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Synthesis and Structure of $Cu_5(BTA)_6(t\text{-}C_4H_9NC)_4$, a Mixed-Valent Copper-Nitrogen Cluster Containing η^3-Benzotriazolate

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Protection of metals with reactive materials capable of forming surface-phase coordination compounds is an area of chemistry which is of considerable scientific and technological importance. In view of the extensive use of benzotriazole as a corrosion inhibitor for copper and its alloys,[1] it is remarkable that, to our knowledge, no copper–benzotriazole complex has been structurally characterized by X-ray diffraction. We report the synthesis and crystal structure of a neutral, highly symmetric complex containing a three-dimensional copper–nitrogen cluster formed by the coordination of η^3-benzotriazolate[2] to copper(I) and copper(II). The central cluster is composed of interconnected copper–nitrogen cycles (azametallocycles) which vary in size and spatial orientation.

The reaction of copper(I) thiophenoxide, benzotriazole, and alkyl isocyanides in dichloromethane at room temperature produces $Cu_5(BTA)_6(RNC)_4$ [BTA = benzotriazolate(1−)]. Since the benzotriazolate ion has a charge of −1, the pentacopper compounds are mixed-valent materials which contain four Cu(I) ions and one Cu(II) ion.[3] The reaction does not occur in the absence of air. Evidently, oxygen oxidizes some of the Cu(I) to Cu(II), which acts as a template for the assembly of the rather complex product. The rate of reaction can be controlled by regulating the partial pressure of oxygen and, in this way, red-orange crystals of $Cu_5(BTA)_6(t\text{-}C_4H_9NC)_4$ suitable for X-ray analysis were obtained. Anal. Calcd for $C_{56}H_{60}Cu_5N_{22}$: C, 49.49; H, 4.45; Cu, 23.38; N, 22.68; S, 0.0. Found: C, 49.3; H, 4.4; Cu, 23.8; N, 22.7; S, <0.3. The infrared spectrum shows a strong band at 2140 cm^{-1} due to *tert*-butyl isocyanide coordinated to the metal. This complex crystallizes in the tetragonal crystal system, space group $P\bar{4}2_1c$, $a = 13.836$ (4) Å, $c = 16.686$ (4) Å, $Z = 2$, $D_{calcd} = 1.413$, $D_{obsd} = 1.41$ (2) Mg m^{-3} (flotation). A total of 1196 unique reflections were measured on an automated four-circle diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) and the θ–2θ scan mode in the range $3.0 \leq 2\theta \leq 45.0°$. Intensity data were corrected for Lorentz and polarization effects but not for absorption (crystal size = 0.10 × 0.11 × 0.11 mm, $\mu = 16.9$ cm^{-1}). The positions of the two independent copper atoms were determined by direct methods (MULTAN)[4] and were verified in a three-dimensional Patterson map.[5] Successive least-squares refinements and Fourier syntheses revealed the positions of the remaining nonhydrogen atoms. Full-matrix least-squares refinement[6] gave a conventional agreement factor $R = 0.063$ for 903 observed reflections with $I \gtrsim 3\sigma(I)$.[7]

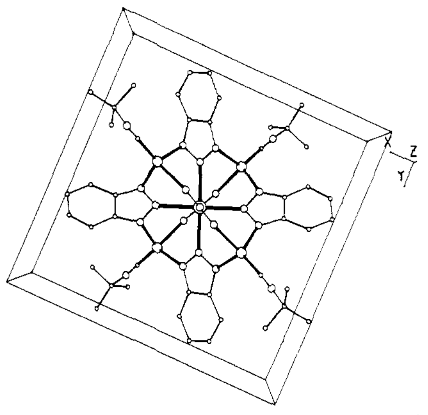

Figure 1. Structure of $Cu_5(BTA)_6(t\text{-}C_4H_9NC)_4$ viewed down a crystallographic $\bar{4}$ axis (parallel to the *z* axis of the unit cell). For clarity, the benzene moieties of the axially coordinated BTA ligands, as well as the entire complex at the origin, have been omitted.[20]

