axis is strictly not present in the methoxo complex, the molecular arrangement is only slightly distorted from this ideal and we shall refer to a pseudo-2-fold axis in this case.

Table III. Fractional Atomic Coordinates for $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]{\cdot}3.36CH_3OH{\cdot}0.7H_2O$ (Esd Values in Parentheses)

atom	*x*	*y*	*z*
Ni(1)	0.0179 (2)	0.18586 (6)	0.2831 (2)
Ni(2)	0.0615 (2)	0.19079 (6)	0.4789 (2)
Ni(3)	0.1333 (2)	0.10210 (6)	0.4890 (2)
Ni(4)	0.0808 (2)	0.09626 (7)	0.2944 (2)
O(1)	0.0789 (8)	0.1447 (3)	0.2078 (8)
O(2)	−0.0281 (7)	0.2279 (3)	0.3740 (7)
O(3)	0.1652 (8)	0.1541 (3)	0.5628 (8)
O(4)	0.1060 (9)	0.0515 (3)	0.4001 (8)
O(5)	0.0226 (7)	0.1376 (3)	0.3859 (7)
O(6)	0.2161 (7)	0.1218 (3)	0.3865 (8)
O(7)	0.1634 (8)	0.1933 (3)	0.3789 (7)
O(8)	−0.1224 (8)	0.1608 (4)	0.2164 (9)
O(9)	−0.0443 (8)	0.1706 (3)	0.5509 (7)
O(10)	0.0152 (9)	0.0965 (3)	0.5621 (9)
O(11)	−0.0704 (9)	0.0847 (4)	0.2314 (9)
N(1)	0.023 (1)	0.2277 (4)	0.184 (1)
N(2)	0.113 (1)	0.2375 (4)	0.5628 (9)
N(3)	0.238 (1)	0.0751 (4)	0.586 (1)
N(4)	0.143 (1)	0.0636 (4)	0.207 (1)
C(1)	0.187 (1)	0.0776 (7)	0.143 (1)
C(2)	0.336 (2)	0.1738 (7)	−0.053 (2)
C(3)	0.077 (1)	0.2251 (5)	0.123 (1)
C(4)	−0.043 (1)	0.2644 (5)	0.189 (1)
C(5)	0.100 (2)	0.3948 (5)	0.359 (2)
C(6)	0.042 (1)	0.2738 (5)	0.547 (1)
C(7)	0.197 (1)	0.2388 (6)	0.625 (1)
C(8)	0.539 (1)	0.2004 (6)	0.815 (1)
C(9)	0.309 (1)	0.0920 (6)	0.645 (1)
C(10)	0.232 (1)	0.0284 (5)	0.582 (1)
C(11)	0.445 (2)	−0.0587 (6)	0.411 (2)
C(12)	0.135 (2)	0.0192 (5)	0.221 (1)
C(13)	0.237 (1)	0.2242 (5)	0.373 (1)
C(14)	0.322 (1)	0.1135 (5)	0.388 (1)
C(15)	−0.222 (2)	0.1731 (7)	0.220 (2)
C(16)	−0.151 (1)	0.1762 (6)	0.517 (1)
C(17)	−0.050 (2)	0.0656 (6)	0.573 (2)
C(18)	−0.131 (1)	0.0583 (6)	0.279 (2)
C(101)	0.138 (1)	0.1522 (5)	0.145 (1)
C(102)	0.1898 (5)	0.105 (1)	0.000 (1)
C(103)	0.205 (1)	0.1963 (6)	0.040 (1)
C(104)	0.263 (2)	0.1645 (7)	0.013 (1)
C(105)	0.253 (1)	0.1271 (6)	0.050 (1)
C(106)	0.196 (1)	0.1207 (5)	0.117 (1)
C(201)	0.000 (1)	0.2673 (5)	0.368 (1)
C(202)	0.035 (1)	0.2900 (4)	0.449 (1)
C(203)	0.065 (1)	0.3309 (5)	0.441 (1)
C(204)	0.063 (1)	0.3504 (5)	0.357 (1)
C(205)	0.025 (1)	0.3266 (5)	0.277 (1)
C(206)	−0.008 (1)	0.2856 (5)	0.282 (1)
C(301)	0.252 (1)	0.1644 (5)	0.620 (1)
C(302)	0.323 (1)	0.1365 (5)	0.659 (1)
C(303)	0.415 (1)	0.1477 (5)	0.719 (1)
C(304)	0.437 (1)	0.1882 (6)	0.747 (1)
C(305)	0.361 (1)	0.2159 (5)	0.712 (1)
C(306)	0.270 (1)	0.2056 (6)	0.649 (1)
C(401)	0.189 (1)	0.0238 (5)	0.405 (1)
C(402)	0.205 (1)	0.0074 (6)	0.322 (1)
C(403)	0.288 (1)	−0.0196 (5)	0.329 (2)
C(404)	0.355 (2)	−0.0308 (6)	0.407 (2)
C(405)	0.331 (1)	−0.0146 (5)	0.486 (2)
C(406)	0.250 (1)	0.0118 (5)	0.487 (1)
O(1ME)	0.471 (1)	0.3164 (4)	0.726 (1)
C(1ME)	0.564 (2)	0.3279 (8)	0.783 (2)
O(2ME)	0.785 (2)	0.1658 (6)	0.754 (1)
C(2ME)	0.753 (3)	0.124 (1)	0.733 (2)
O(3ME)	0.894 (2)	0.0543 (7)	0.060 (2)
C(3ME)	0.928 (3)	0.078 (1)	0.004 (2)
O(4ME)	0.664 (3)	0.453 (1)	0.855 (3)
C(4ME)	0.759 (4)	0.467 (2)	0.915 (4)
O(1W)	0.316 (2)	0.2985 (8)	0.960 (2)

