The crystal structures of some chloromercury(II) anions with Co(III) complexes or protonated polyamines as cations

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(Received June 24, 1991; revised November 4, 1991)

Abstract

The crystal structures have been determined for $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ (**1**) (monoclinic, $P2_1/c$, $a=7.943(2)$, $b=21.070(9)$, $c=12.413(4)$ Å, $\beta=90.33(2)°$, $V=2077.4$ Å^3, $Z=4$); *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ (**2**) (monoclinic, $P2_1/c$, $a=9.110(3)$, $b=8.811(3)$, $c=17.297(6)$ Å, $\beta=90.86(3)°$, $V=1388.4$ Å^3, $Z=2$); $[NH_3(CH_2)_2NH_3][Hg_2Cl_6]$ (**3**) (triclinic, $P\bar{1}$, $a=6.128(1)$, $b=6.984(1)$, $c=8.045(2)$ Å, $\alpha=77.81(2)$, $\beta=85.87(2)$, $\gamma=66.40(2)°$, $V=308.4$ Å^3, $Z=1$); $[NH_3(CH_2)_2(NH_3)]_2[HgCl_4][Cl]_2$ (**4**) (orthorhombic, *Pnma*, $a=122.759(4)$, $b=6.073(2)$, $c=19.829(7)$ Å, $V=1536.5$ Å^3, $Z=4$); $[NH_3(CH_2)_3NH_2(CH_2)_3NH_3]_2[Hg_3Cl_{12}]$ (**5**) (tetragonal, $P4_12_12$, $a=b=12.645(3)$, $c=20.892(8)$ Å, $V=3341$ Å^3, $Z=4$); and $[NH_3(CH_2)_2NH_2(CH_2)_2NH_2(CH_2)_2NH_3][Hg_2Cl_8]$ (**6**) (monoclinic, $P2_1/c$, $a=11.892(3)$, $b=11.872(4)$, $c=14.350(4)$ Å, $\beta=98.25(2)°$, $V=2005$ Å^3, $Z=4$). Four of these six salts show unique Hg(II)–Cl coordination. The anions in **2** and **3** are the previously described dimeric, chloro-bridged, bitetrahedral units, $Hg_2Cl_6^{2-}$. In **3**, the $HgCl_4^{2-}$ anion is polymeric with a single Hg–Cl...Hg bridge, while in **6** two $HgCl_4^{2-}$ units are in much closer association and form linked $Hg_2Cl_8^{4-}$ anions. Of the trimercury(II) anions, $Hg_3Cl_9^{3-}$ in **1** forms $(Hg_3Cl_9^{3-})$ in chains while $Hg_3Cl_{12}^{6-}$ in **5** exists as an isolated anion.

Introduction

Chloromercury(II) anions exhibit a wide structural diversity and frequently a single cation can form salts of quite varied composition [1]. It is also increasingly evident that the formal stoichiometry rarely reflects the nature of the chloromercury(II) anion in the crystal lattice [2, 3]. While spectroscopic techniques can identify Hg–Cl bond lengths to ±0.05 Å, these are not particularly successful at identifying structural units [4], and X-ray crystallography continues to be the only satisfactory tool.

As part of our continuing investigation of salts containing chloromercury(II) anions [2, 3] we report here the structures** of $[Co(NH_3)_6][HgCl_3]_3\cdot H_2O$ (**1**), *trans*-$[CoCl_2(en)_2][HgCl_3]$ (**2**), $[H_2en][HgCl_3]_2$ (**3**), $[H_2en]_2[HgCl_6]$ (**4**), $[H_3dpt]_2[HgCl_4]_3$ (**5**) and $[H_4trien][HgCl_4]_2$ (**6**).

Experimental

$[Co(NH_3)_6][HgCl_3]_3\cdot H_2O$ (**1**) (golden orange needles). Dilute aqueous solutions of $[Co(NH_3)_6]Cl_3$ [5] and $HgCl_2$ in a mole ratio of 1:3 were mixed and allowed to evaporate at room temperature. If a mole ratio of 2:3 is used, then $[Co(NH_3)_6]_2[HgCl_4]_3$ [6] can be isolated. In the presence of HCl, other salts such as $[Co(NH_3)_6][HgCl_5]$ [7, 8] and $[Co(NH_3)_6][Hg_2Cl_7]$ [7] have been characterised.

trans-$[CoCl_2(en)_2][HgCl_3]$ (**2**) (deep green rhombs). Solutions of *trans*-$[CoCl_2(en)_2Cl\cdot HCl\cdot 2H_2O$ [9] (1 g in 50 ml of 3 M HCl at room temperature) and $HgCl_2$ (3 g in 50 ml of 3 M HCl at 60 °C) were mixed and the product crystallised on cooling.

$[H_2en][HgCl_3]_2$ (**3**) (colourless, triclinic crystals). $[H_2en]Cl_2$ (0.8 g, 6.0 mmol) and $HgCl_2$ (1.7 g, 6.3 mmol) were separately dissolved in 50 ml of 60 °C water and the solutions mixed. The product deposited after several days at room temperature in an open beaker.

$[H_2en]_2[HgCl_6]$ (**4**) (colourless, orthorhombic crystals). A procedure similar to that for **3** but using 1.25 g (9.4 mmol) of $[H_2en]Cl_2$ and 1.25 g (4.6 mmol) of $HgCl_2$.

$[H_3dpt]_2[HgCl_4]_3$ (**5**) (colourless, tetragonal crystals). The polyamine (3 ml) was added to 50 ml of 3 M HCl and $HgCl_2$ (5 g) was dissolved in 50 ml of 3 M HCl.

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**The following formula represent the simplest stoichiometry of the salts. Abbreviations used: $en=NH_2(CH_2)_2NH_2$, $H_2en=[NH_3(CH_2)_2NH_3]^{2+}$, $H_3dpt=[NH_3(CH_2)_3NH_2(CH_2)_3NH_3]^{3+}$, $H_4trien=[NH_3(CH_2)_2NH_2(CH_2)_2NH_2(CH_2)_2NH_3]^{4+}$, $H_3dien=[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}$.

