The Crystal Structure of Aquacopper(II)-di-μ-[N,N'-bis(3'-pyridazinecarboxamido)-1,2-ethane]-copper(II) (3 + x) Water; a Dimeric Complex with a Tetradentate Bis-pyridazinecarboxamide Ligand

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Abstract

The dimeric complex $[Cu_2(bpden)_2H_2O]\cdot(3+x)H_2O$ is triclinic, $P\bar{1}$, with $a = 9.038(6)$, $b = 11.535(6)$, $c = 14.834(10)$ Å, $\alpha = 90.74(4)$, $\beta = 105.25(3)$, $\gamma = 98.84(4)°$ and $Z = 2$. The two $bpden^{2-}$ ligands coordinate as N_4 tetradentates via amide nitrogens and 2- and 2'-pyridazine nitrogens {$H_2bpden = N,N'$-bis(3'-pyridazinecarboxamide)-1,2-ethane}. The ligands act as bridging groups, with each copper being bonded in a *trans*-arrangement to one pyridazinecarboxamide chelate from each ligand. The two copper coordination entities are co-axially stacked in an anti-arrangement. The Cu–Cu distance is 3.250 Å. Magnetic susceptibility measurements down to 89 K show no evidence of magnetic interaction. For Cu(1), water coordination produces an approximately trigonal–bipyramidal structure, with the trigonal axis being between the donor nitrogens from two pyridazine groups. The coordination to Cu(2) is tetrahedrally distorted square-planar, with an angle of 36.1° between the two CuN_2 planes associated with the coordinated pyridazinecarboxamides. Four lattice waters have been identified in the structure, but one, OW(5), has an occupancy of 0.56 in the crystal examined. Density measurements suggest, however, that for most crystals the occupancy of OW(5) is close to zero and analytical data on bulk samples consistently indicate a total of four water molecules. The bulk formula is therefore rounded off to $[Cu_2(bpden)_2H_2O]\cdot 3H_2O$. Calculated and experimental X-ray powder patterns are in close agreement for all bulk samples. The reflectance electronic spectrum of the complex contains two bands, at 13 300 and 17 400 cm^{-1}, assigned to Cu(1) and Cu(2) respectively. The structure is unusual in that analogous complexes with deprotonated bis-picolinamide ligands are monomeric with distorted planar N_4 coordination by the ligands.

Introduction

Metal complexes with 3,6-disubstituted pyridazine ligands, and with analogous disubstituted phthalazine ligands, have been extensively studied [1]. The chief interest has been in the formation and study of diimine-bridged complexes with these ligands. In contrast, very little work has been reported on monosubstituted versions of these ligands.

As part of a systematic study of 3-substituted pyridazines, we report the crystal structure of the dimeric complex $[Cu_2(bpden)_2H_2O]\cdot 3H_2O$. The bis-pyridazinecarboxamide compound N,N'-bis(3'-pyridazinecarboxamide)-1,2-ethane(H_2bpden) functions, in its deprotonated form, as a tetradentate bridging ligand in this complex. This appears to be the first report of a complex with a pyridazinecarboxamide ligand. Complexes with the corresponding bis-picolinamide ligands, involving pyridine, are well known [2] and are compared with the bis-pyridazinecarboxamide complex.

Experimental

Preparations

H_2bpden

Ethylenediamine (0.4 g) was added dropwise to a boiling solution of 3-ethylpyridazinecarboxylate [3] (2.0 g) in absolute ethanol (40 ml). The mixture was concentrated to half volume and then left overnight. The precipitate was filtered off, washed with absolute ethanol, and dried over P_2O_5 *in vacuo* (0.95 g, 53%) melting point 292 °C.

Anal. Found: C, 52.9; H, 4.3; N, 30.4. Calc. for $C_{12}H_{12}N_6O_2$: C, 52.9; H, 4.4; N, 30.9%.

$[Cu_2(bpden)_2H_2O]\cdot 3H_2O$

A boiling solution of $Cu(CH_3CO_2)_2\cdot H_2O$ (0.73 g) in water (40 ml) was added to a boiling suspension of H_2bpden (1.0 g) in ethanol (75 ml). Triethylamine (0.8 g) in ethanol (10 ml) was added dropwise to the

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boiling mixture. The mixture was concentrated to half volume and then left for 4 days, yielding greenish-black crystals. These were filtered off, washed with water and ethanol and then air-dried (0.8 g, 60%). *Anal.* Found: C, 39.1; H, 3.7; N, 22.6. Calc. for $Cu_2(C_{12}H_{10}N_6O_2)_2(H_2O)_4$; C, 39.0; H, 3.8; N, 22.7%.

