Synthesis and Characterization of a Series of Functionalized Macrocycles Containing Oxygen and Nitrogen Heteroatoms and their Metal Complexes*

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Abstract

The synthesis and characterization of a series of N-functionalized macrocyclic ligands containing oxygen and nitrogen heteroatoms are reported. These ligands are: 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane-N,N'-diacetic acid (H_2L^1); 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacyclo-heptadecane-N,N',N''-triacetic acid (H_3L^2) and 1,15-diaza-3,4:12,13-,dibenzo-5,8,11-trioxacyclooctadecane-N,N'-diacetic acid (H_2L^3). Some of their transition metal and post transition metal complexes are also reported.

The molecular structure of the complex [NiHL^2-(H$_2$O)]·5H$_2$O was proved by single crystal X-ray analysis. The compound crystallizes in the space group $P2_1/n$, with cell parameters $a = 14.683(2)$, $b = 12.630(4)$, $c = 17.400(2)$ Å, $\beta = 109.01(2)°$, $V = 3051(7)$ Å^3, $D_c = 1.479$ g cm^{-3} and $Z = 4$. The structure was solved by the heavy atom method. The positional and thermal parameters of all non-hydrogen atoms were refined by a full matrix least-squares method to $R = 0.048$ and $R_w = 0.053$ for 3839 observed reflections ($I > 3\sigma(I)$). It is shown that the macrocyclic ligand occupies five coordination positions around the nickel ion with one of the pendant carboxylate groups being uncoordinated. The sixth coordination site is occupied by a water molecule.

Introduction

A number of N-functionalized mixed oxygen—nitrogen donor macrocycles have been reported in recent years [1–6]. These macrocycles have both the structural moieties of crown ether and polyaza macrocycles as well as the N-substituted functional groups. Their specific complexation behaviour is clearly of interest in many areas such as the design of potential lanthanide ion selective reagents [4–6], the design of complexes to act as medical imaging agents [7], and for the treatment of heavy metal intoxication in the case of metal poisoning [1, 3].

We are especially interested in getting a better understanding of the coordination properties of these ligands as well as the stereochemistry that can be achieved. Recently a series of studies of the potential for transition metal ion recognition by some mixed oxygen—nitrogen donor macrocycles has been reported by Lindoy and coworkers [2, 8–10]. By the direct reaction of bromoacetic acid with some of these macrocycles, we have synthesized a series of N-functionalized macrocycles containing oxygen and nitrogen heteroatoms: 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane-N,N'-diacetic acid (H_2L^1); 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacyclohepta-decane-N,N',N''-triacetic acid (H_3L^2) and 1,15-diaza-3,4:12,13-dibenzo-5,8,11-trioxacyclooctadecane-N,N'-diacetic acid (H_2L^3) (Fig. 1). The stereochemistry of H_3L^2 was definitely proved by determining the X-ray structure of its nickel complex, [NiHL^2(H$_2$O)]·5H$_2$O.
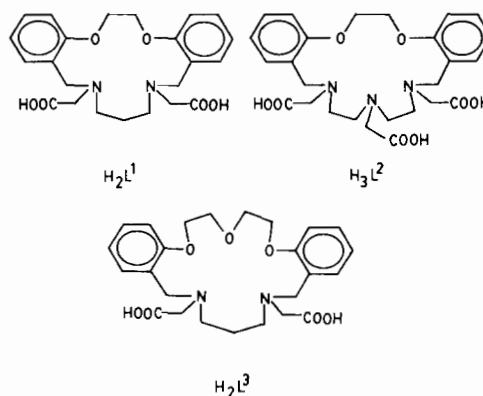

Fig. 1. Structural formulas of H_2L^1, H_3L^2 and H_2L^3.

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Experimental

All chemicals used were of analytical grade. The solvents were purified by conventional methods. The parent macrocycles 1,12-diaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane (I), 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacycloheptadecane (II) and 1,15-diaza-3,4:9,10-dibenzo-5,8,11-trioxacyclooctadecane (III) were prepared by the methods of Lindoy and co-workers [8–10] and characterized by elemental analysis and IR spectroscopy.

