# Synthesis, Spectroscopy, and Crystal Structure of a Thiocyanato-bridged Mixed-valence Copper(I)–Copper(II) Compound with the Ligand 1,6-Bis(5'-methylimidazol-4'-yl)-2,5-dithiahexane[†]

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The synthesis, crystal structure, electronic, and e.s.r. spectra are reported for the complex *catena*-[1,6-bis(5'-methylimidazol-4'-yl)-2,5-dithiahexane]tri-μ-thiocyanato-dicopper(I,II). The complex crystallizes as dark brown octahedra in the space group $P2_1/c$, with $a$ = 13.684(4), $b$ = 9.537(2), $c$ = 18.531(3) Å, β = 108.91(2)°, $Z$ = 4, $R$ = 0.036, $R'$ = 0.039 for 2 936 reflections with $I > 2\sigma(I)$. Each copper(II) ion is surrounded by four nitrogens at 1.968(3), 1.972(3), 2.002(4), and 2.395(4) Å, and two sulphurs at 2.426(1) and 2.814(1) Å. The co-ordination geometry of the copper(II) ion is intermediate between elongated octahedral and square pyramidal. The copper(I) ion is surrounded by three sulphurs and one nitrogen from the bridging thiocyanates in a distorted tetrahedral geometry. Two of the thiocyanate anions bridge to another copper(I) ion and the other two bridge to two different copper(II) ions, resulting in a three-dimensional network.

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Modelling the copper-containing active site of blue copper proteins contributes to the understanding of the relations between the structure and properties of these proteins. From the crystal structure determination of *Populus nigra* plastocyanin[1] and two different azurins[2,3] (*i.e. Alcaligenes denitrificans* and *Pseudomonas aeruginosa*) it is known that the active site is formed by two histidine nitrogens, one methionine thioether sulphur, and one thiolate sulphur of cysteine bonded to the copper ion in a distorted tetrahedral geometry. In the case of azurin from *Alicaligenes denitrificans* indications of a fifth ligand (oxygen from a peptide carbonyl) have been reported.[2]

During the last decade the co-ordination chemistry of azole-containing ligands has been the subject of many studies. Many co-ordination compounds of ligands containing pyrazole, pyridine, or benzimidazole have been reported.[4–7] So far relatively few ligands containing both imidazole and thioether donor atoms have been investigated. Recently, a new method for the synthesis of a large variety of 4(5)-substituted imidazole and thioether-containing ligands has been developed.[8] This method not only provides routes to a large variety of bio-inorganic model systems, but also offers the opportunity to incorporate imidazole chelates in polymers, which may for instance lead to immobilized catalysts and to ion-exchange resins with improved selectively. The study of this new series of ligands has been started with an investigation of the co-ordination chemistry of imidazole derivatives of a few simple thiols, such as 1,3-propanedithiol[9] and 1,2-ethanedithiol. 1,6-Bis(5'-methylimidazol-4'-yl)-2,5-dithiahexane (abbreviated L) forms a variety of complexes with transition-metal ions. The synthesis and characterization of some of these compounds has been described earlier.[8c] The mixed copper(I)–copper(II) thiocyanate compound, described in this paper, was formed from a solution which initially contained only bivalent copper. The stoicheiometry and structure of this compound could not be deduced from spectroscopic and analytical data.

## Experimental

*Syntheses.*—The synthesis of the ligand L will be described elsewhere.[8] Its $^1$H n.m.r. spectrum [solvent $(CD_3)_2SO$, internal standard $SiMe_4$] showed the following signals: 2.19 (s, 6 H, methyl), 2.59 (s, 4 H, $CH_2CH_2$), 3.71 (s, 4 H, $CH_2$), 4.87 (br, NH), and 7.68 p.p.m. (s, 2 H, imidazole).

The mixed-valence co-ordination compound was prepared by dissolving copper(II) nitrate (1 mmol) in ethanol (5 cm$^3$) and ammonium thiocyanate (2 mmol) in water (5 cm$^3$) and adding these two solutions subsequently to a hot suspension of the ligand L (1 mmol) in ethanol (25 cm$^3$). Upon addition of the metal salt the ligand dissolved almost completely. After filtration of the hot reaction mixture, the complex crystallized on cooling as dark brown crystals. After collection of the crystals, a second crop from the filtrate yielded dark green crystals of a compound characterized as $CuL(NCS)(NO_3)$, the structure of which will be solved and described later.

