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Synthesis, Characterization and X-ray Structure of Hetero-polynuclear Thiocyanates of Iron(II) and Mercury(II) with 5,7-Dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine-N^3 and Water as Ligands

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Abstract

The synthesis and characterization of heteronuclear compounds of formula $FeHg(NCS)_4(dmtp)_2(H_2O)_{1.5}$ (I), $FeHg(NCS)_4(dmtp)_2(H_2O)$ (II) and $FeHg(NCS)_4(dmtp)(H_2O)_2 \cdot (Me_2CO)$ (III) with dmtp = 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine ($C_7H_8N_4$) are described. Infrared spectra of these compounds have shown the presence of both S-coordinating and N,S-bridging thiocyanate ligands; moreover, ligand field spectra have indicated an octahedral coordination geometry for the iron ions. The structures of these compounds were elucidated by X-ray diffraction methods. Crystals of I are triclinic, space group $P\bar{1}$, with a = 16.318(10), b = 18.389(14), c = 10.089(4) Å, α = 105.15(4), β = 101.24(6), γ = 83.31(9)°, $Z = 2$; crystals of II are monoclinic, space group $P2_1/n$, with a = 11.599(7), b = 16.541(5), c = 14.766(10) Å, β = 98.47(5)°, Z = 4; crystals of III are monoclinic, space group $P2/n$, with a = 12.285(7), b = 13.689(6), c = 7.562(5) Å, β = 96.28(3)°, Z = 2. The structures were solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to $R = 0.044$ for I, 0.038 for II and 0.058 for III. The structure of I consists of two different octahedral complexes, $[Fe(NCS)_3(dmtp)_2(H_2O)]$ (a) and $[Fe(NCS)_2(dmtp)_2(H_2O)_2]$ (**b**) (in which nitrogen atoms from both thiocyanate groups and dmtp ligands besides water molecules are involved in coordination), and tetrahedral $[Hg(SCN)_4]$ complexes bridging either two or three iron atoms. In II $[Hg(SCN)_4]$ and $[Fe(NCS)_3(dmtp)_2(H_2O)]$ complexes are present, the octahedral iron complex differing from the complex (**a**) only in the mutual orientations of the dmtp molecules. The structure of III consists of $[Hg(SCN)_4]$ and $[Fe(NCS)_3(dmtp)(H_2O)_2]$ complexes together with acetone molecules of crystallization; the octahedral iron complex, involving only one dmtp molecule, can be derived from the complex (**b**) replacing a dmtp molecule by a thiocyanate ligand. The thiocyanate groups which bridge heterometals determine *one*-, *two*- and *three*-dimensional systems in I, III and II respectively.

Introduction

Thiocyanates of first-row transition metals show a great variety of structure types in their coordination compounds [1]. The thiocyanate group can be present in such compounds either as a free anion or coordinated to the metal ion. As a ligand it can be monodentate and bidentate, even bridging three or more metal atoms. The thiocyanate group often acts as a bridging ligand, either through -N-, -S- or -N,S-bridges [1]. The -N,S-bridging behaviour of the thiocyanate group has been found in 1,2,3-triazole derivatives [2–4] and often in heteronuclear compounds [5]. Recently [6] we reported the synthesis and the structure of the tetranuclear complex $Co_2Hg_2(NCS)_8(dmtp)_6(H_2O)_2$, containing two cobalt and two mercury atoms, alternately linked together by thiocyanate groups, thereby forming a non-planar sixteen-membered ring. Identical structures have been found with manganese or nickel replacing cobalt, but not with iron or copper.

In this paper we report the preparation and the structure of three different compounds of iron(II) and mercury(II), containing thiocyanate anions, water and 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine (hereafter abbreviated as dmtp) as ligands.

As pointed out in previous work [3, 6], the dmtp ligand can be compared with the purine system, the difference being in the position of one pyrimidine nitrogen atom, which in dmtp is in a bridge-head position with disappearance of the acidic N-proton of the five-membered ring.

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This paper discusses coordination compounds of purine analogues which are active in several (antimetabolitic) ways in biological systems, where interference with growth of neoplastic tissue and influence on the genetic properties of an organism are important [7].

Experimental

Synthesis and Characterization

The ligand dmtp was synthesized from 2,5-pentanedione and 3-amino-1,2,4-triazole according to a published method [8].

Iron(II) sulphate, mercury(II) thiocyanate and ammonium thiocyanate were used as commercially obtained.

When 1 mmol of $Hg(SCN)_2$ was dissolved in an aqueous solution (10 ml) of NH_4SCN (2 mmol) and this solution added to 10 ml of an aqueous solution of $FeSO_4$ (1 mmol) and dmtp (2 mmol), a yellow solution was obtained, from which yellow crystals separated after several days at room temperature: the compound analyzed as $FeHg(NCS)_4(dmtp)_2(H_2O)_{1.5}$ (**I**). By adding an equal volume of ethanol to the yellow solution, yellow crystals separated whose infrared spectrum and X-ray powder diffractogram were different from the previous ones: they analyzed as $FeHg(NCS)_4(dmtp)_2(H_2O)$ (**II**). Sometimes crystals of **I** and **II** formed simultaneously: they could easily be manually separated, differing in size and shape.

When an aqueous solution of mononuclear $Fe(NCS)_2(dmtp)_2(H_2O)_2$, prepared as previously described [9], was added to an acetone solution of an equimolar amount of $Hg(SCN)_2(dmtp)_2$, also prepared as before [9], a light yellow solution was eventually obtained, after dissolving an initial precipitate by warming up to about 50 °C. Yellow crystals separated upon standing from several hours up to several days. These crystals analyzed satisfactorily as $FeHg(NCS)_4(dmtp)(H_2O)_2(Me_2CO)$ (**III**).

All three compounds were further characterized by infrared spectra, recorded on a Perkin Elmer 580B spectrophotometer in CsCl discs and as nujol mulls, ligand field spectra by means of the diffuse reflectance technique on a Perkin Elmer 330 spectrophotometer, and by X-ray powder diffractograms using a Philips diffractometer.

X-ray Data Collection and Refinement of the Complexes **I**, **II** *and* **III**

A yellow irregularly-shaped crystal of **I** (dimensions *ca.* 0.25 × 0.30 × 0.40 mm), a yellow prismatic crystal of **II** (dimensions *ca.* 0.15 × 0.16 × 0.32 mm) and a yellow flattened crystal of **III** (dimensions *ca.* 0.10 × 0.47 × 0.80 mm) were used for the X-ray analyses. The cell parameters were refined by a least-squares procedure applied to the θ values of 20 (**I**), 23 (**II**) and 25 (**III**) reflections, carefully measured on a Siemens AED single-crystal diffractometer.

The crystal data are as follows:

Complex **I**: $C_{36}H_{38}Fe_2Hg_2N_{24}O_3S_8$, $M = 1624.2$, triclinic, $a = 16.318(10)$, $b = 18.389(14)$, $c = 10.089(4)$ Å, $\alpha = 105.15(4)$, $\beta = 101.24(6)$, $\gamma = 83.31(9)°$, $V = 2859(3)$ Å^3, $Z = 2$, $D_c = 1.89$ g cm^{-3}, $F(000) = 1572$, Mo-Kα radiation, $\lambda = 0.71069$ Å; μ(Mo-Kα) = 61.88 cm^{-1}. Space group $P\bar{1}$ from structure determination.

Complex **II**: $C_{18}H_{18}FeHgN_{12}OS_4$, $M = 803.1$, monoclinic, $a = 11.599(7)$, $b = 16.541(5)$, $c = 14.766(10)$ Å, $\beta = 98.47(5)°$, $V = 2802(3)$ Å^3, $Z = 4$, $D_c = 1.90$ g cm^{-3}, $F(000) = 1552$, Mo-Kα radiation, $\lambda = 0.71069$ Å; μ(Mo-Kα) = 63.12 cm^{-1}. Space group $P2_1/n$ from systematic absences.