0020-1693/92/$5.00

TABLE 1. Crystal data

	$[Co(NH_3)_6][Hg_3Cl_9]H_2O$ (1)	[t-$CoCl_2(en)_2]_2[Hg_2Cl_6]$ (2)	$[H_2en][Hg_2Cl_6]$ (3)	$[H_2en]_2[HgCl_4][Cl]_2$ (4)	$[H_3dpt]_2[Hg_3Cl_{12}]$ (5)	$[H_4trien][Hg_2Cl_8]$ (6)
Molecular formula	$H_{20}N_6OCl_9CoHg_3$	$C_8H_{32}N_8Cl_{10}Co_2Hg_2$	$C_2H_{10}N_2Cl_6Hg_2$	$C_4H_{20}N_4Cl_6Hg$	$C_{12}H_{40}N_6Cl_{12}Hg_3$	$C_6H_{22}N_4Cl_8Hg_2$
Formula weight	1100.0	1114.0	676.01	537.54	1295.7	835.2
Space group	monoclinic	monoclinic	triclinic	orthorhombic	tetragonal	monoclinic
	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pnma$	$P4_12_12$	$P2_1/c$
a (Å)	7.943(2)	9.110(2)	6.128(1)	12.759(4)	12.645(3)	11.892(3)
b (Å)	21.070(9)	8.811(3)	6.984(1)	6.073(2)	12.645(3)	11.872(4)
c (Å)	12.413(4)	17.297(8)	8.045(2)	19.829(7)	20.892(8)	14.350(4)
α (°)	90.0	90.0	77.81(2)	90.0	90.0	90.0
β (°)	90.33(2)	90.86(4)	85.87(2)	90.0	90.0	98.25(2)
γ (°)	90.0	90.0	66.40(2)	90.0	90.0	90.0
V (Å)^3	2077.4	1388.4	308.4	1536.5	3340.7	2005.0
Z	4	2	1	4	4	4
D_{calc} (g/cc)	3.52	2.73	3.64	2.32	2.58	2.77
Temperature	−140	−140	−120	−120	−120	−120
F(000)	1960	1040	298	1016	2392	1528
Absorption coefficient (cm^{-1})	240.58	131.86	261.32	110.50	147.01	164.70
Transmission factor	0.537	0.839	0.137	0.970	0.856	0.581
	0.201	0.467	0.092	0.328	0.624	0.295
R_{merg}	0.0620	0.0243	0.0439	0.0295	0.0472	0.0199
Scan mode	ω	ω	ω	ω	ω	ω
Octants	$h, k, \pm l$	$h, k, \pm l$	$h, \pm k, \pm l$	h, k, l	h, k, l	$h, k, \pm l$
$2\theta_{max}$ (°)	52	52	50	52	55	52
Reflections measured	3922	2748	2432	1793	2288	3890
Reflections used	2480	1993	1082	1053	1389	2213
Parametric reflections	146	136	45	54	104	171
Weighting ($g \times 10^3$)	1.31	2.00	8.58	1.54	1.19	6.00
Anisotropic atoms	Hg, Cl Co, O	all non-H	Hg, Cl	Hg, Cl(1) Cl(3), Cl(4)	Hg, Cl	all non-H
Residuals (e Å^{-3}): max.	3.11	1.00	3.09	1.23	2.16	3.19
Residuals (e Å^3): min	−1.75	−1.57	−6.06	−1.71	−2.31	−1.43
R	4.50	3.37	5.24	3.67	5.91	4.61
R_w	4.56	3.71	5.44	3.66	5.94	4.18
GOF	1.15	0.80	0.66	0.57	1.23	1.16

The 60 °C solutions were mixed in an open beaker and the product deposited overnight at room temperature.

[H_4trien][$HgCl_4$]$_2$ (**6**) (colourless, monoclinic crystals). A procedure similar to that for **5** was used, with 1.3 ml of trien and 4.7 g of $HgCl_2$.

X-ray structure determinations

Intensity data for the six chloromercury(II) salts listed in Table 1 were collected with a Nicolet R3m four circle diffractometer at low temperature (−140 to −120 °C). Graphite monochromated Mo Kα radiation (0.71069 Å) was used, with fixed speed ω scans. Cell parameters were determined by least-squares refinement of 25 accurately centered reflections. During the data collections, the intensities of three standard reflections were monitored at regular intervals and these indicated no significant crystal decomposition. Intensities for which $I > 3\sigma(I)$ were used in the refinement. The collected intensities were corrected for Lorentz, polarisation and absorption effects. The latter, which are considerable for compounds containing Hg, were estimated by face indexing or by using empirical procedures, based on Ψ-scan data, available in the SHELXTL [10] suite of structure solving programmes. We believe that the high absorption corrections required sometimes led to poor refinement, when anisotropic thermal parameters were included.

The structures were solved by conventional Patterson and Fourier methods and refined by blocked-cascade least-squares procedures. The function minimised was $\Sigma w(|F_o| - |F_o|)^2$ where $w = [\sigma^2 F_o + g F_o^2]^{-1}$ (Table 1). In every case, attempts were made to refine all non-hydrogen atoms with anisotropic thermal parameters, but non-positive definite values were sometimes observed for the C and N atoms. The atoms successfully refined are listed in Table 1, and the anisotropic thermal parameters obtained are given in 'Supplementary material'.

In the last cycles of refinement, the appropriate C–H and N–H hydrogen atoms were included in their calculated positions ('Supplementary material'). Highest and lowest residual peak electron densities are given in Table 1. In all cases, these values were found to be close to Hg atom positions. Tables 2–7 list the non-hydrogen atom coordinates for structures **1**–**6**, respectively.

TABLE 2. Non-hydrogen atom coordinates (×10^4) for [$Co(NH_3)_6$][Hg_3Cl_9]·H_2O (**1**)[a]

Atom	*x*	*y*	*z*
Hg(1)	1219(1)	1969(1)	4784(1)
Hg(2)	967(1)	1186(1)	1306(1)
Hg(3)	1382(1)	9771(1)	6285(1)
Co(1)	−3826(3)	1281(1)	−1988(2)
Cl(1)	865(6)	1658(2)	−628(3)
Cl(2)	−1305(7)	422(2)	1250(4)
Cl(3)	−1686(7)	1851(2)	4724(4)
Cl(4)	3901(6)	740(2)	1112(4)
Cl(5)	4110(6)	2070(2)	4967(4)
Cl(6)	1177(7)	2151(2)	2348(4)
Cl(7)	4222(6)	9517(2)	6177(4)
Cl(8)	1278(7)	11010(2)	6646(4)
Cl(9)	−1525(6)	9570(2)	6158(4)
O(1)	6057(21)	1857(5)	2340(12)
N(1)	−2003(20)	655(7)	−1712(13)
N(2)	−5620(19)	1912(6)	−2228(12)
N(3)	−4081(21)	962(7)	−3467(13)
N(4)	6431(21)	3410(7)	4503(13)
N(5)	4438(19)	4328(6)	3463(12)
N(6)	−2127(20)	1891(6)	−2489(12)

[a]See Figs. 1 and 2.

TABLE 3. Non-hydrogen atom coordinates (×10^4) for *trans*-[$CoCl_2(en)_2$]$_2$[Hg_2Cl_6] (**2**)[a]

Atom	*x*	*y*	*z*
Hg(1)	3127(1)	811(1)	339(1)
Co(1)	5043(1)	−2821(1)	2632(1)
Cl(1)	5743(2)	680(3)	914(1)
Cl(2)	7435(2)	−2723(3)	2347(1)
Cl(3)	2627(2)	−2914(3)	2894(1)
Cl(4)	1477(2)	−1128(3)	772(1)
Cl(5)	2667(3)	3286(3)	−137(1)
N(1)	4554(8)	−2604(9)	1534(4)
N(2)	5061(8)	−5008(9)	2441(5)
C(1)	5089(11)	−5287(11)	1594(6)
C(2)	4101(10)	−4106(10)	1222(5)
N(3)	5026(8)	−638(8)	2818(4)
N(4)	5589(9)	−3032(8)	3723(4)
C(3)	4983(10)	−347(11)	3677(5)
C(4)	5956(10)	−1499(12)	4042(6)

[a]See Table 9.

TABLE 4. Non-hydrogen atom coordinates (×10^4) for [H_2en][Hg_2Cl_6] (**3**)[a]

Atom	*x*	*y*	*z*
Hg(1)	1723(1)	2048(1)	4343(1)
Cl(1)	598(7)	2925(6)	7026(5)
Cl(2)	1817(6)	1766(6)	1473(4)
Cl(3)	3821(7)	−2286(6)	5533(5)
N(1)	4749(21)	6644(20)	1653(16)
C(1)	4020(26)	6014(24)	182(20)

[a]See Table 10.

