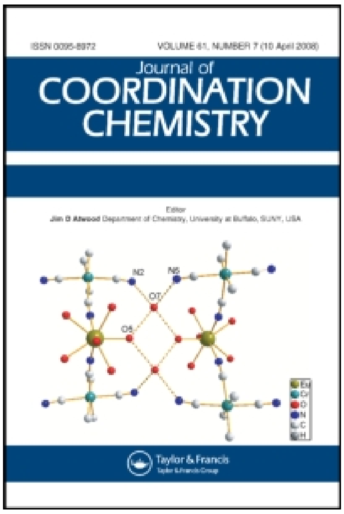


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS, PROPERTIES AND STRUCTURE OF A NOVEL MACROCYCLIC LIGAND

Yin-Han Zhang[a]; Jie-Ying Wu[b]; Yu-Peng Tian[b]; Fu-Xin Xie[b]; Chun-Ying Duan[c]; Zu-Yao Chen[a]
[a] Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui, P.R. China [b] Department of Chemistry, Anhui University, Hefei, Anhui, P.R. China [c] Coordination Chemistry Institute & State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, P.R. China

To cite this Article Zhang, Yin-Han , Wu, Jie-Ying , Tian, Yu-Peng , Xie, Fu-Xin , Duan, Chun-Ying and Chen, Zu-Yao(1999) 'SYNTHESIS, PROPERTIES AND STRUCTURE OF A NOVEL MACROCYCLIC LIGAND', Journal of Coordination Chemistry, 49: 1, 1 — 8

To link to this Article: DOI: 10.1080/00958979908024369

URL: http://dx.doi.org/10.1080/00958979908024369

J. Coord. Chem., 1999, Vol. 49, pp. 1–8
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under
the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

SYNTHESIS, PROPERTIES AND STRUCTURE OF A NOVEL MACROCYCLIC LIGAND

YIN-HAN ZHANG[a,*], JIE-YING WU[b], YU-PENG TIAN[b],
FU-XIN XIE[b], CHUN-YING DUAN[c] and ZU-YAO CHEN[a]

[a]*Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui 230026, P.R. China;* [b]*Department of Chemistry, Anhui University, Hefei, Anhui 230039, P.R. China;* [c]*Coordination Chemistry Institute & State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, P.R. China*

(Received 16 November 1998)

A new ligand, 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxacyclopentadecane, has been synthesized and characterized as the hydrobromide salt, on the bases of analytical data, ^{1}H NMR, IR and FAB mass spectra. An X-ray crystal structure shows the ligand crystallizes in the rhombohedral system, space group $R\bar{3}$, with $a = 35.194(1)$, $b = 35.194(1)$, $c = 10.397(1)$ Å, $\gamma = 120°$, $V = 11152.6(1)$ Å^3, $Z = 18$, refined to $R = 0.061$ for 1120 observed reflections with $I > 3\sigma(I)$ from 3392 independent reflections. Stability constants for 1 : 1 complexes of transition metals and protonation constants for the ligand have been determined by potentiometric titration in 95% ethanol ($I = 0.1$, $(CH_3)_4NCl$) at 25°C.

Keywords: Crystal structure; macrocyclic ligand; stability constants

INTRODUCTION

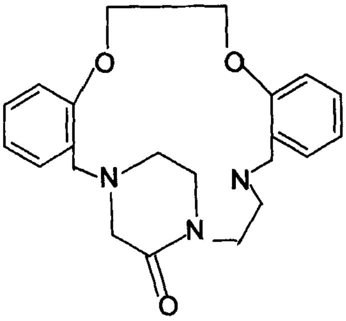
The main aim in macrocyclic design is to synthesize macrocycles which are able to discriminate between different metal cations. Many factors influence the selectivities of macrocycles for cations, such as substituent effects, donor atom type and number.[1–3]

Lindoy and co-workers have studied the effects of mixed nitrogen and oxygen ligands with various pendant carboxylic acid arms on stability and

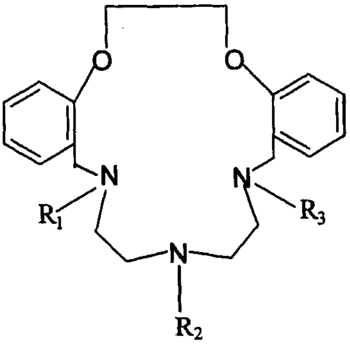
---

[*] Corresponding author.

selectivity.[4–6] In an attempt to further study the properties of new macrocyclic derivatives with varying types and numbers of pendant arms, we have synthesized a new macrocyclic ligand and describe its structure in this paper. Protonation constants for the ligand and stability constants for transition metal complexes have been determined and compared with analogous ligands, as shown below.



