J. Am. Chem. Soc. 1989, 111, 3603–3610

reported.[23] In contrast to the uncoordinated SMe groups in I, the hydrogens on the carbon of the metallacyclopropane in these compounds are inequivalent at ambient temperature. There is also no evidence for a carbene mercaptide form of $ClPt(PPh_3)(CH_2SMe)$. Unlike I, it reacts with PPh_3 to displace the sulfur and give an alkyl complex $ClPt(PPh_3)_2[CH_2SMe]$.[23] In addition, $ClPd(PPh_3)(CH_2SMe)$ reacts with alkyl halides to give a halogen exchanged product $IPd(PPh_3)(CH_2SMe)$,[24] and no alkylation of the sulfur occurs.

It is well documented in the literature[25] that α-heteroatom carbenes tend to be more stable than alkyl-, aryl-, and hydrogen-substituent carbenes because of the stabilizing effect that results from the interaction of the carbene carbon and the lone electron pairs on the heteroatoms. It is therefore understandable why the metallathiacyclopropane I in which such stabilizing groups (SMe) are present is more likely to show evidence for a carbene mercaptide form than the hydrogen-substituted analogues. Other metallathiacyclopropane complexes that are most likely to be in equilibrium with a carbene mercaptide form (eq 11) are also those where the carbene R substituents are stabilizing heteroatom groups.

Acknowledgment. We appreciate the support of this work by the National Science Foundation (Grant No. CHE-8410844 and CHE-8719744). We thank Drs. Vinko Rutar and David Scott for their help in obtaining the temperature-dependent NMR data.

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Synthesis and X-ray Crystal Structures of Ni_4 and Zn_4 Complexes of a Macrocyclic Tetranucleating Ligand

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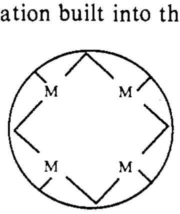
Abstract: Ni_4 and Zn_4 derivatives of the macrocyclic tetra Schiff base (LH_4) formed by condensation of two molecules of 2,6-diformyl-4-methylphenol with two molecules of 2,6-bis(aminomethyl)-4-methylphenol have been isolated. Determination of the structure of $LNi_4(CH_3CO_2)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3){\cdot}4CH_3OH$ by X-ray crystallography reveals four nickels at the corners of a rectangle with edges 2.788 (1) and 2.936 (1) Å; crystal data: monoclinic, space group $C2/c$, $a = 21.494$ (2) Å, $b = 8.996$ (1) Å, $c = 25.451$ (3) Å, $\beta = 93.75$ (1)°, $Z = 4$. An unusual μ_4-hydroxo group is located with its oxygen atom ca. 0.60 Å above the midpoint of the Ni_4 cluster. An unusual, strongly hydrogen bonded $CH_3O{\cdot}H{\cdot}OCH_3^-$ unit with a short O···O separation of 2.509 (7) Å bridges the "face" of the Ni_4 group on the side opposite to the μ_4-OH group, each methoxo oxygen being equally attached to two nickels. The arrangement of the macrocyclic ligand resembles a bowl with the Ni_4 group in the bottom. The $CH_3O{\cdot}H{\cdot}OCH_3^-$ unit is inside the bowl. Two acetate units bridge edges of the Ni_4 group on the outside of the bowl. A similar but less symmetrical bowl-like ligand arrangement is present in $LZn_4(CH_3CO_2)_3(OH){\cdot}2.64CH_3OH{\cdot}2.5H_2O$; crystal data: tetragonal, space group $P\bar{4}2_1c$, $a = 24.835$ (7) Å, $c = 17.172$ (4) Å, $Z = 8$. The Zn_4 group is markedly distorted from a square being no longer planar and having a short diagonal, 3.632 (7) Å, and a long diagonal, 4.742 (7) Å. A hydroxo group bridges the short diagonal with normal Zn–O bonds of length 1.97 (3) and 2.06 (3) Å, but it also interacts less strongly with the other two zincs at distances of 2.17 (2) and 2.60 (2) Å. One acetate bridges the short diagonal on the side opposite to the hydroxo group and on the inside of the bowl. A second acetate bridges an edge of the Zn_4 cluster and the third acetate is monodentate but hydrogen bonded to the hydroxo group. One zinc is intermediate between 4- and 5-coordinate, two are 5-coordinate, and the fourth is 6-coordinate.

It has been proposed that, as a result of an order–disorder-based effect related to the chelate effect, the organization provided by an appropriately designed binucleating ligand may confer unusual structural features and reactivity upon derived binuclear complexes.[1] The recently reported hydration of nitriles to carboxamides catalyzed by dipalladium complexes of binucleating ligands, which proceeds by a bimetallic pathway, provides one example of this sort of unusual reactivity.[2] Complexes in which a single ligand organizes more than two metal centers into some predetermined arrangement may similarly show unique behavior. The present report describes some initial synthetic and structural studies of complexes in which a macrocyclic ligand binds four metal centers in close proximity in a roughly square arrangement as in I. The organization built into these systems may lead to



I

unusual behavior in a number of areas, including the following: (a) Species may be trapped at the central tetrametallic site under circumstances that would be unlikely or impossible in the absence of the order imposed by the tetranucleating ligand. The trapped

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[1] Robson, R. *Inorg. Chim. Acta* **1982**, *57*, 71.

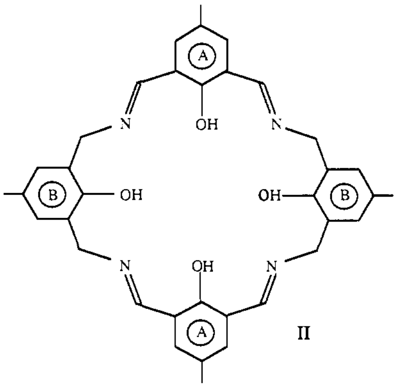
[2] McKenzie, C. J.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1988**, 112.

0002-7863/89/1511-3603$01.50/0

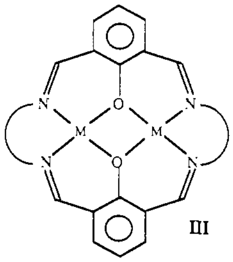
species may in addition be activated toward further reaction in special ways. (b) New types of reaction, either between initially separate species attached to neighboring metal centers or within species attached to more than one metal center, may result. (c) Multielectron reduction or oxidation of substrates may be possible. The relatively accessible arrangement of the four metal centers provided by the organizing ligand may enable substrates to be brought under the influence (not necessarily entirely by direct coordinate bonds) of two or three or even all four metals simultaneously; only a modest 2e change per metal is then required for the transfer of up to 8e either to or from the substrate. Thus for example, the interaction of appropriate complexes of type I with substrates such as O_2 and N_2, which are of considerable chemical, biological, and industrial importance, could prove interesting and possibly useful. Tetramanganese derivatives of type I may provide realistic and useful models for the dioxygen-generating component of the photosynthetic system, which appears to involve four manganese centers in close proximity.[3]

Countless tetranuclear structures are known. Platinous acetate, in the solid phase, contains a square arrangement of four metals[4] similar to that we seek to impose in the present work. Binucleating ligands, under certain circumstances, afford tetranuclear metallic derivatives.[5] Cubane-type structures containing roughly tetrahedral arrangements of metal centers have been intensively studied and now macrocyclic ligands encircling cubane arrangements have been reported.[6] A ligand consisting of four porphyrin nuclei linked together to generate a super-macrocycle has been described[7] and very recently a remarkable complex in which two macrocyclic ligands impose an approximately square arrangement upon four Cu^I centers was reported.[8]

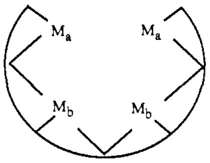
The macrocyclic ligand used in the present work is the tetraphenolate anion derived from II; we represent II as LH_4 below and the ligand present in the complexes as L^{4-}. This constitutes a minor extension of our earlier work with binucleating macrocycles of the general type III, which subsequently have been extensively investigated;[9] the tetranuclear systems promise an even richer chemistry. L^{4-} represents only one of several possible ways of imposing the desired tetranuclear arrangements, which are readily conceived with the background of the synthesis of a range of binucleating systems in mind; thus, for example, it should be possible, by analogy with related binucleating systems,[10] to generate macrocycles with the two phenolate diimine components of L^{4-} replaced by related thiophenolate diimine units. Variants of this sort give us access, in principle, to tetranucleating macrocycles providing central M_4 cavities with a range of sizes that may have a critical effect on their chemistry. Moreover, similar minor modification of procedures used to generate binucleating ligands should afford nonmacrocyclic tetranucleating ligands such as that in IV. These complexes may be sufficiently flexible to allow a much larger variation in the $M_a \cdots M_a$ separation than is possible with the more rigid macrocyclic ligands and additional types of reactivity stemming from this flexibility, such as the "in-plane" introduction of substrates at the $(M_a)_2$ site, may be observable.