Complex **III**: $C_{14}H_{18}FeHgN_8O_3S_4$, $M = 731.0$, monoclinic, $a = 12.285(7)$, $b = 13.689(6)$, $c = 7.562(5)$ Å, $\beta = 96.28(3)°$, $V = 1264(1)$ Å^3, $Z = 2$, $D_c = 1.92$ g cm^{-3}, $F(000) = 704$, Mo-Kα radiation, $\lambda = 0.71069$ Å, μ(Mo-Kα) = 69.87 cm^{-1}. Space group $P2/n$ from systematic absences and structure determination.

Intensities were collected at room temperature using Nb-filtered Mo-Kα radiation for all the compounds with the ω–2θ scan technique. All the reflections in the range of $6 < 2\theta < 48$ for **I**, $6 < 2\theta < 46$ for **II**, and $6 < 2\theta < 56$ for **III** were measured. Of 8719 (**I**), 3878 (**II**) and 3100 (**III**) independent reflections, 4784 (**I**), 1973 (**II**) and 2494 (**III**) having $I > 2\sigma(I)$ were considered observed and used in the analyses. The intensities were corrected for the usual Lorentz and polarization factors; no absorption correction was applied for **I** and **II**, while for **III** corrections for absorption and extinction were applied using the method of Walker and Stuard [10] (absorption correction min–max 0.533–1.914; extinction correction min–max 0.870–1.101). All the structures were solved by Patterson and Fourier methods and the refinements were carried out by least-squares full-matrix cycles, using the SHELX system of computer programs [11]. First isotropic and then anisotropic thermal parameters were estimated for all the non-hydrogen atoms of all compounds (with exception of the acetone atoms of **III**). The hydrogen atoms of the dmtp molecules were placed in their geometrical positions in **II** and **III**, and only for **II** were the hydrogen atoms of the water molecule localized directly from a difference synthesis. The hydrogen atoms were included in the final structure factors with isotropic thermal parameters. The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$; for **II** and **III** unit weights were used in each stage of the refinement, whereas for **I** unit weights were chosen in the first cycles and then the reflections were weighted according to the scheme $w = 0.3741/[\sigma^2(F_o) + 0.005\ F_o^2]$ with $\sigma(F_o)$ based on counting statistics. The final conventional *R* values were 0.044 for **I**, 0.038 for **II** and 0.058 for **III**. Atomic scattering factors, corrected for the anomalous dispersion for Hg, Fe and S atoms were taken from the International Tables [12]. The final atomic coordinates for the non-hydrogen atoms are given in Tables I–III for **I**, **II** and **III** respectively. Atomic coordinates of the hydrogen atoms, atomic thermal parameters and a list of calculated and observed structure factors for all the compounds are available from the authors on request.

TABLE I. Fractional Atomic Coordinates of the Non-Hydrogen Atoms ($\times 10^4$) for **I** with e.s.d.s in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
Hg1	4013(1)	2383(1)	1801(1)
Hg2	731(1)	1900(1)	-346(1)
Fe1	2829(1)	-827(1)	-478(2)
Fe2	2522(1)	3726(1)	6898(2)
S1	4350(3)	1997(2)	-595(4)
S2	4198(3)	1268(2)	2902(4)
S3	2691(3)	3180(2)	2159(4)
S4	5227(3)	3094(3)	3523(5)
S5	2159(3)	1614(2)	-1167(4)
S6	-236(3)	2920(2)	-1222(5)
S7	978(3)	2204(3)	2260(5)
S8	135(3)	614(2)	-1346(6)
O1w	2273(7)	-1830(5)	-1783(10)
O2w	2818(6)	4699(5)	6239(10)
O3w	2202(6)	4511(5)	8726(9)
N1	6056(9)	1552(7)	100(13)
N2	3465(8)	122(7)	754(13)
N3	2811(8)	3106(7)	4920(13)
N4	4308(8)	4264(8)	5053(15)
N5	2270(8)	2843(7)	-2295(13)
N6	880(9)	4091(8)	-453(15)
N7	-577(9)	1760(9)	2419(15)
N8	1705(9)	-177(7)	-946(13)
N31	2994(7)	-1814(6)	-4037(11)
N51	3717(7)	-810(6)	-4288(10)
N71	3948(8)	-109(6)	-3534(12)
N91	3270(7)	-647(6)	-2298(11)
N32	2378(8)	89(6)	3015(11)
N52	1707(7)	-983(7)	3005(12)
N72	1571(8)	-1699(7)	2207(13)
N92	2327(7)	-1064(6)	1242(11)
N33	1309(7)	4591(6)	4318(12)
N53	133(7)	3936(6)	4207(12)
N73	-103(7)	3469(7)	4907(12)
N93	1226(7)	3816(6)	5835(12)
N34	3812(7)	4416(6)	10151(12)
N54	5019(7)	3747(6)	9355(12)
N74	5233(8)	3265(6)	8162(12)
N94	3857(8)	3618(6)	7837(11)
C1	5359(11)	1754(8)	-134(14)
C2	3760(10)	594(9)	1587(16)
C3	2766(9)	3111(8)	3772(15)
C4	4674(9)	3781(9)	4407(17)
C5	2208(8)	2345(8)	-1835(14)
C6	475(12)	3609(9)	-698(15)
C7	61(9)	1925(9)	2356(14)
C8	1049(10)	144(8)	-1116(15)
C11	3579(8)	-1896(9)	-6093(14)
C21	3136(9)	-2213(9)	-5324(14)
C41	3317(8)	-1140(7)	-3573(13)
C61	3905(9)	-1166(9)	-5596(14)
C81	3681(9)	-41(8)	-2356(15)
C101	2781(11)	-2930(8)	-5909(18)
C111	4390(11)	-768(11)	-6244(16)
C12	1660(11)	59(10)	4896(16)
C22	2131(10)	425(9)	4237(16)
C42	2162(8)	-604(7)	2432(13)
C62	1416(10)	-639(11)	4295(15)
C82	1983(10)	-1711(8)	1142(16)
C102	2370(15)	1206(9)	4926(17)
C112	907(10)	-1125(10)	4789(17)
C13	79(10)	4636(8)	2578(15)
C23	908(8)	4841(8)	3226(15)
C43	935(9)	4136(8)	4778(14)
C63	-323(9)	4160(8)	3066(15)
C83	603(10)	3412(8)	5883(15)
C103	1307(11)	5358(8)	2665(16)
C113	-1153(11)	3891(9)	2519(17)
C14	5157(9)	4472(8)	11614(16)
C24	4294(9)	4684(8)	11365(15)
C44	4188(8)	3953(7)	9180(16)
C64	5554(9)	3991(8)	10605(16)
C84	4505(7)	3223(8)	7284(14)
C104	3866(11)	5230(9)	12504(15)
C114	6460(10)	3713(10)	10742(18)

TABLE II. Fractional Atomic Coordinates of the Non-Hydrogen Atoms ($\times 10^4$) for **II** with e.s.d.s in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
Hg	4738(1)	2089(1)	1121(1)
Fe	961(2)	493(1)	3103(1)
S1	6406(3)	3048(3)	1673(3)
S2	5360(4)	679(3)	1235(4)
S3	3023(5)	2689(3)	1814(4)
S4	3860(5)	2462(4)	-551(3)
Ow	1692(8)	-241(6)	2147(6)
N1	5122(11)	4497(8)	1670(8)
N2	3203(15)	-89(10)	814(13)
N3	2065(12)	1433(8)	2730(9)
N4	5228(12)	3728(7)	-968(9)
N31	535(11)	909(7)	683(8)
N51	-1365(11)	1403(7)	782(8)
N71	-2147(11)	1463(7)	1404(9)
N91	-399(11)	909(8)	2038(8)
N32	3743(11)	-598(7)	3490(8)
N52	3577(11)	-684(7)	5076(8)
N72	2826(12)	-413(8)	5653(8)

(continued overleaf)

