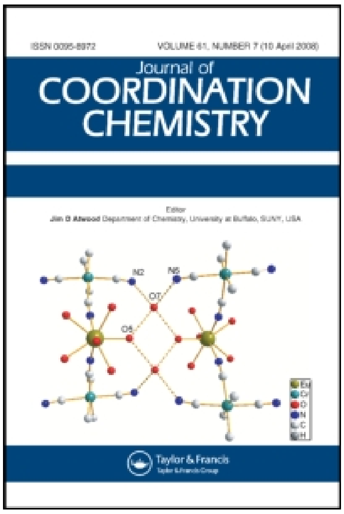

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SYNTHESIS AND CHARACTERIZATION OF A 15-MEMBERED O_2N_2 MACROCYCLE CONTAINING AN *N*-CARBOXYL ACID. THE CRYSTAL STRUCTURE OF COPPER COMPLEX

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The compound (1,2-diaza-3,4;9,10-dibenzo-5,8-dioxacyclopentadecaneacetate, HL) and its complexes ML (M = Cu, Co, Ni) have been prepared and characterized using analytical data, IR, electronic and FAB mass spectra. The copper(II) complex crystal is monoclinic, space group $P2_1/a$ with $a = 12.302(4)$, $b = 13.244(4)$, $c = 15.774(6)$ Å, $\beta = 98.59°$, $V = 2541(1)$ Å^3, $Z = 4$, $\lambda(\mathrm{Mo}K\alpha) = 0.71069$, $R_w = 0.018$ for 3305 observed reflections $[I > 3\sigma(I)]$. It has been found that the copper ion is surrounded by two nitrogen atoms and one oxygen atom from the carboxyl of the ligand and two oxygen atoms of coordinated water molecules in a distorted square pyramidal arrangement. The two ether oxygen atoms of the macrocycle do not coordinate.

Keywords: Copper; nickel; cobalt; macrocycle; X-ray structure

INTRODUCTION

Open-chain complexones such as ethylenediaminetetraacetic acid have long been used in analytical, industrial and medical applications. A number of related *N*-functionalized mixed oxygen and nitrogen donor macrocyclic derivatives incorporating pendant carboxylic acid functional groups have been developed and their complexing properties investigated in recent

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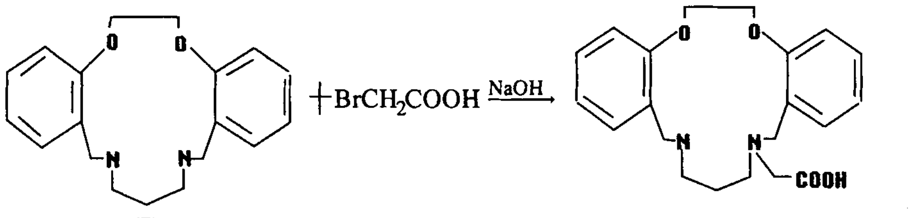
* Corresponding author.

year.[1–6] These macrocycles have both the structural characteristics of crown ether and polyaza macrocycles as well as the *N*-substituted functional group. Their specific complexation behaviour is clearly of interest in many areas such as the design of potential lanthanide ion selective reagents,[7,8] the design of complexes to act as medical imaging agents,[9] and for the treatment of metal poisoning.[10,11]

The majority of the studies has involved O_mN_n ($m = 2, 3, 4$; $n = 2, 3$) donor macrocyclic systems incorporating two or three pendant acid groups as reported by Xu[1,2] and Lindoy.[4] We are especially interested in increasing coordination properties of these ligands, as well as their stereochemistry, and so we have synthesized an *N*-substituted functional ligand containing one carboxyl acid group, 1,12-diaza-3,4,9,10-dibenzo-5,8-dioxyacyclopentadecane-*N*-acetic acid (HL) by the direct reaction of bromoacetic acid with a macrocycle as shown below.



