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The coordination chemistry of macrocyclic 13- and 14-membered dipyridylmethaneamides; crystal structure of the deprotonated Ni(II) complex of 3,15-dioxo-9-ethyl-9-methoxy-1,4,5,6,7,8,10,11,12,13,14,17,18,19,20,21,22,23-octadecadehydro-2,16,22,23-tetraazatetracyclo[15.4.0.$1^{4,8}$.$1^{10,14}$]tricosane

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Abstract

Some 14-membered analogues of previously studied 13-membered macrocyclic dipyridylmethaneamides have been prepared. The ligands form complexes with several metal ions. Spectroscopic studies of Ni(II) and Cu(II) complexes of the deprotonated ligands with both 13- and 14-membered rings have demonstrated that the nickel complexes have square planar coordination while the copper complexes are either square pyramidal or octahedral. A remarkable selectivity was observed in the case of Pd(II) and Ni(II), which formed deprotonated complexes considerably faster with the 13-membered ring than with the higher homologue. The structure of the 13-membered macrocyclic title Ni(II) complex has been determined by X-ray diffraction. Crystal data: $a=8.446(1)$, $b=10.034(1)$, $c=11.209(1)$ Å, $\alpha=84.09(1)$, $\beta=74.33(1)$, $\gamma=87.10(1)°$, triclinic, $P\bar{1}$, $Z=2$. The complex is slightly bent. The four nitrogen atoms adopt a planar coordination geometry with the mean distances Ni–N(amide) = 1.820 and Ni–N(pyridine) = 1.848 Å. The molecules form a layer structure held together by electrostatic interactions besides the van der Waals' forces. The X-ray model was refined to $R=0.033$ for 3936 reflections with $I>3\sigma(I)$.

Introduction

The chemical recognition ability is what renders macrocyclic ligands and their metal complexes important in natural as well as in synthetic systems [1]. Such species participate in diverse processes such as metal ion transport, phase transfer catalysis, separation and metal-catalyzed chemical transformation [2].

We have recently prepared 13-membered tetraaza ligands containing dipyridylmethane and amide subunits. Structural studies of these macrocycles revealed a bowl-shaped conformation both in the solid state and in solution [3, 4]. The compounds are potential tetradentate ligands, since both the dipyridylmethane moiety [5] and the amide groups [6] (the latter either as neutral or anionic entities) have the ability to coordinate metal ions. Neutral amides coordinate either through the nitrogen atom or the carbonyl oxygen, while deprotonated amides coordinate via nitrogen [6]. The latter are strong-field ligands with the ability to stabilize metal ions in high oxidation states, which is of importance in various catalytic processes [7].

Since these macrocycles constitute a new class of ligands with potential application in catalytic processes, it was of interest to study their coordination chemistry. In this paper we report on the preparation of some 14-membered analogues of the previously described 13-membered dipyridylmethaneamides and on the structure and spectroscopic properties of nickel(II), palladium(II) and copper(II) complexes of the deprotonated macrocyclic ligands of both sizes.

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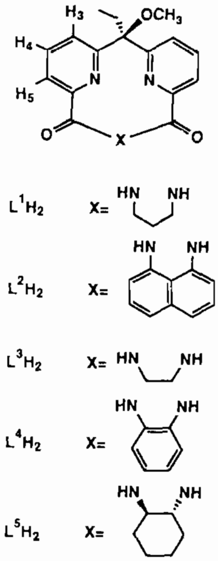

Experimental

Physical measurements

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer in $CDCl_3$ with Me_4Si as internal standard at 400 and 100.6 MHz, respectively. DEPT spectra were recorded to determine carbon multiplicities when appropriate. Visible spectra were recorded on HP 8451A (in the range 300–820 nm) and Pu 8700 spectrometers (300–900 nm), and IR spectra on a Perkin-Elmer 1710 FT spectrometer in KBr. Melting points were corrected with use of standard substances.

