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FULL PAPER

Dicopper complexes derived from 4-amino-2,1,3-benzothiadiazole with versatile co-ordination number and geometry

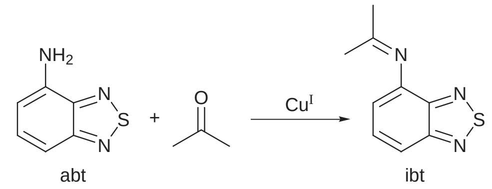
Megumu Munakata,[*,a] **Haiyang He,**[a] **Takayoshi Kuroda-Sowa,**[a] **Masahiko Maekawa**[b] **and Yuichi Suenaga**[a]

[a] *Department of Chemistry, Kinki University, Kowakae 3-4-1, Higashi-Osaka, Osaka 577, Japan*
[b] *Research Institute for Science and Technology, Kinki University, Kowakae 3-4-1, Higashi-Osaka, Osaka 577, Japan*

Three dicopper complexes of 4-amino-2,1,3-benzothiadiazole (abt) have been isolated and structurally characterized. The reaction of $[Cu(CH_3CN)_4][PF_6]$ with abt in THF produced $[Cu_2(abt)_2(CH_3CN)_4][PF_6]_2{\cdot}C_6H_{12}$ **1**$\cdot C_6H_{12}$, while in acetone, Cu^I template Schiff-base condensation of the amino group of abt with solvent was found to give $[Cu_2(ibt)_2(CH_3CN)_4][PF_6]_2$ **2** (ibt = 4-isopropylideneamino-2,1,3-benzothiadiazole). In complex **1** there are two crystallographically independent monomeric units in each of which Cu^I is co-ordinated by one N atom on the ring of abt and two acetonitrile molecules; two units are linked to each other by weak binding of the amino group of abt with Cu^I to give a cyclic dinuclear complex. In complex **2** tetrahedral Cu^I centers are bridged by two ibt molecules in a head-to-tail fashion as in **1**. Both **1** and **2** have the same metallocyclophane skeletons showing an intramolecular stacking interaction between two parallel aromatic rings and a considerably long $Cu \cdots Cu$ separation [7.220(5) Å for **1**, 6.542(4) Å for **2**]. Following the same synthetic strategy as used for the synthesis of **2** another dicopper complex $[Cu_2(ibt)_2][ClO_4]_2$ **3** was obtained, which presents a structural contrast with **2**: two Cu^I centers are linearly co-ordinated by two ibt molecules in a head-to-head arrangement which leads to a twisted conformation with a shorter $Cu \cdots Cu$ distance of 2.699(2) Å. In addition, ^1H NMR measurements reveal that **2** can also be formed directly from **1** in acetone solution.

The considerable interest in a wide range of dinuclear copper complexes may arise partly from some of them acting as model compounds for metalloproteins. An important aspect of these investigations concerns the design of ligands. Among them, imidazole ligands and derived from them a series of cryptand systems with a ternary amino group are prevalent.[1–7] It is noteworthy that the Cu^I co-ordination sphere is made up of three strong binding and a weak interaction in plastocyanin, one of the most accurately determined structures of copper proteins.[8a] The investigation into weak binding in copper complexes allows for a better understanding of the puzzling structure of metalloproteins. However, the structural characterization data in this respect are very limited and need to be systematized.[8] On the other hand, from the standpoint of synthetic chemistry, metallocyclic dinuclear complexes with tetrahedral Cu^I are common,[9] in particular for a large number of double helical complexes,[10,11] whereas those with low co-ordination such as linear Cu^I are rather rare[12,13] and are limited mostly to neutral σ-bond complexes, *e.g.* $[\{Cu[HB(Bu^tpz)_3]_2\}]$ (Bu^tpz = 3-*tert*-butylpyrazol-1-yl),[14] $[Cu_2(mpsa)_2]$ [Hmpsa = (6-methyl-2-pyridyl)trimethylsilylamide].[15]

