

Copper(II) Complex of the Tripodal Ligand Tris((benzimidazol-2-yl)methyl)amine and its Bonding to a Sulfur Ligand of Thiolate Character

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Sletten, J. and Grove, H., 1997. Copper(II) Complex of the Tripodal Ligand Tris((benzimidazol-2-yl)methyl)amine and its Bonding to a Sulfur Ligand of Thiolate Character. – Acta Chem. Scand. 51: 822–831. © Acta Chemica Scandinavica 1997.

Copper(II) complexes of the tripodal ligand tris((benzimidazol-2-yl)methyl)amine, tbima, have been synthesized and structurally characterized. Two different solvates of $\text{Cu}(\text{tbima})(\text{NO}_3)_2$, $[\text{Cu}(\text{tbima})(\text{NO}_3)](\text{NO}_3) \cdot \text{EtOH}$ (**1**) and $[\text{Cu}(\text{tbima})(\text{NO}_3)](\text{NO}_3) \cdot \text{H}_2\text{O}$ (**2**), were isolated. The copper(II)–tbima complex were reacted with a sulfur containing ligand of thiolate character, att, the deprotonated form of 4-amino-1.2.4-triazole-5-thione. The reaction afforded a dinuclear att-bridged Cu^{II} complex, $[\text{Cu}_2(\text{tbima})_2(\text{att})](\text{NO}_3)_3 \cdot \text{H}_2\text{O} \cdot \text{EtOH}$ (**3**). Crystals of all three compounds are triclinic, space group $P\bar{1}$ with $Z=2$. Cell dimensions of compound **1** are $a=9.529(2)$ Å, $b=10.140(1)$ Å, $c=14.423(2)$ Å, $\alpha=86.05(1)^\circ$, $\beta=77.71(1)^\circ$, $\gamma=86.89(1)^\circ$; of compound **2** $a=9.791(3)$ Å, $b=9.644(3)$ Å, $c=13.622(4)$ Å, $\alpha=96.31(2)^\circ$, $\beta=96.93(1)^\circ$, $\gamma=97.08(1)^\circ$; of compound **3** $a=13.339(5)$ Å, $b=14.151(4)$ Å, $c=16.232(6)$ Å, $\alpha=103.05(2)^\circ$, $\beta=108.82(3)^\circ$, $\gamma=93.21(2)^\circ$. The crystal structures at 104 K (**1** and **2**) and 107 K (**3**) have been determined by X-ray diffraction methods. Full-matrix least-squares refinements including 3084, 3219 and 3526 reflections, respectively, converged at R -values of 0.046, 0.035 and 0.044. The results of the structure determinations show that tbima as ligand may allow irregular and unusual coordination geometries. The copper coordination spheres of the two solvates **1** and **2** are significantly different, and none displays the most common type of geometries encountered in Cu^{II} complexes. In both complexes tbima is a tetradentate ligand, and one of the nitrate groups are coordinated in the bidentate, asymmetric mode. The coordination geometry in **1** is elongated octahedral, but with a very strong tetrahedral distortion of the equatorial plane which is defined by the three benzimidazole nitrogen atoms and one nitrate oxygen atom. In compound **2** the interaction with one of the nitrate oxygen atoms is very weak; the remaining five coordinated atoms create a distorted square pyramidal environment for copper, but the axial bond in the pyramid is not the longest bond, as usually found. In compound **3** the two copper atoms have significantly different coordination geometries. Cu1 has an ordinary, but somewhat distorted square pyramidal coordination chromophore with the att chelate (sulfur and amine nitrogen) and two imidazole nitrogen atoms forming the equatorial plane and the tbima amine nitrogen atom forming a weaker axial interaction. Cu2 is also five-coordinated, but the coordination geometry fits neither the square pyramidal nor the trigonal bipyramidal description well. The irregular geometry is probably best described as distorted square pyramidal with a short axial and one long equatorial bond, similar to the situation in complex **2**.

There is considerable interest in preparing and characterizing copper–thiolate complexes that may mimic spectroscopic and/or chemical properties of the copper centres in blue copper proteins. Structural information on Cu^{II} complexes with thiolate ligands is, however, relatively scarce owing to the facile redox reaction converting these species to copper(I) and disulfide. The thiolate function

may be stabilized by steric or electronic constraints, e.g. by introducing multiple bond character at the donor sulfur and appropriate substituents in the ligand molecules.^{1,2} Tripodal, bulky, aromatic ligands may provide protected ‘pockets’ for metal ions, and a copper(II) complex of such a ligand may hence be a useful building block for preparing and isolating copper(II)–thiolate complexes. Previously, utilization of a tripodal pyrazolylborate ligand has allowed the isolation of two

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copper(II)-thiolato complexes; one which has spectroscopic characteristics similar to those of the blue copper proteins, and one which has been shown through an X-ray structure determination to have a rather short Cu^{II}-S bond.³

The tetradentate, tripodal ligand tris((benzimidazol-2-yl)methyl)amine, tbima, is rather bulky, but still quite flexible. Reports on the syntheses and spectroscopic characterization of Cu^{II} complexes of tbima have appeared in the literature.⁴⁻⁷ No crystal structure determinations were, however, reported. We have prepared and structurally characterized two different solvates of Cu(tbima)(NO₃)₂, [Cu(tbima)(NO₃)](NO₃)·EtOH (**1**) and [Cu(tbima)(NO₃)](NO₃)·H₂O (**2**). Their structures (see below) show that tbima as ligand may allow irregular and variable coordination geometries. We have reacted the copper(II)-tbima complex with a sulfur ligand of thiolate character, and have isolated and structurally characterized a stable complex, [Cu₂(tbima)₂(att)](NO₃)₃·H₂O·EtOH (**3**). The sulfur containing ligand used in this work, att, is the deprotonated form of 4-amino-1,2,4-triazole-5-thione. It has been pointed out that heterocyclic, unsaturated compounds with thione substituents may be useful sources of ligands for preparing Cu^{II}-thiolate complexes. While the free ligand may exhibit typical thione character, it may be metal-bonded in its tautomeric thiolate form, or be deprotonated in the reaction.⁸⁻¹⁰

Experimental

Preparation of [Cu(tbima)(NO₃)](NO₃). This compound was prepared by adding a 15 ml warm (50 °C) ethanolic solution of 0.25 mmol (0.100 g) tbima to 0.25 mmol (0.060 g) Cu(NO₃)₂·3H₂O in 10 ml ethanol. Slow evaporation at room temperature afforded deep green crystalline plates of [Cu(tbima)(NO₃)](NO₃)·EtOH (**1**). A sample of these crystals were dissolved in water at 60 °C. Needle-shaped green crystals formed upon cooling and evaporation; another solvate had formed, [Cu(tbima)(NO₃)](NO₃)·H₂O (**2**).

Preparation of [Cu₂(tbima)₂(att)](NO₃)₃. The neutral thione form of the ligand 4-amino-1,2,4-triazole-5-thione, atth, was prepared according to a method described in the literature.¹¹ 1 mmol (0.12 g) atth in 5 ml water/ethanol solution was deprotonated by adding an equimolar amount of LiOH·H₂O dissolved in a minimum volume of water/ethanol. This solution was subsequently added dropwise under stirring to a solution of 1 mmol (0.41 g) tbima and 1 mmol (0.24 g) Cu(NO₃)₂·3H₂O in 15 ml water/ethanol solution. A white precipitate which formed after a few minutes was removed by filtration. The amount of white precipitate was in later experiments reduced by cooling the reactant solutions to ca. 10 °C. A green, microcrystalline solid formed after evaporation at room temperature. The

material was recrystallized from ethanol; thin green plates of [Cu₂(tbima)₂(att)](NO₃)₃·H₂O·EtOH (**3**) formed.

