metal-organic papers

Supramolecular self-assembly *via* inter-ligands hydrogen bonds in [Cu(H$_2$O)$_2$(NO$_3$)$_2$(tb)] (tb is thiabendazole)

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In the title complex, diaquadinitrato[2-(4-thiazolyl)benzimidazole]copper(II), [Cu(NO$_3$)$_2$(C$_{10}$H$_7$N$_3$S)(H$_2$O)$_2$], the Cu atom has a distorted octahedral geometry. Thiabendazole [2-(4-thiazolyl)benzimidazole] acts as a neutral bidentate chelate, coordinating through the imidazole and thiazole N atoms. The equatorial positions are occupied by the two N atoms of the thiabendazole molecule and two O atoms of two water molecules. The axial positions are occupied by two O atoms of two nitrate ions acting as monodentate ligands. The complex units are further self-assembled into a supramolecular motif by extensive inter-ligand O—H···O hydrogen bonds.

Comment

The compound 2-(4-thiazolyl)benzimidazole, also known as thiabendazole (tb), is a well known and widely used anthelmintic for animals and man. It also finds application as a fungistatic agent (Merck Index, 1998). The drug is a bidentate chelating ligand, suggesting the involvement of metal chelation in its mode of action. The structure of thiabendazole is a combination of benzimidazole and thiazole functional units. The imidazole nucleus has been identified as one of the coordinating ligands in copper-containing proteins. It has been suggested that these ligands can serve as biomimetic models for the study of metal sites in complex biological systems (Garcia-Lozano *et al.*, 1996).

(I)
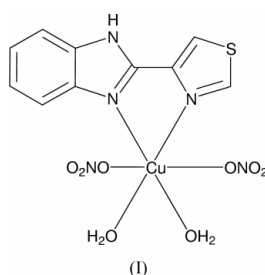
Thiabendazole resembles 2,2'-bipyridine and 1,10-phenanthroline in its metal binding modes. It inhibits the rate of NADH oxidation. A variety of metal complexes of thiabendazole have been reported in the literature (Kowala *et al.*, 1971; Kowala & Wunderlich, 1973; Landschoot *et al.*, 1976; Rong *et al.*, 1991) and also from our laboratory (Umadevi *et al.*, 1995). The design of hydrogen-bonded supramolecular ladders and chains is of current interest (Aitipamula *et al.*, 2002; Stanley *et al.*, 2002). Hydrogen-bonding patterns involving water molecules and anions also play a vital role in supramolecular self-assembly (Prabakaran *et al.*, 2000). The supramolecular self-assembly *via* inter-ligand hydrogen bonds
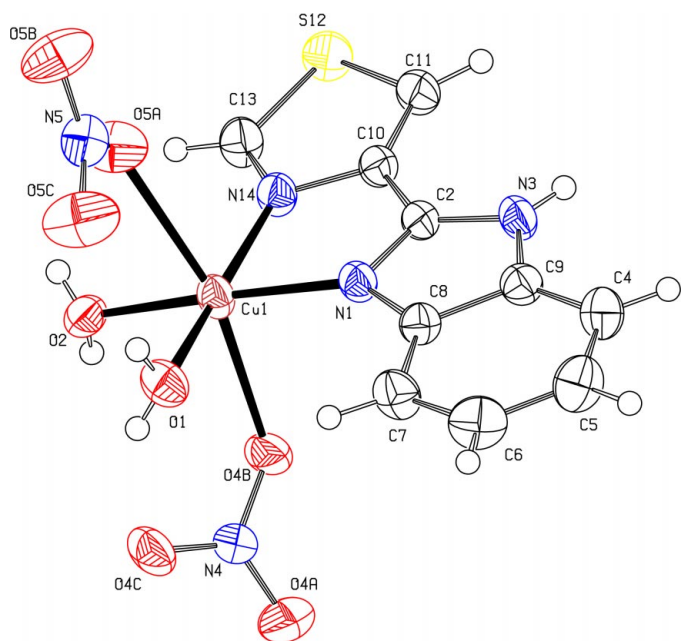
Figure 1
View of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

has also been observed in many crystal structures (Muthiah *et al.*, 2001; Raj *et al.*, 2001). Protonated thiabendazole compounds have been observed to form supramolecular ladders and chains. The crystal structure of the chloro complex of copper with thiabendazole, [CuCl(tb)$_2$]Cl·2H$_2$O (Udupa & Krebs, 1979), has been reported. The present study is aimed at gaining an understanding of the interplay of the coordination and the hydrogen-bonded supramolecular organization of a nitrate complex of copper with thiabendazole, *viz.* [Cu(H$_2$O)$_2$(NO$_3$)$_2$(tb)], (I).

