A Linear Polymeric Copper(II) Complex Bridged Simultaneously by Azido, Nitrato, and Betaine Ligands. Crystal Structure of *catena*-[Bis(μ-(1,1)-azido)bis(μ-nitrato-*O,O'*)bis((μ-trimethylammonio)acetato-*O,O'*)dicopper(II)], $[Cu_2(N_3)_2(NO_3)_2(Me_3NCH_2CO_2)_2]_n$

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Received August 7, 1992

Introduction

Copper(II) complexes with carboxylic acids invariably exhibit oligomeric or polymeric structures in which the carboxylato oxygens coordinate to two copper atoms in the μ-(O,O′)-bridging mode. Typical examples are dimeric copper(II) acetate and its derivatives[1-9] and hexameric copper(II) phenoxyacetate.[10] However the nitrato ligand, NO_3^-, which has often been found to behave as monodentate or a bidentate chelate ligand,[11-19] seldom shows the μ-(O,O′)-bridging mode in its copper(II) complexes. Examples of unsymmetrical μ-(O,O′) nitrato bridging are found in α-$[Cu(NO_3)_2]$,[20] $Cu(NO_3)_2(O_2NMe)$,[21] and $Cu(NO_3)_2(NCMe)_2$.[22] The azido ligand, N_3^-, is also a versatile bridging ligand that can link two copper atoms in either an end-on (μ-1,1)[23-31] or end-to-end (μ-1,3) mode.[32-38]

As a zwitterionic ligand and a neutral analogue of the carboxylate group, betaine ($Me_3NCH_2CO_2$, the IUPAC name is (trimethylammonio)acetate, hereafter referred to as BET) can conceivably function as a μ-(O,O′) bridge between two metal atoms with the insertion of other anionic ligands to form multiligand bridged metal complexes. This expectation has been fulfilled by the synthesis and characterization of the isostructural series of polymeric complexes $M_2(BET)_2(N_3)_4$ (M = Co, Zn, Cd) and $Cd_2(BET)_2(NCO)_4$ in which the metal atoms are bridged by betaine and azide (or isocyanate) ligands.[39] On the other hand, the copper–betaine complex $Cu(BET)_4(NO_3)_2$ has been shown to comprise discrete $Cu(BET)_4^{2+}$ cations with unsymmetrical carboxy chelation and nitrato anions.[40]

In the present study, we report the synthesis of a copper complex bridged by betaine, nitrate, and azide ligands and its structural characterization by single-crystal X-ray analysis. To our knowledge, this is the first example of a polymeric complex bridged simultaneously by three different types of polyatomic ligands although similar triply bridged copper(II) complexes containing at least one monoatomic or diatomic ligand have been reported.[41-43]

Experimental Section

Synthesis. Copper(II) nitrate trihydrate (0.2 g; 0.83 mmol) and betaine (0.4 g, 3.4 mmol) were dissolved together in a minimum amount of distilled water. Absolute ethanol (20 mL) was then added to the solution. Aqueous sodium azide (0.03 g, 0.46 mmol) was introduced dropwisely with gentle stirring until a deep green color appeared. The solution was allowed to stand overnight. The brown precipitate of $Cu(N_3)_2$ was filtered off, and the filtrate was allowed to stand for several days to yield dark green polyhedral crystals of the title compound. Its infrared spectrum was recorded from a KBr pellet in the 4000–400-cm^{-1} range on a Nicolet 205 FTIR spectrometer. The complex exhibits the following IR absorption bands (cm^{-1}): ν(COO) at 1597 vs and 1384 vs, δ(COO) at 730 m ν_{asym}(N_3) at 2101 vs and 2081 vs, and δ(NO_3) at 822 w. The separation (Δ) of 213 cm^{-1} between ν_{asym}(COO) and ν_{sym}(COO) is significantly smaller than that in anhydrous betaine (ν(COO) = 1624 vs, 1388 s cm^{-1}; Δ = 236 cm^{-1})[44] and hence indicative of the bridging and/or chelating mode of the carboxy group.[45] However, the stretching bands of the nitrato group overlap with those of that carboxy group of betaine such that it is difficult to assign their IR frequencies.

X-ray Crystallography. A single crystal of the title complex was used to collect X-ray data at 293 K on a Nicolet R3m/V diffractometer with Mo Kα radiation (λ = 0.710 73 Å) in the ω-scan mode.[46] The intensity data were processed with the profile-fitting procedure[47] and corrected for absorption using azimuthal scan data.[48] Additional details concerning the data collection and analysis are presented in Table I.