Preparation of the ligands

The ligands L^1H_2 and L^2H_2 were prepared under high dilution conditions by the procedure previously described [3]. L^1H_2: 76% crude yield. The product could be purified by column chromatography using EtOAc as eluant or by recrystallization from EtOH or acetone. m.p. 127–130 °C. ^{13}C NMR: 7.33 (CH_3), 28.71 (CH_2), 28.94 (CH_2), 39.89 (CH_2), 51.56 (CH_3), 86.22 (C), 119.70 (CH), 122.48 (CH), 137.24 (CH), 149.22 (C), 159.79 (C) and 164.11 (C). *Anal.* Calc. for $C_{19}H_{22}N_4O_3 \cdot 0.9H_2O$ (the product was hygroscopic and therefore believed to contain some water): C, 61.57; H, 6.47; N, 15.12. Found: C, 61.81; H, 6.41; N, 15.05. L^2H_2: 85% crude yield. A pure product was obtained by column chromatography with EtOAc as the mobile phase or by recrystallization from acetone. m.p. 282–283.5 °C. ^{13}C NMR: 7.48 (CH_3), 28.23 (CH_2), 29.39 (C), 51.73 (CH_3), 54.87 (C), 120.48 (CH), 122.68 (CH), 124.03 (CH), 125.53 (CH), 127.60 (CH), 131.73 (C), 136.56 (C), 138.03 (CH), 149.47 (C), 159.97 (C), 163.53 (C). *Anal.* Calc. for $C_{26}H_{22}N_4O_3$: C, 71.22; H, 5.06; N, 12.78. Found: C, 71.08; H, 5.10; N, 12.80. (^1H NMR spectra of the ligands are presented in Table 1.)

Preparation of the metal complexes

To a boiling solution of the ligand (0.07 mmol) in EtOH was added the appropriate metal acetate (0.1 mmol) in H_2O. The complexes crystallized either directly upon cooling from the reaction mixture or were extracted with CH_2Cl_2 followed by evaporation of the solvent and crystallization of the complex from EtOH. The palladium complexes were prepared from equimolar amounts of the ligand and Na_2PdCl_4 in boiling acetonitrile.

Crystallography

X-ray data collection and processing

The crystals of the title Ni(II) complex, L^4Ni, ($C_{22}H_{18}N_4O_3Ni$, $M_w = 445.12$, triclinic, $P\bar{1}$, $a = 8.446(1)$, $b = 10.034(1)$, $c = 11.209(1)$ Å, $\alpha = 84.09(1)$, $\beta = 74.33(1)$, $\gamma = 87.10(1)°$, $V_c = 909.6(2)$ Å^3, $Z = 2$, $D_c = 1.6252(3)$ Mg m^{-3}, $\mu = 11.03$ cm^{-1}, $F(000) = 460$) were orange regularly shaped octahedral prisms. X-ray diffraction data were obtained from a single crystal with appropriate dimensions ($0.17 \times 0.30 \times 0.37$ mm) at 153(1) K (liquid N_2) using a STOE/AED2 diffractometer equipped with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The ω–2θ scan technique was used with a θ_{max} value of 35°. Five reference reflections were measured once every hour. The intensity instability was <5%. The data reduction included corrections for background, decay, Lorenz and polarization effects, but the relatively weak absorption effects were ignored. The cell parameters were refined against θ values of 40 carefully centered reflections with $30 < 2\theta < 36°$. A total of 8348 reflections was collected with $h < |13|$, $k < |16|$, $0 < l < 18$, of which 8015 were unique, non-zero reflections ($R_{int} = 0.0205$).

Structure determination and refinement

The structure was solved by a combination of heavy atom and direct methods (SHELXS) [8] and refined by full-matrix least-squares treatment using the SHELX program system [9]. The minimized function was $\Sigma w \cdot \Delta(F)^2$. The positions of eight of the hydrogen atoms were derived from difference electron density maps and they were kept riding on their mother atoms during the subsequent calculations. The remaining ten hydrogens were given geometrically assumed positions with C–H = 1.00 Å, which were recalculated after each refinement cycle.

