

Fig. 2. A c projection of the unit-cell contents.

The angles between the ring planes, in the main, are considerably larger than the same angles in the triclinic molecule. The C—Hg bond lengths are within the normal values; for example, 2.09 Å in diphenylmercury (Grdenić, Kamenar & Nagl, 1977) and 2.07–2.13 Å in tribenzo[*b,e,h*][1,4,7]trimercuronin (Brown, Massey & Wickens, 1978) but slightly shorter than the distance (2.090–2.145 Å) found in the triclinic form. As expected for an organomercurial the C—Hg—C bond angles are close to 180°; there are no abnormal intermolecular contacts. The Hg···Hg distances within the heterocyclic ring are 3.461 (1) [Hg(1)—Hg(3)], 3.485 (1) [Hg(2)—Hg(3)] and 3.637 (2) Å [Hg(1)—Hg(2)]. As the van der Waals radius for Hg is thought to be 1.73 Å (Canty & Deacon, 1980) there will presumably be little or no steric strain in the ring.

A view of the unit cell is shown in Fig. 2, and a 'top view' of the molecule shown in Fig. 1 has been deposited.

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Synthesis and X-ray Structure of a Two-Dimensional Thiocyanato-Bridged Mercury(II)–Copper(I) Complex with 5,7-Dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine, [CuHg(μ -SCN)₃(dmtp)₂]

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Abstract. [CuHg(μ -SCN)₃(C₇H₈N₄)₂], $M_r = 734.70$, triclinic, $P\bar{1}$, $a = 8.681(3)$, $b = 17.547(6)$, $c = 8.331(3)$ Å, $\alpha = 99.10(3)$, $\beta = 101.64(2)$, $\gamma = 101.62(3)^\circ$, $V = 1191.0(8)$ Å³, $Z = 2$, $D_x = 2.05$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 76.15$ cm⁻¹, $F(000) = 704$, room temperature, $R = 0.068$ for 3443

independent observed reflections. The crystal structure consists of tetrahedral [Hg^{II}(SCN)₃(dmtp)] and [Cu^I(NCS)₃(dmtp)] coordination units, in which the thiocyanate groups, acting as bridges, are bound *via* S to Hg^{II} and *via* N to Cu^I, in such a way as to determine a two-dimensional arrangement of the units. Unlike the

analogous Hg^{II}-M^{II} compounds (with M^{II} = Co^{II}, Fe^{II}) in which [Hg^{II}(SCN)₄] complexes are present and the dmtp molecules are coordinated only to M^{II}, in the present compound the dmtp molecules are bound to both heterometals.

Introduction. As part of our interest concerning the interactions of N-bridgehead purine analogue ligands, such as 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (abbreviated dmtp) with heavy metals of biological and environmental implication, we have been studying heteronuclear compounds with Hg^{II} and a variety of M^{II} cations resulting in complexes of different type: [CoHg(SCN)₄(dmtp)₃(H₂O)]₂ (I), [FeHg(SCN)₄(dmtp)₂(H₂O)_{1.5}] (II), [FeHg(SCN)₄(dmtp)₂(H₂O)] (III) and [FeHg(SCN)₄(dmtp)(H₂O)₂].acetone (IV). In all these complexes the dmtp molecules are bound to the M^{II} cations only through the triazole N atom corresponding to N(9) in purine ring systems; the SCN groups act both as monodentate (Hg^{II} *via* S) and as bridging (Hg^{II} *via* S and M^{II} *via* N) ligands, forming heterotetranuclear complexes in (I) (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1984) and *one*-, *two*- and *three*-dimensional systems in (II), (IV) and (III) respectively (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1985).

In an attempt to prepare mixed Hg^{II}-Cu^I compounds, a yellow product containing Cu^I was obtained: [CuHg(SCN)₃(dmtp)₂] (V), the structure of which has been fully elucidated only by an X-ray analysis.

Experimental. The ligand dmtp was prepared according to the published method (Bülow & Haas, 1909) from 2,5-pentanedione and 3-amino-1,2,4-triazole.

