complexes from phenoxo-bridged dicopper(I) complexes has been reported by Karlin and co-workers.[50] Furthermore, a recent crystal structure of a (μ-1,2-peroxo)dicopper(II) complex without a bridging ligand between the two copper centers has been reported.[51]

As the addition of base is essential for the oxidation to occur, we speculate that the role of the base is to deprotonate the substrate (ROH) either before or after binding to one or two copper ions in the binuclear complex. This is in line with mechanistic proposals in oxidative phenol coupling.[49,52] Alternative mechanisms as the one shown in Scheme III might be proposed; for instance, the redox reaction of complex **18** with deprotonated substrate is an attractive possibility. This points to a reversal of the sequence, as shown in Scheme III. It should be emphasized that 1 mol of O_2/mol of substrate is consumed, indicating a two-electron-transfer process contrary to four-electron-transfer processes that lead ultimately to H_2O as was observed in copper(II)-mediated oxidative phenol coupling.[49] In situ (catalytic) decomposition of hydroperoxide anion cannot be excluded. In a control experiment adding 30% H_2O_2 to a methanolic solution of **8** and NaOH, we were not able to detect peroxide after 1 h at room temperature, indicating H_2O_2 decomposition.

The presence of a hydroquinone or phenol moiety in the aforementioned ligands is only essential for bridging in the Cu(II) ions, but has, as far as was observed experimentally, no role in the redox process. Furthermore, it can be concluded that the intended application of the hydroquinone moiety as an electron shunt between an external reducing agent and the Cu(II) ions (and thus molecular oxygen) is not possible with the present model system. Appropriate modifications of ligand **1** and complexes derived thereof that fulfill the requirements mentioned above might be obtained by reduction of the imine functionalities. It is expected that this will result in a lowering of the oxidation potential of the hydroquinone moiety.

In conclusion we have reported here the synthesis of a new ligand system **1** containing a hydroquinone moiety capable of forming binuclear complexes. The molecular structure of an unprecedented, stable, binuclear hydroquinone-containing Cu(II) complex **8** was determined. Furthermore, efficient catalytic dehydrogenations of hydroquinone and α-hydroxy ketones using O_2 were found. However, no oxygenation (O-transfer) was achieved so far.

Supplementary Material Available: Listings of crystallographic details, final fractional atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, bond distances and bond angles, and torsion angles (9 pages); a table of F_o and F_c values (7 pages). Ordering information is given on any current masthead page.

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A Tetraazamacrocycle Functionalized with Pendant Pyrazole Groups: Synthesis of the Octadentate Ligand 1,4,7,10-Tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane (L) and Its Transformation to the Ligand 1,4,7-Tris(1-pyrazolylmethyl)-10-((ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane (L′). Structural Characterizations of the Complexes $[NiL]I_2$, $[NiL'](BPh_4)_2 \cdot 2(CH_3)_2CO$, and $[ZnL'](BPh_4)_2 \cdot (CH_3)_2CO$

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The reaction of 1-(hydroxymethyl)pyrazole with 1,4,7,10-tetraazacyclododecane in CH_3CN gives the new pyrazole-containing tetraazamacrocyclic ligand 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane (L). This potentially octadentate ligand gives iron(II), nickel(II), and copper(II) complexes of general formula $[ML]Y_2$ (M = Ni, Y = Br, I, ClO_4; M = Fe, Y = BPh_4; M = Cu, Y = Cl), which have been isolated in the solid state and characterized by means of standard physical–chemical methods. The structure of $[NiL]I_2$ (**1**) in the solid state has been established by X-ray diffraction methods: monoclinic $C2/c$, $a = 15.210$ (7) Å, $b = 11.524$ (3) Å, $c = 17.829$ (8) Å, $\beta = 100.20$ (4)°, $Z = 4$. The complex is six-coordinated, having two pendant arms of the octadentate ligand uncoordinated. The same L ligand reacts with hydrated $NiCl_2$ and respectively hydrated $ZnCl_2$ in an ethanol–acetone solution of $NaBPh_4$, giving the two complexes $[ML'](BPh_4)_2 \cdot n(CH_3)_2CO$ [M = Ni, $n = 2$ (**2**); M = Zn, $n = 1$ (**3**)], where L′ is the new ligand 1,4,7-tris(1-pyrazolylmethyl)-10-((ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane originating from L by substitution of an ethoxo group for the pyrazole group in one of the pendant arms. The crystal structures of these two complexes have been determined by X-ray diffraction: **2**, monoclinic $P2_1/n$, $a = 20.476$ (5) Å, $b = 13.581$ (9) Å, $c = 25.742$ (5) Å, $\beta = 99.83$ (2)°, $Z = 4$; **3**, triclinic $P\bar{1}$, $a = 13.409$ (15) Å, $b = 25.286$ (9) Å, $c = 11.055$ (5) Å, $\alpha = 102.53$ (4)°, $\beta = 113.15$ (7)°, $\gamma = 79.89$ (7)°, $Z = 2$. The nickel complex is six-coordinated, with one pyrazole group and the ethoxo group uncoordinated, whereas the zinc complex is seven-coordinated, with the ethoxo group uncoordinated. A possible mechanism of the ligand transformation is discussed.

Introduction

The coordination properties toward metal ions of macrocycles bearing pendant donor groups from the macrocycle skeleton have recently attracted much interest, mainly as the study of such systems may provide a basis for a better knowledge of the metal environment in some metalloenzymes and metalloproteins. A number of functionalized macrocyclic ligands have now been reported, and most of them contain as pendant donors aliphatic amines,[1] pyridyl groups,[2] carboxylic acids,[3] alcohols and phenols,[4] nitriles,[1a,5] and other donor groups.[5c,6] Only recently attempts to functionalize macrocycles with biomimetic donors have suc-

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ceeded, the ligands so far reported being a bisadenine derivative of 4,13-diaza-18-crown-6,[7] a monopyrazole of 3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene,[2b] and a monoimidazole of cyclam.[8]

In a previous publication we reported a general, high-yielding route for the functionalization of preformed macrocycles bearing secondary amines with imidazoles attached to the macrocycle skeleton through flexible methylene chains.[9] We report here the functionalization of 1,4,7,10-tetraazacyclododecane with four pyrazole groups connected to the macrocycle through methylene chains. Besides their possible biochemical relevance in modeling the donor properties of histidine residues in the binding sites of metalloproteins, pyrazole- and imidazole-functionalized macrocycles are also of more general interest in the field of coordination chemistry.

With the octadentate ligand 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane (L) we have prepared complexes of general formula $[\mathrm{ML}]\mathrm{Y}_2$ (M = Ni, Y = Br, I, ClO_4; M = Fe, Y = BPh_4; M = Cu, Y = Cl). The structure of the complex $[\mathrm{NiL}]\mathrm{I}_2$ (**1**) has been determined by X-ray diffraction. Unexpectedly, the ligand L reacting with either $NiCl_2$ or $ZnCl_2$ in an ethanol–acetone solution of $NaBPh_4$ undergoes replacement of one pendant pyrazole group by an ethoxo group. The new mixed pendant arm macrocycle 1,4,7-tris(1-pyrazolylmethyl)-10-((ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane (L′) gives the two complexes $[\mathrm{ML'}](\mathrm{BPh}_4)_2 \cdot n(\mathrm{CH}_3)_2\mathrm{CO}$ [M = Ni, *n* = 2 (**2**); M = Zn, *n* = 1 (**3**)], whose structures have been determined by X-ray diffraction methods.

Experimental Section

Materials and Reagents. All reagents were reagent grade; solvents were dried according to standard procedures just before their use. The intermediate compounds 1,4,7,10-tetraazacyclododecane[10] and 1-(hydroxymethyl)pyrazole[11] were prepared according to published procedures. Hydrated metal(II) perchlorates and tetrafluoroborates, and the $\mathrm{NiX}_2 \cdot 4\mathrm{EtOH}$ (X = Br, I) salts, were prepared by standard methods.