Results and discussion

The Co(III) cations

The mean Co–N distance of 1.971(7) Å in [$Co(NH_3)_6$][Hg_3Cl_9], is well within the range of 1.94–2.00 Å observed for other $Co(NH_3)_6^{3+}$ salts [11] and

TABLE 5. Non-hydrogen atom coordinates (×10⁴) for $[H_2en]_2[HgCl_4][Cl]_2$ (4)[a]

Atom	*x*	*y*	*z*
Hg(1)	1946(1)	1749(1)	2500
Cl(1)	3963(3)	1875(7)	2500
Cl(2)	1748(3)	−2865(6)	2500
Cl(3)	1493(2)	2098(4)	3668(1)
Cl(4)[b]	4029(2)	2146(4)	4906(1)
N(1)	5006(7)	1357(15)	6389(4)
N(2)	6595(7)	2873(14)	5289(4)
C(1)	5735(8)	3236(19)	6422(5)
C(2)	6747(7)	2899(17)	6039(5)

[a]See Fig.3. [b]Isolated chloride ion.

TABLE 6. Non-hydrogen atom coordinates (×10⁴) for $[H_3dpt]_2[Hg_3Cl_{12}]$ (5)[a]

Atom	*x*	*y*	*z*
Hg(1)	2346(1)	11546(1)	2854(1)
Hg(2)	2846(1)	7154(1)	2500
Cl(1)	2840(6)	7410(6)	1375(3)
Cl(2)	2484(7)	5016(6)	2316(3)
Cl(3)	4005(6)	12312(6)	2505(4)
Cl(4)	565(6)	12204(7)	2710(3)
Cl(5)	2550(7)	9611(6)	2486(4)
Cl(6)	2513(6)	11196(6)	4034(4)
N(1)	9114(23)	843(23)	8804(12)
C(1)	10005(24)	344(23)	8494(14)
C(2)	10481(29)	−485(28)	8938(17)
C(3)	11412(26)	−1069(26)	8611(16)
N(2)	12460(24)	−383(23)	8676(13)
C(4)	13384(33)	−1018(32)	8418(19)
C(5)	14289(26)	−303(26)	8317(15)
C(6)	14798(30)	58(3)	8935(18)
N(3)	15761(19)	771(20)	8760(11)

[a]See Fig. 5 and Table 12.

all N–Co–N angles are within 1° of 90° or 2° of 180° (Table 8).

The 1,2-diaminoethane rings in *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ adopt the δλ conformation, as is observed in all other structural investigations of salts of this cation [12–24], with dihedral angles of +50.5(9)° and −48.4(9)°. Other bond lengths and angles (Table 9) within this cation correspond well with those observed previously [22].

The polyamine cations

The ethylenediammonium cation can adopt either the *gauche* or *trans* configuration [25]. In **3** (Table 10) the configuration is *trans* with the N–C–C–N dihedral angle = 180° and in **4** (Table 11) the configuration is *gauche* with a dihedral angle of 69.2° [25].

TABLE 7. Non-hydrogen atom coordinates (×10⁴) for $[H_4trien)[Hg_2Cl_8]$ (6)[a]

Atom	*x*	*y*	*z*
Hg(1)	2669(1)	1971(1)	1079(1)
Hg(2)	7596(1)	1760(1)	1327(1)
Cl(1)	5222(3)	1676(4)	1102(3)
Cl(2)	8117(4)	2007(4)	2995(3)
Cl(3)	7639(4)	3638(4)	527(3)
Cl(4)	2869(4)	464(4)	2194(3)
Cl(5)	2907(4)	3912(4)	1998(3)
Cl(6)	2623(4)	2821(4)	−457(3)
Cl(7)	7641(4)	211(4)	256(3)
Cl(8)	253(3)	1887(4)	855(3)
N(2)[b]	282(14)	4520(12)	1272(9)
C(4)[c]	4976(17)	4803(15)	9455(11)
C(1)[b]	289(14)	4021(15)	2926(11)
C(3)[b]	−89(14)	5301(14)	475(10)
N(4)[c]	4742(13)	1074(12)	8832(10)
N(1)[b]	−356(12)	4239(14)	3745(9)
C(2)[b]	−157(14)	4802(14)	2132(11)
N(3)[c]	5182(12)	3575(12)	9480(9)
C(5)[c]	5226(14)	3111(16)	8519(10)
C(6)[c]	5582(15)	1872(16)	8523(12)

[a]See Fig. 4 and Table 13. [b]Cation (1), Table 13. [c]Cation (2), Table 13.

The 1,5,9-triazanonanetriammonium cation (Table 12) is more or less linear and dihedral angles along the chain indicate a *trans* (177.7°)-*gauche* (−38.8°)-*trans* (174.0°)-*trans* (165.1°)-*gauche* (+72.4°)-*trans* (178.0°) conformation. The greatest distortion from tetrahedrality occurs at C(2) (111.0°) and C(5) (113.1°) – the central methylene carbon atoms.

Two conformations of the 1,4,7,10-tetraazadecanetetraammonium cation are found in the crystal structure of $[H_4trien][Hg_2Cl_8]$ (**6**) (Table 13). Both are symmetrical with respect to the central C–C bond, but one has the *gauche* (68.1°)-*trans* (172.0°) configuration and the other the *trans* (172.3°)-*trans* (179.2°). The structure of this cation has previously been determined in the $[H_4trien][CuCl_4][Cl]_2$ salt [26].

The $Hg_xCl_y^{n-}$ anions

$[HgCl_3^-]_n$ structures

Three of the salts described here (**1**, **2**, **3**) contain the $Hg_xCl_y^{n-}$ anion with formal stoichiometry $HgCl_3^-$. Previous investigations have shown that this stoichiometry can exist as discrete monomeric $HgCl_3^-$ units [27], $(HgCl_3^-)_n$ chains [28–37] or $Hg_2Cl_6^{2-}$ bitetrahedra [27, 30, 38–45]. The latter arrangement is found in both *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ (**2**) and $[H_2en][Hg_2Cl_6]$ (**3**) and the bond lengths and angles (Tables 9 and 10) are within the ranges previously observed for this dimeric unit [27, 30, 38–45]. The anion arrangement in $[Co(NH_3)_6][HgCl_3]_3$ is, however, unique (Fig. 1). Formally, the $Hg_3Cl_9^{3-}$ unit can be regarded as made up from single chloro-bridged $\{Hg(3)Cl_3^-...Hg(2)Cl_4^{2-}...Hg(1)Cl_2\}_n$ subunits. The central $HgCl_4^{2-}$ sub-unit,

TABLE 8. Bond lengths (Å) and bond angles (°) for $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ (**1**)[a]