We recently[16] reported a number of 2-D polymers of Cu^I complexes with 2,1,3-benzothiadiazole (bdt). Aromatic stacking between bdt molecules plays an important role in the aggregation of individual complexes.[16] As a further study on the syntheses and structures of Cu^I complexes containing btd, here we utilize a ligand, 4-amino-2,1,3-benzothiadiazole (abt) with a 'harder' sp^3 N-donor group attached to the benzene ring of bdt. The interaction of amines with Cu^I was known to be comparatively weak in general, but we have successfully synthesized and authenticated a 2-D three-co-ordinate Cu^I complex from 1-aminopyrene, $[Cu(apyr)_3]ClO_4$.[17] This strong interaction of Cu^I with amino groups was believed to attribute to intra- and inter-molecular stacking of the aromatic rings of the ligands, which is also an important approach to the assembly of supramolecules.[18] In addition to this feature, abt having three potential N-donor atoms was expected to make it possible to bridge two metal centers through different bonding modes and to fine-tune the metal co-ordination sphere.



Scheme 1 Schiff-base condensation of abt with acetone *via* a Cu^I template

In the present work, a dicopper complex with abt, $[Cu_2(abt)_2(CH_3CN)_4][PF_6]_2{\cdot}C_6H_{12}$ **1**$\cdot C_6H_{12}$ was synthesized in a [2+2] manner from $[Cu(CH_3CN)_4]PF_6$ and abt in THF. In addition, Cu^I complexes with ibt, $[Cu_2(ibt)_2(CH_3CN)_4][PF_6]_2$ **2** and $[Cu_2(ibt)_2][ClO_4]_2$ **3** (ibt = 4-isopropylideneamino-2,1,3-benzothiadiazole) were isolated from the appropriate Cu^I cations and abt in acetone by way of a Cu template Schiff-base condensation reaction (Scheme 1). A progressive co-ordination geometry from linearity through trigonal pyramid to tetrahedron for Cu^I was observed in these complexes.

Experimental

All operations were carried out using standard Schlenk techniques under argon. All solvents were dried and distilled by general methods before use. Standard chemicals were obtained from Wako Chemical Co. Japan. 4-Amino-2,1,3-benzothiadiazole (abt) was purchased from Aldrich Chemical Co. and used without further purification. The salt $[Cu(CH_3CN)_4]PF_6$ was prepared according to the literature.[19] Proton NMR spectra were measured on a JEOL GSX-270 FT-NMR spectrometer.

CAUTION: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts should be prepared and handled with great care.

Synthesis

$[Cu_2(abt)_2(CH_3CN)_4][PF_6]_2$ 1. The salt $[Cu(CH_3CN)_4]PF_6$

Table 1 Crystal and refinement data for complexes **1**, **2** and **3***

	1·C_6H_{12}	**2**	**3**
Formula	$C_{20}H_{22}Cu_2F_{12}N_{10}P_2S_2 \cdot C_6H_{12}$	$C_{26}H_{30}Cu_2F_{12}N_{10}P_2S_2$	$C_{18}H_{18}Cl_2Cu_2N_6O_8S_2$
M	483.88 × 2	481.87 × 2	708.49
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	8.129(6)	6.542(4)	11.649(3)
b/Å	18.119(7)	24.682(2)	14.521(2)
c/Å	12.492(7)	11.675(2)	8.221(2)
α/°			94.69(2)
β/°	96.84(6)	97.64(3)	107.94(2)
γ/°			79.49(2)
U/Å^3	1826(1)	1869(1)	1300.3(5)
Z	4	4	2
μ(Mo-Kα)/cm^{-1}	14.65	14.26	20.56
No. reflections measured (unique)	4346	4408	5965
R_{int}	0.042	0.053	0.826
R	0.062	0.045	0.075
R'	0.068	0.053	0.094

* Details in common: $T = 23$ °C.

(0.0932 g, 0.25 mmol) and abt (0.0378 g, 0.25 mmol) were stirred in THF (10 cm^3) under an argon atmosphere for 0.5 h. The resultant orange solution was transferred to a glass tube and layered with cyclohexane and sealed. After standing for 3 d at room temperature orange needle crystals were afforded (Found: C, 27.4; H, 2.7; N, 15.5. $C_{20}H_{22}Cu_2F_{12}N_{10}P_2S_2$ requires C, 27.2; H, 2.5; N, 15.85%). Note: the composition of the product was $[Cu_2(abt)_2(CH_3CN)_4][PF_6]_2 \cdot C_6H_{12}$ according to X-ray diffraction analysis but the solvent cyclohexane molecules were not detected in the measurement of elemental analyses and ^{1}H NMR spectra (see below). It indicated that solvent molecules in this complex were unstable and volatilized from the lattice on standing.