In (I), the Cu atom has a distorted octahedral geometry with one thiabendazole moiety, two water molecules and two nitrate anions. An *ORTEP*II (Johnson, 1976) view is shown in Fig. 1. Thiabendazole acts as a neutral bidentate chelate, coordinating through imidazole and thiazole N atoms. The equatorial positions are occupied by N1 (of the benzimidazole ring) and N14 (of the thiazole ring) of the thiabendazole molecule, and two O atoms of the two water molecules. The axial positions are occupied by two O atoms of the two nitrate ions. The nitrate ions act here as monodentate ligands only. The Cu—O [Cu1—O4B 2.432 (3) Å and Cu1—O5A 2.502 (3) Å] distances to the nitrate ions are significantly larger than the Cu—O [Cu1—O1 1.956 (3) Å and Cu1—O2 1.984 (3) Å] distances to the water molecules and Cu—N [Cu1—N1 2.006 (3) Å and Cu1—N14 2.018 (2) Å] distances to the thiabendazole moiety. The angle [164.4 (1)°] involving the central metal atom and the two O atoms of the two nitrate ions in the axial positions (O5A—Cu1—O4B) deviates from linearity. Also, the angles subtended at the central metal atom by the two diagonal end atoms on the equatorial plane differ significantly from linearity [N1—Cu1—O2 172.3 (1)° and N14—Cu1—O1 172.2 (1)°]. These facts confirm the distorted octahedral geometry around copper.
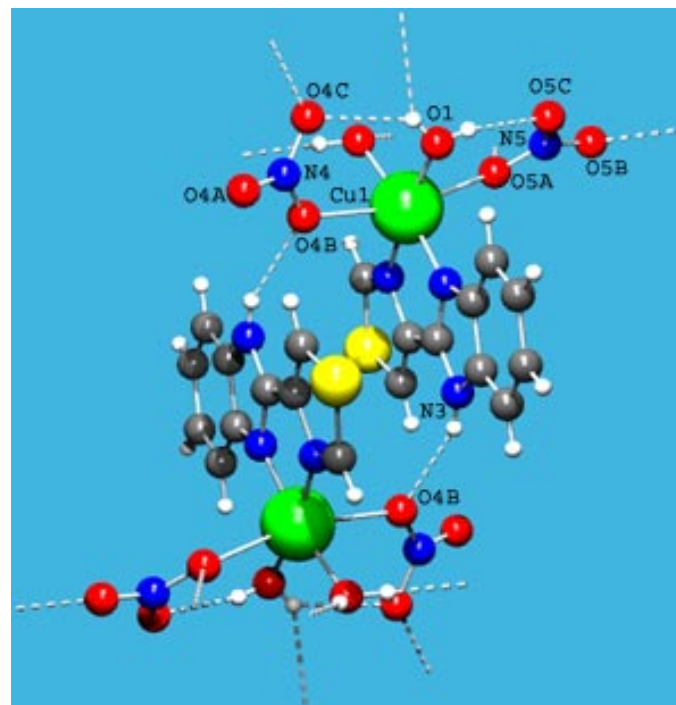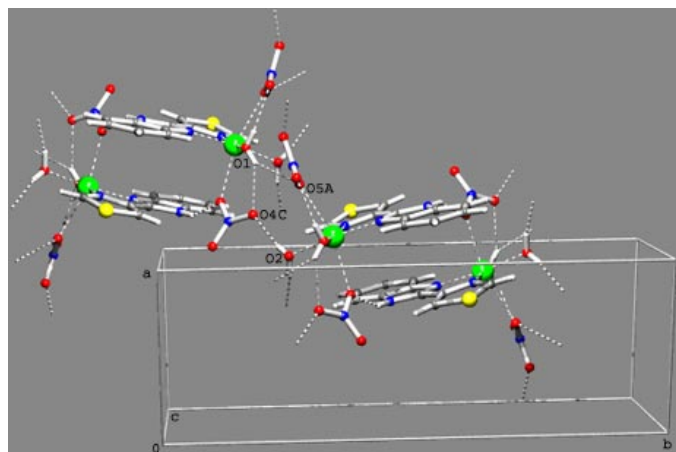

