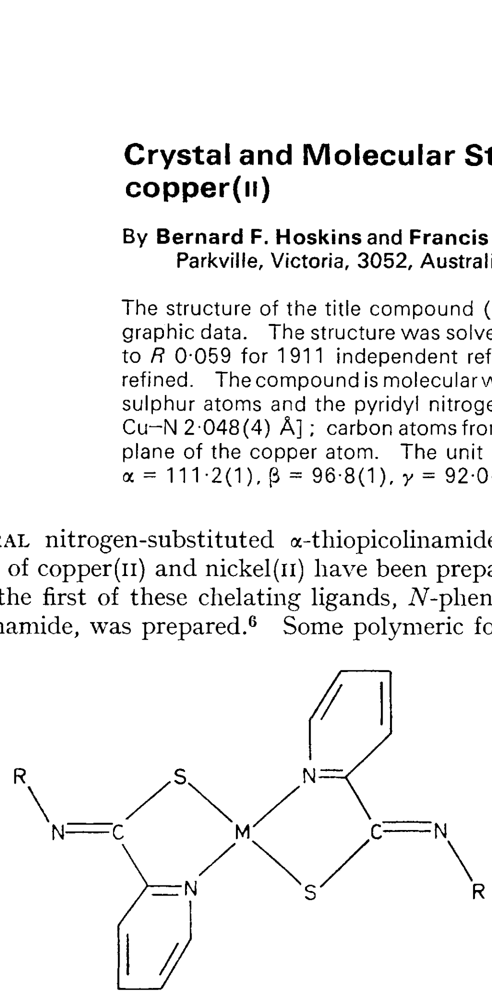
Crystal and Molecular Structure of Bis(*N*-cyclohexylthiopicolinamidato)-copper(II)

By **Bernard F. Hoskins** and **Francis D. Whillans**,*† Department of Inorganic Chemistry, University of Melbourne, Parkville, Victoria, 3052, Australia

The structure of the title compound (I) has been determined from single-crystal three-dimensional *X*-ray photographic data. The structure was solved by Patterson and Fourier methods, and refined by least-squares techniques to *R* 0·059 for 1911 independent reflections. All the hydrogen atoms were located and their parameters were refined. The compound is molecular with the copper atom bonding in a *trans*-square planar manner to the thioamido-sulphur atoms and the pyridyl nitrogen atoms of two *N*-cyclohexylthiopicolinamidato-chelates [Cu–S 2·252(2), Cu–N 2·048(4) Å]; carbon atoms from adjacent molecules are situated at 3·4 Å above and below the co-ordination plane of the copper atom. The unit cell is triclinic with $Z = 1$, $a = 5{\cdot}223(7)$, $b = 10{\cdot}600(4)$, $c = 11{\cdot}573(4)$ Å, $\alpha = 111{\cdot}2(1)$, $\beta = 96{\cdot}8(1)$, $\gamma = 92{\cdot}0(1)°$, space group $P\bar{1}$.

SEVERAL nitrogen-substituted α-thiopicolinamide complexes of copper(II) and nickel(II) have been prepared [1-5] since the first of these chelating ligands, *N*-phenylthiopicolinamide, was prepared.[6] Some polymeric forms of these metal complexes are thermally stable above 300 °C, and this has been attributed to the presence of some electron delocalisation.[2] Spectral evidence [3] has indicated that the *N*-alkylthiopicolinamide complexes of nickel(II) and copper(II) are *trans*-square-planar with the thioamido-sulphur and pyridyl nitrogen atoms of the chelate bonding to the metal atom as in (I). This formulation has been supported by further spectral investigations.[4,5,7] Some complexes involving this type of chelate, however, appear to be bonding to the metal atom *via* the thioamido-nitrogen rather than *via* the sulphur atom; this seems to occur if the chelate is unsubstituted and univalent, as in bis(thiopicolinamidato)-nickel(II),[3] or if the chelate is unsubstituted and molecular, as in the 2-thioamidopyridine complexes of copper-(II).[8] We now report details of the structure of (I), bis-(*N*-cyclohexylthiopicolinamidato)copper(II), by *X*-ray diffraction methods.[9]



(I) R = cyclohexyl, M = Cu^{II}

EXPERIMENTAL

Crystal Data.—$C_{24}H_{30}CuN_4S_2$, $M = 496$, Triclinic, $a = 5{\cdot}223(7)$, $b = 10{\cdot}600(4)$, $c = 11{\cdot}573(4)$ Å, $\alpha = 111{\cdot}2(1)$,

† *Present address:* Preston Institute of Technology, St. Georges Road, Preston, Victoria, 3072, Australia.