TABLE II *(continued)*

Atom	*x/a*	*y/b*	*z/c*
N92	2225(10)	15(7)	4197(8)
C1	5642(12)	3902(10)	1672(9)
C2	4064(17)	244(11)	999(12)
C3	2474(14)	1927(9)	2353(10)
C4	4688(13)	3228(9)	−759(9)
C11	−708(15)	1497(8)	−618(10)
C21	366(15)	1140(9)	−209(11)
C41	−352(14)	1054(7)	1153(11)
C61	−1595(15)	1647(8)	−140(9)
C81	−1482(15)	1145(9)	2137(11)
C101	1361(14)	994(11)	−732(11)
C111	−2758(14)	1991(10)	−479(11)
C12	5103(14)	−1329(10)	4581(13)
C22	4700(14)	−1055(9)	3675(12)
C42	3212(13)	−416(8)	4203(10)
C62	4533(15)	−1135(10)	5296(12)
C82	2024(15)	−19(9)	5094(11)
C102	5300(16)	−1284(12)	2891(13)
C112	4857(17)	−1414(12)	6282(11)

TABLE III. Fractional Atomic Coordinates of the Non-Hydrogen Atoms ($\times 10^4$) for **III** with e.s.d.s in Parentheses.

Atom	*x/a*	*y/b*	*z/c*
Hg	2500	1916(1)	2500
Fe	−988(2)	2183(2)	6912(4)
S1	831(4)	822(4)	2055(7)
S2	2847(4)	2316(6)	−559(8)
S3	4056(5)	1126(4)	4520(9)
S4	1902(5)	3461(4)	4077(9)
O1w	−976(13)	3604(10)	5736(20)
O2w	−2642(14)	1992(11)	5839(25)
N1	−345(16)	1605(14)	4684(25)
N2	667(13)	2394(14)	−1881(24)
N3	3894(15)	−767(13)	3081(25)
N4	3331(19)	4753(14)	2507(31)
N31	−3455(12)	3343(12)	8061(23)
N51	−2592(12)	3771(11)	10892(22)
N71	−1582(13)	3687(12)	11876(18)
N91	−1617(13)	2941(12)	9231(22)
C1	153(14)	1282(13)	3575(24)
C2	1563(15)	2348(16)	−1340(26)
C3	3970(15)	12(14)	3675(27)
C4	2754(21)	4194(16)	3246(39)
C11	−4419(17)	4238(16)	10095(34)
C21	−4351(16)	3815(15)	8443(31)
C41	−2569(15)	3334(12)	9298(26)
C61	−3504(18)	4289(15)	11369(29)
C81	−1045(19)	3164(14)	10834(28)
C101	−3463(23)	4739(20)	13098(40)
C111	−5340(16)	3848(23)	7026(40)
O1	1661(18)	−1985(12)	−2636(31)
C5	1393(18)	−1190(17)	−3337(33)
C6	603(24)	−1163(22)	−4957(44)
C7	1796(25)	−272(25)	2585(49)

The calculations were carried out on the Cyber 76 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (CINECA, Casalecchio, Bologna) and on the GOULD-SEL 32/37 computer of the 'Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma). In addition to the quoted program, ASSORB [13], PLUTO [14] programs were used.

Results and Discussion

General and Spectroscopic Properties

The infrared spectra of the three compounds differ remarkably, not only from each other but also from those of the compounds $[MHg(NCS)_4(dmtp)_3(H_2O)]_2$ with M = Mn, Co, Ni [6]. Minor differences occur between the absorptions that may be ascribed to the dmtp. These minor differences suggest an identical coordination mode (through the usually favoured in the coordination to the metal triazole nitrogen site [3, 4, 6]). The presence of acetone in **III** is easily recognizable by the absorptions in the spectrum (particularly ν_{CO} at 1692 cm^{-1}) (Table IV). Most important are the differences in the absorptions due to the thiocyanate groups: as for all the compounds ν_{CN} absorptions occur at or above 2100 cm^{-1}, so S-bonding or N,S-bridging are expected. As shown by the determination of the crystal structures, in all the compounds the thiocyanate groups are either -N,S-bridging between iron and mercury or are S-bonded to mercury. In fair agreement with the structural results (compounds **I**, **II** and **III** present eight, four and four non-equivalent thiocyanate groups respectively) the ν_{CN} region of the infrared spectra (Table IV) shows at least five, three and three main absorption peaks respectively. In the ν_{CS} region, which is known to be highly diagnostic for the bonding mode of the thiocyanate group [15], ν_{CS} is observed only around 750 cm^{-1} for the bridging mode, or around 700 cm^{-1} for the S-bonding mode. In the far-infrared region, below 500 cm^{-1}, several absorptions are found which can be tentatively assigned to ν_{NCS}, ν_{FeN} and ν_{HgS} vibrations, on the basis of previous observations [9].

All the compounds are as yellow as the previously reported $Fe(NCS)_2(dmtp)_2(H_2O)_2$ [9]. The yellow colour is due to the low energy part of a charge transfer absorption at 340 nm that is present in the electronic spectra of all the compounds.

The ligand-field part of the spectra are also identical, except for some differences in intensity, showing a broad band (asymmetric) around 950 nm (10 500 cm^{-1}). This value is in accordance with what one would expect for iron(II) in a medium strong ligand-field [9] of six ligands in a distorted octahedral geometry.

TABLE IV. Infrared Spectral Properties of I, II and III.

	I	II	III
ν_{CN}	2150 sh, 2135 sh, 2125 vs, 2115 sh, 2100 s	2130 ms, 2108 s, 2095 sh	2140 sh, 2128 s, 2110 s
$2\delta_{NCS}$	928 m, 914 m, 897 w, 850 m	936 w, 929 w, 838 m	878 m
ν_{CS}	755 m, 745 m, 698 w, 690 w	760 w, 750 m, 700 w	750 br (probably together with acetone)
δ_{NCS}	468 w, 453 m, 428 w	468 m, 449 m, 427 m	448 m
ν_{FeO}	445 br		458 m
$\nu_{FeN_{lig}}$, ν_{FeNCS}, ν_{HgSCN}	230 vbr	250 sh, 218 s, vbr	240, 220 vs, vbr
			Acetone absorptions:
			1692, 1418, 1365, 1238, 1089, 993, 543, 397

Description of the Crystal Structure

The crystal structure of **I** consists of two different octahedral iron complexes, $[Fe(NCS)_3(dmtp)_2(H_2O)]$ (**a**) and $[Fe(NCS)_2(dmtp)_2(H_2O)_2]$ (**b**), and tetrahedral $[Hg(SCN)_4]$ units; these last show different behaviour as they bridge either two or three iron atoms. The iron complexes and tetrahedral units of **I** are depicted in Fig. 1 and Fig. 2, respectively. Bond distances and angles in them are given in Table V. The coordination of the iron atom in the complex (**a**) involves two N atoms from dmtp ligands in *trans* positions, an O atom from a water molecule and three N atoms from bridging thiocyanate ligands. The complex (**b**) differs from (**a**) in a second water molecule replacing a thiocyanate group and in the mutual orientations of the dmtp molecules. Complex (**b**) can be described as *trans*(N)*cis*(N′)*cis*(OH_2), where N and N′ are the nitrogen atoms from dmtp and thiocyanate groups respectively.

In **II** $[Fe(NCS)_3(dmtp)_2(H_2O)]$ complexes and $[Hg(SCN)_4]$ units (these last acting only as triple bridges), both depicted in Fig. 3, are present. Bond distances and angles are given in Table VI. The octahedral iron complex is very similar to the complex (**a**) in **I**, differing only in the orientation of the dmtp molecules.