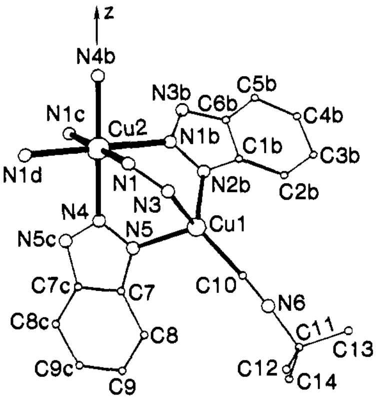

Figure 2. Perspective drawing showing the labeling scheme used. The central nitrogen atoms of the four equatorial BTA ligands illustrated in Figure 1 are oriented to form a plane approximately normal to the plane of the page. Unique atoms are labeled only with atom type and number, while the letters b–d refer to atoms in the following equivalent positions: (b) $1 - y, x, 1 - z$; (c) $1 - x, 1 - y, z$; (d) $y, 1 - x, 1 - z$. Selected interatomic distances and angles follow. Distances: Cu1···Cu2 = 3.638 (2), Cu2–N1 = 2.241 (13), Cu2–N4 = 2.085 (16), Cu1–N3 = 2.013 (14), Cu1–N5 = 2.087 (12), Cu1–N2b = 2.024 (12), Cu1–C10 = 1.882 (17) Å. Angles: N3–Cu1–N5 = 95.3 (5), N3–Cu1–C10 = 121.2 (6), N3–Cu1–N2b = 98.3 (5), N5–Cu1–C10 = 117.0 (6), N5–Cu1–N2b = 94.7 (5), C10–Cu1–N2b = 123.9 (6), Cu1–C10–N6 = 175.8 (1.6)°. The C11–C bond lengths (mean value = 1.44 Å) are shorter than normal, presumably due to the high thermal motion of the methyl groups.

The crystal structure consists of neutral complexes with crystallographic $\bar{4}$ symmetry in which an octahedrally coordinated copper(II) ion is surrounded by four tetrahedrally coordinated copper(I) ions. Tridentate BTA ligands bridge each copper(I)

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(1) Reedijk, J.; Roelofsen, G.; Siedle, A. R.; Spek, A. L. *Inorg. Chem.* **1979**, *18*, 1947–51 and references cited therein.

(2) Other established bonding modes for benzotriazolate are η^1 in *trans*-$(Ph_3P)_2Ir(CO)(BTA)$ (Brown, L. D.; Ibers, J. A.; Siedle, A. R. *Inorg. Chem.* **1978**, *17*, 3026–30), η^2 in $(BTA)_6(CH_2{=}CHCH_2NH_2)_6Ni_3(Ph_3PO)_2$ (Meunier-Piret, J.; Piret, P.; Putzeys, J. P.; Van Meerssche, M. *Acta Crystallogr., Sect. B* **1976**, *32*, 714–7), and η^3 in Tl(BTA) (ref 1).

(3) This has been confirmed by the low-temperature electron spin resonance spectrum of the *tert*-butyl isocyanide derivative (Kokoszka, G. F., et al., to be submitted for publication).

(4) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *27*, 368–76.

(5) All crystallographic calculations (except MULTAN) were performed by using the XRAY76 system (Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H.; Flack, H. XRAY76 Technical Report TR-446, Computer Science Center, University of Maryland, College Park, Md.).

(6) All nonhydrogen atoms were refined anisotropically. The hydrogen atoms on the benzene moieties were held fixed at calculated positions (trigonal geometry, C–H = 1.0 Å) with an isotropic $U = 0.080$ $Å^2$. Due to the apparent disorder of the methyl groups in the *tert*-butyl isocyanide ligand, the methyl hydrogen atoms were not included in the refinement. A difference Fourier map showed no peak greater than 0.54 e $Å^{-3}$.

(7) $R = \sum||F_o| - |F_c|| / \sum|F_o|$. The scattering factors used for C, Cu, and N were those of: Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321–4. For H see: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87. Corrections for anomalous dispersion were applied for copper ($\Delta f' = 0.263$, $\Delta f'' = 1.266$): "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 149.

ion to three symmetry-related copper(I) ions and to the central copper(II) ion. Figure 1 gives a view of the complex down a $\bar{4}$ axis (parallel to the *z* axis of the unit cell). The labeling scheme and selected interatomic distances and angles are given in Figure 2.

There are two complexes in the unit cell with the central Cu2 ions in special positions (0, 0, 0) and $(^1/_2, ^1/_2, ^1/_2)$ with $\bar{4}$ symmetry. Each Cu2 ion is octahedrally coordinated to four equatorial and two axial BTA ligands. The four equatorial BTA ligands illustrated in Figure 1 occupy general positions in the unit cell; their central nitrogen atoms (N1 positions) lie 0.005 (13) Å from the $z = {}^1/_2$ plane ($z = 0$ plane for the complex at the origin) and are coplanar with Cu2. Because N4 lies on a crystallographic $\bar{4}$ axis, a twofold axis relates the two halves of the axial BTA ligands. The central Cu2 ion is also surrounded by four Cu1 ions which lie 2.02 Å alternately above and below the Cu2 basal plane (i.e., the plane defined by Cu2 and the four N1 atoms). The four equatorial BTA ligands define planes (average deviation = 0.008 Å; maximum deviation = 0.017 Å for C4) which make acute angles of 41.7° with the Cu2 basal plane. Because of symmetry considerations, the two planes defined by the axial BTA ligands (average deviation = 0.006 Å; maximum deviation = 0.014 Å for C9) are normal to the Cu2 basal plane.