II



III



IV

A preliminary account of the synthesis and structure of the Ni_4 complex described here has already been published[11] and a short note concerning a Cu_4 complex of a closely related macrocycle appeared very recently.[12]

Results and Discussion

2,6-Bis(aminomethyl)-4-methylphenol. The diamino component of the macrocyclic Schiff base was prepared by a sequence based on the Delépine reaction, which is simpler and more convenient

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Table I. Crystal Data and Details of Crystal Structure Determination of $[LNi_4(CH_3CO_2)_3(OH)(CH_3O{\cdot}H{\cdot}OCH_3)]{\cdot}4CH_3OH$ and $[LZn_4(CH_3CO_2)_3(OH)]{\cdot}$Solvate

	LNi_4	LZn_4
formula	$C_{42}H_{46}N_4Ni_4O_{11}{\cdot}4CH_3OH$	$C_{42}H_{46}N_4O_{11}Zn_4{\cdot}2.64CH_3OH{\cdot}2.5H_2O$
mol wt	1145.8	1174.0
cryst system	monoclinic	tetragonal
space group	*C*2/*c* (No. 15)	$P\bar{4}2_1c$ (No. 114)
a, Å	21.494 (2)	24.835 (7)
b, Å	8.996 (1)	
c, Å	25.451 (3)	17.172 (4) Å
β, deg	93.75 (1)	
vol, $Å^3$	4911.7 (1)	10591 (8)
Z	4	8
ρ(calcd), g cm^{-3}	1.550	1.473
ρ(measd) (by flotation), g cm^{-3}	1.557 (5)	1.526 (5)
cryst dimens (distances in mm from centroid)	±(001) 0.036; ±(110) 0.200; see text (−210) 0.114; (100) 0.300; (1-10) 0.100	
temp, K	295 (1)	295 (1)
radiation (graphite monochromator), Å	Mo Kα radiation; λ 0.71069	
no. of intensity control reflcns	3; meas every 3000 s; no significant variation	3; meas every 3600 s; no significant variation
F(000)	2392	4840
μ, cm^{-1}	15.57	18.74
absorption corrections	applied using SHELX-76[19]	not applied
transmission factors	max 0.8939, min 0.7102	see text
2θ limits	$2 \le 2\theta \le 55°$	$2 \le 2\theta \le 38°$
scan mode	ω:2θ	
instrument	Enraf Nonius CAD-4F diffractometer	
range of *h*, *k*, *l*	$-27 \le h \le 27$ $0 \le k \le 11$ $-33 \le l \le 33$	$-22 \le h \le 22$ $0 \le k \le 22$ $0 \le l \le 15$
no. of reflcns meas	11228	7782
no. of unique reflcns	5628	3729
R_{amal}	0.024	0.037
no. of reflcns used in refinement	2,972 [$I \ge 3\sigma(I)$]	2068 [$I \ge 2\sigma(I)$]
refinement	least-squares; function minimized $\sum w\Delta^2$ where $\Delta = \lVert F_o \rvert - \lvert F_c \rVert$; SHELX-76[19]	
weighting scheme	$w = [k/(\sigma^2_{(F)} + 0.0005F^2)]$ $k = 2.088$	$k = 2.0921$
no. of variables	331	336
final *R*	0.050	0.109
final R_w	0.048	0.093
max. shift/e.s.d. for non-H atom	0.007	0.007
goodness of fit	1.500	1.601
max residual electron density, e $Å^{-3}$	0.78	1.12

than the procedure described in the literature.[13] The action of methanolic HCl upon 2,6-bis(hydroxymethyl)-4-methylphenol gave 2,6-bis(chloromethyl)-4-methylphenol, which was used without isolation for reaction with hexamine to yield the corresponding bis(hexaminiummethyl) dichloride salt in a one-pot sequence. Acid hydrolysis of the salt cleanly afforded the diaminophenol which was conveniently isolated and stored as the monohydrochloride.

$LNi_4(CH_3CO_2)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3)$. The complex was obtained by template condensation in methanol of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride in the presence of excess nickel(II) acetate and acetic acid–sodium acetate buffer. Green monoclinic crystals of the tetramethanolate suitable for X-ray crystallography were grown by vapor diffusion of water into a methanolic solution in the presence of additional nickel acetate.

Crystal data and details of the crystal structure determination are given in Table I. All the hydrogen atoms in the complex molecule were clearly evident in the difference maps. Atomic coordinates are presented in Table II and selected interatomic distances and bond angles are given in Table III.

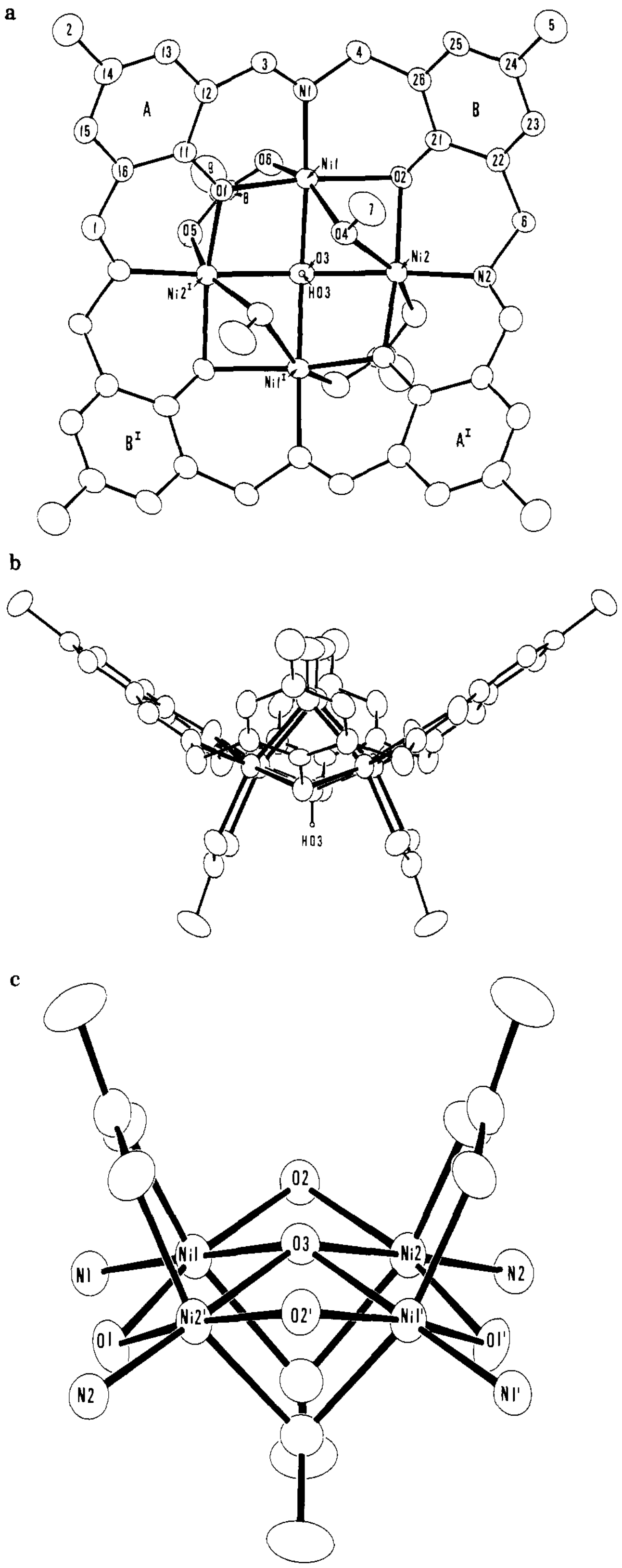

Figure 1. Structure of $LNi_4(CH_3CO_2)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3)$ in the tetramethanolate. (a) view down the 2-fold axis showing the numbering scheme employed (atoms not designated by an atom type are carbon atoms); (b) view approximately perpendicular to the 2-fold axis showing the bowl-like configuration; and (c) coordination environments of the four nickel centers showing the ridged roof arrangement described in the text.