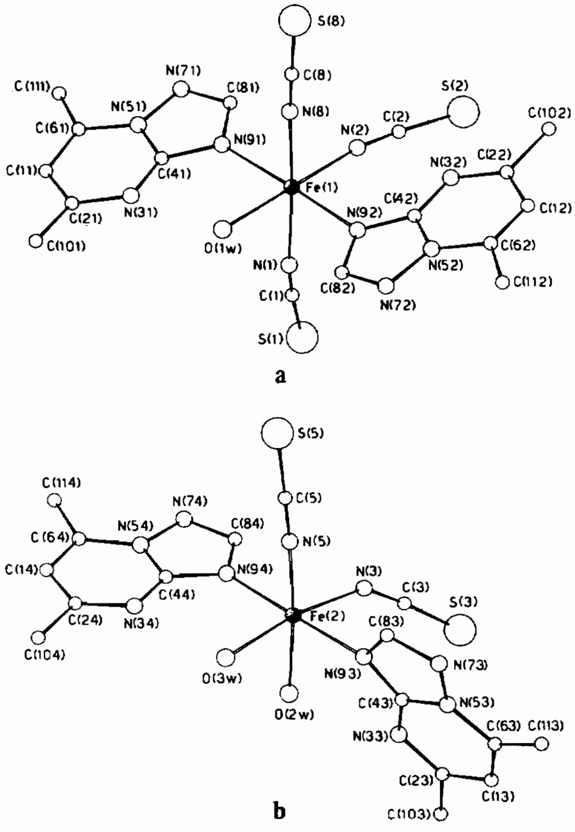

Fig. 1. Perspective view of the octahedral iron complexes, $[Fe(NCS)_3(dmtp)_2(H_2O)]$ (**a**) and $[Fe(NCS)_2(dmtp)_2(H_2O)_2]$ (**b**), in I.

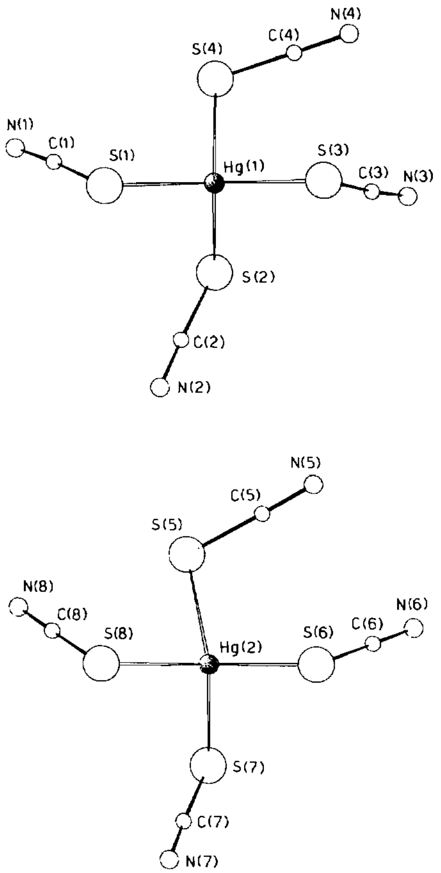

Fig. 2. Perspective view of the tetrahedral [Hg(SCN)$_4$] units in I.

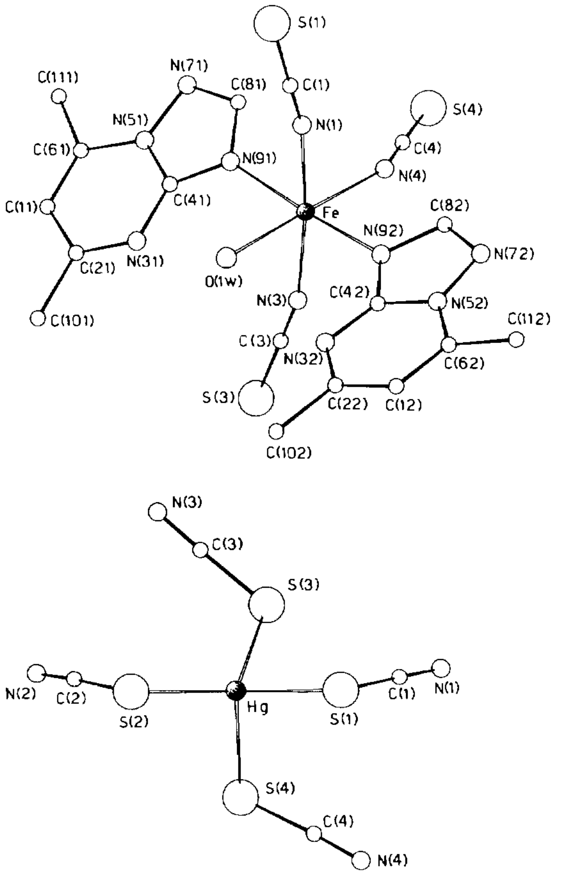

Fig. 3. Perspective view of the octahedral [Fe(NCS)$_3$(dmtp)$_2$(H$_2$O)] complex and of the tetrahedral [Hg(SCN)$_4$] unit in II.

TABLE V. Bond Distances (Å) and Angles (°) in I.

(i) In the coordination sphere of the iron atoms			
Fe(1)–O(1_w)	2.148(9)	Fe(2)–O(2_w)	2.197(11)
Fe(1)–N(1^i)	2.160(14)	Fe(2)–O(3_w)	2.137(9)
Fe(1)–N(2)	2.110(12)	Fe(2)–N(3)	2.135(13)
Fe(1)–N(8)	2.112(14)	Fe(2)–N(5^{ii})	2.109(15)
Fe(1)–N(91)	2.211(13)	Fe(2)–N(93)	2.186(11)
Fe(1)–N(92)	2.215(13)	Fe(2)–N(94)	2.208(12)
O(1_w)–Fe(1)–N(1^i)	86.0(5)	O(2_w)–Fe(2)–O(3_w)	87.3(4)
O(1_w)–Fe(1)–N(2)	175.5(6)	O(2_w)–Fe(2)–N(3)	83.5(5)
O(1_w)–Fe(1)–N(8)	90.3(5)	O(2_w)–Fe(2)–N(5^{ii})	175.2(5)
O(1_w)–Fe(1)–N(91)	89.4(4)	O(2_w)–Fe(2)–N(93)	91.0(5)
O(1_w)–Fe(1)–N(92)	86.8(5)	O(2_w)–Fe(2)–N(94)	87.3(5)
N(1^i)–Fe(1)–N(2)	90.2(6)	O(3_w)–Fe(2)–N(3)	170.1(5)
N(1^i)–Fe(1)–N(8)	176.3(5)	O(3_w)–Fe(2)–N(5^{ii})	88.6(5)
N(1^i)–Fe(1)–N(91)	89.5(5)	O(3_w)–Fe(2)–N(93)	90.3(5)
N(1^i)–Fe(1)–N(92)	91.4(5)	O(3_w)–Fe(2)–N(94)	93.0(4)
N(2)–Fe(1)–N(8)	93.4(6)	N(3)–Fe(2)–N(5^{ii})	100.8(5)
N(2)–Fe(1)–N(91)	88.1(5)	N(3)–Fe(2)–N(93)	86.5(5)
N(2)–Fe(1)–N(92)	95.8(5)	N(3)–Fe(2)–N(94)	90.0(5)
N(8)–Fe(1)–N(91)	90.0(5)	N(5^{ii})–Fe(2)–N(93)	91.5(5)
N(8)–Fe(1)–N(92)	88.9(5)	N(5^{ii})–Fe(2)–N(94)	90.4(5)
N(91)–Fe(1)–N(92)	176.0(5)	N(93)–Fe(2)–N(94)	176.2(5)

(continued on facing page)