Physical measurements. Infrared spectra were recorded with a Nicolet 800 FTIR spectrophotometer as KBr pellets in the 4000–400 cm⁻¹ region. Electronic spectra in solution were recorded using a Varian Cary 1 (200–400 nm) and a HP 8453 (300–1100 nm) spectrophotometer. Analysis of copper content was made with a Perkin-Elmer 5000 atomic absorption spectrophotometer.

Crystal structure determinations and refinements. The crystals were sealed and mounted in paratone-n oil. Diffraction data were collected at 104 K (**1** and **2**) and 107 K (**3**) with an Enraf-Nonius CAD-4 diffractometer, equipped with a liquid-nitrogen cooling device, using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Crystal parameters and refinement results are compiled in Table 1. A total of 4741 (**1**), 4413 (**2**) and 7305 (**3**) unique reflections were recorded to maximum θ values of 25° (**1** and **2**) and 22.5° (**3**). Three reference reflections, monitored during data collections of **2** and **3**, decreased on average by 5.9 and 7.4%, respectively, and increased by 4.4% in the case of **1**. The data were in each case corrected for Lorentz and polarization effects, for linear decay, and for absorption based on ψ -scan measurements using 5 (**1** and **3**) and 6 (**2**) reflections [range of transmission factors 99.92–76.66% (**1**), 99.96–85.81% (**2**) and 99.97–96.23% (**3**)].¹²

The intensity statistics in all three cases suggested a centrosymmetric space group. The structures were solved by direct methods,¹³ and refined by full-matrix least-squares methods. In the course of the refinements it was found that the methyl group of the ethanol molecule in **1** and one of the nitrate groups in **3** were disordered. Two positions of the methyl carbon were refined, the occupancy factors refined to 0.5 for each position. In case of the nitrate group one oxygen and the nitrogen atom had unreasonably high thermal parameters. For the oxygen it was possible to refine two positions, the occupancy factors converging at approximately 0.75 and 0.25, respectively. For the nitrogen atom, refinement of two positions was not successful. All non-hydrogen atoms, except the fractional oxygen atoms of the disordered nitrate group, were anisotropically refined. For compounds **1** and **2** hydrogen atoms, except those bound to the carbon atoms of the ethanol molecule, were located in difference Fourier maps, and were isotropically refined; for compound **3** hydrogen atoms were included at idealized calculated positions and were not refined. Extinction parameters were included and adjusted in the final stages of refinement of **1** ($g = 5.16 \times 10^{-7}$) and **2** ($g = 1.03 \times 10^{-9}$). The refinements, including 3084 (**1**), 3219 (**2**) and 3526 (**3**) reflections with $I > 2\sigma$ converged at $R = 0.046$, 0.034 and 0.044, respectively.

All calculations were carried out with programs in the MolEN system.¹⁴ Neutral atomic scattering factors were

Table 1. Summary of crystallographic data for **1** [Cu(tbima)(NO₃)](NO₃)·C₂H₅OH, **2** [Cu(tbima)(NO₃)](NO₃)·H₂O, and **3** [Cu₂(tbima)₂(att)](NO₃)₃·H₂O·C₂H₅OH.

Compound	1	2	3
Chem. formula	C ₂₆ H ₂₇ CuN ₉ O ₇	C ₂₄ H ₂₃ CuN ₉ O ₇	C ₅₂ H ₅₃ Cu ₂ N ₂₁ O ₁₁ S
FW	641.12	613.06	1307.31
Space group	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)	P $\bar{1}$ (No. 2)
<i>a</i> /Å ^a	9.529(2)	9.791(3)	13.339(5)
<i>b</i> /Å	10.140(1)	9.644(3)	14.151(4)
<i>c</i> /Å	14.423(2)	13.622(4)	16.232(6)
α /°	86.05(1)	96.31(2)	103.05(2)
β /°	77.71(1)	96.93(1)	108.82(3)
γ /°	86.89(1)	97.08(1)	93.21(2)
<i>V</i> /Å ³	1357.3(4)	1256.9(6)	2797(2)
<i>Z</i>	2	2	2
λ /Å	0.710 73	0.710 73	0.710 73
Crystal size/mm	0.37 × 0.36 × 0.03	0.71 × 0.32 × 0.13	0.36 × 0.27 × 0.02
Max-min transmission (%)	99.92–76.66	99.96–85.81	99.97–96.23
<i>T</i> /K	104	104	107
Max. 2 θ /°	50	50	45
Unique refl. measured	4741	4413	7305
Refl. in refinement, <i>N</i> _o	3084 (<i>I</i> > 2 σ)	3219 (<i>I</i> > 2 σ)	3526 (<i>I</i> > 2 σ)
Parameters refined, <i>N</i> _v	486	463	783
$R = \sum F_o - F_c / \sum F_o ^b$	0.046	0.035	0.044
$R_w = [\sum w(F_o - F_c)^2 / \sum w F_o ^2]^{1/2}$	0.051	0.044	0.050
$S = [\sum w(F_o - F_c)^2 / (N_o - N_v)]^{1/2}$	1.749	1.542	1.777

^aCell dimensions based on setting angles of 25 reflections within 2 θ -ranges of 28–44 (**1** and **2**) and 14–23 (**3**). ^bFunction minimized $\sum [w(|F_o| - |F_c|)^2]$, $w = 4F_o^2/\sigma_c^2 + (kF_o^2)^2$, where σ_c is the standard deviation in F^2 based on counting statistics alone, and k equals 0.03 (**1** and **3**) and 0.04 (**2**).

those of Cromer *et al.*¹⁵ Anomalous scattering terms were included in F_{calc} .¹⁶ For non-hydrogen atoms coordinates are listed in Tables 2–4, selected bond distances and angles in Tables 5–7. Supplementary material contains complete lists of atom coordinates, anisotropic thermal parameters, bond lengths and angles, hydrogen bond parameters, least-squares planes, and structure factor tables, and is available from the authors on request.

Results and discussion

On the preparation of the complexes. Previous reports on the synthesis of Cu(tbima)(NO₃)₂ have indicated that different crystal modifications and/or solvates have been isolated depending on solvent systems used.^{4–7} In our preparations we obtained the ethanol and water solvates (compounds **1** and **2**) by crystallization from these solvents. We also observed a third type of crystals, obtained from a 50/50 water/ethanol solution, but these crystals were not of X-ray quality. The white side product obtained in the synthesis of compound **3** were shown by atomic absorption spectroscopy to contain ca. 16% (by weight) copper; as mentioned above, it is probably the product of a redox reaction in which Cu^I is formed.

Infrared and electronic spectra. The peaks at 1460 and 1440 cm⁻¹ of uncomplexed tbima, attributed to the stretching mode for -C=N-C=C-,⁷ are shifted to higher wavenumbers in all three complexes. The fact that one of the imine nitrogen atoms is not coordinated in complex

3 is thus not discernible in the IR spectrum. The two absorptions at 1622 and 1588 cm⁻¹ in uncomplexed tbima, associated with CN stretch in the imidazole ring,⁷ are only marginally shifted (to higher wavenumbers) upon complexation. Complexes **1** and **2** each show two absorptions in the region 800–830 cm⁻¹, associated with the nitrate fundamentals, and several peaks in the combination band region 1720–1770 cm⁻¹, showing the presence of both coordinated and uncoordinated nitrate.^{4,5,17} For complex **3**, on the contrary, only one peak is observed in each of these regions, indicating only uncoordinated nitrate ions.