In the final refinement, the positions of the non-hydrogen atoms were refined together with their anisotropic displacement parameters, and isotropic vibrational parameters were refined for the H atoms.

The methyl groups were treated as rigid. The calculation was terminated when all Δ/σ ratios became less than 0.01, except those of the rotation parameters for the methyl C(25) group, of which the highest was 0.13. The number of refined parameters was 277. The final reliability indices based on 3936 reflections with $I > 3\sigma(I)$ were $R = 0.033$ and $R_w = 0.040$, using the weighting $w = [\sigma^2(F) + 0.0006F^2]^{-1}$. The maximum and minimum $\Delta\rho$ values in the final difference map were 0.23 and -0.14 e Å^{-3}, respectively. All calculations were carried out on a CONVEX C-2100 computer.

Results and discussion

Complexation studies

Macrocyclic ligands L^1H_2 and L^2H_2 were prepared by condensation of 1,1-bis(6-chloroformyl-2-pyridyl)-1-methoxypropane and the appropriate 1,3-diamines in analogy with the procedure previously reported for ligands L^3H_2–L^5H_2 [3]. Metal complexes of the ligands were readily formed upon reaction with metal salts (Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+} and Fe^{2+}) in $EtOH/H_2O$ (Pd(II) complexes were obtained in chloroform or acetonitrile). Studies of molecular models reveal that square planar, pyramidal and octahedral coordination is possible, whereas tetrahedral coordination is sterically unfavourable.

Ligand L^5H_2 in chloroform-d (0.020 M) was also extracted with equal volumes of aqueous solutions containing a twofold excess of Na_2PdCl_4 or a sulfate of Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} or K^+, and the organic phase analyzed by ^1H NMR at intervals. Complex formation under these conditions was observed only with Ni(II) and Pd(II). The palladium salt turned out to be the most reactive one, resulting in quantitative formation of a complex. Ligands with different ring sizes showed different reactivity, however. When a twofold excess of Pd(II) was used in a complexation study with the 13-membered ligand L^3H_2, complete complex formation occurred within 48 h (room temperature, 0.013 M organic phase), whereas a tenfold excess of metal ion was required to achieve complete complexation with the 14-membered ligand L^1H_2. (In this case a by-product of unknown structure was observed). The different reactivity of the ligands was verified in a competing experiment where an aqueous solution of Na_2PdCl_4 was extracted with one equivalent each of L^1H_2 and L^3H_2 in chloroform-d (0.013 M in each ligand), resulting in an approximate 10:90 ratio of L^1Pd and L^3Pd (*c.* 5:95 ratio in the initial part of the reaction). The ratios L^1Pd:L^3Pd and L^1H_2:L^3H_2 did not, however, change upon heating at 50 °C for 24 h, indicating different thermodynamic stabilities of the complexes. A preference for the 13-membered ring was also observed for Ni(II) in a competing experiment using 1 equiv. each of L^1H_2, L^3H_2 and $NiSO_4$. This high selectivity of Pd(II) and Ni(II) for the smaller ligand is noteworthy, since the larger ring would be expected to accommodate the rather large metal ions better. The preference for the smaller ligand may, however, be rationalized as an effect of chelate ring size, since complexes of large metal ions have been shown to be destabilized by six-membered chelate rings and instead to prefer five-membered rings [10].

Spectral data for the ligands and their Ni(II), Pd(II) and Cu(II) complexes are given in Tables 1 and 2.

Spectroscopic studies of the nickel(II) complexes

That deprotonated complexes were formed from ligands L^1H_2–L^5H_2 and nickel(II) acetate is evident from the lack of N–H stretching bands in their IR spectra (Table 2) and from the absence of signals from amide protons in the NMR spectra. A further indication of the formation of deprotonated complexes is the rather large decrease in the carbonyl stretching frequency exhibited by the ligands upon complex formation, as compared to the smaller difference shown by iron and zinc complexes containing neutral ligands [11].

