X-RAY STRUCTURE OF (1,5,9,13-TETRAAZACYCLOHEXADECANE)ZINC(II) TETRABROMOZINCATE

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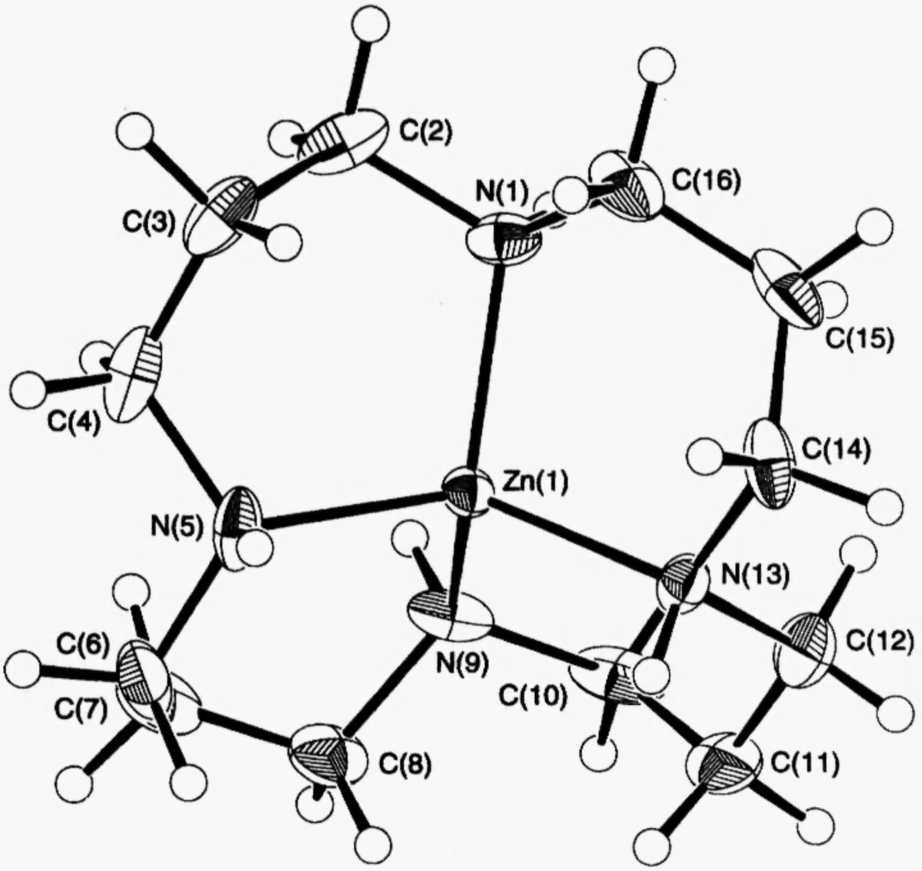

Figure 1. Molecular structure (50% displacement ellipsoids) of the cation in the structure of [ZnL][$ZnBr_4$]. Selected bond distances and angles: Zn(1)-N(1) 2.023(5), Zn(1)-N(5) 2.022(5), Zn(1)-N(9) 2.017(5), and Zn(1)-N(13) 2.013(5) Å; N(1)-Zn(1)-N(5) 105.0(2), N(1)-Zn(1)-N(9) 120.5(2), N(1)-Zn(1)-N(13) 103.6(2), N(5)-Zn(1)-N(9) 103.1(2), N(5)-Zn(1)-N(13) 123.0(2), and N(9)-Zn(1)-N(13) 103.0(2)°.

Comment

The zinc atom in the cation exists in a distorted tetrahedral geometry defined by four nitrogen atoms derived from the macrocyclic ligand. The tetradentate mode of coordination results in the formation of four six-membered rings each of which adopts a chair conformation that is flattened somewhat at the zinc apex. The nitrogen-bound hydrogen atoms adopt a +-+- conformation [1] meaning that they sequentially lie to opposite sides of the macrocycle. The conformation reported here for the cation matches closely that found in the perchlorate analogue

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[1]. The widest angles subtended at the zinc atom, *i.e.* N(1)-Zn(1)-N(9) and N(5)-Zn(1)-N(13), may be related to the close association of the respective pairs of amine-hydrogen atoms with symmetry related $[ZnBr_4]^-$ anions. The closest such interaction of 2.49 Å occurs between N-H(9) and $Br(1)^i$ so that N(9)...Br(1) is 3.403(6) Å and the angle subtended at H(9) is 167° with symmetry operation *i*: *x*, *y*, -1+*z*.

Experimental

Preparation: The macrocyclic ligand, L, was prepared according to previously published procedure [2]. A methanol solution of L (114 mg, 0.5 mmol) and $ZnBr_2$ (225 mg, 1 mmol) was heated at reflux for 1 h. The solution was then taken to dryness and the resulting solid dissolved in acetonitrile/water (1:1, 10 ml). When this mixture was allowed to stand for a few days, a quantity of colourless crystals were deposited. These were filtered off and dried in air. IR (KBr, cm^{-1}): 3224 ν(N-H). FAB mass (m/z): 678 $[ZnL,ZnBr_4]^+$.

Crystallography: An empirical absorption correction was applied [3]. The residual electron density peak (1.19 e $Å^{-3}$) was located near the Br(4) atom.

Table 1. Crystallographic data for $[ZnL][ZnBr_4]$

Formula	$C_{12}H_{28}Br_4N_4Zn_2$	Formula weight	678.8
Crystal system	monoclinic	Space group	$P2_1/n$
a, Å	15.386(5)	*b*, Å	15.668(4)
c, Å	9.036(4)	β, °	103.76(5)
V, $Å^3$	2116(1)	*Z*	4
Crystal size, mm	0.07 x 0.26 x 0.31	Diffractometer	Rigaku AFC7R
Temperature, K	173	μ(Mo-Kα), cm^{-1}	98.45
D_{calcd}, g cm^{-3}	2.131	*F*(000)	1312
θ_{max}, °	27.5	No. reflns meas., unique	5220, 4855
No. reflns with $I \geq 2\sigma(I)$	2588	*R*, *wR* (F^2, obs. data)	0.032, 0.066
R, *wR* (F^2, all data)	0.120, 0.084	No. parameters	200
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0232P)^2 + 1.9103P]$ where $P = (F_o^2 + 2F_c^2)/3$		
GoF	0.99	ρ, e $Å^{-3}$	1.19
Programs used	DIFABS [3], teXsan [4], DIRDIF [5], SHELXL97 [6], ORTEP [7]		
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References

[1] R. Luckay, T.E. Chantson, J.H. Reibenspies and R.D. Hancock, *J. Chem. Soc., Dalton Trans.*, (1995) 1363.
[2] W.L. Smith and K.N. Raymond, *Inorg. Synth.*, **20** (1980) 109.
[3] N. Walker and D. Stuart, *Acta Crystallogr.*, A**39** (1983) 158.
[4] teXsan, Single Crystal Structure Analysis Software, Version 1.04 (1997), Molecular Structure Corporation, The Woodlands, TX, U.S.A.
[5] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, S. García-Granda, R.O. Gould, J.M.M. Smits and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands (1992).
[6] G.M. Sheldrick, SHELXL97, University of Göttingen, Germany (1997).
[7] C.K. Johnson, ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, TN, U.S.A. (1976).

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