Crystal and Molecular Structure of Bis(diethylenetriamine)zinc(II) Dibromide Monohydrate

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The crystal structure of the title compound has been determined from *X*-ray diffractometer data by Patterson and Fourier methods. Crystals are monoclinic, space group $P2_1/c$ with $a = 1381(1)$, $b = 891{\cdot}4(4)$, $c = 1428{\cdot}1(6)$ pm, $\beta = 101{\cdot}23(3)°$, and $Z = 4$. Least-squares refinement of 595 independent observed reflections led to R 0·064. Significant differences in the bonding were found between this structure and the isomorphous copper(II) complex.

In principle, doping a paramagnetic metal-ion into a diamagnetic host-lattice can allow more detailed information to be obtained from e.s.r. experiments on the resulting more magnetically dilute paramagnetic centres. A consequence of this magnetic dilution is the reduction in line-broadening.[1] In particular, the doping of copper(II) ions into zinc(II) lattices might afford a possible probe to the zinc(II) stereochemistry, which is inaccessible through electronic spectral studies. Before applying such techniques to compounds of unknown molecular and crystal structure it is desirable to investigate a system in which the structures of both the host and the inserted ion are known. Preliminary studies[2] indicated that the copper(II) and zinc(II) complexes $[M(dien)_2]Br_2,H_2O$ (dien = diethylenetriamine) were isomorphous. Since the $[Cu(dien)_2]Br_2,H_2O$ structure is known[3] and is suitable for single-crystal spectroscopy[4] the crystal structure of the diamagnetic zinc(II) analogue has been determined and is now reported.

EXPERIMENTAL

Crystals of $[Zn(dien)_2]Br_2,H_2O$ were grown by the slow evaporation of solutions of stoicheiometric amounts of $ZnBr_2$ and diethylenetriamine in water–isopropanol.

Crystal Data.—$C_8H_{28}Br_2N_6OZn$, $M = 479{\cdot}5$, Monoclinic, $a = 1381(1)$, $b = 891{\cdot}4(4)$, $c = 1428{\cdot}1(6)$ pm, $\beta = 101{\cdot}23(3)°$, $U = 1{\cdot}7248 \times 10^9$ pm^3, $D_m = 1{\cdot}72(5)$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}73$ g cm^{-3}, $F(000) = 904$. Mo-K_α radiation, $\lambda = 71{\cdot}07$ pm, μ(Mo-K_α) = 63·78 cm^{-1}. Space group $P2_1/c$ from systematic absences: $(h0l)$ for l odd, $(0k0)$ for k odd.

Crystals were blocks with the {100} and {011} forms well developed. Preliminary space-group and unit-cell data were obtained from precession photographs, and all quantitative *X*-ray data (Zr-filtered Mo-K_α radiation) from a Hilger and Watts four-circle diffractometer controlled by a PDP 8I computer. The maximum and minimum dimensions of the crystal used for data collection were 0·29 and 0·15 mm respectively. Unit-cell parameters were obtained by least-squares refinement of the setting angles of twelve reflections accurately centred in a 3·5 mm diameter circular receiving aperture in a manner outlined by Busing[5] and adapted by us.

Intensity data were collected in the $\omega = \theta$ bisecting mode. Open counter ω-scans indicated the presence of low-intensity satellite peaks close to some reflections on the high-angle side indicating possible imperfections in the crystal. To ensure the recording of all diffracted energy for each reflection, no diffracted beam collimator was used and a large 2θ scan range of 2·0° centred on the calculated peak position was chosen. The scan was composed of 100 steps of 1 s. Stationary-crystal–stationary-background counts of 20 s were recorded at both ends of the scan. Crystal stability was confirmed by the constancy of three reference reflections whose intensities were regularly monitored.