Methanol solutions of **1** and **2** give, as expected, identical electronic spectra, with a broad maximum at 965 nm and a shoulder at 760 nm. The high-energy shoulder may indicate trigonal bipyramidal coordination geometry in solution;^{4,5} however, no definite conclusions may be drawn as reliable criteria for deducing Cu^{II} coordination geometry from electronic spectra have been hard to find.¹⁸ For compound **3** there is, on the other hand, a broad maximum at 690 nm with a low-energy shoulder at 965 nm. The UV bands of tbima (245, 274 and 282 nm) are only marginally blue-shifted in complexes **1–3**; this contrasts with earlier finding where larger shifts have been reported.⁷ The UV region in **3** is practically identical to that of **1** and **2**, in spite of the coordination of att in the former. The intense UV band of neutral atth at 250 nm, probably due to $\pi \rightarrow \pi^*$ and $\sigma \rightarrow \sigma^*$ transitions in the C=S group,¹⁹ is hence not retained in the att complex; this may indicate a significant thiolate character of the coordinated ligand.

Table 2. Atomic coordinates of non-hydrogen atoms for compound **1**, [Cu(tbima)(NO₃)](NO₃) · C₂H₅OH.

Atom	X/a	Y/b	Z/c
Cu	0.18758(6)	0.14147(6)	0.30342(4)
O41	0.1154(3)	−0.0238(3)	0.3866(2)
O42	0.1950(4)	−0.0902(3)	0.2441(2)
O43	0.0844(4)	−0.2257(3)	0.3573(3)
O51	0.4722(4)	0.5026(3)	0.7127(2)
O52	0.3506(4)	0.4452(3)	0.6121(2)
O53	0.5688(4)	0.3689(3)	0.6034(3)
O61	0.1677(4)	0.7106(3)	0.1231(3)
N10	0.1410(4)	0.3507(4)	0.3749(3)
N11	0.2706(4)	0.2605(4)	0.1926(3)
N12	0.2943(4)	0.4606(4)	0.1225(3)
N21	−0.0068(4)	0.1928(4)	0.2813(3)
N22	−0.1937(4)	0.3353(4)	0.2978(3)
N31	0.3506(4)	0.1497(4)	0.3653(3)
N32	0.4669(4)	0.2402(4)	0.4608(3)
N40	0.1318(4)	−0.1165(4)	0.3286(3)
N50	0.4651(4)	0.4390(4)	0.6431(3)
C11	0.1945(5)	0.4495(5)	0.2975(3)
C12	0.2533(5)	0.3905(5)	0.2041(3)
C13	0.3231(5)	0.2490(5)	0.0963(3)
C14	0.3566(5)	0.1376(5)	0.0426(3)
C15	0.4072(5)	0.1560(5)	−0.0521(3)
C16	0.4254(5)	0.2828(5)	−0.0978(3)
C17	0.3904(5)	0.3946(5)	−0.0458(3)
C18	0.3393(5)	0.3752(5)	0.0506(3)
C21	−0.0149(5)	0.3529(5)	0.4038(3)
C22	−0.0741(5)	0.2933(5)	0.3295(3)
C23	−0.0855(5)	0.1689(5)	0.2144(3)
C24	−0.0623(5)	0.0782(5)	0.1445(3)
C25	−0.1615(5)	0.0786(5)	0.0873(3)
C26	−0.2825(5)	0.1662(5)	0.0997(3)
C27	−0.3077(5)	0.2553(5)	0.1695(3)
C28	−0.2068(5)	0.2575(4)	0.2255(3)
C31	0.2218(5)	0.3406(5)	0.4511(3)
C32	0.3497(5)	0.2445(4)	0.4247(3)
C33	0.4800(5)	0.0779(5)	0.3632(3)
C34	0.5366(5)	−0.0335(5)	0.3139(3)
C35	0.6683(5)	−0.0842(5)	0.3290(4)
C36	0.7407(5)	−0.0293(5)	0.3891(3)
C37	0.6850(5)	0.0813(5)	0.4394(3)
C38	0.5539(5)	0.1328(5)	0.4245(3)
C60	0.0206(7)	0.7055(6)	0.1124(6)
C61 ^a	−0.004(1)	0.602(1)	0.0600(9)
C62 ^a	−0.066(1)	0.620(1)	0.1685(9)

^aDisordered atoms, partial occupancy 0.5.

Structural aspects of [Cu(tbima)(NO₃)](NO₃) · EtOH (**1**) and [Cu(tbima)(NO₃)](NO₃) · H₂O (**2**). The complex unit [Cu(tbima)(NO₃)]⁺ in the two solvates are shown in Figs. 1 and 2, respectively. The copper coordination spheres are significantly different in the two compounds, and none displays the type of distorted trigonal bipyramidal structure found in the corresponding complex with the tris(2-benzothiazolylmethyl)amine ligand²⁰ and in two dinuclear compounds containing *N*-methyl- and *N*-ethyl-substituted tbima as capping ligand.^{21,22} The coordination geometry in **1** may be described as elongated octahedral with a very strong tetrahedral distortion of the equatorial plane. The tertiary amine nitrogen and a nitrate oxygen atom bind in axial

Table 3. Atomic coordinates of non-hydrogen atoms for compound **2**, [Cu(tbima)(NO₃)](NO₃) · H₂O.

Atom	X/a	Y/b	Z/c
Cu	0.15762(4)	0.41300(4)	0.21163(3)
O41	−0.0614(3)	0.4507(3)	0.0792(2)
O42	−0.0423(2)	0.4220(2)	0.2364(2)
O43	−0.2333(2)	0.4752(2)	0.1623(2)
O51	−0.4415(3)	0.0845(3)	0.2088(2)
O52	−0.3306(3)	0.1264(2)	0.0904(2)
O53	−0.4317(2)	−0.0822(2)	0.0917(2)
O60	−0.2402(2)	0.2794(3)	0.3432(2)
N10	0.3470(3)	0.4227(3)	0.1367(2)
N11	0.2960(3)	0.3890(3)	0.3350(2)
N12	0.5081(3)	0.3457(3)	0.3855(2)
N21	0.1391(3)	0.2178(3)	0.1519(2)
N22	0.2108(3)	0.0504(3)	0.0549(2)
N31	0.2159(3)	0.6153(3)	0.2290(2)
N32	0.3601(3)	0.7998(3)	0.2011(2)
N400	−0.1149(3)	0.4503(3)	0.1571(2)
N500	−0.3976(3)	0.0440(3)	0.1304(2)
C11	0.4654(3)	0.4133(3)	0.2138(2)
C12	0.4203(3)	0.3819(3)	0.3110(2)
C13	0.3012(3)	0.3585(3)	0.4328(2)
C14	0.2009(3)	0.3541(3)	0.4957(3)
C15	0.2368(4)	0.3174(4)	0.5895(2)
C16	0.3702(4)	0.2836(3)	0.6191(2)
C17	0.4710(3)	0.2895(3)	0.5579(2)
C18	0.4354(3)	0.3309(3)	0.4645(2)
C21	0.3240(4)	0.3019(3)	0.0571(2)
C22	0.2260(3)	0.1880(3)	0.0886(2)
C23	0.0616(3)	0.0893(3)	0.1616(2)
C24	−0.0395(3)	0.0588(3)	0.2206(2)
C25	−0.0984(4)	−0.0810(4)	0.2141(3)
C26	−0.0567(4)	−0.1859(3)	0.1495(3)
C27	0.0446(3)	−0.1569(3)	0.0907(3)
C28	0.1053(3)	−0.0164(3)	0.0987(2)
C31	0.3586(3)	0.5623(3)	0.0990(2)
C32	0.3107(3)	0.6622(3)	0.1751(2)
C33	0.2047(3)	0.7293(3)	0.2984(2)
C34	0.1309(3)	0.7360(3)	0.3787(2)
C35	0.1469(4)	0.8628(4)	0.4385(3)
C36	0.2336(4)	0.9803(4)	0.4184(3)
C37	0.3090(4)	0.9749(3)	0.3400(3)
C38	0.2942(3)	0.8458(3)	0.2804(2)

