

References

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Bis(2-imidazolyl)aminomethane Tris(hydrochloride)

G. MENDOZA-DÍAZ

*Facultad de Química, Universidad de Guanajuato,
Noria Alta s/n, 36050 Guanajuato, Gto, Mexico*

G. J. A. A. KOOLHAAS, W. L. DRIESSEN AND J. REEDIJK

*Leiden Institute of Chemistry, Gorlaeus Laboratories,
Leiden University, PO Box 9502, 2300 RA Leiden,
The Netherlands*

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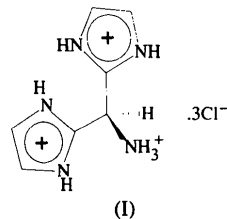
Abstract

Crystals of bis(2-imidazolyl)methylammonium trichloride, C₇H₁₂N₅³⁺·3Cl⁻, are composed of units comprised of the C₇H₁₂N₅³⁺ cation and three chloride anions linked by a two-dimensional network of hydrogen bonds. The two imidazole rings form an angle of 67.1 (2)° with one another. One of the chloride ions forms an intramolecular hydrogen bond between the ammonium residue and one of the imidazole rings.

Comment

Imidazole derivatives are of special importance in biological systems. The imidazole group has many functions such as protein carrier or nucleophilic agent; it is also a structural ligand at the active-site center of many enzymes. It forms part of some hormones and other biomolecules like histamine. This wide biological distribution has attracted the attention of researchers from many different fields, their aim being to understand and mimic the biological activity of these imidazole derivatives. Of special interest are the attempts to mimic the properties of metallo-enzymes and to relate these properties to the structural shape of simple coordination compounds (Bouwman, Driessen & Reedijk, 1990). To gain a better understanding of the relationship between the

structure of the active site and its activity, more data is needed about imidazole compounds coordinated to metal ions, as well as free ligands. The aim of the present study was to determine the molecular structure of bis(2-imidazolyl)aminomethane tris(hydrochloride) (I) [hereafter referred to as (H₃bima)Cl₃], which is necessary for comparative studies of coordination compounds containing this and analogous ligands (Koolhaas, Driessen, van Koningsbruggen, Reedijk & Spek, 1993; Tran *et al.*, 1994; Armstrong, Youinou, Palermo & Holm, 1984).



The molecular structure of the title compound is shown in Fig. 1. The imidazole rings are planar, the largest deviation from the least-squares plane being 0.006 (2) Å for atom N11. The dimensions of both imidazole rings are essentially the same. The angle between the least-squares planes of the imidazole rings is 67.1 (2)°, whereas in the copper complex [Cu₆(tidah)Cl₁₀(H₂O)] [tidah is the anionic form of 1,1,6,6-tetrakis(2-imidazolyl)-2,5-diazahexane], reported previously by Koolhaas, Driessen, van Koningsbruggen, Reedijk & Spek (1993), this angle is 40 (2)°. Crystals of (H₃bima)Cl₃ are comprised of units of the C₇H₁₂N₅³⁺ cation interconnected by seven hydrogen bonds with the three neighboring chloride anions. This hydrogen-bond system forms a polymeric two-dimensional network along the crystallographic planes (100) and (010) (Fig. 2). Only the Cl1 and Cl2 chloride anions are involved in this polymeric structure, whereas Cl3 forms an intramolecular bond between the ammo-

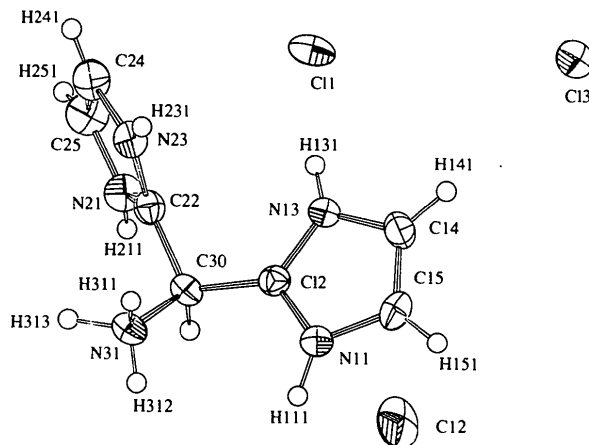


Fig. 1. TME plot (PLATON93; Spek, 1993) of bis(2-imidazolyl)aminomethane tris(hydrochloride). The displacement ellipsoids are drawn at the 50% probability level and H atoms are represented as small circles of arbitrary size.

