Inorganica Chimica Acta, *77* (1983) L113–L115

The Crystal and Molecular Structure of Bis(biguanide)copper(II) Chloride Dihydrate

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Received April 11, 1983

Introduction

Metal biguanide complexes have attracted considerable attention since the original work of Ray and Saha [1].

The ligand, biguanide, is useful as an analytical agent capable of complexing a range of metal ions [2]. The nature of the bonding of biguanide to metals had been investigated using UV spectroscopy [3] and X-ray methods [4–6]. This resulted in the structure determination of bis(biguanide)nickel(II) chloride dihydrate, [$Ni(BigH)_2Cl_2 \cdot 2H_2O$)], [4] and ethylenebis(biguanide)copper(II) chloride monohydrate, [$Cu(enBigH)_2Cl_2 \cdot H_2O$], [5]. However the structural characteristic of the Cu(II) analogue of biguanide [$Cu(BigH)_2Cl_2 \cdot 2H_2O$] have only been alluded to [6]. The current work on the series relates to the determination of the X-ray structure of this analogue.

Experimental

The title compound was prepared by reacting biguanide and copper(II) chloride [7]. Red needle-like crystals grew from a matrix of smaller needles out of an aqueous solution. These needles showed perfect cleavage across the prisms, (the direction of the c crystallographic axis). A cleaved crystal (0.22 X 0.13 X 0.13 mm) was used.

Crystal Data

$C_4H_{18}Cl_2CuN_{10}O_2$, $Mr = 372.6$, triclinic, space group $P\bar{1}$, $a = 6.801(3)$, $b = 9.582(1)$, $c = 12.485(2)$ Å, $\alpha = 68.65(1)$, $\beta = 72.91(2)$, $\gamma = 78.74(2)$, $V = 720.7$ Å^3, $Z = 2$, $D_c = 1.72$ g cm^{-3}, $D_f = 1.74$ g cm^{-3}, $F(000) = 382$, μ(Mo-$K\alpha$) = 19.6 cm^{-1}.

Data Collection, Structure Solution and Refinement

Intensity data were collected from a single crystal using a Nonius CAD-4 automatic diffractometer (graphite monochromated Mo-$K\alpha$ radiation, $\lambda = 0.71069$ Å). Of 3317 reflections collected up to $2\theta_{max} = 54°$, 1519 with $I > 2.5\sigma(I)$ were considered observed and were used in structure analysis. No corrections were made for absorption. The structure was solved by direct methods using SHELX 76 [8] and refined to final residuals $R = 0.043$ and $Rw = 0.041$, with anisotropic thermal parameters on all non-hydrogens. The value of w used in the weighting scheme was $w = 1.6/(\sigma^2 Fo + 5.0 \times 10^{-3}\ Fo^2)$. Hydrogens were located from a difference-Fourier synthesis and included in the refinement at fixed positions with their isotropic U values also fixed at 0.05 Å^2. Two intense low angle reflections (2 0 0; 0 1 0) were considered to be affected by extinction and were removed before the final refinement cycle. Scattering factors used were those of Cromer and Mann [9] (non-hydrogens) and Stewart *et al.* [10] (hydrogen), while Cu and Cl were corrected for anomalous dispersion [11].

Atomic positional parameters are listed in Table I while interatomic distances and angles are given in Table II. Structure factors and anisotropic thermal parameters are available on request from the authors.

Discussion

The molecular configuration and atom numbering scheme are shown in Fig. 1. The complex is square planar with Cu lying 0.043(2) Å out of the coordination plane, and comparable Cu–N bond lengths [1.949(5) Å mean]. These distances and the N–M–N angles are more regular than the values for the unsymmetrical square planar Cu[en$(BigH)_2$], [1.933–1.989 Å] [4]. These values are slightly longer than the corresponding metal–N bond distances in the isomorphous and isostructural $Ni(BigH)_2Cl_2 \cdot 2H_2O$ [1.81–1.89 Å (mean 1.84(3) Å) [4]. The comparative cell data for the Ni(II) analogue are: $a = 6.85(2)$, $b = 9.48(3)$, $c = 12.50(3)$ Å, $\alpha = 112.8(3)$, $\beta = 100.5(3)$, $\gamma = 100.2(3)°$, $V = 708$ Å^3, $Z = 2$, $D_c = 1.73$ g cm^{-3} [4].

This higher precision determination has given the hydrogen positions particularly for those about the guanidine ligand. Although these positional parameters atoms have not refined, they were located with a high degree of certainty. The protons are trigonally disposed about the six-membered chelate ring consistent with the expected delocalization of electrons about the ring, while those on the terminal amine groups are tetrahedral (sp^3). The C–N bond distances found from this determination may be classified into three distinct types.

a. C–N(H,M) 1.281–1.301 Å [1.297(7) Å mean]
b. C–N(H,H) 1.328–1.362 Å [1.341(7) Å mean]

0020-1693/83/$3.00

TABLE I. Atomic Coordinates (×10^4) except Hydrogens (×10^3).