The crystal contains, together with lattice methanol, neutral molecules of composition $LNi_4(CH_3CO_2)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3)$, various aspects of the structure of which are represented in Figure

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[13] Mazurek, W.; Bond, A. M.; Murray, K. S.; O'Connor, M. J.; Wedd, A. G. *Inorg. Chem.* **1985**, *24*, 2484.

Table II. Fractional Atomic Coordinates for the Non-Hydrogen Atoms of $[LNi_4(CH_3CO_2)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3)]{\cdot}4CH_3OH$[a]

atom	*x*	*y*	*z*
Ni1	0.51381 (3)	0.02946 (11)	0.67201 (3)
Ni2	0.59389 (3)	0.02984 (11)	0.76274 (3)
O1	0.4288 (2)	−0.0561 (5)	0.6694 (2)
O2	0.6075 (2)	0.0912 (5)	0.6849 (1)
O3	0.5000 (–)	0.0961 (7)	0.7500 (–)
O4	0.5461 (2)	−0.1501 (4)	0.7222 (2)
O5	0.3953 (2)	0.2369 (5)	0.7040 (2)
O6	0.4755 (2)	0.2358 (5)	0.6510 (2)
O7	0.6402 (3)	0.3926 (8)	0.6763 (3)
O8	0.4825 (4)	0.2798 (10)	0.5427 (3)
N1	0.5222 (2)	−0.0388 (6)	0.5989 (2)
N2	0.6805 (2)	−0.0391 (6)	0.7786 (2)
C1	0.2991 (3)	−0.1209 (7)	0.6828 (2)
C2	0.2939 (3)	−0.4109 (8)	0.5168 (3)
C3	0.4827 (3)	−0.1140 (7)	0.5702 (2)
C4	0.5796 (2)	0.0124 (7)	0.5758 (2)
C5	0.7745 (3)	−0.2977 (9)	0.5865 (3)
C6	0.7241 (3)	0.0163 (8)	0.7408 (2)
C7	0.5724 (3)	−0.2877 (8)	0.7071 (3)
C8	0.4297 (3)	0.2957 (8)	0.6711 (3)
C9	0.4142 (4)	0.4554 (8)	0.6560 (3)
C11	0.3965 (3)	−0.1297 (7)	0.6328 (2)
C12	0.4225 (3)	−0.1671 (7)	0.5849 (2)
C13	0.3882 (3)	−0.2544 (7)	0.5481 (2)
C14	0.3291 (3)	−0.3079 (7)	0.5567 (2)
C15	0.3023 (3)	−0.2642 (7)	0.6018 (2)
C16	0.3340 (3)	−0.1733 (7)	0.6400 (2)
C21	0.6489 (3)	0.0056 (6)	0.6602 (2)
C22	0.7060 (2)	−0.0377 (8)	0.6866 (2)
C23	0.7455 (3)	−0.1354 (7)	0.6623 (2)
C24	0.7319 (3)	−0.1881 (7)	0.6117 (3)
C25	0.6779 (3)	−0.1371 (8)	0.5851 (2)
C26	0.6372 (3)	−0.0406 (8)	0.6080 (2)
C27	0.6251 (5)	0.4273 (12)	0.6233 (4)
C28	0.4388 (5)	0.3551 (15)	0.5196 (4)

[a] The atoms of the two independent methanol molecules are designated C27, O7 and C28, O8.

Table III. Selected Interatomic Dimensions for $LNi_4(CH_3CO_2)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3){\cdot}4CH_3OH$

	Distances (Å)		
Ni1···Ni2	2.788 (1)	Ni1···Ni2^a	2.936 (1)
Ni1···Ni1^a	4.052 (1)	Ni2···Ni2^a	4.046 (1)
Ni1–O1	1.980 (4)	Ni1–O2	2.094 (4)
Ni1–N1	1.979 (5)	Ni1–O3	2.113 (2)
Ni1–O4	2.146 (4)	Ni1–O6	2.086 (5)
Ni2–O1^a	1.982 (5)	Ni2–O2	2.095 (3)
Ni2–N2	1.979 (4)	Ni2–O3	2.109 (2)
Ni2–O4	2.145 (4)	Ni2–O5	2.053 (5)
O1–C11	1.305 (7)	O2–C21	1.361 (7)
O3–HO3	0.74 (6)	O4–C7	1.424 (8)
O5–C8	1.268 (9)	O4···O4^a	2.509 (7)
	Angles (deg)		
O1–Ni1–N1	89.3 (2)	O5^a–Ni2–O2	97.6 (2)
O1–Ni1–O3	87.5 (2)	O5^a–Ni2–O3	83.6 (2)
O1–Ni1–O2	169.9 (2)	O5^a–Ni2–N2	96.9 (3)
O2–Ni1–N1	94.8 (2)	O5^a–Ni2–O4	157.0 (2)
O2–Ni1–O3	88.3 (2)	O1^a–Ni2–O2	169.8 (2)
O4–Ni1–O1	89.4 (2)	Ni1–O1–Ni2^a	95.6 (2)
O4–Ni1–O2	80.6 (2)	Ni1–O1–C11	131.9 (4)
O4–Ni1–O3	73.4 (2)	Ni2^a–O1–C11	132.1 (4)
O4–Ni1–N1	106.3 (2)	Ni1–O2–Ni2	83.5 (2)
O6–Ni1–O1	89.4 (2)	Ni1–O2–C21	115.4 (3)
O6–Ni1–O2	99.4 (2)	Ni2–O2–C21	115.1 (3)
O6–Ni1–O3	84.9 (2)	Ni1–O3–Ni2	82.7 (2)
O6–Ni1–O4	158.3 (2)	Ni1–O3–Ni2^a	88.1 (2)
O6–Ni1–N1	95.4 (2)	Ni1–O3–Ni1^a	147.0 (3)
N1–Ni1–O3	176.8 (2)	Ni2–O3–Ni2^a	147.2 (3)
N2–Ni2–O1^a	89.0 (2)	HO3–O3–Ni1	106.5 (15)
N2–Ni2–O2	95.0 (2)	HO3–O3–Ni2	106.4 (15)
N2–Ni2–O3	176.4 (2)	Ni1–O4–Ni2	81.0 (2)
O3–Ni2–O1^a	87.5 (2)	O3–Ni2–O2	88.4 (2)
O4–Ni2–O1^a	89.3 (2)	O4–Ni2–O2	80.6 (2)
O4–Ni2–O3	73.5 (2)		

[a] $1 - x, y, 1.5 - z$.

1. The molecule is situated around a crystallographic 2-fold axis of symmetry, the four nickel ions being located at the corners of a rectangle perpendicular to the axis that closely approximates to a square (Ni(1)···Ni(2) 2.788 (1), Ni(1)···Ni(2′) 2.936 (1), Ni(1)···Ni(1′) 4.052 (1), Ni(2)···Ni(2′) 4.046 (1) Å). The LNi_4 unit resembles a bowl, as can be seen in Figure 1b, the dialdehyde-derived benzene rings (referred to below as rings A, as in II) being inclined at 34.6° to the Ni_4 plane and the diamine-derived benzene rings (referred to below as rings B, as in II) being inclined at 38.3°, all on the same side of the metal plane. An acetate unit bridges each pair of nickels associated with the A-type phenolate residues (i.e. Ni(1) + Ni(2′) and Ni(1′) + Ni(2)) on the underside of the molecular bowl, in the view represented in Figure 1b.

