

Fig. 1. Stereoscopic view of the complex.

regular octahedral coordination. In fact, the N(3)–Ni–N(5) angle of 98.0 (3)° approaches that of 98.5 (2)° found in the distorted tetrahedral Ni(POB)₂Cl₂ complex. The benzimidazole portions of both POB ligands are planar, the dihedral angle between them being 44.8 (3)°.

The oxazine rings are in essentially similar conformations with chiral centres at C(2) and C(18). In the POB ligand with chiral centre C(2) the phenyl substituent is in the pseudo-axial position resulting in *R* chirality, whereas in the other POB ligand this substituent is in the pseudo-equatorial position conferring *S* chirality on C(18) – see Fig. 1. This contrasts with the Ni(POB)₂Cl₂ compound where although both oxazine rings are still in similar conformations they now have identical configurations with the phenyl substituents pseudo-equatorial in both. Inspection of a model of the present complex demonstrates that intramolecular steric hindrance causes the oxazine ring and substituents to occupy the aforementioned conformations. An example of this is the phenyl group in POB 1 in the pseudo-axial position, which is very nearly

parallel [8.8 (6)°] to the NO₃ group 1 [N(1)O(1)–O(2)O(3)]; however, if it were in the pseudo-equatorial position as in POB 2 it would come into close contact with nitrate group 1. We can see that the close proximity of the two bulky POB ligands has caused significant conformational changes.

The complex crystallizes with one molecule of solvent, CH₃CN. The solvent molecule is not coordinated in any way and controlled heating at 330 K resulted in complete solvent removal. There are no unusual intermolecular contacts.

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The Structure of Bis[(*R,S*)-*N,N'*-bis(5-methyl-2-thienylmethylene)-1,2-cyclohexanediamine]copper(I) Trifluoromethanesulfonate, C₃₆H₄₄CuN₄S₄⁺.CF₃SO₃⁻

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Abstract. *M_r* = 873.65, monoclinic, *P*2₁/*c*, *a* = 13.948 (3), *b* = 19.338 (6), *c* = 19.811 (3) Å, β = 126.35 (2)°, *V* = 4304 (2) Å³, *Z* = 4, *D_m* = 1.347, *D_x* = 1.348 g cm⁻³, Cu *K*α, λ = 1.5418 Å, μ = 33.3 cm⁻¹, *F*(000) = 1816, *T* = 295 K, final *R* = 0.086 for 2985 unique observed reflections with *I* > 2.5σ(*I*).

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The crystal is twinned (63:37) on (100). The Cu^I in this 1:2 complex with an N₄S₄ donor set has a coordination sphere consisting of four nitrogen atoms and two sulfur atoms in a distorted octahedral arrangement. Only two of the nitrogen atoms show normal coordination geometry with Cu–N = 1.907 (9) and 1.92 (1) Å. The other two nitrogen atoms coordinate to Cu with the Cu significantly out of the C=N double-bond plane and with Cu–N = 2.25 (1) and 2.51 (1) Å. The two S atoms are at 2.960 (5) and 3.155 (5) Å with unfavorable bonding geometry.

Introduction. In the search for model compounds that can mimic one or more of the unusual specific physical and chemical properties of Cu^I-containing proteins we have investigated the coordination properties of Cu^I O₃SCF₃ with the neutral N₂S₂ ligand system (*R,S*)-1,2-(5-*R*-thiophene-2-CH=N)cyclohexane (*R* = H, CH₃) (van Stein, 1984). In this study we included the corresponding Ag^I complexes to obtain detailed information concerning the coordination properties of this polydentate system to the *Ib* metals in solution with NMR techniques. The N₂S₂ system produces both dinuclear [M₂(N₂S₂)₂](O₃SCF₃)₂ and mononuclear [M(N₂S₂)₂](O₃SCF₃) complexes with *M* = Cu^I, Ag^I. The synthesis, characterization, dynamic behavior in solution as studied by ¹H, INEPT ¹⁵N (van Stein, van Koten, Vrieze, Brevard & Spek, 1984) and INEPT ¹⁰⁹Ag (van Stein, van Koten, Vrieze, Brevard & Spek, 1984; Brevard, van Stein & van Koten, 1981) NMR spectroscopy of these complexes as well as the X-ray crystal and molecular structures of the dinuclear complex [Ag₂(N₂S₂)₂](O₃SCF₃)₂ (5-*R* = H) (van Stein, van Koten, Blank, Taylor, Vrieze, Spek, Duisenberg, Schreurs & Kojić-Prodić, 1984) and the mononuclear complex [Ag(N₂S₂)₂](O₃SCF₃) (van Stein, van Koten, Vrieze, Spek, Klop & Brevard, 1985) have been reported in separate papers. In order to test the validity of the assumption that Cu^I can be replaced by Ag^I with retention of the structural features an X-ray structure determination has been carried out on the mononuclear Cu^I complex [Cu(N₂S₂)₂](O₃SCF₃) (5-*R* = CH₃). A further aspect of the latter complex is the presence of eight potential donor atoms that can coordinate to the metal *Ib* center. The present Cu^I structure allows a comparison of the extent of interaction of these donor sites in the respective Cu^I and Ag^I complexes. The results of this study have been published in a preliminary form (van Stein, van Koten, Spek, Duisenberg & Klop, 1983; van Stein, van Koten, Spek & Klop, 1983).