L_1



L_2 $R_1=R_2=R_3=H$

L_3 $R_1=R_2=R_3=CH_2COOH$

L_4 $R_1=R_3=H$, $R_2=CH_2CH_2NH_2$

EXPERIMENTAL

All chemical reagents were commercial products of analytical grade. The solvents were purified by conventional methods. The parent macrocycle 1,12,15-triaza-3,4:8,9-dibenzo-5,8-dioxacyclooctadecane was synthesized previously.[7]

Synthesis of Ligand (L_1)

Some 50 cm^3 of a dry methanol solution 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) at 10°C. The mixture was added in portions to a mixture of parent macrocycle (27.3 g, 0.08 mol) and powdered anhydrous sodium carbonate (0.1 mol) in 400 cm^3 of methanol, 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 was filtered off, and the solution was acidified to pH 5.5–6.5 with hydrobromic acid. The product precipitated as a white solid. Yield: 32%. *Anal.* Calc. for $C_{22}H_{29}N_3O_3Br_2$ (%): C, 40.51; H, 5.34; N, 7.73, Found: C, 40.49; H, 5.50; N, 7.76. IR (cm^{-1}): 1625 ($\nu_{C=O}$); ^1H NMR (D_2O): δ3.2 (1H, NH^+), δ3.4–3.9 (8H, NCH_2), δ4.1 (2H, CH_2O), δ4.36 (4H, $ArCH_2$), δ4.5–4.6 (2H, NH_2^+), δ4.8 (4H, OCH_2), δ7.0–7.5 (8H, Ar); FAB-Ms: *m/e* 382.

Potentiometric Determinations

Potentiometric measurements and computation of the protonation and stability constants were carried out by procedures described previously.[8] Typical concentrations of experimental solutions were 2.00×10^{-3} mol · dm^{-3} of ligand and 0.100 mol dm^{-3} of KOH, and initial solution volumes were 50.0 cm^3. Twenty experimental data points were recorded by the titration for measurement of protonation constants. Three parallel titrations were performed for determination of the error. Standard stock solutions were prepared from analytical grade $Cu(ClO_4)_2$, $Ni(ClO_4)_2$, $Co(ClO_4)_2$, $Zn(Ac)_2$ and $Cd(NO_3)_2$. The meter-glass electrode system was calibrated by standard acid with KCl at 0.100 mol dm^{-3} as the supporting electrolyte to read hydrogen ion concentration, $[H^+]$, directly so that the measured value was $-\log[H]$.

Crystal Data

Data were collected at 294 K on a Rigaku RAXIS IIC imaging-plate diffractometer using MoKα radiation from a rotating-anode generator operating at 50 kV and 90 mA (exposure 8 min per frame). Absorption corrections were made using the ABSCOR program based on Fourier coefficient fitting to the intensities of symmetry-equivalent reflections.[9] The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL.[10] All non-hydrogen atoms were refined anisotropically to a final $R = 0.061$, $R_w = 0.1814$ for 1120 observed reflections with $I > 3\sigma(I)$ from 3392 independent reflections. All the hydrogen atoms were placed in calculated positions (C–H, 0.96 Å), assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic U of the atoms to which they are attached, and allowed to ride on their respective parent atoms. The contributions of these hydrogen atoms were included in the structure factors calculations. All computations were carried out on a 586 computer using the SHELXTL program package, Analytical expressions of neutral atom scattering factors were employed and anomalous corrections were incorporated.[11]

RESULTS AND DISCUSSION

Protonation and Stability Constants

The protonation constants K were determined potentiometrically by titrating the respective ligand hydrochlorides with base. Protonation constants of L_1 and analogous ligands are listed in Table I.

For L_1, there are three nitrogen donor groups. Log K_1 refers to protonation of substituted nitrogen (N1); Log K_2 refers to protonation of a second amine nitrogen atom; Log K_3 corresponds to protonation of other substituted nitrogen of the macrocycle. Negative charge on nitrogen decreases owing to conjugation between N and C=O, as demonstrated by the crystal structure of L_1. Ether oxygen donors of the ligand are too weakly basic to be protonated.

The interaction of ligand L_1 and transition metal (Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}) has been studied in 95% ethanol solution ($I = 0.1$, $(CH_3)_4NCl$, 25°C). Stability constants for 1 : 1complexes are listed in Table II.