The structure was solved by Patterson and Fourier techniques and subjected to full-matrix least-squares refinement. All non-hydrogen atoms

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Table I. Data Collection and Processing Parameters

mol formula: $Cu_2(Me_3NCH_2CO_2)_2(N_3)_2(NO_3)_2$
mol wt: 569.50
color and habit: dark green polyhedron
unit cell parameters: a = 19.958 (6) Å; b = 9.103 (2) Å; c = 13.180 (1) Å; β = 120.00 (2)°; V = 2052.8 (9) Å^3; Z = 4; $F(000)$ = 1160
density (measd): 1.82 g/cm^3
density (calcd): 1.84 g/cm^3
space group: $C2/c$ (No. 15)
radiation: graphite-monochromatized Mo Kα, λ = 0.710 73 Å
std reflcns: $(12,0,\bar{8})$, $(7,3,\bar{6})$
intens variation: ±2%
R_{int} (from merging of equiv reflcns): 0.022
abs coeff: 2.15 mm^{-1}
crystal size: 0.40 × 0.42 × 0.42 mm^3
mean μr: 0.444
transm factors: 0.506–0.586
scan type and rate: ω-scan; 3-21–14.01 deg min^{-1}
scan range: 0.65° below Kα_1 to 0.65° above Kα_2
bkgd counting: stationary counts for one-fifth of the scan time at each end of scan range
collcn range: $+h,+k,\pm l$; $2\theta_{max} = 60°$
no. of unique data measd: 2895
no. of obsd data with $I \geq 3\sigma(I)$, n: 2194
no. of variables, p: 148
$R_F = \sum||F_o| - |F_c|| / \sum|F_o|$: 0.063
weighting scheme: $w = [\sigma^2(F_o) + 0.0001|F_o|^2]^{-1}$
$R_G = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$: 0.059
$S = [\sum w(|F_o| - |F_c|)^2 / (n - p)]^{1/2}$: 2.675
residual extrema in final difference map: −2.31 to +1.23 e Å^{-3}

Table II. Atomic Coordinates (×10^4) and Equivalent Isotropic Thermal Parameters (Å^2 × 10^4 for Cu, Å^2 × 10^3 for Others)

	x	y	z	U_{eq}[a]
Cu(1)	0	0	0	205 (3)
Cu(2)	0	1081 (1)	−2500	200 (3)
N(2)	−268 (2)	−406 (3)	−1640 (3)	24 (1)
N(3)	−591 (2)	−1552 (4)	−2094 (3)	29 (2)
N(4)	−905 (3)	−2632 (5)	−2521 (4)	53 (2)
N(5)	1643 (2)	831 (4)	121 (3)	31 (2)
O(3)	1244 (2)	1110 (4)	583 (3)	53 (2)
O(4)	1347 (2)	790 (7)	−946 (3)	81 (2)
O(5)	2341 (2)	585 (5)	734 (3)	58 (2)
O(1)	−541 (2)	1957 (3)	−450 (2)	30 (1)
O(2)	−423 (2)	2689 (3)	−1986 (3)	31 (1)
C(1)	−696 (2)	2765 (4)	−1309 (3)	22 (2)
C(2)	−1276 (3)	4020 (5)	−1663 (3)	27 (2)
N(1)	−1599 (2)	4417 (3)	−880 (3)	21 (1)
C(3)	−975 (3)	4988 (5)	279 (4)	45 (2)
C(4)	−2011 (3)	3165 (5)	−705 (5)	49 (3)
C(5)	−2173 (3)	5647 (5)	−1479 (4)	38 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

were refined anisotropically. The hydrogen atoms were generated geometrically (C–H = 0.96 Å) and included in structure-factor calculations with assigned isotropic thermal parameters (0.08 Å^2). Computations were performed on a DEC MicroVAX-II computer using the program package SHELTXL-PLUS.[49] Analytic expressions of neutral atomic scattering factors were used, and anomalous dispersion corrections were incorporated.[50] The atomic coordinates and equivalent isotropic thermal parameters of the non-hydrogen atoms are tabulated in Table II, and selected bond lengths and angles are given in Table III; lists of the remaining bond lengths and angles, hydrogen atomic coordinates, and anisotropic thermal parameters are available as supplementary material.