An unusual μ_4-hydroxo unit is located on the 2-fold axis at the

Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2$ (Esd Values in Parentheses)[a]

	Distances		
Ni(1)···Ni(2)	2.771 (1)	Ni(1)···Ni(1′)	4.099 (2)
Ni(1)···Ni(2′)	3.058 (2)	Ni(2)···Ni(2′)	4.131 (2)
Ni–O(1)	1.994 (5)	Ni(1)–O(2)	2.070 (5)
Ni(1)–N(1)	1.972 (6)	Ni(1)–O(4)	2.090 (5)
Ni(1)–O(3)	2.176 (3)	Ni(1)–O(5)	2.071 (6)
Ni(2)–O(1′)	2.002 (6)	Ni(2)–O(2)	2.104 (6)
Ni(2)–N(2)	1.984 (7)	Ni(2)–N(3)	2.071 (7)
Ni(2)–O(3)	2.128 (2)	Ni(2)–O(4)	2.271 (5)
O(1)–C(11)	1.319 (9)	O(2)–C(21)	1.370 (9)
O(4)–C(7)	1.41 (1)	N(1)–C(3)	1.29 (1)
N(1)–C(4)	1.45 (1)	N(2)–C(1′)	1.29 (1)
N(2)–C(6)	1.46 (1)	N(3)–N(4)	1.20 (1)
N(4)–N(5)	1.13 (1)	C(1)–C(16)	1.46 (1)
C(2)–C(14)	1.52 (1)	C(3)–C(12)	1.45 (1)
C(4)–C(26)	1.52 (1)	C(5)–C(24)	1.50 (1)
C(6)–C(22)	1.50 (1)	O(3)–H(03)	0.8 (1)
O(4)···O(4′)	2.492 (7)	O(5)···N(3)	2.82 (1)
	Angles		
O(1)–Ni(1)–O(2)	174.4 (3)	O(1)–Ni(1)–N(1)	91.0 (3)
O(1)–Ni(1)–O(4)	93.4 (2)	O(1)–Ni(1)–O(3)	84.1 (2)
O(1)–Ni(1)–O(5)	89.1 (3)	O(2)–Ni(1)–N(1)	94.2 (3)
O(2)–Ni(1)–O(4)	83.3 (2)	O(2)–Ni(1)–O(3)	90.6 (2)
O(2)–Ni(1)–O(5)	92.9 (3)	N(1)–Ni(1)–O(4)	103.3 (3)
N(1)–Ni(1)–O(3)	174.8 (3)	N(1)–Ni(1)–O(5)	92.6 (3)
O(4)–Ni(1)–O(3)	75.2 (2)	O(4)–Ni(1)–O(3)	163.9 (3)
O(3)–Ni(1)–O(3)	89.2 (3)	O(1′)–Ni(2)–O(2)	165.1 (3)
O(1′)–Ni(2)–N(2)	90.4 (3)	O(1′)–Ni(2)–N(3)	95.9 (3)
O(1′)–Ni(2)–O(3)	85.2 (3)	O(2)–Ni(2)–N(2)	93.0 (3)
O(2)–Ni(2)–N(3)	98.0 (3)	O(2)–Ni(2)–O(3)	91.0 (3)
N(2)–Ni(2)–N(3)	98.1 (3)	N(2)–Ni(2)–O(3)	175.5 (3)
N(3)–Ni(2)–O(11)	83.3 (3)	O(1′)–Ni(2)–O(4)	86.8 (2)
O(2)–Ni(2)–O(4)	78.3 (2)	N(2)–Ni(2)–O(4)	106.4 (3)
O(4)–Ni(2)–N(3)	155.3 (3)	O(4)–Ni(2)–O(3)	72.5 (2)
Ni(1)–O(1)–Ni(2′)	99.9 (3)	Ni(2)–O(4)–C(7)	129.5 (5)
Ni(1)–O(1)–C(11)	129.9 (4)	Ni(2′)–O(1)–C(11)	130.2 (4)
Ni(1)–O(2)–Ni(2)	83.2 (2)	Ni(1)–O(2)–C(21)	117.3 (4)
Ni(2)–O(2)–C(21)	116.4 (4)	Ni(1)–O(3)–Ni(1′)	140.7 (3)
Ni(1)–O(3)–Ni(2)	80.1 (2)	Ni(1)–O(3)–Ni(2′)	90.5 (2)
Ni(2)–O(3)–Ni(2′)	152.2 (3)	Ni(1)–O(4)–Ni(2)	78.8 (2)
H(03)–O(3)–Ni(1)	110 (4)	H(03)–O(3)–Ni(2)	104 (4)
Ni(1)–O(4)–C(7)	125.8 (5)	Ni(1)–N(1)–C(3)	125.6 (5)
Ni(1)–N(1)–C(4)	115.5 (5)	C(3)–N(1)–C(4)	118.2 (5)
Ni(2)–N(2)–C(1)	127.1 (5)	Ni(2)–N(2)–C(6)	114.0 (5)
C(1)–N(2)–C(6)	118.9 (5)	Ni(2)–N(3)–N(4)	128.5 (6)
N(3)–N(4)–N(5)	177.7 (6)	N(2)–C(1)–C(16′)	126.1 (6)
N(1)–C(3)–C(12)	127.0 (6)	N(1)–C(4)–C(26)	113.1 (6)
N(2)–C(6)–C(22)	110.4 (6)	O(1)–C(11)–C(12)	120.9 (5)
O(1)–C(11)–C(16)	121.2 (5)	C(3)–C(12)–C(11)	124.9 (6)
C(3)–C(12)–C(13)	115.9 (6)	C(2)–C(14)–C(13)	121.4 (6)
C(1′)–C(16)–C(11)	124.7 (6)	C(1′)–C(16)–C(15)	115.0 (6)
O(2)–C(21)–C(22)	120.6 (5)	O(2)–C(21)–C(26)	121.2 (5)
C(6)–C(22)–C(21)	120.8 (6)	C(6)–C(22)–C(23)	119.1 (6)
C(5)–C(24)–C(23)	121.4 (7)	C(5)–C(24)–C(25)	121.5 (7)
C(4)–C(26)–C(21)	120.5 (6)	C(4)–C(26)–C(25)	119.2 (6)