The nickel(II) complex of ligand L^1H_2 is yellow with an absorption in the visible region at 412 nm in EtOH, suggesting a square planar coordination [12], which is in analogy with similar previously described non-cyclic bipyridineamides [13]. The extinction coefficient is somewhat higher than expected (*c.* 2500 l mol^{-1} cm^{-1}) suggesting that the d–d transition may be obscured by a charge transfer band [14].

The coordination geometry of nickel(II) is usually sensitive to variation in, for example, solvent, pH and temperature, with high temperature, polar solvents and high pH values favouring a change from square planar to octahedral coordination [15]. However, very small frequency shifts were observed in solvents with superior coordinating properties such as DMSO (absorption at 408 nm) or upon the addition of a ligand such as pyridine, demonstrating the non-tendency of the complex to change the coordination geometry from square planar to octahedral.

The electron spectra of the remaining nickel(II) complexes (L^2Ni–L^5Ni) have absorption bands close to that of L^1Ni (Table 2), suggesting square planar structures for these complexes too.

The ^1H NMR spectra of the nickel(II) complexes all show similar features. Electron donation from the pyridine nitrogen to the metal is evidenced by the downfield shift of the aromatic protons of the pyridine nuclei compared to the free ligand. Rather large upfield shifts of the protons of the methoxy groups and the methylene protons of the ethyl group were also observed, due to shielding of these protons by the metal ion.

TABLE 1. ^1H NMR data for ligands L^1H_2–L^5H_2 and their nickel(II) and some palladium(II) complexes[a]

Compound	CH_3CH$_2$	CH$_3$$CH_2$	OCH$_3$	H$_3$	H$_5$	H$_4$	CONH	Other protons
L^1H_2	0.70	2.68	3.58	7.73	7.92	7.78	8.75	1.98 (2H), 3.55 (2H), 3.92 (2H)
L^1Ni	0.78	2.03	3.18	7.77	7.95	8.09		1.77 (2H), 2.97 (2H), 3.24 (2H)
L^1Pd	0.64	2.04	3.225	7.89	8.06	8.17		1.90 (2H)
L^2H_2	0.77	2.84	3.68	7.78	8.04	7.84	11.06	7.54 (2H), 7.78 (2H), 8.39 (2H)
L^2Ni	0.77	2.28	3.28	7.78	8.11	8.11		7.34 (2H), 7.47 (2H), 8.70 (2H)
L^3H_2	0.73	2.46	3.45	7.75	7.95	7.86	8.82	3.56 (2H), 3.77 (2H)
L^3Ni	0.73	2.02	3.17	7.75	7.79	8.09		3.7 (4H)
L^3Pd	0.73	2.09	3.220	7.78	7.86	8.12		3.95–4.11 (4H)
L^4H_2	0.69	2.59	3.60	7.83	8.04	7.91	10.85	7.28 (2H), 8.09 (2H)
L^4Ni	0.73	2.03	3.18	7.76	7.83	8.11		6.92 (2H), 8.14 (2H)
L^5H_2	0.72	2.48, 2.75	3.58	7.60–7.86			8.14, 8.89	1.36–1.61 (3H), 1.81 (1H), 1.89 (1H), 2.18 (1H), 2.60 (1H), 2.81 (1H), 3.43 (1H), 3.60 (1H)
L^5Ni	0.72	1.98, 2.03	3.15	7.71–7.78		8.07, 8.08		1.25–1.42 (2H), 1.49 (1H), 1.59 (1H), 1.66–1.74 (2H), 3.04 (1H), 3.13 (1H), 3.41 (1H), 3.48 (1H)

[a]Chemical shifts in ppm downfield from Me_4Si. Spectra were obtained at 400 MHz in $CDCl_3$.