Crystallography

Crystal data

$Cu_2(C_{12}H_{10}N_6O_2)_2(H_2O)_{4.6}$, $M = 750.46$, triclinic, space group $P\bar{1}$, $a = 9.038(6)$, $b = 11.535(6)$, $c = 14.834(10)$ Å, $\alpha = 90.74(4)$, $\beta = 105.25(3)$, $\gamma = 98.84(4)°$, $D_c = 1.69$ g cm^{-3}, $Z = 2$, μ(Mo) 15.17 cm^{-1}. Crystal size: 0.12 × 0.19 × 0.05 mm.

Structure determination

Intensities for 5173 reflexions were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode, using graphite monochromatized molybdenum radiation (λ 0.7107 Å) and $2\theta_{max}$ of 50°. Data were corrected for absorption. A total of 3215 reflexions with $I > 3\sigma(I)$ were considered observed, and were used for least-squares refinement after structure solution by direct phasing and Fourier methods. Non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen atoms were located in difference Fouriers and given isotropic temperature parameters equivalent to those of the atoms to which bonded.

Five water molecules were identified, comprising four lattice waters and one bonded to Cu(1). Density measurement indicated that the sample was inhomogeneous, with the bulk of crystals having a density of 1.67 g cm^{-3}, corresponding to four waters. A small number of crystals clearly had greater density, ranging up to about 1.69 g cm^{-3}, and it seemed likely one of these had been chosen. The thermal parameters for OW(5) were abnormally high, so its occupancy was allowed to vary. This converged to a value of 0.56(2), consistent with a density of 1.69 g cm^{-3}, and the thermal parameters became acceptable. Microanalyses consistently indicated a total of four waters, so bulk samples appear to have an average OW(5) occupancy close to zero. The calculated X-ray powder diffraction patterns, based on 0.56 or zero OW(5) water molecules, were virtually identical, and very closely agreed with all experimental patterns. Accordingly, the structure is taken to refer to the system with $(3 + x)$ lattice waters. The formula is rounded to $[Cu_2(bpden)_2H_2O]\cdot 3H_2O$ for bulk samples, in view of their near zero average occupancy values for OW(5).

The final residuals R, R_w were 0.037, 0.046. Reflexion weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography [4]. Structure solution was by MULTAN 80 [5], and refinement used BLOCKLS, a local version of ORFLS [6]. A Cyber 172 computer was used for all calculations.

Results and Discussion

An ORTEP-II diagram [7] of the structure is shown in Fig. 1 with the atoms labelled. Final atomic

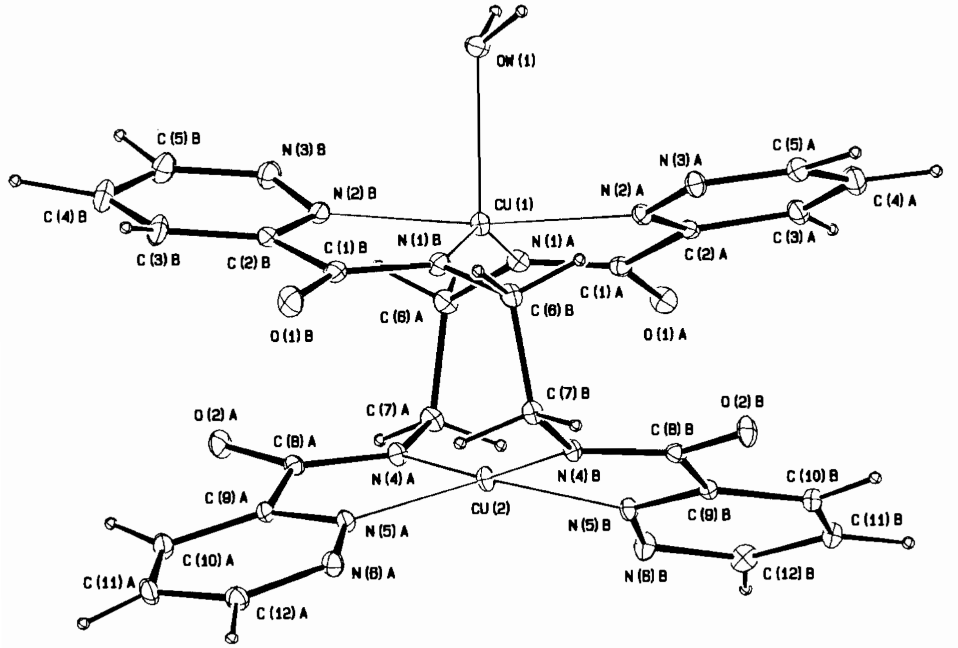

Fig. 1. A perspective drawing of the $[Cu_2(bpden)_2H_2O]$ molecule with atom labelling.