Experimental. All crystals of the batch showed external twinning signs. Block-shaped (0.22 × 0.32 × 0.32 mm) brown specimen mounted on glass fiber. Data collected on Enraf–Nonius CAD-4F diffractometer, Ni-filtered Cu *K*α radiation. Nature of twinning analyzed from

setting angles of 25 reflections found by automatic search program. The twin lattice consists of a superposition (rotated over 180° about **a***) of two monoclinic lattices with the observed reflections fitting in at least one of them. The twin lattice has orthorhombic symmetry of index 6, *i.e.* one out of the six reflections coincides with (non-)equivalent reflections (*h, k, 6l* of lattice *A* with *h + 5l, k, 6l* of lattice *B*). Twin ratio determined as 63:37 from comparison of intensities of equivalent resolved reflections. Unit-cell dimensions from least-squares treatment of setting angles of 25 reflections (9.5 < θ < 19.7°). *D_m* by flotation in 1,2-dibromoethane – *n*-heptane. Intensity data collected for major crystal component (ω/2θ scan; 0.1 < θ < 50°; *h* 0→13, *k* 0→19, *l* –19→19; 4411 reflections). Reference reflection 002 showed only statistical fluctuations. Data corrected for twinning overlap, Lorentz–polarization and absorption (Gaussian, corrections from 1.937 to 2.648). Unique set of 2986 reflections with *I* > 2.5σ(*I*) used in structure determination (Patterson and Fourier methods) and refinement by blocked full-matrix least squares on *F* with unit weights (*SHELX76*; Sheldrick, 1976). Hydrogen atoms introduced at calculated positions and refined in riding mode on carrier atom with one overall isotropic temperature factor. All non-hydrogen atoms refined with anisotropic thermal parameters. Convergence at *R* = 0.086 [*wR* = 0.090; *S* = 3.5; (Δ/σ)_{max} = 0.6; 2985 reflections; 479 parameters]. One reflection (020) left out of final refinement cycles (extinction suspected). Max. residual density 0.68 e Å^{–3} in region of probably somewhat disordered anion. Min. residual density –0.43 e Å^{–3}. Scattering factors from Cromer & Mann (1968); anomalous dispersion from Cromer & Liberman (1970). Calculations carried out on either the Cyber-175 of the University of Utrecht with programs of *EUCLID* (geometry calculations and illustrations) (Spek, 1982) or on the in-house Eclipse S/230 mini-computer with a locally modified version of *SHELX76*.†

Discussion. Final atomic parameters are given in Table 1.

The monoclinic unit cell contains four O₃SCF₃ anions and four [Cu(N₂S₂)₂] cations (Fig. 1). The geometry of the cation with the adopted numbering is shown in Fig. 2. The complex exhibits approximate twofold axial symmetry along the bisector of the S(1)–Cu(1)–S(3) angle, being roughly parallel with **c***. Bond distances and angles for the non-hydrogen atoms are given in Table 2. The two independent cyclohexane