$[Cu_2(ibt)_2(CH_3CN)_4][PF_6]_2$ 2. The salt $[Cu(CH_3CN)_4]PF_6$ (0.1677 g, 0.45 mmol) and abt (0.068 g, 0.45 mmol) were stirred under an argon atmosphere in acetone (10 cm^3) for 0.5 h. The resultant orange solution was transferred to a glass tube and layered with cyclohexane and sealed. After standing for 7 d at room temperature orange brick crystals were afforded (Found: C, 32.2; H, 2.8; N, 14.3. $C_{26}H_{30}Cu_2F_{12}N_{10}P_2S_2$ requires C, 32.4; H, 3.1; N, 14.5%).

$[Cu_2(ibt)_2][ClO_4]_2$ 3. Copper(II) perchlorate hexahydrate (0.0593 g, 0.16 mmol) and copper plates were stirred under an ethylene atmosphere in acetone (8 cm^3) for 0.5 h to give a colorless solution, then abt (0.0484 g, 0.32 mmol) was added and stirred under an argon atmosphere for 10 min to yield a red solution. The resultant solution was transferred to a glass tube and layered with *n*-hexane and sealed. After standing for 3 d at room temperature deep red plate crystals were obtained (Found: C, 30.5; H, 2.3; N, 11.6. $C_{18}H_{18}Cl_2Cu_2N_6O_8S_2$ requires C, 30.5; H, 2.6; N, 11.9%).

Crystallography

The unit-cell data and intensities were collected on a Rigaku AFC-5R or -6S four-circle diffractometer with graphite-monochromated Mo-Kα ($\lambda = 0.71069$ Å). The structures were solved by a direct method (MITHRIL)[20] and refined by full-matrix least-squares minimization of $\Sigma w(|F_o|-|F_c|)^2$ with anisotropic thermal parameters for all the non-hydrogen atoms. Isotropic hydrogen atoms were located by Fourier-difference synthesis and refined on the associated atoms. All of the calculations were performed using the TEXSAN package[21] on a micro VAX computer. Reliability factors are defined as $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$, where $w = 4F_o^2/\sigma^2(F_o^2)$. Relevant crystal data for complexes **1**–**3** are listed in Table 1.

CCDC reference number 186/927.

See http://www.rsc.org/suppdata/dt/1998/1499/ for crystallographic files in .cif format.

Results and Discussion

Synthesis of complexes

Dinuclear Cu^I complex **1** was prepared by mixing abt with $[Cu(CH_3CN)_4]PF_6$ in THF at room temperature. Crystals suitable for X-ray diffraction were afforded by diffusion of cyclohexane into these solutions. Attempts to isolate similar species from $Cu(ClO_4)$ and abt in THF have been unsuccessful. However, when THF was replaced with acetone as solvent the unexpected complex $[Cu_2(ibt)_2][ClO_4]_2$ **3** was formed and indicated that copper(I) acted as a template for the Schiff-base condensation of abt and solvent. In contrast, general Schiff-base condensation reactions with ketones are carried out under rigorous conditions. Although a variety of metal ions were found to be effective templating ions for this reaction, including Cu^{II},[22] to our knowledge, examples of Cu^I are hardly seen. The synthetic utilization of this Cu^I template Schiff-base condensation reaction offered a convenient path to the rational design of complexes such as **1** with general bis(N donor) ligands (sp^2 N). Accordingly this approach was used for further investigation of the interaction of abt with $[Cu(CH_3CN)_4]PF_6$ in acetone. A similar reaction was observed and $[Cu_2(ibt)_2(CH_3CN)_4][PF_6]$ **2** was isolated in crystalline form. X-Ray crystallographic determinations confirmed the formula of all three complexes.