TABLE V *(continued)*

(ii) in the coordination sphere of the mercury atoms			
Hg(1)–S(1)	2.486(5)	Hg(2)–S(5)	2.575(6)
Hg(1)–S(2)	2.539(5)	Hg(2)–S(6)	2.534(5)
Hg(1)–S(3)	2.495(5)	Hg(2)–S(7)	2.502(5)
Hg(1)–S(4)	2.594(5)	Hg(2)–S(8)	2.542(5)
S(1)–Hg(1)–S(2)	111.2(2)	S(5)–Hg(2)–S(6)	116.3(2)
S(1)–Hg(1)–S(3)	117.8(2)	S(5)–Hg(2)–S(7)	108.6(3)
S(1)–Hg(1)–S(4)	110.2(3)	S(5)–Hg(2)–S(8)	99.8(2)
S(2)–Hg(1)–S(3)	113.0(3)	S(6)–Hg(2)–S(7)	110.4(3)
S(2)–Hg(1)–S(4)	94.9(2)	S(6)–Hg(2)–S(8)	111.1(3)
S(3)–Hg(1)–S(4)	107.2(2)	S(7)–Hg(2)–S(8)	110.2(2)
(iii) in the thiocyanate groups			
S(1)–C(1)	1.66(2)	S(5)–C(5)	1.67(2)
C(1)–N(1)	1.15(2)	C(5)–N(5)	1.15(2)
S(2)–C(2)	1.67(1)	S(6)–C(6)	1.73(2)
C(2)–N(2)	1.12(2)	C(6)–N(6)	1.11(2)
S(3)–C(3)	1.64(2)	S(7)–C(7)	1.66(2)
C(3)–N(3)	1.15(2)	C(7)–N(7)	1.14(2)
S(4)–C(4)	1.63(2)	S(8)–C(8)	1.64(2)
C(4)–N(4)	1.14(2)	C(8)–N(8)	1.16(2)
Hg(1)–S(1)–C(1)	96.4(5)	Hg(2)–S(5)–C(5)	102.3(6)
S(1)–C(1)–N(1)	175(1)	S(5)–C(5)–N(5)	178(1)
C(1)–N(1)–Fe(1^{i})	161(1)	C(5)–N(5)–Fe(2^{iii})	174(1)
Hg(1)–S(2)–C(2)	101.7(6)	Hg(2)–S(6)–C(6)	96.5(7)
S(2)–C(2)–N(2)	176(2)	S(6)–C(6)–N(6)	173(2)
C(2)–N(2)–Fe(1)	168(1)	Hg(2)–S(7)–C(7)	94.7(6)
Hg(1)–S(3)–C(3)	93.6(6)	S(7)–C(7)–N(7)	177(2)
S(3)–C(3)–N(3)	176(1)	Hg(2)–S(8)–C(8)	94.1(7)
C(3)–N(3)–Fe(2)	145(1)	S(8)–C(8)–N(8)	179(1)
Hg(1)–S(4)–C(4)	98.8(7)	C(8)–N(8)–Fe(1)	173(1)
S(4)–C(4)–N(4)	178(2)		
(iv) in the organic ligands			
C(11)–C(21)	1.42(2)	C(12)–C(22)	1.43(3)
C(21)–N(31)	1.36(2)	C(22)–N(32)	1.34(2)
N(31)–C(41)	1.34(2)	N(32)–C(42)	1.31(2)
C(41)–N(51)	1.35(2)	C(42)–N(52)	1.37(2)
N(51)–C(61)	1.39(2)	N(52)–C(62)	1.43(2)
C(11)–C(61)	1.43(2)	C(12)–C(62)	1.34(2)
N(71)–C(81)	1.31(2)	N(52)–N(72)	1.37(2)
C(81)–N(91)	1.38(2)	N(72)–C(82)	1.37(2)
C(41)–N(91)	1.38(1)	C(82)–N(92)	1.35(2)
N(51)–N(71)	1.37(1)	C(42)–N(92)	1.33(2)
C(21)–C(101)	1.43(2)	C(22)–C(102)	1.48(2)
C(61)–C(111)	1.47(3)	C(62)–C(112)	1.52(3)
C(21)–C(11)–C(61)	124(1)	C(22)–C(12)–C(62)	121(1)
C(11)–C(21)–N(31)	120(1)	C(12)–C(22)–N(32)	123(1)
C(21)–N(31)–C(41)	115(1)	C(22)–N(32)–C(42)	117(1)
N(31)–C(41)–N(51)	126(1)	N(32)–C(42)–N(52)	123(1)
C(41)–N(51)–C(61)	123(1)	C(42)–N(52)–C(62)	122(1)
N(51)–C(61)–C(11)	111(1)	N(52)–C(62)–C(12)	114(1)
N(51)–C(41)–N(91)	108(1)	N(52)–C(42)–N(92)	107(1)
C(41)–N(51)–N(71)	112(1)	C(42)–N(52)–N(72)	112(1)
N(51)–N(71)–C(81)	103(1)	N(52)–N(72)–C(82)	100(1)
N(71)–C(81)–N(91)	115(1)	N(72)–C(82)–N(92)	115(1)
C(81)–N(91)–C(41)	103(1)	C(82)–N(92)–C(42)	105(1)

(continued overleaf)

TABLE V *(continued)*

C(81)–N(91)–Fe(1)	127.6(9)	C(82)–N(92)–Fe(1)	123.5(9)
C(41)–N(91)–Fe(1)	129.3(9)	C(42)–N(92)–Fe(1)	130.2(9)
C(13)–C(23)	1.43(2)	C(14)–C(24)	1.41(2)
C(23)–N(33)	1.33(2)	C(24)–N(34)	1.33(2)
N(33)–C(43)	1.31(2)	N(34)–C(44)	1.32(2)
C(43)–N(53)	1.37(2)	C(44)–N(54)	1.35(2)
N(53)–C(63)	1.37(2)	N(54)–C(64)	1.39(2)
C(13)–C(63)	1.39(2)	C(14)–C(64)	1.37(2)
N(53)–N(73)	1.37(2)	N(54)–N(74)	1.37(2)
N(73)–C(83)	1.37(2)	N(74)–C(84)	1.33(2)
C(83)–N(93)	1.34(2)	C(84)–N(94)	1.34(2)
C(43)–N(93)	1.33(2)	C(44)–N(94)	1.36(2)
C(23)–C(103)	1.49(2)	C(24)–C(104)	1.54(2)
C(63)–C(113)	1.45(2)	C(64)–C(114)	1.50(2)
C(23)–C(13)–C(63)	120(1)	C(24)–C(14)–C(64)	122(1)
C(13)–C(23)–N(33)	121(1)	C(14)–C(24)–N(34)	122(1)
C(23)–N(33)–C(43)	119(1)	C(24)–N(34)–C(44)	116(1)
N(33)–C(43)–N(53)	122(1)	N(34)–C(44)–N(54)	124(1)
C(43)–N(53)–C(63)	123(1)	C(44)–N(54)–C(64)	122(1)
N(53)–C(63)–C(13)	114(1)	N(54)–C(64)–C(14)	113(1)
N(53)–C(43)–N(93)	109(1)	N(54)–C(44)–N(94)	107(1)
C(43)–N(53)–N(73)	110(1)	C(44)–N(54)–N(74)	111(1)
N(53)–N(73)–C(83)	102(1)	N(54)–N(74)–C(84)	102(1)
N(73)–C(83)–N(93)	114(1)	N(74)–C(84)–N(94)	114(1)
C(83)–N(93)–C(43)	105(1)	C(84)–N(94)–C(44)	105(1)
C(83)–N(93)–Fe(2)	126(1)	C(84)–N(94)–Fe(2)	130(1)
C(43)–N(93)–Fe(2)	127(1)	C(44)–N(94)–Fe(2)	125(1)

(v) probable hydrogen bonds

O(1$_w$)•••N(31)	2.76(2)
O(1$_w$)•••N(7^{iv})	2.71(2)
O(2$_w$)•••N(33)	2.81(1)
O(2$_w$)•••N(4)	2.86(2)
O(3$_w$)•••N(34)	2.75(1)
O(3$_w$)•••N(6^{ii})	2.71(2)

Asymmetric units

i $1 - x, -y, -z$
ii $x, y, 1 + z$
iii $x, y, z - 1$
iv $-x, -y, -z$

TABLE VI. Bond Distances (Å) and Angles (°) in **II**.