The stereochemistry about Cu2 is unusual in that it is an undistorted octahedron of a compressed form. Cu2 is coordinated to four equatorial and two axial BTA ligands at the N1 and N4 positions, respectively (Figure 2). While the two Cu2–N4 bond distances are typical, the four Cu2–N1 distances are longer than those usually found for nitrogen coordinated to copper(II).[8,9] Similar copper(II)–nitrogen distances have been observed in $Cu(dien)_2(NO_3)_2$[10] and $Cu(V)_2(MEEN)$,[11] compounds in which the copper(II) ion has distorted, compressed octahedral geometry.

The coordination geometry about Cu1 is approximately tetrahedral but, as shown in Figure 2, there are significant deviations from the ideal angles. Cu1 is coordinated to one *tert*-butyl isocyanide ligand and to three different BTA ligands (two equatorial, one axial) at the N2, N3, and N5 positions. The Cu1–C10 distance of 1.882 (17) Å and Cu1–C10–N6 angle of 175.8 (1.6)° are in general agreement with the respective values of 1.81 (15) Å and 180 (2)° found for $CuI(CNCH_3)$.[12] The coordination distances to Cu1 are close to those reported for copper(I)–cyanide complexes in which Cu–N distances are typically 2.0 Å and Cu–C distances are approximately 1.9 Å with a nearly linear Cu–C–N angle.[13,14]

As a tridentate ligand, BTA is involved in two types of copper–nitrogen–copper bridges. Bridging between Cu2 and Cu1 is accomplished via the central and an adjacent nitrogen atom of a BTA ligand. The four symmetry-related Cu1 ions are bridged by the two nitrogen atoms adjacent to the central nitrogen of a BTA ligand in a manner analogous to the imidazolate bridge in $[Cu_2(bpim)(im)]_2(NO_3)_4 \cdot 4H_2O$.[15] The axial BTA ligands bridge two Cu1 ions situated on the same side of the Cu2 basal plane, while the equatorial BTA ligands bridge Cu1 ions on opposite sides of the Cu2 basal plane.

Reference to Figure 1 shows that $Cu_5(BTA)_6(t\text{-}C_4H_9NC)_4$ contains a Cu_4N_{12} ring, which we refer to as an azametallocyclic ring. The view of the complex presented in Figure 1 suggests a striking resemblance to a phthalocyanine; however, $Cu_5(BTA)_6(t\text{-}C_4H_9NC)_4$ is far more complex and fundamentally different. There are two additional Cu_4N_{12} rings,[16] as well as many larger and smaller azametallocyclic rings, which may be defined in this three-dimensional complex. Unlike the C_8N_8 macrocycle in phthalocyanine, each Cu_4N_{12} ring is nonplanar, with the four copper(I) ions in a ruffled arrangement. Thus, conjugation between the BTA anions and their coordinated copper(I) is probably severely inhibited because of the tetrahedral geometry about copper(I). In this regard, the established architecture for $Cu_5(BTA)_6(t\text{-}C_4H_9NC)_4$ is similar to the nonplanar macrocycle proposed to be present in the pentacopper(II) compound $Cu_5(BTA)_6(acac)_4$.[17] By replacing tetrahedral copper(I) with planar silver(I) or gold(I), it may be possible to synthesize compounds with planar, conjugated azametallocyclic rings similar to the C_8N_8 macrocycle in phthalocyanine. In addition, the use of divalent metal ions other than copper(II) in a template synthesis analogous to that described for this compound may lead to a broad class of new metal–nitrogen clusters.

The reaction of benzotriazole with metallic copper leads initially to copper(I) benzotriazolate[18,19] which subsequently oxidizes in air. The structure described herein shows how the benzotriazolate anion, acting as a tridentate ligand, can bridge multiple sites containing both copper(I) and copper(II). It is possible that similar bonding is involved in the corrosion-resistant surface phase produced on the bulk metal.

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Supplementary Material Available: Tables of atomic positional and thermal parameters and a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Evidence for a Novel Carbene–Carbene Rearrangement of a New Foiled Methylene[1]

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While cyclopropylidene (**1**) undergoes a carbene–carbene rearrangement with a 1,3-carbon shift, **1** → **2**,[2] 2-vinylcyclobutylidene (**3**) surprisingly does not.[3] Different methods of

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