Figure 2
A view of the hydrogen-bonded dimer-like arrangement in (I).

The bite angle (N1—Cu1—N14) of the thiabendazole ligand in this compound is 81.4 (1)°. The values of the corresponding angle in other complexes are: 75.6 (7) and 78.4 (7)° in [CoCl$_2$(tb)$_2$]·XH$_2$O (Kowala & Wunderlich, 1973), 77.18 (8) and 76.87 (7)° in [CoCl$_2$(tb)$_2$]·H$_2$O (Umadevi *et al.*, 1995), 78.6 (2) and 80.6 (2)° in [CuCl(tb)$_2$]Cl·2H$_2$O (Udupa & Krebs, 1979), and 80.7 (5)° in [PtBr$_2$(tb)] (Rong *et al.*, 1991). The twist between the planar thiazole and benzimidazole moieties of thiabendazole is 9.96 (2)° in the free ligand (Trus & Marsh, 1973), the value in this complex being 6.46 (19)°. The values of the corresponding angle in other complexes are: 9.81 (14) and 7.91 (3)° in [CuCl(tb)$_2$]Cl·2H$_2$O (Udupa & Krebs, 1979), 4.85 (17) and 4.34 (11)° in [CoCl$_2$(tb)$_2$]·XH$_2$O (Kowala & Wunderlich, 1973), and 1.71 (2) and 3.95 (3)° in [CoCl$_2$(tb)$_2$]·H$_2$O (Umadevi *et al.*, 1995). Thus, as in many other complexes, the thiabendazole ligand maintains a near planar geometry. Selected geometric parameters are shown in Table 1.

The inter-ligand hydrogen bonds involve the water molecules, nitrate ions and the NH group of the thiabendazole moiety. Two centrosymmetrically related metal complex units constitute a hydrogen-bonded dimeric unit, as shown in Fig. 2. A hydrogen-bonded dimer involving an SO$_3$$^-$ ion and a coordinated water molecule has also been observed in the crystal structure of the sulfoxine complex, [Ni(HQS)-(H$_2$O)$_4$]·H$_2$O (Raj *et al.*, 2001). Fig. 3 shows the π–π-stacking interaction between the two thiabendazole moieties. The centroid-to-centroid distance between the thiazole and imidazole rings is 3.808 (3) Å, and between the thiazole and benzene rings is 3.892 (3) Å. It is interesting to note that a similar π–π-stacking interaction plays a vital role in the

Figure 3
A view of the π–π-stacking interaction between two benzimidazole moieties in (I).

Figure 4
The supramolecular ladder-like arrangement in (I).

stabilization of the crystal structure of the sulfoxine complex [Ni(HQS)(H$_2$O)$_4$]·H$_2$O (Raj *et al.*, 2001). These dimeric units are further organized *via* O—H···O hydrogen bonds involving the water molecules and the nitrate ions, leading to the formation of a supramolecular ladder, with thiabendazole moieties acting as the rungs, as shown in Fig. 4. The metal complex units also form a hydrogen-bonded supramolecular motif (zigzag chain) along the *c* direction, as shown in Fig. 5. The crystal structure is further stablilized by C—H···O hydrogen bonds. The hydrogen-bonding geometry is given in Table 2.
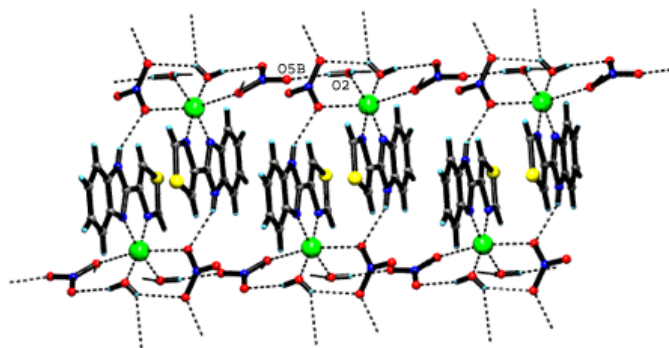
Experimental