A standard deviation was assigned to each measured intensity according to the expression: $\sigma(I) = [c + (t_c/t_b)^2(B_1 + B_2) + (pI)^2]^{\frac{1}{2}}$, where c is the scan count, B_1 and B_2 are the background counts, t_c and t_b are scan and background times respectively, and p is an empirical coefficient[6] of the nett count I which was given the value 0·05. The two equivalent forms $\{hkl\}$ and $\{h\bar{k}l\}$ were collected in the quadrant of reciprocal space where h was positive and $0° < 2\theta < 36°$. The $\{hkl\}$ reflections were also measured in the quadrant where h and k were positive and $36° < 2\theta < 40°$. The 2951 reflections were corrected for crystal absorption using a Gaussian integration technique, the transmission coefficients lying between 0·45 and 0·24. After absorption correction the equivalent reflections were averaged yielding 1606 reflections of which 596 had intensities $I > 2{\cdot}5\sigma(I)$. Of these the low-angle reflection (100) was rejected as the counter had been obscured by the diffractometer beam-stop during intensity collection.

Solution and Refinement of the Structure.—The positions of the zinc and two bromine atoms were obtained from a three-dimensional Patterson synthesis. A series of difference Fourier maps and least-squares cycles led to the positions of all other non-hydrogen atoms. The isostructural relationship with the copper complex was confirmed.

The full-matrix least-squares refinements were based on the structure factor F and the function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where the weight, w, was $4F_o{}^2/[\sigma(F_o)^2]^2$. The scattering factor curves used for all atoms were taken from ref. 7, the values for zinc and bromine being corrected for anomalous dispersion with values $\Delta f'$ and

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[1] G. F. Kokoszka and G. Gordon, in 'Technique of Inorganic Chemistry,' eds. H. B. Jonassen and A. Weissberger, Interscience, New York, vol. VII, 1968, p. 202.

[2] B. J. Hathaway, personal communication.

[3] F. S. Stephens, *J. Chem. Soc.* (*A*), 1969, 2233.

[4] B. J. Hathaway, M. J. Bew, D. E. Billing, R. J. Dudley, and P. Nicholls, *J. Chem. Soc.* (*A*), 1969, 2312.

[5] W. R. Busing, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, p. 319.

[6] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 1967, **6**, 197.

[7] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962.

$\Delta f''$ from ref. 8. For final refinement, the thermal vibration of the zinc and bromine atoms were described by the six-parameter ellipsoid model, other atoms being treated isotropically. Hydrogen atoms were not included in the calculations. At convergence, R was 0·064, and R' 0·074 for all 595 reflections $\{R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$.

Final positional and thermal parameters of all non-hydrogen atoms are in Table 1, and the root-mean square amplitude of vibration for the atoms which are refined anisotropically in Table 2. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21050 (3 pp., 1 microfiche).*

TABLE 1

Atomic co-ordinates and thermal parameters

	x	y	z	10^4B*/pm^2
Zn	−0·2379(3)	0·1098(6)	0·0638(3)	†
Br(1)	0·4617(3)	0·2704(6)	0·3605(3)	†
Br(2)	−0·0915(2)	0·4556(6)	0·2933(2)	†
O	−0·375(2)	0·041(4)	0·297(2)	7·0(3)
N(1)	−0·171(2)	0·054(4)	0·214(2)	3·9(7)
N(2)	−0·256(2)	−0·133(4)	0·055(2)	3·5(7)
N(3)	−0·295(2)	0·085(4)	−0·093(2)	4·0(8)
N(4)	−0·085(2)	0·145(4)	0·029(2)	3·8(7)
N(5)	−0·225(2)	0·347(4)	0·076(2)	2·6(6)
N(6)	−0·391(2)	0·168(4)	0·086(2)	2·5(6)
C(1)	−0·176(3)	−0·118(6)	0·224(2)	3·3(8)
C(2)	−0·173(3)	−0·189(5)	0·129(2)	3·8(8)
C(3)	−0·259(3)	−0·177(6)	−0·043(3)	4·8(9)
C(4)	−0·323(3)	−0·076(5)	−0·106(2)	3·3(9)
C(5)	−0·066(3)	0·304(5)	0·029(2)	4·2(9)
C(6)	−0·164(2)	0·397(4)	0·005(2)	2·5(7)
C(7)	−0·328(3)	0·419(5)	0·056(2)	3·4(8)
C(8)	−0·385(3)	0·332(5)	0·114(2)	3·0(9)

