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Synthesis and Spectroscopic Characterization of a New Class of Heterotetranuclear Compounds with Thiocyanate Groups as Bridging Ligands. The X-ray Structure of Bis-(μ-tetrakis(thiocyanato-*S*)mercury(II)-*N,N'*)diaquahexakis-(5.7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine-N^3) dicobalt(II)

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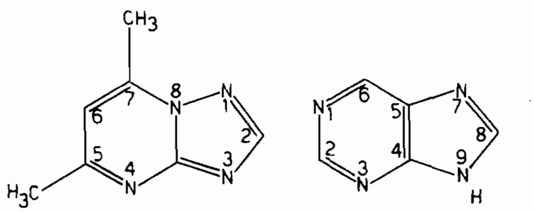
The synthesis and characterization of a novel type of heterotetranuclear compounds of general formula $[MHg(dmtp)_3(SCN)_4(H_2O)]_2$ *[M = Mn, Co, Ni(II) and dmtp = 5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidine] are described. Infrared spectra show the presence of both S-coordinating and N,S-bridging thiocyanate ligands. Ligand-field spectra indicate an ocahedral coordination geometry for the transition-metal ions. The structure of one of the three, mutually isomorphous, compounds was determined by X-ray diffraction methods. Crystals of* $[CoHg(dmtp)_3(SCN)_4(H_2O)]_2$ *are triclinic, space groups* $P\bar{1}$ *with* a = *11.481(9),* b = *13.975(11),* c = *11.479(8) Å,* α = *101.08(6),* β = *90.11(7),* γ = *77.24(6)°, Z = 1. The structure was solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least-squares to R = 0.038 for 2392 independent observed reflections. The structure consists of centrosymmetric heterotetranuclear complexes formed by thiocyanate groups bridging heterometals. Mercury is tetrahedrally coordinated by sulphur atoms from thiocyanate groups (Hg–S bonds ranging from 2.457 to 2.601 Å), two of which bridge two centrosymmetric Co atoms. Three N atoms from dmtp ligands and one oxygen from a water molecule complete the octahedral coordination of Co (Co–N bonds: 2.11, 2.14 and 2.18 Å; Co–*O_w *bond: 2.08 Å). Intramolecular hydrogen bonds between water hydrogens and N atom sfrom a dmtp molecule and a non-bridging thiocyanate group respectively stabilize the tetranuclear species. Magnetic susceptibility studies indicate that the magnetic exchange between the metal ions is very weak.*

Introduction

The increasing interest in the development of the metal complexes of heterocyclic ligands has led us to the use of 5,7-dimethyl[1,2,4]triazolo[1,5-*a*] pyrimidine (abbreviated dmtp) [1, 2], a ligand whose skeleton differs from the purine system in having a pyrimidine nitrogen atom in a bridgehead position.



IUPAC Numbering Schemes of dmtp and purine molecules

Although three nitrogen atoms are available for coordination, steric reasons hamper coordination at N_1 and N_4, and so far only N_3 coordination has been observed [1–3].

Using thiocyanate transition metal compounds, the following stoichiometries have been obtained: $M(dmtp)_2(H_2O)_2(NCS)_2$ for M = Mn, Fe, Co, Ni, Cd [1], $Cu_2(dmtp)_4(NCS)_4$ (a dimer which exists in two isomers) [2,4], $Zn(dmtp)_2(NCS)_2$ (a tetra-

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hedral species) [1], $Hg(dmtp)_2(SCN)_2$ (a tetrahedral species containing S-bonded thiocyanate) [1], $Pt(dmtp)_4Pt(SCN)_6$ (a mixed valence compound [2].

It appeared interesting to study the mixed metal species with $Hg(SCN)_2$ to see whether the coordination of NCS could be influenced by Hg or the other metal ions and to see if bridging thiocyanate could be obtained. Therefore, the coordination of dmtp was studied in the presence of a 1:1 mixture of metal isothiocyanates. The results of the Mn-Hg, Co-Hg and Ni-Hg systems are described in the present paper together with the crystal structure of the compound $[CoHg(dmtp)_3(SCN)_4(H_2O)]_2$.