1 F. Lions and K. V. Martin, *J. Amer. Chem. Soc.*, 1958, **80**, 1591.
2 K. V. Martin, *J. Amer. Chem. Soc.*, 1958, **80**, 233.
3 R. W. Kluiber, *Inorg. Chem.*, 1965, **4**, 829, 1047.
4 G. V. Glazneva, E. K. Mamaeva, and A. P. Zeif, *Zhur. obschei Khim.*, 1966, **36** (8), 1499 (*Chem. Abs.*, 1967, **66**, 18652*m*).
5 W. W. Fee and J. D. Pulsford, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 227.
6 H. D. Porter, *J. Amer. Chem. Soc.*, 1954, **76**, 127.
7 I. V. Miroshnichenko, G. M. Larin, and E. G. Rukhadze, *Teor. i. eksp. Khim.*, 1966, **2** (3), 409 (*Chem. Abs.*, 1967, **66**, 24301*n*).
8 G. J. Sutton, *Austral. J. Chem.*, 1964, **17**, 1360; 1966, **19**, 2059.
9 B. F. Hoskins and F. D. Whillans, *Inorg. Nuclear Chem. Letters*, 1970, **6**, 85.

$\beta = 96{\cdot}8(1)$, $\gamma = 92{\cdot}0(1)°$, $U = 591$ Å^3. $D_m = 1{\cdot}391(3)$, $Z = 1$, $D_c = 1{\cdot}393$ g cm^{-3}, $F(000) = 263$. Space group $P\bar{1}$ (C_i^1; No. 2). Cu-$K_{\bar{\alpha}}$ radiation, $\lambda = 1{\cdot}5418$ Å, $\mu = 29{\cdot}63$ cm^{-1}. Single-crystal precession, oscillation, and equi-inclination Weissenberg photographs; empirical absorption and secondary extinction corrections applied.

The bronze-red crystals were needles (along the *a* axis) with a hexagonal cross-section. The space group was determined from preliminary cone axis and precession photographs; unit-cell dimensions were determined by least-squares methods from twenty-six high-angle K_{α_1} and K_{α_2} reflections observed in calibrated zero-level equi-inclination Weissenberg photographs taken about each of the three axes.

Data Collection and Reduction.—Equi-inclination Weissenberg photographs of the 0—4*kl*, *h*0—2*l*, and *hk*0—3 layers were collected by use of the multiple-film technique. For the *nkl* layers a needle crystal $0{\cdot}93 \times 0{\cdot}13 \times 0{\cdot}17$ mm was used and for the other layers a crystal $0{\cdot}37 \times 0{\cdot}30 \times 0{\cdot}25$ mm. [Absorption corrections for upper-level equi-inclination Weissenberg reflections from a completely irradiated, cylindrical, crystal are less prone to error if the cylinder length to diameter ratio is large.[10]] The intensities of all visually observed reflections were used as input to a computer programme [11] (which made corrections for Lorentz, polarisation, absorption, and secondary extinction effects and which scaled, sorted, and weighted the resulting data); equivalent terms were averaged to give 1911 independent observations. During the structure determination this programme was rerun in order to provide an improved interlayer scaling, to weight the structure amplitudes more appropriately, and to correct the intensity data for secondary extinction.

The absorption correction was interpolated from values given by Bond [12] for a cylinder (*nkl* layers, μR 0·22) and for a sphere (*hnl* and *hkn* layers, μR 0·48). The interlayer scaling was based upon a least-squares method in which the term $\Sigma w_{ij}(k_j J_{ji} - k_i J_{ij})^2$ [this expression, without the weight w_{ij}, has been recommended by Dickerson [13]] was minimised where w_{ij} is the number of common reflections observed in the layers *i* and *j*, k_i is the scale factor for layer *i*, and J_{ij} is the sum of $|F_o|$ for reflections in layer *i* which were observed in layer *j*. The Zachariasen correction for secondary extinction [14] was applied owing to the considerable diminution of intensity observed for high-intensity reflections; the empirical constant, *c*, in Zachariasen's expression was assigned a value of $3{\cdot}5 \times 10^{-5}$. The weight, *w*, assigned to each unique reflection was $w = n/(0{\cdot}4 - 0{\cdot}033|F_o| + 0{\cdot}006|F_o|^2)$ for $|F_o| < 30$ and $w = n/(6|F_o| - 168)$ for $|F_o| \geqslant 30$, where *n* is the number of axes about which the reflection had been observed.