Table III. Selected Bond Lengths (Å) and Angles (deg)[a]

Cu(1)···Cu(2)	3.436 (1)	Cu(1)–N(2)	1.985 (4)
Cu(1)–O(3)	2.419 (4)	Cu(1)–O(1)	1.997 (3)
Cu(2)–N(2)	1.992 (4)	Cu(2)–O(4)	2.446 (3)
Cu(2)–O(2)	1.960 (4)		
N(2)–Cu(1)–O(1)	91.6 (1)	N(2)–Cu(1)–O(3)	95.5 (2)
N(2)–Cu(2)–O(4)	86.9 (2)	O(3)–Cu(1)–O(1)	92.6 (1)
N(2)–Cu(2)–N(2b)	95.5 (2)	N(2)–Cu(2)–O(2)	91.0 (2)
O(2)–Cu(2)–O(2b)	84.6 (2)	O(2)–Cu(2)–N(2b)	167.9 (1)
O(4)–Cu(2)–N(2b)	84.8 (2)	O(2)–Cu(2)–O(4b)	83.5 (2)
O(4)–Cu(2)–O(4b)	167.7 (3)	O(4)–Cu(2)–O(2)	105.8 (2)
Cu(1)–N(2)–N(3)	118.9 (3)	Cu(1)–N(2)–Cu(2)	119.5 (2)
Cu(1)–O(1)–C(1)	129.6 (3)	Cu(1)–O(3)–N(5)	124.5 (3)
Cu(2)–O(2)–C(1)	134.4 (3)	Cu(2)–N(2)–N(3)	121.5 (3)
N(2)–N(3)	1.207 (5)	Cu(2)–O(4)–N(5)	131.0 (4)
N(5)–O(3)	1.246 (8)	N(3)–N(4)	1.142 (5)
N(5)–O(5)	1.232 (5)	N(5)–O(4)	1.224 (5)
O(2)–C(1)	1.260 (7)	O(1)–C(1)	1.248 (5)
O(3)–N(5)–O(4)	120.5 (4)	N(2)–N(3)–N(4)	179.1 (6)
O(4)–N(5)–O(5)	119.1 (5)	O(3)–N(5)–O(5)	120.4 (4)
		O(1)–C(1)–O(2)	127.7 (4)

[a] Symmetry codes: (a) $-x, -y, -z$; (b) $-x, y, -\frac{1}{2} - z$.

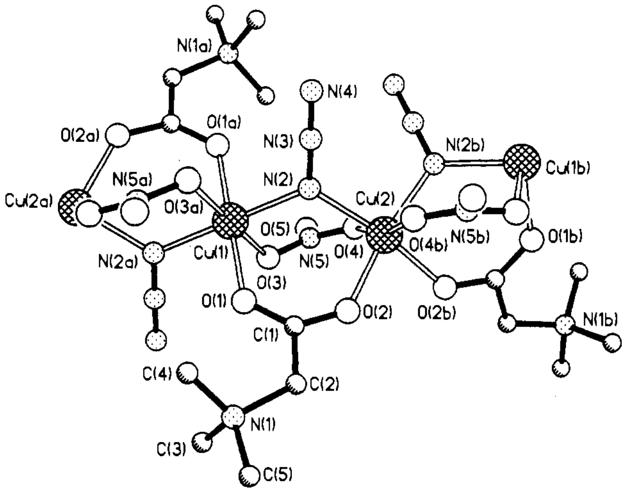

Figure 1. Perspective view showing the coordination geometry about the Cu(1) and Cu(2) atoms along the polymeric chain, as well as the numbering scheme. Symmetry codes are given in Table III.

Discussion

The structure contains copper atoms in two crystallographically and chemically different environments, as illustrated in Figure 1. Atom Cu(1), located at an inversion center in Wyckoff position 4(a), is trans-coordinated by two carboxy oxygens from different betaines, two azido nitrogens, and two nitrato oxygens in a distorted octahedral environment. The other atom Cu(2), lying on a 2-fold axis in Wyckoff position 4(e), is trans-coordinated by two nitrato oxygens and cis-coordinated by two carboxy oxygens and two azido nitrogens to adopt another distorted octahedral geometry. Every pair of adjacent copper atoms, separated by a nonbonded distance of 3.436 (1) Å, are simultaneously bridged by an azido group, a nitrato group, and the carboxy group of a betaine ligand to build up a linear zigzag polymeric chain running parallel to the c axis. These three different ligands extend outward from the backbone of the chain and away from one another in order to reduce steric hindrance. The crystal structure is composed of a packing of polymeric chains.