Compound (I) was prepared by mixing an aqueous methanolic solution of copper nitrate and thiabendazole (obtained from Merck, Sharp & Dohme Inc, USA) in a 1:1 molar ratio. The solution was warmed over a water bath for a few minutes. The resulting solution was allowed to cool slowly to room temperature. Green plate-like crystals were obtained after a few days.

Crystal data

[Cu(NO$_3$)$_2$(C$_{10}$H$_7$N$_3$S)(H$_2$O)$_2$]	$D_x = 1.856$ Mg m^{-3}
$M_r = 424.86$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 7.580$ (4) Å	reflections
$b = 20.065$ (5) Å	$\theta = 10$–15°
$c = 10.606$ (2) Å	$\mu = 1.63$ mm^{-1}
$\beta = 109.51$ (3)°	$T = 293$ (2) K
$V = 1520.4$ (10) Å^3	Plate, green
$Z = 4$	$0.3 \times 0.3 \times 0.2$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.020$
	$\theta_{max} = 25.0°$
ω–2θ scans	$h = 0 \to 9$
Absorption correction: ψ scan	$k = 0 \to 23$
(North *et al.*, 1968)	$l = -12 \to 11$
$T_{min} = 0.89$, $T_{max} = 0.99$	2 standard reflections
2857 measured reflections	frequency: 60 min
2649 independent reflections	intensity decay: none
2057 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.029$	$+ 1.6719P]$
$wR(F^2) = 0.077$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{max} = 0.001$
2649 reflections	$\Delta\rho_{max} = 0.35$ e Å^{-3}
271 parameters	$\Delta\rho_{min} = -0.26$ e Å^{-3}
All H-atom parameters refined	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.0008 (4)
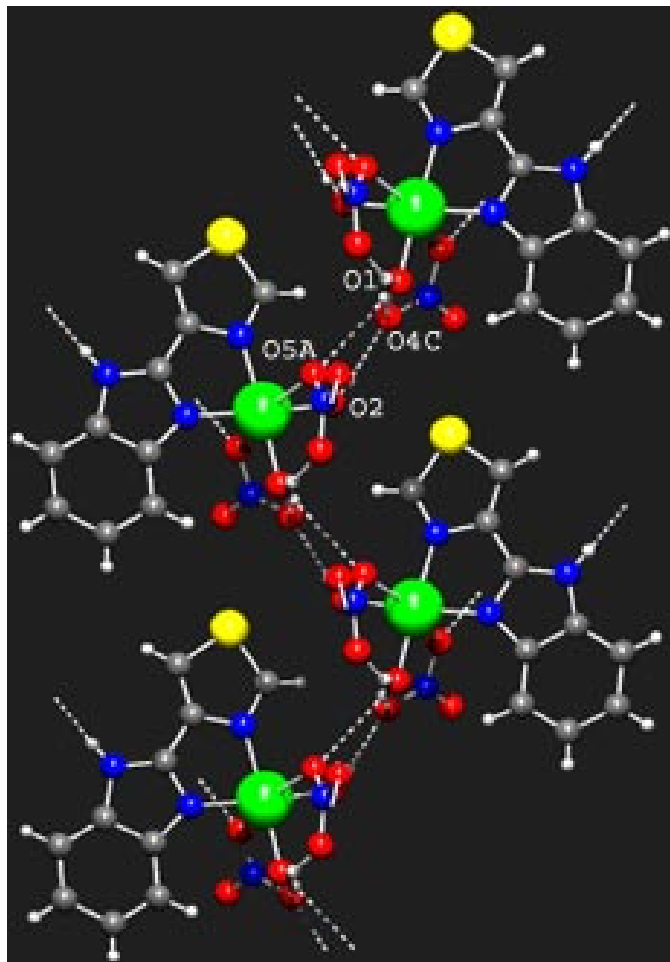
Figure 5
The zigzag chain motif in (I).