Structure Determination and Refinement.—Since $Z = 1$, the copper atom was assigned to a centre of symmetry. The positions of all non-hydrogen atoms were located from a three-dimensional Patterson synthesis. After their positional and individual isotropic thermal parameters had been refined initially from difference syntheses, refinement was continued by minimising $\Sigma w(|F_o| - |F_c|)^2$ by least squares using the computer programme ORFLS.[15] After some refinement these atoms were assigned individual anisotropic thermal factors.

All hydrogen atoms were located without difficulty from a subsequent difference synthesis; their positional parameters and isotropic temperature factors were refined using a block-diagonal least-squares procedure.[16] Both the convergence of the parameters of the hydrogen atoms and the observation-to-parameter ratio of 9·5 : 1 justified the inclusion of hydrogen atoms in the refinement.

When empirical secondary extinction corrections and improvements to the interlayer scaling were applied to the data late in the refinement process *R* dropped from 0·087 to 0·059 and *R'* was 0·073.* All positional and thermal parameters converged in the refinement; no shift in a parameter was $> 0{\cdot}05\ \sigma$.

Scattering factor curves used were for divalent copper ion and for neutral sulphur, carbon, and nitrogen atoms; [17a] those for copper and sulphur were corrected for the effects of anomalous dispersion.[17a] The curve used for the hydrogen atoms was that calculated [18] for a bonded atom.

TABLE 1

Final fractional co-ordinates

Atom	$10^4\ x/a$	$10^4\ y/b$	$10^4\ z/c$
Cu	5000(0)	5000(0)	5000(0)
S	6227(2)	4614(1)	6766(1)
N(1)	2022(5)	3549(3)	4668(3)
C(1)	−5(7)	3284(4)	3747(3)
C(2)	−1929(7)	2263(4)	3507(4)
C(3)	−1815(7)	1473(4)	4230(4)
C(4)	214(7)	1755(3)	5189(3)
C(5)	2085(6)	2789(3)	5387(3)
C(6)	4311(6)	3093(3)	6416(3)
N(2)	4595(5)	2214(3)	6918(3)
C(7)	6783(6)	2387(3)	7888(3)
C(8)	7295(7)	998(3)	7927(3)
C(9)	9533(9)	1093(4)	8927(4)
C(10)	9049(11)	2062(5)	1 0200(4)
C(11)	8512(9)	3463(4)	1 0187(4)
C(12)	6285(7)	3359(4)	9172(3)
Atom	$10^3\ x/a$	$10^3\ y/b$	$10^3\ z/c$
H(1)	1(7)	394(4)	321(4)
H(2)	−377(10)	210(6)	275(5)
H(3)	−319(7)	66(4)	396(4)
H(4)	38(6)	131(4)	574(3)
H(5)	829(6)	280(4)	774(3)
H(6)	774(7)	29(4)	709(4)
H(7)	570(7)	53(4)	814(3)
H(8)	1 127(10)	137(6)	863(5)
H(9)	961(7)	13(4)	906(4)
H(10)	737(6)	169(3)	1 037(3)
H(11)	993(10)	210(6)	1 093(5)
H(12)	1 016(9)	395(5)	1 005(5)
H(13)	791(6)	398(4)	1 100(4)
H(14)	484(6)	298(3)	943(3)
H(15)	615(7)	431(4)	902(3)

In the difference synthesis calculated after the final cycle of refinement, three peaks (0·50, 0·43, 0·40; 0·45, 0·46, 0·40; and 0·58, 0·40, 0·40) with electron-density differences between 0·6 and 0·7 e$^-$ Å^{-3} were found *ca.* 1·2 Å from the copper atom, indicating an inadequate description of the

* $R' = \Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega(|F_o|)^2$.