TABLE 2. Spectroscopic data for ligands L^1H_2–L^5H_2 and their nickel(II) and copper(II) complexes[a]

Compound	IR (cm^{-1})		λ_{max} (nm)	Colour
	(NH)	(CO)		
L^1H_2	3360	1673		
L^1Ni		1620	408	yellow
L^1Cu		1615	498	violet
L^2H_2	3305, 3325	1675		
L^2Ni		1626	412	red
L^3H_2	3264, 3300	1674		
L^3Ni		1626	430	yellow
L^3Cu		1617	485	violet
L^4H_2	3260, 3340	1699		
L^4Ni		1636	410	orange
L^5H_2	3302, 3346	1686, 1660		
L^5Ni		1635	430	yellow

[a]IR spectra were recorded in KBr and UV–Vis spectra in DMSO.

The ligands undergo a conformational change upon coordination. This change is evident from a comparison of the ^1H NMR spectrum of the chiral ligand L^5H_2 with that of its Ni(II) complex. For example, in the free ligand the chemical shift difference of the diastereotopic methylene proton is as high as 0.26 ppm, whereas in the nickel complex it is reduced to only 0.05 ppm. Decreased shift differences were also observed for the protons in the cyclohexane ring which are related by the twofold rotational axis present in the free amine, indicating a flattening of the structure.

In order to get more exact information about the conformational changes upon coordination and about the coordination geometry around the nickel cation we investigated the structure of the L^4Ni complex also by X-ray diffraction.

Crystallographic description of the L^4Ni complex

A perspective drawing of the molecule, with crystallographic numbering of the atoms, is shown in Fig. 1. The final fractional atomic coordinates are listed in Table 3, distances and bond angles concerning the coordination around the Ni ion are shown in Table 4, and selected conformational features are given in Table 5. Figure 2 is a stereoscopic packing illustration, and Table 6 lists the intermolecular distances shorter than 3.6 Å.

Earlier X-ray studies of five conformers of related tetraaza ring compounds [3, 4] showed that the C(9)–O(24) bond (see Fig. 1) is nearly co-planar with

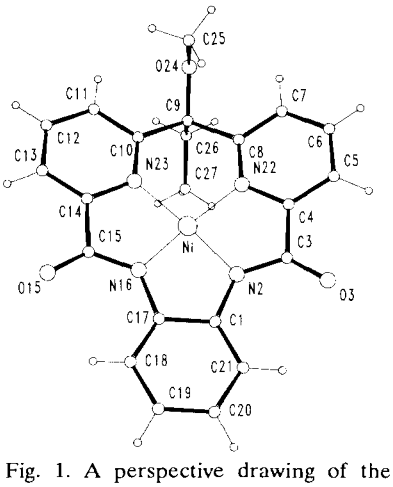

Fig. 1. A perspective drawing of the L^4Ni complex with the crystallographic numbering of the atoms.

TABLE 3. Fractional atomic coordinates and equivalent isotropic[a] displacement parameters for the non-hydrogen atoms in the L^{4}Ni complex with e.s.d.s in parentheses