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond lengths and angles involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39898 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
Cu(1)	0.1462 (1)	-0.1870 (1)	0.2742 (1)	0.0725 (6)
S(1)	0.3322 (3)	-0.2484 (2)	0.4390 (2)	0.106 (1)
S(2)	-0.1233 (4)	-0.0488 (2)	0.1473 (3)	0.125 (2)
S(3)	0.2307 (3)	-0.0650 (2)	0.4037 (2)	0.080 (1)
S(4)	0.2677 (4)	-0.3369 (3)	0.2289 (3)	0.133 (2)
S(5)	0.7369 (5)	-0.3001 (4)	0.8756 (4)	0.155 (2)
F(1)	0.601 (1)	-0.3964 (9)	0.792 (1)	0.254 (3)
F(2)	0.780 (1)	-0.4213 (9)	0.857 (1)	0.259 (3)
F(3)	0.696 (1)	-0.3575 (9)	0.7486 (8)	0.245 (3)
O(1)	0.737 (1)	-0.3122 (7)	0.9461 (6)	0.155 (3)
O(2)	0.851 (1)	-0.275 (1)	0.902 (1)	0.242 (4)
O(3)	0.639 (2)	-0.252 (1)	0.817 (1)	0.291 (3)
N(1)	0.2890 (7)	-0.1669 (5)	0.2856 (5)	0.065 (3)
N(2)	0.0638 (8)	-0.1209 (5)	0.1413 (5)	0.075 (3)
N(3)	0.0382 (7)	-0.1841 (5)	0.3041 (5)	0.066 (3)
N(4)	0.0363 (8)	-0.2808 (5)	0.2022 (6)	0.074 (3)
C(1)	0.414 (1)	-0.313 (1)	0.587 (1)	0.175 (3)
C(2)	0.442 (1)	-0.2806 (8)	0.5325 (9)	0.119 (3)
C(3)	0.550 (1)	-0.2757 (8)	0.5491 (9)	0.119 (3)
C(4)	0.542 (1)	-0.2414 (7)	0.4825 (8)	0.087 (3)
C(5)	0.430 (1)	-0.2226 (6)	0.4193 (8)	0.076 (3)
C(6)	0.3966 (9)	-0.1867 (6)	0.3453 (7)	0.069 (3)
C(7)	0.279 (1)	-0.1263 (6)	0.2181 (7)	0.071 (3)
C(8)	0.296 (1)	-0.0503 (7)	0.2404 (8)	0.091 (3)
C(9)	0.284 (1)	-0.0078 (8)	0.1694 (8)	0.113 (3)
C(10)	0.167 (1)	-0.0203 (8)	0.0867 (8)	0.106 (3)
C(11)	0.153 (1)	-0.0951 (8)	0.0672 (7)	0.099 (3)
C(12)	0.155 (1)	-0.1410 (7)	0.1320 (7)	0.081 (3)
C(13)	-0.039 (1)	-0.1304 (6)	0.0806 (7)	0.082 (3)
C(14)	-0.139 (1)	-0.1037 (7)	0.0776 (9)	0.098 (3)
C(15)	-0.257 (1)	-0.1131 (9)	0.014 (1)	0.137 (3)
C(16)	-0.325 (2)	-0.077 (1)	0.026 (1)	0.166 (3)
C(17)	-0.278 (2)	-0.038 (1)	0.090 (1)	0.149 (3)
C(18)	-0.318 (2)	0.007 (1)	0.127 (1)	0.230 (3)
C(19)	0.371 (1)	0.0470 (7)	0.5034 (9)	0.113 (3)
C(20)	0.259 (1)	0.0073 (6)	0.4631 (8)	0.087 (3)
C(21)	0.164 (1)	0.0214 (7)	0.4623 (8)	0.091 (3)
C(22)	0.072 (1)	-0.0261 (7)	0.4194 (8)	0.087 (3)
C(23)	0.095 (1)	-0.0768 (6)	0.3839 (7)	0.076 (3)
C(24)	0.023 (1)	-0.1360 (6)	0.3418 (7)	0.075 (3)
C(25)	-0.0427 (9)	-0.2440 (6)	0.2780 (7)	0.066 (3)
C(26)	0.017 (1)	-0.2994 (7)	0.3417 (7)	0.085 (3)
C(27)	-0.060 (1)	-0.3656 (7)	0.3154 (7)	0.090 (3)
C(28)	-0.093 (1)	-0.3902 (6)	0.2310 (8)	0.095 (3)
C(29)	-0.154 (1)	-0.3336 (6)	0.1657 (7)	0.083 (3)
C(30)	-0.0767 (9)	-0.2688 (6)	0.1918 (7)	0.072 (3)
C(31)	0.030 (1)	-0.3086 (7)	0.1406 (8)	0.088 (3)
C(32)	0.128 (1)	-0.3293 (7)	0.1415 (9)	0.089 (3)
C(33)	0.137 (1)	-0.3422 (9)	0.0786 (9)	0.113 (3)
C(34)	0.230 (2)	-0.362 (1)	0.094 (1)	0.154 (3)
C(35)	0.321 (1)	-0.3625 (9)	0.174 (1)	0.135 (3)
C(36)	0.442 (2)	-0.381 (1)	0.214 (1)	0.200 (3)
C(37)	0.709 (2)	-0.360 (1)	0.825 (1)	0.186 (4)