[10] C. W. Burnham, *Amer. Mineral.*, 1966, **51**, 159.
[11] F. D. Whillans, Ph.D. thesis, University of Melbourne, 1971.
[12] 'International Tables for *X*-Ray Crystallography,' vol. II, Kynoch Press, Birmingham, 1967, Tables 5.3.5B and 5.3.6B.
[13] R. E. Dickerson, *Acta Cryst.*, 1959, **12**, 610.
[14] W. H. Zachariasen, *Acta Cryst.*, 1963, **16**, 1139.
[15] W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory Report ORNL TM 305, Oak Ridge, Tennessee, 1962.
[16] F. R. Ahmed, Report NRC 10, Division of Pure Physics, National Research Council, Ottawa, 1966.
[17] Ref. 12, vol. III, 1962, (*a*) pp. 202—7, 214; (*b*) pp. 273—6.
[18] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

copper atom. At the position of the sulphur atom the electron-density difference was at a minimum ($-0.60\,e^- Å^{-3}$); because the chelate was anionic the conversion to a scattering curve for a positive sulphur ion was felt to be unjustified. No other peaks had an electron density difference $>0.47\,e^- Å^{-3}$.

Final calculated structure factors and observed structure amplitudes are listed in Supplementary Publication No. SUP 21060 (7 pp.),* together with all thermal data; this data includes anisotropic temperature factors for non-hydrogen atoms, isotropic temperature factors for hydrogen atoms, the root-mean-square components of the thermal displacement of the non-hydrogen atoms along the principal axes of their respective thermal ellipsoids, and also in the direction of any bonds, and the angles between each of the principal axes of these ellipsoids and an approximately orthogonal set of axes based upon the co-ordination sphere of the copper atom. Final fractional co-ordinates for the atoms are in Table 1.

RESULTS AND DISCUSSION

Intermolecular Structure.—The crystals are composed of discrete monomeric molecules (Figure 1). Because each

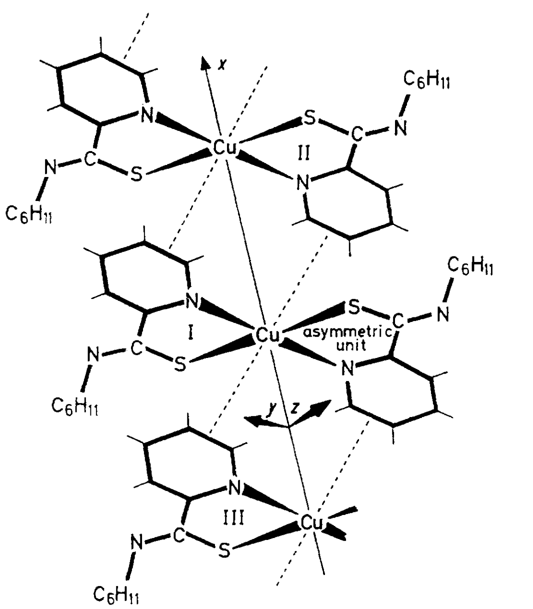


FIGURE 1 The stacking of the molecules along the *a* axis. Contacts between atoms of different chelates are given in Table 3, where Roman numeral superscripts are defined

unit cell of the crystal contains one molecule only, the shortest distance between the copper atoms of adjacent molecules is the unit-cell length *a* (5·22 Å). For efficient packing these molecules are stacked along the *a* axis in a slanting fashion with the normal of the co-ordination plane of the copper atom making angles of 49, 126, and 109° with the *a*, *b*, and *c* axes respectively [see plane (1), Table 2]. This stacking places carbon atoms [C(1) and C(2)] of one of the chelates of each of the two adjacent molecules, and their attached hydrogen atoms [H(1) and H(2)], very close to the normal of the co-ordination plane passing through the copper atom of the asymmetric unit (Figure 1).

All unique intra- and inter-molecular non-bonding contacts are listed in Table 3. Two axial copper–carbon