Experimental

Synthesis and Characterization

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

Metal nitrates and thiocyanates were used as obtained commercially. The mononuclear compounds were prepared as described before [1]. The compounds of general formula $MHg(dmtp)_3(SCN)_4(H_2O)$ were all synthesized by the following procedure (M = Mn, Co, Ni): a solution of 2 mmol of $Hg(SCN)_2(dmtp)_2$ in 20 ml of acetone was added to a solution of 2 mmol of $M(NCS)_2(dmtp)_2(H_2O)_2$ in 20 ml aqueous aceton (20/80) at 40 °C. Crystals were formed upon cooling slowly to room temperature. The Ni and Mn compounds usually yield finely divided microcrystalline powders, whereas in the case of the Co compound crystals suitable for X-ray analysis were formed. The solids were isolated by filtration, washed with aqueous acetone and finally dried *in vacuo.*

All three compounds had excellent elemental analyses (M, C, H, N, S), performed by Microanalytical Laboratory Pascher, Bonn. The compounds were characterized by infrared spectra (recorded on a Perkin Elmer 580 instrument in KBr discs and as Nujol mulls), ligand-field spectra (obtained as diffuse reflectance spectra on a Beckman DK-2 instrument) and X-ray powder diagrams (using a Guinier type camera).

X-ray Data Collection and Refinement

A yellow-orange crystal (of dimensions 0.06 × 0.10 × 0.20 mm) was used for the X-ray analysis. Unit cell parameters, preliminarly determined from rotation and Weissenberg photographs, were refined by a least-squares procedure applied to the 29 values of accurately measured reflections on a Siemens AED single-crystal diffractometer. Crystal data are as follows: $C_{50}H_{52}Co_2Hg_2N_{32}O_2S_8$, M = 1908.6, triclinic, $a = 11.481(9)$, $b = 13.975(11)$, $c = 11.479(8)$ Å, $\alpha = 101.08(6)$, $\beta = 90.11(7)$, $\gamma = 77.24(6)^\circ$; $V = 1761(2)$ Å^3, $Z = 1$. $D_c = 1.80$ g cm^{-3}, μ(MoKα) = 50.97 cm^{-1}, space group: $P\bar{1}$ from structure determination.

A total of 4746 independent reflections with θ in the range 3–24° were measured on the same diffractometer using the Nb-filtered MoKα radiation and the $\theta/2\theta$ scan technique. 2392 reflections, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The structure amplitudes were obtained after the usual Lorentz and polarization corrections; no corrections were applied for the absorption effects. Data were placed on an approximate absolute scale by means of a Wilson plot which also provided the average overall temperature factor.

The structure was solved by Patterson and Fourier methods. The refinement was carried out by least-squares full-matrix cycles using the SHELX system of computer programs [6] with first isotropic and then anisotropic thermal parameters for all the non hydrogen atoms. The H(1) and H(2) hydrogen atoms of the water molecule, localized in a ΔF map but not refined and the other hydrogen atoms, placed in their geometrically calculated positions, were all included in the final structure-factor calculation with isotropic thermal parameters (mean values of the thermal parameters of the atoms to which they are attached). The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$; unit weights were chosen in the first cycles, and then the reflections were weighted according to the scheme $w = 0.2472/[\sigma^2(F_o) + 0.0042F_o^2)]$ with $\sigma(F_o)$ based on counting statistics. The final R and R_w values were 3.8% and 3.9% respectively (observed reflections only). Atomic scattering factors, corrected for the anomalous dispersion of Hg and Co, were taken from the International Tables [7]. The final coordinates for the non-hydrogen and hydrogen atoms are given in Tables I and II respectively. The thermal parameters and a list of observed and calculated structure factors are available from the authors on request.

Results and Discussion

General and Spectroscopic Properties

The IR spectra of the three compounds are almost identical and suggest mutual isomorphism for M = Mn, Co and Ni. In the case of M = Fe, three mutually different compounds were found, all different from the Mn, Co and Ni compounds. The results of this work will be published later.

The IR spectra show the presence of bands originating from dmtp and from the NCS anion. In addition, some bands were observed in the far-IR spectra. The bands not due to the ligand are summarised in Table III, together with the ligand-field maxima of the Co and the Ni compounds.