[a] A prime refers to the transformation $1 - x, y, {}^1/_2 - z$.

bottom of the bowl with the O–H directed downward. The nickel centers are arranged approximately at the corners of a rectangle, and the four Ni-OH bonds are approximately equal in length and somewhat elongated (see below). Associated with the four centers on the inside of the bowl is an unprecedented $CH_3O{\cdot}H{\cdot}OCH_3^-$ bridging system which can be regarded as two methoxo units each bridging an opposite edge of the Ni_4 rectangle with a proton forming a hydrogen bond between the two oxygens. The three compounds differ in the nature of the bridging or pseudobridging species represented in Figure 5 as X-Y (X-Y = $CH_3CO_2^-$ or HO–H···N_3^- or $CH_3O{\cdot}H{\cdot}OCH_3^-$) which project downward from the convex underside of the molecular bowl.

In all three cases the nickel centers have distorted octahedral environments and the Ni_4 core can be regarded as four octahedra each of which shares an edge with one neighbor, a face with another, and a vertex with all three neighbors.

Structural Features Specific to the Azido Complex. The crystal of the azido complex contains discrete neutral $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2]$ molecules, and no lattice solvent is present. Views of the molecule down the 2-fold axis and approximately perpendicular to the axis are given in Figures 1 and 3, respectively, and structural data are presented in Table IV.

Two types of nickel are present; coordinated to Ni(1) is an aquo ligand, and coordinated to Ni(2) is a monodentate azide. Nickel–ligand bond distances are normal except for those to the μ_4-OH (Ni(1)–O(3) = 2.176 (3) Å; Ni(2)–O(3) = 2.128 (3) Å) and those from Ni(2) to the bridging methoxide (2.271 (5) Å). While the four nickel centers in the acetato complex are effectively coplanar and are distorted only slightly from a square (Ni···Ni "edge" separations, 2.788 (1) and 2.936 (1) Å), those in the azido complex show a bigger difference in the Ni···Ni edge separations and are significantly displaced from their mean plane (Ni(1)···Ni(2) = 2.771 (1), Ni(1)···Ni(2′) = 3.058 (2), Ni(1)···Ni(1′) = 4.099 (2), and Ni(2)···Ni(2′) = 4.131 (2) Å; Ni(2) and Ni(2′) 0.22 Å nearer the bottom of the bowl than Ni(1) and Ni(1′)).

The environment of the μ_4-OH is much as in the acetato complex with somewhat elongated Ni–O bonds (above) and with O(3) displaced 0.623 Å from the Ni_4 mean plane.

The $CH_3O{\cdot}H{\cdot}OCH_3^-$ bridging system is less symmetrical than that in the acetato complex, Ni(2)–O(4) being distinctly longer (2.271 (5) Å) than Ni(1)–O(4) (2.090 (5) Å). The hydrogen-bonded O···O separation is short (2.492 (7) Å as compared with 2.509 (7) Å in the acetato complex).