*Characterization.*—Metal analyses were carried out complexometrically with ethylenediaminetetra-acetate (edta) as the complexing agent. Infrared spectra in the range 4 000—180 cm$^{-1}$ for samples pelleted in KBr were recorded on a Perkin-Elmer spectrophotometer, equipped with a PE data station. Electronic spectra (28 000—5 000 cm$^{-1}$) were recorded on a Perkin-Elmer 330 spectrophotometer, also equipped with a PE data station, in methanol solution or for the solid in standard reflectance mode. E.s.r. spectra of the powdered copper(II) compounds were obtained with a Varian spectrometer at $X$-band frequency at room temperature and 77 K (liquid nitrogen), those of frozen solutions of the copper compounds in methanol were recorded at 77 K.

*Crystallography.*—*Crystal data.* $C_{15}H_{18}Cu_2N_7S_5$, $M_r$ = 583.748, monoclinic, $a$ = 13.684(4), $b$ = 9.537(2), $c$ = 18.531(3) Å, β = 108.91(2)°, $U$ = 2 287.60 Å$^3$ by least-squares refinement of diffractometer angles for 24 reflections, λ(Mo-$K_\alpha$) = 0.710 73 Å, $T$ = 293 K, space group $P2_1/c$, $Z$ = 4, $D_c$ = 1.695 g cm$^{-3}$, μ(Mo-$K_\alpha$) = 23.21 cm$^{-1}$, $F$(000) = 1 184.21.

*Data collection and structure refinement.* A single crystal of approximate dimensions 0.40 × 0.35 × 0.28 mm, mounted in a glass capillary, was used for data collection. Cell dimensions were determined by least-squares refinement of the setting angles of 24 reflections ($10 < \theta < 12°$). The data collection was carried out on a four-circle Enraf-Nonius CAD4 diffractometer.

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[†] *catena*-[1,6-Bis(5'-methylimidazol-4'-yl)-2,5-dithiahexane-2$N^{3'}S^2S^5$]-tri-μ-thiocyanato-dicopper(I,II).

*Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

*Non-S.I. unit employed:* G = 10$^{-4}$ T.

**Table 1.** Positional parameters [ $\times 10^5$ for Cu(01) and Cu(02) and $\times 10^4$ for S(04)—S(53)] for the non-hydrogen atoms in $[Cu_2L(NCS)_3]$

| Atom | *X/a* | *Y/b* | *Z/c* | Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|---|---|---|---|
| Cu(01) | 66 849(4) | 2 961(7) | 46 375(4) | C(22) | 6 482(4) | 262(6) | 7 187(3) |
| Cu(02) | 85 433(4) | 14 050(5) | 80 687(3) | N(23) | 7 142(2) | 624(4) | 7 845(2) |
| S(04) | 9 116(1) | −868(1) | 7 775(1) | C(24) | 6 754(3) | 100(5) | 8 395(3) |
| C(05) | 9 572(4) | −1 725(5) | 8 697(3) | C(25) | 5 851(3) | −577(5) | 8 044(3) |
| C(06) | 8 803(4) | −1 648(5) | 9 129(3) | C(26) | 5 111(5) | −1 306(8) | 8 352(5) |
| S(07) | 8 692(1) | 106(1) | 9 464(1) | N(31) | 8 115(3) | 3 318(4) | 8 296(2) |
| C(10) | 10 324(3) | −228(5) | 7 697(3) | C(32) | 7 606(3) | 4 219(5) | 8 374(2) |
| N(11) | 11 604(3) | 2 530(4) | 9 024(2) | S(33) | 6 864(1) | 5 500(1) | 8 477(1) |
| C(12) | 10 595(3) | 2 781(5) | 8 884(3) | N(41) | 6 084(3) | −1 128(4) | 5 139(2) |
| N(13) | 10 029(2) | 1 842(4) | 8 409(2) | C(42) | 5 434(3) | −1 601(5) | 5 321(3) |
| C(14) | 10 726(3) | 949(5) | 8 245(2) | S(43) | 4 509(1) | −2 282(1) | 5 599(1) |
| C(15) | 11 701(3) | 1 355(5) | 8 625(2) | N(51) | 8 245(3) | 1 772(5) | 6 736(2) |
| C(16) | 12 716(4) | 773(8) | 8 631(4) | C(52) | 8 254(3) | 1 513(5) | 6 133(3) |
| C(20) | 7 305(4) | 277(7) | 9 218(3) | S(53) | 8 331(1) | 1 137(1) | 5 284(1) |
| N(21) | 5 700(3) | −450(5) | 7 283(3) | | | | |