TABLE I. Fractional Atomic Coordinates of the Non-hydrogen Atoms ($\times 10^4$) with E.S.D. s in Parentheses.

	x/*a*	y/*b*	z/*c*
Hg	5510(1)	8033(1)	763(1)
Co	6662(1)	8187(1)	5864(1)
S1	4035(3)	8147(3)	2528(3)
S2	6377(3)	9544(3)	1345(3)
S3	7212(4)	6524(3)	538(4)
S4	4171(5)	7822(4)	−893(3)
Ow	7926(7)	7056(6)	4806(7)
N1	5652(10)	8321(7)	4370(9)
N2	4666(10)	10725(7)	3031(10)
N3	8534(14)	7118(12)	2488(13)
N4	3512(14)	6155(12)	−339(15)
N31	7216(10)	5916(8)	7001(9)
N51	5222(9)	5780(7)	6596(8)
N71	4221(9)	6287(8)	6181(9)
N91	5738(9)	7080(7)	6171(8)
N32	9167(9)	9423(8)	6781(9)
N52	8366(9)	10600(7)	5603(8)
N72	7528(10)	10743(8)	4818(9)
N92	7523(9)	9342(7)	5491(8)
N33	9488(10)	6817(8)	6570(9)
N53	9187(10)	7697(8)	8549(9)
N73	8360(11)	8436(9)	9232(10)
N93	7709(9)	8054(7)	7360(8)
C1	4968(10)	8245(9)	3605(12)
C2	5338(12)	10235(9)	2340(11)
C3	7989(16)	6885(14)	1717(17)
C4	3781(16)	6831(12)	−551(14)
C11	6389(14)	4563(10)	7459(12)
C21	7357(13)	5063(10)	7418(10)
C41	6140(13)	6264(9)	6614(10)
C61	5318(13)	4922(10)	7019(11)
C81	4572(12)	7069(10)	5934(10)
C101	8537(12)	4684(10)	7893(12)
C111	4239(12)	4459(10)	6998(13)
C12	9941(13)	10916(11)	6781(12)
C22	9928(13)	10001(11)	7176(12)
C42	8365(11)	9760(9)	5994(10)
C62	9132(13)	11206(10)	6001(12)
C82	7026(12)	9970(10)	4784(11)
C102	10806(14)	9646(12)	8040(13)
C112	9004(14)	12167(8)	5488(13)
C13	10935(13)	6514(11)	8026(13)
C23	10550(13)	6334(10)	6872(13)
C43	8797(13)	7492(10)	7413(10)
C63	10250(13)	7202(12)	8888(13)
C83	7488(12)	8620(10)	8463(11)
C103	11334(13)	5580(10)	5897(13)
C113	10526(14)	7513(13)	10176(10)

TABLE II. Fractional Atomic Coordinates ($\times 10^4$) of the Hydrogen Atoms.

	x/*a*	y/*b*	z/*c*
H1	8637	7023	5450
H2	8149	7225	4060
H11	6517	3901	7841
H81	3987	7650	5575
H101	8530	4000	8196
H102	8714	5237	8627
H103	9226	4539	7202
H111	4464	3787	7362
H112	3976	4275	6093
H113	3509	4985	7524
H12	10582	11355	7103
H82	6284	9856	4237
H104	11363	10177	8286
H105	11358	8926	7639
H106	10335	9577	8823
H114	9654	12576	5869
H115	8115	12628	5701
H116	9154	11968	4535
H13	11793	6098	8236
H83	6671	9181	8712
H107	12159	5248	6262
H108	11529	5953	5204
H109	10872	5002	5532
H117	11386	7075	10348
H118	9845	7389	10740
H119	10545	8297	10360