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TABLE 2

Equations of mean planes in the form $lX + mY + nZ + d = 0$,* and in square brackets, distances (Å × 10^3) of relevant atoms from the planes

	l	m	n	d	χ^2
Plane (1)					
Cu, S, N(1)	0·6620	−0·5655	−0·4918	3·2716	0
Plane (2):					
Cu, N(1), C(5), C(6), S	0·7171	−0·5062	−0·4791	2·9194	10300
[Cu 0, N(1) −167, C(5) −1, C(6) 255, S −22]					
Plane (3)					
Cu N(1), C(1)—(6) S, N(2)	0·6866	−0·5027	−0·5252	3·2088	77000
[Cu, 0, N(1) −110, C(1) −282, C(2) −297, C(3) −134, C(4) 12, C(5) 18, C(6) 192, S −124, N(2) 562, C(7) 820, H(1) −404, H(2) −529, H(3) −58, H(4) 75]					
Plane (4)					
N(1), C(1)—(5)	0·6364	−0·4449	−0·6302	3·7620	27
[N(1) 8, C(1) −8, C(2) −5, C(3) 11, C(4) −3, C(5) −6, Cu 90, H(1) −19, H(2) −101, H(3) 106, H(4) −43]					
Plane (5)					
S, C(5), C(6), N(2)	0·6965	−0·2519	−0·6719	3·8653	2·6
[S 0, C(5) 1, C(6) −5, N(2) 1, Cu 689, C(7) 62]					

* Where X, Y, and Z are orthogonal co-ordinates related to the fractional co-ordinates by: $X = x + y\cos\gamma + z\cos\beta$, $Y = y\sin\gamma + z(\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma$, and $Z = z\{\sin^2\beta - [(\cos\alpha - \cos\beta\cos\gamma)/\sin\gamma]^2\}^{\frac{1}{2}}$.

TABLE 3

Intra- and inter-molecular contacts (Å) <3·5 Å for non-hydrogen atoms and <3·25 Å for those involving hydrogen

(*a*) Intramolecular contacts			
S ··· N(1)	2·929	S ··· H(1^{I})	2·44
S ··· N(1^{I})	3·155	S ··· H(5)	2·75
N(2) ··· H(4)	2·42	C(8) ··· C(11)	2·936
C(7) ··· H(4)	3·80	C(9) ··· C(12)	2·938
C(7) ··· C(10)	2·937		
H(6) ··· H(7)	1·66	H(12) ··· H(13)	1·68
H(8) ··· H(9)	1·80	H(14) ··· H(15)	1·81
H(10) ··· H(11)	1·38		
(*b*) Intermolecular contacts			
Cu ··· C(1^{II})	3·396	Cu ··· H(1^{II})	3·497
Cu ··· C(2^{II})	3·366	Cu ··· H(2^{II})	3·376
C(6) ··· C(3^{II})	3·43	C(1) ··· N(1^{III})	3·46
C(7) ··· H(4^{II})	3·20	C(3) ··· H(6^{V})	3·05
C(9) ··· H(14^{II})	3·21	C(4) ··· H(6^{V})	3·07
H(5) ··· C(4^{II})	3·06	C(3) ··· H(4^{VI})	3·08
H(8) ··· N(2^{II})	3·11	C(3) ··· H(7^{VI})	3·21
H(8) ··· C(12^{II})	3·14	C(4) ··· H(4^{VI})	3·02
H(1) ··· N(1^{III})	3·21	N(2) ··· H(3^{VI})	2·88
H(11) ··· C(1^{IV})	3·03	C(8) ··· H(3^{VI})	2·88
H(11) ··· C(2^{IV})	3·18		

Roman numeral superscripts denote the following transformations:

I $1 - x, +1 - y, 1 - z$	II $1 + x, y, z$
III $-x, 1 - y, 1 - z$	IV $1 + x, y, 1 + z$
V $1 - x, -y, 1 - z$	VI $-x, -y, 1 - z$

contacts [Cu · · · C(1^{II}) 3·396(6) and Cu · · · C(2^{II}) 3·366(5) Å] indicate some interaction, since as they are *ca.* 0·5 Å shorter than the calculated van der Waals distance [19] of 3·9 Å (assuming a copper radius of 1·5 Å normal to the co-ordination plane); this is consistent with the considerable development of the crystals along the *a* direction. While these contacts are similar to those (3·37 and 3·39 Å) observed [20] in square-planar bis-(*N*-2-hydroxyethylsalicylaldimino)copper(II) and those (3·38 and 3·49 Å) [21] in square-planar anhydrous *NN'*-ethylenebis(acetylacetoneiminato)copper(II), they are longer than those [22] in bis(acetylacetonato)copper(II) (2·84 Å) and bis(ethylacetylacetonato)copper(II) (3·10 Å).

