[Bis(4,5-diisopropyl-1-methyl-2-imidazolyl) ketone]dibromozinc(II)

By Randy J. Read and Michael N. G. James

MRC Group in Protein Structure and Function, Department of Biochemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2H7

Abstract. [Zn($C_{21}H_{34}N_4O$)Br$_2$], $C_{21}H_{34}Br_2N_4OZn$, $M_r = 583.71$, orthorhombic, $Pna2_1$, $a = 18.554$ (5), $b = 18.885$ (5), $c = 8.633$ (3) Å, $Z = 4$, $D_m = 1.44$ (1), $D_c = 1.282$ (not including solvent), $D_c = 1.443$ Mg m^{-3} (including one molecule of dimethylformamide per asymmetric unit), μ(Cu $K\alpha$) = 4.48 mm^{-1}. Final $R = 0.073$ for 1817 reflections with $I > 3\sigma(I)$. The molecule is a conjugated, planar system, which crystallizes with one disordered solvent molecule (probably dimethylformamide) per asymmetric unit. The Zn^{II} is coordinated in a distorted tetrahedral manner to the two unsubstituted imidazole N atoms and the two Br atoms.

Introduction. Organic compounds in which imidazole N atoms are coordinated to Zn^{II} are of interest as possible synthetic analogues of the active site of carbonic anhydrase, the enzyme which catalyzes the equilibrium

$$CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-.$$
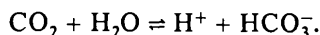
The active site of this enzyme includes three histidine residues which are coordinated to Zn^{II} in an approximately tetrahedral configuration through imidazole N atoms. The fourth ligand is probably a water molecule or hydroxyl ion (Liljas *et al.*, 1972). The title compound was synthesized by J. Huguet in the laboratory of R. S. Brown as part of a series of syntheses intended to create an active-site analogue (Brown & Huguet, 1980).

The compound was recrystallized by controlled evaporation from dimethylformamide (DMF). Preliminary oscillation and Weissenberg photographs showed *mmm* symmetry and systematic absences *h0l*, $h = 2n + 1$; *0kl*, $k + l = 2n + 1$, which determine the space group $Pna2_1$.

Intensity data were collected from a single crystal (0.20 × 0.22 × 0.28 mm) on a Picker FACS-1 diffractometer with Ni-filtered Cu $K\alpha$ radiation, using the diffractometer computing and controlling system of Lenhert (1975). The unit-cell parameters (see *Abstract*) were determined by least-squares refinement of the positions of 15 accurately centered reflections. Crystal decay was monitored and corrected with six control reflections; their intensities gradually decreased throughout the data collection to an average final value

about 3.0% less than their average intial value. 4173 reflections in the range $4.5° < 2\theta < 110.0°$ were measured in the $\theta/2\theta$ scan mode, to obtain 2206 unique reflections with 1817 having $I > 3\sigma(I)$.

The measured intensities were corrected for absorption by the empirical method of North, Phillips & Mathews (1968) (maximum absorption-correction factor = 1.114). Correction for Lorentz and polarization effects and all structure solution and refinement calculations were performed with the programs of the XRAY 70 system (Stewart, Kundell & Baldwin, 1970). The positions of the two Br and single Zn atoms were determined from a sharpened, origin-removed Patterson map, and the z coordinate of Br(1) (see Fig. 1) was set as 0.0. The remaining non-hydrogen atoms were positioned using Fourier methods. A full-matrix least-squares refinement of the atomic coordinates and thermal parameters was carried to convergence at $R = 0.073$ and $R_w = 0.097$. At an intermediate stage of refinement calculated and observed $|F|$'s were compared. Six reflections (011, 110, 111, 210, 230 and 310) were deemed to suffer from secondary extinction, and were ignored in further cycles of refinement. Anisotropic thermal parameters were ultimately used for all atoms except C(8), C(9) and C(10); anisotropic thermal parameters for these atoms could not be refined successfully. The H atoms could not be visualized in a difference Fourier map calculated after
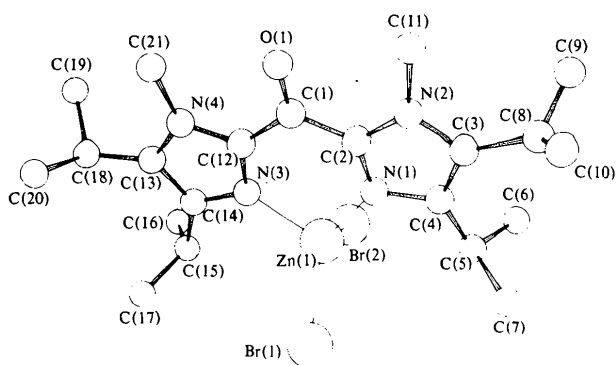

Fig. 1. *PLUTO* (W. D. S. Motherwell) drawing of the title compound. Atoms are represented by spheres of arbitrary radius and coordination bonds are represented by thin lines.

the refinement had converged. Final positional and thermal parameters are listed in Table 1.*

Atomic scattering factors were those of Cromer & Mann (1968); anomalous-dispersion corrections were obtained from *International Tables for X-ray Crystallography* (1974).