Synthesis of 1,4,7,10-Tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane (L). A solution of the preformed macrocycle[10] (30 mmol, 5.17 g) and of 1-(hydroxymethyl)pyrazole[11] (120 mmol, 11.8 g) in CH_3CN (80 mL) was stirred at room temperature for 4 days in a closed vessel. The yellowish solution was allowed to evaporate under reduced pressure at room temperature. The viscous oil so obtained was placed in the refrigerator at −5 °C until crystallization of the mass occurred. A share of the crude product (1 g), which is very hygroscopic, was dissolved in dichloromethane (10 mL) and passed down a basic alumina column (15-cm length by 2-cm diameter). The column was eluted with dichloromethane–methanol (10:1, 200 mL), and the extracts were evaporated to give fairly pure ligand that was satisfactorily employed in the synthesis of the complexes. ^{1}H NMR ($CDCl_3$, δ): 2.83 (s, 16 H, CH_2), 5.04 (s, 8 H, CH_2), 6.25 (t, 4 H, CH, J = 2.0 Hz), 7.44 (d, 4 H, CH, J = 1.9 Hz), 7.71 (d, 4 H, CH, J = 2.0 Hz).

Synthesis of the Complexes. All of the complexes were prepared by mixing warm solutions (20–30 mL) of the L ligand (1 mmol) and of the appropriate metal salt in 1:1 molar ratio. Solvents were methanol, ethanol, acetone, acetonitrile, or their mixtures. When appropriate, the stoichiometric amount of $NaBPh_4$ dissolved in 10 mL of either acetone or ethanol was employed. The crystalline products were collected by suction filtration, washed with small amounts of suitable solvents followed by diethyl ether, and finally dried in a vacuum oven. Recrystallization from suitable solvents gave analytically pure products. The iron(II) complex was prepared under a prepurified nitrogen atmosphere. In some cases the complexes precipitated in a short time; otherwise the solutions of the reactants were allowed to slowly evaporate at room temperature. Details of the syntheses and analytical data are reported below.

$[\mathrm{FeL}](\mathrm{BPh}_4)_2$. Anhydrous $FeBr_2$ in acetone and the ligand in ethanol were mixed together, followed by the addition of $NaBPh_4$ in ethanol. White crystals soon formed, which were recrystallized from acetonitrile–butanol. The complex is soluble in hot acetonitrile.

Anal. Calcd for $C_{72}H_{76}N_{12}B_2Fe$: C, 72.9; H, 6.45; N, 14.2. Found: C, 72.3; H, 6.74; N, 14.2.

$[\mathrm{NiL}]\mathrm{X}_2$ (X = Br, I, ClO_4). The appropriate nickel(II) salt [$\mathrm{NiX}_2 \cdot 4\mathrm{EtOH}$ or hydrated $Ni(ClO_4)_2$] in ethanol and the ligand in acetone were mixed together. Mauve crystals were soon obtained. Slow evaporation of the solution in a dry atmosphere at room temperature gave crystals of $[\mathrm{NiL}]\mathrm{I}_2$ suitable for X-ray analysis. Solubility: X = Br, CH_3CN, CH_3OH, H_2O, DMSO; X = I, DMSO, H_2O (slightly); X = ClO_4, CH_3CN, DMSO.

Anal. Calcd for $C_{24}H_{36}N_{12}Br_2Ni$: C, 40.5; H, 5.10; N, 23.6. Found: C, 40.4; H, 5.30; N, 23.3. Calcd for $C_{24}H_{36}N_{12}I_2Ni$: C, 35.8; H, 4.51; N, 20.9. Found: C, 35.8; H, 4.44; N, 20.4. Calcd for $C_{24}H_{36}N_{12}Cl_2O_8Ni$: C, 38.4; H, 4.84; N, 22.4. Found: C, 38.8; H, 5.02; N, 22.1.

$[\mathrm{CuL}]\mathrm{Cl}_2$. Hydrated $CuCl_2$ and the ligand in acetone were employed, and turquoise crystals were soon obtained. The complex is soluble in DMSO and, slightly, in H_2O and CH_3OH.

Anal. Calcd for $C_{24}H_{36}N_{12}Cl_2Cu$: C, 46.0; H, 5.79; N, 26.8. Found: C, 45.4; H, 5.90; N, 26.1.

$[\mathrm{NiL'}](\mathrm{BPh}_4)_2 \cdot 2(\mathrm{CH}_3)_2\mathrm{CO}$. To a solution formed by hydrated $NiCl_2$ in ethanol and by the ligand L in acetone was added a solution of $NaBPh_4$ in ethanol. The resulting solution was allowed to stand in a desiccator until lilac crystals were obtained. The compound was recrystallized from acetone–ethanol. Crystals suitable for X-ray diffraction were obtained by slow evaporation in a desiccator of a dilute solution of the complex in an ethanol–acetone mixture. The complex is soluble in $(CH_3)_2CO$, CH_3CN, CH_2Cl_2, and $CHCl_3$.

Anal. Calcd for $C_{77}H_{90}N_{10}B_2O_3Ni$: C, 72.0; H, 7.06; N, 10.9; Ni, 4.57. Found: C, 72.1; H, 6.89; N, 11.7; Ni, 5.02.

$[\mathrm{ZnL'}](\mathrm{BPh}_4)_2 \cdot (\mathrm{CH}_3)_2\mathrm{CO}$. The complex was obtained as the above nickel derivative of L′, starting from hydrated $ZnCl_2$. The complex is soluble in $(CH_3)_2CO$ and DMSO.

Anal. Calcd for $C_{74}H_{84}N_{10}B_2O_2Zn$: C, 72.1; H, 6.87; N, 11.4; B, 1.75; Zn, 5.30. Found: C, 71.6; H, 6.93; N, 11.0; B, 1.78; Zn, 5.40.

Physical Measurements. Magnetic susceptibility measurements were made on solid samples at room temperature by the Faraday method with an automated magnetometer DMS-5. Electronic spectra were recorded in the range 300–2000 nm with a Perkin-Elmer Lambda 9 spectrophotometer. Concentrations of the solutions in CH_3CN, CH_3OH, DMSO, or water were about 10^{-3} mol dm^{-3}. The solution spectrum of the iron(II) complex was carried out in a N_2 atmosphere. Infrared spectra were recorded with a Perkin-Elmer 283 grating spectrophotometer on a Nujol mull and KBr plates. ^{1}H NMR spectra were recorded with a Bruker MSL 200 spectrometer on 0.1 mol dm^{-3} solutions in deuterated chloroform or acetone. Chemical shifts are reported on the δ scale relative to internal standard $SiMe_4$. Positive chemical shifts are downfield with respect to $SiMe_4$. Coupling constants are in hertz. Abbreviations: s, singlet; d, doublet; t, triplet.

X-ray Structural Determinations. The mauve crystals of the compound $[\mathrm{NiL}]\mathrm{I}_2$ (**1**), grown in the form of elongated prisms, did not present well-defined faces. The lilac crystals of $[\mathrm{NiL'}](\mathrm{BPh}_4)_2 \cdot 2(\mathrm{CH}_3)_2\mathrm{CO}$ (**2**) were in form of bulky prisms. Those of the uncolored $[\mathrm{ZnL'}](\mathrm{BPh}_4)_2 \cdot (\mathrm{CH}_3)_2\mathrm{CO}$ (**3**) derivative were obtained as small prisms that did not provide good quality material for X-ray diffraction. Crystal data for the three compounds are given in Table I. A CAD4 diffractometer and

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Table I. Crystallographic Data for $[NiL]I_2$ (**1**), $[NiL'](BPh_4)_2 \cdot 2(CH_3)_2CO$ (**2**), and $[ZnL'](BPh_4)_2 \cdot (CH_3)_2CO$ (**3**)[a]

