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Synthesis and Structure of μ-3,3'-[1,2-ethanediyl-bis(nitrilomethylidyne)-bis(2-hydroxybenzoato)] aquadicopper(II) Hydrate

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Abstract

The complex μ-3,3'-[1,2-ethanediyl-bis(nitrilomethylidyne)-bis(2-hydroxybenzoato)] aquadicopper(II) hydrate, $C_{18}H_{16}N_2O_8Cu_2$, was isolated from an attempted preparation of a copper lanthanum binuclear complex. The dark purple crystals are monoclinic, space group $P2_1/n$, with 4 molecules per unit cell; dimensions $a = 13.961(5)$, $b = 11.787(3)$, $c = 11.622(3)$ Å and $\beta = 113.09(2)^\circ$. The final R was 0.046 for the 2062 reflections used in the analysis. The Cu atom in the N_2O_2 cavity is five coordinate with Cu–N distances of 1.879 and 1.880 Å and Cu–O distances of 1.898 and 1.900 Å. A water molecule at 2.557 Å completes the square pyramidal arrangement. The second Cu in the O_4 cavity is square planar, with Cu–O distances to the bridging oxygens of 1.914 and 1.909 Å and to the carboxy oxygens of 1.871 and 1.882 Å. A survey of copper complexes in a square planar N_2O_2 arrangement has led to the equation ΔCu from the N_2O_2 plane = 0.822 – 0.275 (Cu–O axial distance) with a correlation coefficient of 0.98 for the 12 structures in which the Cu atom is bonded to a fifth oxygen atom. A model for the transition from square planar to square pyramidal geometry is proposed.

Introduction

Metal complexes of binuclear ligands continue to be of interest for a variety of reasons [1, 2]. In spite of the large number of binuclear complexes which have been reported there are only a few examples of binuclear complexes proportedly containing a lanthanide ion [3, 4]. In fact there are to our knowledge no structural studies of binuclear complexes containing a lanthanide ion. The ligand 3,3'-[1,2-ethanediylbis(nitrilomethylidyne)] bis(2-hydroxybenzoic acid) [5], H_4fsaen, seemed ideally suited to prepare a lanthanide–transition metal binuclear complex. Previous studies had suggested that a copper ion would coordinate preferentially to the N_2O_2 cavity leaving the O_4 cavity available for a second ion. Since the lanthanide ions are known to prefer oxygen donors, the empty O_4 cavity appeared to be an ideal coordination site for a lanthanide ion. A similar strategy was reported recently [3] during the course of our studies. The product of our reactions was a dark purple product which our crystal structure study has revealed is the dicopper complex $Cu(H_2O)$-Cufsaen·H_2O. The dark purple color is distinctly different from the previously reported yellow brown [5] and green [6] crystals for the identical stoichiometry.

Experimental

The 3-formylsalicylic acid was prepared by the reported method [7]. The bright yellow H_4fsaen (0.3561 g, 1.0 mmol) was refluxed with copper acetate (0.1997 g, 1.0 mmol) in ethanol for 12 h. Lanthanum acetate (1.0 mmol) dissolved in 45 ml of DMSO was added to the yellow–green slurry. The volume of the solution was increased to 200 ml by the addition of DMSO and then heated for 2 h. The solution was filtered. Deep purple crystals formed slowly as the DMSO evaporated. Because the color was markedly different from the reported dicopper complexes, an X-ray diffraction study was carried out.

The intensity data were measured using a P$\bar{1}$ diffractometer with nickel filtered Cu Kα radiation to a 2θ limit of 110°. A variable speed (2° to 24°/min) scan technique was used. The structure was solved using MULTAN and refined by least-square techniques. The crystal data and other details are given in Table I. The final positional parameters are given in Table II. The atomic numbering and the thermal ellipsoids are illustrated in Fig. 1. Tables of the thermal parameters for the non-hydrogen atoms, hydrogen atom coordinates and the observed and calculated structure amplitudes have been deposited. Copies are available from the Editor-in-Chief or the author (G.J.P.).