Bond lengths (Å)			
Hg(1)–Cl(3)	2.321(5)	Hg(1)–Cl(5)	2.316(5)
Hg(1)–Cl(6)	3.049(5)	Hg(1)–Cl(1a)	2.950(4)
Hg(1)–Cl(8a)	3.070(4)	Hg(2)–Cl(1)	2.600(4)
Hg(2)–Cl(2)	2.420(5)	Hg(2)–Cl(4)	2.526(5)
Hg(2)–Cl(6)	2.414(4)	Hg(3)–Cl(7)	2.323(5)
Hg(3)–Cl(8)	2.650(4)	Hg(3)–Cl(9)	2.352(5)
Hg(3)–Cl(2a)	3.087(5)	Co(1)–N(1)	1.987(15)
Co(1)–N(2)	1.970(15)	Co(1)–N(3)	1.964(16)
Co(1)–N(6)	1.966(15)	Co(1)–N(4a)	1.972(16)
Co(1)–N(5a)	1.968(15)	Cl(1)–Hg(1b)	1.950(4)
Cl(2)–Hg(3a)	3.087(5)	Cl(8)–Hg(1a)	3.070(4)
N(4)–Co(1a)	1.972(16)	N(5)–Co(1a)	1.968(15)
Bond angles (°)			
Cl(3)–Hg(1)–Cl(5)	176.1(2)	Cl(3)–Hg(1)–Cl(6)	88.7(2)
Cl(5)–Hg(1)–Cl(6)	95.2(2)	Cl(3)–Hg(1)–Cl(1a)	90.4(1)
Cl(5)–Hg(1)–Cl(1a)	91.2(1)	Cl(6)–Hg(1)–Cl(1a)	72.8(1)
Cl(3)–Hg(1)–Cl(8a)	88.0(1)	Cl(5)–Hg(1)–Cl(8a)	88.6(2)
Cl(6)–Hg(1)–Cl(8a)	146.0(1)	Cl(1a)–Hg(1)–Cl(8a)	141.0(1)
Cl(1)–Hg(2)–Cl(2)	102.0(2)	Cl(1)–Hg(2)–Cl(4)	94.5(2)
Cl(2)–Hg(2)–Cl(4)	115.9(2)	Cl(1)–Hg(2)–Cl(6)	100.1(1)
Cl(2)–Hg(2)–Cl(6)	128.7(2)	Cl(4)–Hg(2)–Cl(6)	107.7(2)
Cl(7)–Hg(3)–Cl(8)	105.5(2)	Cl(7)–Hg(3)–Cl(9)	155.2(1)
Cl(8)–Hg(3)–Cl(9)	99.1(2)	Cl(7)–Hg(3)–Cl(2a)	93.0(2)
Cl(8)–Hg(3)–Cl(2a)	87.8(1)	Cl(9)–Hg(3)–Cl(2a)	91.0(2)
N(1)–Co(1)–N(2)	178.6(6)	N(1)–Co(1)–N(3)	90.3(6)
N(2)–Co(1)–N(3)	91.1(6)	N(1)–Co(1)–N(6)	89.3(6)
N(2)–Co(1)–N(6)	90.5(6)	N(3)–Co(1)–N(6)	89.8(6)
N(1)–Co(1)–N(4a)	89.2(6)	N(2)–Co(1)–N(4a)	89.5(6)
N(3)–Co(1)–N(4a)	179.2(6)	N(6)–Co(1)–N(4a)	90.8(6)
N(1)–Co(1)–N(5a)	91.6(6)	N(2)–Co(1)–N(5a)	88.6(6)
N(3)–Co(1)–N(5a)	88.5(6)	N(6)–Co(1)–N(5a)	178.0(7)
N(4a)–Co(1)–N(5a)	91.0(6)	Hg(2)–Cl(1)–Hg(1b)	102.2(1)
Hg(2)–Cl(2)–Hg(3a)	94.5(2)	Hg(1)–Cl(6)–Hg(2)	115.2(2)
Hg(3)–Cl(8)–Hg(1a)	121.4(2)		

[a] See Figs. 1 and 2.

linked on either side by chloro bridges to $HgCl_3^-$ and $HgCl_2$ with Hg...Cl distances of 3.087(5) and 3.049(5) Å, respectively, has bond lengths and angles (Table 8) very similar to those found in isolated $HgCl_4^{2-}$ units [2, 3, 46–61]. Hg(3) is also four-coordinate, with two short (2.323(5), 2.352(5) Å), one moderate (2.650(4) Å), and one long (3.087(5) Å, bridging) Hg–Cl bonds. The Cl(8) atom, at an Hg(3)–Cl(8) distance of 2.650(4) Å acts as the connector, joining the $Hg_3Cl_9^-$ units into chains. Hg(1), at the other end of the repeat unit, is formally five-coordinate, with three long (3.049(5), 3.070(4) and 2.950(4) Å) and two short (2.321(5), 2.316(5) Å) Hg–Cl bonds. It is one of these (Hg(1)–Cl(1a) at 2.950(4) Å) that provides 'cross-linking' between the chains (Fig. 2).

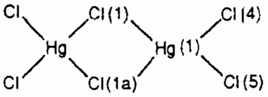
$[HgCl_4^{2-}]_n$ structures

Salts **5** and **6**, $[H_3dpt]_2[HgCl_4]_3$ and $[H_3trien][HgCl_4]_2$, have $HgCl_4^{2-}$ as the formal stoichiometry, and this unit also appears in $[H_2en]_2[HgCl_4][Cl]_2$ (**4**). In none of these salts is the more or less isolated pseudo-tetrahedral $HgCl_4^{2-}$ anion observed. Three unique $(HgCl_4^{2-})_n$ structures are found. In **4** the $HgCl_4^{2-}$ units are linked into chains (Fig. 3), each Hg atom being five-coordinate with a fifth Hg...Cl distance at 3.277

TABLE 9. Bond lengths (Å) and bond angles (°) for *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ (**2**)[a]

Bond lengths (Å)			
Hg(1)–Cl(1)	2.571(2)	Hg(1)–Cl(4)	2.402(2)
Hg(1)–Cl(5)	2.367(2)	Hg(1)–Cl(1a)	2.748(2)
Co(1)–Cl(2)	2.243(2)	Co(1)–Cl(3)	2.255(2)
Co(1)–N(1)	1.954(8)	Co(1)–N(2)	1.955(8)
Co(1)–N(3)	1.951(7)	Co(1)–N(4)	1.954(8)
Cl(1)–Hg(1a)	2.748(2)	N(1)–C(2)	1.49(1)
N(2)–C(1)	1.49(1)	C(1)–C(2)	1.51(1)
N(3)–C(3)	1.51(1)	N(4)–C(4)	1.49(1)
C(3)–C(4)	1.48(1)		
Bond angles (°)			
Cl(1)–Hg(1)–Cl(4)	115.4(1)	Cl(1)–Hg(1)–Cl(5)	109.5(1)
Cl(4)–Hg(1)–Cl(5)	131.0(1)	Cl(1)–Hg(1)–Cl(1a)	85.9(1)
Cl(4)–Hg(1)–Cl(1a)	98.6(1)	Cl(5)–Hg(1)–Cl(1a)	103.5(1)
Cl(2)–Co(1)–Cl(3)	178.9(1)	Cl(2)–Co(1)–N(1)	89.5(2)
Cl(3)–Co(1)–N(1)	89.4(2)	Cl(2)–Co(1)–N(2)	89.4(2)
Cl(3)–Co(1)–N(2)	90.5(2)	N(1)–Co(1)–N(2)	86.3(3)
Cl(2)–Co(1)–N(3)	90.5(2)	Cl(3)–Co(1)–N(3)	89.6(2)
N(1)–Co(1)–N(3)	93.5(3)	N(2)–Co(1)–N(3)	179.8(5)
Cl(2)–Co(1)–N(4)	88.9(2)	Cl(3)–Co(1)–N(4)	92.2(2)
N(1)–Co(1)–N(4)	178.4(3)	N(2)–Co(1)–N(4)	93.8(3)
N(3)–Co(1)–N(4)	86.3(3)	Hg(1)–Cl(1)–Hg(1a)	94.1(1)
Co(1)–N(1)–C(2)	108.9(6)	Co(1)–N(2)–C(1)	109.2(6)
N(2)–C(1)–C(2)	106.7(8)	N(1)–C(2)–C(1)	107.3(7)
Co(1)–N(3)–C(3)	109.3(5)	Co(1)–N(4)–C(4)	108.9(6)
N(3)–C(3)–C(4)	106.2(8)	N(4)–C(4)–C(3)	109.4(8)