SCHEME 1

EXPERIMENTAL

All chemical reagents were commercial products of analytical grade. Solvents were purified by conventional methods. The parent macrocycle 1,12-diaza-3,4,9,10-dibenzo-5,8-dioxyacyclopentadecane was prepared following methods previously reported by Lindoy and coworkers.[12]

Microanalyses were carried out on a elemental analyzer. IR spectra were recorded in KBr pellet on an FT IR spectrophotometer. Electronic spectra of DMF solutions were run on a UV-240 spectrophotometer. Fast atom bombardment mass spectra were measured on a VG auto-Spec instrument using Cs as the fast atom.

Preparation of the Ligand

A dry methanol solution (50 cm^3) of sodium hydroxide (0.05 mol) was added to 50 cm^3 of a dry methanol solution of bromoacetic acid (7 g, 0.05 mol) below 10°C. The above mixture was added stepwise to a mixture of parent macrocycle (25 g, 0.08 mol) and powdered anhydrous sodium carbonate (0.1 mol) in 150 cm^3 of methanol during about 1 h, then refluxed with stirring for 24 h. The mixture was cooled and the white precipitate of sodium hydrogen carbonate was filtered off. After nearly complete evaporation of the solvent, distilled water (200 cm^3) was added to the residue, the white precipitate of unreacted parent macrocycle filtered off, and the solution was acidified to pH 8 with hydrobromic acid. The product HL precipitated as a white solid. Yield, 70%. Empirical formula and analytical data are given in Table I.

Syntheses of the Complexes

Metal nitrate (0.6 mmol) was added to a solution of HL (0.5 mmol) in 20 cm^3 of anhydrous ethanol, with refluxing for 30 min. The complexes were obtained upon standing; solids were washed with ethanol and air-dried. Empirical formulae and analytical data are given in Table I. Crystals of the copper complex suitable for X-ray diffraction were obtained by recrystallization of CuL from water.

Crystal Structure Determination

A blue, single crystal $[CuL(H_2O)_2]NO_3 \cdot 2H_2O]$ obtained by dissolving CuL in water and evaporating for several days was selected for X-ray analysis. A crystal with dimensions 0.3 × 0.5 × 0.6 mm was mounted on a Rigaku AFC5R diffractometer with graphite-monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71069$). A total of 3600 unique reflections were measured using the $\omega/2\theta$ scan mode ($1° < \theta < 25°$) of which 3305 with $I > 3\sigma(I)$ were counted as being observed. The intensities were corrected for Lp factors as well as for empirical absorption using the psi-scan technique. The linear absorption coefficient is 9.19 cm^{-1}. The structure was solved by direct methods and a

TABLE I Composition and analytical data for the ligand and its complexes*

Compound	*Analyses* (%)			*IR data* (cm^{-1})				
	C	*H*	*N*	ν_{OH}	ν_{CO}	ν_{As-O-C}	ν_{NO}	ν_{Ar}
$C_{21}H_{31}N_2O_{6.5}$	60.71	7.52	6.74	3434	1602	1239		1599, 1495
	(60.64)	(7.56)	(6.38)					1453, 762
$C_{21}H_{33}N_3O_{11}Cu$	44.48	5.87	7.40	3376	1621		1386, 1042	1604, 1455
	(44.50)	(6.02)	(7.46)				829	1494
$C_{21}H_{26}N_3O_{4.5}Co$	50.32	5.23	(8.54)	3446	1599	1219	1414, 1353	1587, 1495
	(50.50)	(5.34)	(8.41)				1014	1456
$C_{21}H_{28}N_3O_{8.5}Ni$	48.45	5.45	8.62	3453	1587	1229	1413, 1338	1599, 1494
	(48.77)	(5.77)	(8.31)				1035	1459

* Calc. in parentheses.

difference Fourier synthesis and refined with unit weights by full-matrix least-squares methods with anisotropic thermal parameters for all non-H atoms; H atoms were fixed geometrically and not refined. The final R and R_w values are 0.060 and 0.081 respectively. The weight, W, is defined as $1/\sigma(F^2)$; $S=2.17$; $(\Delta/\sigma)_{\max}=0.02$; $\Delta\rho_{\max}=1.30\,\mathrm{e\,Å^{-3}}$; $\Delta\rho_{\min}=-0.866\,\mathrm{e\,Å^{-3}}$. All calculations were performed on a VAX computer using SDP programs.