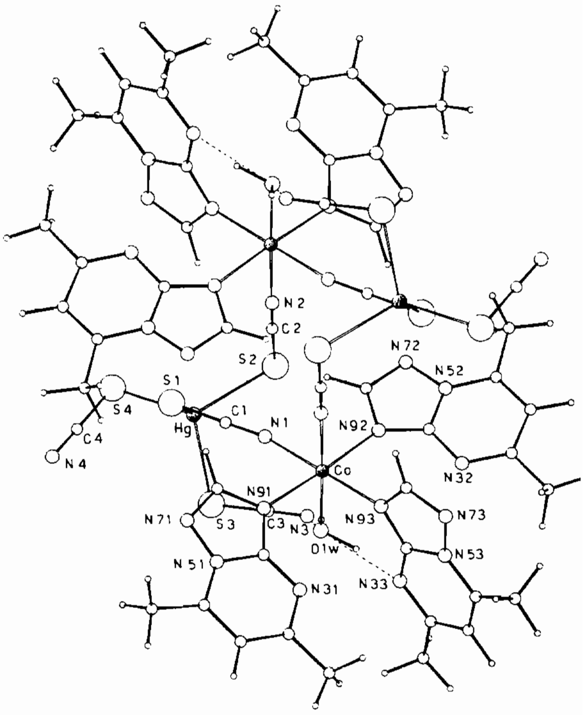

Fig. 1. Perspective view of the heterotetranuclear complex.

The X-ray powder diagrams of all three compounds are essentially the same and indicate that the metal environments are the same. The ligand-field maxima of the Co and the Ni compounds agree with distorted octahedral coordination geometry. Assuming that the water molecule is coordinating,

TABLE III. Spectral Information[a] of $[M(dmtp)_3(H_2O)(NCS)_2Hg(SNC)_2]_2$, M = Mn, Co, Ni; Thiocyanate and Metal–Ligand Vibrations. Ligand Field Maxima (cm^{-1}) for M = Co, Ni.

	Mn	Co	Ni
ν_{CN}	2120s(sh), 2150s, 2095ms	2135vs, 2118ms, 2100s	2135s, 2105ms, 2095ms
$2\delta_{NCS}$	923m, 860m	930m, 860m	928m
ν_{CS}	756w, 748w, 696mw	753mw, 700w	752w, 698w
δ_{NCS}	462w, 426m	470w, 426w	468w, 430w
ν_{MO}	449m	456m	453m
ν_{MN}	226m, 205w(sh), 188m	246w(sh), 229w(sh), 194w(sh)	257w(sh), 240m, 203w(sh)
ν_{HgS}	215w(sh)	212m	220m
Ligand field	–	9200, 20300	9800, 13900sh, 16400, 28200

[a] All values in cm^{-1}.

TABLE IV. Bond Distances (A) and Angles (°).

i) in the coordination polyhedra			
Co–N(1)	2.083(10)	Co–N(91)	2.140(10)
Co–N(2^i)	2.118(11)	Co–N(92)	2.177(10)
Co–O$_w$	2.082(8)	Co–N(93)	2.108(9)
N(1)–Co–N(2^i)	91.6(4)	N(2^i)–Co–N(93)	89.0(4)
N(1)–Co–O$_w$	88.8(4)	O$_w$–Co–N(91)	88.8(3)
N(1)–Co–N(91)	87.9(4)	O$_w$–Co–N(92)	92.2(3)
N(1)–Co–N(92)	89.2(4)	O$_w$–Co–N(93)	90.7(3)
N(1)–Co–N(93)	179.0(4)	N(91)–Co–N(92)	176.9(4)
N(2^i)–Co–O$_w$	176.8(4)	N(91)–Co–N(93)	92.8(4)
N(2^i)–Co–N(91)	88.0(4)	N(92)–Co–N(93)	90.1(4)
N(2^i)–Co–N(92)	91.0(4)		
Hg–S(1)	2.602(4)	Hg–S(3)	2.511(5)
Hg–S(2)	2.506(5)	Hg–S(4)	2.457(5)
S(1)–Hg–S(2)	104.2(1)	S(2)–Hg–S(3)	107.2(1)
S(1)–Hg–S(3)	112.4(1)	S(2)–Hg–S(4)	123.4(2)
S(1)–Hg–S(4)	99.6(1)	S(3)–Hg–S(4)	109.7(1)
ii) in the thiocyanate groups			
S(1)–C(1)	1.640(13)	S(3)–C(3)	1.677(18)
C(1)–N(1)	1.182(16)	C(3)–N(3)	1.122(19)
S(2)–C(2)	1.653(13)	S(4)–C(4)	1.660(18)
C(2)–N(2)	1.120(17)	C(4)–N(4)	1.125(19)
S(1)–C(1)–N(1)	178.9(9)	C(2)–N(2)–Co^i	170.5(10)
C(1)–S(1)–Hg	98.2(5)	S(3)–C(3)–N(3)	178.3(12)
C(1)–N(1)–Co	165.4(9)	C(3)–S(3)–Hg	99.6(7)
S(2)–C(2)–N(2)	177.2(9)	S(4)–C(4)–N(4)	178.8(13)
C(2)–S(2)–Hg	99.5(5)	C(4)–S(4)–Hg	95.1(6)
iii) in the organic ligands			
C(11)–C(21)	1.443(19)	C(42)–N(92)	1.314(15)
C(11)–C(61)	1.357(19)	N(52)–N(72)	1.326(14)