All four aromatic C_6 rings are inclined on the same side of the Ni_4 mean plane, the diamine-derived ring at a dihedral angle of 34.5° and the dialdehyde-derived ring at 32.8°. While the dialdehyde-derived phenoxide oxygen center O(1) is essentially planar (displaced 0.01 Å from the plane of the three connected atoms), the diamine-derived O(2) is very markedly pyramidal, lying ca. 0.65 Å from the plane of its bonded atoms. These geometrical features are clearly evident in the view presented in Figure 3. The diimine component of the macrocycle consisting of the C_6 ring, O(1), and the flanking imines C(3)N(1) and C(1)N(2′) together with the coordinated Ni(1) and Ni(2′) forms an essentially planar block, as is evident in Figure 3, where this system is viewed "edge-on". By contrast considerable twisting from coplanarity occurs within the diamine-derived component; the strongly pyramidal nature of O(2) together with the twist of the CH_2–N units around the C(26)–C(4) and C(22)–C(6) bonds leads to N(1) and N(5) and the two associated nickels, Ni(1) and Ni(2), being far from coplanar with the diamine C_6 ring. These are the crucial stereochemical features leading to the general bowllike form of the molecule. The "equatorial" coordination system associated with Ni(1) and Ni(2′) (i.e. O(1), N(1), N(2′), O(2′), O(3), O(2) and Ni(1) and Ni(2′) themselves) is close to planar. This planar unit and the symmetry-related one associated with Ni(1′) and Ni(2) are hinged along the shared O(2), O(3), O(2′) edge, the dihedral angle between their mean planes being 48.2°.

The two azido and two aquo ligands are located on the underside of the molecular bowl. A particular azide is much closer to one of its neighboring water molecules than the other. The N(3)···O(5′) separation of 2.82 (1) Å and also the orientation of the azide unit around the Ni(2)–N(3) bond are strongly indicative of an O(5′)–H···N(3) hydrogen bond. This hydrogen-bonded pair of ligands is coordinated to the pair of nickels, Ni(1) and Ni(2′), associated with the planar diimine component; effectively the three-atom-bridging acetate group of the acetato complex has been replaced by the $H_2O{\cdot}N_3^-$ association acting as a single three-atom-bridging unit.

The azido complex is exceptional among derivatives of L in not having lattice solvent in the crystal. Efficient molecular packing is achieved in this case by hydrogen bonding interactions between

Table V. Selected Interatomic Distances (Å) and Angles (deg) for $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]{\cdot}3.36CH_3OH{\cdot}0.7H_2O$

Distances

Ni(1)···Ni(2)	2.765 (4)	Ni(1)···Ni(3)	4.077 (3)	O(6)–C(14)	1.42 (2)	O(7)–C(13)	1.42 (2)
Ni(1)···Ni(4)	3.023 (3)	Ni(2)···Ni(3)	3.028 (3)	O(8)–C(15)	1.39 (3)	O(9)–C(16)	1.40 (2)
Ni(2)···Ni(4)	4.109 (4)	Ni(3)···Ni(4)	2.751 (4)	O(10)–C(17)	1.36 (3)	O(11)–C(18)	1.45 (3)
Ni(1)–O(1)	2.00 (1)	Ni(1)–O(2)	2.07 (1)	N(1)–C(3)	1.25 (2)	N(1)–C(4)	1.49 (2)
Ni(1)–O(5)	2.15 (1)	Ni(1)–O(7)	2.13 (1)	N(2)–C(6)	1.45 (2)	N(2)–C(7)	1.27 (2)
Ni(1)–O(8)	2.07 (1)	Ni(1)–N(1)	1.99 (1)	N(3)–C(9)	1.25 (2)	N(3)–C(10)	1.52 (2)
Ni(2)–O(2)	2.094 (9)	Ni(2)–O(3)	2.02 (1)	N(4)–C(1)	1.28 (2)	N(4)–C(12)	1.46 (2)
Ni(2)–O(5)	2.18 (1)	Ni(2)–O(7)	2.18 (1)	C(1)–C(106)	1.46 (3)	C(3)–C(102)	1.47 (2)
Ni(2)–O(9)	2.02 (1)	Ni(2)–N(2)	1.97 (1)	C(4)–C(206)	1.49 (2)	C(6)–C(202)	1.49 (2)
Ni(3)–O(3)	1.99 (1)	Ni(3)–O(4)	2.07 (1)	C(7)–C(306)	1.44 (2)	C(9)–C(302)	1.47 (3)
Ni(3)–O(5)	2.181 (9)	Ni(3)–O(6)	2.12 (1)	C(404)–C(11)	1.49 (4)	C(304)–C(8)	1.54 (2)
Ni(3)–O(10)	2.07 (1)	Ni(3)–N(3)	1.95 (1)	C(204)–C(5)	1.52 (2)	C(104)–C(2)	1.53 (4)
Ni(4)–O(1)	2.01 (1)	Ni(4)–O(4)	2.08 (1)	C(10)–C(406)	1.54 (2)	C(12)–C(402)	1.60 (2)
Ni(4)–O(5)	2.14 (1)	Ni(4)–O(6)	2.155 (9)	O(6)···O(7)	2.42 (1)	O(8)···O(11)	2.56 (2)
Ni(4)–O(11)	2.05 (1)	Ni(4)–N(4)	1.96 (2)	O(9)···O(10)	2.53 (1)	O(1ME)–C(1ME)	1.38 (3)
O(1)–C(101)	1.34 (2)	O(2)–C(201)	1.34 (2)	O(2ME)–C(2ME)	1.44 (4)	O(3ME)–C(3ME)	1.27 (5)
O(3)–C(301)	1.31 (2)	O(4)–C(401)	1.41 (2)	O(4ME)–C(4ME)	1.44 (6)		