For L_1, formation of equilibrium is very slow, and the formation constants are small compared with the corresponding parent macrocycle L_2 and

TABLE I Protonation constants of macrocyclic ligands (±0.05) at 25°C

Ligand	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$
L_1	10.21	6.85	3.91	
L_2^6	9.47	8.27	2.35	
L_3^4	10.33	9.30	3.70	2.10
L_4^{12}	9.90	8.78	3.15	2.08

TABLE II Log K values for metal complex formation (±0.2) at 25°C

Ligand	Co	Ni	Cu	Zn	Cd
L_1	4.6	5.8	8.9	5.0	[d]
L_2^6	7.6	10.0	14.4	7.5	8.7
L_3^4	14.2	> 15	[d]	14.5	[d]
L_4^{12}	11.5	11.8	12.3	12.5	

[d] Precipitation occurred.

substituted macrocyclic ligands, L_3 and L_4. Oxygen atoms do not coordinate with the transition metals. It has been found that it is more difficult to form complexes for substituted macrocyclic ligands than unsubstituted macrocyclic ligands. X-ray crystal structures and molecular model studies of the complexes of macrocycles containing *N*-benzyl[13] and *N*-cyanoethyl[14] arms indicate the substituents greatly restrict the formation of complexes.

Crystal structures show that ether oxygen atoms of the unsubstituted parent macrocycle participate in the formation of complexes,[15] but those of *N*-substituted macrocycle do not coordinate with the metal ion[16] in general when pendant arms are present on the macrocycle. The results confirm that ether oxygen atoms are less capable of binding than the amine nitrogen atoms of the macrocyclic ligands.

Crystal Structure

Crystal data for the ligand (L_1) are given in Table III and final atomic coordinates in Table IV. Selected bond distances and angles are listed in Table V. An ORTEP plot of the macrocycle is displayed in Figure 1 C–N bonds, 1.414(1) Å, because of conjugate effects between C–O and N(2).

TABLE III Crystal data and structure refinement details for the ligand

Empirical formula	$C_{22}H_{29}Br_2N_3O_3$
Formula weight	543.29
Temperature (K)	296(2)
Wavelength (Å)	0.71073
Crystal system	R_3
Space group	Rhombohedral
Unit cell dimensions	
a (Å)	35.194(1)
c (Å)	10.397(1)
Volume (Å^3)	11152.6(12)
Z	18
D_c (mg m^{-3})	1.451
μ (mm^{-1})	3.297
F(000)	4932
Crystal size (mm^3)	0.63 × 0.35 × 0.22
Colour	Colourless
θ range for data collection (°)	2.00–25.00
Reflections collected	3705
Independent reflections	3392 ($R(int) = 0.025$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3392/0/271
Goodness-of-fit on F^2	1.045
Final R indices ($I > 2\sigma(I)$)	
R	0.0621
R_w	0.181

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$). $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	*y/b*	*z/c*	*U(eq)*
Br (1)	374(1)	8080(1)	− 9155(1)	65(1)
Br(2)	− 160(1)	8681(1)	− 2793(1)	85(1)
O(1)	− 784(2)	7161(1)	− 8428(4)	71(2)
O(2)	− 374(1)	7252(1)	− 5967(4)	68(2)
O(3)	− 894(1)	8005(1)	− 6158(4)	66(2)
N(1)	− 983(1)	8005(2)	− 9641(5)	47(2)
N(2)	− 426(2)	8500(2)	− 7568(5)	47(2)
N(3)	− 60(2)	8196(2)	− 5276(6)	59(2)
C(1)	− 753(2)	7778(2)	− 10201(7)	52(2)
C(2)	− 1061(2)	7293(2)	− 10366(6)	54(2)
C(3)	− 1354(2)	7123(2)	− 11390(7)	68(2)
C(4)	− 1641(2)	6674(3)	− 11512(8)	76(3)
C(5)	− 1638(2)	6396(2)	− 10626(8)	71(3)
C(6)	− 1351(2)	6556(2)	− 9610(8)	70(2)
C(7)	− 1062(2)	6997(2)	− 9461(7)	55(2)
C(8)	− 537(2)	6962(2)	− 8033(7)	89(2)
C(9)	− 597(2)	6857(2)	− 6714(8)	77(3)
C(10)	− 342(2)	7214(2)	− 4671(7)	59(2)
C(11)	− 575(2)	6824(2)	− 3999(8)	67(2)
C(12)	− 525(2)	6819(2)	− 2672(8)	74(3)
C(13)	− 238(2)	7207(2)	− 2063(7)	71(2)
C(14)	− 16(2)	7588(2)	− 2706(7)	63(2)
C(15)	− 53(2)	7598(2)	− 4027(7)	53(2)
C(16)	204(2)	8010(2)	− 4806(7)	61(2)
C(17)	179(2)	8590(2)	− 6103(7)	58(2)
C(18)	− 112(2)	8757(2)	− 6563(7)	62(2)
C(19)	− 325(2)	8657(2)	− 8887(6)	57(2)
C(20)	− 720(2)	8490(2)	− 9714(7)	56(2)
C(21)	− 1133(2)	7881(2)	− 8278(6)	56(2)
C(22)	− 799(2)	8142(2)	− 7253(6)	53(2)