Infrared spectra and UV–Vis spectra were obtained with a Nicolet 170Sx and a Shimadzu UV-240 spectrometer, respectively. ^{1}H NMR spectra were recorded on a JEOL FX-90Q spectrometer. Conductivity measurements were made with a DDS-11A conductometer. Microanalyses were determined by Professor Chen Shunxi, Centre of Structure and Elemental Analysis, China University of Science and Technology.

Syntheses of the Ligands

KHL$^1\cdot 3H_2O$ (A)

To 7 g (0.05 mmol) of bromoacetic acid in 30 ml dry methanol, 0.05 mol of KOH in 70 ml dry methanol was added. Then 6.3 g (0.02 mmol) of I in 100 ml dry methanol and 7.6 g (0.055 mol) of powdered anhydrous potassium carbonate were added. The mixture was refluxed with stirring for 10 h, then cooled and the white precipitate of KHCO$_3$ was filtered off. After nearly complete evaporation of the solvent, the residue was dissolved in a minimum of water and the solution was acidified to pH 2 with concentrated hydrobromic acid. The product KHL$^1\cdot 3H_2O$ (A) precipitated as white or light cream crystals upon standing. The free form of H$_2$L^1 has not been obtained. Yield 7.3 g (70%). *Anal.* Found: C, 52.72; H, 6.20; N, 5.01. Calc. for C$_{23}$H$_{33}$KN$_2$O$_9$ (M_r 520.61): C, 53.06; H, 6.39; N, 5.38%. IR (KBr, cm^{-1}): 1728 (COOH), 1623 (COO$^-$), 1599-(sh), 1495, 1453, 1392, 762 (Ar). ^{1}H NMR (D$_2$O): δ 2.30 (2H, –CH$_2$–), 3.26 (4H, N–CH$_2$–), 3.66 (4H, CH$_2$COO$^-$), 4.44 (4H, Ar–CH$_2$–), 4.53 (4H, O–CH$_2$–), 6.9–7.5 (8H, Ar). ^{13}C NMR (D$_2$O): δ 21.78, 22.18 (–CH$_2$CH$_2$CH$_2$–), 53.72 (N–CH$_2$–), 57.03, 57.36, 57.81 (Ar–CH$_2$–), 69.01 (–O–CH$_2$–), 114.78, 119.2, 124.34, 135.07, 135.65, 159.78 (Ar), 172.33 (COO$^-$).

H$_3$L$^2\cdot 2HBr\cdot 6H_2O$ (B)

By a similar procedure to that described above, 6.25 g (0.02 mol) of II yielded H$_3$L$^2\cdot 2HBr\cdot 6H_2O$ as white or light cream crystals. Yield 10.2 g (*c.* 65%). *Anal.* Found: C, 40.00; H, 6.04; N, 5.26. Calc. for C$_{26}$H$_{47}$Br$_2$N$_3$O$_{14}$ (M_r 785.466): C, 39.75; H, 6.03; N, 5.35%. IR (KBr cm^{-1}): 2500–2300 (NH$^+$), 1738 (COOH), 1633 (COO$^-$), 1604, 1496, 1454, 760 (Ar).

^{1}H NMR (D$_2$O) δ 3.66br (8H, –NCH$_2$–), 3.9 (4H, Ar–CH$_2$–), 4.88br (10H, –OCH$_2$–, N–CH$_2$–COO$^-$), 6.9–7.5 (8H, Ar).

H$_2$L$^3\cdot 3HBr\cdot 4.5H_2O$ (C)

By a similar procedure to that described above, 7.25 g (0.02 mol) of III yielded H$_2$L$^3\cdot 3HBr\cdot 4.5H_2O$ (C) as light cream crystals. Yield 10.4 g (*c.* 65%). *Anal.* Found: C, 37.74; H, 5.38; N, 3.64. Calc. for C$_{25}$H$_{44}$Br$_3$N$_2$O$_{11}$ (M_r 796.322): C, 37.70; H, 5.57; N, 3.52%. IR (KBr, cm^{-1}): 2600–2300 (NH$^+$), 1739 (COOH), 1641, 1630 (COO$^-$), 1604, 1495, 1452, 764 (Ar). ^{1}H NMR (D$_2$O) δ 2.6 (2H, –CH$_2$–), 3.39 (4H, N–CH$_2$–), 3.83 (4H, Ar–CH$_2$–), 4.06–4.26 (8H, –OCH$_2$–), 6.98–7.6 (Ar).