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TABLE I. X-ray Diffraction Data

(A) Crystal data

Formula: $C_{18}H_{16}N_2O_8Cu_2$
Formula Weight: 515.412 amu
Crystal System: monoclinic
Space Group: $P2_1/n$
$a = 13.961(5)$ Å
$b = 11.787(3)$ Å
$c = 11.622(3)$ Å
$\alpha = 90.0°$
$\beta = 113.09(2)°$
$\gamma = 90.0°$
$V = 1759.3(8)$ Å^3
$Z = 4$
$D_m = 1.93$ g cm^{-3}
$D_c = 1.95$ g cm^{-3}
Crystal dimensions = 0.41 × 0.23 × 0.21 mm
$\mu =$ cm^{-1}

(B) Solution and refinement

Reflections measured: 4146 (Cu Kα–Ni filter)
Reflections used: 2062 ($I \geqslant 2.0\ \sigma(I)$)
Number of variables: 271 ($w = 1/\sigma^2(F_o)$)
$R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o| = 0.046$
$GOF = 0.54$

TABLE II. Final Positional Parameters (×10^4) for the Non-hydrogen Atoms in Cu(H_2O)Cufsaen·H_2O

Atom	x	y	z
Cu(1)	1725(1)	4472(1)	6084(1)
Cu(2)	604(1)	2698(1)	6847(1)
O(1)	4020(3)	3660(4)	5020(5)
O(2)	2893(3)	4385(4)	5676(4)
O(3)	1713(3)	2863(3)	6303(4)
O(1')	856(4)	7718(3)	5903(5)
O(2')	1570(3)	6058(3)	5959(4)
O(3')	592(3)	4292(3)	6596(4)
O(W1)	1786(4)	2465(4)	9159(5)
O(W2)	6189(4)	3946(4)	5783(5)
N(1)	546(4)	1106(4)	6778(5)
N(1')	−625(4)	2675(4)	7144(4)
C(1)	2994(5)	2318(5)	5547(5)
C(2)	2221(5)	2045(5)	5967(5)
C(3)	1932(5)	889(5)	6017(5)
C(4)	2499(6)	46(6)	5705(6)
C(5)	3272(6)	310(6)	5319(6)
C(6)	3519(5)	1427(6)	5227(5)
C(7)	3331(5)	3518(6)	5421(6)
C(8)	1118(5)	479(5)	6416(6)
C(9)	−195(5)	651(5)	7264(6)
C(1')	107(4)	6231(5)	6611(5)
C(2')	−27(4)	5071(5)	6792(5)
C(3')	−839(5)	4726(5)	7163(5)
C(4')	−1437(5)	5560(6)	7436(6)
C(5')	−1245(5)	6702(6)	7345(6)
C(6')	−501(5)	7023(5)	6908(6)
C(7')	888(5)	6701(5)	6133(6)
C(8')	−1136(5)	3551(6)	7229(5)
C(9')	−1063(5)	1524(5)	7072(7)

Results and Discussion

The most surprising result of our study was the fact that the purple crystals were, in fact, the dicopper complex. A complex with a stoichiometry of [Cu_2fsaen]·$2H_2O$ had been reported by two groups [5, 6]. In one case the compound was said to be brown [5] and in the other green [6]. Unfortunately, neither study included a crystal structure so that the nature of the solid was not established unequivocally. The methanol solvate Cu(CH_3OH)Cufsaen [8] was reported to be blue–black which is certainly closer to

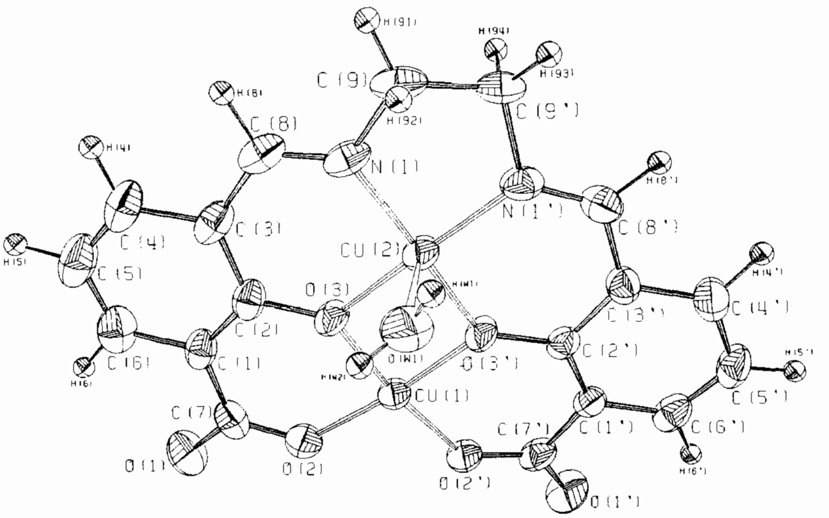

Fig. 1. An ORTEP drawing of the Cu_2fsaen(H_2O) complex illustrating the atomic numbering and thermal ellipsoids. The hydrogen atoms were assigned a B of 1.0 so that they would not dominate the drawing.