The attempt to stabilize the divalence of the Cu atom in complexes as [M^{II}Hg(SCN)₄(dmtp)_x(H₂O)_y] met with only partial success. The solution, prepared with Cu^{II} cations according to the previously described method (Biagini Cingi *et al.*, 1984) produces a mixture of green (apparently containing Cu^{II}) and yellow crystals. Only the yellow crystals could be separated and analysed as [CuHg(SCN)₃(dmtp)₂].

Yellow prismatic crystal 0.08 × 0.19 × 0.37 mm, Siemens AED diffractometer, Nb-filtered Mo K α , 21 reflections for lattice-parameter measurements; 5012 independent reflections with 3 ≤ θ ≤ 27° (-10 ≤ *h* ≤ 10, -22 ≤ *k* ≤ 22, 0 ≤ *l* ≤ 10), 3443 with *I* > 2 σ (*I*), no significant intensity deterioration of standard reflection (242). Lp correction, absorption ignored. Patterson and Fourier methods; full-matrix least-squares refinement, anisotropic for non-H atoms (SHELX76, Sheldrick, 1976); H in calculated positions and included in final structure-factor calculations with isotropic thermal parameters; $\sum w|\Delta F|^2$ minimized, final *R* = 0.068 and *wR* = 0.088, unit weights; (Δ/σ)_{max} = 0.08, final $\Delta\rho$ excursions ≤ |0.8| e Å⁻³, atomic scattering factors (anomalous dispersion of Hg and Cu

Table 1. Fractional atomic coordinates (×10⁴) with equivalent isotropic thermal parameters for the non-H atoms, with e.s.d.'s in parentheses

	$B_{eq} = \frac{2}{3}\pi^2 \text{trace } U.$			
	x	y	z	$B_{eq}(\text{\AA}^2)$
Hg	2633 (1)	7756 (1)	9486 (1)	2.94 (2)
Cu	-1519 (3)	7087 (1)	3318 (3)	3.11 (6)
S(1)	906 (7)	6329 (3)	8814 (6)	3.41 (14)
S(2)	3980 (6)	8245 (3)	12482 (6)	3.35 (14)
S(3)	3642 (6)	8133 (3)	7062 (6)	3.59 (14)
N(1)	-723 (22)	6690 (10)	11327 (21)	3.72 (56)
N(2)	6691 (20)	7567 (10)	12861 (20)	3.28 (46)
N(3)	471 (23)	7768 (12)	4946 (20)	4.30 (59)
N(31)	1569 (20)	9357 (10)	11890 (18)	3.15 (49)
N(51)	-1173 (18)	9057 (8)	10437 (18)	2.43 (44)
N(71)	-2207 (20)	8516 (9)	9059 (21)	3.39 (46)
N(91)	325 (21)	8287 (9)	9468 (20)	3.38 (51)
N(32)	-3273 (18)	6269 (8)	6470 (17)	2.75 (42)
N(52)	-2655 (19)	5051 (8)	5417 (18)	2.88 (42)
N(72)	-2032 (22)	4736 (9)	4146 (20)	3.57 (50)
N(92)	-2056 (19)	6036 (9)	4126 (18)	3.03 (45)
C(1)	-59 (23)	6536 (10)	10292 (23)	2.85 (54)
C(2)	5557 (23)	7823 (11)	12636 (20)	2.67 (51)
C(3)	1691 (24)	7894 (11)	5785 (22)	3.22 (52)
C(11)	-282 (26)	10120 (11)	12655 (23)	3.30 (59)
C(21)	1257 (25)	9947 (11)	12879 (21)	3.18 (49)
C(41)	321 (22)	8919 (10)	10661 (21)	2.54 (50)
C(61)	-1554 (24)	9665 (11)	11399 (24)	3.07 (56)
C(81)	-1212 (24)	8115 (11)	8594 (24)	3.07 (54)
C(101)	2684 (29)	10444 (15)	14269 (24)	5.24 (68)
C(111)	-3226 (27)	9780 (12)	10977 (30)	4.00 (73)
C(12)	-3797 (24)	5111 (12)	7686 (24)	3.43 (58)
C(22)	-3831 (24)	5897 (12)	7596 (23)	3.31 (54)
C(42)	-2698 (21)	5817 (10)	5385 (21)	2.59 (48)
C(62)	-3203 (23)	4657 (11)	6557 (23)	3.09 (51)
C(82)	-1672 (26)	5363 (11)	3434 (24)	3.57 (60)
C(102)	-4529 (27)	6379 (13)	8789 (23)	4.13 (68)
C(112)	-3102 (31)	3819 (12)	6468 (28)	4.89 (80)

atoms) from *International Tables for X-ray Crystallography* (1974); calculations performed on the Cyber 76 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord Orientale, Casalecchio (Bologna) with financial support from the University of Parma.*

Discussion. The atomic coordinates for the non-H atoms are listed in Table 1.