TABLE I. Final Atomic Parameters and the Isotropic Equivalent of the Anisotropic Temperature Factor[a]

	x	y	z	B_{eq} (Å^2)		x	y	z	B_{eq} (Å^2)
Cu(1)	0.5680(1)	0.6993(1)	0.1723(0)	2.48(2)	N(1)B	0.6502(3)	0.8164(3)	0.2786(3)	2.56(2)
Cu(2)	0.3640(1)	0.6292(1)	0.3199(0)	2.48(2)	N(2)B	0.4533(5)	0.8323(3)	0.1181(3)	2.78(2)
O(1)A	0.3769(4)	0.3586(3)	0.0943(3)	3.49(11)	N(3)B	0.3660(5)	0.8317(4)	0.0300(3)	3.95(11)
O(2)A	0.0405(4)	0.7587(3)	0.1258(2)	3.68(12)	N(4)B	0.5703(4)	0.6407(3)	0.4054(2)	2.09(12)
N(1)A	0.4161(4)	0.5628(3)	0.1062(3)	2.53(12)	N(5)B	0.3715(4)	0.4559(3)	0.3292(3)	2.35(12)
N(2)A	0.6968(4)	0.5681(3)	0.2125(3)	2.33(12)	N(6)B	0.2541(5)	0.3694(3)	0.2899(3)	3.03(12)
N(3)A	0.8437(5)	0.5845(4)	0.2640(3)	2.98(13)	C(1)B	0.5929(6)	0.9157(4)	0.2709(4)	3.02(13)
N(4)A	0.2015(4)	0.6344(3)	0.2053(3)	2.35(11)	C(2)B	0.4861(6)	0.9262(4)	0.1765(4)	3.09(11)
N(5)A	0.2965(4)	0.7798(3)	0.3519(3)	2.41(12)	C(3)B	0.4216(8)	1.0267(5)	0.1496(5)	4.95(12)
N(6)A	0.3470(5)	0.8403(3)	0.4341(3)	2.92(13)	C(4)B	0.3299(9)	1.0273(6)	0.0622(5)	5.90(13)
C(1)A	0.4586(6)	0.4584(4)	0.1192(3)	2.57(15)	C(5)B	0.3064(8)	0.9286(6)	0.0050(5)	5.10(15)
C(2)A	0.6240(5)	0.4640(4)	0.1722(3)	2.39(14)	C(6)B	0.7591(5)	0.8005(4)	0.3694(4)	2.87(14)
C(3)A	0.7003(6)	0.3665(5)	0.1800(4)	3.49(18)	C(7)B	0.6766(5)	0.7508(4)	0.4408(3)	2.39(18)
C(4)A	0.8515(7)	0.3816(5)	0.2322(4)	4.19(20)	C(8)B	0.6254(5)	0.5415(4)	0.4230(3)	2.30(20)
C(5)A	0.9166(6)	0.4932(5)	0.2746(4)	3.72(18)	C(9)B	0.5077(5)	0.4341(4)	0.3796(3)	2.13(18)
C(6)A	0.2517(6)	0.5627(5)	0.0594(3)	3.00(15)	C(10)B	0.5397(6)	0.3213(4)	0.3910(4)	2.87(15)
C(7)A	0.1500(5)	0.5472(4)	0.1260(3)	2.66(14)	C(11)B	0.4222(6)	0.2301(4)	0.3492(4)	3.19(14)
C(8)A	0.1359(5)	0.7297(4)	0.1962(3)	2.55(14)	C(12)B	0.2813(6)	0.2608(5)	0.3008(4)	3.52(14)
C(9)A	0.1826(5)	0.8085(4)	0.2835(3)	2.45(14)	OW(1)	0.7230(4)	0.7549(3)	0.0788(2)	3.08(14)
C(10)A	0.1093(6)	0.9038(4)	0.2943(4)	3.26(17)	OW(2)	1.0618(4)	0.6558(3)	0.5057(3)	5.71(17)
C(11)A	0.1581(6)	0.9645(4)	0.3783(4)	3.57(18)	OW(3)	0.9125(5)	1.1506(4)	0.3701(4)	6.51(18)
C(12)A	0.2789(6)	0.9304(4)	0.4469(4)	3.23(17)	OW(4)	0.0569(5)	0.2380(4)	0.0764(3)	6.06(17)
O(1)B	0.6197(5)	0.9996(3)	0.3303(3)	4.35(13)	OW(5)	−0.0705(15)	0.0946(10)	0.1911(8)	10.94(13)
O(2)B	0.7563(4)	0.5273(3)	0.4694(3)	3.46(11)					

[a] e.s.d.s. are given in parentheses.