TABLE III. Summary of Metal–Ligand Distances in Several CuMfsaen Complexes

	Refcode [reference] M					
	a, Cu	HCBZCU [8] Cu	BIHZEX [9] Ni	FSCUCO [10] Co	BIGFAY [11] VO	FSALCM [12] Mg
Cu(2)–N(1)	1.879(5)	1.895(4)	1.902(3)	1.882(5)	1.895(8)	1.917(3)
Cu(2)–N(1′)	1.880(6)	1.907(4)	1.907(3)	1.888(5)	1.878(9)	[b]
Cu(2)–O(3)	1.898(5)	1.924(3)	1.892(3)	1.893(4)	1.912(9)	1.920(3)
Cu(2)–O(3′)	1.900(4)	1.902(3)	1.896(3)	1.882(4)	1.958(8)	[b]
Cu-axial	2.557(5)	2.266(4)	[c]	2.784(5)	2.304(8)	[c]
Cu–M	2.949(1)	2.942(1)	2.975(1)	2.953(2)	2.989(4)	3.001(4)
M–O(3)	1.914(4)	1.919(3)	2.022(3)	2.022(4)	2.014(8)	2.049(3)
M–O(3′)	1.909(5)	1.929(3)	2.018(3)	1.978(4)	1.978(8)	[b]
M–O(2)	1.871(5)	1.884(3)	1.986(3)	1.941(4)	1.901(9)	1.978(3)
M–O(2′)	1.882(4)	1.873(3)	1.989(3)	1.954(4)	1.893(7)	[b]
M-axial	[c]	[c]	2.069(3)	2.072(5)	1.576(9)	2.115(3)
M-axial	[c]	[c]	2.111(3)	[c]	[c]	[b]
ΔCu[d]	0.145	0.205	0.014	0.031	0.176	0.000

The refcode for the entry in the Cambridge Crystallographic Data is given with the type of M. The first column gives the values found in the present study. The atomic numbering is given in Fig. 1. [a] Present study. [b] Identical to the value above by symmetry. [c] The distance does not exist in the complex. [d] The deviation of the Cu atom from the N_2O_2 plane.

our color. The intriguing question is whether the products reported earlier [5, 6] represent complexes in which the copper ion is not present in both cavities.

A summary of the geometries of the various CuMfsaen complexes, M = Cu, Ni, Co, VO and Mg, are given in Table III. The Cu–N distances range from 1.880 to 1.917 Å, with an average of 1.896(14) Å. The Cu–O distances vary from 1.882 to 1.958 Å with an average of 1.908(20) Å. However, the Cu–O distances appear, reasonably, to be somewhat dependent on the second metal ion in the complex.

The binding of an axial group on the Cu in the N_2O_2 cavity appears to depend on the nature of the metal in the O_4 cavity. The Cu–O(axial) distances vary from 2.266(4) to 2.784(5) Å, appearing to reflect the influence of the other metal ion in the O_4 cavity. The displacement of the Cu atom from the N_2O_2 plane appears to be dependent on the length of the axial ligand (see Table III). With no axial group, the Cu atom lies in the N_2O_2 plane but as an axial group approaches (2.784, 2.557, 2.304, 2.266 Å), the deviation increases (0.031, 0.145, 0.176, 0.105 Å). In the latter four cases the displacement of the Cu atom is toward the axial ligand.

To investigate the correlation of the displacement of Cu from the N_2O_2 plane with the Cu–O axial distance, we searched the Cambridge Crystallographic Data file for copper compounds containing an O–C–C–C–N–C–C–N–C–C–C–O chain. The environment around Cu out to 2.9 Å and the displacement of Cu from the least-squares plane through the N_2O_2 atoms were calculated for the 42 structures for which the coordinates were available. In the structures with no axial group the displacement of the Cu atom was generally very small, 0.029(20) Å for 29 structures. The 13 structures in which the Cu–O axial distance was less than 2.9 Å are summarized in Table IV and illustrated in Fig. 2. Excluding the point for SPACOM, which involves a methyl group on the 1,2-diaminopropane chain, the points fall on the line ΔCu = 0.822 – 0.275(Cu–O axial), with a correlation coefficient of $r = 0.98$. The correlation is very good considering the fact that a range of different struc-

TABLE IV. Summary of the Cu–O Axial Distance and Displacement of the Cu Atom from the N_2O_2 Plane for Complexes with an O–C–C–C–N–C–C–N–C–C–C–O Backbone

Refcode[a]	Reference	Cu–O axial	ΔCu
ACIMCU	13	2.428	0.138
BEWRAW	14	2.803	0.052
BIGFAY	11	2.305	0.176
CHLSAC	15	2.789	0.049
CUEHAP	16	2.645	0.110
CURAPN	17	2.319	0.192
CUSAFA	18	2.813	0.056
ENPCUA	19	2.534	0.131
FPESCU	20	2.801	0.059
FSCUCO	10	2.784	0.031
HCBZCU	8	2.267	0.205
SEACOP	21	2.412	0.157
SPACOM	22	2.526	0.187
This work		2.557	0.145

[a] The refcode corresponds to that found in the Cambridge Crystallographic Datafile.