positions [Cu–N10 = 2.401(4) Å, Cu–O42 = 2.547(3) Å], while three benzimidazole nitrogen atoms of the tripodal ligand and a nitrate oxygen atom are equatorially bonded [Cu–N(eq) = 1.958–1.985(4) Å, Cu–O41 = 2.053(3) Å]. The marked tetrahedral distortion is evident from the atomic deviations from a best least-squares plane defined by O41, N11, N12, N13 (0.36, 0.38, −0.38, −0.36 Å) and the dihedral angle Cu, N11, N21/Cu, N31, O41 of 30.8° (Supplementary material, Table S6A). In compound **2** the ligand atoms are the same as in **1**, but a different and unusual, irregular coordination geometry is found. The interaction with one of the nitrate oxygen atoms is very weak [Cu–O41 = 2.718(3) Å] and may be considered a semi-coordination;²³ the remaining five-coordinated atoms create a distorted square pyramidal environment for copper, but the axial bond in the pyramid [Cu–N11 = 2.080(3) Å] is not the longest bond, as usually found. The tertiary amine nitrogen binds in equatorial position

Table 4. Atomic coordinates of non-hydrogen atoms for compound **3**, [Cu₂(tbima)₂(att)](NO₃)₃ · H₂O · C₂H₅OH.

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Cu1	0.79133(8)	0.48296(7)	0.75629(6)	C21	0.8866(7)	0.3484(6)	0.5852(5)
Cu2	0.51609(7)	0.19340(7)	0.80159(6)	C22	0.9327(6)	0.2761(6)	0.6336(5)
S	0.6398(2)	0.3812(1)	0.7344(1)	C23	0.9858(6)	0.1905(6)	0.7301(6)
O11	0.2110(4)	0.4574(4)	0.0400(4)	C24	1.0063(7)	0.1507(7)	0.8021(6)
O12	0.0818(4)	0.5231(4)	-0.0396(4)	C25	1.0357(7)	0.0570(7)	0.7931(6)
O13	0.1358(4)	0.3945(4)	-0.1042(4)	C26	1.0440(7)	0.0055(7)	0.7129(7)
O21	0.2179(5)	0.7600(5)	0.7395(4)	C27	1.0255(7)	0.0430(7)	0.6387(7)
O22	0.1756(5)	0.8242(5)	0.6251(4)	C28	0.9958(7)	0.1367(7)	0.6487(6)
O23	0.0743(6)	0.6995(5)	0.6206(4)	C31	0.8393(7)	0.5088(6)	0.5815(5)
O31	0.2957(6)	0.3919(6)	0.6184(5)	C32	0.7389(7)	0.5414(6)	0.5932(5)
O32	0.1796(6)	0.3679(6)	0.6741(6)	C33	0.6136(6)	0.5815(6)	0.6448(5)
O33 ^a	0.2144(8)	0.5068(7)	0.6415(6)	C34	0.5479(7)	0.5990(6)	0.6968(5)
O34 ^a	0.138(2)	0.390(2)	0.555(2)	C35	0.4576(7)	0.6409(6)	0.6636(6)
O40	0.0890(7)	0.2126(6)	0.4716(5)	C36	0.4325(7)	0.6631(6)	0.5805(6)
O80	0.2390(6)	0.1575(5)	0.3905(4)	C37	0.4976(7)	0.6452(6)	0.5282(5)
N10	0.8885(5)	0.4469(5)	0.6410(4)	C38	0.5883(7)	0.6043(6)	0.5631(5)
N11	0.9170(5)	0.5899(4)	0.7989(4)	C41	0.2872(6)	0.2147(7)	0.7904(6)
N12	1.0698(5)	0.6611(5)	0.7975(4)	C42	0.3699(6)	0.2822(6)	0.8731(5)
N21	0.9446(5)	0.2761(5)	0.7176(4)	C43	0.5219(6)	0.3451(5)	0.9792(5)
N22	0.9626(6)	0.1942(5)	0.5895(4)	C44	0.6291(6)	0.3701(5)	1.0353(5)
N31	0.7099(5)	0.5407(5)	0.6626(4)	C45	0.6513(6)	0.4365(6)	1.1186(5)
N32	0.6689(6)	0.5777(5)	0.5314(4)	C46	0.5694(6)	0.4759(6)	1.1448(5)
N40	0.3431(5)	0.1545(5)	0.7355(4)	C47	0.4645(6)	0.4522(5)	1.0899(5)
N41	0.4721(5)	0.2800(4)	0.8930(4)	C48	0.4419(6)	0.3863(5)	1.0068(5)
N42	0.3461(4)	0.3438(4)	0.9367(4)	C51	0.3207(6)	0.1788(6)	0.6463(5)
N51	0.5026(5)	0.1436(4)	0.6737(4)	C52	0.4124(6)	0.1548(5)	0.6160(5)
N52	0.4152(5)	0.1448(5)	0.5326(4)	C53	0.5722(6)	0.1246(5)	0.6257(5)
N61	0.4946(5)	0.0628(4)	0.8379(4)	C54	0.6766(6)	0.1070(6)	0.6520(5)
N62	0.3847(5)	-0.0757(5)	0.8062(4)	C55	0.7256(7)	0.0924(7)	0.5887(6)
N71	0.8769(4)	0.4081(4)	0.8397(4)	C56	0.6726(7)	0.0983(6)	0.5015(6)
N72	0.8116(4)	0.3383(4)	0.8546(4)	C57	0.5676(8)	0.1138(6)	0.4720(5)
N73	0.7501(5)	0.2250(4)	0.9042(4)	C58	0.5166(7)	0.1260(6)	0.5359(5)
N74	0.6652(4)	0.2525(4)	0.8406(4)	C61	0.3185(6)	0.0485(6)	0.7215(5)
N100	0.1445(5)	0.4581(5)	-0.0338(4)	C62	0.3969(6)	0.0127(6)	0.7894(5)
N200	0.1597(6)	0.7603(6)	0.6638(5)	C63	0.5471(6)	0.0028(5)	0.8884(5)
N300	0.2196(6)	0.4090(6)	0.6322(5)	C64	0.6497(6)	0.0193(6)	0.9515(5)
C11	0.9992(7)	0.4902(6)	0.6993(6)	C65	0.6829(6)	-0.0536(6)	0.9929(5)
C12	0.9944(6)	0.5812(6)	0.7657(5)	C66	0.6153(7)	-0.1412(6)	0.9706(6)
C13	0.9418(6)	0.6842(5)	0.8576(5)	C67	0.5143(7)	-0.1584(6)	0.9088(6)
C14	0.8880(6)	0.7334(6)	0.9092(5)	C68	0.4801(6)	-0.0856(6)	0.8688(5)
C15	0.9334(6)	0.8287(6)	0.9589(5)	C71	0.8345(5)	0.2794(6)	0.9103(5)
C16	1.0265(7)	0.8731(5)	0.9563(6)	C72	0.7029(6)	0.3213(5)	0.8116(5)
C17	1.0811(6)	0.8250(5)	0.9048(5)	C81	0.217(1)	0.1633(8)	0.3004(6)
C18	1.0375(6)	0.7289(5)	0.8555(5)	C82	0.3086(9)	0.1379(9)	0.2675(7)

^aDisordered atoms, partial occupancy O33 = 0.75, O34 = 0.25.

in this description, and is the longest bond [Cu–N10 = 2.219(3) Å]. A similar coordination geometry has been reported in a squarato-bridged dinuclear copper(II) complex,²⁴ where the bond length to an equatorial water molecule is appreciably longer than a corresponding axial bond length. The atomic deviations from a best least-squares plane defined by O42, N10, N21, N31 are 0.06, 0.08, -0.07, -0.07 Å, respectively, revealing a weak tetrahedral distortion. The Cu atom is displaced by 0.28 Å in the direction of the axial N11 atom.

