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A metallopolymer, $[Cu(abt)]_{\infty}$ (abt, 2-aminobenzenethiol) with novel structural patterns resembling black phosphorus

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Dedicated to Prof. Gerd Meyer on the occasion of his 60th birthday.

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1. Introduction

Copper complexes of N, S ligands are of interest as models for the Cu_A center of cytochrome-c-oxidase (CcO), which is involved in the final step of cell respiration catalysing reduction of molecular oxygen to water [1–5]. 2-Aminobenzenethiol (abt) belongs to the group of arvl N. S donor ligands, which are capable of forming $[Cu(\mu_x-S)_xN]_n$ cyclic frameworks of varying nuclearities [6–16]. Recently we reported a N,S ligand, iso-abt, which forms tetranuclear and dodecanuclear copper(I) complexes with trigonal [Cu(μ - $S_{2}N_{4}$ butterfly or tetrahedral $[Cu(\mu_{3}-S)_{3}N]_{12}$ double wheel architectures [6]. The known complexes contain N-substituted N,S ligands, which are derived from abt, and this ligand is an example that can stabilise both copper(I) and copper(II) centers. The coordination chemistry of abt has been investigated for the cases of vanadium and iron, and the ligand is viable to the formation of radicals and it is redox non-innocent towards iron [17-23]. It formed the complex anion $[V(SNH_2C_6H_4)_2(SNHC_6H_4)]^-$ wherein three abt ligands are bound to vanadium(III), and it can coordinate

ABSTRACT

A copper(I) complex of 2-aminobenzenethiol, $[Cu(abt)]_{\infty}(1)$, has been synthesized and characterized. The crystal structure determination indicates a two-dimensional metallopolymeric network formed by edge and corner sharing $[Cu(\mu_3-S)N]$ coordination tetrahedra wherein the copper(I) centers are coordinated to three bridging thiolate donors and the amino group of 2-aminobenzenethiolate. The copper, the sulfur and the nitrogen atoms form sub-lattices that reveal independently striking similarities to the double-layers present in black phosphorus.

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to iron as *o*-aminothiophenolate(1–) forming (μ -{S,S})[Fe^{II}(abt)₂]₂ or in addition as iminothionebenzosemiquinonate(1–) π radical in its oxidized form, (iibs)[–], forming [Fe^{II}(abt)₂(iibs)][–]. A complex formulated as {Cu^{II}(abt)} has been synthesized earlier but structural information is yet not known [24–29]. To investigate complexes with [Cu(μ_x -S)_xN]_n cores of varying nuclearities we synthesised the copper(1) complex of abt, [Cu(abt)]_∞ (1). Herein we report the synthesis and describe a novel structural pattern associated with copper complexes derived from bifunctional N/S donor ligands.

2. Experimental

2.1. Synthesis of $[Cu(abt)]_{\infty}$ (1)

The reaction was carried out under a dinitrogen atmosphere using Schlenk technique.

2-Aminobenzenethiol (125 mg, 1 mmol) was treated with triethylamine (0.100 mL, 1 mmol) in DMF (60 mL) under N₂ atmosphere and after stirring for 20 min, CuI (180 mg, 1 mmol) was added. Stirring was continued for 2 h at 24 °C followed by diffusion of diethylether vapours into the reaction mixture for 19 h. The vapour diffusion of diethyl ether was then discontinued and the reaction flask was tightly closed under N₂ atmosphere and left in





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the refrigerator for a period of 3 days, which led to the formation of extremely air sensitive white single crystals of **1**. Data for **1**: Yield, 43%; C, H, N analysis (%), *Anal.* Calc. for C₆H₆CuNS: C, 38.35; H, 3.19; N, 7.45. Found: C, 38.16; H, 2.89; N, 7.69%. IR (KBr): ν (cm⁻¹) 3328(w), 3211(w), 1579(s), 1544(s), 1468(s), 1437(s), 1280(m), 929(s), 809(s), 746(s) (s, strong; m, medium; w, weak). ¹H NMR (500 MHz, DMSO-d₆, 298 K): δ (ppm) 7.10 (t, 1H), 7.01 (d, 1H), 6.73 (d, 1H), 6.43 (t, 1H), 5.43 (s, 2H).