RESULTS AND DISCUSSION

IR Spectra

IR data for the ligand and complexes are given in Table I. The spectra indicated ionic NO_3^- for the copper complex (1386 cm^{-1}), but not for cobalt and nickel complexes. Absorption is shifted to 1414 cm^{-1} and 1413 cm^{-1}, respectively, because NO_3^- coordinates both nickel and cobalt.

FAB Mass Spectrometry

There has been a great deal of interest in the last few years in using new mass spectrometric techniques for the characterization of transition metal complexes;[13] fast atom bombardment mass spectrometry and liquid secondary ion mass spectrometry have produced significant results. Although several studies on organometallic and coordination compounds using these methods have been reported,[13-15] only a few examples for macrocyclic O_mN_n (m = 2, 3; n = 2, 3, 4) ligands are known.[6]

We have undertaken a FAB-MS study in order to characterize the ligand and complexes. Results are shown in Table II. Data serve an important role in confirming the monomeric [1 + 1] parent macrocycle and bromoacetic acid constitution. Besides peaks corrosponding to ligand (HL^+) at (*m*/*z* 370), $[CuL-H]^+$ at (*m*/*z* 433), $[CoL-H]^+$ at (*m*/*z* 429) and $[NiL-H]^+$ at (*m*/*z* 428), new peaks for the ligand at (*m*/*z* 740) appear in the spectra. When the experiment is carried out under standard conditions using dimethyl sulfoxide as solvent, ligand interchange to give a dimer by H-bonding is observed.

Electronic Spectra

Absorption maxima of solution spectra in the ultraviolet and visible region are collected in Table II.

Absorption spectra of the samples in DMF exhibit *d*–*d* bands in the visible region and $d\pi(M)\rightarrow\pi^*$ ligand-to-metal charge transfer bands in the

TABLE II Electronic spėctra for the ligand and its complexes

Compound	*Electronic spectra*		*FAB-MS*	
	Transition(ϵ')	*Assignment*	*(m/z)*	*Assignment*
$HL \cdot 2.5H_2O$			370	HL^+
$[CuL(H_2O)_2]NO_3 \cdot 2H_2O$	688.4 (120)	${}^Be_g \rightarrow {}^2T_{2g}$	529	$Cu(L-2H)^+$
$CoLNO_3 \cdot 0.5H_2O$	327.5 (86)	${}^4T_{1g} \rightarrow {}^4T_{2g}$	489	$Co(L-2H)^+$
	510 (51)	${}^4T_{1g} \rightarrow {}^4A_{2g}$		
$NiLNO_3 \cdot 1.5H_2O$	367 (67)	${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$	488	$Ni(L-2H)^+$
	598.5 (43)	${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$		
	888 (75)	${}^3A_{2g} \rightarrow {}^3T_{2g}(F)$		

ultraviolet region. The most intense LMCT feature has a maximum at 270 nm ($\epsilon' = 315$) for the ligand, at 278 nm ($\epsilon' = 452$) for Cu, at 272 nm ($\epsilon' = 533$) for cobalt and at 275 nm ($\epsilon' = 376$) for nickel.

Crystal Structure Study

Coordinates and equivalent thermal parameters for non-hydrogen atoms are listed in Table III, and bondlengths and angles in Table IV. The crystal structure of the copper complex consists of copper(II) ion, deprotonated ligand, two molecules of coordinated water, two molecules of crystalline water and uncoordinated nitrate anions. The two ether oxygen atoms of the macrocyclic ligand do not coordinate with the metal ion. A perspective view of the structure and the packing of molecules in unit cell of copper complex are shown in Figures 1 and 2.