	1	2	3
formula	$C_{24}H_{36}N_{12}NiI_2$	$C_{77}H_{90}B_2N_{10}NiO_3$	$C_{74}H_{84}B_2N_{10}O_2Zn$
fw	805.15	1283.97	1232.55
cryst system	monoclinic	monoclinic	triclinic
space group	$C2/c$	$P2_1/n$[b]	$P\bar{1}$
a, Å	15.210 (7)	20.476 (5)	13.409 (15)
b, Å	11.524 (3)	13.581 (9)	25.286 (9)
c, Å	17.829 (8)	25.742 (5)	11.055 (5)
α, deg	90	90	102.53 (4)
β, deg	100.20	99.83	113.15 (7)
γ, deg	90	90	79.89 (7)
V, Å^3	3076 (2)	7053 (5)	3347 (4)
Z	4	4	2
d(calcd), g cm^{-3}	1.738	1.209	1.222
μ(Mo Kα), cm^{-1}	26.54	7.89	4.25
R[c]	0.043	0.065	0.084
R_w[d]	0.048	0.071	0.089

[a] L = 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane; L′ = 1,4,7-tris(1-pyrazolylmethyl)-10-((ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane. [b] Alternative setting of $P2_1/c$ (No. 14 of ref 12). [c] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

Table II. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[NiL]I_2$ (**1**)[a,b]

atom	x	y	z	U_{eq}, Å^2
I	6286 (1)	1692 (1)	1132 (1)	71 (1)
Ni[c]	5000	2845 (1)	7500	33 (1)
N1	4318 (4)	1729 (4)	6633 (3)	39 (3)
N2	3841 (3)	2432 (5)	8021 (3)	38 (3)
N3	4037 (4)	3591 (5)	6055 (3)	46 (4)
N4	4498 (4)	4074 (5)	6697 (3)	43 (3)
N5	2643 (4)	3445 (5)	8548 (3)	47 (4)
N6	2845 (5)	3967 (6)	9230 (4)	63 (4)
C1	3810 (5)	889 (6)	7015 (4)	46 (4)
C2	3303 (5)	1494 (6)	7563 (4)	45 (4)
C3	4237 (5)	2016 (6)	8793 (4)	45 (4)
C4	4994 (5)	1175 (7)	8758 (4)	49 (4)
C5	3684 (5)	2422 (6)	6084 (4)	48 (4)
C6	3300 (5)	3491 (6)	8047 (4)	44 (4)
C7	3929 (6)	4337 (8)	5476 (4)	63 (6)
C8	4326 (7)	5350 (8)	5736 (5)	74 (6)
C9	4681 (6)	5151 (6)	6493 (4)	55 (5)
C10	1816 (5)	3014 (6)	8423 (5)	55 (5)
C11	1458 (6)	3251 (7)	9055 (6)	67 (6)
C12	2118 (6)	3836 (8)	9536 (5)	70 (6)

[a] In this and the following tables of atomic parameters, coordinates are multiplied by 10^4 and temperature factors by 10^3; standard deviations in the least significant digit(s) are in parentheses. [b] The isotropic equivalent thermal parameter is defined as $(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$. [c] Atom in special position, on a 2-fold axis.

graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) were used for all operations. Unit cell parameters were determined by least-squares refinement of 24 reflections in each case, having $18 < 2\theta < 24°$ (**1**), $26 < 2\theta < 34°$ (**2**), or $18 < 2\theta < 22°$ (**3**). Intensity data were collected at room temperature by the ω–2θ scan technique. The intensities of three standard reflections, monitored periodically throughout the data collections, did not reveal any systematic trends. Data sets were corrected for absorption empirically once the structures had been solved.[13] The principal computer programs used in the crystallographic calculations are given in ref 14.

The structure of compound **1** was solved by Patterson and Fourier methods and refined by full-matrix least squares in which the function $\sum w(|F_o| - |F_c|)^2$ was minimized, with weights $w = [\sigma^2(F_o) + gF_o^2]^{-1}$. The NiL^{2+} cation was found to possess 2-fold symmetry, the Ni atom lying on a binary axis. Only half of the L ligand and one I atom, in addition to Ni in a special position, were therefore located and refined. Since one of the two symmetry-independent pyrazole groups is uncoordinated, the position of the unsubstituted N atom on its ring, i.e. the orientation of the ring with respect to 180° rotations about the C–N (pyrazole) bond of the pendant arm, had to be assigned. This was achieved by comparing (1) the peak heights from ΔF maps for the two alternative N/C sites of the ring [5.6 and 4.9 e Å^{-3}, respectively, for N(6) and C(10) of the final model], (2) the equivalent isotropic temperature factors for the two sites from sets of refinements in which the N and C form factors were exchanged between the two sites, or the 0.5N + 0.5C form factor was assigned to both, and (3) R values from such refinement (on the basis of Hamilton's test,[15] the hypothesis of the alternative orientation of the ring with respect to that finally chosen, as well as the hypothesis of disordered orientation, could both be rejected at the 0.005 level). Moreover, residual density (0.5 e Å^{-3}) was detected on a ΔF map close to the position expected for the H atom attached to the final C(10) site, but not to the N(6) one, such H atom contribution being excluded from the calculation of the ΔF map. Also the pattern of nonbonded interactions (see Results) and agreement between the geometries of the two symmetry-independent pyrazole groups in the cation were in favor of the final model. In the final cycles all non-hydrogen atoms were refined anisotropically. H atoms, introduced in calculated positions (C–H = 0.96 Å), were assigned isotropic temperature factors 20% larger than the equivalent isotropic temperature factors of the corresponding C atoms. The final residuals were R = 0.043 and R_w = 0.048 for 177 parameters and 1654 data with $I > 3\sigma(I)$.

The structure of **2** was solved by direct methods and refined by procedures analogous to those followed for **1**, except as noted below. Of the two uncoordinated pendant groups in this structure only one was found to be an unmodified 1-pyrazolylmethyl group as in the original L ligand. Its orientation was assigned by procedures similar to those already described for **1**. The other uncoordinated arm was found to consist of a tetraatomic arrangement finally identified as an (ethyloxy)methyl chain, where the ethoxo group replaces the pyrazole group of the original L ligand. The nature of the atoms forming such arrangement was determined by examining the trends in values of the temperature factors along the chain, resulting from refinements in which the C, N, or O scattering factors were assigned to the two inner sites of the chain, the C form factor being always assigned to the extremal sites. A smooth trend in U_{eq} values was provided only by the –C–O–C–C model, which was assumed to be correct. Alternative choices produced notably different, and unsatisfactory, results: e.g. assigning the N, rather than O, form factor to the second atom of the chain involved a 40% decrease in its U_{eq}. Moreover, the above model was supported by the R criterion and by the peak heights in ΔF maps (3.7, 5.7, 2.7, 2.7 e Å^{-3}, in the above order) besides being chemically sound. In the final model for **2** all non-hydrogen atoms were refined anisotropically, except the B atoms and the central C atoms of the solvent molecules; both the phenyl and methyl groups were refined as rigid bodies. Convergence was attained at R = 0.065 and R_w = 0.071 for 5560 data and 737 parameters refined in two blocks.

The structure of compound **3** was solved by heavy-atom methods and refined by full-matrix least squares with H atoms in calculated positions and rigid group refinement for the phenyl and methyl groups. The unique free arm of the ligand in this seven-coordinate complex was assumed to consist of an (ethyloxy)methyl chain on the basis of ΔF maps (1.6, 2.0, 1.4, 1.3 e Å^{-3} peak heights in the same order as for **2**) and by analogy with the structure of compound **2**. Due to the scarcity and poor quality of data for this compound anisotropic temperature factors were only assigned to the metal atom, to the non-hydrogen atoms of the free arm, and to the peripheral atoms of the solvate acetone molecule. The

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(13) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(14) (a) Sheldrick, G. M. *SHELX, a Program for Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976. (b) Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Crystallogr.* **1989**, *22*, 389. (c) Johnson, C. K. ORTEP-II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976. (d) Nardelli, M. PARST. *Comput. Chem.* **1983**, *7*, 95.