Atom	x	y	z	U_{eq}[a] (Å^2)
Ni	0.2339(1)	0.0689(1)	0.2769(1)	0.0137(1)
N(2)	0.2790(3)	0.0026(2)	0.4225(2)	0.017(1)
C(3)	0.1886(3)	0.0549(2)	0.5260(2)	0.018(1)
O(3)	0.1780(3)	0.0164(2)	0.6363(2)	0.026(1)
C(4)	0.0899(3)	0.1747(2)	0.4896(2)	0.016(1)
C(5)	−0.0168(3)	0.2505(3)	0.5744(2)	0.020(1)
C(6)	−0.1038(3)	0.3567(3)	0.5286(2)	0.020(1)
C(7)	−0.0803(3)	0.3846(2)	0.4013(2)	0.018(1)
C(8)	0.0265(3)	0.3030(2)	0.3197(2)	0.014(1)
C(9)	0.0583(3)	0.3397(2)	0.1783(2)	0.015(1)
O(24)	−0.0865(2)	0.4041(2)	0.1554(2)	0.020(1)
C(25)	−0.2261(3)	0.3180(3)	0.1795(3)	0.026(1)
C(26)	0.1881(3)	0.4513(2)	0.1384(2)	0.020(1)
C(27)	0.3573(3)	0.4106(3)	0.1551(3)	0.025(1)
C(10)	0.1135(3)	0.2276(2)	0.0908(2)	0.016(1)
C(11)	0.0924(3)	0.2475(3)	−0.0297(2)	0.022(1)
C(12)	0.1503(3)	0.1518(3)	−0.1121(2)	0.022(1)
C(13)	0.2310(3)	0.0366(3)	−0.0758(2)	0.020(1)
C(14)	0.2514(3)	0.0225(2)	0.0426(2)	0.017(1)
C(15)	0.3404(3)	−0.0958(3)	0.0932(2)	0.019(1)
O(15)	0.3949(3)	−0.1911(2)	0.0313(2)	0.030(1)
N(16)	0.3458(3)	−0.0766(2)	0.2097(2)	0.018(1)
C(1)	0.3771(3)	−0.1158(2)	0.4126(2)	0.018(1)
C(17)	0.4119(3)	−0.1623(2)	0.2926(2)	0.018(1)
C(18)	0.5027(3)	−0.2811(3)	0.2679(3)	0.023(1)
C(19)	0.5601(4)	−0.3514(3)	0.3627(3)	0.028(1)
C(20)	0.5307(3)	−0.3032(3)	0.4788(3)	0.028(1)
C(21)	0.4395(3)	−0.1848(3)	0.5045(3)	0.022(1)
N(22)	0.1085(3)	0.2010(2)	0.3650(2)	0.015(1)
N(23)	0.1925(3)	0.1164(2)	0.1244(2)	0.014(1)

[a] $U_{eq}=(1/3)\Sigma_i\Sigma_j U_{ij} a^*_i\, a^*_j\, \mathbf{a}_i \cdot \mathbf{a}_j$.

TABLE 4. The geometry of the coordination around the Ni(II) ion in the L^{4}Ni complex. Ni–N and N...N distances (Å) and N–Ni–N angles (°) with e.s.d.s in parentheses

Distances		Angles	
Ni–N(2)	1.826(2)	N(2)–Ni–N(16)	86.8(1)
Ni–N(16)	1.815(2)	N(2)–Ni–N(22)	87.0(1)
Ni–N(22)	1.848(2)	N(2)–Ni–N(23)	173.5(1)
Ni–N(23)	1.847(2)	N(16)–Ni–N(22)	172.0(1)
N(2)...N(16)	2.501(3)	N(16)–Ni–N(23)	87.2(1)
N(2)...N(22)	2.529(3)	N(22)–Ni–N(23)	98.8(1)
N(16)...N(23)	2.525(3)		
N(22)...N(23)	2.806(3)		

TABLE 5. Selected torsion angles and conformational features, calculated for the L^{4}Ni complex with e.s.d.s in parentheses

Selected torsional angles (°)[a, b]	
N(2)–C(3)–C(4)–N(22)	1.9(3)
N(2)–C(1)–C(17)–N(16)	2.3(3)
N(23)–C(14)–C(15)–N(16)	−2.4(3)
C(7)–C(8)–C(9)–O(24)	−31.0(3)
C(11)–C(10)–C(9)–O(24)	35.6(3)
C(7)–C(8)–C(9)–C(26)	80.8(3)
C(11)–C(10)–C(9)–C(26)	−76.4(3)
N(22)–C(8)–C(9)–O(24)	154.0(2)
N(23)–C(10)–C(9)–O(24)	−149.7(2)
N(22)–C(8)–C(9)–C(26)	−94.2(3)
N(23)–C(10)–C(9)–C(26)	98.3(3)
C(1)–N(2)–C(3)–C(4)	−173.8(2)
C(1)–N(2)–C(3)–O(3)	4.9(4)
N(22)–C(4)–C(3)–O(3)	−176.9(2)
(C17)–N(16)–C(15)–C(14)	177.9(1)
C(17)–N(16)–C(15)–O(15)	−1.7(4)
N(23)–C(14)–C(15)–O(15)	177.2(2)

Least-squares planes[c, d]