[a] Atom numbering schemes:



and

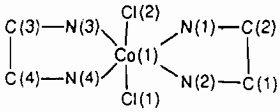


TABLE 10. Bond lengths (Å) and bond angles (°) for $[H_2en][Hg_2Cl_6]$ (**3**)[a]

Bond lengths (Å)			
Hg(1)–Cl(1)	2.349(4)	Hg(1)–Cl(2)	2.353(4)
Hg(1)–Cl(3)	2.751(3)	Hg(1)–Cl(3a)	2.811(5)
Cl(3)–Hg(1a)	2.811(5)	C(1)–C(1a)	1.51(3)
N(1)–C(1)	1.50(2)	Hg(1)...Hg(1a)	3.946
Bond angles (°)			
Cl(1)–Hg(1)–Cl(2)	165.1(1)	Cl(1)–Hg(1)–Cl(3)	95.6(1)
Cl(2)–Hg(1)–Cl(3)	94.3(1)	Cl(1)–Hg(1)–Cl(3a)	93.8(1)
Cl(2)–Hg(1)–Cl(3a)	97.4(1)	Cl(3)–Hg(1)–Cl(3a)	89.6(1)
Hg(1)–Cl(3)–Hg(1a)	90.4(1)	N(1)–C(1)–C(1a)	110(2)

[a] Atom numbering schemes: N(1)–C(1)–C(1a)–N(1a) and

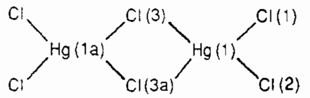


TABLE 11. Bond lengths (Å) and bond angles (°) for $[H_2en]_2[HgCl_4][Cl]_2$ (**4**)[a]

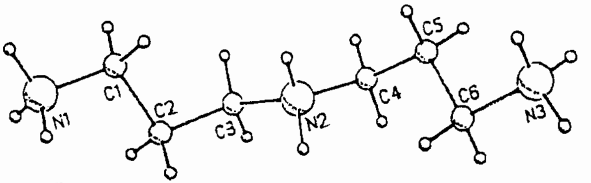
Bond lengths (Å)			
Hg(1)–Cl(1)	2.575(4)	Hg(1)–Cl(2)	2.891(4)
Hg(1)–Cl(3)	2.396(2)	Hg(1)–Cl(3a)	2.396(2)
N(1)–C(1)	1.47(1)	N(2)–C(2)	1.50(1)
C(1)–C(2)	1.51(1)	Hg(1)–Cl(2a)	3.277
Bond angles (°)			
Cl(1)–Hg(1)–Cl(2)	96.9(1)	Cl(1)–Hg(1)–Cl(3)	103.8(1)
Cl(2)–Hg(1)–Cl(3)	93.8(1)	Cl(1)–Hg(1)–Cl(3a)	103.8(1)
Cl(2)–Hg(1)–Cl(3a)	93.8(1)	Cl(3)–Hg(1)–Cl(3a)	150.2(1)
N(1)–C(1)–C(2)	114.3(9)	N(2)–C(2)–C(1)	112.9(8)
Hg(1)–Cl(2a)–Hg(1a)	170.4		

[a] Atom numbering schemes: N(1)–C(1)–C(2)–N(2) and Fig. 3.

TABLE 12. Bond lengths (Å) and bond angles (°) for $[H_3dpt]_2[Hg_3Cl_{12}]$ (**5**)[a]

Bond lengths (Å)			
Hg(1)–Cl(3)	2.425(7)	Hg(1)–Cl(4)	2.420(8)
Hg(1)–Cl(5)	2.580(8)	Hg(1)–Cl(6)	2.518(8)
Hg(2)–Cl(1)	2.377(7)	Hg(2)–Cl(2)	2.771(8)
Hg(2)–Cl(5)	3.130(8)	Hg(2)–Cl(1′)	2.377(7)
Hg(2)–Cl(2′)	2.771(8)	Hg(2)–Cl(5′)	3.130(8)
N(1)–C(1)	1.44(4)	C(1)–C(2)	1.53(5)
C(2)–C(3)	1.55(5)	C(3)–N(2)	1.59(5)
N(2)–C(4)	1.52(5)	C(4)–C(5)	1.47(5)
C(5)–C(6)	1.52(5)	C(6)–N(3)	1.56(5)
Bond angles (°)			
Cl(3)–Hg(1)–Cl(4)	129.1(3)	Cl(3)–Hg(1)–Cl(5)	101.7(3)
Cl(4)–Hg(1)–Cl(5)	112.5(3)	Cl(3)–Hg(1)–Cl(6)	107.0(3)
Cl(4)–Hg(1)–Cl(6)	105.1(2)	Cl(5)–Hg(1)–Cl(6)	96.7(3)
Cl(1)–Hg(2)–Cl(2)	89.7(2)	Cl(1)–Hg(2)–Cl(5)	81.7(2)
Cl(2)–Hg(2)–Cl(5)	161.5(2)	Cl(1)–Hg(2)–Cl(1′)	168.7(4)
Cl(2)–Hg(2)–Cl(1′)	96.8(2)	Cl(5)–Hg(2)–Cl(1′)	89.4(2)
Cl(1)–Hg(2)–Cl(2′)	96.8(2)	Cl(2)–Hg(2)–Cl(2′)	110.0(4)
Cl(5)–Hg(2)–Cl(2′)	87.4(2)	Cl(1′)–Hg(2)–Cl(2′)	89.7(2)
Cl(1)–Hg(2)–Cl(5′)	89.4(2)	Cl(2)–Hg(2)–Cl(5′)	87.4(2)
Cl(5)–Hg(2)–Cl(5′)	76.3(3)	Cl(1′)–Hg(2)–Cl(5′)	81.7(2)
Cl(2′)–Hg(2)–Cl(5′)	161.5(2)	Hg(1)–Cl(5)–Hg(2)	162.1(4)
N(1)–C(1)–C(2)	110(2)	C(1)–C(2)–C(3)	111(3)
C(2)–C(3)–N(2)	110(3)	C(3)–N(2)–C(4)	109(3)
N(2)–C(4)–C(5)	109(3)	C(4)–C(5)–C(6)	113(3)
C(5)–C(6)–N(3)	108(3)		

[a] Atom numbering schemes:



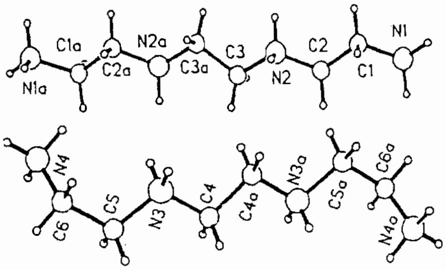
and Fig. 5.