In the crystal structure of (V) distorted tetrahedral [Hg^{II}(SCN)₃(dmtp)] and [Cu^I(NCS)₃(dmtp)] units, represented in Fig. 1, are present. Relevant bond distances and angles are given in Table 2. In both coordination polyhedra the dmtp molecule acts as a monodentate ligand involving the preferred site in the coordination to the metal, the N(9) (Biagini Cingi, Manotti Lanfredi, Tiripicchio, Haasnoot & Reedijk, 1983, 1984, 1985), and the three thiocyanate groups all behave as bridging ligands and coordinate through S to Hg^{II} and through N to Cu^I. The bond lengths in the coordination polyhedra are in good agreement with the literature values for similar coordinations.

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42676 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The thiocyanate groups are nearly linear. Even if the N(3)–C(3) and C(3)–S(3) bond lengths in the N(3)–C(3)–S(3) group agree with a relevant *sp* hybridization of the N(3) atom, the Cu–N(3)–C(3) angle [155 (2)°] shows a remarkable departure from linearity. Such deviations, however, appear to be quite common for *M*–N–C angles in isothiocyanates.

The structural parameters of the two independent dmtp molecules are quite regular; both are planar [maximum deviations from the mean planes through the two molecules are 0.03 (2) Å for C(111) and 0.03 (2) Å for C(102) respectively]. Even though in (V) the behaviour of the dmtp molecule as a ligand is normal, it is noteworthy that (V) represents the first example of a heterometal compound containing dmtp molecules coordinated to different metals. In fact in the previous dmtp heteronuclear complexes (I)–(IV) only tetrahedral [Hg(SCN)₄] complexes involving either terminal or bridging thiocyanate groups have been

found and the dmtp molecules were coordinated only to the non-mercury metals. This fact could be explained by the different acid character of the cations (Singh, 1980), 'soft' for Hg^{II} and 'harder' for Co^{II} and Fe^{II}; the N-bonding of the organic ligand both to Hg^{II} and Cu^I in the present compound could be ascribed to the similar soft character of these cations, the slight difference between them being manifested by the S-bonding to Hg^{II} and the N-bonding to Cu^I of the thiocyanate groups. The thiocyanate groups, bridging two adjacent heterometals, determine a layered arrangement of the complexes, shown in Fig. 2. The dmtp molecules linked to different metals are orthogonal, the dihedral angle between the mean planes through them being 88 (3)°. The mutual orientation of the dmtp molecules and the

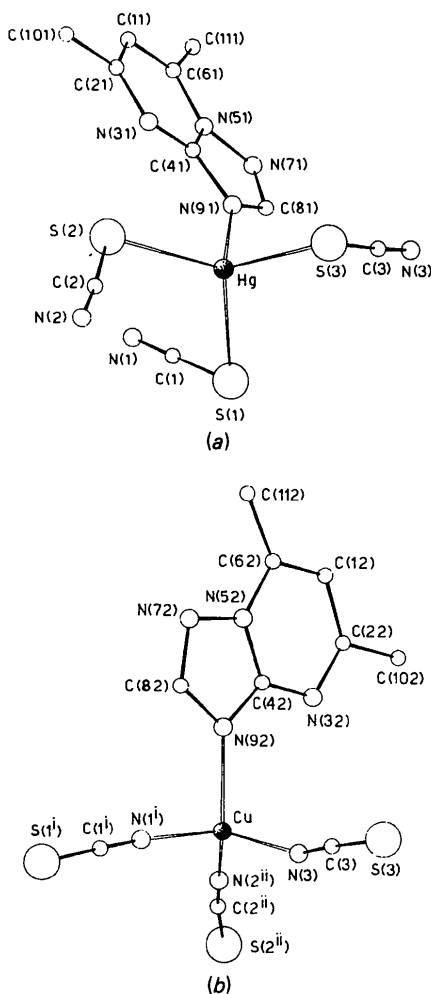


Fig. 1. Tetrahedral coordination around (a) Hg^{II} and (b) Cu^I in (V).