* B values are the parameters in the isotropic factor expression $\exp[-B(\sin\theta)^2/\lambda^2]$. † These atoms were refined anisotropically; the β values which are the coefficients in the anisotropic temperature factor expression $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ with coefficients:

	$10^8\beta_{11}$	$10^8\beta_{22}$	$10^8\beta_{33}$	$10^8\beta_{12}$	$10^8\beta_{13}$	$10^8\beta_{23}$
Zn	29(3)	101(9)	37(3)	3(5)	−2(2)	−2(5)
Br(1)	35(2)	157(1)	65(3)	−7(5)	−4(2)	−8(5)
Br(2)	34(2)	195(1)	41(2)	−7(5)	−8(2)	−5(5)

TABLE 2

Root-mean-square amplitudes of vibration (pm) of the anisotropically refined atoms

	Max.	Intermediate	Min.
Zn	21·8(8)	19·9(9)	15·4(7)
Br(1)	27·1(6)	25·1(9)	17·1(6)
Br(2)	28·1(8)	23·5(5)	15·2(6)

DISCUSSION

Although this compound is isostructural with the corresponding copper(II) complex with discrete monomeric $[Zn(dien)_2]^{2+}$ cations, bromide ions, and a molecule of water in the lattice, there are significant variations in the bonding of the two cations. The bond lengths and angles of the $[Zn(dien)_2]^{2+}$ cation (Figure) are tabulated in Table 3 together with those of $[Cu(dien)_2]^{2+}$.

TABLE 3

Comparison of the bond distances (pm) and bond angles (°) for the copper(II)[a] and zinc(II)[b] complexes $[M(dien)_2]Br_2,H_2O$

(*a*) Distances

	Zn	Cu		Zn	Cu
M–N(1)	222(3)	235(3)	M–N(4)	228(3)	213(2)
M–N(2)	218(4)	204(2)	M–N(5)	213(3)	203(3)
M–N(3)	224(3)	246(3)	M–N(6)	227(3)	207(2)
N(1)–C(1)	154(6)	145(4)	N(4)–C(5)	144(5)	145(4)
C(1)–C(2)	150(5)	153(4)	C(5)–C(6)	157(5)	150(5)
C(2)–N(2)	148(4)	148(4)	C(6)–N(5)	150(4)	149(4)
N(2)–C(3)	145(4)	149(3)	N(5)–C(7)	153(4)	143(4)
C(3)–C(4)	145(5)	150(4)	C(7)–C(8)	147(5)	157(4)
C(4)–N(3)	149(5)	151(4)	C(8)–N(6)	151(5)	147(4)

(*b*) Angles

N(1)–M–N(2)	81(1)	79·9(9)	N(2)–M–N(6)	98(1)	96·6(9)
N(1)–M–N(3)	161(1)	157(1)	N(3)–M–N(4)	87·5(9)	88·4(9)
N(1)–M–N(4)	91(1)	89·7(9)	N(3)–M–N(5)	101(1)	102(1)
N(1)–M–N(5)	98(1)	100(1)	N(3)–M–N(6)	90·4(9)	88·4(9)
N(1)–M–N(6)	98(1)	100(1)	N(4)–M–N(5)	79(1)	83(1)
N(2)–M–N(3)	80(1)	78·0(9)	N(4)–M–N(6)	159(1)	163(1)
N(2)–M–N(4)	103(1)	99·1(9)	N(5)–M–N(6)	80(1)	82(1)
N(2)–M–N(5)	178(1)	178(1)			