(Å). Even though this distance is at the extreme end of potential Hg...Cl interactions [62], very large distortions occur at the $HgCl_4^{2-}$ center and the normal range of 'tetrahedral' angles 100–121° [58] is expanded to 94–150° in **4** (Table 11). The linking of $HgCl_4^{2-}$ groups is even more marked in **6** and **5** where $Hg_2Cl_8^{4-}$ and $Hg_3Cl_{12}^{6-}$ units can be recognised. In **6**, the $Hg_2Cl_8^{4-}$ anion (Fig. 4) has next nearest Hg...Cl distances at 3.328 Å (Hg(2)–Cl(8), along the chain) and 3.204 Å (Hg(1)–Cl(7), chain cross-links). Within the

TABLE 13. Bond lengths (Å) and bond angles (°) for $[H_4trien][Hg_2Cl_8]$ (**6**)[a]

Bond lengths (Å)			
Hg(1)–Cl(4)	2.385(4)	Hg(1)–Cl(5)	2.644(4)
Hg(1)–Cl(6)	2.412(4)	Hg(1)–Cl(8)	2.841(4)
Hg(2)–Cl(1)	2.791(4)	Hg(2)–Cl(2)	2.398(4)
Hg(2)–Cl(3)	2.507(5)	Hg(2)–Cl(7)	2.398(5)
N(2)–C(3)	1.48(2)	N(2)–C(2)	1.44(2)
C(4)–N(3)	1.48(2)	C(4)–C(4A)	1.62(3)
C(1)–N(1)	1.51(2)	C(1)–C(2)	1.50(2)
C(3)–C(3A)	1.58(3)	N(4)–C(6)	1.48(2)
N(3)–C(5)	1.50(2)	C(5)–C(6)	1.53(3)
Bond angles (°)			
Cl(4)–Hg(1)–Cl(5)	108.9(1)	Cl(4)–Hg(1)–Cl(6)	155.5(2)
Cl(5)–Hg(1)–Cl(6)	94.4(1)	Cl(4)–Hg(1)–Cl(8)	92.9(1)
Cl(5)–Hg(1)–Cl(8)	96.9(1)	Cl(6)–Hg(1)–Cl(8)	91.2(1)
Cl(1)–Hg(2)–Cl(2)	103.4(1)	Cl(1)–Hg(2)–Cl(3)	93.7(1)
Cl(2)–Hg(2)–Cl(3)	109.1(2)	Cl(1)–Hg(2)–Cl(7)	90.8(1)
Cl(2)–Hg(2)–Cl(7)	134.8(2)	Cl(3)–Hg(2)–Cl(7)	112.5(2)
C(3)–N(2)–C(2)	114(1)	N(3)–C(4)–C(4A)	106(1)
N(1)–C(1)–C(2)	109(1)	N(2)–C(3)–C(3A)	109(2)
N(2)–C(2)–C(1)	112(1)	C(4)–N(3)–C(5)	112(1)
N(3)–C(5)–C(6)	113(1)	N(4)–C(6)–C(5)	114(1)

[a] Atom numbering schemes:



and Fig. 4.

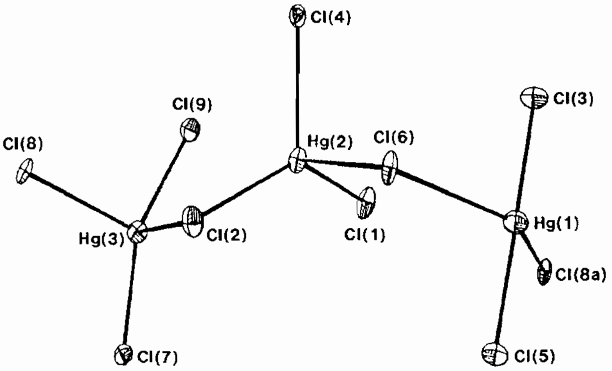


Fig. 1. The numbering scheme adopted for the $(Hg_3Cl_9^{3-})_n$ chains in $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$. There are 'cross links' between the chains with Hg(1)–Cl(1a) = 2.950 Å (Table 8).

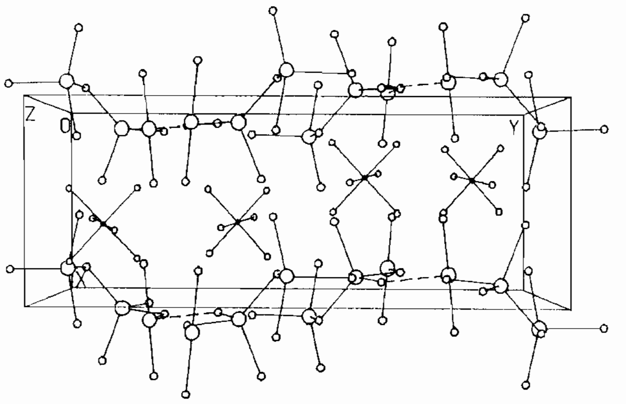


Fig. 2. A packing diagram for $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ showing the chloro-mercury(II) chains developed in this structure. Oxygen atoms have been omitted.

anion (Table 13), the bridging Cl atom has the longest Hg–Cl distances (3.045(4) and 2.792(4) Å). Thus we now can recognise isolated $HgCl_4^{2-}$ anions [58], $HgCl_4^{2-}$ units associated via Cl...Cl attractive forces [2, 63], $(HgCl_4^{2-})_n$ chains with Hg...Cl bridging at 3.28 Å, more discrete $Hg_2Cl_8^{4-}$ units with Hg–Cl bridging at 3.05 Å, and finally $Hg_3Cl_{12}^{6-}$.

Isolated $Hg_3Cl_{12}^{6-}$ anions are observed in $[H_3dpt]_2[Hg_3Cl_{12}]$ (Fig. 5). The two terminal Hg atoms in this anion adopt four-coordination, but the central Hg atom has the rather rare [64] six-coordination. Bond lengths about the central centrosymmetric six-coordinate Hg(2) atom are of the [2+2+2] type viz. 2.377(7)×2, 2.771(8)×2 and 3.130(8) Å×2 with the longer bonds being associated with the bridging chlorine atoms. These in turn are linked to the terminal 'tetrahedral' Hg atoms at a distance of 2.580(8) which is at the long end of the range observed for isolated $HgCl_4^{2-}$ anions (2.36–2.61 Å, mean 2.50 Å).

While the six chloro ligands are symmetrically arranged about the central Hg(2) atom, distortions of up to 18° from octahedral ideality are observed (Table 12).

The closest Hg...Cl distance between the anions (Hg(1)...Cl(1)) is 3.79 Å, and is of the same magnitude as the interionic Cl...Cl distances. Recently [65] the structure of another chloromercury(II) salt of a triprotonated polyamine with stoichiometry $[H_3dien]_2[HgCl_8]$ has been described. Here the cation is counterbalanced with three isolated chloride ions and one five-coordinate $HgCl_5^{3-}$ ion, i.e. $[H_3dien]_2[HgCl_5][Cl]_3$.