Crystal-structure determinations

$[Cu_2(abt)_2(CH_3CN)_4][PF_6]_2 \cdot C_6H_{12}$ 1·C_6H_{12}. The crystal-structure determination revealed that orange crystals of **1** consist of $[Cu_2(abt)_2(CH_3CN)_4]^{2+}$ cations, PF_6^- anions and cyclohexane molecules. The cation involves two crystallographically symmetrical $[Cu(abt)(CH_3CN)_2]^+$ units from which every amino group is co-ordinated weakly to the other Cu^I center. The perspective view of the asymmetric unit of the crystal structure with the atom labeling scheme is illustrated in Fig. 1. The PF_6^- anions and cyclohexane molecules of **1**·C_6H_{12} are omitted for clarity. Selected bond distances and angles are listed in Table 2 (including those for complexes **2** and **3**). Two abt molecules bridge two Cu^I centers *via* the thiadiazole-N atoms and the amino groups in a head-to-tail fashion to give a metallocyclophane which has a rectangular cavity with a Cu···Cu separation of 7.220(5) Å and with two parallel benzothiadiazole planes in a staggered conformation (anti-parallel, see also Fig. 2). The plane-to-plane distance of 3.36 Å indicates

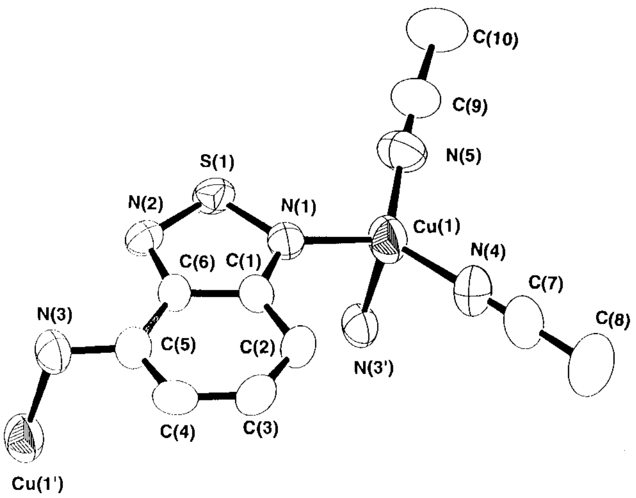


Fig. 1 Perspective view of the unsymmetrical unit of complex **1**

Table 2 Selected bond distances (Å) and angles (°) for complexes **1**–**3**

Complex **1**			
Cu(1)–N(1)	2.022(6)	Cu(1)–N(4)	1.936(9)
Cu(1)–N(5)	1.936(9)	Cu(1)–N(3′)	2.422(8)
N(1)–Cu(1)–N(4)	117.0(3)	N(1)–Cu(1)–N(5)	113.2(3)
N(4)–Cu(1)–N(5)	122.1(3)	N(1)–Cu(1)–N(3′)	100.7(2)
N(3′)–Cu(1)–N(4)	101.0(3)	N(3′)–Cu(1)–N(5)	96.1(3)
Complex **2**			
Cu(1)–N(1)	2.117(3)	Cu(1)–N(3)	1.988(4)
Cu(1)–N(4)	2.005(4)	Cu(1)–N(5′)	2.078(3)
N(1)–Cu(1)–N(3)	111.0(1)	N(1)–Cu(1)–N(4)	108.1(2)
N(1)–Cu(1)–N(5′)	107.9(1)	N(3)–Cu(1)–N(4)	108.5(2)
N(3)–Cu(1)–N(5′)	114.8(1)	N(4)–Cu(1)–N(5′)	106.3(1)
Complex **3**			
Cu(1)–N(1)	1.943(8)	Cu(1)–N(3)	1.949(9)
Cu(2)–N(5)	1.911(8)	Cu(2)–N(6)	1.908(8)
N(1)–Cu(1)–N(3)	172.4(4)	N(5)–Cu(2)–N(6)	160.6(3)
Cu(2)–Cu(1)–N(1)	87.3(2)	Cu(2)–Cu(1)–N(3)	85.2(3)
Cu(1)–Cu(2)–N(5)	80.7(2)	Cu(1)–Cu(2)–N(6)	80.0(2)

the existence of π–π interactions between the benzothiadiazole ligands.[16]