The structure determination demonstrates that the coordination number of copper atoms is five. The five atoms N(1), N(2), O(3), O(8) and O(9) which coordinate to copper form a distorted tetragonal pyramid with geometric parameter ($\tau = 0.23$).[16] Two atoms, N(1), N(2), from the macrocyclic ligand, one carboxyl oxygen, O(3), and two oxygen atoms, O(8), O(9), from coordinated water make up the equatorial plane, which satisfies the equation $0.4905X + 0.8692Y - 0.0629Z - 1.3013 = 0$. The copper atom is 0.168 Å above the equatorial plane towards O(9) with Cu–O(9) 2.130 Å. An EPR spectrum of the copper complex (5×10^{-3} M in ethanol) at room and liquid nitrogen temperatures gives $g_{\parallel} > g_{\perp}$ ($g_{\parallel} = 2.189$, $g_{\perp} = 2.015$).[17]

The equivalent isotropic displacement of the three oxygen atoms in NO_3^- is much larger than the other atoms, and the distances of the three N–O bonds are not equal; O(7)–N(3) [1.16(1) Å] is much shorter than the usual N–O bond distance. This may be attributable to vibration and rotation of NO_3^-, but there is no disorder.

The structures of the parent macrocyclic complexes ML (M = Cu,[18] Ni,[19] Zn[20]) have been reported. The ether oxygen atoms of the parent macrocycle

TABLE III Atomic coordinates and thermal parameters

Atom	x/a	y/b	z/c	B_{eq}	*Atom*	x/a	y/b	z/c	B_{eq}
Cu	0.4425(5)	0.0237(5)	0.6898(4)	1.8	C(4)	0.0653(6)	−0.1178(5)	0.5677(5)	4.7
O(1)	0.3427(4)	−0.1879(3)	0.7396(3)	3.4	C(5)	0.1004(5)	−0.0557(5)	0.6359(5)	3.5
O(2)	0.5597(4)	−0.2237(4)	0.8050(3)	4.5	C(6)	0.1962(5)	−0.0768(4)	0.6932(4)	2.4
O(3)	0.3455(3)	0.0469(3)	0.5837(2)	2.5	C(7)	0.2358(5)	−0.0088(4)	0.7665(4)	2.3
O(4)	0.1967(3)	0.1314(3)	0.5271(2)	2.8	C(8)	0.3441(5)	0.1364(4)	0.8252(4)	2.8
O(5)	1.0240(5)	0.1648(5)	0.8012(4)	7.0	C(9)	0.4218(5)	0.0832(5)	0.8945(4)	3.3
O(6)	0.9133(6)	0.1374(6)	0.6939(5)	8.9	C(10)	0.5337(5)	0.0632(5)	0.8716(4)	3.5
O(7)	0.9169(9)	0.0410(8)	0.7996(7)	12.8	C(11)	0.6512(5)	−0.0448(6)	0.7986(4)	3.9
O(8)	0.5293(3)	−0.0624(3)	0.6187(2)	2.8	C(12)	0.6934(5)	−0.1166(7)	0.8695(4)	4.3
O(9)	0.5383(4)	0.1636(3)	0.0806(3)	3.5	C(13)	0.7834(6)	−0.0931(8)	0.9331(5)	6.1
O(10)	0.1032(3)	0.3368(3)	0.5185(3)	3.13	C(14)	0.8181(8)	−0.163(1)	0.9958(6)	7.9
O(11)	0.2393(4)	0.4941(3)	0.5978(3)	3.53	C(15)	0.767(1)	−0.253(1)	0.9974(6)	9.3
N(1)	0.3124(3)	0.0750(3)	0.7455(3)	1.8	C(16)	0.6776(8)	−0.2782(7)	0.9353(5)	6.7
N(2)	0.5339(4)	−0.0137(4)	0.8024(3)	2.5	C(17)	0.6426(7)	−0.2093(7)	0.8715(4)	4.6
N(3)	0.9490(5)	0.1124(5)	0.7684(4)	4.7	C(18)	0.4774(7)	−0.2994(6)	0.8101(5)	5.1
C(1)	0.2512(5)	−0.1665(4)	0.8607(4)	2.7	C(19)	0.3938(6)	−0.2853(5)	0.7339(5)	4.5
C(2)	0.2141(6)	−0.2279(5)	0.6110(5)	4.1	C(20)	0.2528(5)	0.1417(4)	0.6783(4)	2.3
C(3)	0.1235(7)	−0.2027(6)	0.5554(5)	4.7	C(21)	0.2633(4)	0.1031(4)	0.5894(3)	2.2

TABLE IV Selected bondlengths (Å) and angles (deg.)