Supplementary material

Tables of structure factors, hydrogen atom coordinates and anisotropic thermal parameters are available from the authors.

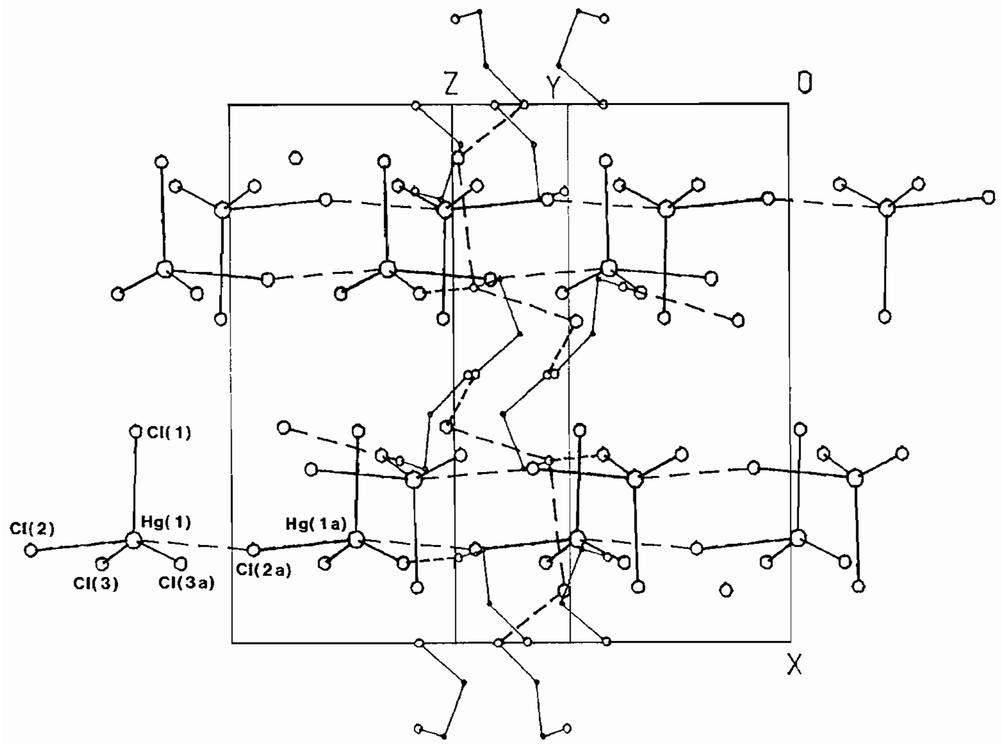


Fig. 3. A packing diagram for $[H_2en]_2[HgCl_4][Cl]_2$ (4) showing the $\{HgCl_4^{2-}\}_n$ chain and the atom numbering scheme adopted in Tables 5 and 11.

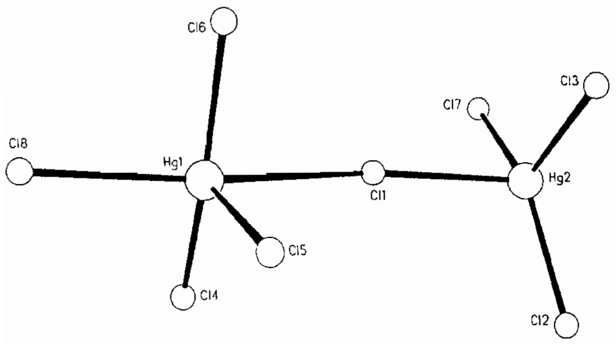


Fig. 4. A view of the $Hg_2Cl_8^{4-}$ unit in $[H_4trien][Hg_2Cl_8]$ (6).

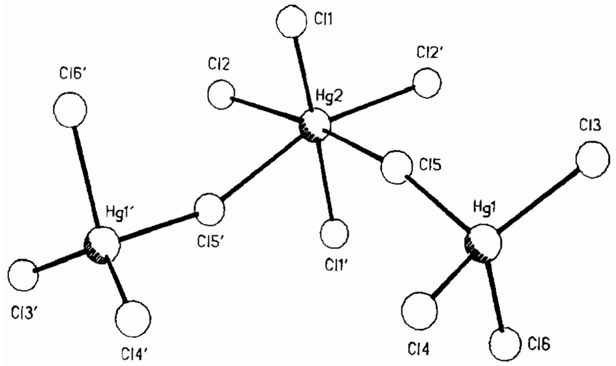


Fig. 5. A view of the $Hg_3Cl_{12}^{6-}$anion in $[H_3dpt]_2[Hg_3Cl_{12}]$ (5) showing the atom numbering scheme adopted in Tables 6 and 12.

Acknowledgements

We thank the New Zealand Universities Grants Committee for funds to purchase instruments used in this research and Huo Wen thanks the same organisation for the award of a post-graduate scholarship.