Atom	x/a	y/b	z/c
Cu	2345(1)	−530.1(8)	10598.1(6)
Cl(1)	3755(3)	2193(2)	4959(1)
Cl(2)	−1823(3)	−4033(2)	18382(2)
W(1)	−3344(13)	4798(7)	11166(6)
W(2)	2001(7)	−3516(6)	15864(4)
N(1)	2620(8)	−1409(6)	9372(4)
C(2)	2982(9)	−775(7)	8228(5)
N(2)	3222(9)	−1510(6)	7471(4)
N(3)	3094(7)	750(6)	7701(4)
C(4)	3027(9)	1794(7)	8231(5)
N(4)	3172(8)	3200(6)	7488(4)
N(5)	2833(8)	1416(5)	9363(4)
N(6)	1958(7)	−2483(5)	11815(4)
C(7)	1817(8)	−2861(6)	12931(5)
N(7)	1707(9)	−4281(6)	13680(5)
N(8)	1758(7)	−1847(5)	13477(4)
C(9)	1846(8)	−315(6)	12946(5)
N(9)	1726(8)	407(6)	13726(4)
N(10)	2001(7)	305(5)	11834(4)
Hw(11)	−179	488	1087
Hw(12)	−408	447	1191
Hw(21)	−123	374	1331
Hw(22)	292	−303	1536
H(1)	271	−246	967
H(3)	345	113	681
H(21)	340	−252	784
H(22)	345	−97	677
H(41)	321	355	677
H(42)	289	413	779
H(5)	264	224	957
H(6)	175	−336	1155
H(71)	208	−493	1340
H(72)	194	−452	1440
H(8)	141	−221	1435
H(91)	235	−20	1442
H(92)	168	125	1336
H(10)	244	138	1156

TABLE II. Bond Distances (Å) and Angles (°).

Distances		Angles	
Cu–N(1)	1.949(5)	N(1)–Cu–N(5)	89.0(2)
Cu–N(5)	1.953(5)	N(1)–Cu–N(6)	90.7(2)
Cu–N(6)	1.941(5)	N(1)–Cu–N(10)	178.7(2)
Cu–N(10)	1.952(5)	N(5)–Cu–N(6)	178.1(2)
N(1)–C(2)	1.301(7)	N(5)–Cu–N(10)	91.3(2)
C(2)–N(2)	1.328(8)	N(6)–Cu–N(10)	89.0(2)
C(2)–N(3)	1.374(8)	N(1)–C(2)–N(2)	124.1(6)
N(3)–C(4)	1.376(8)	N(1)–C(2)–N(3)	121.8(5)
C(4)–N(4)	1.332(8)	N(2)–C(2)–N(3)	114.1(5)
C(4)–N(5)	1.297(8)	C(2)–N(3)–C(4)	127.9(5)
N(6)–C(7)	1.284(7)	N(3)–C(4)–N(4)	114.3(5)
C(7)–N(7)	1.344(8)	N(3)–C(4)–N(5)	121.8(6)
C(7)–N(8)	1.365(7)	N(4)–C(4)–N(5)	123.9(6)
N(8)–C(9)	1.379(7)	N(6)–C(7)–N(7)	124.0(5)
C(9)–N(9)	1.363(8)	N(6)–C(7)–N(8)	122.9(5)
C(9)–N(10)	1.281(7)	N(7)–C(7)–N(8)	113.0(5)
		C(7)–N(8)–C(9)	126.6(5)
		N(8)–C(9)–N(9)	113.1(5)
		N(8)–C(9)–N(10)	122.9(5)
		N(9)–C(9)–N(10)	124.0(5)
		Cu–N(1)–C(2)	129.5(4)
		Cu–N(5)–C(4)	129.5(4)
		Cu–N(6)–C(7)	129.1(4)
		Cu–N(10)–C(9)	128.8(4)

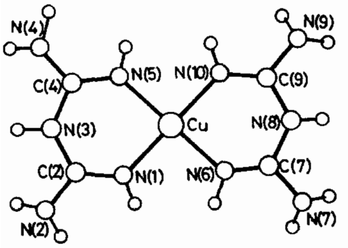

Fig. 1. Molecular configuration and atom naming scheme.

c. C–N(H,C) 1.365–1.379 Å [1.373(7) Å mean]
All the C–N bond lengths point towards some significant double bond character.

Type (a) bonds lengths are considerably shorter than the expected value and this may be attributed to electron withdrawal from N as a result of metal coordination. Similar observations have been made for C–N distances in coordinated heterocyclic systems *e.g.* pyridine in [$Cu_2(2,4,5\text{-}T)_4(py)_2$] [12], [1.31(3) Å]. Although the other types are similar they are different from type (a), which suggests some delocalization, but the location of the protons on the terminal amine groups tends to preclude this.

The metal-complex molecules are stacked down the *a* crystal axis (Fig. 2) with the chloride counter

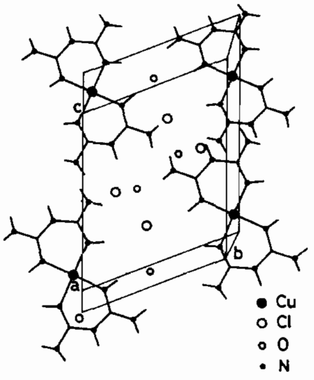

Fig. 2. Packing in the cell viewed perpendicular to *bc*.

ions and water molecules providing further stability *via* hydrogen bonds to amino and imino nitrogens.

Acknowledgements

The authors wish to thank the Australian and Indian Governments for financial support through the Bilateral Science and Technology Agreements to enable one of us (CHLK) to work at the Indian Institute of Technology, Madras. The authors also thank Professor P. T. Manoharan of the Indian Regional and Sophisticated Instrument Centre. Madras, for use of a diffractometer and Dr. Mary Truter of the Rothamsted Experimental Station, Harpenden, Herts., U.K. for computer facilities. Two of us (GS and EJO'R) thank the Queensland Institute of Technology for the time required to work on this project.

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