Discussion. The imidazole rings and carbonyl group of the molecule comprise a conjugated, planar system (see Fig. 1). These 12 atoms and Zn have an overall r.m.s. deviation of 0·025 Å from a least-squares plane. Fig. 1 shows that the whole molecule (including the substituents on the imidazole rings) has approximate *mm*2 symmetry, although this symmetry is not used in the crystal packing [Fig. 2(*a*)]. Examination of Table 2 shows that, with few exceptions, bond lengths and angles involving corresponding atoms are, as expected, not significantly different from one another.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35586 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
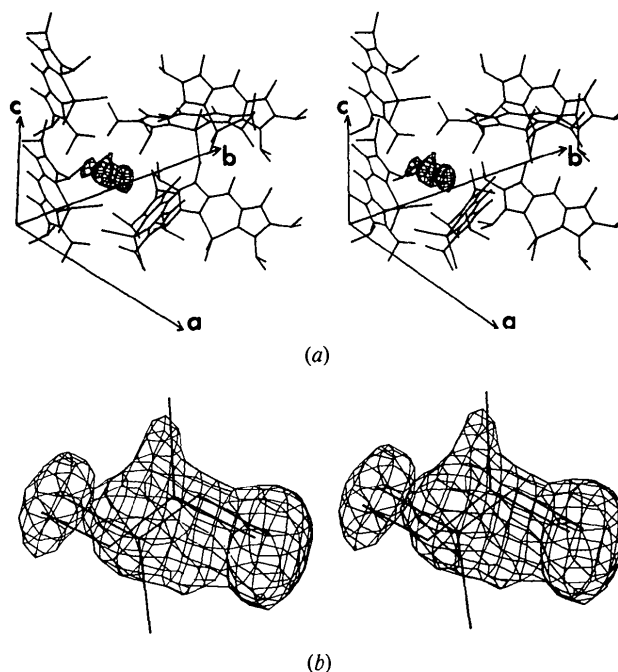

(*a*)

(*b*)

Fig. 2. Disordered solvent electron density in the crystal structure. (*a*) Stereoscopic view of the residual electron density, contoured at 0·50 e Å^{-3}, in its environment in the unit cell. (*b*) View from a similar orientation of the same electron density, together with two attempts to fit DMF models to this density. Both (*a*) and (*b*) were made with the use of an MMS-X interactive graphics system.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters* (Å^2) (*e.s.d.'s in parentheses*)

C(8), C(9) and C(10) were refined with isotropic thermal parameters. For all other atoms, equivalent isotropic [$B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$] temperature factors are given.

	x	y	z	B_{eq}
C(1)	1341 (7)	−118 (7)	5434 (15)	5·3 (3)
C(2)	1986 (7)	−268 (6)	4493 (15)	5·2 (3)
C(3)	2946 (7)	−863 (8)	3667 (21)	6·6 (4)
C(4)	2849 (6)	−249 (6)	2780 (22)	6·1 (4)
C(5)	3281 (9)	41 (10)	1501 (25)	8·1 (5)
C(6)	4077 (13)	242 (16)	1987 (44)	12·3 (9)
C(7)	3274 (14)	−435 (12)	53 (40)	11·4 (9)
C(8)	3522 (11)	−1417 (11)	3518 (29)	8·9 (4)
C(9)	4002 (21)	−1532 (22)	4780 (57)	14·5 (9)
C(10)	3270 (15)	−2111 (14)	2957 (40)	11·4 (6)
C(11)	2248 (8)	−1458 (8)	5872 (23)	7·8 (5)
C(12)	915 (5)	525 (5)	5173 (13)	4·4 (3)
C(13)	30 (6)	1292 (7)	5444 (14)	5·2 (3)
C(14)	485 (6)	1520 (6)	4262 (15)	4·6 (3)
C(15)	450 (6)	2162 (6)	3238 (17)	5·4 (3)
C(16)	576 (17)	2865 (8)	4162 (29)	10·8 (8)
C(17)	−222 (9)	2204 (9)	2261 (26)	8·3 (5)
C(18)	−662 (8)	1664 (8)	5995 (18)	6·4 (4)
C(19)	−628 (12)	1842 (12)	7763 (30)	10·1 (7)
C(20)	−1351 (11)	1288 (11)	5545 (33)	9·4 (6)
C(21)	−33 (8)	221 (7)	7167 (16)	6·2 (4)
N(1)	2240 (5)	109 (5)	3349 (12)	4·9 (3)
N(2)	2391 (5)	−843 (6)	4706 (15)	6·0 (3)
N(3)	1028 (5)	1034 (4)	4134 (13)	4·6 (2)
N(4)	284 (5)	668 (5)	5955 (11)	4·5 (2)
O(1)	1150 (7)	−539 (6)	6418 (16)	8·7 (4)
Br(1)	1378 (1)	955 (1)	0	6·4 (1)
Br(2)	2658 (1)	1988 (1)	2994 (3)	7·5 (1)
Zn	1850 (1)	1050 (1)	2544 (2)	4·9 (1)