(15) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

Table III. Positional Parameters and Isotropic Thermal Parameters for $[NiL'](BPh_4)_2{\cdot}2(CH_3)_2CO$ (**2**)[a,b]

atom	x	y	z	U_{eq}/U, Å^2	atom	x	y	z	U_{eq}/U, Å^2
Ni	2724 (1)	2620 (1)	4811 (1)	40 (1)	C51	9512 (2)	1802 (3)	3695 (2)	48 (3)
N1	3401 (2)	3374 (3)	4401 (2)	42 (3)	C52	9509 (2)	1859 (3)	3153 (2)	67 (4)
N2	3305 (2)	3386 (3)	5495 (2)	44 (3)	C53	9894 (2)	1210 (3)	2914 (2)	74 (4)
N3	3272 (2)	1379 (3)	5184 (2)	49 (3)	C54	10283 (2)	505 (3)	3216 (2)	78 (4)
N4	2627 (2)	1679 (3)	4110 (2)	49 (3)	C55	10286 (2)	448 (3)	3757 (2)	87 (5)
N5	2496 (2)	4502 (3)	4316 (2)	47 (3)	C56	9901 (2)	1097 (3)	3997 (2)	71 (4)
N6	2175 (2)	3867 (3)	4596 (2)	45 (3)	C61	8984 (2)	3678 (3)	3686 (2)	54 (4)
N7	3221 (3)	4462 (4)	6250 (2)	62 (3)	C62	8402 (2)	4232 (3)	3627 (2)	87 (5)
N8	3262 (3)	5440 (5)	6168 (3)	94 (4)	C63	8375 (2)	5153 (3)	3385 (2)	107 (5)
N9	2192 (2)	1046 (3)	5362 (2)	56 (3)	C64	8930 (2)	5522 (3)	3202 (2)	92 (5)
N10	1982 (2)	1907 (3)	5110 (2)	49 (3)	C65	9512 (2)	4968 (3)	3261 (2)	80 (4)
O1	1830 (2)	2637 (3)	3603 (2)	76 (3)	C66	9539 (2)	4047 (3)	3503 (2)	73 (4)
C1	3934 (3)	3825 (4)	4788 (2)	54 (4)	C71	764 (2)	2656 (2)	442 (1)	44 (3)
C2	3660 (3)	4188 (4)	5259 (2)	50 (3)	C72	857 (2)	1816 (2)	150 (1)	51 (3)
C3	3783 (3)	2675 (4)	5798 (2)	57 (4)	C73	683 (2)	1828 (2)	−398 (1)	60 (4)
C4	3900 (3)	1770 (4)	5480 (3)	59 (4)	C74	416 (2)	2678 (2)	−655 (1)	59 (4)
C5	3372 (3)	671 (4)	4763 (3)	66 (4)	C75	323 (2)	3517 (2)	−363 (1)	55 (4)
C6	2765 (3)	672 (4)	4325 (3)	66 (4)	C76	497 (2)	3506 (2)	185 (1)	47 (3)
C7	3128 (3)	1982 (5)	3775 (3)	62 (4)	C81	1846 (2)	3118 (3)	1166 (1)	41 (3)
C8	3669 (3)	2638 (4)	4064 (2)	57 (4)	C82	2217 (2)	2976 (3)	765 (1)	51 (3)
C9	3023 (3)	4127 (4)	4065 (2)	51 (3)	C83	2882 (2)	3259 (3)	842 (1)	65 (4)
C10	2198 (3)	5384 (4)	4268 (3)	65 (4)	C84	3174 (2)	3685 (3)	1318 (1)	73 (4)
C11	1671 (3)	5346 (5)	4530 (3)	71 (4)	C85	2803 (2)	3827 (3)	1718 (1)	72 (4)
C12	1681 (3)	4388 (4)	4726 (2)	56 (4)	C86	2139 (2)	3544 (3)	1642 (1)	58 (4)
C13	2878 (3)	3830 (5)	5847 (2)	55 (4)	C91	1093 (2)	1552 (3)	1366 (2)	47 (3)
C14	3532 (4)	4211 (6)	6726 (3)	89 (4)	C92	566 (2)	900 (3)	1228 (2)	59 (4)
C15	3778 (4)	5037 (7)	6957 (3)	107 (5)	C93	553 (2)	15 (3)	1502 (2)	75 (4)
C16	3616 (4)	5797 (7)	6607 (4)	97 (5)	C94	1067 (2)	−218 (3)	1912 (2)	88 (4)
C17	2892 (3)	928 (5)	5563 (3)	61 (4)	C95	1594 (2)	435 (3)	2050 (2)	89 (4)
C18	1685 (3)	492 (5)	5448 (3)	73 (4)	C96	1607 (2)	1320 (3)	1777 (2)	62 (4)
C19	1118 (3)	981 (5)	5233 (3)	81 (4)	C101	599 (2)	3420 (3)	1408 (1)	44 (3)
C20	1322 (3)	1840 (5)	5026 (3)	62 (4)	C102	646 (2)	4439 (3)	1358 (1)	57 (4)
C21	1966 (3)	1669 (4)	3772 (3)	65 (4)	C103	230 (2)	5056 (3)	1587 (1)	71 (4)
C22	1303 (5)	2771 (6)	3205 (4)	129 (5)	C104	−233 (2)	4653 (3)	1865 (1)	80 (4)
C23	1259 (4)	3788 (6)	3047 (3)	119 (5)	C105	−281 (2)	3634 (3)	1915 (1)	68 (4)
C31	9371 (2)	2734 (2)	4622 (2)	46 (3)	C106	135 (2)	3017 (3)	1686 (1)	52 (3)
C32	9773 (2)	3549 (2)	4774 (2)	57 (4)	B1	9030 (3)	2577 (5)	3981 (3)	48 (2)
C33	10072 (2)	3663 (2)	5299 (2)	65 (4)	B2	1067 (3)	2686 (4)	1093 (3)	41 (2)
C34	9970 (2)	2961 (2)	5673 (2)	70 (4)	O2	4127 (6)	2358 (5)	2919 (3)	213 (5)
C35	9568 (2)	2145 (2)	5521 (2)	68 (4)	C111	4199 (5)	2119 (7)	2498 (4)	107 (3)
C36	9269 (2)	2032 (2)	4995 (2)	60 (4)	C112	3741 (7)	1499 (9)	2186 (6)	216 (7)
C41	8265 (2)	2083 (3)	3926 (2)	51 (4)	C113	4772 (6)	2475 (8)	2283 (5)	180 (7)
C42	8023 (2)	1481 (3)	3497 (2)	66 (4)	O3	7554 (5)	3022 (6)	1568 (3)	211 (6)
C43	7369 (2)	1148 (3)	3425 (2)	80 (5)	C121	7262 (6)	3243 (8)	1899 (5)	129 (3)
C44	6958 (2)	1417 (3)	3781 (2)	77 (4)	C122	6563 (7)	3456 (10)	1788 (5)	202 (7)
C45	7201 (2)	2019 (3)	4210 (2)	67 (4)	C123	7548 (10)	3306 (15)	2410 (5)	343 (8)
C46	7854 (2)	2352 (3)	4282 (2)	59 (4)					

[a] Atoms Ni–C23 belong to the $[NiL']^{2+}$ cation, C31–B2 to the BPh_4^- anions, and O2–C123 to the acetone solvate molecules. [b] The equivalent isotropic thermal parameter is defined as in Table II; the temperature factors for atoms refined isotropically are of the form $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

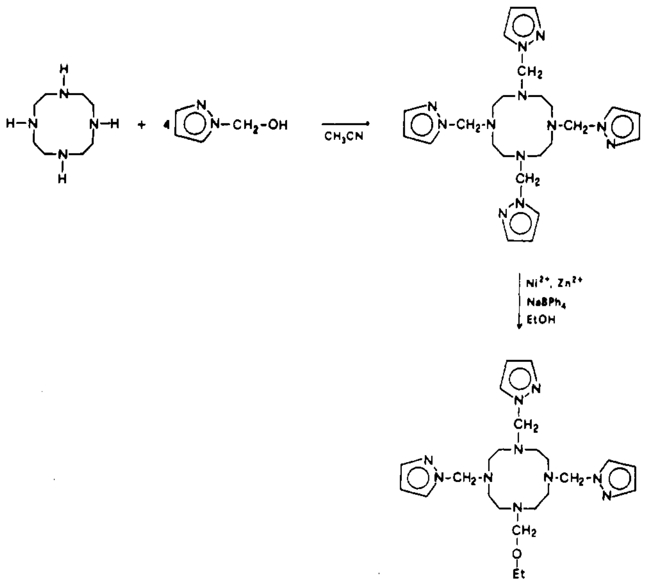
C–C and C–O distances in this molecule were constrained to a fixed ratio. The final residuals were $R = 0.084$ and $R_w = 0.089$ for 2526 data and 311 parameters.