On the inside of the bowl a methoxo unit bridges each pair of nickels associated with the B-type phenolate rings (i.e. Ni(1) + Ni(2) and Ni(1′) + Ni(2′)). The methoxo oxygen centers are markedly pyramidal, as can be seen in Figure 1a; each oxygen atom can be regarded as providing a lone pair of electrons directed toward its symmetry-related partner. A hydrogen atom is clearly evident between the two oxygen centers yielding a hydrogen bonded $(CH_3O{\cdot}H{\cdot}OCH_3)^-$ system with a very short oxygen–oxygen separation of 2.509 (7) Å. The existence of H-bonded bridges of the type $(RO{\cdot}H{\cdot}OR)^-$ (where R = H or alkyl) in certain complexes of binucleating ligands has been proposed previously;[10a,14] in the case of a dicopper complex of this type a $(CH_3O{\cdot}H{\cdot}OCH_3)^-$ bridge with a very short H-bonded O···O separation of 2.35 Å has been confirmed by X-ray crystallography.[10b] The $H_3O_2^-$ bridging system has attracted recent attention and structural studies reveal short oxygen–oxygen separations in the range 2.45–2.55 Å.[15] The $(CH_3O{\cdot}H{\cdot}OCH_3)^-$ bridge in the present tetranickel complex differs from these other examples in that each oxygen atom is attached to two metal centers, not one, and in this regard is, to the best of our knowledge, without precedent.

A central μ_4-hydroxo group, O(3) in Figure 1, essentially equidistant from all four metals (Ni(1)–O(3) 2.113 (2) and Ni(2)–O(3) 2.109 (2) Å), is located 0.60 Å out of the Ni_4 plane on the side opposite to the $CH_3O{\cdot}H{\cdot}OCH_3^-$ system. The O(3)–H bond is coincident with the 2-fold molecular axis, the hydrogen pointing away from the Ni_4 plane. This hydroxo group, attached equally to four metal centers, while being capable formally of providing only three pairs of electrons, is to our knowledge unprecedented. A comparable μ_4 chloro center is present in the $Sb_4Cl_{12}O^{2-}$ ion,[16] but the availability of d atomic orbitals on the chlorine can be used to account for its participation in four bonds to the antimony centers. One of the features of potential interest that we anticipate for complexes of these tetranucleating ligands is that species may be trapped at the central tetrametallic site under unusual circumstances; the remarkable environment imposed upon the hydroxo group in the present case provides encouragement that other examples await discovery.

The molecular symmetry approximates very closely to C_{2v}, so that all four methylene groups of the macrocycle are essentially equivalent. One CH bond of each methylene can be described as "axial", being close to parallel with the 2-fold axis, while the other CH bonds are "equatorial", being found approximately in the plane of the associated B-type benzene ring.

The immediate coordination environment of the tetranuclear core is represented in Figure 1c. Each nickel is surrounded by an O_5N distorted octahedral set of ligand atoms. The macrocyclic ligand supplies two oxygen donors plus one nitrogen donor to each nickel and these, together with the μ_4 hydroxo group, provide an

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Table IV. Fractional Atomic Coordinates for the Non-Hydrogen Atoms of $LZn_4(CH_3CO_2)_3(OH){\cdot}2.64CH_3OH{\cdot}2.5H_2O$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Zn1	−0.2917 (2)	−0.2214 (2)	0.0377 (4)	C6	−0.295 (2)	−0.289 (2)	0.298 (2)	C206	−0.358 (1)	−0.174 (1)	0.193 (2)
Zn2	−0.2783 (2)	−0.3191 (2)	0.1361 (3)	C7	−0.320 (1)	−0.377 (1)	0.273 (2)	C301	−0.308 (2)	−0.441 (2)	0.157 (3)
Zn3	−0.2367 (2)	−0.4038 (2)	0.0188 (4)	C8	−0.417 (2)	−0.549 (3)	0.246 (3)	C302	−0.313 (2)	−0.492 (2)	0.120 (3)
Zn4	−0.3029 (2)	−0.3227 (2)	−0.0723 (3)	C9	−0.292 (2)	−0.508 (2)	0.044 (2)	C303	−0.349 (2)	−0.529 (2)	0.148 (3)
N1	−0.350 (2)	−0.167 (2)	0.049 (3)	C10	−0.239 (2)	−0.502 (2)	−0.064 (3)	C304	−0.370 (2)	−0.516 (2)	0.219 (3)
N2	−0.297 (1)	−0.333 (2)	0.244 (2)	C11	−0.327 (2)	−0.534 (2)	−0.317 (3)	C305	−0.358 (2)	−0.464 (2)	0.258 (3)
N3	−0.258 (1)	−0.481 (1)	0.010 (2)	C12	−0.279 (2)	−0.342 (1)	−0.240 (2)	C306	−0.328 (2)	−0.429 (2)	0.230 (3)
N4	−0.310 (1)	−0.314 (2)	−0.186 (2)	C13	−0.379 (2)	−0.358 (2)	0.041 (3)	C401	−0.265 (1)	−0.419 (1)	−0.146 (2)
O1	−0.325 (1)	−0.2420 (9)	−0.064 (2)	C14	−0.428 (2)	−0.394 (2)	0.075 (2)	C402	−0.282 (2)	−0.406 (2)	−0.223 (2)
O2	−0.291 (1)	−0.2328 (9)	0.149 (2)	C15	−0.155 (2)	−0.345 (2)	0.108 (3)	C403	−0.300 (1)	−0.443 (2)	−0.274 (2)
O3	−0.276 (1)	−0.402 (1)	0.118 (2)	C16	−0.102 (2)	−0.346 (2)	0.144 (3)	C404	−0.304 (2)	−0.494 (2)	−0.262 (2)
O4	−0.250 (1)	−0.383 (1)	−0.090 (2)	C17	−0.192 (2)	−0.189 (2)	0.017 (3)	C405	−0.279 (2)	−0.514 (2)	−0.196 (3)
O5	−0.362 (1)	−0.363 (1)	−0.030 (2)	C18	−0.141 (3)	−0.148 (2)	0.002 (4)	C406	−0.264 (2)	−0.478 (2)	−0.136 (3)
O6	−0.365 (1)	−0.321 (1)	0.083 (2)	C101	−0.371 (1)	−0.223 (1)	−0.103 (2)	O1Me	−0.097 (2)	−0.292 (2)	−0.094 (3)
O7	−0.194 (1)	−0.328 (1)	0.152 (2)	C102	−0.405 (1)	−0.182 (1)	−0.070 (2)	C1Me	−0.126 (3)	−0.323 (3)	−0.150 (4)
O8	−0.164 (1)	−0.382 (1)	0.057 (2)	C103	−0.445 (2)	−0.166 (2)	−0.115 (2)	O2Me	−0.469 (2)	−0.248 (2)	−0.437 (3)
O9	−0.227 (1)	−0.173 (1)	0.026 (2)	C104	−0.461 (2)	−0.176 (2)	−0.183 (3)	C2Me	−0.493 (3)	−0.293 (3)	−0.457 (5)
O10	−0.169 (2)	−0.243 (2)	0.003 (2)	C105	−0.427 (2)	−0.222 (2)	−0.216 (3)	O3Me	−0.007 (3)	0.404 (3)	0.403 (5)
O11	−0.2614 (9)	−0.3023 (9)	0.021 (2)	C106	−0.384 (2)	−0.242 (2)	−0.180 (2)	C3Me	0.040 (2)	0.404 (2)	0.320 (3)
C1	−0.347 (2)	−0.282 (2)	−0.217 (3)	C201	−0.330 (1)	−0.217 (2)	0.203 (2)	O1W	0.000 (−)	0.500 (−)	0.256 (6)
C2	−0.511 (2)	−0.163 (2)	−0.227 (3)	C202	−0.333 (2)	−0.244 (1)	0.276 (3)	O2W	0.500 (−)	0.000 (−)	0.376 (4)
C3	−0.385 (2)	−0.159 (2)	0.006 (2)	C203	−0.365 (2)	−0.227 (2)	0.328 (3)	O3W	0.053 (2)	0.431 (2)	0.502 (3)
C4	−0.350 (1)	−0.135 (1)	0.120 (2)	C204	−0.399 (2)	−0.185 (2)	0.311 (2)	O4W	0.037 (3)	0.502 (3)	0.376 (5)
C5	−0.445 (2)	−0.170 (2)	0.373 (3)	C205	−0.396 (2)	−0.152 (2)	0.252 (2)	O5W	0.084 (3)	0.500 (3)	0.452 (4)