niium residue and one of the imidazole rings (Table 3). The donor—H···acceptor angles are in the range 143–172°. The N···Cl distances in the hydrogen bonds that form part of the two-dimensional network are between 3.017 (3) and 3.048 (3) Å, whereas the N···Cl3 distances are 3.140 (3) and 3.187 (3) Å, for atoms N21 and N31, respectively. It appears that the angle between the two imidazole rings is related to the latter hydrogen bond. Stacking seems to exist between the imidazole rings, with an interplanar angle of 2.4 (2)° between the least-squares planes. However, a translation parallel to these planes is observed. This translation generates a 'stair-step' arrangement of the imidazole rings of adjacent asymmetric units.

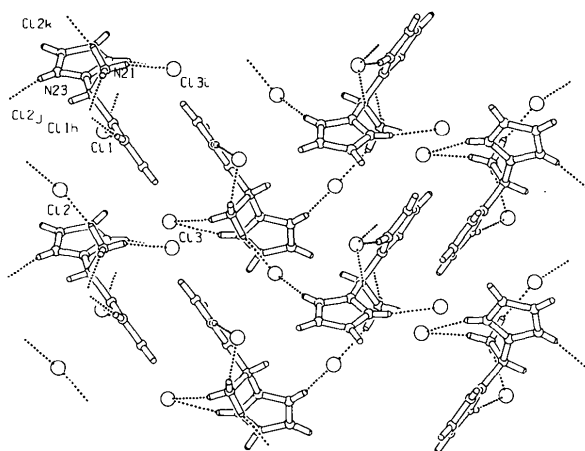
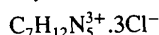


Fig. 2. View of the crystal packing (PLUTON92; Spek, 1992) of bis(2-imidazolyl)aminomethane tris(hydrochloride) in the *b* direction showing a partial view of the network of hydrogen bonds and the 'stair-step' arrangement between the imidazole rings.

Experimental

Crystal data



$M_r = 272.56$

Orthorhombic

$P2_12_12_1$

$a = 7.265 (2) \text{ \AA}$

$b = 7.557 (2) \text{ \AA}$

$c = 21.910 (7) \text{ \AA}$

$V = 1202.9 (6) \text{ \AA}^3$

$Z = 4$

$D_x = 1.505 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4
diffractometer

$\omega/2\theta$ scans

Absorption correction:
none

2993 measured reflections

2993 independent reflections

1964 observed reflections

$[I_{\text{net}} > 2\sigma(I_{\text{net}})]$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 24
reflections

$\theta = 10\text{--}12^\circ$

$\mu = 0.74 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Prism

$0.40 \times 0.25 \times 0.20 \text{ mm}$

Light pink

$\theta_{\text{max}} = 34.88^\circ$

$h = 0 \rightarrow 11$

$k = 0 \rightarrow 12$

$l = 0 \rightarrow 35$

3 standard reflections

frequency: 90 min

intensity decay: 13.73%

Refinement

Refinement on F

$R = 0.041$

$wR = 0.052$

$S = 1.826$

1960 reflections

184 parameters

All H atoms refined
isotropically

Weighting scheme based
on measured e.s.d.'s

$(\Delta/\sigma)_{\text{max}} = 0.072$

$\Delta\rho_{\text{max}} = 0.499 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.522 \text{ e \AA}^{-3}$

Atomic scattering factors
from *International Tables*
for *X-ray Crystallography*
(1974, Vol. IV, Tables
2.2B and 2.3.1)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

U_{iso} for H atoms; $U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$ for others.