Syntheses of the Complexes

A solution of compound **A** or **B** or **C** (0.5 mmol) in methanol or water was added to the required metal salt (1 mmol) in methanol or water. The pH was adjusted to 5 with KOH. The mixture was stirred and heated for 1 h; the corresponding metal complex crystals were obtained upon standing. These were collected and air dried. Satisfactory microanalyses (Table 1) were obtained for all complexes. The IR data of these complexes are given in Table 2 with their assignments.

Crystallographic Study

Light blue crystals suitable for X-ray determination were obtained under a controlled rate of evaporation of the aqueous solution of [NiHL^2-(H$_2$O)]·5H$_2$O, M_r 680.35, space group $P2_1/n$, a = 14.683(2), b = 12.630(4), c = 17.400(2) Å, β = 109.01(2)°, Z = 4, V = 3051(7) Å^3, D_c = 1.479 g cm^{-3}, μ = 7.056 cm^{-1}.

Three-dimensional X-ray diffraction data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation using ω–2θ scan mode. A total of 5861 reflections was measured in the range of 2 $\leqslant$ 2θ $\leqslant$ 50°. Corrections were made for Lorentz, polarization and empirical X-ray absorption effects. Positions of the metal atoms were solved by the heavy atom method and the positions of other non-hydrogen atoms were located by difference Fourier syntheses. The positional and thermal parameters of all non-hydrogen atoms were refined by a full matrix least-squares method to R = 0.048 and R_w = 0.053 for 3839 observed reflections with $I > 3\sigma(I)$. The final atomic coordinates are listed in Table 3.

Results and Discussion

In the previous method [11] of preparing complexon-like macrocyclic ligands, neutralization of the alkylating agents, chloroacetic acid or bromoacetic acid, was carried out in cold water solution and

TABLE 1. Analyses and yield of complexes

Compound	Colour	Analyses (%)[a]			Yield (%)
		C	H	N	
$K_2L^1 \cdot 5H_2O$ (1)	colourless	46.12 (46.45)	6.38 (6.10)	4.63 (4.71)	90
$Li_2L^1 \cdot 8H_2O$ (2)	colourless	47.08 (47.26)	7.50 (7.24)	4.86 (4.79)	90
$CuL^1 \cdot 3H_2O$ (3)	blue	50.41 (50.77)	5.60 (5.93)	4.89 (5.15)	80
$CoL^1 \cdot 3H_2O$ (4)	light brown—red	51.04 (51.21)	5.71 (5.98)	5.21 (5.19)	75
$NiL^1 \cdot 3H_2O$ (5)	green	51.00 (51.21)	5.76 (5.98)	5.09 (5.20)	80
$ZnL^1 \cdot 3H_2O$ (6)	colourless	50.34 (50.60)	5.65 (5.91)	5.11 (5.13)	70
$CdL^1 \cdot 2H_2O$ (7)	colourless	48.32 (48.05)	5.03 (5.26)	4.74 (4.87)	85
$HgL^1 \cdot H_2O$ (8)	colourless	43.02 (42.82)	4.58 (4.38)	4.37 (4.34)	60
$KH_2L^2 \cdot 2HCl$ (9)	colourless	49.49 (49.84)	5.62 (5.47)	6.77 (6.71)	75
$Cu_2BrL^2 \cdot 3H_2O$ (10)	light blue	40.31 (40.37)	4.52 (4.69)	5.52 (5.43)	80
$CoHL^2 \cdot 4.5H_2O$ (11)	light reddish brown	47.97 (47.78)	5.98 (6.17)	6.21 (6.43)	70
$KNiL^2 \cdot 6H_2O$ (12)	light blue	43.65 (43.47)	5.63 (5.89)	5.95 (5.85)	85
$NiHL^2(H_2O) \cdot 5H_2O$ (13)	light blue	45.84 (45.90)	6.41 (6.37)	6.12 (6.18)	85
$CdHL^2 \cdot HBr \cdot 5H_2O$ (14)	colourless	38.91 (39.19)	5.07 (5.31)	5.10 (5.27)	80
$(HgCl)_2HL^2 \cdot 2HBr$ (15)	white	27.11 (27.22)	3.07 (2.90)	3.68 (3.66)	65
$K_2L^3 \cdot 7H_2O$ (16)	colourless	44.54 (44.50)	6.30 (6.57)	4.09 (4.15)	85
$CuL^3 \cdot 5H_2O$ (17)	blue	47.88 (48.11)	6.37 (6.46)	4.46 (4.49)	80
$CoL^3 \cdot 3H_2O$ (18)	pink	51.20 (51.46)	5.92 (6.22)	4.84 (4.80)	70
$NiL^3 \cdot 3H_2O$ (19)	light green	51.40 (51.48)	5.94 (6.22)	5.00 (4.80)	75
$ZnL^3 \cdot 1.5H_2O$ (20)	colourless	53.39 (53.34)	6.09 (5.91)	5.01 (4.98)	70
$CdL^3 \cdot 4.5H_2O$ (21)	colourless	45.30 (45.22)	5.82 (5.92)	4.38 (4.22)	70
$Hg_2Cl_3HL^3 \cdot 3H_2O$ (22)	colourless	29.42 (29.06)	3.82 (3.61)	2.81 (2.71)	65