[a] Site occupation for solvent molecules: O1Me–C1Me 1.00 (2), O3Me–C3Me 0.82 (2), O2W 0.38 (2), O4W 0.49 (2), O2Me–C2Me 0.82 (2), O1W 0.25 (2), O3W 0.76 (2), and O5W 0.59 (2).

essentially square-planar O_3N arrangement around each metal. These square planes are approximately coplanar for Ni(1) and Ni(2′), i.e. the nickels shared by one of the A-type phenolate units. The pair of nickels associated with the second A-type phenolate, i.e. Ni(2) and Ni(1′), likewise have an essentially coplanar pair of O_3N square planes, but this second plane makes a dihedral angle of 46.4° with the first. The entire set of all the macrocyclic donor atoms plus the four metal centers plus the central hydroxo oxygen resembles a ridged roof; when viewed from the angle represented in Figure 1c, the ridge being provided by O(2)···O(3)···O(2′) which are almost co-linear. The pseudo-octahedral nickel environments are completed by acetate bridges, one above each of the roof planes, and by the methoxo bridges below (as viewed from the angle represented in Figure 1c). The metal–ligand atom distances are unexceptional except for those to the μ_4-OH (2.113 (2) and 2.109 (2) Å) and those to the methoxo centers (2.146 (4) and 2.145 (4) Å), which are somewhat longer than usual Ni^{II}–O bonds, but then these donors in any case are unusual. The very close approximation to C_{2v} symmetry for the isolated molecule is apparent in the almost identical environments observed for Ni(1) and Ni(2) indicated in Table III.

Bridging phenolates are generally close to planar at the oxygen center and the oxygens of the A-type phenolates (O(1) and O(1′)) in the present example are of this common type. The B-type phenolate oxygens (O(2) and O(2′)) are, by contrast, markedly pyramidal, resembling those observed in a dicopper complex of a binucleating ligand based, as in the present case, on a substituted 2,6-bis(aminomethyl)phenol.[17]

The only d ↔ d bands observable in the diffuse reflectance spectrum of the Ni_4 complex are ν_1 and ν_2 ($^3T_{2g} \leftarrow {}^3A_{2g}$ and $^3T_{1g} \leftarrow {}^3A_{2g}$ respectively in O_h symmetry), ν_3 being obscured by intense bands of non d ↔ d origin. ν_2 appears at 16.3×10^3 cm^{-1} and ν_1 is split into two components (11.5×10^3 and 8.5×10^3 cm^{-1}) consistent with the low-symmetry six-coordinate environments of the nickel(II) centers. The room temperature magnetic moment is 3.0 μ_B per nickel center. The IR spectrum shows the imine stretching frequency, $\nu_{C=N}$, as a strong band at 1645 cm^{-1} and the acetate bands at ca. 1420 cm^{-1} ($\nu_{OCO(sym)}$) and ca. 1550 cm^{-1} ($\nu_{OCO(asym)}$), both of which partially overlap ligand bands. When a KBr disc of the Ni_4 complex is dried at 140 °C under vacuum a weak but sharp peak at ca. 3610 cm^{-1} becomes discernible, which very likely corresponds to ν_{OH} of the central μ_4 hydroxo group.

Table V. Selected Interatomic Dimensions for $LZn_4(CH_3CO_2)_3(OH){\cdot}2.64CH_3OH{\cdot}2.5H_2O$

	Distances (Å)		
Zn1···Zn2	2.975 (8)	Zn1···Zn3	4.742 (7)
Zn1···Zn4	3.158 (8)	Zn2···Zn3	3.090 (8)
Zn2···Zn4	3.632 (7)	Zn3···Zn4	3.034 (7)
Zn1O1	2.00 (3)	Zn1–O2	1.93 (4)
Zn2–O2	2.18 (2)	Zn2–O3	2.08 (3)
Zn3–O3	1.96 (3)	Zn3–O4	1.97 (3)
Zn4–O4	2.02 (3)	Zn4–O1	2.08 (2)
Zn1–N1	1.99 (5)	Zn2–N2	1.94 (4)
Zn3–N3	2.00 (3)	Zn4–N4	1.97 (4)
Zn1–O11	2.17 (2)	Zn2–O11	2.06 (3)
Zn4–O11	1.97 (3)	Zn1–O9	2.02 (3)
Zn2—O7	2.12 (3)	Zn3–O8	2.00 (3)
Zn4–O5	1.92 (3)		
	Angles (deg)		
N1–Zn1–O1	88 (2)	N2–Zn2–O3	89 (2)
N1–Zn1–O2	91 (2)	N2–Zn2–O7	95 (2)
N1–Zn1–O9	101 (2)	N2–Zn2–O11	178 (2)
N1–Zn1O11	154 (2)	O2–Zn2–O3	173 (1)
O1–Zn1–O2	146 (1)	O2–Zn2–O7	103 (1)
O1–Zn1–O9	113 (1)	O2–Zn2–O11	86 (1)
O1–Zn1–O11	78 (1)	O3–Zn2–O7	84 (1)
O2–Zn1–O9	100 (1)	O3–Zn2–O11	93 (1)
O2–Zn1–O11	90 (1)	O7–Zn2–O11	87 (1)
O9–Zn1–O11	105 (1)	N3–Zn3–O3	88 (1)
N2–Zn2–O2	93 (2)	N3–Zn3–O4	98 (1)
N3–Zn3–O8	122 (1)	Zn1–O2–Zn2	93 (1)
O3–Zn3–O4	137 (1)	Zn2–O3–Zn3	100 (2)
O3–Zn3–O8	99 (1)	Zn3–O4–Zn4	99 (2)
O4–Zn3–O8	113 (1)	Zn1–O1–Zn4	101 (1)
N4–Zn4–O1	87 (2)	Zn1O11–Zn2	89 (1)
N4–Zn4–O4	89 (2)	Zn1–O11–Zn4	100 (1)
N4–Zn4–O5	111 (2)	Zn2–O11–Zn4	128 (2)
N4–Zn4–O11	145 (2)	O1–Zn4–O4	154 (1)
O1–Zn4–O5	106 (1)	O1–Zn4–O11	81 (1)
O4–Zn4–O5	100 (1)	O4–Zn4–O11	88 (1)
O5–Zn4–O11	103 (1)		

$LZn_4(CH_3CO_2)_3(OH)$. Condensation of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride in the presence of excess zinc acetate and acetic acid–sodium acetate in methanol gave solvated $LZn_4(CH_3CO_2)_3(OH)$ as a yellow crystalline solid. Tetragonal crystals suitable

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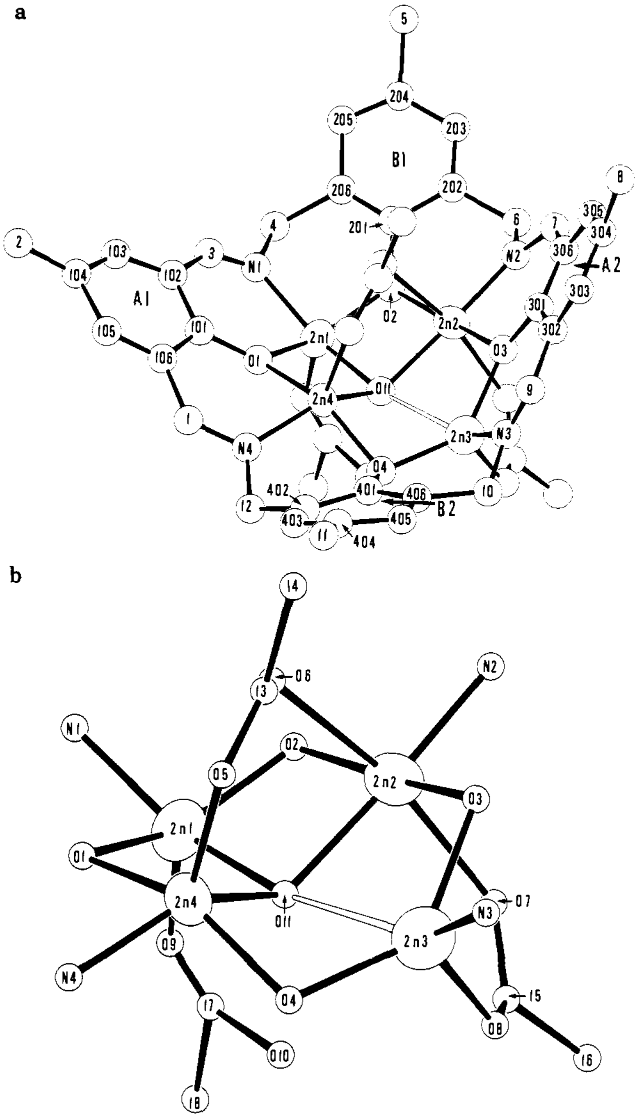