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.956 (3)	O4C—N4	1.247 (4)
Cu1—O2	1.984 (3)	O5A—N5	1.246 (4)
Cu1—O4B	2.432 (3)	O5B—N5	1.238 (4)
Cu1—O5A	2.502 (3)	O5C—N5	1.238 (4)
Cu1—N1	2.006 (3)	N1—C8	1.395 (4)
Cu1—N14	2.018 (2)	N1—C2	1.325 (4)
S12—C11	1.705 (4)	N3—C9	1.390 (4)
S12—C13	1.699 (4)	N3—C2	1.340 (4)
O4A—N4	1.214 (4)	N14—C13	1.305 (4)
O4B—N4	1.268 (4)	N14—C10	1.380 (4)
O1—Cu1—O2	92.00 (13)	C2—N3—C9	107.2 (3)
O1—Cu1—O4B	89.03 (12)	O4A—N4—O4C	121.6 (3)
O1—Cu1—O5A	89.02 (12)	O4B—N4—O4C	118.7 (3)
O1—Cu1—N1	93.19 (11)	O4A—N4—O4B	119.7 (3)
O1—Cu1—N14	172.14 (14)	O5A—N5—O5C	120.3 (3)
O2—Cu1—O4B	82.98 (11)	O5A—N5—O5B	119.7 (3)
O2—Cu1—O5A	81.59 (11)	O5B—N5—O5C	119.9 (3)
O2—Cu1—N1	172.25 (13)	Cu1—N14—C13	135.2 (2)
O2—Cu1—N14	94.01 (12)	Cu1—N14—C10	113.84 (19)
O4B—Cu1—O5A	164.37 (9)	C10—N14—C13	110.7 (3)
O4B—Cu1—N1	91.36 (11)	N1—C2—C10	118.7 (3)
O4B—Cu1—N14	96.72 (10)	N3—C2—C10	128.3 (3)
O5A—Cu1—N1	104.24 (11)	N1—C2—N3	113.0 (3)
O5A—Cu1—N14	86.86 (10)	N1—C8—C7	131.0 (3)
N1—Cu1—N14	81.36 (10)	N1—C8—C9	108.7 (3)
C11—S12—C13	90.13 (17)	N3—C9—C8	105.6 (3)
Cu1—O4B—N4	123.1 (2)	N3—C9—C4	132.0 (3)
Cu1—O5A—N5	124.22 (19)	N14—C10—C2	112.8 (3)
Cu1—N1—C2	113.1 (2)	N14—C10—C11	114.9 (3)
Cu1—N1—C8	140.94 (19)	S12—C11—C10	109.8 (3)
C2—N1—C8	105.4 (2)	S12—C13—N14	114.4 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O5C	0.73 (5)	2.03 (5)	2.724 (5)	161 (5)
O1—H1B···O4C	0.71 (6)	2.18 (6)	2.759 (5)	139 (6)
O1—H1B···O5A[i]	0.71 (6)	2.58 (6)	3.172 (4)	142 (6)
O2—H2A···O4C[ii]	0.71 (3)	2.03 (4)	2.731 (4)	170 (4)
O2—H2B···O5B[iii]	0.82 (5)	2.00 (5)	2.783 (5)	159 (4)
N3—H3···O4B[iv]	0.78 (3)	2.11 (3)	2.825 (4)	154 (4)
C11—H11···O4A[iv]	0.90 (3)	2.45 (3)	3.332 (5)	166 (3)
C13—H13···O4C[ii]	0.90 (4)	2.57 (4)	3.278 (5)	135 (3)
C13—H13···O5C[v]	0.90 (4)	2.34 (4)	3.104 (5)	142 (3)

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x - 1, y, z$; (iv) $-x, 1 - y, 1 - z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$.

H atoms were located from a difference Fourier map and were refined isotropically.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *PLATON* (Spek, 1997).

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