(i) In the coordination sphere of the iron atom

Fe–O$_w$	2.130(10)	Fe–N(4^{ii})	2.147(14)
Fe–N(1^{i})	2.128(13)	Fe–N(91)	2.169(12)
Fe–N(3)	2.137(14)	Fe–N(92)	2.165(11)
O$_w$–Fe–N(1^{i})	88.0(5)	N(1^{i})–Fe–N(92)	87.2(5)
O$_w$–Fe–N(3)	86.1(5)	N(3)–Fe–N(4^{ii})	92.1(5)
O$_w$–Fe–N(4^{ii})	177.8(4)	N(3)–Fe–N(91)	89.0(5)
O$_w$–Fe–N(91)	91.1(4)	N(3)–Fe–N(92)	95.3(5)
O$_w$–Fe–N(92)	89.7(4)	N(4^{ii})–Fe–N(91)	87.6(5)
N(1^{i})–Fe–N(3)	173.6(5)	N(4^{ii})–Fe–N(92)	91.8(5)
N(1^{i})–Fe–N(4^{ii})	93.8(5)	N(91)–Fe–N(92)	175.7(5)
N(1^{i})–Fe–N(91)	88.7(5)		

(continued on facing page)

TABLE VI *(continued)*

(ii) in the coordination sphere of the mercury atom			
Hg–S(1)	2.542(4)	Hg–S(3)	2.567(6)
Hg–S(2)	2.440(5)	Hg–S(4)	2.602(5)
S(1)–Hg–S(2)	111.8(2)	S(2)–Hg–S(3)	125.5(2)
S(1)–Hg–S(3)	103.2(2)	S(2)–Hg–S(4)	111.3(2)
S(1)–Hg–S(4)	109.2(2)	S(3)–Hg–S(4)	93.9(2)
(iii) in the thiocyanate groups			
S(1)–C(1)	1.67(2)	S(3)–C(3)	1.67(2)
C(1)–N(1)	1.15(2)	C(3)–N(3)	1.13(2)
S(2)–C(2)	1.66(2)	S(4)–C(4)	1.65(2)
C(2)–N(2)	1.14(3)	C(4)–N(4)	1.11(2)
Hg–S(1)–C(1)	98.6(5)	Hg–S(3)–C(3)	105.7(6)
S(1)–C(1)–N(1)	179(1)	S(3)–C(3)–N(3)	177(1)
C(1)–N(1)–Fe^{iii}	169(1)	Hg–S(4)–C(4)	101.7(5)
Hg–S(2)–C(2)	98.7(7)	S(4)–C(4)–N(4)	175(1)
S(2)–C(2)–N(2)	176(2)	C(4)–N(4)–Fe^{iv}	157(1)
		C(3)–N(3)–Fe	164(1)
(iv) in the organic ligands			
C(11)–C(21)	1.43(2)	C(12)–C(22)	1.42(2)
C(21)–N(31)	1.36(2)	C(22)–N(32)	1.34(2)
N(31)–C(41)	1.34(2)	N(32)–C(42)	1.33(2)
C(41)–N(51)	1.35(2)	C(42)–N(52)	1.37(2)
N(51)–C(61)	1.41(2)	N(52)–C(62)	1.34(2)
C(61)–C(11)	1.35(2)	C(62)–C(12)	1.36(3)
N(51)–N(71)	1.39(2)	N(52)–N(72)	1.38(2)
N(71)–C(81)	1.34(2)	N(72)–C(82)	1.32(2)
C(81)–N(91)	1.34(2)	C(82)–N(92)	1.38(2)
C(41)–N(91)	1.34(2)	C(42)–N(92)	1.35(2)
C(21)–C(101)	1.50(2)	C(22)–C(102)	1.48(3)
C(61)–C(111)	1.48(2)	C(62)–C(112)	1.52(2)
C(21)–C(11)–C(61)	122(1)	C(22)–C(12)–C(62)	121(2)
C(11)–C(21)–N(31)	121(1)	C(12)–C(22)–N(32)	121(1)
C(21)–N(31)–C(41)	116(1)	C(22)–N(32)–C(42)	116(1)
N(31)–C(41)–N(51)	124(1)	N(32)–C(42)–N(52)	124(1)
C(41)–N(51)–C(61)	123(1)	C(42)–N(52)–C(62)	123(1)
N(51)–C(61)–C(11)	114(1)	N(52)–C(62)–C(12)	115(2)
N(91)–C(41)–N(51)	108(1)	N(92)–C(42)–N(52)	109(1)
C(41)–N(51)–N(71)	112(1)	C(42)–N(52)–N(72)	110(1)
N(51)–N(71)–C(81)	99(1)	N(52)–N(72)–C(82)	103(1)
N(71)–C(81)–N(91)	117(1)	N(72)–C(82)–N(92)	115(1)
C(81)–N(91)–C(41)	103(1)	C(82)–N(92)–C(42)	104(1)
C(41)–N(91)–Fe	129(1)	C(42)–N(92)–Fe	133(1)
C(81)–N(91)–Fe	127(1)	C(82)–N(92)–Fe	123(1)
(v) in the water molecule			
O_w–H(1)	1.18	H(1)–O_w–H(2)	110
O_w–H(2)	1.18		
(vi) hydrogen bonds			
O_w···N(32)	2.92(1)	O_w–H(1)–N(32)	163
H(1)···N(32)	1.77	H(1)–O_w–N(32)	10
O_w···N(31)	3.04(1)	O_w–H(2)–N(31)	128
H(2)···N(31)	2.16	H(32)–O_w–N(31)	34
O_w···N(2)	2.83(2)	O_w–H(2)–N(2)	118
H(2)···N(2)	2.07	H(2)–O_w–N(2)	40

(continued overleaf)

TABLE VI *(continued)*

Asymmetric units

i	$1/2 - x, -1/2 + y, 1/2 - z$	iii	$1/2 - x, 1/2 + y, 1/2 - z$
ii	$-1/2 + x, 1/2 - y, 1/2 + z$	iv	$1/2 + x, 1/2 - y, -1/2 + z$

The structure of **III** consists of octahedral [Fe$(NCS)_3$(dmtp)$(H_2O)_2$] complexes, with nitrogen atoms from thiocyanate groups in mutual *fac* positions, and [Hg$(SCN)_4$] units bridging three iron atoms together with acetone molecules of crystallization. The iron and mercury complexes are represented in Fig. 4. Bond distances and angles are given in Table VII. The octahedral iron complex, in which only one dmtp molecule is coordinated, can be derived from complex (**b**) replacing a dmtp molecule by a thiocyanate ligand.

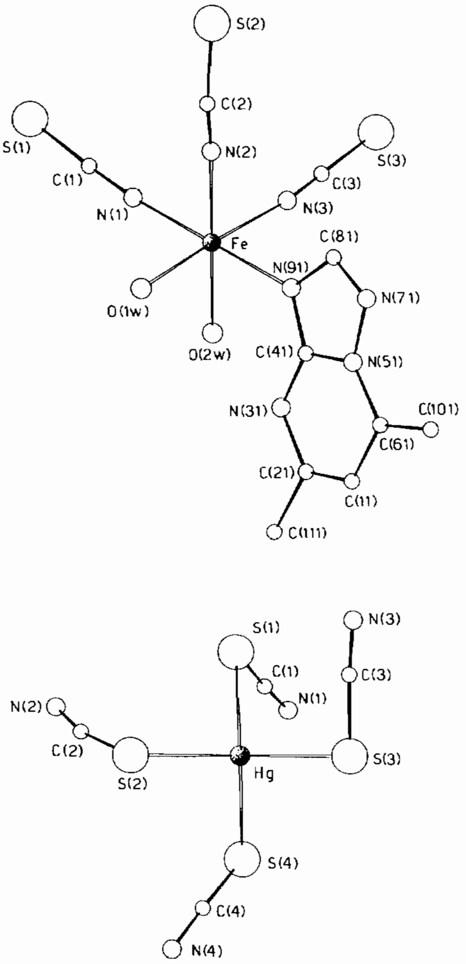

Fig. 4. Perspective view of the octahedral [Fe$(NCS)_3$(dmtp)$(H_2O)_2$] complex and of the tetrahedral [Hg$(SCN)_4$] unit in **III**.