TABLE V Selected bond lengths (Å) and bond angles (°) for the structure

O1	C7	1.371(86)	O1	C8	1.422(9)
O2	C10	1.364(8)	O2	C9	1.434(8)
O3	C22	1.217(7)	N(1)	C20	1.482(7)
N1	C21	1.499(8)	N1	C1	1.508(8)
N2	C22	1.326(7)	N2	C19	1.455(8)
N2	C18	1.460(8)	N3	C16	1.462(9)
N3	C17	1.485(8)	C1	C2	1.507(8)
C2	C3	1.392(9)	C2	C7	1.403(10)
C3	C4	1.394(10)	C4	C5	1.347(11)
C5	C6	1.371(10)	C6	C7	1.374(9)
C8	C9	1.408(10)	C10	C11	1.387(9)
C10	C15	1.392(8)	C11	C12	1.392(11)
C12	C13	1.380(10)	C13	C14	1.346(10)
C14	C15	1.382(10)	C15	C16	1.505(9)
C17	C18	1.493(10)	C19	C20	1.486(9)
C21	C22	1.512(8)			

TABLE V (*Continued*)

C7	O1	C8	120.3(6)	C10	O2	C9	118.2(5)
C20	N1	C21	108.1(5)	C20	N1	C1	113.6(4)
C21	N1	C1	114.6(5)	C22	N2	C19	122.1(6)
C22	N2	C18	119.7(5)	C19	N2	C18	118.2(4)
C16	N3	C17	114.8(5)	C2	C1	N1	111.7(4)
C3	C2	C7	118.0(6)	C3	C2	C1	122.2(6)
C7	C2	C1	119.9(6)	C2	C3	C4	121.1(7)
C5	C4	C3	119.8(7)	C4	C5	C6	120.0(6)
C5	C6	C7	121.9(7)	O1	C7	C6	122.2(7)
O1	C7	C2	118.6(5)	C6	C7	C2	119.2(7)
C9	C8	O1	111.2(7)	C8	C9	O2	109.6(6)
O2	C10	C11	123.9(6)	O2	C10	C15	115.9(6)
C11	C10	C15	120.2(7)	C10	C11	C12	119.7(6)
C13	C12	C11	118.5(7)	C14	C13	C12	122.1(7)
C13	C14	C15	120.3(6)	C14	C15	C10	119.0(6)
C14	C15	C16	122.7(6)	C10	C15	C16	118.2(6)
N3	C16	C15	113.6(5)	N3	C17	C18	111.9(5)
N2	C18	C17	116.1(6)	N2	C19	C20	113.1(5)
N1	C20	C19	110.2(6)	N1	C21	C22	115.7(5)
O3	C22	N2	123.6(6)	O3	C22	C21	116.1(5)
N2	C22	C21	120.2(6)				

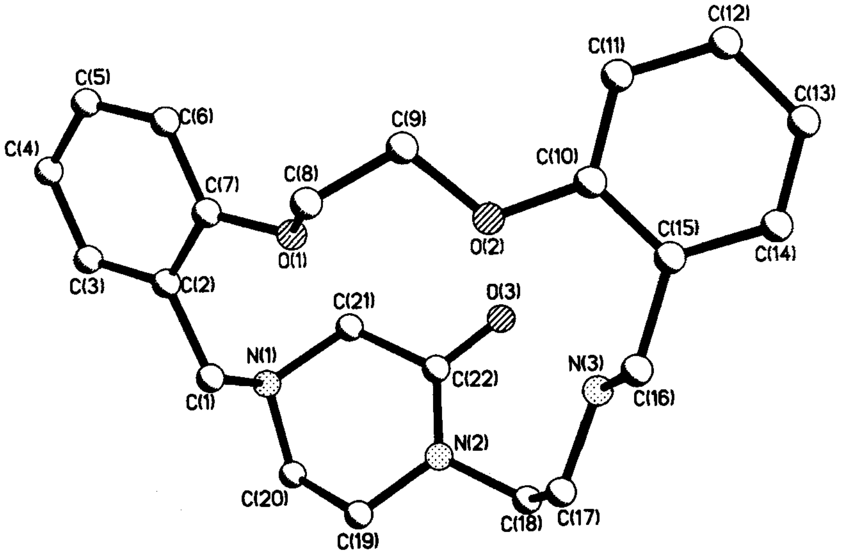


FIGURE 1 ORTEP plot of L_1 with atomic numbering scheme (Br ion is omitted for clarity).