TABLE II. Selected Bond Length (Å) and Bond Angle (°) Data

Cu(1)–N(1)A	1.978(4)	Cu(2)–N(4)A	1.941(4)
Cu(1)–N(1)B	1.971(4)	Cu(2)–N(4)B	1.944(3)
Cu(1)–N(2)A	2.049(4)	Cu(2)–N(5)A	2.018(4)
Cu(1)–N(2)B	2.040(4)	Cu(2)–N(5)B	2.016(4)
Cu(1)–OW(1)	2.250(3)	Cu(1)–Cu(2)	3.250(1)
N(1)A–Cu(1)–N(2)A	80.5(2)	N(1)B–Cu(1)–OW(1)	102.3(1)
N(1)A–Cu(1)–N(1)B	151.2(2)	N(2)B–Cu(1)–OW(1)	85.4(1)
N(1)A–Cu(1)–N(2)B	99.8(2)	N(4)A–Cu(2)–N(5)A	82.1(2)
N(1)A–Cu(1)–OW(1)	106.5(1)	N(4)A–Cu(2)–N(4)B	160.2(2)
N(2)A–Cu(1)–N(1)B	102.7(2)	N(4)A–Cu(2)–N(5)B	102.8(2)
N(2)A–Cu(1)–N(2)B	172.5(2)	N(5)A–Cu(2)–N(4)B	102.5(2)
N(2)A–Cu(1)–OW(1)	87.3(1)	N(5)A–Cu(2)–N(5)B	153.3(2)
N(1)B–Cu(1)–N(2)B	80.8(2)	N(4)B–Cu(2)–N(5)B	81.9(1)

parameters are listed in Table I and selected bond length and bond angle data are given in Table II. Two tetradentate deprotonated bpden^{2-} ligands act as bridging groups between a five-coordinate copper and a four-coordinate copper. Each copper is bonded in a *trans*-arrangement to one pyridazinecarboxamide chelate from each ligand. Amide nitrogen coordination occurs, as is usual for deprotonated amide [2, 8, 9]. Coordination by each pyridazine 2-nitrogen atom also occurs, resulting in N_4 coordination to each copper. A coordinated water molecule produces a five-coordinate structure for Cu(1).

The two copper coordination entities are coaxially stacked. The ligands are disposed in an anti-arrangement, *i.e.* the $(NN')(NN')$ rotation sequences for the coppers are in opposite senses, where (NN') refers to the pyridazine and amide nitrogen donors for one chelate.

The coordination geometry about Cu(1) is close to trigonal bipyramidal. The trigonal axis is between the pyridazine nitrogens N(2)A and N(2)B, with the N(2)A–Cu(1)–N(2)B angle being 172.5°, close to the ideal value of 180°. The trigonal plane involves the water oxygen OW(1) and the amide nitrogens N(1)A and N(1)B. The OW(1), N(1)A, N(1)B, Cu(1) grouping is a well-defined plane, the sum of the bond angles to Cu(1) being 360.0°. The Cu(1) atom deviates by 0.022 Å from the OW(1), N(1)A, N(1)B plane. The angles in the trigonal plane from OW(1), N(1)A and N(1)B to Cu(1) are 106.5°, 151.2° and 102.3°, distorted from the ideal value of 120°. The angles from the axial bonds, N(2)A–Cu(1) and N(2)B–Cu(1), to the OW(1), N(1)A, N(1)B trigonal plane are 78.0° and 79.4°, showing distortion from the ideal angle of 90°.

The coordination geometry about Cu(2) is a tetrahedrally distorted planar arrangement. The pyridazinecarboxamide groups are twisted so that the angle between the Cu(2), N(4)A, N(5)A and Cu(2), N(4)B, N(5)B planes is 36.1°, compared to 0° for a planar arrangement and 90° for a tetrahedral arrangement.

The pyridazinecarboxamide chelate groups, such as N(1)A, C(1)A, C(2)A, N(2)A, are slightly distorted from co-planarity with their adjacent pyridazine groups. This is shown by the NCCN torsional angles which are 11.3°, 6.0°, 8.5° and 2.0° for the chelate groups which involve the amide nitrogens N(1)A, N(1)B, N(4)A and N(4)B, respectively. The Cu–N distances for the four-coordinate Cu(2) are shorter than the corresponding Cu–N distances for five-coordinate Cu(1), in keeping with the greater electron acceptor power associated with a lower coordination number.