Table 2. Bond distances (Å) and angles (°)

(i) In the coordination sphere of the Hg ^{II} atom			
Hg–S(1)	2.557 (5)	Hg–S(3)	2.487 (6)
Hg–S(2)	2.465 (5)	Hg–N(91)	2.372 (19)
S(1)–Hg–S(2)	113.4 (2)	S(1)–Hg–N(91)	91.9 (5)
S(1)–Hg–S(3)	112.7 (2)	S(2)–Hg–N(91)	97.9 (4)
S(2)–Hg–S(3)	127.2 (2)	S(3)–Hg–N(91)	104.9 (4)
(ii) In the coordination sphere of the Cu ^I atom			
Cu–N(1 ⁱ)	2.00 (2)	Cu–N(3)	1.99 (2)
Cu–N(2 ⁱⁱ)	1.91 (2)	Cu–N(92)	2.06 (2)
N(1 ⁱ)–Cu–N(2 ⁱⁱ)	115.6 (7)	N(1 ⁱ)–Cu–N(92)	98.7 (7)
N(1 ⁱ)–Cu–N(3)	103.9 (8)	N(2 ⁱⁱ)–Cu–N(92)	114.1 (7)
N(2 ⁱⁱ)–Cu–N(3)	115.9 (8)	N(3)–Cu–N(92)	106.7 (7)
(iii) In the thiocyanate groups			
S(1)–C(1)	1.66 (2)	C(2)–N(2)	1.16 (3)
C(1)–N(1)	1.16 (3)	S(3)–C(3)	1.74 (2)
S(2)–C(2)	1.67 (2)	C(3)–N(3)	1.10 (2)
Hg–S(1)–C(1)	91.9 (7)	C(2)–N(2)–Cu ^{iv}	176 (2)
S(1)–C(1)–N(1)	179 (2)	Hg–S(3)–C(3)	92.1 (7)
C(1)–N(1)–Cu ^{iv}	170 (2)	S(3)–C(3)–N(3)	177 (2)
Hg–S(2)–C(2)	100.9 (6)	C(3)–N(3)–Cu	155 (2)
S(2)–C(2)–N(2)	175 (2)		
(iv) In the organic ligands			
C(11)–C(21)	1.41 (3)	C(12)–C(22)	1.40 (3)
C(21)–N(31)	1.32 (3)	C(22)–N(32)	1.34 (3)
N(31)–C(41)	1.33 (2)	N(32)–C(42)	1.34 (2)
C(41)–N(51)	1.35 (2)	C(42)–N(52)	1.36 (2)
N(51)–C(61)	1.37 (3)	N(52)–C(62)	1.36 (3)
C(11)–C(61)	1.37 (2)	C(12)–C(62)	1.38 (3)
N(51)–N(71)	1.39 (2)	N(52)–N(72)	1.37 (2)
N(71)–C(81)	1.30 (3)	N(72)–C(82)	1.34 (3)
C(81)–N(91)	1.33 (2)	C(82)–N(92)	1.36 (3)
C(41)–N(91)	1.37 (2)	C(42)–N(92)	1.35 (2)
C(21)–C(101)	1.52 (2)	C(22)–C(102)	1.50 (3)
C(61)–C(111)	1.49 (3)	C(62)–C(112)	1.48 (3)
C(21)–C(11)–C(61)	121 (2)	C(22)–C(12)–C(62)	121 (2)
C(11)–C(21)–N(31)	123 (2)	C(11)–C(22)–N(32)	124 (2)
C(21)–N(31)–C(41)	116 (2)	C(22)–N(32)–C(42)	114 (2)
N(31)–C(41)–N(51)	123 (2)	N(32)–C(42)–N(52)	124 (2)
C(41)–N(51)–C(61)	124 (2)	C(42)–N(52)–C(62)	123 (2)
N(51)–C(61)–C(11)	114 (2)	N(52)–C(62)–C(12)	114 (2)
N(51)–C(41)–N(91)	110 (2)	N(52)–C(42)–N(92)	109 (2)
C(41)–N(91)–C(81)	100 (2)	C(42)–N(92)–C(82)	103 (2)
N(91)–C(81)–N(71)	120 (2)	N(92)–C(82)–N(72)	115 (2)
C(81)–N(71)–N(51)	100 (2)	C(82)–N(72)–N(52)	102 (2)
N(71)–N(51)–C(41)	110 (1)	N(72)–N(52)–C(42)	111 (1)
C(11)–C(21)–C(101)	121 (2)	C(12)–C(22)–C(102)	121 (2)
N(31)–C(21)–C(101)	115 (2)	N(32)–C(22)–C(102)	116 (2)
C(11)–C(61)–C(111)	127 (2)	C(12)–C(62)–C(112)	128 (2)
N(51)–C(61)–C(111)	119 (2)	N(52)–C(62)–C(112)	118 (2)
Hg–N(91)–C(81)	138 (1)	Cu–N(92)–C(82)	122 (1)
Hg–N(91)–C(41)	122 (1)	Cu–N(92)–C(42)	134 (3)