Three bond angles around the Cu center in the plane defined by N(1), N(4) and N(5) are 122.1(3), 117.0(3) and 113.2(3)° respectively and amount to 352.3°. The copper atom deviates from this plane by 0.3 Å. These values indicate that copper adopts a distorted trigonal pyramidal rather than tetrahedral geometry. The Cu–N distances in the basal plane are normal and fall in the range of typical Cu–N distances of four-co-ordinate Cu^I complexes;[23] whereas the apical Cu–N (amine) distance of 2.422(8) Å is a little longer. The few Cu^I–N (amine) distances reported in the literature show a wide variation [from 1.869(4) to 2.59(1) Å].[2,8,24] The Cu–N (amine) distance presented indicates a weak binding of amine to Cu^I in both $[Cu(abt)(CH_3CN)_2]^+$ units. Although co-ordination of the amino group with Cu^{II} is easier than with Cu^I, a few examples with a longer Cu–N distance are observed.[25,26] For example, in $[CuL_2][ClO_4]_2$ [L = bis(benzimidazol-2-ylmethyl)amine] the amino nitrogen is located at an axial position with a Cu–N distance of 2.579(6) Å.[25] Obviously, one weak bond introduced at the four-co-ordinate coppers favors the preferential generation of trigonal-pyramidal geometry.

$[Cu_2(ibt)_2(CH_3CN)_4][PF_6]_2$ 2. The molecular structure of **2** has a very similar skeleton to **1**, as shown in Fig. 2. Two ibt molecules bridge two copper centers in a head-to-tail arrangement to form a metallocyclophane with a Cu · · · Cu separation of 6.542(4) Å and an interplane distance of 3.26 Å. The most remarkable difference for **2** is that the Cu^I atoms adopt perfect tetrahedral geometry with four nearly equivalent Cu–N distances and with N–Cu–N angles ranging from 106.3(1) to 114.8(1)°. The structural framework of **1** and **2** resembles those of various [*n*,*n*]cyclophane molecules.[27]

$[Cu_2(ibt)_2][ClO_4]_2$ 3. Complex **3** exhibits a twisted dimeric structure in which each copper is linearly co-ordinated by two different ibt molecules in a head-to-head fashion, in marked contrast with **2**, as depicted in Fig. 3. This head-to-head arrangement forces the two copper atoms into close proximity. The Cu(1) · · · Cu(2) distance of 2.699(2) Å is considerably shorter than that in **1** and **2**, but longer than the Cu–Cu distance of 2.56 Å in metallic copper. There remain arguments as to whether a metal–metal interaction exists or not between d^{10} metal atoms.[28]

Two types of Cu^I center appear in **3**. The Cu(1) atom has a nearly linear geometry with an N(1)–Cu(1)–N(3) angle of 172.4(4)°. The Cu(1)–N distances of 1.943(8) and 1.949(9) Å are slightly longer, but within the range of those found in the two-co-ordinate complexes: $[Cu(2,6\text{-}Me_2py)_2][ClO_4]$ [1.936(5) Å],[29] $[Cu(2,6\text{-}Me_2py)_2][NO_3]$ [1.956(5), 1.966(5) Å],[29] $[Cu(napy)]_2[ClO_4]_2$ [1.908(5), 1.909(5) Å; napy = 1,8-naphthyridine],[12] $[Cu(xypz)]_2[BF_4]_2$ [1.873(4), 1.875(4) Å; xypz = α,α′-bis(3,5-dimethylpyrazolyl)-*m*-xylene].[13] The Cu(2) center is bonded to two imine-N of ibt; the N(5)–C(2)–N(6) angle of 160.6(3)° deviates markedly from linearity as a result of the bridging cyclic structure. The closest Cu–O (ClO_4^-) distances of 2.52(3) and 2.50(1) Å indicate that the perchlorate anions are not co-ordinated. As expected, the Cu–N (heterocycle) distance decreases from 2.117 Å in complex **2**, through 2.022 Å in **1**, to 1.946 (average) Å in **3** and the co-ordination number at copper decreases from four to two.