the Cu atoms significantly out of the C=N plane. The coordination geometry of Cu with the four nitrogen atoms may be described as distorted trigonal pyramidal

Table 2. Bond distances (Å) and angles (°) for the non-hydrogen atoms

Cu(1)–N(1)	1.907 (9)	C(8)–C(9)	1.55 (2)
Cu(1)–N(2)	2.51 (1)	C(9)–C(10)	1.50 (2)
Cu(1)–N(3)	1.92 (1)	C(10)–C(11)	1.48 (2)
Cu(1)–N(4)	2.25 (1)	C(11)–C(12)	1.55 (2)
S(1)–C(2)	1.67 (2)	C(13)–C(14)	1.46 (2)
S(1)–C(5)	1.70 (2)	C(14)–C(15)	1.37 (2)
S(2)–C(14)	1.65 (2)	C(15)–C(16)	1.31 (3)
S(2)–C(17)	1.76 (2)	C(16)–C(17)	1.27 (3)
S(3)–C(20)	1.72 (1)	C(17)–C(18)	1.45 (3)
S(3)–C(23)	1.71 (1)	C(19)–C(20)	1.48 (2)
S(4)–C(32)	1.68 (1)	C(20)–C(21)	1.34 (2)
S(4)–C(35)	1.71 (2)	C(21)–C(22)	1.39 (2)
N(1)–C(6)	1.30 (1)	C(22)–C(23)	1.35 (2)
N(1)–C(7)	1.48 (2)	C(23)–C(24)	1.42 (2)
N(2)–C(12)	1.44 (2)	C(25)–C(26)	1.48 (2)
N(2)–C(13)	1.22 (1)	C(25)–C(30)	1.55 (2)
N(3)–C(24)	1.29 (2)	C(26)–C(27)	1.55 (2)
N(3)–C(25)	1.48 (1)	C(27)–C(28)	1.52 (2)
N(4)–C(30)	1.48 (2)	C(28)–C(29)	1.51 (2)
N(4)–C(31)	1.29 (2)	C(29)–C(30)	1.53 (2)
C(1)–C(2)	1.49 (3)	C(31)–C(32)	1.41 (2)
C(2)–C(3)	1.34 (2)	C(32)–C(33)	1.35 (3)
C(3)–C(4)	1.42 (3)	C(33)–C(34)	1.21 (3)
C(4)–C(5)	1.35 (2)	C(34)–C(35)	1.32 (3)
C(5)–C(6)	1.43 (2)	C(35)–C(36)	1.42 (3)
C(7)–C(8)	1.51 (2)	S(5)–C(37)	1.43 (2)
C(7)–C(12)	1.58 (2)	F(1)–C(37)	1.42 (3)
S(5)–O(1)	1.42 (2)	F(2)–C(37)	1.43 (3)
S(5)–O(2)	1.43 (1)	F(3)–C(37)	1.41 (3)
S(5)–O(3)	1.48 (2)		
N(1)–Cu(1)–N(2)	79.5 (4)	N(2)–C(12)–C(11)	112 (1)
N(1)–Cu(1)–N(3)	156.0 (4)	C(7)–C(12)–C(11)	105 (1)
N(1)–Cu(1)–N(4)	120.6 (4)	N(2)–C(13)–C(14)	122 (1)
N(2)–Cu(1)–N(3)	110.7 (4)	S(2)–C(14)–C(13)	123 (1)
N(2)–Cu(1)–N(4)	91.7 (4)	S(2)–C(14)–C(15)	110 (1)
N(3)–Cu(1)–N(4)	81.7 (4)	C(13)–C(14)–C(15)	126 (2)
C(2)–S(1)–C(5)	91.8 (7)	C(14)–C(15)–C(16)	112 (2)
C(14)–S(2)–C(17)	91.9 (9)	C(15)–C(16)–C(17)	120 (2)
C(20)–S(3)–C(23)	92.3 (7)	S(2)–C(17)–C(16)	106 (2)
C(32)–S(4)–C(35)	92.6 (8)	S(2)–C(17)–C(18)	116 (2)
Cu(1)–N(1)–C(6)	127 (1)	C(16)–C(17)–C(18)	137 (2)
Cu(1)–N(1)–C(7)	117.9 (7)	S(3)–C(20)–C(19)	122 (1)
C(6)–N(1)–C(7)	115 (1)	S(3)–C(20)–C(21)	109.4 (9)