In both complexes the flexibility of the tbima ligand is evident. The ligand is distorted from the idealized trigonal geometry to give room for the coordinated nitrate. The dihedral angles between the planes of the benzimidazole groups with atom numbering A2X and A3X are 9.1 and

11.1° for **1** and **2**, respectively, while the corresponding angles between the A1X/A2X and A1X/A3X groups are 109.4, 103.0° (**1**) and 83.2, 90.6° (**2**). The strain introduced in the ligand molecule through this distortion is also revealed by the fact that the chelate rings N10,C21,C22,N21 and N10,C31,C32,N31 deviate appreciably from planarity in both molecules while the N10,C11,C12,N11 chelate in each case is almost planar (Tables S6A and S6B). In copper(II) complexes of two closely related tripodal ligands, tris(benzothiazol-2-ylmethyl)amine and tris(*N*-methylbenzimidazol-2-ylmethyl)amine, much smaller deviations from the regular trigonal arrangement have been observed.^{20,21} A recent structure determination of manganese(II)-tbima reveals the presence of two different complex units in the

Table 5. Selected bond distances (in Å) and angles (in °) in compound 1, [Cu(tbima)(NO₃)](NO₃)·C₂H₅OH.

Copper coordination sphere				Cu–N10–C11	104.9(3)	N10–C11–C12	113.5(4)
Cu–O41	2.053(3)	Cu–N11	1.985(4)	Cu–N10–C21	101.0(3)	N11–C12–N12	111.6(4)
Cu–O42	2.547(3)	Cu–N21	1.981(4)	Cu–N10–C31	104.5(3)	N11–C12–C11	124.1(4)
Cu–N10	2.401(4)	Cu–N31	1.958(4)	C11–N10–C21	113.5(4)	N12–C12–C11	124.3(5)
O41–Cu–O42	55.1(1)	O42–Cu–N31	107.1(1)	C11–N10–C31	114.0(4)	N11–C13–C18	109.4(4)
O41–Cu–N10	117.3(1)	N10–Cu–N11	80.3(1)	C21–N10–C31	116.7(4)	N12–C18–C13	104.5(4)
O41–Cu–N11	162.3(1)	N10–Cu–N21	78.0(1)	Cu–N11–C12	116.7(3)	N10–C21–C22	108.7(4)
O41–Cu–N21	92.5(2)	N10–Cu–N31	78.0(1)	Cu–N11–C13	136.6(3)	N21–C22–N22	111.3(4)
O41–Cu–N31	91.6(1)	N11–Cu–N21	89.0(2)	C12–N11–C13	105.4(4)	N21–C22–C21	122.0(4)
O42–Cu–N10	170.3(1)	N11–Cu–N31	94.5(2)	C12–N12–C18	109.0(5)	N22–C22–C21	126.7(5)
O42–Cu–N11	107.1(1)	N21–Cu–N31	154.8(2)	Cu–N21–C22	115.9(3)	N21–C23–C28	108.6(4)
O42–Cu–N21	95.6(1)			Cu–N21–C23	136.1(1)	N22–C28–C23	105.2(4)
				C22–N21–C23	106.6(4)	N10–C31–C32	109.0(4)
				C22–N22–C28	108.3(4)	N31–C32–N32	112.9(4)
				Cu–N31–C32	118.9(3)	N31–C32–C31	122.0(4)
				Cu–N31–C33	135.7(3)	N32–C32–C31	125.0(4)
				C32–N31–C33	105.4(4)	N31–C33–C38	108.7(4)
				C32–N32–C38	107.7(4)	N32–C38–C33	105.2(4)
Imidazolyl–amine moiety				Coordinated nitrate			
N10–C11	1.472(6)	N31–C32	1.329(6)	O41–N40	1.283(5)	O43–N40	1.230(5)
N10–C21	1.454(6)	N31–C33	1.393(6)	O42–N40	1.256(5)		
N10–C31	1.465(6)	N32–C32	1.326(6)				
N11–C12	1.337(6)	N32–C38	1.393(6)				
N11–C13	1.383(6)	C11–C12	1.497(7)	O41–N40–O42	117.7(4)	Cu–O41–N40	104.7(3)
N12–C12	1.328(7)	C13–C18	1.400(7)	O41–N40–O43	119.2(4)	Cu–O42–N40	82.2(3)
N12–C18	1.379(7)	C21–C22	1.490(7)	O42–N40–O43	123.1(4)		
N21–C22	1.330(6)	C23–C28	1.413(7)				
N21–C23	1.384(6)	C31–C32	1.518(7)				
N22–C22	1.353(6)	C33–C38	1.400(7)				
N22–C28	1.380(6)						

crystal structure; one in which tbima essentially retains its trigonal geometry, and one where a distortion similar to those observed in **1** and **2** is found.²⁵

The nitrate ligands may in both complexes be considered unsymmetrically bidentate,¹⁷ although in **2** one of the Cu–O bonds is very weak. Unsymmetrically bidentate as well as symmetrically bidentate, monodentate, and bridging coordination modes have been observed in copper(II)–nitrate complexes.¹⁷ The coordinated nitrate in **1** and **2**, respectively, deviates significantly from three-

fold symmetry, the strongly coordinated oxygen being associated with the longest, the semi-coordinated with the intermediate N–O bond, and the chelate O–N–O angle being less than 120°. These features are characteristic in unsymmetrically bidentate nitrate groups.¹⁷ The non-coordinated nitrate ions have close to three-fold symmetry.

The crystal packing in the two solvates is depicted in Figs. 3 and 4, respectively. Compound **2** has a somewhat more dense packing than compound **1** (Table 1, cell

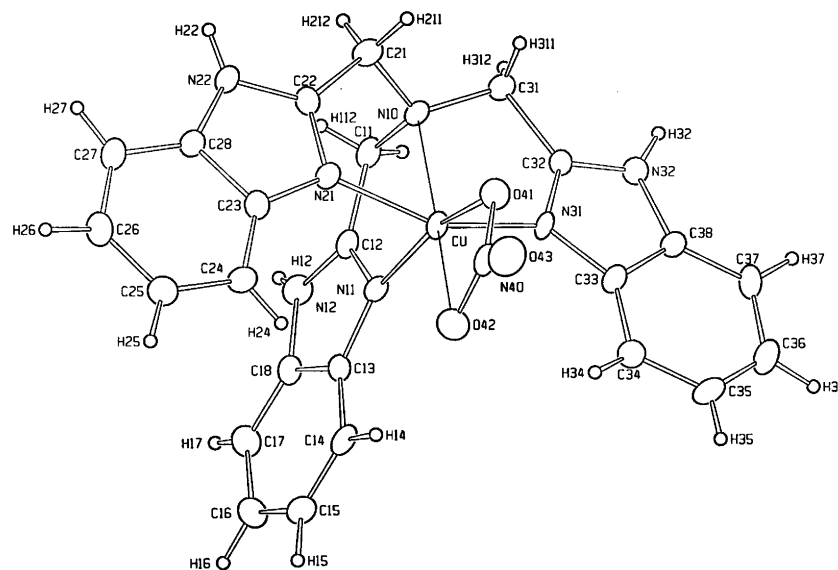


Fig. 1. Complex unit, [Cu(tbima)(NO₃)]⁺ of compound 1, [Cu(tbima)(NO₃)](NO₃)·EtOH. Thermal ellipsoids are plotted at the 50% probability level.