Intramolecular Structure.—The copper atom is bonded in a *trans*-manner to two chelating ligands *via* the thioamido-sulphur atoms and the pyridyl-nitrogen atoms (Figure 2); the copper atom and its four donor atoms are

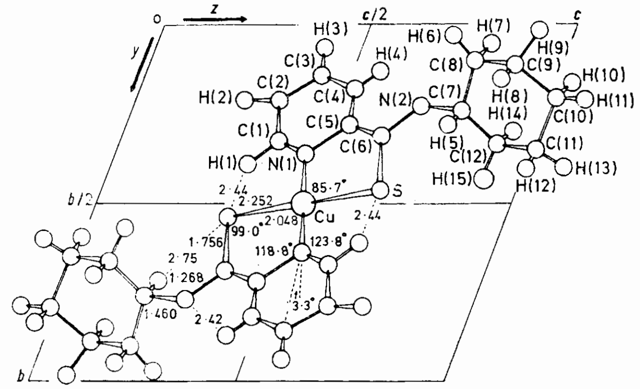

FIGURE 2 The molecule viewed along the *a* axis of the unit cell. Important dimensions are given in Å and degrees. The atoms of one chelate are related to those of the other chelate by the symmetry transformation: $1 - x$, $1 - y$, $1 - z$

exactly coplanar, a restriction imposed by the crystal symmetry.

The nine non-hydrogen atoms of the thioamido-[S,C(5), C(6), N(2)] and pyridyl [N(1), C(1)—(5)] moieties of each ligand are significantly non-coplanar; the substantial deviations from the mean plane of 0·28 and 0·30 Å for the carbon atoms [C(1) and C(2)] and the even greater deviations of 0·4 and 0·5 Å for their attached hydrogen atoms [H(1) and H(2)] towards the copper atom in the adjacent molecule provide further evidence for an intermolecular interaction [see plane (3) Table 2]. Further, it appears as though the thioamido-moiety is twisted about the single bond [C(5)–C(6)] with respect to the pyridyl ring so that the dihedral angle between these two planes is 11·9° [see planes (4) and (5) Table 2]. This twist is apparently caused by intrachelate [H(4) · · · N(2) 2·42 Å] and intramolecular [S · · · H(1^{I}) 2·44 Å] contacts, which are less than calculated van der Waals distances [19] by *ca.* 0·2 and 0·5 Å. The carbon atom of the N(2)–C(7) bond is bent away from the pyridyl moiety in order to prevent a close contact with hydrogen H(4), and deviates only 0·06 Å from the plane of the thioamido-moiety. The resulting contact S · · · H(5), between the sulphur atom and the hydrogen atom attached to C(7), is *ca.* 0·15 Å shorter than the calculated van der Waals contact.[19] It is likely that this conformation results in minimal repulsion, in view of the presence of approximately planar molecules above and below the asymmetric unit.

The five-membered chelate ring [Cu,N(1),C(5),C(6), and S] is significantly non-coplanar with a maximum deviation of 0·25 Å [plane (2) Table 2]. While the Cu–S distance [2·252(2) Å] is significantly shorter than the mean (2·32 Å) reported for the Cu–S bonds in the square pyramidal bis(*NN*-di-R-dithiocarbamato)copper(II) compounds [R = Et [23] or Pr^{n} (ref. 24)], it agrees favourably with that (2·26—2·27 Å) in 2-keto-3-ethoxybutyraldehydebis(thiosemicarbazone)copper(II), Cu(kts),[25] a square-planar complex with two sulphur and two nitrogen atoms in a square plane about the copper atom. The extent of Cu–S double bonding in these compounds is difficult to gauge as an unusually short Cu–S distance of 1·85 Å has been reported [26] for bis-(dithizonato)copper(II). While the S–C(6) distance [1·756(4) Å] is shorter than the paraffinic carbon to sulphur distance (1·81 Å [27]), it is longer than those (*ca.* 1·71 Å) in the thiourea molecule [27] and the trithiocarbonate ion; [28] one estimate [29] of a sulphur–carbon double-bond distance is 1·61 Å. The Cu–N(1) distance [2·048(4) Å] is considered to be a little longer than is usually found for this type of bond, *e.g.* Cu–N 1·97—1·98 Å in Cu(kts).[25] This bond lengthening seems to arise from a steric crowding of the two chelates about the copper atom; note the S · · · H(1^{I}) contact in Figure 2.