Atoms involved in the LS plane calculation	The atoms are co-planar within (Å)	Selected atomic deviations (Å) from the plane
N(2)–C(3)–C(4)–N(22)	0.020(3)	Ni: 0.2301(5)
N(2)–C(1)–C(17)–N(16)	0.024(3)	Ni: 0.0460(5)
N(16)–C(15)–C(14)–N(23)	0.026(3)	Ni: 0.1058(5)
N(2)–C(3)–C(4)–N(22)–Ni	0.156(3)	Ni: 0.0044(5)
N(2)–C(1)–C(17)–N(16)–Ni	0.045(3)	Ni: 0.0009(5)
N(16)–C(15)–C(14)–N(23)–Ni	0.084(3)	Ni: 0.0020(5)
C(10)–N(23)–Ni–N(22)–C(8)	0.110(3)	Ni: 0.0027(5), C(9): 0.379(3)
N(2)· ·N(16)· ·N(23)· ·N(22)	0.045(2)	Ni: 0.0622(5)

Ring puckering coordinates for the N(22)–C(8)–C(9)–C(10)–N(23)–Ni ring[e]

ϕ_2 (°)	−8.8(5)
Q_{tot} (Å)	0.268(2)
θ (°)	105.7(4)

[a] Right-hand rule according to Klyne and Prelog [16]. [b] e.s.d.s are calculated according to Stanford and Waser [17]. [c] The least-squares planes are calculated according to Nardelli *et al.* [18]. [d] See 'Supplementary material'. [e] Puckering parameters are calculated according to Cremer and Pople [19].

the nearest C–C and C–N bonds of the pyridine rings, thus giving rise to a bowl-like conformation for these metal-free ligands. In the present complex, however, the ring is flattened, which brings the four coordinating nitrogen atoms into suitable positions around the metal ion. Accordingly, the mean values of the N–C–C(9)–O(24) and the C–C–C(9)–O(24) torsion angles [16, 17], which are ±178(±6) and 7(±7)° in the free ligands (averaged for five conformers [3, 4]), are changed in the Ni(II) complex to 152 (±3) and 33 (±3)°, respectively. Moreover, the dihedral angle [18] between the pyridine rings is increased from approximately 90° in the free ligands (the mean value with the root mean square deviation in angular brackets is 92[10]°) to 161.1(1)° in the present complex. The flattened ring conformation leads to altered directions also for the ethyl and the methoxy substituents at C(9). Hence, the C(25)–O(24)–C(9)–C(26) and the O(24)–C(9)–C(26)–C(27) torsion angles, which have the mean values ±51 (±3) and ±55 (±2)°, respectively, in the metal-free ligands, became 177.0(2) and 179.1(2)° in the nickel complex.

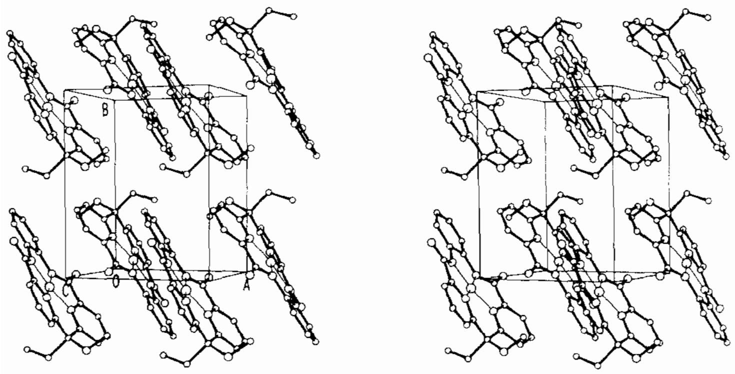

Fig. 2. A stereoscopic packing illustration of L^4Ni complex. The layers are parallel to the *110* direction and neighbouring layers contain molecules with opposite orientations.