Table 6. Selected bond distances (in Å) and angles (in °) in compound **2**, [Cu(tbima)(NO₃)](NO₃)·H₂O.

Copper coordination sphere				Cu–N10–C11	107.0(2)	N10–C11–C12	112.9(3)
Cu–O41	2.718(3)	Cu–N11	2.080(3)	Cu–N10–C21	106.7(2)	N11–C12–N12	112.6(3)
Cu–O42	2.037(2)	Cu–N21	1.945(3)	Cu–N10–C31	104.7(2)	N11–C12–C11	125.0(3)
Cu–N10	2.219(3)	Cu–N31	1.944(3)	C11–N10–C21	112.1(3)	N12–C12–C11	122.4(3)
				C11–N10–C31	111.9(3)	N11–C13–C18	108.2(3)
O41–Cu–O42	52.15(8)	O42–Cu–N31	96.5(1)	C21–N10–C31	113.8(3)	N12–C18–C13	106.0(3)
O41–Cu–N10	108.96(9)	N10–Cu–N11	83.0(1)	Cu–N11–C12	111.1(2)	N10–C21–C22	107.6(3)
O41–Cu–N11	167.83(9)	N10–Cu–N21	80.6(1)	Cu–N11–C13	142.1(2)	N21–C22–N22	112.5(3)
O41–Cu–N21	89.01(9)	N10–Cu–N31	79.6(1)	C12–N11–C13	106.1(3)	N21–C22–C21	121.2(3)
O41–Cu–N31	88.8(1)	N11–Cu–N21	95.3(1)	C12–N12–C18	107.2(3)	N22–C22–C21	126.2(3)
O42–Cu–N10	161.00(9)	N11–Cu–N31	91.4(1)	Cu–N21–C22	116.4(2)	N21–C23–C28	108.1(3)
O42–Cu–N11	115.8(1)	N21–Cu–N31	158.1(1)	Cu–N21–C23	137.4(2)	N22–C28–C23	105.7(3)
O42–Cu–N21	99.3(1)			C22–N21–C23	106.0(3)	N10–C31–C32	106.6(3)
				C22–N22–C28	107.7(3)	N31–C32–N32	113.3(3)
				Cu–N31–C32	116.7(2)	N31–C32–C31	119.7(3)
				Cu–N31–C33	136.4(2)	N32–C32–C31	126.9(3)
				C32–N31–C33	105.5(3)	N31–C33–C38	108.3(3)
				C32–N32–C38	106.4(3)	N32–C38–C33	106.4(3)
Imidazolyl–amine moiety				Coordinated nitrate			
N10–C11	1.487(4)	N31–C32	1.319(4)	O41–N400	1.239(4)	O43–N400	1.221(4)
N10–C21	1.477(4)	N31–C33	1.393(4)	O42–N400	1.294(4)		
N10–C31	1.489(4)	N32–C32	1.348(4)				
N11–C12	1.305(4)	N32–C38	1.384(4)				
N11–C13	1.392(4)	C11–C12	1.496(5)				
N12–C12	1.354(4)	C13–C18	1.400(4)	O41–N400–O42	118.6(3)	Cu–O41–N400	78.8(2)
N12–C18	1.369(4)	C21–C22	1.502(5)	O41–N400–O43	122.9(3)	Cu–O42–N400	109.9(2)
N21–C22	1.316(4)	C23–C28	1.400(5)	O42–N400–O43	118.5(3)		
N21–C23	1.399(4)	C31–C32	1.494(5)				
N22–C22	1.340(4)	C33–C38	1.400(5)				
N22–C28	1.381(5)						

volume and density). This is evidenced by a more pronounced overlap between benzimidazole moieties of neighbouring molecules in **2** and the presence of a hydrogen bond between the water molecule and the uncoordinated nitrate in **2**; a corresponding contact between the ethanol of crystallization and nitrate in **1** is not established. In other respects the hydrogen bonding patterns are very similar in the two compounds. The three imidazole N–H groups participate in hydrogen

bonds to uncoordinated nitrate and ethanol (**1**) or water (**2**). Ethanol (**1**) and water (**2**) also form hydrogen bonds to the coordinated nitrate.

*Structural aspects of [Cu₂(tbima)₂(att)](NO₃)₃·H₂O·EtOH (**3**).* The complex unit [Cu₂(tbima)₂(att)]³⁺ is shown in Fig. 5. The monodeprotonated form of 4-amino-1,2,4-triazole-5-thione, att, functions as a bridging, bidentate (sulfur and amino group) and mono-

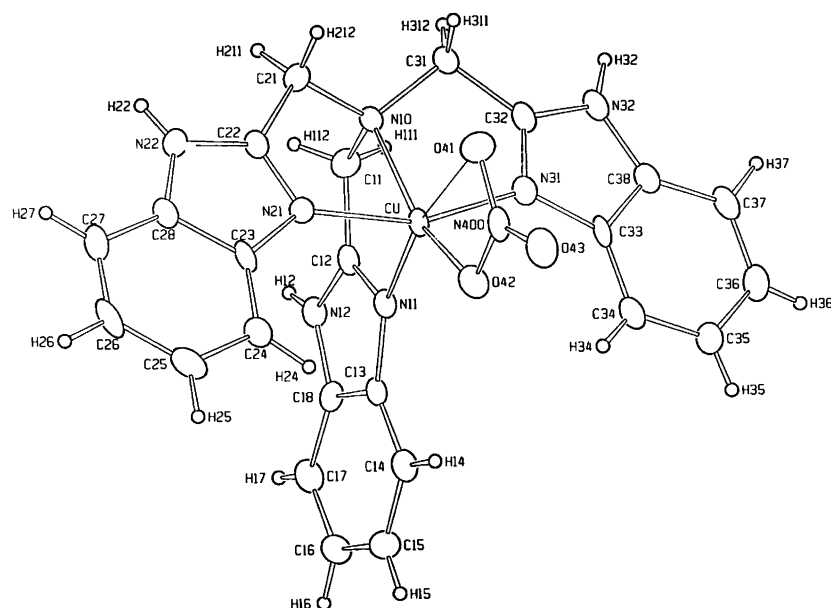


Fig. 2. Complex unit, [Cu(tbima)(NO₃)]⁺ of compound **2**, [Cu(tbima)(NO₃)](NO₃)·H₂O. Thermal ellipsoids are plotted at the 50% probability level.

Table 7. Selected bond distances (in Å) and angles (in °) in compound **3**, [Cu₂(tbima)₂(att)](NO₃)₃ · H₂O · C₂H₅OH.