2.2. X-ray structure analysis

The X-ray intensities were collected on a Bruker AXS Smart APEX CCD diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct and conventional Fourier methods and refined on F^2 by full-matrix least-squares techniques [30]. All non-hydrogen atoms were refined anisotropically, H atoms at idealized positions in riding mode. Selected crystallographic data of compound **1** are given in Table 1.

2.3. Other physical measurements

Spectra were recorded using the following spectrometers: NMR, Bruker WMX 500; IR, Nicolet P510. The elemental analyses were performed on a Perkin Elmer Analysator Model 240.

3. Results and discussion

The polymeric complex **1** is shown in part in Chart 1. The complex was prepared by the reaction of 2-aminobenzenethiol and CuI in DMF. White single crystals of $[Cu(abt)]_{\infty}$ composition formed over a period of three days after vapour diffusion of diethyl ether. Complex **1** was characterized by IR, elemental analysis, ¹H NMR and X-ray crystallography. The IR spectrum (KBr disc) of **1** showed NH₂ peaks at v (cm⁻¹), 3328 and 3211. The polymeric complex is insoluble in all common solvents and sparingly soluble in

Table 1

Crystal data for $[Cu(abt)]_{\infty}$ (1).

| Empirical formula | C ₆ H ₆ CuNS |
|----------------------------------------------------------|-----------------------------------------|
| Formula weight | 187.72 |
| T (K) | 120(2) |
| Wavelength Mo Ka (Å) | 0.71073 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | |
| a (Å) | 13.786(1) |
| b (Å) | 7.081(1) |
| <i>c</i> (Å) | 6.173(1) |
| β (°) | 96.2(2) |
| Volume (Å ³) | 599.14 |
| Ζ | 4 |
| Density (Mg/m ³) | 2.081 |
| Absorption coefficient (mm ⁻¹) | 3.875 |
| F(000) | 376 |
| Crystal size (mm) | $0.40 \times 0.20 \times 0.03$ |
| θ Range for data collection | 1.49-28.26° |
| Index ranges | -16 < h < 18, -9 < k < 9, -8 < l < 8 |
| Reflections collected | 7277 |
| Independent reflections | $1483 [R_{int} = 0.0312]$ |
| Completeness to $\theta = 28.26^{\circ}$ | 99.8% |
| Absorption correction | semi-empirical from equivalents |
| Refinement method | full-matrix least-squares on F^2 |
| Data/restraints/parameters | 1483/1/90 |
| Goodness-of-fit (GOF) on F^2 | 1.118 |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.0219, wR_2 = 0.0570$ |
| R indices (all data) | $R_1 = 0.0229, wR_2 = 0.0576$ |
| Largest difference in peak and hole (e Å ⁻³) | 0.528 and -0.317 |



Chart 1. Structural subunit of the polymeric complex **1** with the characteristic $\{Cu(\mu_3-S)N\}$ core highlighted by thick lines.

DMSO- d_6 . The ¹H NMR in DMSO- d_6 indicated signals (two triplets and two doublets) corresponding to the protons of 2-aminobenzenethiolate.

3.1. Structure of 1

The X-ray structure determination of **1** indicates that the complex is polymeric with 1:1 metal to ligand composition. The structure consists of sheets expanding infinitely along two directions via the copper(I) center, coordinated nitrogen and sulfur donors of the ligand. The nitrogen and sulfur atoms of an abt ligand are coordinated to two different copper(I) centers. A fragment of the polymeric structure of **1** is shown in Fig. 1, and the bond lengths and valence angles are given in Table 2. The structure can be primarily considered as a network of dinuclear {Cu(abt)}₂ cores with tetracoordinated copper(I) centers. The links between these cores are formed by the μ_3 -bridging thiolate donors wherein each copper(I) center is coordinated in a pseudo-tetrahedral fashion by a terminal nitrogen and three μ_3 -bridging thiolates. The three Cu–S bond