Scattering factors for the neutral atoms and the anomalous dispersion corrections for the metal atoms were taken from ref 16. Tables II–IV contain lists of atomic positional parameters and isotropic or equivalent isotropic thermal parameters for **1**–**3**. Values of selected bond distances and angles for the three compounds appear in Tables V–VII. Available as supplementary material are details on data collections and structure refinements, lists of anisotropic thermal parameters for the three compounds, extended tables of bond distances and angles, lists of hydrogen atom coordinates, and tables of observed and calculated structure factors. See the paragraph at the end of this paper regarding supplementary material.

Results

Complexes with the Ligand L. The new ligand 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane (L) has been prepared in a high yield by the one-step reaction of the preformed macrocycle 1,4,7,10-tetraazacyclododecane with 1-(hydroxymethyl)pyrazole in a CH_3CN solution at room tem-

Scheme I



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(16) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 71, 148.

Table IV. Positional Parameters and Isotropic Thermal Parameters for $[ZnL'](BPh_4)_2\cdot(CH_3)_2CO$ (**3**)[a,b]

atom	x	y	z	U_{eq}/U, Å^2	atom	x	y	z	U_{eq}/U, Å^2
Zn	1654 (2)	2156 (1)	4585 (2)	41 (1)	C45	−199 (8)	10203 (3)	3334 (8)	49 (5)
N1	3291 (10)	2648 (5)	5596 (12)	41 (4)	C46	781 (8)	9871 (3)	3735 (8)	39 (4)
N2	3223 (10)	1485 (5)	4861 (13)	50 (4)	C51	3008 (8)	9280 (4)	4810 (9)	40 (4)
N3	1280 (10)	1628 (5)	2538 (12)	44 (4)	C52	3862 (8)	9595 (4)	5136 (9)	41 (4)
N4	1359 (12)	2753 (6)	3209 (14)	53 (4)	C53	4472 (8)	9778 (4)	6470 (9)	48 (5)
N5	2115 (11)	3138 (6)	6739 (13)	52 (4)	C54	4228 (8)	9646 (4)	7478 (9)	56 (5)
N6	1374 (11)	2781 (5)	6026 (12)	46 (4)	C55	3374 (8)	9332 (4)	7152 (9)	53 (5)
N7	2453 (11)	1203 (6)	6178 (13)	54 (4)	C56	2764 (8)	9149 (4)	5818 (9)	41 (4)
N8	1601 (11)	1573 (5)	5735 (13)	47 (4)	C61	1957 (8)	8418 (4)	3064 (9)	34 (4)
N9	−456 (11)	1629 (6)	2524 (13)	51 (4)	C62	1004 (8)	8225 (4)	2086 (9)	53 (5)
N10	−312 (12)	2032 (6)	3581 (14)	60 (4)	C63	816 (8)	7684 (4)	1927 (9)	65 (5)
O1	−88 (19)	3440 (9)	2054 (23)	225 (14)	C64	1582 (8)	7336 (4)	2746 (9)	67 (5)
C1	4319 (14)	2272 (7)	5941 (18)	66 (6)	C65	2536 (8)	7529 (4)	3724 (9)	58 (5)
C2	4193 (13)	1750 (7)	4998 (17)	51 (5)	C66	2724 (8)	8070 (4)	3883 (9)	50 (5)
C3	2932 (15)	1039 (7)	3744 (17)	68 (6)	C71	4921 (9)	6574 (4)	−258 (11)	49 (5)
C4	2267 (14)	1260 (7)	2474 (17)	58 (5)	C72	4229 (9)	7025 (4)	8 (11)	59 (5)
C5	907 (15)	1957 (7)	1484 (18)	65 (5)	C73	3742 (9)	7028 (4)	917 (11)	75 (6)
C6	1491 (15)	2475 (7)	1986 (17)	64 (5)	C74	3948 (9)	6581 (4)	1560 (11)	74 (6)
C7	2118 (14)	3191 (8)	3865 (19)	72 (6)	C75	4641 (9)	6130 (4)	1294 (11)	65 (5)
C8	3241 (13)	2968 (7)	4593 (16)	56 (5)	C76	5127 (9)	6127 (4)	385 (11)	59 (5)
C9	3246 (16)	3003 (8)	6800 (19)	81 (6)	C81	4448 (10)	6428 (5)	−2950 (10)	66 (6)
C10	1777 (16)	3559 (8)	7466 (19)	71 (6)	C82	3347 (10)	6468 (5)	−3139 (10)	61 (5)
C11	733 (18)	3476 (9)	7252 (21)	92 (7)	C83	2575 (10)	6329 (5)	−4413 (10)	75 (6)
C12	511 (16)	3004 (8)	6370 (19)	74 (6)	C84	2903 (10)	6149 (5)	−5498 (10)	83 (6)
C13	3452 (17)	1268 (9)	6072 (20)	87 (6)	C85	4004 (10)	6109 (5)	−5308 (10)	97 (7)
C14	2235 (15)	868 (8)	6843 (18)	64 (5)	C86	4777 (10)	6248 (5)	−4034 (10)	76 (6)
C15	1249 (15)	1023 (7)	6820 (17)	59 (5)	C91	6477 (9)	6096 (5)	−1370 (12)	69 (6)
C16	838 (16)	1460 (8)	6126 (18)	71 (6)	C92	6277 (9)	5551 (5)	−1644 (12)	71 (6)
C17	454 (14)	1274 (7)	2339 (18)	59 (5)	C93	7135 (9)	5140 (5)	−1547 (12)	104 (7)
C18	−1528 (16)	1591 (8)	1784 (19)	71 (6)	C94	8193 (9)	5274 (5)	−1177 (12)	107 (7)
C19	−2109 (18)	1955 (8)	2374 (20)	79 (6)	C95	8393 (9)	5819 (5)	−904 (12)	107 (7)
C20	−1354 (17)	2241 (9)	3466 (21)	86 (6)	C96	7535 (9)	6230 (5)	−1000 (12)	70 (6)
C21	213 (30)	3047 (14)	2892 (27)	208 (16)	C101	5764 (8)	7202 (5)	−1231 (10)	62 (5)
C22	−1106 (25)	3561 (17)	1366 (43)	281 (16)	C102	5174 (8)	7548 (5)	−2155 (10)	62 (5)
C23	−1278 (25)	3976 (18)	605 (41)	283 (16)	C103	5391 (8)	8091 (5)	−1881 (10)	71 (6)
C31	2901 (8)	9067 (3)	2188 (9)	34 (4)	C104	6197 (8)	8286 (5)	−684 (10)	79 (6)
C32	3521 (8)	8598 (3)	1848 (9)	31 (4)	C105	6787 (8)	7940 (5)	241 (10)	79 (6)
C33	4098 (8)	8606 (3)	1044 (9)	44 (5)	C106	6571 (8)	7398 (5)	−33 (10)	63 (5)
C34	4056 (8)	9083 (3)	579 (9)	43 (5)	B1	2238 (15)	9067 (8)	3199 (18)	38 (5)
C35	3437 (8)	9552 (3)	919 (9)	40 (4)	B2	5447 (16)	6572 (8)	−1472 (20)	51 (6)
C36	2860 (8)	9545 (3)	1723 (9)	38 (4)	O2	2624 (23)	4305 (11)	6255 (24)	234 (14)
C41	1095 (8)	9497 (3)	2788 (8)	30 (4)	C111	3040 (27)	4714 (11)	6516 (30)	171 (11)
C42	429 (8)	9455 (3)	1441 (8)	38 (4)	C112	3228 (36)	5087 (14)	7734 (39)	264 (16)
C43	−551 (8)	9787 (3)	1040 (8)	47 (5)	C113	3363 (38)	4794 (14)	5488 (39)	287 (16)
C44	−866 (8)	10161 (3)	1987 (8)	48 (5)					

[a] Atoms Zn–C23 belong to the $[ZnL']^{2+}$ cation, C31–B2 to the BPh_4^- anions, and O2–C113 to the acetone solvate molecule. [b] The equivalent isotropic thermal parameter is defined as in Table II, and the isotropic temperature factor, as in Table III.