Cu(1)–N(2)–C(12)	96.1 (7)	C(19)–C(20)–C(21)	128 (1)
Cu(1)–N(2)–C(13)	119.8 (9)	C(20)–C(21)–C(22)	115 (1)
C(12)–N(2)–C(13)	116 (1)	C(21)–C(22)–C(23)	112 (1)
Cu(1)–N(3)–C(24)	129.0 (8)	S(3)–C(23)–C(22)	110.9 (9)
Su(1)–N(3)–C(25)	116.4 (8)	S(3)–C(23)–C(24)	123 (1)
C(24)–N(3)–C(25)	115 (1)	C(22)–C(23)–C(24)	126 (1)
Cu(1)–N(4)–C(30)	103.3 (7)	N(3)–C(24)–C(23)	128 (1)
Cu(1)–N(4)–C(31)	125.0 (9)	N(3)–C(25)–C(26)	110.0 (9)
C(30)–N(4)–C(31)	118 (1)	N(3)–C(25)–C(30)	107 (1)
S(1)–C(2)–C(3)	119.9 (9)	C(26)–C(25)–C(30)	111 (1)
S(1)–C(2)–C(3)	114 (1)	C(25)–C(26)–C(27)	113 (1)
C(1)–C(2)–C(3)	126 (1)	C(26)–C(27)–C(28)	109 (1)
C(2)–C(3)–C(4)	110 (1)	C(27)–C(28)–C(29)	111 (1)
C(3)–C(4)–C(5)	113 (1)	C(28)–C(29)–C(30)	112 (1)
S(1)–C(5)–C(4)	111 (1)	N(4)–C(30)–C(25)	106.8 (9)
S(1)–C(5)–C(6)	124.1 (9)	N(4)–C(30)–C(29)	113 (1)
C(4)–C(5)–C(6)	125 (1)	C(25)–C(30)–C(29)	109 (1)
N(1)–C(6)–C(5)	125 (1)	N(4)–C(31)–C(32)	126 (1)
N(1)–C(7)–C(8)	110 (1)	S(4)–C(32)–C(31)	124 (1)
N(1)–C(7)–C(12)	110 (1)	S(4)–C(32)–C(33)	104 (1)
C(8)–C(7)–C(12)	112 (1)	C(31)–C(32)–C(33)	131 (1)
C(7)–C(8)–C(9)	110 (1)	C(32)–C(33)–C(34)	120 (2)
C(8)–C(9)–C(10)	112 (1)	C(33)–C(34)–C(35)	116 (2)
C(9)–C(10)–C(11)	109 (1)	S(4)–C(35)–C(34)	107 (1)
C(10)–C(11)–C(12)	114 (1)	S(4)–C(35)–C(36)	122 (2)
N(2)–C(12)–C(7)	107 (1)	C(34)–C(35)–C(36)	131 (2)
O(1)–S(5)–O(2)	110 (1)	F(1)–C(37)–F(2)	93 (1)
O(1)–S(5)–O(3)	110 (1)	F(1)–C(37)–F(3)	96 (2)
O(1)–S(5)–C(37)	114 (1)	S(5)–C(37)–F(1)	120 (2)
O(2)–S(5)–O(3)	112 (1)	F(2)–C(37)–F(3)	97 (2)
O(2)–S(5)–C(37)	108 (1)	S(5)–C(37)–F(2)	122 (2)
O(3)–S(5)–C(37)	103 (1)	S(5)–C(37)–F(3)	122 (2)

rings are both in the chair conformation with average torsion angle 57.6 (6)° for C(7)–C(12) and 56.8 (6)° for C(25)–C(30). Their two chemically equivalent side chains are in equatorial and axial positions respectively [torsion angles: N(1)–C(7)–C(12)–N(2) = 60 (1)°; N(3)–C(25)–C(30)–N(4) = 54 (1)°]. The thiophene rings are approximately coplanar with the C=N moiety [torsion angles: S(1)–C(5)–C(6)–N(1) = 3 (2); S(2)–C(14)–C(13)–N(2) = 10 (2); S(3)–C(23)–C(24)–N(3) = -9 (2); S(4)–C(32)–C(31)–N(4) = 14 (2)°].