[a]Calculated values are given in parentheses.

TABLE 2. Infrared spectra of metal complexes (cm^{-1})

Compound	ν(COOH)	ν(COO$^-$)	ν(NH$^+$)	ν(Ar−O−C)	ν(Ar)
1		1628		1225	1494, 1454, 762
2		1629		1225	1494, 1452, 762
3		1639		1223	1489, 1450, 760
4		1617		1223	1496, 1451, 751
5		1632		1237	1491, 1458, 755
6		1657		1229	1490, 1455, 758
7		1586		1221	1489, 1450, 758
8		1654		1224	1496, 1447, 754
9	1739	1639	2500(br)	1248	1494, 1451, 765
10		1604		1228	1491, 1451, 762
11	1723	1600		1226	1489, 1451, 762
12		1598		1228	1488, 1452, 762
13	1721	1600		1227	1490, 1451, 763
14	1721	1605	2500(br)	1235	1496, 1449, 763
15	1724	1629	2500(br)	1249	1495, 1452, 760
16		1640		1241	1495, 1452, 764
17		1655		1245	1494, 1459, 764
18		1616		1241	1492, 1449, 756
19		1616		1242	1492, 1450, 757
20		1622		1247	1495, 1452, 763
21		1623		1242	1492, 1448, 759
22	1728	1623		1248	1495, 1452, 758

TABLE 3. Atomic coordinates and thermal parameters for NiHL^2(H$_2$O)·5H$_2$O with e.s.d.s in parentheses