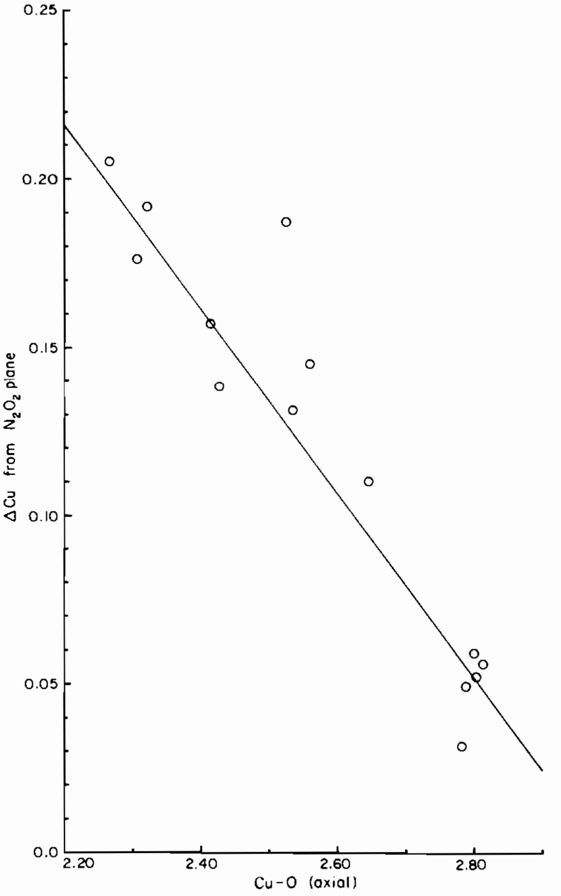

Fig. 2. A plot of the displacement of the Cu atom from the N_2O_2 plane *versus* the Cu–O distance to a fifth axial group. The straight line follows the equation ΔCu(in Å) = 0.822 – 0.275(Cu–O distance in Å).

tural types are included. These data must represent a view of the transition from a square planar copper complex to that of a square pyramidal complex. As a fifth ligand approaches a square planar copper complex, the copper atom is displaced from the plane toward the incoming atom. The model is reasonable for the general case of the addition of a fifth ligand to a square planar complex or the dissociation of a ligand from a square pyramidal complex. However, additional studies are required to establish the generality of the model.

The bond distances in the ligand are presented in Table V. The C–C distances in the two phenyl rings average 1.396(20) Å, the expected value. The C–C, C–N and C=N distances in the Schiff base portion are all close to the expected values. The C(1)–C(7) and C(3)–C(8) distances are significantly different, surprisingly. Presumably the different substituents on C(7) and C(8) alter the stability of resonance forms involving the C–C ring bonds.

TABLE V. Distances in the fsaen Ligands. The A Values are between Unprimed Atoms and the B Values between Primed Atoms

Atoms	A	B
C(7)–O(1)	1.233(9)	1.225(8)
C(7)–O(2)	1.284(8)	1.293(8)
C(7)–C(1)	1.515(10)	1.510(10)
C(1)–C(2)	1.386(10)	1.407(8)
C(2)–C(3)	1.428(9)	1.422(9)
C(3)–C(4)	1.404(10)	1.404(10)
C(4)–C(5)	1.357(12)	1.384(10)
C(5)–C(6)	1.376(11)	1.376(10)
C(6)–C(1)	1.412(10)	1.393(9)
C(2)–O(3)	1.342(8)	1.340(8)
C(3)–C(8)	1.468(10)	1.456(9)
C(8)–N(1)	1.273(9)	1.281(9)
N(1)–C(9)	1.461(10)	1.477(8)
C(9)–C(9′)	1.537(9)	

The fact that the lanthanide atom did not enter the O_4 is not completely surprising. The size of the O_4 cavity found in all the reported fsaen complexes is too small to accommodate a large lanthanide ion. The possibility of the lanthanide sitting up out of the cavity with additional ligands to achieve a coordination number of around 8 must be excluded by the proximity of the Cu ion. Consequently, the construction of suitable ligands for binuclear complexes involving a transition metal and a lanthanide must involve cavities of widely different sizes.

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