**Table 2.** Selected bond distances (Å) and angles (°) in $[Cu_2L(NCS)_3]$ with their estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Cu(01) ··· Cu(02) | 6.126 3(8) | Cu(02)–S(07) | 2.814(1) |
| Cu(01)–N(41) | 1.970(4) | Cu(02)–N(13) | 1.968(3) |
| Cu(01)–S(33) | 2.367(1) | Cu(02)–N(23) | 1.972(3) |
| Cu(01)–S(43) | 2.446(2) | Cu(02)–N(31) | 2.002(4) |
| Cu(01)–S(53) | 2.324(1) | Cu(02)–N(51) | 2.395(4) |
| Cu(02)–S(04) | 2.426(1) | | |
| S(33)–Cu(01)–N(41) | 112.9(1) | S(07)–Cu(02)–N(23) | 78.6(1) |
| S(33)–Cu(01)–S(43) | 110.2(1) | S(07)–Cu(02)–N(31) | 98.5(1) |
| S(33)–Cu(01)–S(53) | 102.2(1) | S(07)–Cu(02)–N(51) | 161.7(1) |
| N(41)–Cu(01)–S(43) | 105.2(1) | N(13)–Cu(02)–N(23) | 168.7(2) |
| N(41)–Cu(01)–S(53) | 118.5(1) | N(13)–Cu(02)–N(31) | 94.7(2) |
| S(43)–Cu(01)–S(53) | 107.7(1) | N(13)–Cu(02)–N(51) | 96.5(1) |
| S(04)–Cu(02)–S(07) | 83.1(1) | N(23)–Cu(02)–N(31) | 93.3(2) |
| S(04)–Cu(02)–N(13) | 83.4(1) | N(23)–Cu(02)–N(51) | 90.6(1) |
| S(04)–Cu(02)–N(23) | 88.8(1) | N(31)–Cu(02)–N(51) | 96.9(2) |
| S(04)–Cu(02)–N(31) | 177.6(1) | Cu(02)–S(04)–C(05) | 103.2(2) |
| S(04)–Cu(02)–N(51) | 81.9(1) | Cu(02)–S(04)–C(10) | 95.0(2) |
| S(07)–Cu(02)–N(13) | 92.2(1) | | |