Figure 2. Structure of $LZn_4(CH_3CO_2)_3(OH)$ in the hydrate/methanolate. (a) A general view of the molecule showing the numbering scheme employed for the metal atoms and the atoms in the macrocyclic ligand (atoms not designated by an atom type are carbon atoms). (b) Coordination environments of the four zinc centers including the numbering scheme for the acetate ligands.

for X-ray crystallography were grown by vapor diffusion of water into a methanolic solution in the presence of additional zinc acetate.

Crystal data and details of the crystal structure determination are given in Table I. Table IV gives atomic coordinates. Selected interactomic distances and bond angles can be found in Table V.

The crystal of composition $LZn_4(CH_3CO_2)_3(OH)\cdot 2.64CH_3OH\cdot 2.5H_2O$ contains discrete molecules of formulation $LZn_4(CH_3CO_2)_3(OH)$, whose structure is represented in Figure 2. The molecule is completely lacking in symmetry. Zn(1) and Zn(4) are 5-coordinate, Zn(2) 6-coordinate, and Zn(3) intermediate between 4- and 5-coordinate. The general bowl-like arrangement seen in the Ni_4 complex is present in the Zn_4 complex in less symmetrical form. The four benzene rings are all inclined on the same side of the Zn_4 cluster at the following angles to the mean plane through the metals: A(1) 33°, A(2) 58°, B(1) 39°, B(2) 23°.

The four zinc centers are not coplanar, the Zn(1)–Zn(2)–Zn(4) plane being inclined to the Zn(2)–Zn(3)–Zn(4) plane at an angle of 32.4°. The two "diagonals", Zn(2)···Zn(4) and Zn(1)···Zn(3) differ significantly in length, being 3.632 (7) and 4.742 (7) Å, respectively. Other metal-metal separations are as follows: Zn(1)···Zn(2) 2.975 (8), Zn(2)···Zn(3) 3.090 (8), Zn(3)···Zn(4) 3.034 (7), and Zn(4)···Zn(1) 3.158 (8) Å.

A very asymmetrically attached acetate unit bridges the short diagonal on the inside of the bowl. O(5) of this acetate is strongly bonded to Zn(4) at a distance of 1.92 (3) Å, while the other acetate oxygen, O(6), interacts more weakly with Zn(2) at a distance of 2.34 (3) Å. A second acetate unit bridges an edge of the Zn_4 cluster, namely Zn(2)···Zn(3), on the opposite side to the first acetate. The third acetate is essentially monodentate being bound to Zn(1) on the outside of the bowl. However, the noncoordinated oxygen, O(10), of this acetate is within hydrogen bonding distance of the hydroxo group, O(11), the separation being 2.74 (5) Å. This hydroxo oxygen is attached to Zn(2) and Zn(4) by "normal" bonds (O(11)–Zn(2) 2.06 (3) Å and O(11)–Zn(4) 1.97 (3) Å) to Zn(1) by a weaker bond (O(11)–Zn(1) 2.17 (2) Å) and the interaction with the fourth zinc is even weaker (O(11)–Zn(3) 2.60 (3) Å).

The phenolic oxygen centers of the diamino components, O(2) and O(4), are, as in the Ni_4 structure, markedly pyramidal being displaced 0.476 and 0.474 Å, repsectively, from the planes of the directly bonded atoms. The dialdehyde-derived phenolic centers, O(1) and O(3), are less planar than the corresponding centers in the Ni_4 structure, but not so strongly pyramidal as O(2) and O(4); displacements from the planes of the bonded atoms are 0.252 Å for O(1) and 0.147 Å for O(3).

The donor atoms N(2), O(2), O(11), O(4), and N(3) are very close to coplanar (rms deviation 0.072 Å) as are N(1), O(2), O(11), O(4), and N(4) (rms deviation 0.107 Å), the dihedral angle between the two planes being 40°. This feature is similar to that in the Ni_4 structure where the comparable "roof-ridge" dihedral angle was 46.4°.

The ^1H and ^{13}C NMR spectra of the Zn_4 complex in $CDCl_3$ are consistent with the persistence in solution of a molecular arrangement very similar to that observed in the crystal structure. The presence of three different sorts of acetate unit is indicated by three broad but distinct resonances at 2.35, 2.08, and 0.93 ppm in the ^1H NMR spectrum, the latter very probably corresponding to the monodentate acetate; the ^{13}C spectrum however reveals only two of the three different sorts of acetate, two carboxylate carbons at 180.5 and 180.0 ppm and two broadened acetate methyl carbons at 20.0 and 19.7 ppm being observed. The four CH_2 groups give rise to a quartet in the ^1H NMR spectrum (δ = 4.11 and 5.54 ppm; J = 12.8 Hz), indicating that the two protons within each CH_2 are locked in very different environments, i.e. "axial" and "equatorial"; evidently the molecular bowl turns inside-out at room temperature at a negligible rate on the NMR time scale. Even at 100 °C in $C_6D_5NO_2$ the CH_2 signal has only started to broaden, the quartet structure being still apparent with maxima at 4.25, 4.36, 5.45, and 5.55 ppm. Although the NMR features derived from the acetate units point to asymmetry in the molecule, those arising from the macrocycle, listed below, seem to be so insensitive to this asymmetry that they appear as though the molecule had C_{2v} symmetry: CH_2, singlet in ^{13}C NMR (65.8 ppm) and quartet in ^1H NMR as described above; imine CH=N, singlet in both ^1H NMR (8.20 ppm, 4H) and ^{13}C NMR (166.2 ppm); CH_3, 2 singlets in both ^1H NMR (2.21, 2.23, 6 H each) and ^{13}C NMR (23.6, 22.9 ppm); aromatic CH, 2 singlets in ^1H NMR (7.13, 6.82 ppm, 4 H each) and 2 singlets in ^{13}C NMR identified by off-resonance (140.2, 129.9 ppm); quaternary aromatic C, 6 singlets only, identified by off-resonance (165.1, 158.7, 125.5, 125.2, 124.8, 121.3 ppm).

The IR spectrum of the Zn_4 complex in the solid phase (KBr disc) is less well defined than that of the Ni_4 complex, as is consistent with the lack of symmetry in the former case. A broad imine band, $\nu_{C=N}$, at 1650 cm^{-1} is observed and acetate features in the 1420- and 1550–1560-cm^{-1} regions are much broader than in the Ni_4 spectrum.