Atom	x	y	z	B_{eq}
Ni	0.19700(4)	0.17650(5)	0.03597(3)	2.18(1)
O1	0.3588(3)	0.3219(4)	0.2397(2)	5.9(1)
O2	0.2421(2)	0.2331(3)	0.1504(2)	2.89(7)
O3	−0.0898(2)	0.1345(3)	−0.0193(2)	3.70(8)
O4	0.0623(2)	0.1783(3)	0.0418(2)	2.93(7)
O5	0.4146(3)	0.1204(3)	−0.1218(2)	4.57(9)
O6	0.1412(3)	0.5514(3)	−0.0522(2)	4.66(9)
O7	0.0891(3)	0.5790(3)	0.0516(2)	4.62(9)
O8	0.2358(3)	0.1244(3)	−0.2409(2)	5.00(1)
O15	0.2210(2)	0.0232(3)	0.0807(2)	3.13(7)
O16	0.0896(3)	0.2873(5)	0.2113(2)	6.9(1)
O17	0.2282(4)	0.0086(4)	0.2391(3)	8.2(2)
O18	0.2476(5)	0.1903(6)	0.3397(3)	10.6(2)
O19	0.0766(5)	0.5127(5)	0.2191(4)	10.5(2)
O20	0.0950(3)	−0.2646(3)	−0.1038(2)	4.19(9)
N1	0.3479(3)	0.1997(3)	0.0490(2)	2.61(8)
N12	0.1195(3)	0.1287(3)	−0.0883(2)	2.45(8)
N15	0.1795(3)	0.3358(3)	−0.0127(2)	2.52(8)
C2	0.4006(3)	0.1058(4)	0.0323(3)	3.0(1)
C3	0.4955(3)	0.1329(4)	0.0185(3)	3.5(1)
C4	0.4979(3)	0.1453(4)	−0.0605(3)	3.7(1)
C6	0.4058(4)	0.1412(6)	−0.2033(3)	5.7(2)
C7	0.3186(4)	0.0871(6)	−0.2556(3)	5.9(2)
C9	0.1548(4)	0.0611(4)	−0.2691(3)	3.9(1)
C10	0.1155(3)	0.0203(4)	−0.2127(3)	3.2(1)
C11	0.1621(3)	0.0398(4)	−0.1222(3)	3.2(1)
C13	0.1173(4)	0.2259(4)	−0.1370(3)	3.6(1)
C14	0.1061(4)	0.3243(4)	−0.0946(3)	3.5(1)

(continued)

TABLE 3. *(continued)*

Atom	x	y	z	B_{eq}
C16	0.2760(4)	0.3710(4)	−0.0102(3)	3.9(1)
C17	0.3432(3)	0.2827(4)	−0.0124(3)	4.00(1)
C18	0.3949(4)	0.2383(5)	0.1325(3)	4.3(1)
C19	0.3265(4)	0.2676(4)	0.1780(3)	3.2(1)
C20	0.0205(3)	0.1003(4)	−0.0895(3)	3.0(1)
C21	−0.0041(3)	0.1420(4)	−0.0176(3)	2.6(1)
C22	0.1416(4)	0.4056(4)	0.0372(3)	3.3(1)
C23	0.1218(4)	0.5211(4)	0.0118(3)	3.5(1)
C24	0.5822(4)	0.1774(5)	−0.0732(4)	4.8(1)
C25	0.6635(4)	0.1951(5)	−0.0083(4)	5.3(2)
C26	0.6643(4)	0.1806(5)	0.0700(4)	5.2(2)
C27	0.5790(4)	0.1492(4)	0.0831(4)	4.2(1)
C28	0.0327(4)	−0.0410(4)	−0.2421(3)	3.7(1)
C29	−0.0097(5)	−0.0607(5)	−0.3237(3)	4.8(1)
C30	0.0314(5)	−0.0188(5)	−0.3777(3)	5.4(2)
C31	0.1123(5)	0.0421(5)	−0.3515(3)	4.9(1)

alkylation of the macrocyclic amine was also carried out in a water-containing medium. It takes as long as 24 h to complete the reaction and for most of the reaction time the pH of the reaction solution must be maintained between 9 and 10. Obviously, the reaction conditions are difficult to control and hydrolysis of the alkylating agents is unavoidable under such circumstances. In this paper, neutralization of the alk. lating agent and alkylation of the macrocyclic amines are carried out in dry methanol medium and powdered anhydrous K_2CO_3 is used to neutralize the HBr produced by the alkylation reaction. This procedure is very convenient and the hydrolysis side reaction can also be avoided.

Metal Complexes

Ligands H_2L^1, H_3L^2 and H_2L^3 have six, eight and seven potential coordinating atoms, respectively. Their metal complexes were studied in part in solution, but mainly by preparing several crystalline compounds. According to the elemental analyses, these ligands form complexes with transition metals, post transition metals as well as certain large metal ions. Their lanthanide complexes will be reported subsequently.