Fig. 1. Structure of a fraction of polymeric **1** with the thiolate-bridged copper(I) site. The ligand spheres around copper(I) viz., Cu(1A), Cu(1C), Cu(1D), Cu(1E), Cu(1F), Cu(1G) and the S-donors S(1A), S(1C), S(1AC) and S(1AA) are incomplete and terminated for clarity.

| Table 2 | | |
|--------------------|--------------------|-------------------------------|
| Selected distances | [Å] and angles [°] | for $[Cu(abt)]_{\infty}$ (1). |

| Bond lengths | Bond angles | Bond lengths | Bond angles |
|--------------|-------------|----------------------|-------------|
| Cu(1)-N(1) | 2.1749(14) | N(1)-Cu(1)-S(1)#1 | 112.47(4) |
| Cu(1)-S(1)#1 | 2.2713(4) | N(1)-Cu(1)-S(1)#2 | 114.58(4) |
| Cu(1)-S(1)#2 | 2.3327(4) | S(1)#1-Cu(1)-S(1)#2 | 114.982(15) |
| Cu(1)-S(1) | 2.4002(4) | N(1)-Cu(1)-S(1) | 92.19(4) |
| S(1)-C(1) | 1.7805(16) | S(1)#1-Cu(1)-S(1) | 132.207(13) |
| S(1)-Cu(1)#3 | 2.2713(4) | S(1)#2-Cu(1)-S(1) | 87.470(15) |
| S(1)-Cu(1)#2 | 2.3327(4) | C(1)-S(1)-Cu(1)#3 | 99.88(5) |
| N(1)-C(2)#4 | 1.423(2) | C(1)-S(1)-Cu(1)#2 | 115.88(5) |
| C(1) - C(6) | 1.399(2) | Cu(1)#3-S(1)-Cu(1)#2 | 103.387(16) |
| C(1) - C(2) | 1.401(2) | C(1)-S(1)-Cu(1) | 127.77(5) |
| C(6) - C(5) | 1.386(2) | Cu(1)#3-S(1)-Cu(1) | 115.721(16) |
| C(2) - C(3) | 1.390(2) | Cu(1)#2-S(1)-Cu(1) | 92.530(15) |
| C(2)-N(1)#4 | 1.423(2) | C(2)#4-N(1)-Cu(1) | 123.83(10) |
| C(3) - C(4) | 1.393(2) | C(6)-C(1)-C(2) | 118.89(14) |
| C(5)-C(4) | 1.387(2) | C(6)-C(1)-S(1) | 119.78(12) |
| | | | |

Symmetry transformations used to generate equivalent atoms: #1 - x, y - 1/2, -z + 1/2; #2 - x, -y + 2, -z; #3 - x, y + 1/2, -z + 1/2; #4 - x, -y + 2, -z + 1.

lengths are different and range from 2.271(3) via 2.333(1) to 2.400 Å, the shortest one being exocyclic with respect to the Cu_2S_2 core portion. The short contacts existing throughout the lattice between the N- or S-donors and the neighbouring copper(I) ions are covalent bonds, which lead to the formation of a two-dimensional coordination polymer.

The structure of **1** viewed down the *x*-axis followed by the removal of carbon and hydrogen atoms presents an inspiring polymeric design incorporating both 10-membered {CuSCCNCuSCCN} and 4-membered {CuSCuS} rings. The crystal packing of **1** seen along the *z*-axis presents isolated sheets with distances being 2.583 Å for nearest intermolecular H…H contacts. The metallopolymer **1** shows close structural resemblance to black phosphorus, which is a two-dimensional double-layer lattice. The structure of black phosphorus is composed of puckered layers with 6-membered rings, and each phosphorus is bound to three nearest neighbours [31]. Similarly the structure of **1** contains interpenetrating double-layers formed by the $(Cu-S)_{\infty}$ network wherein the copper and sulfur atoms are oriented in a zig-zag fashion as shown in Fig. 2.