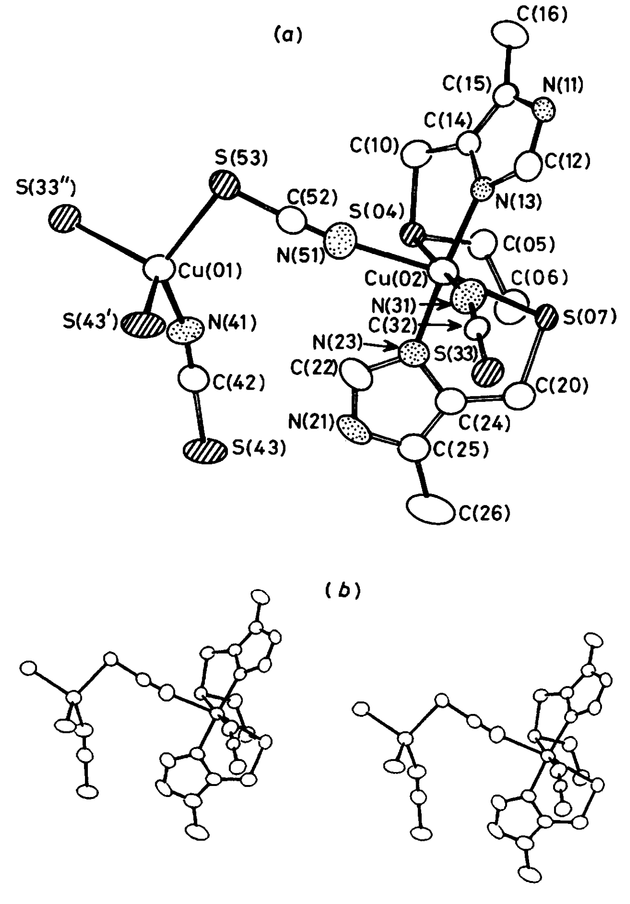

**Figure 1.** (*a*) ORTEP drawing of $[Cu_2L(NCS)_3]$ with thermal ellipsoids at 50% probability, showing the atomic numbering scheme. The hydrogen atoms have been omitted for clarity. The atoms S(43′) and S(33″), which have been added, are at the positions $1 - x$, $-y$, $1 - z$ and $x$, $\frac{1}{2} - y$, $z - \frac{1}{2}$ respectively; (*b*) stereoview of $[Cu_2L(NCS)_3]$

Graphite-monochromatized Mo-$K_\alpha$ radiation was used: 5 734 reflections were measured ($2.0 < \theta < 27.5°$, $-17 < h < 17$, $0 < k < 12$, $0 < l < 24$), of which 5 568 were unique; of these, 2 936 were considered as observed [$I > 2\sigma(I)$]. The scanning rate was adjusted to the required precision of $\sigma(I)/I = 0.01$, with a maximum scan time of 90 s per reflection. Intensities were corrected for background. The instrument and crystal stability were checked every 5 400 s of radiation time by measuring three reflections: no significant changes in the intensities were observed.

Intensities were corrected for Lorentz and polarization effects. The calculations were performed on the Leiden University Computer (IBM 3083), using a local set of computer programs. Scattering factors and anomalous dispersion corrections were taken from ref. 10. The structure was solved by direct methods (yielding first the heavy metals), followed by normal heavy-atom procedures and refined by full-matrix least-squares calculations. The refinement was considered to be complete when the changes in the parameters were smaller than one-third of the standard deviations. Hydrogen atoms were located from Fourier-difference maps, and their positional and isotropic thermal parameters were refined also. The thermal parameters of the non-hydrogen atoms were refined anisotropically. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. At the final stage the conventional discrepancy index $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ had been reduced to 0.036. The weighted factor $R' = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ had been reduced to 0.039. The fractional co-ordinates of the non-hydrogen atoms of of $[Cu_2L(NCS)_3]$ are listed in Table 1, relevant bond distances and angles of the non-hydrogen atoms in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond distances and angles.

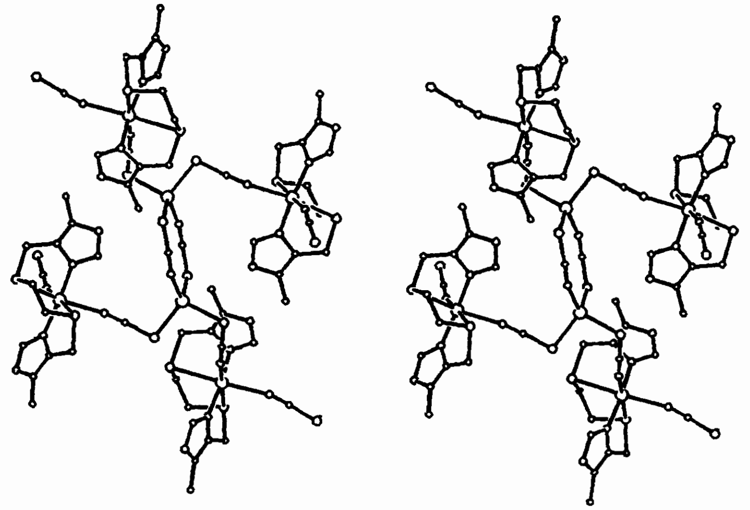

**Figure 2.** Stereo ORTEP drawing of a part of the extended network formed by the bridging thiocyanates in [$Cu_2L(NCS)_3$]