It is very interesting to compare the colour of the solid complexes and the solution (ethanol–water, 4:1) spectra (Fig. 2) of the copper complexes, $CuL^1 \cdot 3H_2O$, $Cu_2BrL^2 \cdot 3H_2O$ and $CuL^3 \cdot 5H_2O$. Both of the solids $CuL^1 \cdot 3H_2O$ and $CuL^3 \cdot 5H_2O$ are blue, while the solid $Cu_2BrL^2 \cdot 3H_2O$ is light blue. On the other hand, the spectra of CuL^1 and CuL^3 are very similar and show one transition with a maximum at *c.* 620 nm, while the spectrum of Cu_2BrL^2 shows a transition with a maximum at *c.* 740 nm. These spectra indicate that the Cu_2BrL^2 complex has a much lower
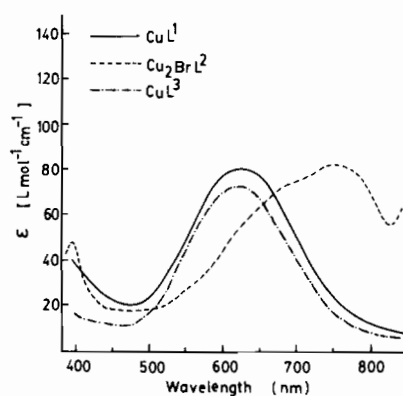

Fig. 2. Electronic spectra for the complexes shown in ethanol–water (4:1) medium.

ligand field than the CuL^1 and CuL^3 complexes. This is probably due to the fact that the two copper atoms of Cu_2BrL^2 share the three amine nitrogen donors and the three pendant carboxylate groups of the macrocyclic ligand H_3L^2, while each of the central atoms of CuL^1 and CuL^3 is coordinated with two amine nitrogen donors and two pendant carboxylate groups, because the amine donors produce a rather strong ligand field which causes the absorption band to move from the far red to the middle of the red region of the spectrum. The spectra strongly suggest that in solution the copper atoms of Cu_2BrL^2 might keep their 'sharing' binuclear structure.

Structure of $[NiHL^2(H_2O)] \cdot 5H_2O$

The crystal consists of monomeric complex molecules of the indicated formula, a molecule of coordinated water and five molecules of crystalline water. The structure of the macrocyclic complex is shown in

TABLE 4. Selected bond distances (Å) and angles (°) in $[NiHL^2(H_2O)]\cdot5H_2O$

Distances

Ni–O2	2.013(2)	C6–C7	1.474(7)	N1–C18	1.473(4)
Ni–O4	2.013(2)	C7–O8	1.403(5)	C18–C19	1.541(5)
Ni–O15	2.074(2)	O8–C9	1.384(5)	C19–O1	1.232(4)
Ni–N1	2.173(3)	C9–C10	1.389(4)	C19–O2	1.252(4)
Ni–N12	2.175(3)	C10–C11	1.518(4)	N12–C20	1.491(4)
Ni–N15	2.165(3)	C11–N12	1.497(4)	C20–C21	1.507(5)
N1–C2	1.495(4)	N12–C13	1.486(4)	C21–O3	1.253(4)
C2–C3	1.528(5)	C13–C14	1.480(5)	C21–O4	1.254(4)
C3–C4	1.395(5)	C14–N15	1.488(4)	N15–C22	1.465(4)
C4–O5	1.371(5)	N15–C16	1.478(4)	C22–C23	1.524(5)
O5–C6	1.406(5)	C16–C17	1.498(5)	C23–O6	1.295(6)
C17–N1	1.483(4)	C23–O7	1.209(4)		