Metal-Free Macrocyclic Derivatives. The diprotonated, metal-free macrocyclic derivative $(LH_6)(BF_4)_2$ was obtained by addition of excess aqueous HBF_4 to a solution of $LZn_4(CH_3CO_2)_3(OH)$ in methanol. Hydrolytic disruption of the Schiff base macrocycle, leading to the separation of 2,6-diformyl-4-methylphenol, occurred if the acidified mixture was heated for some time. The ^1H NMR spectrum of $(LH_6)(BF_4)_2$ in dimethyl sulfoxide-d_6

solution at room temperature indicates that the six protons within the macrocyclic cavity are not undergoing rapid exchange but rather are of two distinct types; a broad 4-proton band at 13.1 ppm corresponds to four phenolic protons and a broad 2-proton band at 9.62 ppm to two protonated imines. In view of the scope for internal hydrogen bonding it is surprising that all six protons do not exchange more rapidly. The imine CH protons appear as a broadened pair of bands at 8.89 and 8.98 ppm, one corresponding to the two protonated imine units and the other to the two unprotonated imines. Addition of D_2O causes the imine CH resonances to sharpen to a singlet at the same time as the separate OH and NH resonances disappear; under these conditions exchange of the six internal H/D with the large excess of external H/D is sufficiently rapid to render all four imine CH's equivalent. The four methylene groups give rise to a somewhat broadened single band at 4.84 ppm in contrast to the quartet, discussed above, observed for the Zn_4 complex; this implies that if, as seems likely on the basis of models, the macrocycle adopts the bowl-like conformation seen in the crystal structures of the Ni_4 and the Zn_4 complexes, the bowl is able to turn inside-out relatively rapid in the absence of the constraints imposed by coordinated metal centers. Evidently the asymmetry introduced by the essentially localized protonation of two of the four imine nitrogens has no significant effect on the chemical shifts of the protons associated with the four toluene residues which appear as single bands at 7.72 and 7.23 ppm (aromatic CH, 4 H each) and 2.22 and 2.19 ppm (CH_3, 6 H each). In the IR spectrum of solid $LH_6(BF_4)_2$ two resolved C=N stretching bands are observed at 1640 and 1660 cm^{-1}, one corresponding to the protonated imines and the other to the unprotonated imines.

Reaction of the monohydrochloride of 2,6-bis(aminomethyl)-4-methylphenol with 2,6-diformyl-4-methylphenol in boiling methanol gave $(LH_6)Cl_2$ as an orange crystalline solid. This compound was too insoluble to afford useful NMR data but its IR spectrum (KBr disk) showed the same pair of resolved C=N stretching bands at 1640 and 1660 cm^{-1} as was observed for $(LH_6)(BF_4)_2$.

Conclusions

The results described here establish the general feasibility of constructing polydentate ligands that bind four metal ions in close proximity in a roughly planar, roughly square arrangement that is relatively accessible to external substrates. Many variants on the building blocks used for the tetranucleating ligand are clearly possible and we regard the present examples as prototypes for a potentially extensive and useful series of tetranuclear species with a variety of metals in a variety of oxidation states and with an approximately predeterminable range of metal–metal separations. The unusual environments of the central hydroxy groups in the complexes described here point to the potential offered by these and similar organized ligand–M_4 combinations to impose unusual environments upon a range of trapped species. The differences between the Ni_4 and Zn_4 structures demonstrate that the LM_4 unit is able to flex to accommodate significantly varible metal–metal separations. This flexibility may prove to be a most useful structural characteristic in future catalytic applications (compared with the relatively fixed intermetallic spacing on the surface of a catalytic metal or metal oxide) allowing the MM separations to vary as required during a multistep catalytic process.

Experimental Section

2,6-Bis(aminomethyl)-4-methylphenol Monohydrochloride. A solution of hydrogen chloride (64 g) in methanol (150 mL) was added at room temperature to solid 2,6-bis(hydroxymethyl)-4-methylphenol[18] (20.0 g, 0.12 mol). The suspension was stirred, the solid dissolving completely within ca. 10 min. After 2 h at room temperature the solution was evaporated under reduced pressure at ≤35 °C to a colorless, crystalline residue. A solution of hexamine (37.3 g, 0.27 mol) in methanol (750 mL) at room temperature was added rapidly and with vigorous stirring to the solid residue which dissolved within seconds. After an additional few seconds a fine microcrystalline colorless solid separated. The mixture was allowed to stand at room temperature for 15 min and then the solid was collected, washed with ice cold methanol, and dried under vacuum at room temperature. Yield 45.0 g, 78% based on the bis(hexaminium) dichloride formulation. The bis-(hexaminium) dichloride salt (24.9 g, 0.051 mol) suspended in a mixture of ethanol (10 mL) and concentrated aqueous hydrochloric acid (30 mL, 32%) was heated and evaporated in an open beaker. The solid dissolved completely as the mixture reached the boiling point and within a few minutes a copious colorless precipitate separated. The mixture was continuously evaporated at atmospheric pressure in an open beaker with the addition of ethanol from time to time to maintain the volume approximately constant for 2 h. Further concentrated aqueous hydrochloric aid (20 mL, 32%) and added and evaporation, with the occasional addition of ethanol to keep the volume approximately constant, was continued for 2 h. The mixture was evaporated to dryness under vacuum yielding a mixture of ammonium chloride and 2,6-bis(aminomethyl)-4-methylphenol dihydrochloride. Concentrated aqueous ammonia (7 mL, 25% solution) was added with stirring to a solution of the residue in water (85 mL). The mixture was maintained at 0 °C for 1 h and the yellow precipitate was collected and dried under vacuum over calcium chloride. Yield of crude 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride 7.9 g. The product could be recrystallized from either methanol or aqueous methanol as pale yellow needles. Anal. Calcd for $C_9H_{15}ClN_2O\cdot{}^1/_6H_2O$: C, 52.6; H, 7.5; N, 13.6; Cl, 17.2. Found: C, 52.9; H, 7.2; N, 13.4; Cl, 16.6. ^1H NMR (D_2O), δ 2.19 (s, 3 H, CH_3), 4.08 (s, 4 H, benzylic CH_2), 7.04 (s, 2 H, arom.).

$LNi_4(CH_3CO_2)_2(OH)(CH_3O\cdot H\cdot OCH_3)\cdot H_2O$. A solution of sodium acetate (1.07 g, 13 mmol) in water (8 mL) was added to a solution of nickel(II) acetate tetrahydrate (1.61 g, 6.5 mmol) and acetic acid (0.73 g, 13 mmol) in hot methanol (40 mL). To this nearly boiling solution were added, in quick succession, a solution of 2,6-diformyl-4-methylphenol (0.46 g, 2.8 mmol) in methanol (40 mL) followed by 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride (0.57 g, 2.8 mmol) in methanol (100 mL). The resulting mixture was filtered at its boiling point and the filtrate was evaporated at atmospheric pressure until solid started to appear. Upon cooling the mixture deposited green crystals of $LNi_4(CH_3CO_2)_2(OH)(CH_3O\cdot H\cdot OCH_3)\cdot 4CH_3OH$, which were collected, washed with methanol, dried under vacuum at 80 °C, and then exposed to the atmosphere to yield the monohydrate. Yield, 1.03 g, 71%. Recrystallization from methanol containing nickel acetate tetrahydrate (ca. 1/4 the weight of the complex) followed by drying under vacuum at 80 °C and exposure to the atmosphere gave an analytically pure sample of the monohydrate. Anal. Calcd for $C_{42}H_{48}N_4O_{12}Ni_4$: C, 48.7; H, 4.7; N, 5.4; Ni, 22.7. Found: C, 48.6; H, 4.5; N, 5.4; Ni, 22.4.

$LZn_4(CH_3CO_2)_3(OH)\cdot 2.5H_2O$. A solution of sodium acetate (1.02 g, 12.4 mmol) in water (10 mL) was added to a solution of zinc acetate dihydrate (1.65 g, 7.5 mmol) and acetic acid (0.45 g, 7.5 mmol) in methanol (70 mL). To the resulting solution at its boiling point were added, in quick succession, a solution of 2,6-diformyl-4-methylphenol (0.69 g, 4.2 mmol) in methanol (50 mL) followed by 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride (0.85 g, 4.2 mmol) in methanol (170 mL). The resulting mixture was filtered at its boiling point and the filtrate was evaporated at atmospheric pressure to a volume of ca. 100 mL. Addition of water (300 mL) gave a yellow precipitate. The suspension so formed was heated on the steam bath (20 h) during which time the initially amorphous suspended solid was replaced by microcrystalline material. The solid was collected, washed with methanol, dried under vacuum at 80 °C, and then exposed to the atmosphere. Yield 1.54 g. Recrystallization from methanol followed by drying at 80 °C under vacuum and then exposure to the atmosphere gave an analytically pure sample of $LZn_4(CH_3CO_2)_3(OH)\cdot 2.5H_2O$. Anal. Calcd for $C_{42}H_{47}O_{13.5}N_4Zn_4$: C, 46.5; H, 4.4; N, 5.2. Found: C, 46.5; H, 3.6; N, 5.4.