The Fe–N distances found in **I**, **II** and **III**, involving the nitrogen atoms from bridging thiocyanate ligands and from dmtp molecules, are respectively in the ranges 2.10(2)–2.16(1) and 2.16(1)–2.25(2) Å, in good agreement with those observed for the octahedrally coordinated iron complexes with isothiocyanate groups, 2.102(3)–2.156(11) Å [16, 17] and with imidazole ligands, 2.16(1)–2.24(1) Å [18].

In the tetrahedral [Hg$(SCN)_4$] units of all the examined complexes the thiocyanate groups are bridging or terminal hydrogen-bonded acceptor ligands, the Hg–S distances being in the range 2.440(5)–2.602(5) Å, the first value being among the shortest ones found in the Hg(II) thiocyanates [9, 19].

The different orientations of the dmtp ligands in the iron complexes are probably determined by intramolecular hydrogen bonds between coordinated water molecules and N(3) pyrimidine nitrogen atoms from dmtp. In **I** the O(1w), O(2w) and O(3w) water molecules form probable hydrogen bonds with the N(31), N(33) and N(34) atoms respectively; in **II** both dmtp molecules are hydrogen-bonded through N(31) and N(32) to the water molecule of the complex; in **III** the N(31) atom is probably involved in a hydrogen bonding with the O(2w) water molecule. These intramolecular hydrogen bonds determine an indirect chelation of the dmtp molecules, as mentioned in a previous work [6]. All the five-membered pseudo-chelate rings are not planar, the N(9) and N(3) atoms having the greatest deviations from the mean plane passing through the atoms of the ring. In all the compounds the dmtp ligands, always coordinated through the metal triazole nitrogen site [3, 6], show normal bond lengths and angles with the nine-framework of the organic ligand planar. This is in contrast with what found in the previously analyzed [CoHg$(SCN)_4$$(dmtp)_3(H_2O)]_2$ compound [6], in which only the framework of the dmtp molecules, not involved in an interligand hydrogen bonding, is planar.

In **I** all the tetrahedral [Hg$(SCN)_4$] complexes join, through two thiocyanate groups, the octahedral iron complexes in helicoidal chains whereas a half of these acting as triply bridging connect the chains in ribbons running along *c* (Fig. 5). The packing of the ribbons (Fig. 6) is determined by stacking interactions involving dmtp molecules

TABLE VII. Bond Distances (Å) and Angles (°) in **III**.

(i) In the coordination sphere of the iron atom			
Fe–O(1_w)	2.140(14)	Fe–N(2^i)	2.155(16)
Fe–O(2_w)	2.120(17)	Fe–N(3^{ii})	2.142(18)
Fe–N(1)	2.093(20)	Fe–N(91)	2.246(17)
O(1_w)–Fe–O(2_w)	90.2(6)	O(2_w)–Fe–N(91)	87.6(6)
O(1_w)–Fe–N(1)	89.4(7)	N(1)–Fe–N(2^i)	88.3(7)
O(1_w)–Fe–N(2^i)	90.3(6)	N(1)–Fe–N(3^{ii})	92.2(7)
O(1_w)–Fe–N(3^{ii})	176.5(7)	N(1)–Fe–N(91)	174.6(7)
O(1_w)–Fe–N(91)	85.6(6)	N(2^i)–Fe–N(3^{ii})	92.9(7)
O(2_w)–Fe–N(1)	94.3(7)	N(2^i)–Fe–N(91)	89.8(7)
O(2_w)–Fe–N(2^i)	177.4(7)	N(3^{ii})–Fe–N(91)	92.9(7)
O(2_w)–Fe–N(3^{ii})	86.6(7)		
(ii) in the coordination sphere of the mercury atom			
Hg–S(1)	2.532(5)	Hg–S(3)	2.553(6)
Hg–S(2)	2.459(6)	Hg–S(4)	2.574(6)
S(1)–Hg–S(2)	103.2(2)	S(2)–Hg–S(3)	117.5(2)
S(1)–Hg–S(3)	111.8(2)	S(2)–Hg–S(4)	109.9(2)
S(1)–Hg–S(4)	106.2(2)	S(3)–Hg–S(4)	107.7(2)
(iii) in the thiocyanate groups			
S(1)–C(1)	1.62(2)	S(3)–C(3)	1.65(2)
C(1)–N(1)	1.18(3)	C(3)–N(3)	1.16(3)
S(2)–C(2)	1.62(2)	S(4)–C(4)	1.62(3)
C(2)–N(2)	1.13(2)	C(4)–N(4)	1.22(3)
Hg–S(1)–C(1)	98.5(7)	Hg–S(3)–C(3)	98.5(7)
S(1)–C(1)–N(1)	179(2)	S(3)–C(3)–N(3)	179(2)
C(1)–N(1)–Fe	170(2)	C(3)–N(3)–Fe^{iv}	171(2)
Hg–S(2)–C(2)	95.0(7)	Hg–S(4)–C(4)	95.7(9)
S(2)–C(2)–N(2)	178(2)	S(4)–C(4)–N(4)	175(2)
C(2)–N(2)–Fe^{iii}	168(2)		
(iv) in the organic ligand			
C(11)–C(21)	1.39(3)	N(51)–N(71)	1.38(2)
C(21)–N(31)	1.33(3)	N(71)–C(81)	1.30(3)
N(31)–C(41)	1.35(2)	C(81)–N(91)	1.37(3)
C(41)–N(51)	1.35(2)	C(41)–N(91)	1.29(2)
N(31)–C(61)	1.41(3)	C(61)–C(101)	1.44(4)
C(61)–C(11)	1.40(3)	C(21)–C(111)	1.53(3)
C(21)–C(11)–C(61)	121(2)	C(41)–N(51)–N(71)	110(1)
C(11)–C(21)–N(31)	122(2)	N(51)–N(71)–C(81)	102(1)
C(21)–N(31)–C(41)	118(2)	N(71)–C(81)–N(91)	114(2)
N(31)–C(41)–N(51)	121(2)	C(81)–N(91)–C(41)	105(2)
C(41)–N(51)–C(61)	123(2)	C(41)–N(91)–Fe	128(1)
N(51)–C(61)–C(11)	114(2)	C(81)–N(91)–Fe	127(1)
N(91)–C(41)–N(51)	109(2)		
(v) in the acetone molecule			
O(1)–C(5)	1.24(3)	O(1)–C(5)–C(7)	122(2)
C(5)–C(6)	1.48(4)	O(1)–C(5)–C(6)	120(2)
C(5)–C(7)	1.44(4)	C(6)–C(5)–C(7)	118(2)
(vi) probable hydrogen bonds			
O(1_w)···N(4^v)	2.80(3)	O(2_w)···N(31)	2.76(2)
O(1_w)···N(71^{iii})	2.93(2)	O(2_w)···O(1^{ii})	2.67(3)
Asymmetric units	i $x, y, 1 + z$	iv $1/2 + x, -y, -1/2 + z$	
	ii $-1/2 + x, -y, 1/2 + z$	v $-1/2 + x, 1 - y, 1/2 + z$	
	iii $x, y, -1 + z$		