Angles

O2–Ni–O4	87.62(9)	Ni–N12–C20	105.85(19)	N1–C18–C19	114.73(29)
O2–Ni–O15	89.97(9)	Ni–N15–C14	103.94(21)	C18–C19–O1	117.32(33)
O2–Ni–N1	81.54(10)	Ni–N15–C16	106.13(20)	C18–C19–O2	117.21(30)
O2–Ni–N12	168.07(10)	Ni–N15–C22	110.27(20)	O1–C19–O2	125.46(35)
O2–Ni–N15	90.91(10)	N1–C2–C3	114.18(28)	C11–N12–C20	110.40(26)
O4–Ni–O15	92.36(10)	C2–C3–C4	119.78(33)	C13–N12–C20	110.58(27)
O4–Ni–N1	168.10(10)	C3–C4–O5	116.01(32)	N12–C20–C21	113.61(27)
O4–Ni–N12	81.29(9)	C4–O5–C6	120.49(32)	C20–C21–O3	117.68(30)
O4–Ni–N15	90.88(10)	O5–C6–C7	108.25(36)	O3–C21–O4	123.61(32)
O15–Ni–N1	92.52(10)	C6–C7–O8	111.21(40)	O4–C21–C20	118.65(29)
O15–Ni–N12	94.83(10)	C7–O8–C9	115.99(34)	C14–N15–C22	109.27(26)
O15–Ni–N15	176.68(10)	O8–C9–C10	118.11(33)	C16–N15–C22	110.33(28)
N1–Ni–N12	109.09(10)	C9–C10–C11	121.46(35)	N15–C22–C23	118.46(31)
N1–Ni–N15	84.44(10)	C10–C11–N12	115.17(28)	C22–C23–O6	117.25(32)
N12–Ni–N15	84.93(10)	C11–N12–C13	109.18(27)	C22–C23–O7	119.11(37)
Ni–O2–C19	117.93(22)	N12–C13–C14	113.20(27)	O6–C23–O7	123.46(36)
Ni–O4–C21	117.90(20)	C13–C14–N15	113.34(29)	C2–C3–C27	121.17(35)
Ni–N1–C2	116.61(20)	C14–N15–C16	116.59(28)	O5–C4–C24	123.98(38)
Ni–N1–C17	102.32(20)	N15–C16–C17	114.23(30)	C17–N1–C18	111.89(30)
Ni–N1–C18	106.41(21)	C16–C17–N1	112.60(30)	O8–C9–C31	120.73(38)
Ni–N12–C11	116.70(20)	C17–N1–C2	109.02(26)	Ni–N12–C13	104.17(19)
C2–N1–C18	110.39(27)				
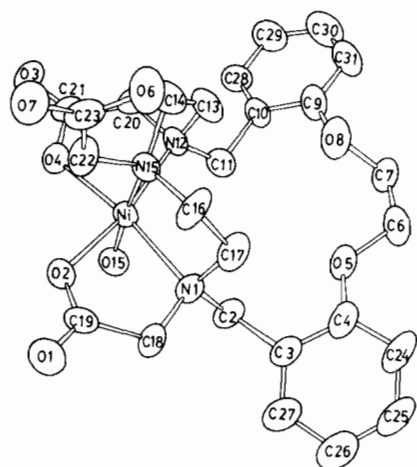
Fig. 3. Structure of $[NiHL^2(H_2O)]\cdot5H_2O$. The crystalline water molecules have been omitted for clarity.

the drawing of the molecule (Fig. 3). Most crystalline water molecules are bonded with the carboxylate oxygen atoms through hydrogen bondings. Selected bond distances and angles are given in Table 4.

The nickel atom in the complex is six coordinated to the three nitrogen atoms of the macrocycle and two oxygen atoms of two pendant carboxylate groups, with the three nitrogen atoms of the 1,4,7-triazaneptane unit arranged in a facial configuration. The ether oxygen atoms and one of the pendant carboxylate groups of the macrocyclic ligand are uncoordinated. A distorted octahedral coordination geometry is completed by a coordinated water molecule.

Lindoy et al. [12] have reported the structure of two octahedral nickel complexes with the parent O_2N_3 macrocycle (II). In the case of $[Ni(II)(NCS)_2]_2$, the nickel atom achieves a pseudo octahedral

geometry in which the ether oxygen atoms of the macrocycle are also not coordinated, and the three nitrogen atoms of its 1,4,7-triazaneptane unit are also arranged in a facial configuration. The Ni–N bond lengths in this complex are 2.128(9), 2.095(10) and 2.104(8) Å, respectively. The values are typical for the octahedral triplet ground state Ni(II) coordinated to a second amine group. In $[NiHL^2(H_2O)] \cdot 5H_2O$ the Ni–N(tertiary) distances (2.173(3), 2.175-(3) and 2.165(3) Å, respectively) are longer than that of Ni–N(secondary) in $[Ni(II)(NCS)_2]_2$. This is probably because the Ni–N bond to the tertiary nitrogen is lengthened by steric effects in $[NiHL^2-(H_2O)] \cdot 5H_2O$.

Acknowledgements

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