$LH_6(BF_4)_2$. Aqueous tetrafluoroboric acid (1 mL, ca. 40% solution) was added with stirring to a supersaturated solution of the Zn_4 complex (0.164 g) in methanol (10 mL) (obtained by evaporating at atmospheric pressure a solution initially in 20 mL of methanol). The orange crystalline solid that separated was quickly collected, washed well with methanol, dried at 80 °C under vacuum, and then equilibrated in air. Yield 0.113 g. Anal. Calcd for $LH_6(BF_4)_2\cdot H_2O$, i.e., $C_{36}H_{40}B_2F_8N_4O_5$: C, 55.4; H, 5.1; N, 7.2; F, 19.5. Found: C, 55.5; H, 4.8; N, 7.2; F, 19.3.

LH_6Cl_2. A solution of 2,6-bis(aminomethyl)-4-methylphenol monohydrochloride (0.263 g, 1.30 mmol) together with acetic acid (0.168 g, 2.8 mmol) in boiling methanol (15 mL) was added to a solution of 2,6-diformyl-4-methylphenol (0.213 g, 1.30 mmol) in boiling methanol (15 mL). The resulting clear yellow solution, in an enclosed vessel, was heated in a bath maintained at 58–60 °C for 20 h during which time orange crystals gradually separated. The solid was collected, washed with methanol, and dried under vacuum at 80 °C. Yield 0.318 g, 74%. Anal. Calcd for $C_{36}H_{38}Cl_2N_4O_4$: C, 65.4; H, 5.8; N, 8.5; Cl, 10.7. Found: C, 65.5; H, 6.0; N, 8.4, Cl, 10.6.

Physical Measurements. ^1H and ^{13}C NMR spectra were recorded on a JEOL FX100 and a JEOL FX400 spectrometer. Infrared spectra were recorded as KBr disks on a JASCO A302 spectrophotometer. Microanalyses were performed by Amdel, the Australian Microanalytical Service, and Analytisch Laboratorien, Engelskirchen, West Germany. Magnetic suspectibilities were determined by the Gouy method with $\mathrm{HgCo(SCN)_4}$ as calibrant.

Crystal Structure Determination for [$\mathbf{LNi_4(CH_3CO)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3)}$]·$\mathbf{4CH_3OH}$. Green crystals of $\mathrm{LNi_4(CH_3CO)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3){\cdot}4CH_3OH}$ were grown from a methanolic solution in the presence of additional nickel acetate by the slow transfer of water vapor. Intensity data were collected from a crystal mounted in an arbitrary orientation and sealed in a Lindemann glass capillary together with mother liquor. Crystal data and details of data collection are listed in Table I. Accurate values of the unit cell parameters and the orientation matrix were determined by a least-squares procedure using the angular settings of 25 carefully centered reflections. Corrections for Lorentz, polarization, and absorption effects were applied,[19,20] but no correction was made for extinction; absorption corrections were numerically evaluated by a Gaussian integration to a precision of 0.5%.[19]

The structure was solved by using the direct methods routine of SHELXS-86.[21] The asymmetric unit is composed of half a formula unit, the molecule being situated around a 2-fold axis of symmetry $(^1/_2, y, ^3/_4)$. All non-hydrogen atoms with the exception of the acetate, methoxy, and methanol of solvation were revealed in the *E* map;[21] the remaining non-H atoms were found in subsequent difference maps.[19] The structure was refined by using the full-matrix least-squares facility of the SHELX-76 system,[19] which minimizes the function given in Table I. Anisotropic thermal parameters were assigned to all of the non-hydrogen atoms. Initially, unit weights were used but in the final stages of refinement, the weighting scheme of the form given in Table I was applied.

All the hydrogen atoms of the macrocyclic ligand were clearly apparent in the difference map and were included in the model of their calculated positions. A common isotropic thermal parameter was refined for each H-atom type viz. methyl, methylene, etc. A subsequent difference map showed the hydrogen atom of the hydroxyl group to be located on the 2-fold axis of symmetry and its *y*-coordinate and isotropic thermal parameter were included in the refinement; these parameters converged satisfactorily. The hydrogen atom participating in the hydrogen bond between the two symmetry related OMe groups was also evident in the difference map. Although the maximum of this electron density was on the 2-fold axis the distribution was elongated along the line joining the two oxygen atoms, suggesting that the hydrogen atom is disordered across the 2-fold axis. This atom was included in the refinement and confined to the 2-fold axis. Neither the *y*-coordinate nor the isotropic thermal parameter would converge so that the *y*-coordinate was fixed at the value observed in the difference map; the thermal parameter only was refined. The hydrogen atoms of the methanol of solvation were not apparent and were not included in the model. Values of R, R_w, and k at convergence are given in Table I together with the value of the maximum residual electron density. The scattering factors of C, H, N, and O were as incorporated in the SHELX-76 system.[19] Those for atomic nickel were taken from ref 22 and corrected for real and imaginary anomalous dispersion effects.[22] All calculations were performed on the VAX 11/780 and VAX 11/8650 computers at the University of Melbourne Computer Centre.

Crystal Structure Determination for [$\mathbf{LZn_4(CH_3CO_2)_3(OH)}$]·Solvate. Yellow crystals of $\mathrm{LZn_4(CH_3CO_2)_3(OH){\cdot}}$solvate, the composition of which is given in Table I, were obtained from a solution of the complex in methanol in the presence of additional zinc acetate by the slow transfer of water vapor. Crystal data and data collection parameters are listed in Table I; details of data collection and structure solution are similar to those given for the $\mathrm{Ni_4}$ complex. All of the small irregular crystals investigated in a preliminary study were weakly scattering. That chosen for the data collection was approximately 0.1 mm across; the data were limited to $2\theta = 38°$. Accurate measurement of the crystal faces proved difficult, and in view of this, the relatively low value of the linear absorption coefficient, and the relatively small size of the crystal, absorption corrections were not performed. The asymmetric unit consists of one formula unit, and the four zinc atoms were revealed on the *E* map.[21] The remaining non-hydrogen atoms of the macrocycle and ten of the twelve acetate non-hydrogen atoms were located in subsequent difference maps. Satisfactory refinement of this model only occurred when constraints were initially applied to the bond lengths of the macrocyclic ligand. These distances were initially set to the average value observed for comparable bonds in the nickel structure and were included as parameters in the refinement. During the constrained refinement, the uncoordinated oxygen and methyl carbon of the monodentate acetate were revealed in the difference map. Anisotropic thermal parameters were only assigned to the metal atoms and for the final unconstrained refinement cycles a weighting scheme of the form given in Table I was applied. Electron density consistent with hydrogen atoms was observed near the macrocycle and the acetate groups. Although not all H-atoms were observed, all H atoms were included in the model at their calculated positions with an assignment of the same isotropic thermal parameter as the carbon atom to which they are bonded. Electron density due to solvent molecules was observed in the difference map, and these were included in the model as either methanol or water depending upon the proximity of other atoms. The solvent atoms were assigned a common isotropic thermal parameter and the site occupations were included as parameters in the refinement. Details of the values of R, R_w, k, and maximum residual electron density at convergence are given in Table I. The scattering factors for zinc, corrected for real and imaginary anomalous dispersion,[22] were taken from ref 22. The solvent structure was difficult to define and the discrepancy between the observed and calculated values for the density indicates that not all of the solvent could be located.

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Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom parameters, intramolecular dimensions, intermolecular contacts, and mean planes data for the $\mathrm{LNi_4(CH_3CO)_2(OH)(CH_3O{\cdot}H{\cdot}OCH_3){\cdot}4CH_3OH}$ and $\mathrm{LZn_4(CH_3CO_2)_3OH{\cdot}}$solvate structure (32 pages); listing of structure factors (30 pages). Ordering information is given on any current masthead page.

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