Angles

O(1)–Ni(1)–O(2)	172.8 (5)	O(1)–Ni(1)–O(5)	86.1 (5)	Ni(1)–O(5)–Ni(4)	89.6 (5)	Ni(2)–O(5)–Ni(3)	87.9 (5)
O(1)–Ni(1)–O(7)	90.8 (5)	O(1)–Ni(1)–O(8)	84.9 (5)	Ni(2)–O(5)–Ni(4)	143.9 (6)	Ni(3)–O(5)–Ni(4)	79.1 (4)
O(1)–Ni(1)–N(1)	89.2 (6)	O(2)–Ni(1)–O(5)	90.7 (5)	Ni(3)–O(6)–Ni(4)	80.1 (5)	Ni(3)–O(6)–C(14)	126.0 (9)
O(2)–Ni(1)–O(7)	82.1 (5)	O(2)–Ni(1)–O(8)	101.4 (5)	Ni(4)–O(6)–C(14)	128.5 (9)	O(7)–O(6)–C(14)	117.1 (9)
O(2)–Ni(1)–N(1)	93.7 (6)	O(5)–Ni(1)–O(7)	75.3 (5)	Ni(1)–O(7)–Ni(2)	79.8 (5)	Ni(1)–O(7)–C(13)	125.5 (9)
O(5)–Ni(1)–O(8)	85.6 (5)	O(5)–Ni(1)–N(1)	175.0 (6)	Ni(2)–O(7)–C(13)	126.8 (9)	O(6)–O(7)–C(13)	119.2 (9)
O(7)–Ni(1)–O(8)	160.8 (6)	O(7)–Ni(1)–N(1)	102.9 (6)	Ni(1)–O(8)–C(15)	129 (1)	O(11)–O(8)–C(15)	121 (1)
O(8)–Ni(1)–N(1)	95.8 (6)	O(2)–Ni(2)–O(3)	169.4 (5)	Ni(2)–O(9)–C(16)	122.3 (9)	O(10)–O(9)–C(16)	115 (1)
O(2)–Ni(2)–O(5)	89.4 (5)	O(2)–Ni(2)–O(7)	80.5 (5)	Ni(3)–O(10)–C(17)	134 (1)	O(9)–O(10)–C(17)	121 (1)
O(2)–Ni(2)–O(9)	102.2 (5)	O(2)–Ni(2)–N(2)	93.9 (6)	Ni(4)–O(11)–C(18)	119 (1)	O(8)–O(11)–C(18)	117 (1)
O(3)–Ni(2)–O(5)	86.6 (5)	O(3)–Ni(2)–O(7)	88.9 (5)	Ni(1)–N(1)–C(3)	125 (1)	Ni(1)–N(1)–C(4)	114 (1)
O(3)–Ni(2)–O(9)	87.6 (5)	O(3)–Ni(2)–N(2)	89.1 (6)	C(3)–N(1)–C(4)	121 (1)	Ni(2)–N(2)–C(6)	113.0 (9)
O(5)–Ni(2)–O(7)	73.7 (5)	O(5)–Ni(2)–O(9)	87.8 (5)	Ni(2)–N(2)–C(7)	127 (1)	C(6)–N(2)–C(7)	121 (1)
O(5)–Ni(2)–N(2)	173.6 (6)	O(7)–Ni(2)–O(9)	161.3 (5)	Ni(3)–N(3)–C(9)	127 (1)	Ni(3)–N(3)–C(10)	113.4 (9)
O(7)–Ni(2)–N(2)	101.3 (6)	O(9)–Ni(2)–N(2)	96.9 (6)	C(9)–N(3)–C(10)	119 (1)	Ni(4)–N(4)–C(1)	126 (1)
O(3)–Ni(3)–O(4)	173.5 (5)	O(3)–Ni(3)–O(5)	87.2 (5)	Ni(4)–N(4)–C(12)	113 (1)	C(1)–N(4)–C(12)	121 (1)
O(3)–Ni(3)–O(6)	92.0 (5)	O(3)–Ni(3)–O(10)	84.2 (5)	N(4)–C(1)–C(106)	127 (1)	N(1)–C(3)–C(102)	127 (1)
O(3)–Ni(3)–N(3)	87.8 (6)	O(4)–Ni(3)–O(5)	89.7 (5)	N(1)–C(4)–C(206)	110 (1)	N(2)–C(6)–C(202)	109 (1)
O(4)–Ni(3)–O(6)	81.7 (5)	O(4)–Ni(3)–O(10)	101.3 (6)	N(2)–C(7)–C(306)	126 (1)	N(3)–C(9)–C(302)	126 (1)
O(4)–Ni(3)–N(3)	95.2 (6)	O(5)–Ni(3)–O(6)	74.8 (5)	N(3)–C(10)–C(406)	112 (1)	N(4)–C(12)–C(402)	109 (1)