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
N11	1.0116 (4)	0.2341 (4)	0.6739 (1)	0.030 (1)
C12	0.9067 (5)	0.3571 (4)	0.6480 (1)	0.024 (1)
N13	0.9750 (4)	0.5141 (4)	0.6629 (1)	0.029 (1)
C14	1.1261 (5)	0.4905 (5)	0.6994 (2)	0.032 (2)
C15	1.1501 (5)	0.3153 (5)	0.7073 (2)	0.035 (2)
N21	0.5396 (4)	0.5846 (4)	0.6313 (1)	0.029 (1)
C22	0.6331 (4)	0.4832 (4)	0.5928 (1)	0.026 (1)
N23	0.6012 (4)	0.5424 (4)	0.5368 (1)	0.032 (1)
C24	0.4846 (6)	0.6854 (5)	0.5400 (2)	0.040 (2)
C25	0.4454 (5)	0.7130 (5)	0.5989 (2)	0.037 (2)
C30	0.7427 (4)	0.3208 (4)	0.6080 (1)	0.026 (1)
N31	0.6214 (5)	0.1860 (4)	0.6374 (1)	0.033 (1)
C11	0.9005 (2)	0.8815 (1)	0.61496 (4)	0.0424 (4)
C12	0.2904 (2)	0.2025 (2)	0.55421 (4)	0.0559 (6)
C13	0.5963 (1)	0.4112 (1)	0.76013 (3)	0.0334 (4)
H111	1.001 (7)	0.118 (7)	0.664 (2)	0.06 (1)
H131	0.941 (6)	0.618 (6)	0.649 (2)	0.04 (1)
H141	1.200 (6)	0.584 (6)	0.716 (2)	0.04 (1)
H151	1.241 (6)	0.252 (6)	0.732 (2)	0.06 (1)
H211	0.538 (6)	0.589 (6)	0.668 (2)	0.04 (1)
H231	0.642 (5)	0.493 (5)	0.507 (1)	0.021 (8)
H241	0.442 (6)	0.746 (6)	0.505 (2)	0.033 (9)
H251	0.367 (7)	0.790 (7)	0.621 (2)	0.06 (1)
H301	0.788 (7)	0.267 (6)	0.572 (2)	0.05 (1)
H311	0.591 (5)	0.215 (5)	0.675 (1)	0.020 (8)
H312	0.662 (8)	0.079 (8)	0.636 (2)	0.07 (2)
H313	0.496 (7)	0.190 (7)	0.615 (2)	0.06 (1)

Table 2. Selected geometric parameters (\AA , °)

N11—C12	1.329 (4)	N11—H111	0.91 (5)
N11—C15	1.388 (5)	N13—H131	0.88 (4)
C12—N13	1.327 (4)	C14—H141	0.96 (4)
C12—C30	1.505 (4)	C15—H151	0.98 (4)
N13—C14	1.371 (4)	N21—H211	0.80 (4)
C14—C15	1.346 (5)	N23—H231	0.80 (3)
N21—C22	1.326 (4)	C24—H241	0.94 (4)
N21—C25	1.383 (5)	C25—H251	0.94 (5)
C22—N23	1.326 (4)	C30—H301	0.95 (4)
C22—C30	1.500 (4)	N31—H311	0.87 (3)
N23—C24	1.375 (5)	N31—H312	0.86 (6)
C24—C25	1.339 (5)	N31—H313	1.04 (5)
C30—N31	1.494 (4)		
C12—N11—C15	109.4 (3)	N21—C22—C30	127.2 (3)
N11—C12—N13	107.9 (3)	N23—C22—C30	125.0 (3)
N11—C12—C30	125.1 (3)	C22—N23—C24	109.1 (3)
N13—C12—C30	127.0 (3)	N23—C24—C25	107.6 (3)
C12—N13—C14	109.0 (3)	N21—C25—C24	106.2 (3)
N13—C14—C15	107.9 (3)	C12—C30—C22	113.6 (2)
N11—C15—C14	105.8 (3)	C12—C30—N31	109.8 (2)
C22—N21—C25	109.5 (3)	C22—C30—N31	109.9 (3)
N21—C22—N23	107.6 (3)		