Table V. Selected Bond Distances (Å) and Angles (deg) for $[NiL]I_2$ (**1**)[a]

	(a) Bond Distances		
Ni–N1	2.134 (5)	Ni–N4	2.062 (5)
Ni–N2	2.186 (5)		
	(b) Bond Angles		
N1–Ni–N1′	105.9 (2)	N2–Ni–N2′	154.8 (2)
N1–Ni–N2	81.5 (2)	N2–Ni–N4	102.5 (2)
N1–Ni–N2′	83.5 (2)	N2–Ni–N4′	94.7 (2)
N1–Ni–N4	80.7 (2)	N4–Ni–N4′	93.2 (2)
N1–Ni–N4′	171.9 (2)		

[a] Primed atoms are related to the corresponding unprimed ones through a 2-fold axis passing through the Ni atom position.

Table VI. Selected Bond Distances (Å) and Angles (deg) for $[NiL'](BPh_4)_2\cdot 2(CH_3)_2CO$ (**2**)

	(a) Bond Distances		
Ni–N1	2.140 (5)	Ni–N4	2.194 (5)
Ni–N2	2.209 (4)	Ni–N6	2.055 (4)
Ni–N3	2.157 (4)	Ni–N10	2.057 (5)
	(b) Bond Angles		
N1–Ni–N2	82.1 (2)	N2–Ni–N10	104.8 (2)
N1–Ni–N3	105.2 (2)	N3–Ni–N4	83.0 (2)
N1–Ni–N4	81.3 (2)	N3–Ni–N6	169.3 (2)
N1–Ni–N6	81.0 (2)	N3–Ni–N10	80.0 (2)
N1–Ni–N10	172.1 (2)	N4–Ni–N6	106.8 (2)
N2–Ni–N3	81.1 (2)	N4–Ni–N10	93.7 (2)
N2–Ni–N4	153.0 (2)	N6–Ni–N10	94.8 (2)
N2–Ni–N6	91.3 (2)		

perature (Scheme I) by a procedure similar to that already reported for primary and secondary amines.[11b] Characterization of the ligand was carried out through its ^1H NMR spectrum (see Experimental Section). The reaction of the octadentate ligand L with some metal(II) salts in equimolar ratios gave a number of crystalline compounds having the general formula $[ML]Y_2$ (M = Ni, Y = Br, I, ClO_4; M = Fe, Y = BPh_4; M = Cu, Y = Cl). The electronic spectra of the complexes were recorded on solid samples and in solution. Absorption maxima in the visible region are reported in Table VIII together with magnetic moment values. Visible spectra exhibited by the nickel(II) and copper(II) complexes in the solid state are quite similar to those of the same compounds in solution. In the case of the $[NiL]Y_2$ complexes the spectra are similar to each other, irrespective of the counterion present and of the solvent. These spectra are all indicative of a MN_6 coordination sphere and, consequently, of a six-coordinate ligand. The crystal structure of the complex $[NiL]I_2$ determined by X-ray analysis (vide infra) has confirmed that the ligand is six-coordinated to the nickel atom. The electronic spectrum of the colorless iron(II) complex, both in the solid state and in CH_3CN solution, is essentially featureless in the range 500–2000

Table VII. Selected Bond Distances (Å) and Angles (deg) for $[ZnL'](BPh_4)_2\cdot(CH_3)_2CO$ (3)

	(a) Bond Distances		
Zn–N1	2.458 (12)	Zn–N6	2.084 (13)
Zn–N2	2.421 (13)	Zn–N8	2.173 (14)
Zn–N3	2.277 (13)	Zn–N10	2.474 (14)
Zn–N4	2.249 (14)		
	(b) Bond Angles		
N1–Zn–N2	75.2 (4)	N3–Zn–N4	76.1 (5)
N1–Zn–N3	120.1 (4)	N3–Zn–N6	156.7 (5)
N1–Zn–N4	76.1 (5)	N3–Zn–N8	100.4 (5)
N1–Zn–N6	73.9 (5)	N3–Zn–N10	70.7 (5)
N1–Zn–N8	114.4 (5)	N4–Zn–N6	90.9 (5)
N1–Zn–N10	157.6 (4)	N4–Zn–N8	168.9 (5)
N2–Zn–N3	75.7 (5)	N4–Zn–N10	89.0 (5)
N2–Zn–N4	117.8 (5)	N6–Zn–N8	88.7 (5)
N2–Zn–N6	127.6 (5)	N6–Zn–N10	90.1 (5)
N2–Zn–N8	70.7 (5)	N8–Zn–N10	79.9 (5)
N2–Zn–N10	129.8 (5)		

Table VIII. Electronic Spectra and Effective Magnetic Moments of the Complexes[a]

complex	μ_{eff}, μ_B[b] (293 K)	state[c]	λ, nm (ε, cm² mmol⁻¹)
$[FeL](BPh)_2$[d]	4.96	dr	<500
		CH_3CN	320 (5.5)
$[NiL]Br_2$	3.05	dr	365, 542, 625 sh, 825 sh, 1030
		DMSO	375 (37), 535 (22), 630 sh, 840 sh, 1055 (36)
		CH_3OH	376 (39), 538 (21), 620 sh, 830 sh, 1060 (30)
		H_2O	375 (33), 535 (22), 630 sh, 820 sh, 1050 (38)
$[NiL]I_2$	3.00	dr	370, 530, 620 sh, 1040
		DMSO	375 (40), 535 (26), 1045 (42)
$[NiL](ClO_4)_2$	3.12	dr	375, 535, 620 sh, 830 sh, 1040
		DMSO	368 (41), 530 (27), 625 sh, 830 sh, 1035 (39)
$[NiL'](BPh_4)_2$	3.14	dr	370, 530, 825 sh, 1065
		CH_3CN	370 (43), 530 (23), 625 sh, 825 sh, 1020 (44)
$[CuL]Cl_2$	1.73	dr	750
		DMSO	759 (496)

[a] L = 1,4,7,10-tetrakis(1-pyrazolylmethyl)-1,4,7,10-tetraazacyclododecane; L′ = 1,4,7-tris(1-pyrazolylmethyl)-10-((ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane. [b] $1\ \mu_B = 9.274 \times 10^{-24}$ J T^{-1}. [c] dr = diffuse reflectance; solutions in acetonitrile and in dimethyl sulfoxide are about 10^{-3} M; solutions in water and in methanol are about 10^{-2} M. [d] No d–d transition observable in the range 500–2000 nm.

nm, and d–d transitions are hardly observable. This spectrum is not typical of six-coordinate high-spin iron(II) complexes.[17] In view of the denticity of the L ligand, a coordination number greater than six cannot be ruled out for the $[FeL](BPh_4)_2$ complex. Unfortunately, it has been impossible up to now to obtain crystals of the above compound suitable for X-ray investigations.

The $[NiL]Br_2$ complex exhibits remarkable resistance toward ligand dissociation even in strong mineral acids. For instance, attack by a large excess of $HClO_4$ in about 0.10 M concentration (more than 100:1 molar ratio) for a long time (about 1 month) is required in order to attain complete decomposition of the complex. The great stability of the complexes is also indicated by the fact that the $[FeL](BPh_4)_2$ derivative is considerably inert toward aerial oxidation not only in the solid state but even in CH_3CN solution, from which the complex can be recovered unchanged in air.