O(5)–Ni(3)–O(10)	85.6 (5)	O(5)–Ni(3)–N(3)	174.7 (6)	O(1)–C(101)–C(106)	120 (1)	O(1)–C(101)–C(102)	121 (1)
O(6)–Ni(3)–O(10)	160.2 (5)	O(6)–Ni(3)–N(3)	104.0 (6)	C(1)–C(106)–C(101)	123 (1)	C(1)–C(106)–C(105)	115 (1)
O(10)–Ni(3)–N(3)	95.3 (6)	O(1)–Ni(4)–O(4)	169.4 (5)	C(105)–C(104)–C(2)	124 (2)	C(103)–C(104)–C(2)	119 (2)
O(1)–Ni(4)–O(5)	86.2 (5)	O(1)–Ni(4)–O(6)	88.8 (5)	C(3)–C(102)–C(101)	124 (1)	C(3)–C(102)–C(103)	117 (1)
O(1)–Ni(4)–O(11)	89.3 (6)	O(1)–Ni(4)–N(4)	88.6 (6)	O(2)–C(201)–C(206)	121 (1)	O(2)–C(201)–C(202)	120 (1)
O(4)–Ni(4)–O(5)	90.5 (5)	O(4)–Ni(4)–O(6)	80.6 (5)	C(4)–C(206)–C(201)	125 (1)	C(4)–C(206)–C(205)	116 (1)
O(4)–Ni(4)–O(11)	100.7 (6)	O(4)–Ni(4)–N(4)	94.0 (6)	C(205)–C(204)–C(5)	127 (1)	C(203)–C(204)–C(5)	119 (1)
O(5)–Ni(4)–O(6)	74.9 (5)	O(5)–Ni(4)–O(11)	86.7 (5)	C(6)–C(202)–C(201)	124 (1)	C(6)–C(202)–C(203)	117 (1)
O(5)–Ni(4)–N(4)	173.6 (6)	O(6)–Ni(4)–O(11)	161.6 (6)	O(3)–C(301)–C(306)	120 (1)	O(3)–C(301)–C(302)	122 (1)
O(6)–Ni(4)–N(4)	101.4 (6)	O(11)–Ni(4)–N(4)	96.9 (6)	C(7)–C(306)–C(301)	125 (1)	C(7)–C(306)–C(305)	115 (1)
Ni(1)–O(1)–Ni(4)	98.0 (5)	Ni(1)–O(1)–C(101)	127.5 (9)	C(305)–C(304)–C(8)	123 (1)	C(303)–C(304)–C(8)	122 (1)
Ni(4)–O(1)–C(101)	129.2 (9)	Ni(1)–O(2)–Ni(2)	83.1 (4)	C(9)–C(302)–C(301)	124 (1)	C(9)–C(302)–C(303)	115 (1)
Ni(1)–O(2)–C(201)	117.7 (8)	Ni(2)–O(2)–C(201)	118.3 (8)	O(4)–C(401)–C(406)	123 (1)	O(4)–C(401)–C(402)	118 (1)
Ni(2)–O(3)–Ni(3)	98.1 (6)	Ni(2)–O(3)–C(301)	128.4 (9)	C(10)–C(406)–C(401)	120 (1)	C(10)–C(406)–C(405)	120 (1)
Ni(3)–O(3)–C(301)	127.7 (9)	Ni(3)–O(4)–Ni(4)	83.0 (5)	C(405)–C(404)–C(11)	122 (2)	C(403)–C(404)–C(11)	126 (2)
Ni(3)–O(4)–C(401)	116.4 (9)	Ni(4)–O(4)–C(401)	118.9 (9)	C(12)–C(402)–C(401)	123 (1)	C(12)–C(402)–C(403)	121 (1)
Ni(1)–O(5)–Ni(2)	79.3 (4)	Ni(1)–O(5)–Ni(3)	140.5 (6)				

a coordinated water of one molecule and the pyramidal phenolic oxygen atom of another with an O(2)···O(5) separation of 2.841 (8) Å. In this way each molecule is involved in four hydrogen bonds, two to one neighbor and two to another.