Bond lengths and angles in the imidazole rings and N—Zn coordination distances were compared with those in related compounds (Harding & Cole, 1963; Kretsinger, Cotton & Bryan, 1963) and did not differ significantly. The Zn—Br distance appears to be sensitive to the nature of the other ligands in the coordination sphere (Crotty, Anderson, Glick & Oliver, 1977; DeSimone & Stucky, 1971; Zakrzewski & Lingafelter, 1970); it is, however, not significantly different from that in dibromobis(γ-picoline)zinc(II) (Fanfani, Nunzi & Zanazzi, 1972), in which Zn also has two aromatic N atoms and two Br atoms in its coordination sphere.

The Zn coordination sphere is strongly distorted from a regular tetrahedron. The Br(1)—Zn—Br(2) angle is large (116·5°), probably to minimize Br—Br interactions, and the N(1)—Zn—N(3) angle is small (91·3°). The Br—Zn—Br angle in dibromobis(γ-picoline)zinc(II) is also large (120·9°), but the N—Zn—N angle is not nearly as small (101·6°), perhaps because the two separate γ-picoline ligands do not impose the same strain as the bidentate ligand of the title compound.

After the molecular model had been refined, one prominent region of electron density remained in the asymmetric unit in a difference map [Fig. 2(*a*)]. This residual electron density appears to represent a

Table 2. *Bond lengths* (Å) *and angles* (°) (*e.s.d.'s in parentheses*)

C(1)—C(2)	1·47 (2)		C(12)—N(4)	1·38 (1)
C(1)—C(12)	1·47 (2)		C(13)—C(14)	1·39 (2)
C(1)—O(1)	1·22 (2)		C(13)—C(18)	1·54 (2)
C(2)—N(1)	1·31 (2)		C(13)—N(4)	1·34 (2)
C(2)—N(2)	1·33 (2)		C(14)—C(15)	1·50 (2)
C(3)—C(4)	1·40 (2)		C(14)—N(3)	1·37 (1)
C(3)—C(8)	1·50 (3)		C(15)—C(16)	1·57 (2)
C(3)—N(2)	1·37 (2)		C(15)—C(17)	1·51 (2)
C(4)—C(5)	1·47 (3)		C(18)—C(19)	1·56 (3)
C(4)—N(1)	1·41 (2)		C(18)—C(20)	1·51 (3)
C(5)—C(6)	1·58 (3)		C(21)—N(4)	1·47 (2)
C(5)—C(7)	1·54 (4)		N(1)—Zn	2·041 (9)
C(8)—C(9)	1·42 (5)		N(3)—Zn	2·053 (10)
C(8)—C(10)	1·47 (4)		Zn—Br (1)	2·371 (2)
C(11)—N(2)	1·56 (2)		Zn—Br (2)	2·353 (2)
C(12)—N(3)	1·33 (1)			