Bond	*Dist.*	*Bond*	*Dist.*	*Bond*	*Dist.*	*Bond*	*Dist.*
Cu–O(3)	1.9294	Cu–O(8)	2.0146	Cu–N(1)	2.0544	Cu–N(2)	2.017(5)
O(1)–C(1)	1.378(7)	O(1)–C(19)	1.444(7)	O(2)–C(17)	1.363(9)	O(2)–C(18)	1.441(5)
O(0)–C(21)	1.270(6)	O(4)–C(21)	1.239(6)	O(5)–N(3)	1.207(8)	O(6)–N(3)	1.237(8)
O(7)–N(3)	1.16(1)	N(1)–C(7)	1.524(7)	N(1)–C(8)	1.499(7)	N(1)–C(20)	1.486(7)
N(2)–C(10)	1.493(8)	N(2)–C(11)	1.511(7)	C(1)–C(2)	1.388(9)	C(1)–C(6)	1.395(8)
C(2)–C(3)	1.35(7)	C(3)–C(4)	1.36(1)	C(4)–C(5)	1.37(1)	C(5)–C(6)	1.402(8)
O(1)–C(1)	1.378(7)	O(1)–C(19)	1.444(7)	O(2)–C(17)	1.363(9)	O(2)–C(18)	1.441(5)
C(6)–C(7)	1.4908)	C(8)–C(9)	1.5148	C(9)–C(10)	1.4989	C(11)–C(12)	1.50(1)
C(12)–C(13)	1.41(1)	C(12)–C(17)	1.38(1)	C(13)–C(14)	1.38(1)	C(14)–C(15)	1.35(2)
C(15)–C(16)	1.40(2)	C(16)–C(17)	1.38(1)	C(18)–C(19)	1.47(1)	C(20)–C(21)	1.517(8)

Angle	(°)	*Angle*	(°)	*Angle*	(°)
O(3)–Cu–O(8)	85.3(2)	O(3)–Cu–N(1)	84.1(2)	O(3)–Cu–N(2)	173.8(2)
O(8)–Cu–N(1)	159.7(2)	O(8)–Cu–N(2)	94.5(2)	N(1)–Cu–N(2)	94.1(2)
C(1)–O(1)–C(19)	117.5(5)	C(17)–O(2)–C(18)	120.5(6)	Cu–O(3)–C(21)	115.4(3)
Cu–N(1)–C(7)	113.5(3)	Cu–N(1)–C(8)	114.6(3)	Cu–N(1)–C(20)	103.0(3)
C(7)–N(1)–C(8)	107.7(4)	C(7)–N(1)–C(20)	109.5(4)	C(8)–N(1)–C(20)	108.3(4)
Cu–N(2)–C(10)	114.6(4)	Cu–N(2)–C(11)	116.2(4)	C(10)–N(2)–C(11)	108.7(5)
O(5)–N(3)–O(6)	113.1(8)	O(5)–N(3)–O(7)	124.9(9)	O(6)–N(3)–O(7)	121.7(9)
O(1)–C(1)–C(2)	123.5(6)	O(1)–C(1)–C(6)	116.4(5)	C(2)–C(1)–C(6)	120.1(6)
C(1)–C(2)–C(3)	123.5(6)	C(2)–C(2)–C(4)	120.7(7)	C(3)–C(4)–C(5)	119.7(7)
C(4)–C(5)–C(6)	121.5(7)	C(1)–C(6)–C(5)	117.2(6)	C(1)–C(6)–C(7)	121.0(5)
C(5)–C(6)–C(7)	121.7(5)	N(1)–C(7)–C(6)	114.3(4)	N(1)–C(8)–C(9)	114.2(5)
C(8)–C(9)–C(10)	114.4(5)	N(2)–C(10)–C(9)	113.5(5)	N(2)–C(11)–C(12)	111.7(5)
C(11)–C(12)–C(13)	122.5(8)	C(11)–C(12)–C(17)	118.3(6)	C(13)–C(12)–C(17)	119.2(7)
C(12)–C(13)–C(14)	119(1)	C(13)–C(14)–C(15)	121(1)	C(14)–C(15)–C(16)	121(1)
C(15)–C(16)–C(17)	119(1)	O(2)–C(17)–C(12)	113.3(6)	O(2)–C(17)–C(16)	126(1)
C(12)–C(17)–C(16)	120.9(9)	O(2)–C(18)–C(19)	106.1(6)	O(1)–C(19)–C(18)	108.7(6)
N(1)–C(20)–C(21)	111.0(4)	O(3)–C(21)–O(4)	124.1(5)	O(3)–C(21)–C(20)	116.2(5)
O(4)–C(21)–C(20)	119.6(5)				