Symmetry code: (i) *x*, *y*, $-1 + z$; (ii) $-1 + x$, *y*, $-1 + z$; (iii) *x*, *y*, $1 + z$; (iv) $1 + x$, *y*, $1 + z$.

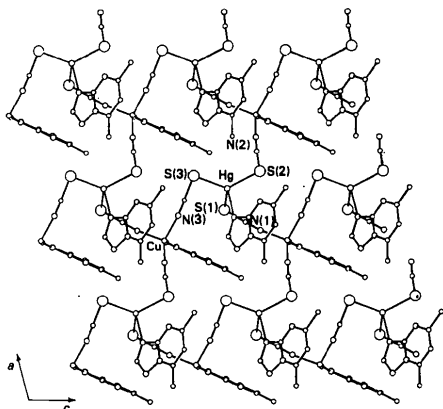


Fig. 2. Projection along *b* of the structure of (V).

differences found in the dimensions of the NCS groups and in the Cu–N–C angles can be attributed, respectively, to steric demand and steric strain of the organic and inorganic ligands in the linkage of the complexes. In the earlier-studied heterometal dmtp compounds the non-bridgehead pyrimidine N atom from dmtp was involved in intramolecular hydrogen bonds with coordinated water molecules which determined, apart from the packing, the orientation of the organic ligands. Although in the present compound the distance C(81)⋯N(32) of

3.37 (2) Å is rather long, the distance H(81)⋯N(32) = 2.45 Å and the angle C(81)–H(81)–N(32) = 142°, with H in a calculated position, suggest a weak interaction between the non-bridgehead pyrimidine N atoms from dmtp bonded to Cu^I and the C–H group from dmtp linked to Hg^{II}.

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Structure of 2-Oxatricyclo[6.4.0.0^{3,6}]dodeca-1(12),8,10-trien-7-ol

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Abstract. C₁₁H₁₂O₂, *M_r* = 176.2, monoclinic, *C*2/*c*, *a* = 23.575 (6), *b* = 7.591 (1), *c* = 10.056 (4) Å, β = 101.92 (3)°, *V* = 1760.8 Å³, *Z* = 8, *D_x* = 1.33, *D_m* = 1.34 g cm⁻³, λ(Mo *K*α) = 0.7107 Å, μ = 0.98 cm⁻¹, *F*(000) = 752, *T* = 293 K. Final *R* = 0.051 for 930 observed reflections. The study establishes the stereo-

chemistry at the ring junction as *cis* and the hydroxy group in the *endo* configuration. Bond lengths and angles are normal. The four-membered ring is planar to within ±0.01 Å.

Introduction. In connection with a comprehensive programme devoted to the synthesis of *A*-ring aromatic tricothecane analogues (Anderson & Lee, 1980) and related sesquiterpenes, compounds of type (1) were

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