There are two different C–N bond distances in the thioamido-moiety: N(2)–C(7) 1·460(4) Å does not differ significantly from the 1·472 Å given for a C–N single-bond,[27] but N(2)–C(6) 1·268(4) Å is indicative of a double bond. A smooth curve through the points 1·475, 1·345, and 1·158 Å for the lengths of carbon–nitrogen single, aromatic, and triple bonds [17b,27] suggests a double-bond length of 1·26 Å, a value close to that of 1·27 Å found in dimethylglyoxime.[27]

The cyclohexyl substituent has a chair conformation. The lack of significant distortion of this conformation is indicated both by the three carbon to opposite-carbon

[19] L. Pauling, in 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1963, pp. 228—9, 260—3.
[20] E. R. Boyco, *Acta Cryst.*, 1963, **A16**, 64.
[21] D. Hall, A. D. Rae, and T. N. Waters, *J. Chem. Soc.*, 1963, 5897; *Proc. Chem. Soc.*, 1962, **143**; D. Hall, A. J. McKinnon, J. M. Waters, and T. N. Waters, *Nature*, 1964, **201**, 607; D. Hall, H. J. Morgan, and T. N. Waters, *J. Chem. Soc. (A)*, 1966, 677.
[22] G. A. Barclay and A. Cooper, *J. Chem. Soc.*, 1965, 3746.
[23] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 886; B. H. O'Connor and E. N. Maslen, *Acta Cryst.*, 1966, **21**, 828.
[24] A. Pignedoli and G. Peyronel, *Gazzetta*, 1962, **92**, 745.
[25] M. R. Taylor, E. J. Gabe, J. P. Glusker, J. A. Minkin, and A. L. Patterson, *J. Amer. Chem. Soc.*, 1966, **88**, 1845; W. E. Blumberg and J. Peisach, *J. Chem. Phys.*, 1968, **49**, 1793.
[26] R. F. Bryan and P. M. Knopf, *Proc. Chem. Soc.*, 1961, 203.
[27] *Chem. Soc. Special Publ.*, No. 11, 1958, and No. 18, 1965.
[28] E. Philippot and O. Lindqvist, *Acta Cryst.*, 1970, **B26**, 877.
[29] B. R. Penfold, *Acta Cryst.*, 1953, **6**, 707.

TABLE 4

Molecular geometry

(*a*) Bond lengths (Å)

Cu–S	2·252(2)	C(7)–C(12)	1·531(5)
Cu–N(1)	2·048(4)	C(1)–H(1)	1·09(4)
N(1)–C(1)	1·353(5)	C(2)–H(2)	1·18(5)
N(1)–C(5)	1·351(4)	C(3)–H(3)	1·03(4)
C(1)–C(2)	1·378(5)	C(4)–H(4)	0·91(4)
C(2)–C(3)	1·380(5)	C(7)–H(5)	0·95(4)
C(3)–C(4)	1·380(5)	C(8)–H(6)	1·05(4)
C(4)–C(5)	1·378(5)	C(8)–H(7)	1·05(4)
C(5)–C(6)	1·497(5)	C(9)–H(8)	1·07(6)
S–C(6)	1·756(4)	C(9)–H(9)	1·09(4)
C(6)–N(2)	1·268(4)	C(10)–H(10)	1·02(3)
N(2)–C(7)	1·460(4)	C(10)–H(11)	0·90(5)
C(7)–C(8)	1·521(5)	C(11)–H(12)	1·05(5)
C(8)–C(9)	1·517(6)	C(11)–H(13)	0·99(4)
C(9)–C(10)	1·518(6)	C(12)–H(14)	0·97(3)
C(10)–C(11)	1·526(6)	C(12)–H(15)	1·09(4)
C(11)–C(12)	1·522(5)		

(*b*) Angles (°)