Structure of $[NiL]I_2$ (1). The structure consists of $[NiL]^{2+}$ cations and I^- anions. The cation (Figure 1) possesses C_2 symmetry, a 2-fold axis passing through the metal atom. The nickel atom is six-coordinated, with approximate octahedral geometry, by the four nitrogen atoms of the macrocycle and two pyrazole nitrogens belonging to nonadjacent pendant arms of the L ligand, the other two arms being uncoordinated. The four amine nitrogens span two contiguous faces of the distorted octahedron about the nickel atom, and the pyrazole nitrogens occupy the remaining pair of cis positions in the coordination polyhedron. The main deviations from the idealized geometry, possibly imposed by geometric requirements of the ligand, are due to (1) incomplete folding of the 12-membered ring, revealed by the 105.9 (2)° N(1)–Ni–N(1)′ angle, larger than the expected 90° angle for the idealized geometry and (2) inability of the nitrogen atoms of the macrocycle bearing dangling groups to reach trans positions in the coordination sphere. As a consequence of the latter constraint, the N(2)–Ni–N(2)′ angle [154.8 (2)°] is smaller than the expected 180° for the octahedral coordination geometry and all donor atoms of the macrocycle are forced to lie on one side of the metal atom. The nickel atom is constrained by symmetry to lie on the least-squares plane, defined by the atoms N(1), N(4), N(4)′, and N(1)′, which deviate by ≤0.10 (1) Å from the plane, but it is highly displaced, by 0.90 (1) Å, from the best plane through the nitrogen atoms of the macrocycle, which in turn lie in pairs at 0.38 or 0.42 Å on opposite sides of that plane. The Ni–N distances (Table V) formed by the pyrazole nitrogens are shorter than those formed by the amine ones, in agreement with what is generally observed,[9,18] both sets of distances being in the ranges of values found for nickel complexes formed by other macrocycles.[9,18,19] However, detailed comparisons are not possible, as such values are rather dispersed, mainly as a consequence of geometric constraints imposed by the nature of the specific macrocycles and of the substituents in their pendant arms.

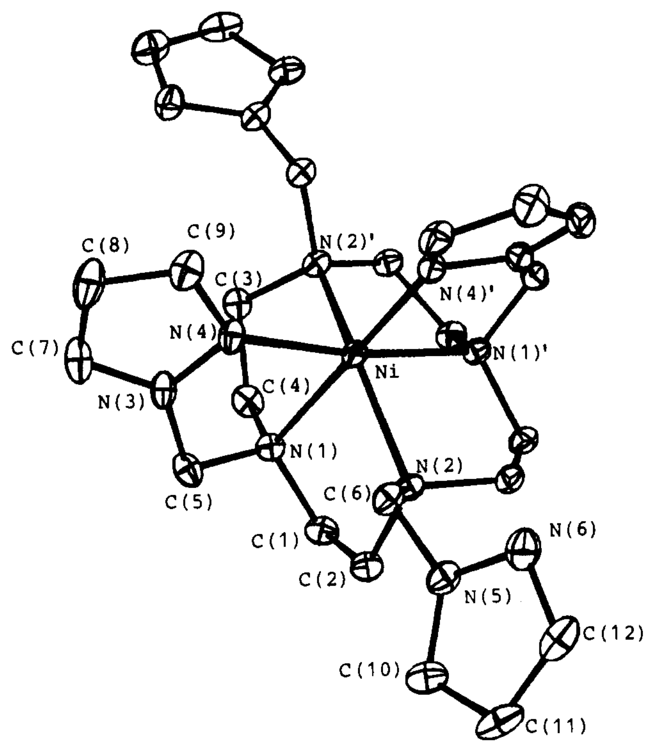

Figure 1. Perspective view of the cation in the structure of $[NiL]I_2$ (1), with 20% probability ellipsoids. The primed N atoms are related to the corresponding unprimed ones through a 2-fold axis passing through the Ni atom position. Only symmetry-independent carbon atoms are labeled.

Complexes with the Ligand L′. Attempts to isolate complexes of cobalt(II), nickel(II), and zinc(II) of general formula $[ML](BPh_4)_2$ failed. Instead the two complexes $[ML'](BPh_4)_2\cdot n(CH_3)_2CO$ (M = Ni, n = 2; M = Zn, n = 1) were obtained with the new ligand L′ = 1,4,7-tris(1-pyrazolylmethyl)-10-((ethyloxy)methyl)-1,4,7,10-tetraazacyclododecane originated from the ligand L by substitution of an ethoxo group

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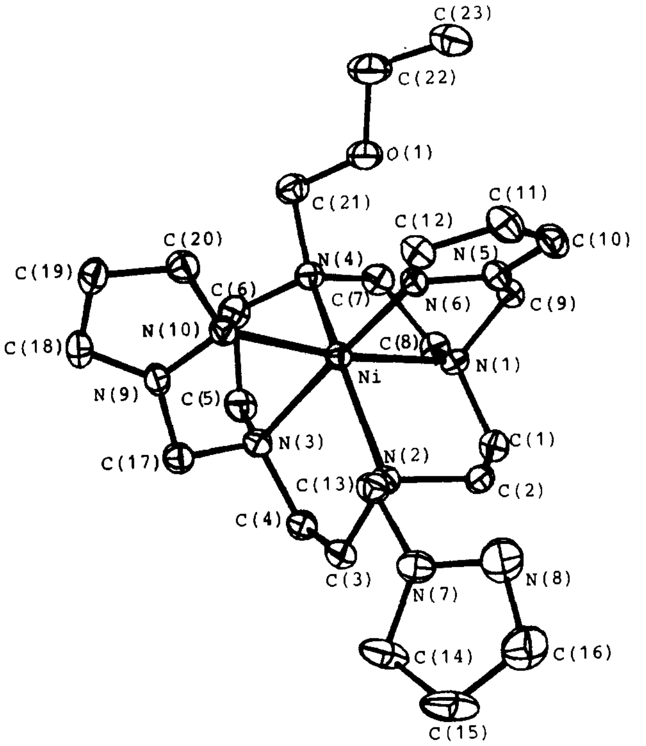

Figure 2. View of the cation in the structure of $[NiL'](BPh_4)_2 \cdot 2(CH_3)_2CO$ (**2**), with 20% probability ellipsoids.

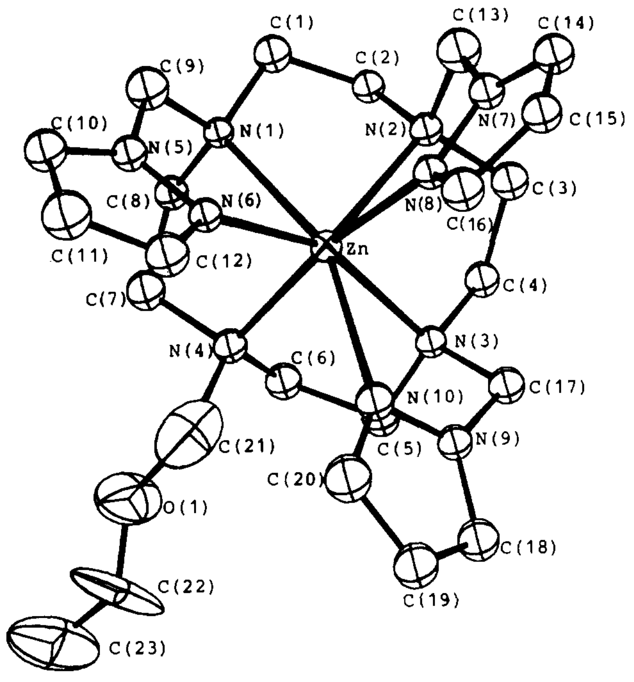

Figure 3. View of the cation in the structure of $[ZnL'](BPh_4)_2 \cdot (CH_3)_2CO$ (**3**), with 20% probability ellipsoids.

for a pyrazole group. Such displacement of one pyrazole group occurs when an acetone solution of the $[ML]^{2+}$ (M = Ni, Zn) complex is allowed to stand with BPh_4^- in ethanol.