Other bond lengths and angles are within ranges of the reported values.[17,18] Protonated N atoms in the macrocycle are N1 and N3. A six-membered ring (N1, C21, C22, C19, N2 and C20) is due to the *N*,*N*-substituent. N1, C21, C22, C19, N2 and O3 form a plane with mean deviation 0.05 Å. C20 is

0.63 Å from the plane. The O1, O2, N1, N2 and N3 atoms of the macrocycle ring also lie in a plane with mean deviation 0.09 Å. The dihedral angle between the two planes is 56.7°.

The crystal structure is stabilized by intramolecular hydrogen bonds. N3 and N1 and Br(2) form two intermolecular hydrogen bonds (Br(2)$\cdots$N(3) = 3.213(1) Å; Br(1)$\cdots$N(1) = 3.177(2) Å).

Acknowledgements

This work was supported by the Youth Fund of the University of Science and Technology of China and the National Nature Science Foundation of China.

References

[1] R.M. Izatt and J.J. Christensen, Eds., *Synthesis of Macrocycles: The design of Selective Complexing Agents* (Wiley-Interscience, New York, 1987).
[2] L.F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes* (Cambridge University Press, Cambridge, 1989).
[3] V. Alexander, *Chem. Rev.*, **95**, 273 (1995).
[4] K.R. Adam, A.J. Leong, L.F. Lindoy, P. Hendry, S.V. Smith and D. Yellowlees, *J. Coord. Chem.*, **19**, 189 (1988).
[5] K.R. Adam, L.F. Lindoy and R.J. Smith, *J. Chem. Soc., Chem. Commun.*, 812 (1979).
[6] K.R. Adam, L.F. Lindoy, H.C. Lip and J.H. Rea, *J. Chem. Soc., Dalton Trans.*, 74 (1981).
[7] K.R. Adam, A.J. Leong, L.F. Lindoy, H.C. Lip, B.W. Skelton and A.H. White, *J. Am. Chem. Soc.*, **105**, 4645 (1983).
[8] K.R. Adam, G. Anderegg, L.F. Lindoy, H.C. Lip, M. Mcpartlin, J.H. Rea, R.J. Smith and P.A. Tasker, *J. Am. Chem. Soc.*, **19**. 4645 (1980).
[9] T. Higashi, ABSCOR (Rigaku Corporation, Tokyo, 1995).
[10] SHELXTL (Version 5.0, 1995) Reference Manual (Siemens Industrial Autom, Inc, Analytical Instrumentation, USA, 1995).
[11] *International Tables for X-ray Crystallography*, Vol. C, Ed. A.J.C. Wilson (Kluwer Academic Publishers, Dordrecht, 1992).
[12] Unpublished data.
[13] L.F. Lindoy, *Pure Appl. Chem.*, **61**, 1575 (1989).
[14] X. Xu, Q. Lou, F. Xie and S. Ni, *Synth. React. Inorg. Met-org. Chem.*, **27**, 1059 (1997).
[15] (a) K.R. Adam, G. Anderegg, L.F. Lindoy, H.C. Lip, M. McPartlin, J.H. Rea and R.J. Smith, *Inorg. Chem.*, **19**, 2956 (1980); (b) D.E. Fenton, B.P. Murphy, A.J. Leong, L.F. Lindoy, A. Bashall and M. McPartlin, *J. Chem. Soc., Dalton Trans.*, 2543 (1987).
[16] (a) Y.H. Zhang, Y.P. Tian, F.X. Xie, Z.Y. Chen and H. Zhang, *J. Coord. Chem.* (in press); (b) J.D. Xu, S.S. Ni, K.S. Cui and Z.Q. Zhi, *Inorg. Chim. Acta*, **171**, 239 (1990).
[17] J.F. Desreux, *Inorg. Chem.*, **19**, 1319 (1980).
[18] R.B. Lauffer, *Chem. Rev.*, **87**, 901 (1987).