Solution behavior

The successful syntheses of complexes **1** and **2** from the same reactant aroused our interest enough to investigate their solution behavior, as complex **1** may be looked upon as an intermediate of **2** during the Cu template Schiff-base condensation reaction. Indeed, after redissolution of a crystal of $[Cu_2(abt)_2(CH_3CN)_4][PF_6]_2$ **1** in CD_3COD_3, two sets of aromatic signals were detected in the ^1H NMR spectrum. Resonances at δ 6.75 (d), 7.25 (d) and 7.52 (t) are shifted a little downfield compared to metal-free abt [6.68 (d), 7.21 (d) and 7.43 (t)] and are consequently assigned to **1** (abt species). The more downfield set of aromatic protons at δ 7.42 (d), 7.80 (t) and 7.97 (d) is assigned to **2** (ibt species) because $[Cu_2(ibt)_2][ClO_4]_2$ **3** exhibited a similar ^1H NMR spectrum pattern in CD_3OD; resonances at δ 7.20 (overlap), 7.69 (t) and 7.90 (d) for ibt ligand. It came as a surprise in the measurement of **3** to observe signals of the abt species again at δ 6.65 (d), 7.20 (overlap) and 7.44 (t). This species was proposed to come from the hydrolysis of ibt in **3** in CD_3OD solution containing water as an impurity. The present work reveals that the Cu^I ion can act as a suitable template for the Schiff-base condensation of abt where an amine complex is observed as an intermediate.

Acknowledgements

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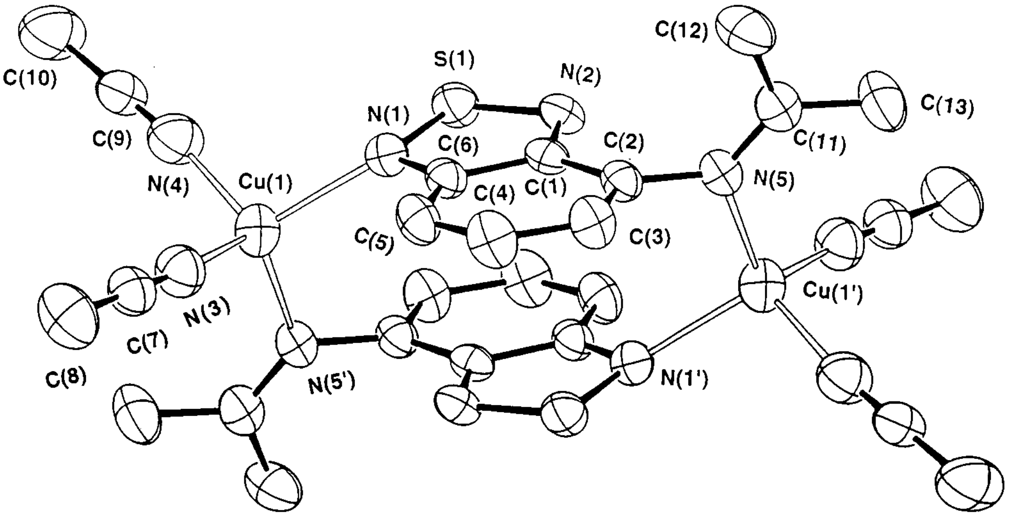

Fig. 2 Perspective view of complex **2**

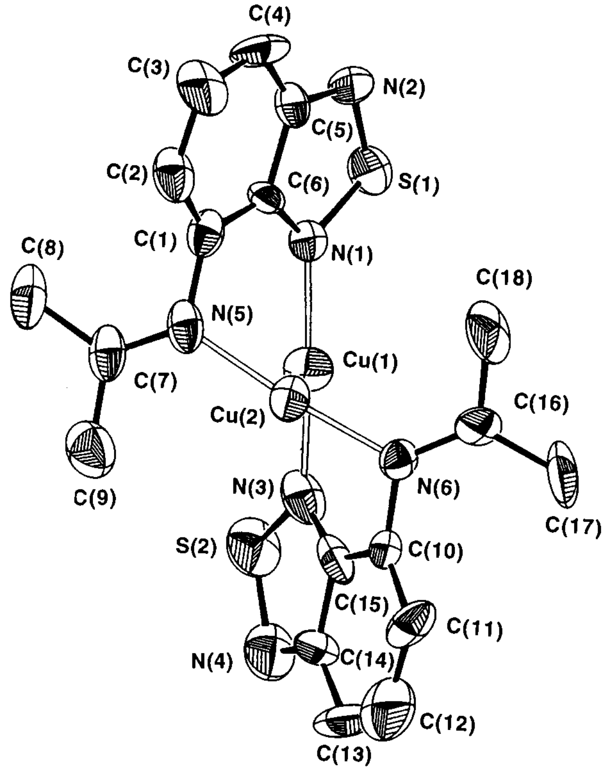

Fig. 3 Perspective view of complex **3**

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