Crystal Structures of $[NiL'](BPh_4)_2 \cdot 2(CH_3)_2CO$ (2) and $[ZnL'](BPh_4)_2 \cdot (CH_3)_2CO$ (3). In the structure of **2**, consisting of $[NiL']^{2+}$ cations, BPh_4^- anions, and interposed $(CH_3)_2CO$ solvate molecules, the cation (Figure 2 and Table VI) exhibits coordination geometry closely similar to that found for the $[NiL]^{2+}$ cation in **1**. The arrangement of the L′ ligand matches that of L in **1**, if the substitution of an ethoxo group for the pyrazole in one of the uncoordinated arms is disregarded. As a result of the conformation attained by the macrocycle in compounds **1** and **2**, all pendant arms are forced to point toward one side with respect to the plane through the macrocycle nitrogens. In particular, the N–C bonds involving the amine nitrogens and belonging to the coordinated arms in either structure form angles in the 34–40° range with the normal to the above plane; the corresponding N–C bonds of the free arms form angles in the 55–58° range. By inspection of Figures 1 and 2 the uncoordinated pyrazole groups in both structures are seen to be equally oriented, in the left–right sense already discussed in the Experimental Section, with respect to the molecular frame. Consideration of intramolecular nonbonded distances suggests that this is dictated by the different space requirements of the unsubstituted N atom of pyrazole compared to a C–H group: of the two sites available to N through 180° rotations of the pyrazole plane about the C–N(pyrazole) bond of the pendant arm, the unsubstituted nitrogen atom is found to occupy the site having more stringent steric requirements.

In the structure of compound **3**, consisting of $[ZnL']^{2+}$ cations, BPh_4^- anions, and solvate $(CH_3)_2CO$ molecules, the metal atom in the cation (Figure 3) is seven-coordinated by the four nitrogen atoms of the macrocycle and the three N donor atoms of the pyrazole groups of the L′ ligand. Such a high coordination number is achieved at the expense of some long Zn–N distances (Table VII), those formed by the amine nitrogens ranging 2.25–2.46 Å and those of the pyrazole ones 2.08–2.47 Å. The conformational rearrangement undergone by the macrocycle on going from the structures of the nickel compounds to that of the zinc derivative essentially consists of an increase of the N(1)–M–N(3) angle and a notable decrease of the N(2)–M–N(4) one (N labels as for **2** or **3**). As a result, these angles attain comparable values in **3**: 120.1 (4) and 117.8 (5)°, respectively. The nitrogen atoms of the macrocycle in **3** lie on a plane much more closely, within 0.02 (1) Å, than in the other structures. With reference to the view along the normal to the above plane, given in Figure 3, the coordination geometry in the zinc cation may be tentatively described as that of a square prism with the planes of the basal faces respectively defined by the macrocycle and the pyrazole nitrogens, having however a vacant donor site on the latter face. The metal atom is displaced by 1.19 (1) and 1.36 (1) Å from the planes of the basal faces in the above order; these planes form a 1.3 (5)° angle with each other. As a consequence of the rearrangement, described above, undergone by the ligand on going from the nickel compounds to the zinc one, the N–C bonds of the pendant arms, formed by the amine nitrogens of **3**, deviate by 48–55° from the normal to the plane through the same nitrogen atoms, therefore spanning a narrower range in the values of such angles than the corresponding bonds in the other structures.

NMR Spectrum of $[ZnL'](BPh_4)_2 \cdot (CH_3)_2CO$. The ^1H NMR spectrum of the complex in $(CD_3)_2CO$ at room temperature exhibits the BPh_4^- multiplets (7.47, 7.01, and 6.86 ppm) at the expected shifts and shows in addition three well-separated groups of sharp signals, due to the hydrogen atoms of the macrocycle, to those of the CH_2 bridging groups, and to the pyrazole hydrogens. The ethylene protons of the tetraazacyclododecane ring give a complex multiplet centered at 3.29 ppm, the hydrogen atoms of the methylene chains yield six singlets (4.64, 4.68, 5.07, 5.30, 5.35, and 5.41 ppm), the (C4)H hydrogens of the pyrazole groups present triplets (6.48, 6.50, and 6.68 ppm; $J = 2.0$ Hz), and finally the (C3)H and (C5)H hydrogens give doublets (7.81, 7.91, 8.12, and 8.30 ppm; $J = 2.0$ Hz). A high-field triplet (1.09 ppm; $J = 7.1$ Hz) is assigned to the CH_3 of the ethoxo group; the CH_2 resonances of this group, which are not observed, are probably masked by the intense multiplet at 3.29 ppm. The relative intensities of the signals due to the ethoxo group, the macrocycle, the CH_2 chains, the pyrazole groups, and the tetraphenylborate anions are in agreement with the expected values. The numerous signals observed, in particular for the pyrazole and CH_2 chains, might be accounted for by the presence of at least two species in solution differing in coordination number or coordination geometry about the metal atom.

Discussion

The new functionalized macrocycles L and L′ here reported have been found to behave as strong ligands toward some transition metals. Two of the results here reported deserve further comment, namely the seven-coordination of the metal atom in the $[ZnL']^{2+}$ cation and the solvolysis of the L ligand. The coordination number 7 found for the complex **3** is rather uncommon for zinc(II) complexes.[20] While in some of the examples reported up to now it seems to be strongly favored by the geometric requirements of the ligands employed, in the present case it may be allowed by a combination of factors, like the number of available donor atoms, the absence of stereochemical requirements due to the d^{10} electronic configuration of the zinc(II) ion, the ligand flexibility, and limited steric hindrance of the pyrazole groups.

The substitution reaction undergone by one pendant arm of the L ligand was unexpected. In fact, to the best of our knowledge, cleavage of a C–N(pyrazole) bond followed by formation of a C–O(ether) linkage had never been reported previously for complexes with ligands bearing R_2N-CH_2–pyrazole moieties.[21] In the present case the reaction occurs in very mild conditions when either a nickel(II) or a zinc(II) salt is allowed to stand for a prolonged time in an ethanolic solution of both the ligand and $NaBPh_4$. Several experiments carried out in a variety of solvents, using anions different from BPh_4^- (e.g. BF_4^- or PF_6^-) have provided no evidence that the displacement reaction had taken place. A reasonable mechanism of the displacement reaction involving the BPh_4^- anion is as follows:

$$BPh_4^- + C_2H_5OH \rightarrow BPh_3 + Ph + C_2H_5O^-$$

It is accepted that the BPh_4^- anion undergoes a slow dissociation reaction in protic solvents.[22] Once formed, the ethoxo anion can compete with the pyrazole group for the linkage to the methylene chain.[23] The displacement reaction should involve an uncoordinated pendant arm, rather than a coordinated one. This is supported by the chemical behavior of the hexadentate ligand 1,4,7-tris(1-pyrazolylmethyl)-1,4,7-triazacyclodecane, L″, which is similar to L apart from the lesser denticity. The L″ ligand, which forms stable $[ML''](BPh_4)_2$ 3d metal complexes with all pendant groups coordinated,[24] does not undergo transformations in the experimental conditions in which the L → L′ transformation occurs. Moreover, an uncoordinated pyrazole group should allow rearrangements of the CH_2 carbon atom from sp^3 to the sp^2 hybridization required by the transition state of the replacement reaction if an S_N2 mechanism is operative.

The $[FeL](BPh_4)_2$ complex has been obtained with the intact L ligand even in presence of the BPh_4^- anion. This may be due to the fact that the compound crystallizes immediately after the addition of the BPh_4^- solution to that of the reactants so that the slow replacement process does not occur.

Supplementary Material Available: Full details of the crystal data and crystallographic data collections for **1**–**3** (Table SI), thermal parameters for **1**–**3** (Tables SII–SIV), bond distances (Tables SV–SVII) and angles (Tables SVIII–SX) for **1**–**3**, and hydrogen atom coordinates for **1**–**3** (Tables SXI–SXIII) (28 pages); listings of observed and calculated structure factors for **1**–**3** (47 pages). Ordering information is given on any current masthead page.

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(23) Following the suggestion of a reviewer, an acetonitrile solution of $[NiL](BF_4)_2$ has been treated with an equimolar amount of sodium ethoxide in ethanol in order to support the proposed reaction mechanism. Indeed, by concentration of the solution in a stream of N_2 at room temperature, a compound that analyzed as $[NiL'](BF_4)_2$ was obtained.

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