	Zn	Cu
M–N(1)–C(1)	107(2)	105(2)
N(1)–C(1)–C(2)	109(3)	110(3)
C(1)–C(2)–N(2)	110(3)	108(3)
C(2)–N(2)–M	103(2)	110(2)
C(2)–N(2)–C(3)	118(3)	111(2)
M–N(2)–C(3)	108(3)	113(2)
N(2)–C(3)–C(4)	110(4)	107(2)
C(3)–C(4)–N(3)	115(3)	111(2)
C(4)–N(3)–M	105(2)	102(2)
M–N(4)–C(5)	108(3)	109(2)
N(4)–C(5)–C(6)	112(3)	108(3)
C(5)–C(6)–N(5)	105(3)	109(3)
C(6)–N(5)–M	107(2)	105(2)
C(6)–N(5)–C(7)	112(3)	117(3)
M–N(5)–C(7)	110(2)	111(2)
N(5)–C(7)–C(8)	105(3)	108(3)
C(7)–C(8)–N(6)	112(3)	105(2)
C(8)–N(6)–M	104(2)	112(2)

[a] Ref. 3. [b] This work.

TABLE 4

Equations of the planes of best fit given in the form $lX + mY + nZ - p = 0$. The deviations (pm) of the most relevant atoms from the planes are given in square brackets

	l	m	n	p
Plane (1): N(1)—(3)	0·9678	−0·1515	−0·2010	−3·5445
[C(1) 12, C(2) 78, C(3) 56, C(4) −8]				
Plane (2): N(4)—(6)	−0·1700	0·1612	0·9722	0·0265
[C(5) 18, C(6) 86, C(7) 61, C(8) −15]				
Plane (3): N(2), N(4)—(6)	−0·1764	0·0754	−0·9814	−0·1465
[N(2) −5, N(4) 7, N(5) −8, N(6) 7, Zn −5]				
Plane (4): N(1)—(3), N(5)	0·9782	−0·0658	−0·1972	−3·5966
[N(1) 7, N(2) −8, N(3) 7, N(5) 6, Zn −3]				

Table 4 lists the planes formed by the approximately octahedral array of nitrogen atoms around the zinc(II) ion.

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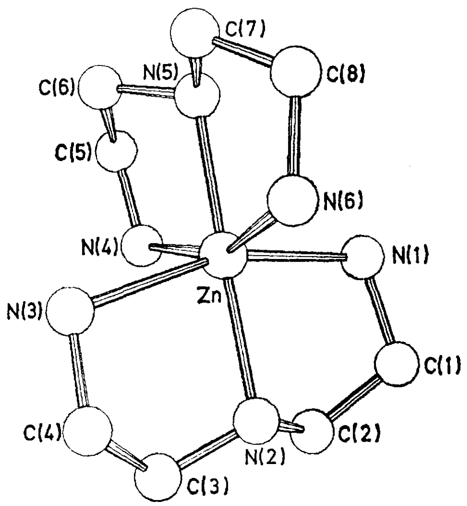
* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

[8] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

The bonds to the secondary nitrogen atoms, as in the copper(II) complex, are shorter than the others, 213(3) and 218(4) pm *vs*. a mean of 225 pm, but the tetragonal distortion found in the copper(II) chromophore is clearly not present. From this it would appear that the marked tetragonal distortion in the copper(II) complex, as evidenced by the considerable lengthening of two *trans* Cu–N bonds, with simultaneous contraction of the other in-plane bonds, is due to the stereochemical requirements of the copper(II) ion. On the other hand, the angular distortions from a regular octahedral geometry are not significantly different between the two structures and can be ascribed to the constraining influence of the diethylenetriamine molecules. The considerable rearrangement of nitrogen atoms around the zinc(II) ion causes simultaneous changes within the diethylenetriamine molecules, and although the pattern of these changes is consistent with the rearrangement the individual differences are not significant.



A general view of the cation $Zn(dien)^{2+}$ showing atom labelling

However, the significant differences between the two metal-ion chromophores should make it possible to determine through e.s.r. experiments whether the copper(II) ion doped in the isostructural zinc(II) compound will adapt to the host lattice, affording a useful stereochemical probe, or whether it tends to impose its own preferred configuration on the host site.

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