Copper coordination spheres				C21–N10–C31	108.9(7)	C51–N40–C61	110.0(7)
Cu1–N10	2.578(7)	Cu2–N40	2.185(7)	Cu1–N11–C12	121.0(6)	Cu2–N41–C42	116.1(6)
Cu1–N11	2.018(7)	Cu2–N41	1.966(7)	Cu1–N11–C13	133.6(6)	Cu2–N41–C43	137.6(6)
Cu1–N31	1.939(7)	Cu2–N51	1.981(7)	C12–N11–C13	105.2(7)	C42–N41–C43	106.3(7)
Cu1–S	2.295(2)	Cu2–N61	2.095(7)	C12–N12–C18	106.4(7)	C42–N42–C48	107.8(7)
Cu1–N71	2.011(7)	Cu2–N74	1.955(7)	C22–N21–C23	105.7(8)	Cu2–N51–C52	114.3(6)
				C22–N22–C28	107.8(9)	Cu2–N51–C53	136.5(6)
N10–Cu1–N11	73.4(3)	N40–Cu2–N41	81.8(3)	Cu1–N31–C32	120.6(7)	C52–N51–C53	106.1(7)
N10–Cu1–N31	77.5(3)	N40–Cu2–N51	78.0(3)	Cu1–N31–C33	134.7(6)	C52–N52–C58	106.8(8)
N10–Cu1–N71	96.4(3)	N40–Cu2–N61	80.4(3)	C32–N31–C33	104.5(8)	Cu2–N61–C62	111.1(6)
N10–Cu1–S	119.3(2)	N40–Cu2–N74	164.7(3)	C32–N32–C38	107.7(8)	Cu2–N61–C63	143.2(6)
N11–Cu1–N31	92.4(3)	N41–Cu2–N51	149.2(3)	N10–C11–C12	108.2(8)	C62–N61–C63	105.3(7)
N11–Cu1–N71	90.5(3)	N41–Cu2–N61	97.8(3)	N11–C12–N12	113.9(8)	C62–N62–C68	107.7(7)
N11–Cu1–S	167.3(2)	N41–Cu2–N74	99.0(3)	N11–C12–C11	122.7(8)	N40–C41–C42	108.9(7)
N31–Cu1–S	89.7(2)	N51–Cu2–N61	101.5(3)	N12–C12–C11	123.3(8)	N41–C42–N42	112.9(8)
N31–Cu1–N71	172.1(3)	N51–Cu2–N74	94.6(3)	N11–C13–C18	108.1(8)	N41–C42–C41	123.1(8)
N71–Cu1–S	89.0(2)	N61–Cu2–N74	114.4(3)	N12–C18–C13	106.5(7)	N42–C42–C41	123.8(8)
				N10–C21–C22	116.5(8)	N41–C43–C48	107.7(7)
Imidazolyl-amine moiety				N21–C22–N22	112(1)	N42–C48–C43	105.3(7)
N10–C11	1.48(1)	N40–C41	1.49(1)	N21–C22–C21	127(1)	N40–C51–C52	106.9(8)
N10–C21	1.48(1)	N40–C51	1.50(1)	N22–C22–C21	120(1)	N51–C52–N52	113.3(8)
N10–C31	1.47(1)	N40–C61	1.47(1)	N21–C23–C28	110(1)	N51–C52–C51	120.1(8)
N11–C12	1.31(1)	N41–C42	1.30(1)	N22–C28–C23	105(1)	N52–C52–C51	126.6(8)
N11–C13	1.40(1)	N41–C43	1.41(1)	N10–C31–C32	113.2(8)	N51–C53–C58	107.6(8)
N12–C12	1.35(1)	N42–C42	1.33(1)	N31–C32–N32	112.8(9)	N52–C58–C53	106.1(8)
N12–C18	1.38(1)	N42–C48	1.40(1)	N31–C32–C31	125.4(9)	N40–C61–C62	111.5(7)
N21–C22	1.32(1)	N51–C52	1.31(1)	N32–C32–C31	121.8(9)	N61–C62–N62	112.1(8)
N21–C23	1.39(1)	N51–C53	1.39(1)	N31–C33–C38	109.5(9)	N61–C62–C61	122.4(8)
N22–C22	1.37(1)	N52–C52	1.34(1)	N32–C38–C33	105.4(9)	N62–C62–C61	125.3(8)
N22–C28	1.38(1)	N52–C58	1.38(1)			N61–C63–C68	109.9(8)
N31–C32	1.30(1)	N61–C62	1.34(1)			N62–C68–C63	105.0(8)
N31–C33	1.41(1)	N61–C63	1.38(1)	Bridging aminotriazolethiolate			
N32–C32	1.35(1)	N62–C62	1.35(1)	S–C72	1.696(9)	N73–N74	1.406(9)
N32–C38	1.37(1)	N62–C68	1.39(1)	N71–N72	1.393(8)	N73–C71	1.29(1)
C11–C12	1.50(1)	C41–C42	1.51(1)	N72–C71	1.34(1)	N74–C72	1.31(1)
C13–C18	1.41(1)	C43–C48	1.39(1)	N72–C72	1.37(1)		
C21–C22	1.47(1)	C51–C52	1.49(1)				
C23–C28	1.42(1)	C53–C58	1.41(1)	Cu1–S–C72	94.4(3)	Cu2–N74–C72	126.7(6)
C31–C32	1.50(1)	C61–C62	1.46(1)	Cu1–N71–N72	111.9(5)	N73–N74–C72	109.3(7)
C33–C38	1.38(1)	C63–C68	1.41(1)	N71–N72–C71	131.2(7)	N72–C71–N73	111.9(7)
				N71–N72–C72	122.0(7)	S–C72–N72	122.3(7)
Cu1–N10–C11	100.5(5)	Cu2–N40–C41	109.8(5)	C71–N72–C72	106.8(6)	S–C72–N74	130.7(7)
Cu1–N10–C21	124.3(5)	Cu2–N40–C51	104.3(5)	N74–N73–C71	105.0(6)	N72–C72–N74	107.0(7)
Cu1–N10–C31	100.6(6)	Cu2–N40–C61	107.2(5)	Cu2–N74–N73	124.0(5)		
C11–N10–C21	110.6(8)	C41–N40–C51	110.8(8)				
C11–N10–C31	111.2(7)	C41–N40–C61	114.2(7)				

dentate ligand (deprotonated triazole nitrogen). The two copper atoms have significantly different coordination geometries: Cu1, the metal site bonded to the att chelate, is close to square pyramidal with two imidazole nitrogen atoms [Cu1–N11 = 2.018(7) Å, Cu1–N31 = 1.939(7) Å], sulfur [Cu1–S = 2.295(2) Å] and att amine nitrogen [Cu1–N71 = 2.011(7) Å] as equatorial ligands, and with the tbima amine nitrogen in the axial position [Cu1–N10 = 2.578(7) Å]. There is a significant tetrahedral distortion, with S, N11, N31, N71 deviating by –0.17, –0.19, 0.19, 0.18 Å from a least-squares plane defined by these atoms, and the dihedral angle S, N71, Cu1/N11, N31, Cu1 being 14.7°. Cu(1) is displaced by 0.05 Å from the mean plane towards the apical ligand. At this coordination site one leg of the terminal tripodal

tbima ligand is twisted away from the metal, leaving space for bidentate binding of att. Cu2 is also five-coordinated, but the geometry fits neither the elongated square pyramidal nor the trigonal bipyramidal description well. The best equatorial plane in a square pyramidal model (N40, N41, N51, N74) will give a short axial bond [Cu2–N61 = 2.095(7) Å] and one long equatorial bond [Cu2–N40 = 2.185(7) Å], thus resembling the coordination geometry of compound **2**. The tetrahedral distortion of the equatorial plane (atomic deviations –0.09, 0.08, 0.09, –0.08 Å) is also comparable to that in **2**, and Cu2 is displaced by 0.35 Å towards the strongly bonded apical ligand. It is to be noted that the other axial position in this description is screened by the att sulfur atom [Cu2–S = 3.599(3) Å, S–Cu2–N61 = 159.0(1)°], quite