Numerous structure determinations have been reported for copper(II) complexes of tetradentate bis-picolinamide ligands analogous to H_2bpden [10–12]. No example appears to have been reported of a deprotonated bis-picolinamide functioning as a bridging ligand. Instead, each dinegative deprotonated bis-picolinamide ligand produces distorted planar N_4 coordination to an individual metal. This leads to a *cis*-arrangement of the picolinamide groups, in contrast to the *trans*-arrangement with the present ligand. The structural dimensions of the present ligand are similar to those for bis-picolinamides [11]. The Cu–N(amide) distances for the complex, in the range 1.941–1.978 Å, overlap with the range of 1.911–1.955 Å observed for copper(II) deprotonated bis-picolinamide complexes. The Cu N-(pyridazine) distances for the complex, at 2.016–2.049 Å, are in the range 2.009–2.074 Å found for Cu–N(pyridine) distances in analogous bis-picolinamide systems. The pyridazinecarboxamide chelate coordination angles, of the type N(1)A–Cu(1)–N(2)A, are in the range 80.5°–82.1°, and overlap the range of 80.7°–83.0° for deprotonated bis-picolinamide copper(II) complexes.

The reflectance electronic spectrum of the complex has bands at 13 300 and 17 400 cm^{-1}, in keeping with the presence of two independent copper atoms with four- and five-coordinate structures. The band at 13 300 cm^{-1} is assigned to Cu(1) which has a trigonal bipyramidal structure. In support of this, a similar band in the range 12 500–13 400 cm^{-1} is found in the spectra of some trigonal bipyramidal copper(II) complexes, with chromophores of the type CuN_4O and CuN_4Cl [13]. This assignment might seem to be in contradiction to the spectral results for a series of copper(II) complexes with deprotonated bis-picolinamide ligands. These complexes have five-coordinate CuN_4O structures and their electronic spectra have a band in the range 17 500–19 600 cm^{-1} [14–16]. The structures are, however, square-based pyramidal with apical water molecules, and complexes with this geometry may have spectra with higher frequency bands than found with related trigonal bipyramidal complexes [13, 17].

We assign the absorption band at 17 400 cm^{-1} to Cu(2) which has a tetrahedrally distorted planar structure. We are not aware of other CuN_4 systems with distortions similar to that found with Cu(2). However, two four-coordinate complexes with CuN_2O_2 chromophores display tetrahedral distortions from planarity of 34.4° and 36.0°, respectively, similar to the value of 36.1° for Cu(2) [18]. In their spectra, these complexes have a single asymmetric band, occurring at 16 000 cm^{-1} for the former complex and 17 100 cm^{-1} for the latter complex, both resembling the band assigned to Cu(2).

The magnetic moment of $[Cu_2(bpden)_2H_2O]\cdot 3H_2O$ is 1.77 BM at 304 K and 1.72 BM at 89 K, with a Weiss θ constant of –7 K, showing little significant indication of magnetic exchange. Strong super-exchange via the ligand amidoethane linkage is not likely. The Cu(1)–Cu(2) distance is 3.250 Å.

It is interesting that the non-deprotonated form of the bis-picolinamide ligand *N*,*N*′-bis(2′-pyridinecarboxamide)-1,3-propane (H_2bppn) yields the dimeric complexes $[Cu_2(H_2bppn)_2(SO_4)_2]\cdot 13H_2O$ and $[Cu_2(bppnH_2)_2Cl_2]SO_4\cdot 8H_2O$ [19, 20]. These complexes are structurally similar to $[Cu_2(bpden)_2H_2O]\cdot 3H_2O$ in that they are co-axially stacked dimers. However, the non-deprotonated ligand bppnH_2 coordinates via the amide oxygen, giving N_2O_2 coordination, in contrast to the N_4 coordination in the deprotonated bis-pyridazinecarboxamide complex. The Cu–Cu distances in the bppnH_2 complexes are 3.9 and 3.948 Å respectively. Studies of magnetic properties and of ESR spectra suggest that $[Cu_2(H_2bppn)_2(SO_4)_2]\cdot 13H_2O$ is very weakly antiferromagnetic, the Weiss θ constant being –4 K [19].

Supplementary Material

All atom and thermal parameters and all interatomic distances, angles and torsional angles, as well as structure factor listings are available from the authors on request.

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