References

1 J. Reedijk, Methyl cyanide as a ligand, *Doctoral Thesis,* University of Leiden, 1968, p. 41.
2 D. A. House, V. McKee and W. T. Robinson, *Inorg. Chim. Acta, 157* (1989) 15.
3 D. A. House, V. McKee and W. T. Robinson, *Inorg. Chim. Acta, 160* (1989) 71.
4 L. V. Konovalov and K. A. Davarski, *J. Coord. Chem., 14* (1986) 201.
5 G. G. Schlessinger, *Inorganic Laborator Preparations,* Chemical Publishing Co., New York, 1962, p. 176.
6 M. C. Cimolino and R. G. Linck, *Inorg. Chem., 20* (1981) 3499.
7 A. W. Herlinger, J. N. Brown, M. A. Dwyer and S. F. Pavkovic, *Inorg. Chem., 20* (1981) 2366.
8 W. Clegg, *J. Chem. Soc., Dalton Trans.,* (1982) 593.
9 G. G. Schlessinger, *Inorganic Laborator Preparations,* Chemical Publishing Co., New York, 1962, p. 237.
10 G. M. Sheldrick, *SHELXTL User Manual,* Revision 5, Nicolet XRD Corp., Madison, WI, 1986.
11 D. A. House, in G. Wilkinson (ed.), *Comprehensive Coordination Chemistry,* Vol. 2, Pergamon, Oxford, 1987, p. 26.
12 A. Nakahara, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Jpn. 25* (1952) 331.
13 A. Becker, G. Grosse and K. Pleith, *Z. Kristallogr., 112* (1959) 375; *Naturwissenschaften, 42* (1955) 254.
14 S. Ooi and H. Kuroya, *Bull. Chem. Soc. Jpn., 36* (1963) 1083.
15 K. Bordersen, J. Rath and G. Thiele, *Z. Anorg. Allg. Chem., 394* (1972) 13.
16 K. Maroy, *Acta Chem. Scand., 27* (1973) 1705.
17 Yu. A. Simonov, L. I. Landa, N. N. Proskina, T. I. Malinovskii and A. V. Ablov, *Sov. Phys. Crystallogr., 18* (1973) 333; *Kristallografiya, 18* (1973) 530; *C. A., 79* (1973) 58765.
18 J. Roziere and J. M. Williams, *Inorg. Chem., 15* (1976) 1175; J. M. Williams, *Inorg. Nucl. Chem. Lett., 3* (1967) 297.
19 J. Bordner, Z. Z. Hugus, Jr. and W. M. Shirley, *Cryst. Struct. Commun., 5* (1976) 691.
20 A. S. Foust, V. Janickis and K. Maroy, *Inorg. Chem., 19* (1980) 1040.
21 A. S. Foust, V. Janickis and K. Maroy, *Inorg. Chem., 19* (1980) 1044.
22 A. S. Foust and V. Janickis, *Inorg. Chem., 19* (1980) 1048.
23 U. Schubert, B. Zimmer-Gasser, K. C. Dash and G. R. Chaudhury, *Cryst. Struct. Commun., 10* (1981) 239.
24 E. C. Niederhoffer, R. Peascoe, P. R. Rudolf, A. Clearfield and A. E. Martell, *Acta Crystallogr., Sect. C, 42* (1986) 568; L. Campanella, *Bull. Chem. Soc. Jpn., 41* (1968) 2814.
25 D. A. House, in G. Wilkinson (ed.), *Comprehensive Coordination Chemistry,* Vol. 2, Pergamon, Oxford, 1987, p. 30.
26 G. C. DeFotis, E. M. McGhee, I. Bernal and D. B. Losee, *J. Appl. Phys., 61* (1987) 3298.
27 R. C. Larock, L. D. Burns, S. Varaparth, C. E. Russell, J. W. Richardson, Jr., M. N. Janakiraman and R. A. Jacobson, *Organometallics, 6* (1987) 1780.
28 J. K. Mohana Rao and R. K. Rajaram, *Z. Kristallogr., 160* (1982) 219.
29 K. Weidenhammer and M. L. Ziegler, *Z. Anorg. Allg. Chem., 434* (1977) 152.
30 T. J. Kistenmacher, M. Rossi, C. C. Chiang, R. P. Van Duyne and A. R. Siedle, *Inorg. Chem., 19* (1980) 3604.
31 J. Pickardt and T. Schendler, *Z. Naturforsch., Teil B, 37* (1982) 930.
32 L. Book, A. J. Carty and C. Chieh, *Can. J. Chem., 59* (1981) 138.
33 M. Sikirica, D. Grdenic and I. Vickovic, *Cryst. Struct. Commun., 11* (1982) 1299.
34 P. M. Boorman, C. L. Meril, W. A. Shantha Nandana and J. F. Richardson, *J. Chem. Soc., Dalton Trans.,* (1986) 1251.
35 P. Biscarini, L. Fusina, G. Nivellini and G. Pelizzi, *J. Chem. Soc., Dalton Trans.,* (1977) 664.
36 N. Korfer and H. Fuess, *Z. Kristallogr., 183* (1988) 27.
37 M. Sandstrom and D. H. Liem, *Acta Chem. Scand., Ser. A, 32* (1978) 509.
38 M. N. Ponnsuswamy and J. Trotter, *Acta Crystallogr., Sect. C, 40* (1984) 1671.
39 K. Brodersen and G. Pezzei, *Z. Anorg. Allg. Chem., 499* (1983) 169.
40 P. L. Goggin, P. King, D. M. McEwan, D. G. Taylor, P. Woodward and M. Sandstrom, *J. Chem. Soc., Dalton Trans.,* (1982) 875.
41 R. P. Shibaeva and L. P. Rozenberg, *Sov. Phys. Crystallogr., 26* (1981) 695; *C. A., 96* (1982) 27120.
42 E. I. Zhilaeva, R. N. Lyubovskaya, M. L. Khidekel, R. P. Shibaeva, L. P. Rozenberg, M. A. Simmonov, O. Ya. Neiland and D. B. Bite, *Dokl. Akad. Nauk. SSSR, 250* (1980) 868; *C. A., 93* (1980) 46478.

43 P. S. Chaari, A. Ben Salah, T. Jouni and A. Daoud, *Acta Crystallogr., Sect. C, 45* (189) 1495.

44 D. J. Shi and M. Kaneko, *J. Photochem. Photobiol. A: Chem., 51* (1990) 155.

45 G. Chessa, G. Marangoni, B. Pitteri, V. Bertolasi, V. Ferretti and G. Gilli, *J. Chem. Soc., Dalton Trans.*, (1990) 915.

46 A. Ben Salah, J. W. Bats, R. Kalus, H. Fuess and A. Daoud, *Z. Anorg. Allg. Chem., 493* (1982) 173.

47 A. Ben Salah, J. W. Bats, H. Fuess and A. Daoud, *Inorg. Chim. Acta, 63* (1982) 169.

48 A. Ben Salah, J. W. Bats, H. Fuess and A. Daoud, *Z. Kristallogr., 164* (1983) 259.

49 N. Hadjiliadis, A. Hyannopoulos and R. Bau, *Inorg. Chim. Acta, 69* (1983) 109.

50 R. Mason, G. B. Robertson and G. A. Rusholme, *Acta Crystallogr., Sect. B, 30* (1974) 894.

51 I. D. Vessosi, A. Benedetti, A. Albinati, F. Ganazoli, F. Cariati and L. Pelliciari, *Inorg. Chim. Acta, 90* (1984) 1.

52 S. A. Linde, A. Y. Mikhailova, V. I. Pakhomov, V. V. Kirilenko and V. G. Shulga, *Koord. Khim., 9* (1983) 998; *C. A., 99* (1983) 149952.

53 N. W. Alcock, E. M. Curzon and P. Moore, *J. Chem. Soc., Dalton Trans.*, (1984) 2813.

54 N. W. Alcock, E. H. Curzon, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, (1979) 1987.

55 M. R. Burke and M. F. Richardson, *Inorg. Chim. Acta, 69* (1983) 29.

56 L. Menabue, G. C. Pellacani, A. Albinati, F. Ganazoli, F. Cariati and G. Rassu, *Inorg. Chim. Acta, 58* (1982) 227.

57 W. Clegg, M. L. Brown and L. J. A. Wilson, *Acta Crystallogr., Sect. B, 32* (1976) 2905.

58 L. Book and T. C. W. Mak, *Inorg. Chim. Acta, 77* (1983) L57.

59 G. Ferguson, J. A. D. Jeffreys and G. A. Sim, *J. Chem. Soc. B*, (1966) 454.

60 J. A. D. Jeffreys, G. A. Sim, R. H. Burnell, W. I. Taylor, R. E. Corbett, J. Murray and B. J. Sweetman, *Proc. Chem. Soc.*, (1963) 171.

61 G. Cheesa, G. Marangoni, B. Pitteri, V. Bertolasi, V. Ferretti and G. Gilli, *J. Chem. Soc., Dalton Trans.*, (1988) 1479.

62 L. G. Kuz'mina and Y. T. Struchkov, *Croat. Chem. Acta, 57* (1984) 701; *C. A., 102* (1985) 203994.

63 J. A. R. P. Sarma and G. R. Desiraju, *Acc. Chem. Res., 19* (1986) 222.

64 K. Brodersen, K. P. Jensen and G. Thiele, *Z. Naturforsch., Teil B, 35* (1980) 259; *C. A., 93* (1980) 105117.

65 L. P. Gattaglia, A. B. Conradi, L. Antolini, T. Manfredini, L. Menabue, G. C. Pellacani and G. Ponticelli, *J. Chem. Soc., Dalton Trans.*, (1986) 2529.