Although the ligand system N₂S₂ is potentially quadridentate, only the nitrogen atom of the equatorial cyclohexane ring substituent has a normal coordination geometry [Cu(1)–N(1) = 1.907 (9); Cu(1)–N(3) = 1.92 (1) Å; N(1)–Cu(1)–N(3) = 156.0 (4)°] to Cu. The nitrogen atoms of the axial substituents of the two ligands have N...Cu = 2.25 (1) and 2.51 (1) Å with

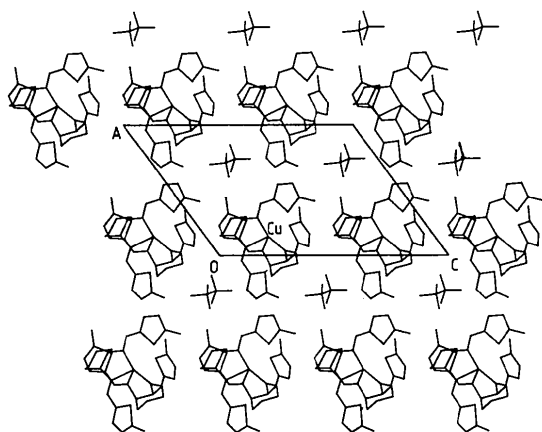


Fig. 1. Projection of part of the structure down the b axis of molecules related by the c -glide operation. A similar layer of molecules, generated by the 2_1 axis at $x = 0$, $z = \frac{1}{4}$, completes the structure.

[base N(1),N(3),N(4); apex N(2)]. The coordination sphere is completed with one thiophene S atom of each ligand: $\text{Cu}(1)\cdots\text{S}(1) = 2.960(5) \text{ \AA}$ and $\text{Cu}(1)\cdots\text{S}(3) = 3.155(5) \text{ \AA}$, resulting in a distorted octahedral N_4S_2 coordination. However, the $\text{Cu}\cdots\text{S}$ interaction is probably rather weak in view of the unfavorable coordination geometry and the large distance as compared to that found in other Cu^{I} complexes: e.g. $2.328(7)$, $2.324(8) \text{ \AA}$ (Drew, Cairns, McFall & Nelson, 1980).

The present structure is very similar to that of the corresponding Ag complex, which crystallizes in $P\bar{1}$ (van Stein, van Koten, Vrieze, Spek, Klop & Brevard, 1984). However, the detailed coordination geometry in the Ag complex is different, probably due to the larger radius of Ag.

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Guanidinium Tetraborate(2–) Dihydrate, $(\text{CH}_6\text{N}_3)_2[\text{B}_4\text{O}_5(\text{OH})_4]\cdot 2\text{H}_2\text{O}$

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Abstract. $M_r = 347.4$, triclinic, $P\bar{1}$, $a = 8.443(10)$, $b = 12.560(15)$, $c = 7.290(10) \text{ \AA}$, $\alpha = 106.76(5)$, $\beta = 103.87(6)$, $\gamma = 90.38(7)^\circ$, $V = 716.25 \text{ \AA}^3$, $Z = 2$,

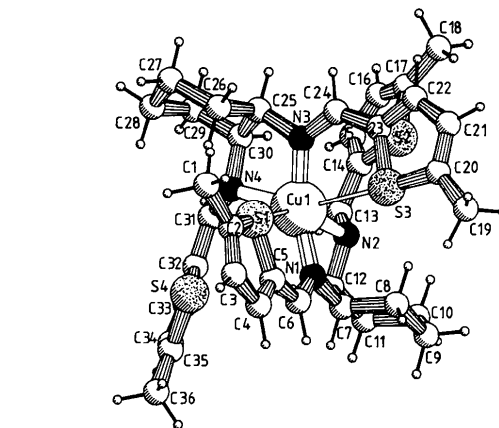


Fig. 2. Drawing of the cation showing the approximate twofold axial symmetry along the bisector of the angle $\text{S}(1)\text{--Cu}(1)\text{--S}(3)$ and the adopted numbering.

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