N(1)–Cu–S	85·7(1)°	H(1)–C(1)–N(1)	115(2)
Cu–S–C(6)	99·0(1)	H(1)–C(1)–C(2)	123(2)
Cu–N(1)–C(1)	123·8(3)	H(2)–C(2)–C(1)	122(3)
Cu–N(1)–C(5)	118·8(2)	H(2)–C(2)–C(3)	119(3)
C(1)–N(1)–C(5)	117·4(3)	H(3)–C(3)–C(2)	117(2)
N(1)–C(1)–C(2)	122·7(4)	H(3)–C(3)–C(4)	125(2)
C(1)–C(2)–C(3)	119·3(4)	H(4)–C(4)–C(3)	124(2)
C(2)–C(3)–C(4)	118·3(4)	H(4)–C(4)–C(5)	116(2)
C(3)–C(4)–C(5)	119·8(3)	H(5)–C(7)–N(2)	112(2)
C(4)–C(5)–N(1)	122·3(3)	H(5)–C(7)–C(8)	110(2)
C(4)–C(5)–C(6)	120·3(3)	H(5)–C(7)–C(12)	104(2)
N(1)–C(5)–C(6)	117·5(3)	H(6)–C(8)–C(7)	115(2)
C(5)–C(6)–S	116·0(3)	H(6)–C(8)–C(9)	106(2)
C(5)–C(6)–N(2)	116·0(3)	H(7)–C(8)–C(7)	113(2)
S–C(6)–N(2)	128·0(3)	H(7)–C(8)–C(9)	106(2)
C(6)–N(2)–C(7)	120·1(3)	H(8)–C(9)–C(8)	108(3)
N(2)–C(7)–C(8)	108·3(3)	H(8)–C(9)–C(10)	114(3)
N(2)–C(7)–C(12)	112·0(3)	H(9)–C(9)–C(8)	110(2)
C(8)–C(7)–C(12)	110·4(3)	H(9)–C(9)–C(10)	102(2)
C(7)–C(8)–C(9)	111·5(3)	H(10)–C(10)–C(9)	106(2)
C(8)–C(9)–C(10)	110·9(3)	H(10)–C(10)–C(11)	105(2)
C(9)–C(10)–C(11)	111·8(4)	H(11)–C(10)–C(9)	124(4)
C(10)–C(11)–C(12)	110·9(3)	H(11)–C(10)–C(11)	113(4)
C(11)–C(12)–C(7)	111·4(3)	H(12)–C(11)–C(10)	111(3)
Cu–N(1)–C(3)	176·7(2)	H(12)–C(11)–C(12)	109(3)
		H(13)–C(11)–C(10)	107(2)
H(6)–C(8)–H(7)	105(3)	H(13)–C(11)–C(12)	106(2)
H(8)–C(9)–H(9)	112(3)	H(14)–C(12)–C(11)	103(2)
H(10)–C(10)–H(11)	93(4)	H(14)–C(12)–C(7)	110(2)
H(12)–C(11)–H(13)	112(3)	H(15)–C(12)–C(11)	111(2)
H(14)–C(12)–H(15)	120(3)	H(15)–C(12)–C(7)	102(2)

distances of 2·936—2·938 Å, and by its constituent three mean planes, each through four of the six carbon atoms of the cyclohexyl ring. The maximum deviation of an atom defining any of three planes was $<2\sigma_{rms}$. The axial [H(5), H(7), H(8), H(10), H(12), and H(14)] and equatorial atoms [N(2), H(6), H(9), H(11), H(13), and H(15)] of this substituent were identified without difficulty.

The bond lengths and angles of the cyclohexyl substituent (Table 4) provide a means of gauging the validity of the estimated standard deviation values for the atomic positional parameters of the atoms. The C–C bond lengths range from 1·517(6) to 1·531(5) Å, mean 1·522 Å, and the C–H bond lengths from 0·90(5) to 1·09(4) Å, mean 1·02 Å. The C–C–C bond angles range from 110·4(3) to 111·8(4)°, mean 111·1°, and the C–C–H bond angles from 102(2) to 124(4)°, mean 109°. Assuming that the bond parameters in each of these four groups are equivalent to each other, an analysis suggests that the positional σ values, as determined from the full-matrix least-squares procedure, have been underestimated and that they should be multiplied by 1·2 and 1·5 for the non-hydrogen and hydrogen atoms respectively. Had the secondary extinction corrections and improved inter-layer scaling not been applied, the resulting σ values would have been overestimated by *ca.* 25%.

Both the thermal displacements of the non-hydrogen atoms and the relatively small angles between the major principal axis of vibration of most of these atoms and the normal to the Cu–S–N(1) plane indicate that the molecules have a significant out-of-plane thermal translation. The sulphur atom seems to have a thermal motion normal to the Cu–S–N(1) plane relatively larger than the motion of adjoining atoms, suggesting a dynamic twisting of the thioamido-moiety about the C(5)–C(6) bond.

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