(continued on facing page)

TABLE IV. *(continued)*

C(21)–N(31)	1.345(18)	N(52)–C(62)	1.370(17)
C(21)–C(101)	1.485(18)	C(62)–C(112)	1.545(18)
N(31)–C(41)	1.333(18)	N(72)–C(82)	1.326(18)
C(41)–N(51)	1.371(17)	C(82)–N(92)	1.344(16)
C(41)–N(91)	1.327(17)	C(13)–C(23)	1.390(19)
N(51)–N(71)	1.348(14)	C(13)–C(63)	1.351(19)
N(51)–C(61)	1.361(17)	C(23)–N(33)	1.337(18)
C(61)–C(111)	1.517(19)	C(23)–C(103)	1.518(19)
N(71)–C(81)	1.323(18)	N(33)–C(43)	1.333(16)
C(81)–N(91)	1.368(17)	C(43)–N(53)	1.376(15)
C(12)–C(22)	1.439(19)	C(43)–N(93)	1.329(17)
C(12)–C(62)	1.341(19)	N(53)–N(73)	1.357(16)
C(22)–N(32)	1.338(18)	N(53)–C(63)	1.360(18)
C(22)–C(102)	1.487(19)	C(63)–C(113)	1.512(18)
N(32)–C(42)	1.362(16)	N(73)–C(83)	1.348(17)
C(42)–N(52)	1.335(16)	C(83)–N(93)	1.349(15)
C(21)–C(11)–C(61)	120.2(12)	N(72)–N(52)–C(42)	110.1(9)
C(11)–C(21)–N(31)	121.7(11)	C(12)–C(62)–N(52)	118.1(12)
C(11)–C(21)–C(101)	121.2(10)	C(12)–C(62)–C(112)	125.2(12)
N(31)–C(21)–C(101)	117.1(11)	N(52)–C(62)–C(112)	116.7(10)
C(21)–N(31)–C(41)	116.3(10)	N(52)–N(72)–C(82)	102.9(9)
N(31)–C(41)–N(51)	123.1(10)	N(72)–C(82)–N(92)	114.0(10)
N(51)–C(41)–N(91)	107.1(10)	C(42)–N(92)–C(82)	103.0(9)
C(41)–N(51)–C(61)	122.7(10)	C(23)–C(13)–C(63)	120.9(12)
N(71)–N(51)–C(41)	111.9(9)	C(13)–C(23)–N(33)	121.9(12)
C(11)–C(61)–N(51)	115.9(11)	C(13)–C(23)–C(103)	120.8(12)
C(11)–C(61)–C(111)	125.2(12)	N(33)–C(23)–C(103)	117.3(11)
N(51)–C(61)–C(111)	118.9(11)	C(23)–N(33)–C(43)	118.0(10)
N(51)–N(71)–C(81)	102.0(9)	N(33)–C(43)–N(53)	120.5(11)
N(71)–C(81)–N(91)	114.4(10)	N(53)–C(43)–N(93)	109.3(9)
C(41)–N(91)–C(81)	104.7(9)	C(43)–N(53)–C(63)	122.8(10)
C(22)–C(12)–C(62)	117.9(12)	N(73)–N(53)–C(43)	109.9(9)
C(12)–C(22)–N(32)	123.0(11)	C(13)–C(63)–N(53)	115.9(11)
C(12)–C(22)–C(102)	120.1(12)	C(13)–C(23)–C(113)	128.4(12)
N(32)–C(22)–C(102)	116.9(12)	N(53)–C(63)–C(113)	115.7(11)
C(22)–N(32)–C(42)	116.2(19)	N(53)–N(73)–C(83)	101.9(9)
N(32)–C(42)–N(52)	121.9(10)	N(73)–C(83)–N(93)	115.3(10)
N(52)–C(42)–N(92)	110.0(9)	C(43)–N(93)–C(83)	103.6(9)
C(42)–N(52)–C(62)	122.7(9)		