TABLE 6. Intermolecular contact distances (Å) less than 3.6 Å between the non-hydrogen atoms with e.s.d.s in parentheses

N(2)...C(5)	3.44(1)	O(3)...C(12)	3.20(1)
N(2)...C(21)	3.38(1)	O(3)...C(13)	3.40(1)
N(16)...C(5)	3.55(1)	O(15)...C(14)	3.37(1)
N(16)...C(13)	3.51(1)	O(15)...C(25)	3.44(1)
N(22)...C(3)	3.57(1)	O(15)...C(27)	3.42(1)

The tetraaza ring functions as a tetradentate ligand, forming one six-membered and three five-membered chelate rings around the Ni^{2+} cation. The five-membered rings are flat with N–C–C–N torsion angles near 0° (see Table 5) whereas the six-membered ring is puckered [19] by having C(9) significantly out of the plane of the five other ring atoms, i.e. indicating a near half-boat conformation with an approximate mirror plane through C(9) and the metal atom. This was also confirmed by a calculation according to Duax *et al.* [20], yielding a low value of one asymmetry parameter only, namely $\Delta C_s(\mathrm{Ni}) = 0.026(1)°$.

The four nitrogen atoms form a square planar coordination around the nickel ion. The sum of the four N–Ni–N angles is 359.8°. The average Ni–N(amide) and Ni–N(pyridine) distances are 1.820 and 1.848 Å, respectively. Comparison with corresponding Ni–N coordination bond lengths, observed in related complexes such as the [*N,N′*-bis(2-pyridinecarboxamido)-*trans*-1,2-cyclohexane]nickel(II) with Ni–N(amide) = 1.868(7), Ni–N(pyridine) = 1.944(8) Å [21], and the disodium triglycylglycinatonickelate(II)hydrates with Ni–N(amino) = 1.924, Ni–N(peptide) = 1.830, 1.820 and 1.870 Å [22] indicates that the Ni cation is somewhat more tightly bound by the present macrocyclic ligand than by the related 'open-chain' ligands.

The covalent bond lengths and bond angles are generally in agreement with the expected values. Worth mentioning, however, is that the C(1)–C(17) aromatic bond (1.419(4) Å) is slightly elongated, whereas the other five C–C bonds in the benzene ring have the expected length (av. 1.393(4) Å). Nevertheless, similar lengthening of corresponding aromatic bonds has been observed in related copper complexes with C–C distances of 1.428(4) [23] and 1.429(11) [24] Å.

In the crystal, the complex molecules are packed so as to form a layer structure (Fig. 2). The layers are stacked parallel to the *110* direction, and neighbouring layers contain molecules with opposite orientations. Examination of the shorter intermolecular contacts (Table 6) gives an indication that the crystal structure is stabilized also by electrostatic interactions besides the ordinary van der Waals' forces.

Spectroscopic studies of the copper(II) complexes

The copper(II) complexes of L^1H_2 and L^3H_2 were isolated from ethanol as violet crystals, which decomposed in air. Their IR spectra are consistent with the formation of deprotonated complexes (Table 2). The crystals dissolved in DMSO and in ethanol to yield violet solutions, whereas green $CHCl_3$ solutions were obtained. L^1Cu showed absorption bands in the visible region at 498, 594 and 626 nm in DMSO, EtOH and $CHCl_3$, respectively, which indicate either an octahedral coordination with two apically situated water molecules or a pentacoordinated complex. The latter situation would result also in an absorption at lower energy [12]. Examination of the spectral region 400–900 nm did indeed reveal a band with a maximum above 900 nm, suggesting a pyramidal rather than octahedral structure for the copper complex, which is in analogy with similar non-cyclic ligands [13].

Supplementary material

Lists of the bond distances and bond angles involving the non-hydrogen atoms (Tables 7 and 8), fractional atomic coordinates of the hydrogen positions and their isotropic displacement parameters (Table 9), bond distances and bond angles involving the hydrogen atoms (Table 10 and 11), a full list of the calculated least-square planes (equations, atomic displacements and dihedral angles) (Table 12), anisotropic displacement parameters of the non-hydrogen atoms (Table 13) and a list of the F_o–F_c values for the L^4Ni complex are available from authors A.E. and I.C.

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