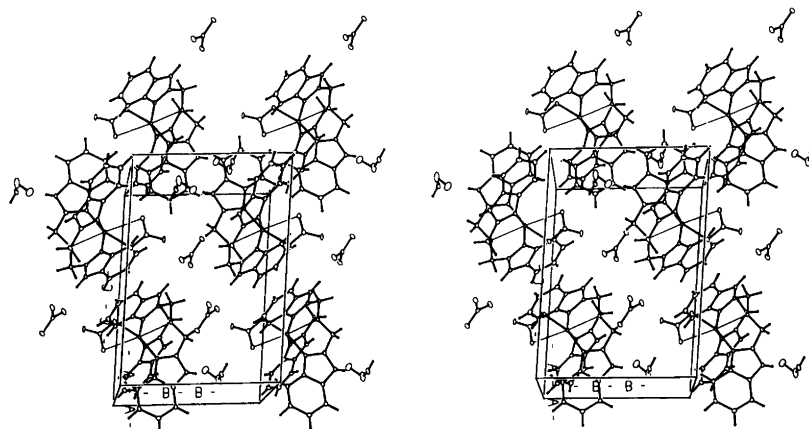


Fig. 3. Crystal packing of compound 1, $[\text{Cu}(\text{tbima})(\text{NO}_3)](\text{NO}_3) \cdot \text{EtOH}$.

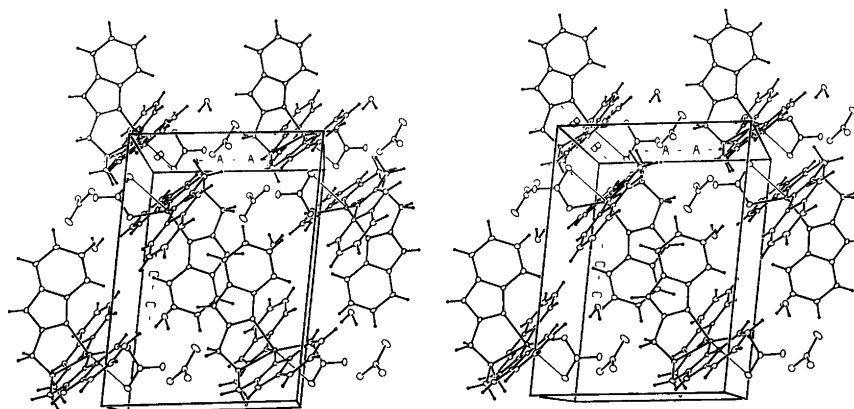


Fig. 4. Crystal packing of compound 2, $[\text{Cu}(\text{tbima})(\text{NO}_3)](\text{NO}_3) \cdot \text{H}_2\text{O}$.

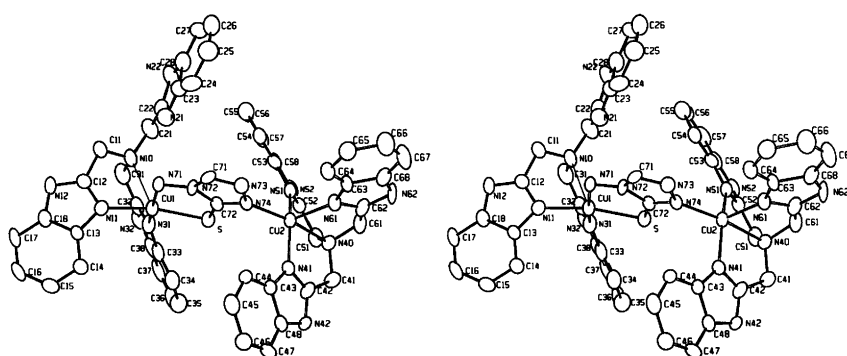


Fig. 5. Stereo view of the complex unit, $[\text{Cu}_2(\text{tbima})_2(\text{att})]^{3+}$ of compound 3, $[\text{Cu}_2(\text{tbima})_2(\text{att})](\text{NO}_3)_3 \cdot \text{H}_2\text{O} \cdot \text{EtOH}$. Thermal ellipsoids are plotted at the 50% probability level.

analogous to the weak Cu–O interaction in **2**. An alternative description of the coordination would be a distorted trigonal bipyramidal geometry with axial bonds $\text{Cu}2\text{--N}40 = 2.185(7) \text{ \AA}$ and $\text{Cu}2\text{--N}74 = 1.955(7) \text{ \AA}$, and the three imidazole nitrogen atoms defining the equatorial plane [$\text{Cu}2\text{--N} 1.966(7)\text{--}2.095(7) \text{ \AA}$]. The copper atom does not fit the equatorial plane, but is displaced by 0.35 \AA from this plane in the direction of the bridging

group. Also the angles in the equatorial plane deviate appreciably from 120° [$97.8(3)\text{--}149.2(3)^\circ$]. A similar model has been used to describe the coordination geometry in a dinuclear complex with tris(*N*-methylbenzimidazol-2-ylmethyl)amine as terminal ligand;²¹ in this case, however, the deviation from trigonal symmetry is less pronounced than in **3**. The distorted shortened square pyramidal model seems to be the better choice

for describing Cu₂ in compound **3**. The dihedral angles between the benzimidazole planes of the tbima ligand bonded to Cu₂ range from 104.0(2) to 141.2(2)°, thus the distortion from three-fold symmetry in this ligand is smaller than found in **1** and **2**.

The bridging ligand, att, is planar within the limits of experimental errors. Cu₁ and Cu₂ deviate by -0.168 Å and 0.036 Å, respectively, from the plane of the bridge. The dihedral angle between att and the equatorial plane of Cu₁ is 10.0°. Att makes an angle of 106.3° with the equatorial plane of Cu₂ in the square pyramidal description (N40,N41,N51,N74), and an angle of 91.0° with the equatorial plane defined in the trigonal bipyramidal description (N41,N51,N61). The intramolecular Cu₁...Cu₂ distance across the att bridge is 5.677(1) Å.

The Cu₁-S bond in **3** [2.295(2) Å] is found to be significantly shorter than the corresponding bond in a square pyramidal copper(II) complex with the neutral, protonated atth ligand [2.340(1) Å].²⁶ This change is to be expected given the higher degree of thiolate sulfur character in the deprotonated ligand. The Cu-S bond length in **3** also compares nicely with the distances observed in two other square pyramidal complexes where partial thiolate character is attained through deprotonation of a heterocycle [Cu-S 2.308(3) Å, 2.292(2) Å].^{27,28} Only in a case where the heterocycle is built into a frame which gives a ligand that imposes a near tetrahedral geometry on the copper(II) ion, has Cu-S distances close to 2.20 Å been observed [2.209(1) and 2.227(1) Å],²⁹ thus approaching the distance quoted for Cu^{II}-S(cys) in the oxidized form of plastocyanin [2.13(2) Å].³⁰

Acknowledgement. Thanks are due to Anne Gulbrandsen Frøystein for performing the atomic spectroscopy analysis.

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Received November 11, 1996.