## Results and Discussion

*Description of the Structure.*—From the metal content of the obtained crystals the stoicheiometry $Cu_2L(NCS)_3$ was deduced (Found: Cu, 21.8. Calc. Cu, 21.8%), and this can now be understood from the *X*-ray structure. An ORTEP[11] projection of the molecular entity $Cu_2L(NCS)_3$ and the atomic labelling are given in Figure 1. An impression of the network structure, formed by the bridging of the thiocyanate anions, is depicted in Figure 2. Because of the extended network in three dimensions, only a small part with two copper(I) ions and four copper(II) ions can be shown. From the stoicheiometry of the compound it was inferred that half the copper ions has to be present in the univalent state and the other half in the bivalent state. However, from the *X*-ray data alone it cannot be decided which of the two metal ions in the asymmetric unit is the copper(II) and which is the copper(I). From the preference of copper(I) for a tetrahedral rather than an octahedral co-ordination geometry and from the preference of copper(I) for sulphur atoms rather than nitrogen-donor atoms, a very good guess about the valence state of the copper ions can be made.

The copper(I) ion is surrounded by one nitrogen and three sulphur atoms from four bridging thiocyanates in a geometry close to tetrahedral (angles between 102.2 and 118.5°). The distances are about normal for copper–nitrogen and –sulphur being 2.0 and 2.4 Å respectively (Table 2). The copper(II) ion is surrounded by two nitrogens from the thiocyanates and two nitrogens and two thioether sulphurs from the ligand L. The equatorial ligands are at normal distances (2.4 for sulphur, 2.0 Å for nitrogen) but the axial ligands are at very large distances. At first sight it seems that the copper(II) ion is in a square-pyramidal geometry with the axial thiocyanate nitrogen at a distance of 2.4 Å. The second thioether sulphur of the ligand L is at a very large, though semi-co-ordinating, distance of 2.81 Å. The co-ordination angles copper(II)–thioether sulphur–carbon are 88.5 and 94.6°, indicating that a lone pair of the sulphur is directing towards the copper(II) ion. Although the ligand L is symmetrical, in this case it chelates asymmetrically. In earlier crystal structures on related ligands the two sulphur atoms are at equal distances, *i.e.* either short ($\approx$2.4 Å)[12] or long ($\approx$2.8—2.9 Å).[9] In the present case the ligand is bonded asymmetrically to the metal ion, with distances of 2.4 and 2.8 Å. The four atoms N(13), N(23), N(31), and S(04) comprising the equatorial plane have deviations of less than 0.09 Å. The copper(II) ion is coplanar with the four donor atoms (distance to the least-squares plane 0.06 Å). From these data, the copper ion is not in a square-pyramidal geometry, because in that case the metal ion would be lying above the plane. Now it is clear that the S(07) sulphur atom 'pulls' the metal back into the plane, in accordance with an elongated octahedral geometry.

The imidazole nitrogen–copper–thioether sulphur bonding angles are about 78°. As can be deduced from other crystal structures with similar ligands,[8b,9] this angle is about the maximum which can be reached for this type of ligands, as a result of the constraints in the 'bridge.' The two imidazole rings are planar, with deviations from the least-squares plane of about 0.004 Å. The copper ion lies almost in the imidazole plane with a deviation of about 0.1 Å.

From i.r. data for this compound it was inferred that two different thiocyanate species had to be present (see below). Indeed there are two differently bridging $NCS^-$ species. One $NCS^-$ ion bridges between two copper(I) ions, forming $Cu_2(NCS)_2$ units, and the other two $NCS^-$ ions bridge between a copper(I) and a copper(II) ion. However, the difference in bond lengths and angles between the thiocyanate ions are only very small, the largest difference being encountered between the axial and equatorial bond lengths of N(31) and N(51). The thiocyanates are essentially linear.