Structural Features Specific to the Methoxo Complex. Views of the molecule along the pseudo-2-fold axis looking down into the molecular bowl and approximately perpendicular to the axis are given in Figures 2 and 4, respectively. Structural data are presented in Table V.

The four Ni centers are closer to planar than those in the azido complex, being displaced only 0.031 Å from the mean plane. The Ni_4 arrangement is close to rectangular (Ni(1)···Ni(2) = 2.765 (4), Ni(1)···Ni(4) = 3.023 (3), Ni(2)···Ni(3) = 3.028 (3), Ni(3)···Ni(4) = 2.751 (4), Ni(1)···Ni(3) = 4.077 (3), and Ni(2)···Ni(4) = 4.109 (4) Å)

Bonds to the μ_4-OH are similar in length to those in the acetato and azido complexes (2.15 (1) to Ni(1), 2.18 (1) to Ni(2), 2.181 (9) to Ni(3), and 2.14 (1) Å to Ni(4)) and the μ_4-O is displaced a similar distance (0.70 Å) from the Ni_4 mean plane.

Two types of $CH_3O{\cdot}H{\cdot}OCH_3^-$ unit are present, one bridging the Ni_4 rectangular "face", the other bridging the rectangle edges Ni(1)···Ni(4) and Ni(2)···Ni(3). The face-bridging $CH_3O{\cdot}H{\cdot}OCH_3^-$ is more symmetrically bonded to the four nickel centers than that in the azido complex (Ni(3)–O(6) = 2.12 (1), Ni(4)–O(6) = 2.155 (9), Ni(1)–O(7) = 2.13 (1) and Ni(2)–O(7) = 2.18 (1) Å), and the O(6)···O(7) hydrogen-bonded distance is extremely short, 2.42 (1) Å. The edge-bridging $CH_3O{\cdot}H{\cdot}OCH_3^-$ units, in which each oxygen is bonded to a single nickel, show significantly shorter Ni–O separations (Ni(1)–O(8) = 2.07 (1), Ni(2)–O(9) = 2.02 (1), Ni(3)–O(10) = 2.07 (1) and Ni(4)–O(11) = 2.05 (1) Å) and significantly longer O···O separations (O(8)···O(11) = 2.56 (2) and O(9)···O(10) = 2.53 (1) Å) than the face-bridging units.

The methoxo complex molecule is more deeply dished than the

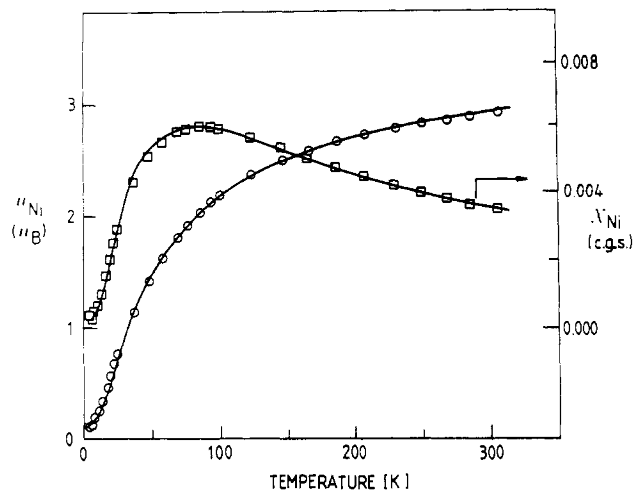

Figure 6. Temperature dependence of molecular susceptibility per Ni (□) and of magnetic moment per Ni (○) for the azido complex $LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2$. The solid lines represent the least-squares best-fit to eq 1 using $g = 2.17$, $\chi_{TIP} = 480 \times 10^{-6}$ cgs, and $J = -28.5$ cm^{-1}.

acetato or azido complexes. The diamine-derived phenoxy centers; like those in the acetato and azido complexes, are markedly pyramidal, the distances from the planes of the three bonded atoms being 0.622 Å for O(2) and 0.644 Å for O(4). The C_6 rings of the diamine components are inclined at 34.4 and 34.6° to the Ni_4 mean plane. As in the acetato and azido complexes, the entire "equatorial" coordination system surrounding the pair of nickels, Ni(1) and Ni(4), associated with one diimine component (i.e. O(2), N(1), O(1), N(4), O(4), O(5), Ni(1), and Ni(4)) is close to planar and is inclined at a dihedral angle of 52.8° to the corresponding nearly planar coordination system associated with Ni(2) and Ni(3). The diimine C_6 rings are particularly steeply inclined to the Ni_4 mean plane (dihedral angles 49.8 and 49.2°). This feature arises from the fact that, in addition to the pronounced folding around the shared O(2)···O(5)···O(4) "hinge" of the two sets of nearly planar coordination systems described above, O(1) and O(3) themselves are pyramidal, as can be clearly seen in Figure 2 (distance from the plane of the three bonded atoms is 0.219 Å for O(1) and 0.225 Å for O(3)). As a consequence of this marked inclination of the diimine C6 rings, the methyl carbons C(2) and C(8) are considerably closer together than C(5) and C(11), as can be seen in Figure 2, in contrast to the other LNi_4 complexes, where the analogous Me···Me separations are nearly equal (e.g. see Figure 1).