Table 3. Hydrogen-bond distances (Å) to Cl⁻ ions

C11...H11 ⁱ	2.21 (5)	C11...N11 ⁱ	3.069 (3)
C11...H13 ⁱ	2.14 (4)	C11...N13	3.017 (3)
C11...H31 ⁱⁱ	2.33 (6)	C11...N31 ⁱ	3.106 (3)
C12...H313	2.00 (5)	C12...N31	3.020 (3)
C12...H231 ⁱⁱ	2.27 (3)	C12...N23 ⁱⁱ	3.049 (3)
C13...H21 ⁱ	2.47 (4)	C13...N21	3.140 (3)
C13...H311	2.39 (3)	C13...N31	3.187 (3)

Symmetry codes: (i) $x, 1 + y, z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

The title compound was prepared by the procedure reported by Joseph, Leigh & Swain (1977). 0.5 g of the crude compound was dissolved in 25 ml of a water/ethanol mixture (1:1 v/v). Crystals were grown by slow evaporation. After 20 d, crystals were filtered off, washed with a small amount of cold solvent, dried in a flow of air and crystallized in the form of slightly pink elongated prisms with well developed faces.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *Xtal3.2 ADDREF SORTRF* (Hall, Flack & Stewart, 1992). Program(s) used to solve structure: *Xtal3.2*. Program(s) used to refine structure: *Xtal3.2 CRYLSQ*. Molecular graphics: *PLATON93* (Spek, 1993) and *PLUTON92* (Spek, 1992). Software used to prepare material for publication: *Xtal3.2 BONDLA CIFIO*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, including bond angles involving H atoms, have been deposited with the IUCr (Reference: BK1097). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl *N*-(4-Chlorophenylaminothiocarbonyl)benzimidate

BECHIR HAJJEM, TAHAR JOUINI, ABDALLAH HARIZI AND BELGACEM BACCAR

Département de Chimie, Faculté des Sciences, 1060 Campus Universitaire, Tunis, Tunisia

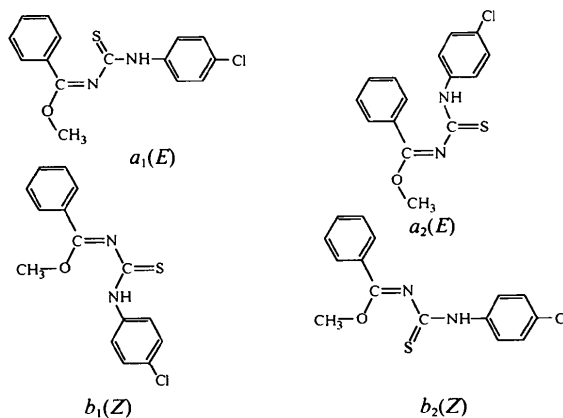
(Received 22 June 1994; accepted 13 October 1994)

Abstract

The conformation of the title compound, C₁₅H₁₃ClN₂OS, corresponds to that of methyl 4-chloro-*N*-(2-tolyl)benzimidate [Kallel, Hajjem, Baccar & Svoboda (1992). *Acta Cryst.* **C48**, 536–538]. The planes composed of atoms O, C8, N2 and N2, C7, S make an angle of 104.3 (2)° with one another. The two phenyl rings are not coplanar. The N—H bond participates in intermolecular hydrogen bonding.

Comment

The reaction of 4-chlorophenylthioisocyanate with methyl benzimidate leads to the formation of methyl *N*-(4-chlorophenylaminothiocarbonyl)benzimidate. This method of preparation has been described previously (Etienne, Le Berre, Lonchambon, Roques & Lemmens, 1976). Four stereoisomers may exist for the title compound. They are characterized as *a*₁(*E*), *a*₂(*E*), *b*₁(*Z*) and *b*₂(*Z*). ¹H and ¹³C NMR spectroscopic analysis confirms that the title compound exists in one isomeric form and X-ray diffraction studies show this configuration to be *a*₁(*E*).



Adjacent molecules in the crystal are linked by an N—H...S hydrogen bond [N1...S(-x, -y, 1-z) 3.382 (2), H1...S 2.58 (2) Å and N1—H1...S 167 (2)°]. The geometrical conformation *a*₁(*E*) adopted by the