In the bridging skeleton, the azido ligand is linked to copper atoms in an end-on (μ-1,1) fashion and the carboxy group of the betaine ligand adopts an almost *syn–syn* μ-O,O′ arrangement with torsion angles Cu(1)–O(1)–C(1)–C(2) = 164.9 (3)°, and Cu(2)–O(2)–C(1)–C(2) = −152.1 (3)°, but the nitrato group functions in a nonplanar *syn*–skew μ-O,O′ mode with torsion angles Cu(1)–O(3)–N(5)–O(5) = −133.9 (4)° and Cu(2)–O(4)–N(5)–O(5) = 176.9 (4)°. This unusual nonplanar *syn*–skew bridging mode of the nitrato group is seldom found in other metal complexes.

The data in Table III show that the copper–carboxy oxygen bonds are significantly stronger than the copper–nitrato oxygen

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Table IV. Metal–Metal Separation (Å) and Angles M(1)–N(2)–M(2) and O(1)–C(1)–O(2) (deg) for Some Related Complexes Containing Betaine and Azido Ligands

compounds	M(1)···M(2)	M(1)–N(2)–M(2)[a]	angle O(1)–C(1)–O(2)	refs
$Co_2(BET)_2(N_3)_4$	3.209 (2)	96.8 (1) 97.2 (1)	128.2 (3)	unpublished
$Zn_2(BET)_2(N_3)_4$	3.230 (3)	96.9 (1) 97.1 (1)	129.0 (4)	unpublished
$Cd_2(BET)_2(N_3)_4$	3.451 (2)	95.4 (1) 95.5 (1)	128.4 (4)	39
$Cd_2(BET)_2(NCO)_4$	3.406 (1)	93.7 (1) 94.0 (1)	128.6 (5)	39
$Cu_2(BET)_2(N_3)_2(NO_3)_2$	3.436 (1)	119.5 (2)	127.7 (4)	this work

[a] Two values are shown for different bridging azides in the complex.

Table V. Metal–Azide and Nitrogen–Nitrogen Bond Lengths (and Their Differences) (Å) for Some Complexes Containing Betaine and Azido Ligands

compounds	M(1)–N(2)[a]	M(2)–N(2)[a]	N(2)–N(3)[a]	N(3)–N(4)[a]	difference[b]	refs
$Co_2(BET)_2(N_3)_4$	2.129 (3)	2.163 (2)	1.185 (4)	1.149 (4)	0.036	unpublished
	2.128 (2)	2.150 (2)	1.180 (4)	1.135 (4)	0.045	
$Zn_2(BET)_2(N_3)_4$	2.143 (4)	2.166 (3)	1.192 (5)	1.153 (5)	0.039	unpublished
	2.116 (3)	2.200 (4)	1.168 (5)	1.146 (6)	0.022	
$Cd_2(BET)_2(N_3)_4$	2.328 (4)	2.339 (3)	1.190 (5)	1.145 (5)	0.045	39
	2.295 (3)	2.366 (4)	1.169 (5)	1.128 (6)	0.041	
$Cu_2(BET)_2(N_3)_2(NO_3)_2$	1.985 (4)	1.992 (4)	1.207 (5)	1.142 (5)	0.065	this work

[a] Two values appear since two different briding azides are bound to the same pair of metal atoms. [b] Difference = [bond length of N(2)–N(3)] – [bond length of N(3)–N(4)].

ones (difference ~0.5 Å) such that steric overcrowding of the ligands around the metal atom is relieved by twisting the nitrato group into a *syn*–skew mode. The copper···copper separation (3.436 (1) Å) is accordingly quite long, giving rise to an unusually large Cu(1)–N(2)–Cu(2) angle of 119.5 (2)° as compared to values observed for other related polymeric metal–betaine–pseudohalide complexes (average M–N–M ~ 96° as shown in Table IV) and copper–azide complexes in which the Cu–N–Cu angles for the μ-1,1-bridge mode range from 94.6 to 111.2°.[25–30] The short copper–azido nitrogen bonds reveal stronger coordination bond strengths and hence the difference between the N–N bond lengths within the azido ligand is more obvious when compared with those found in similar complexes (Table V). However, the O–C–O angle of the betaine ligand is slightly smaller than those of other *syn*–*syn* bridged metal complexes (also see Table IV) in spite of the large copper···copper separation.

Acknowledgment. This work was supported by a Hong Kong Research Grants Council Earmarked Grant for Research A/C No. 221600010.

Supplementary Material Available: Tables of additional bond lengths and angles, anisotropic thermal parameters, and hydrogen atomic coordinates (2 pages). Ordering information is given on any current masthead page.