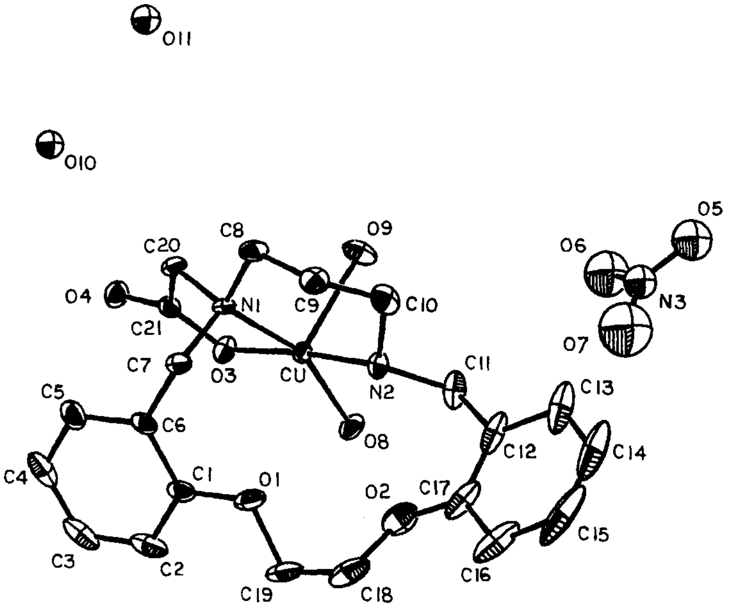


FIGURE 1 Structure of the title complex.

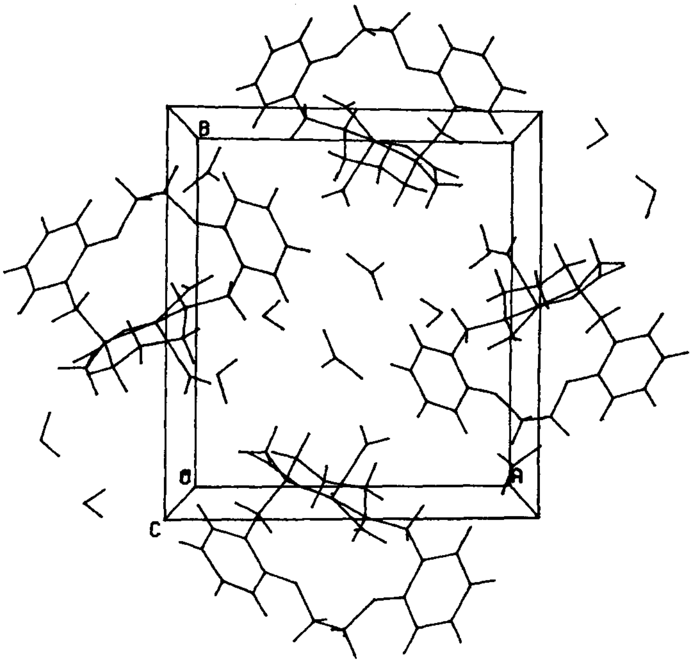


FIGURE 2 Packing in the unit cell.

coordinated to copper and nickel, but not to zinc. The interactions of metal ions with mixed donor macrocycles containing pendant acid functions have also been studied.[1,2,4] The ether oxygen atoms appeared to not bind to the metal. This is taken as evidence that ether oxygen atoms are less capable of binding than the amine nitrogen atoms in the macrocyclic ligands, in general, when pendant carboxylic functions are present.

Supplementary Data

Full lists of H atom positions, anisotropic thermal parameters and observed and calculated structure factors are available from the anthors on request.

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