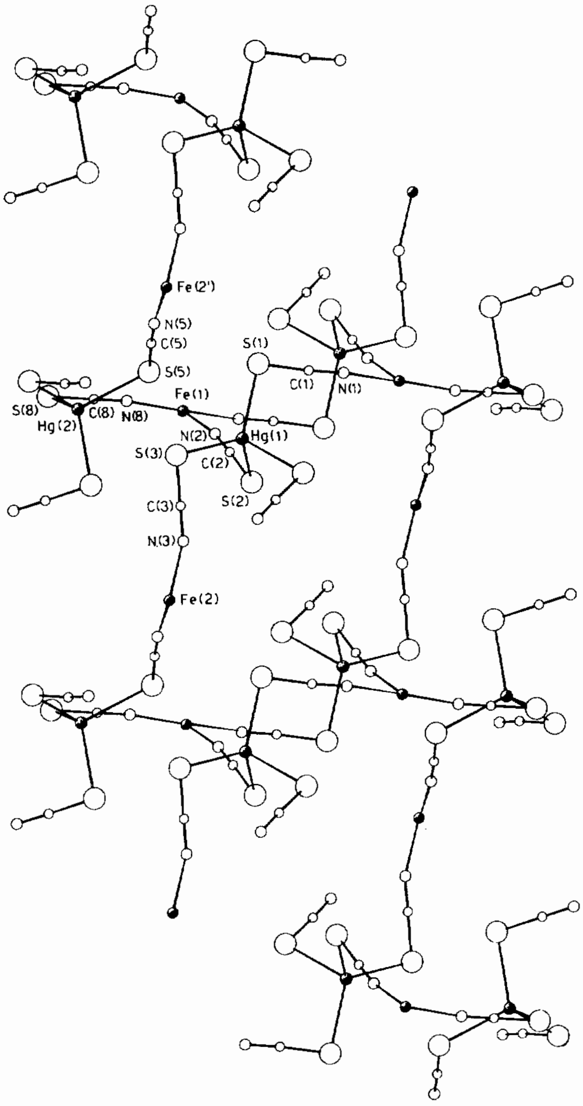

Fig. 5. Ribbons, running along *c*, of iron octahedra and mercury tetrahedra in I (the dmtp molecules are omitted for clarity).

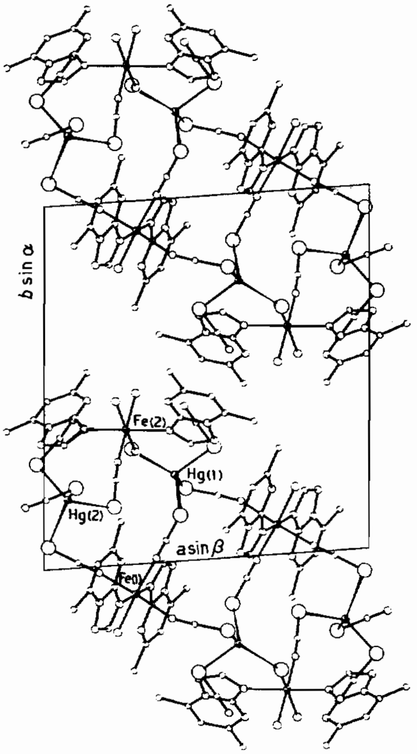

Fig. 6. Projection along *c* of the structure of I.

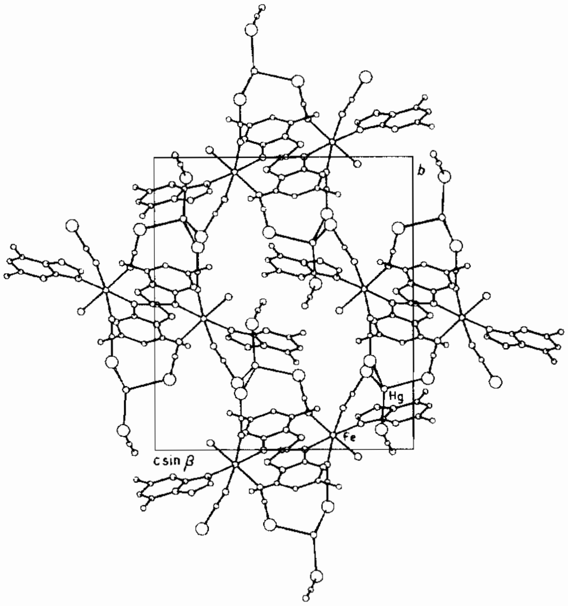

Fig. 7. Projection along *a* of the structure of II.

from ribbons related by inversion centers at 0 1/2 1/2 and 1/2 1/2 1/2 (the mean separation between the nine-ring framework is 3.4 Å) and by hydrogen bonds between water molecules and nitrogen atoms from monodendate thiocyanate groups.

Tetrahedral $[Hg(SCN)_4]$ units, all triply bridging octahedral iron complexes, form a three-dimensional network in **II** (Fig. 7) and layers parallel to (010) in **III** (Fig. 8), these last containing acetone molecules linked by hydrogen bonds to the water molecules of the same layer. Hydrogen bonds involving water molecules and nitrogen atoms from monodentate thiocyanate groups also contribute to the tridimensional network in **II** and to the linkage of the layers in **III**. Moreover, in **III** the triazole nitrogen atom N(71) is involved in an intermolecular hydrogen bond with the water molecule of an adjacent iron complex.

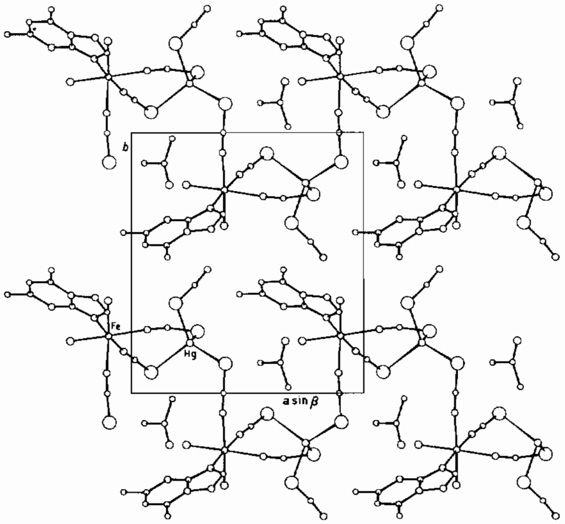

Fig. 8. Projection along *c* of the structure of III.

References

1 M. Kabešová and J. Gažo, *Chem. Zvesti, 34*, 800 (1980).

2 L. R. Groeneveld, G. Vos, G. C. Verschoor and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, 620 (1982).

3 M. Biagini Cingi, A. M. Manotti Lanfredi, A. Tiripicchio, J. G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta, 72*, 81 (1983).

4 J. G. Haasnoot, W. L. Driessen and J. Reedijk, *Inorg. Chem., 23*, 2803 (1984).

5 P. P. Singh, *Coord. Chem. Rev., 32*, 33 (1980).

6 M. Biagini Cingi, A. M. Manotti Lanfredi, A. Tiripicchio, J. G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta, 86*, 137 (1984).

7 J. Gut, *Adv. Heterocyclic Chem., 1*, 189 (1963).

8 C. Bülow and K. Haas, *Ber. Dtsch. Chem. Ges., 42*, 4638 (1909).

9 J. Dillen, A. Th. Lenstra, J. G. Haasnoot and J. Reedijk, *Polyhedron, 2,* 195 (1983).

10 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A:, 39*, 158 (1983).

11 G. M. Sheldrick, 'SHELX-76', System of Computing Programs, University of Cambridge, 1976.

12 'International Tables for X-ray Crystallography, Vol. IV', Kynoch Press, Birmingham, England, 1974.

13 F. Ugozzoli, 'ASSORB', A Program for Walker and Stuard's Absorption Correction, University of Parma, Italy, 1983.

14 W. D. S. Motherwell, 'PLUTO', University of Cambridge, 1976.

15 R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, *Coord. Chem. Rev., 6*, 407 (1971).

16 D. W. Engelfriet and G. C. Verschoor, *Acta Crystallogr., Sect. B:, 37*, 237 (1981).

17 G. L. Long, G. Galeazzi, U. Russo, G. Valle and S. Calogero, *Inorg. Chem., 22*, 507 (1983).

18 V. R. Lehnert and F. Seel, *Z. Anorg. Allg. Chem., 444*, 91 (1978).

19 E. C. Alyea, G. Ferguson and R. J. Restivo, *J. Chem. Soc., Dalton Trans.*, 1845 (1977).