C(2)—C(1)—C(12)	121 (1)		C(15)—C(14)—N(3)	122 (1)
C(2)—C(1)—O(1)	120 (1)		C(14)—C(15)—C(16)	112 (1)
C(12)—C(1)—O(1)	120 (1)		C(14)—C(15)—C(17)	114 (1)
C(1)—C(2)—N(1)	127 (1)		C(16)—C(15)—C(17)	111 (1)
C(1)—C(2)—N(2)	123 (1)		C(13)—C(18)—C(19)	112 (1)
N(1)—C(2)—N(2)	110 (1)		C(13)—C(18)—C(20)	114 (1)
C(4)—C(3)—C(8)	128 (2)		C(19)—C(18)—C(20)	113 (2)
C(4)—C(3)—N(2)	104 (1)		C(2)—N(1)—C(4)	107 (1)
C(8)—C(3)—N(2)	128 (2)		C(2)—N(1)—Zn	127·3 (8)
C(3)—C(4)—C(5)	130 (1)		C(4)—N(1)—Zn	125·8 (9)
C(3)—C(4)—N(1)	108 (1)		C(2)—N(2)—C(3)	111 (1)
C(5)—C(4)—N(1)	121 (1)		C(2)—N(2)—C(11)	127 (1)
C(4)—C(5)—C(6)	114 (2)		C(3)—N(2)—C(11)	122 (1)
C(4)—C(5)—C(7)	113 (2)		C(12)—N(3)—C(14)	108 (1)
C(6)—C(5)—C(7)	111 (2)		C(12)—N(3)—Zn	125·3 (7)
C(3)—C(8)—C(9)	119 (2)		C(14)—N(3)—Zn	126·3 (7)
C(3)—C(8)—C(10)	115 (2)		C(12)—N(4)—C(13)	108·0 (9)
C(9)—C(8)—C(10)	108 (2)		C(12)—N(4)—C(21)	125 (1)
C(1)—C(12)—N(3)	128 (1)		C(13)—N(4)—C(21)	127 (1)
C(1)—C(12)—N(4)	123 (1)		N(1)—Zn—N(3)	91·3 (4)
N(3)—C(12)—N(4)	109 (1)		N(1)—Zn—Br(1)	112·4 (3)
C(14)—C(13)—C(18)	126 (1)		N(1)—Zn—Br(2)	111·9 (3)
C(14)—C(13)—N(4)	107 (1)		N(3)—Zn—Br(1)	110·1 (3)
C(18)—C(13)—N(4)	126 (1)		N(3)—Zn—Br(2)	112·0 (3)
C(13)—C(14)—C(15)	131 (1)		Br(1)—Zn—Br(2)	116·5 (1)
C(13)—C(14)—N(3)	107 (1)			

disordered substituent, probably a solvent DMF molecule; the calculated crystal density agrees within 0·2% with the observed value when one molecule of DMF is included in the asymmetric unit (see *Abstract*).

Several attempts were made to fit a model of DMF into this electron density using an interactive graphics system. Two of the resulting models are shown in Fig. 2(*b*). None of these models, however, adequately fits the observed electron density.

Some residual electron density was also found associated with the isopropyl group comprised of C(8), C(9) and C(10). This suggests that static disorder in their positions may be a factor contributing to the failure of the anisotropic-thermal-motion model to describe these atoms. It is interesting to note that the closest contact distance calculated between the non-hydrogen atoms of the DMF molecules and the complex molecule involves C(9). It seems probable that the disorder seen in this isopropyl group results from its close contact with the neighboring disordered solvent molecule.

References

BROWN, R. S. & HUGUET, J. (1980). *Can. J. Chem.* **58**, 889–901.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

CROTTY, D. E., ANDERSON, T. J., GLICK, M. D. & OLIVER, J. P. (1977). *Inorg. Chem.* **16**, 2346–2350.

DeSIMONE, R. E. & STUCKY, G. D. (1971). *Inorg. Chem.* **10**, 1808–1812.

FANFANI, L., NUNZI, A. & ZANAZZI, P. F. (1972). *Acta Cryst.* B**28**, 323–325.

HARDING, M. M. & COLE, S. J. (1963). *Acta Cryst.* **16**, 643–650.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 149–150. Birmingham: Kynoch Press.

KRETSINGER, R. H., COTTON, F. A. & BRYAN, R. F. (1963). *Acta Cryst.* **16**, 651–657.

LENHERT, P. G. (1975). *J. Appl. Cryst.* **8**, 568–570.

LILJAS, A., KANNAN, K. K., BERGSTEN, P.-C., WAARA, I., FRIDBORG, K., STRANDBERG, B., CARLBOM, U., JARUP, L., LOVGREN, S. & PETEF, M. (1972). *Nature (London) New Biol.* **235**, 131–137.

NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). *The XRAY 70 system.* Computer Science Center, Univ. of Maryland, College Park, Maryland.

ZAKRZEWSKI, G. & LINGAFELTER, E. C. (1970). *Inorg. Chim. Acta*, **4**, 251–257.