Magnetic Properties. The essential constancy in the J values for the three compounds (acetato, -33.3 cm^{-1} azido, -28.5 cm^{-1} methoxo, -30.0 cm^{-1}) simply quantifies the similarity in the observed χ/T plots and suggests that the magntic interactions within the essentially common tetranuclear core are little influenced by the "external" X-Y moieties shown in Figure 5. Indeed, the excellent fits to eq 1 suggest that little would be gained by employing tetranuclear models e.g. of a rectangular type incorporating three J values appropriate to dissimilar edge and diagonal interactions. The "pair of dimers" model, in fact, is quite consistent with the structural features of the Ni_4 core environment. The key features to concentrate on are the "equatorial" bridging groups between the Ni atoms since these will provide the most important superexchange pathways between the $d_{x^2-y^2}$ orbitals of the $S = 1$ Ni^{II} centers. The dialdehyde imine components (i.e. those encompassing Ni(1), Ni(2′) and Ni(2), Ni(1′) in Figure 1) provide an essentially coplanar coordinating environment with a trigonal-planar phenolate O(1) bridging atom, a situation known in related binuclear macrocyclic systems of types $L'Ni_2Cl_2{\cdot}2H_2O$ ($J = -27$ cm^{-1})[11] and $[L'Ni_2(py)_4](BF_4)_2$ ($J = -23$ cm^{-1})[12] to provide antiferromagnetic exchange of magnitude very similar to that observed here and independent of axial ligand variations. These two internally coplanar Ni_2 components are hinged together by the roof ridge provided by the pyramidal phenolate oxygens of the diamine components and the central μ_4-OH. Magnetic interaction between these markedly inclined planar Ni_2 blocks would be expected to be weak despite the shorter Ni···Ni distances (ca. 2.8 Å) and smaller Ni–O–Ni angles (ca. 83°) than those within the blocks. In a recent binuclear macrocyclic example containing this diamine component (the reduced version of L′ above) coupling does indeed appear to be negligible;[13] surprisingly, the bridging geometry in this example is more like that in the dialdehyde component in the present systems than the diamine component.

In a more general comparison of J values with other O-bridged octahedral Ni^{II} species of the small cluster type, we note that net ferromagnetism (J ca. $+7$ cm^{-1}) characterizes the cubane tetramers of the type $[Ni(OCH_3)(Sal)(C_2H_5OH)]_4$;[14] here the methoxo O atom provides 90° bridges to three adjacent Ni atoms. The trimeric $[Ni(acac)_2]_3$ behaves likewise. Antiferromagnetism ($J = -20$ cm^{-1}) was noted for the binuclear complex $[Ni_2(cyclam)_2(C_2O_4)](NO_3)_2$, in which the bridging O atoms of the oxalate occupied cis-positions[15] and also in various triketone complexes (J ca. -13 cm^{-1}), the structures of which show overall coplanarity and a bridge geometry rather like that in the present dialdehyde imine moiety.[16] Even weaker antiferromagnetic coupling has been noted in two triply-bridged binuclear complexes $[Ni_2bimp(\mu\text{-}OAc)_2]ClO_4$ ($J = -1.9$ cm^{-1}), containing a phenolate bridging O atom and two tertiary amino "arms" within the bimp ligand,[17] and in $(Ni_2(tacn)_2(\mu\text{-}OH)(\mu\text{-}OAc)_2]ClO_4$ ($J = -4.5$ cm^{-1}), which contains a μ-hydroxo bridge.[18] In both of these systems the Ni···Ni distance and Ni–O–Ni angles are larger than those in the present dialdehyde imine or diamine components, but the Ni···Ni distances are shorter than in the μ-oxalato example cited above. Thus, while some broad trends are emerging in the relationship between structure and magnetic exchange in Ni^{II}···Ni^{II} systems,[19] the fine detail noted in Cu^{II}···Cu^{II} chemistry is not yet forthcoming. Nevertheless data of the present kind should prove useful in modeling the electronic structure of polynuclear Ni^{II} sites in enzymes such as urease[20] ($J = -6.3$ cm^{-1}).

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Supplementary Material Available: Tables S-I–S-IV, listing anisotropic thermal parameters, H-atom coordinates, least-squares planes, and intermolecular contacts for $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)(N_3)_2(H_2O)_2]$, and Tables S-V–S-VIII, listing the corresponding data for $[LNi_4(OH)(CH_3O{\cdot}H{\cdot}OCH_3)_3]{\cdot}3.36CH_3OH{\cdot}0.7H_2O$ (21 pages); Tables S-IX and S-X, listing structure factors for the two compounds (21 pages). Ordering information is given on any current masthead page.

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