*Spectral Properties.*—The solid-state e.s.r. spectrum of [$Cu_2L(NCS)_3$] is typical for an elongated geometry with a $d_{x^2-y^2}$ ground state. Both at room temperature and at 77 K the spectrum is rhombic ($g_1$ = 2.24, $g_2$ = 2.09, $g_3$ = 2.04). The e.s.r. powder spectrum does not show copper hyperfine splitting, which is likely to be the result of a small coupling between the copper(II) ions. The diffuse reflectance spectrum shows a ligand-field maximum at 15 300 with a shoulder at 10 500 $cm^{-1}$ and a charge-transfer band at 28 800 $cm^{-1}$. The latter band is ascribed to either a $\pi$(imidazole) to copper(II) transition[13] or a thioether sulphur to copper(II) transition.[14] A sulphur–copper charge-transfer band has been found in many compounds with short Cu–S distances with similar ligands.[14] Infrared spectra obtained in the solid state show the presence of ligand bands, in some cases shifted or split as a result of co-ordination. The thiocyanate vibrations at 2 080 and 2 104 $cm^{-1}$ indicate that two different $NCS^-$ species are present, in agreement with the described crystal structure.

Ligand-field and e.s.r. spectra were also recorded in methanol solution under various conditions. The solution obtained is green, quite different from the dark brown colour of the solid. The ligand-field spectrum of the methanol solution again shows one band with a shoulder, but now at 16 100 and 11 900 $cm^{-1}$ respectively, and a charge-transfer band at about 28 000 $cm^{-1}$. The e.s.r. spectra of the frozen solution (77 K) of $[Cu_2L(NCS)_3]$ show hyperfine splittings with $A_{\parallel} = 130$ G. The spectrum is rhombic ($g_1 = 2.24$, $g_2 = 2.08$, $g_3 = 2.03$). Comparison of the spectra in the solid state and in solution gives rise to the suspicion that the mixed-valence compound is not present as such in solution, despite the fact that it can be recrystallized from methanol.

*Comparison with Related Structures.*—The molecular structure of the compound appears to be of great interest in view of the structures of compounds with similar ligands published earlier by our laboratory and other groups. The most striking feature of the present compound is its formation through *spontaneous* reduction of a solution containing *only* copper(II) ions. The compound $[Cu_2(pabd)(NCS)_3]$, where pabd is the tridentate nitrogen-donor ligand *NN*-bis(3,5-dimethylpyrazol-1-ylmethyl)aminobenzene, is also formed through spontaneous reduction of half of the copper(II) ions present in the initial solution.[15] The structures of these two compounds show remarkable similarities. Both have an infinite chain of copper(I) and copper(II) with bridging thiocyanate anions. Further, the copper(I) ion is in a distorted tetrahedral environment of three sulphurs and one nitrogen of the thiocyanates. The largest difference between the structures is the geometry around the copper(II) ion. In the present structure the copper(II) ion is in an elongated octahedral geometry, with one thioether sulphur at a very long semi-co-ordinating distance of 2.8 Å. In the pabd compound the copper(II) ion is in a square-pyramidal geometry, simply because no other ligand donor atom is available. The spectral properties of both compounds match in many ways.[16] The mixed-valence pyrazole-containing compound has a ligand-field absorption (solid reflectance) at 13 500 $cm^{-1}$ and a charge-transfer band at 27 000 $cm^{-1}$. In both compounds the charge-transfer band is likely to originate from an azole-to-copper transition rather than from a thioether-sulphur-to-copper transition, simply because in the pabd compound no thioether sulphurs are present. The other possibility, of intervalence copper(II)–thiocyanate–copper(I) charge transfer is less acceptable because analogous bands have been observed in non-mixed-valence complexes of these ligands with other anions.[16]

A mixed-valence copper(I)–copper(II) cluster has been reported by Bharadwaj *et al.*,[17] formed by $N_2S_2$ donor sets. The compound consists, however, of discrete $Cu^I{}_2Cu^{II}{}_3$ clusters, and no extended network is obtained. A two-dimensional complex of copper(I) and mercury(II) with bridging thiocyanates has been reported by Biagini Cingi *et al.*[18] In this compound the copper ion is co-ordinated by three thiocyanate nitrogens and one ligand nitrogen in a distorted tetrahedron; the mercury ion is in a tetrahedron formed by the three thiocyanate sulphurs and one ligand nitrogen, the ligand being 5,7-dimethyl[1,2,4]-triazolo[1,5-*a*]pyrimidine.

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