Asymmetric units:
i) 1 – x, 2 – y, 1 – z

a chromophore MN_5O would be expected. The crystal-field splitting 10 *Dq* of such a chromophore would be about 1000 cm^{-1} (*cf.* 970–990 cm^{-1} in the chromophore MN_4O_2 for related compounds [1]). This agrees well with the present results. This would leave no more than two ligands for the Hg(II) ions, which is unlikely unless some of the NCS or dmtp ligands would bridge between Hg and the transition metal. To investigate this possibility, magnetic susceptibility measurements at low temperatures were performed (2–80 K) to detect possible M–M interactions. The results, however, indicate that such interactions – if present at all – are at best very weak. Therefore an X-ray analysis on the compound with M = Co was undertaken to find out details of the structure.

Crystal and Molecular Structure of $[CoHg(dmtp)_3(SCN)_4(H_2O)]_2$

In the crystal structure centrosymmetric heterotetranuclear complexes, represented in Fig. 1, are present. Interatonic bond distances and angles are given in Table IV. Two centrosymmetric related $Hg(SCN)_4$ units containing Hg atoms tetrahedrally coordinated by sulphur atoms from thiocyanate groups (two acting as bridging ligands) join two centrosymmetric Co atoms whose octahedral coordination involves three additional N atoms from dmtp ligands and a water molecule. In the CoN_5O chromophore the two N atoms from bridging thiocyanate groups are in *cis* position, the water molecule is coordinated *trans* to a bridging thiocyanate and the three N atoms from dmtp ligands are in mutual *mer* positions. All the dmtp molecules act as monodentate ligands in the coordination to the metal triazole nitrogen site [1–3]. Intramolecular hydrogen bonds occur between the coordinated water molecule and the N(3) nitrogen atom from an adjacent monodentate thiocyanate group ($O_w \cdots N(3)$ = 2.774(18), $H_2 \cdots N(3)$ = 1.83 Å, N(3)–O_w–H(2) = 12°, N(3)–H(2)–O_w = 161°) and also the non-bridging pyrimidine nitrogen atom from a dmtp ligand ($O_w \cdots N(33)$ = 2.722(14), $H(1) \cdots N(33)$ = 1.64 Å, N(33)–O_w–H_1 = 9°, N(33)–H(1)–O_w = 165°). This hydrogen bonding apparently stabilizes the tetranuclear species; Co–N–C–S–Hg frameworks have been observed in other compounds and in particular in $CoHg(SCN)_4(pyridine)_2$ [8], where HgS_4 tetrahedra and $CoN_4(pyridine)_2$ octahedra are connected by bridging thiocyanate groups in a three-dimensional arrangement. In fact in this last structure each of the HgS_4 tetrahedra is attached to four different $CoN_4(pyridine)_2$ units, each of which is, in turn, connected to four different HgS_4 units. A comparison of the relevant features of this structure with the present one shows that the Hg–S bond distances, the S–Hg–S and Hg–S–C angles of the $Hg(SCN)_4$ groups agree very well, excepting those involving one thiocyanate group. In fact in the present compound the S(4)–C(4)–N(4) thiocyanate group behaves as a monodentate ligand so that the Hg–S(4) distance and Hg–S(4)–C(4) angle are shorter and narrower, respectively, than the others involving thiocyanates of different behaviour (bridging or monodentately hydrogen bonded acceptor ligands). The thiocyanate groups are linear with normal S–C and N–C bond lengths. The Co coordination polyhedron is slightly distorted with Co–N and Co–O bond lengths, in good agreement with the values of the literature for a similar coordination. While in the structure of $CoHg(SCN)_4(pyridine)_2$ only one of the two independent Co–N–C groups is significantly bent [164.0(8)°], in the present compound both Co–N–C groups show remarkable departure from the linearity (165.4(9) and 170.5(10)°). In the tetranuclear complex the $Hg \cdots Hg$, $Co \cdots Co$ and $Hg \cdots Co$ distances are 6.282(6), 5.959(8) and 5.965(5) Å respectively and show no M–M interactions, in good agreement with the magnetic susceptibility measurements. The hydrogen bond of the water molecule with the pyrimidine nitrogen of a dmtp molecule determines an indirect chelation of the dmtp molecule, which seems to be of some interest. We have noted in several metal complexes containing purine derivatives as ligands that the purine system usually takes part in interligand hydrogen bonding with suitable donors in the coordination sphere, as a water molecule, utilizing generally carbonyl [9–10] or amine [11–12] exocyclic groups and forming six-membered pseudo-chelate rings. Here the five-membered pseudo-chelate ring involves an endocyclic nitrogen of a fused ring system which, as already mentioned, is similar to the purine skeleton. This ring is roughly planar, the maximum deviations from the plane passing through N(93), Co, O_w, N(33), C(43) being –0.05 and 0.04 Å for the N(93) and N(33) atoms, respectively.