As such the overall structure of **1** is composed of three doublelayered sub-lattices viz., the copper sub-lattice, the sulfur sub-lattice and the nitrogen sub-lattice, which are each composed of sheared 6-membered rings in the chair conformation. The nitrogen sub-lattice is the replica of the black phosphorus structure whereas the Cu and S sub-lattices are more distorted compared with the black phosphorus structure due to shear imposed on the 6-membered basic building blocks. The copper, sulfur and nitrogen sublattices extracted from the structure of **1** along with the structure of the black phosphorus are displayed in Fig. 3. The copper and the sulfur sub-lattices are nearly identical but differently orientated in space; their 6-membered rings are both in comparable dimensions in contrast to that of the nitrogens, which are



Fig. 2. Fraction of the double-layered zig-zag $(Cu-S)_{\infty}$ network in the structure of 1.



Fig. 3. (a) The copper sub-lattice; (b) the sulfur sub-lattice, (c) the nitrogen sub-lattice extracted from the structure of 1 and (d) structure of black phosphorus.



Fig. 4. Polyhedral representation of the $\{Cu(\mu_3-S)N\}_{\infty}$ (1), $\{Cu(\mu_3-S)N\}_{12}$ (2) and $\{Cu(\mu-S)N\}_4$ (3) cores.

significantly different. The intra-layer distances in the copper, sulfur and nitrogen sub-lattices are 1.660, 2.187 and 3.812 Å, respectively. By superposition of the three individual sub-lattices, the overall {Cu(μ_3 -S)N} core in **1** is obtained.

The formation of the polymeric network of **1** is a result of the less commonly observed tetrahedral connectivity of Cu^I. Each $\{Cu(\mu_3-S)_3N\}$ coordination tetrahedron is connected to five other ones, to the first one by an edge-sharing interaction and to the remaining ones by vertex-sharing modes (Fig. 4, 1). Since the corner defined by N is not shared, a two-dimensional polymeric structure is formed rather than a three dimensional one. In the cyclic $\{Cu_2S_2\}$ units the μ_3 -bridging sulfur donors are located within the sum of their van der Waals radii (S…S 3.272 Å) and the Cu^I…Cu^I intermetallic separation within the rhomb is 3.420 Å. The copper(I) complex of N-methylated ligand, N,N'-dimethylaminobenzenethiol is neutral and trinuclear with μ_2 -bridging thiolate donors and the geometry around the Cu^I centers is trigonal planar [10]. On the other hand, the Cu^I complexes of the imino derivatives of 2-aminobenzenethiol are tetranuclear with trigonal geometry or octanuclear or dodecanuclear with pseudo-tetrahedral geometries around the Cu^I centers (Fig. 4, 2 and 3).

The trigonal butterfly-type architecture (Fig. 4, 3) is formed by $[Cu(\mu-S)_2N]$ corner sharing triangles whereas the double wheel architecture is formed by the $[Cu(\mu_3-S)_3N]$ adjacent edge-sharing tetrahedra (Fig. 4, 2) [6]. In all of the reported examples, the Cu–S–Cu bridging angles (ca. $64^{\circ}-74^{\circ}$) are acute and the Cu¹...Cu¹ distances are short (ca. 2.67 Å). But in the complex **1**, these angles are around 92°, and the intermetallic separations are significantly longer (ca. 3.420 Å). The structural features of $[Cu(abt)]_{\infty}$ prove that the geometry of the $[Cu(\mu_3-S)_3N]$ core is governed by the type of polyhedral connectivity, which in turn depends upon the steric demands of the ligand. Thus the N-substituted compounds form oligomers whereas the unsubstituted abt forms a polymer with unique tetrahedral connectivity.

4. Conclusions

The metallopolymer $[Cu(abt)]_{\infty}(1)$ described hitherto has been synthesized and its structure has been determined, which indicates the formation of a two-dimensional polymeric structure. Furthermore, three interpenetrating double-layered sub-lattices, formed by Cu, S and N, respectively, can be identified, which show close structural relationships with similar double-layers present in black phosphorus. The structure of **1** with its unique tetrahedral connectivity is a novel addition to the class of copper(I) oligomeric complexes of N/S ligands, which form complexes of varying nuclearities.

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Appendix A. Supplementary material

CCDC 730041 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.ica.2010.03.008.

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