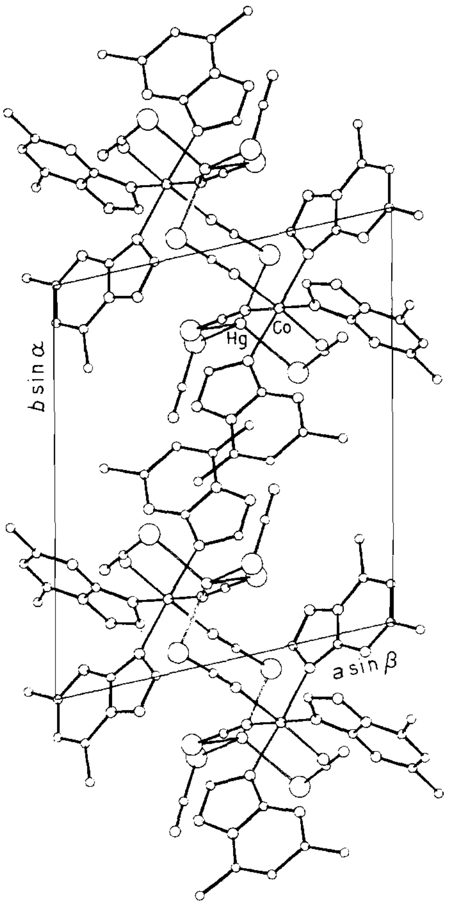

Fig. 2. Projection of the structure along *c*.

The bond lengths and angles in the coordinated dmtp molecules are in excellent agreement with those found in other crystal structures of metal complexes with dmtp ligand [1, 2]. The analysis of the planarity data of the dmtp molecules shows that the framework of the organic, usually planar, ligand is slightly but significantly distorted from planarity only for the dmtp molecule involved in interligand hydrogen bonding. This is probably the origin of the lack of planarity. The dihedral angle between the mean planes through triazole and pyrimidine rings of this dmtp molecule is only 2.3°.

The mean planes through the skeleton of the three dmtp ligands make angles with the equatorial plane containing the three N atoms from organic ligands of 33, 90 and 17° consecutively, probably according to the steric demand of the bulky dmtp molecules.

The packing of the complexes is shown in Fig. 2. The inversion-related (about 0,0,0) tetranuclear complexes show significant overlap of a third of the dmtp molecules (the mean separation between the ring-frameworks is 3.39(1) Å). Therefore the packing in the lattice is determined both by stacking interactions and by van der Waals contacts.

Further studies on this ligand system will deal with other mixed-metal combinations and with derivatives of dmtp.

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