Synthesis and Characterization of Pentagonal-bipyramidal Mercury(II) Complexes with 2,6-Diacetylpyridine Bis(2′-pyridylhydrazone). *X*-Ray Structure of [2,6-Diacetylpyridine bis(2′-pyridylhydrazone)]mercury(II) Tetrachloromercurate(II)†

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The ligand 2,6-diacetylpyridine bis(2′-pyridylhydrazone) (H_2dapp) reacts in ethanol with $HgCl_2$ or $Hg(ClO_4)_2{\cdot}3H_2O$ to give the charged species [Hg(H_2dapp)][$HgCl_4$] (**1**) or [Hg(H_2dapp)(H_2O)$_2$][ClO_4]$_2$ (**2**) respectively. Starting from $HgCl_2$ in the presence of perchlorate ions the mixed chloro–aqua complex [Hg(H_2dapp)Cl(H_2O)][ClO_4] (**3**) is obtained. Complexes (**1**), (**2**), and (**3**) can be deprotonated to the neutral species [Hg(dapp)] (**4**) under basic conditions. The complexes have been characterized by a number of physicochemical measurements including the *X*-ray analysis of (**1**). Crystals of (**1**) are monoclinic, space group $P2_1/n$, with unit-cell dimensions a = 12.271(5), b = 15.948(6), c = 12.703(6) Å, β = 109.06(3)°, and Z = 4. The structure has been solved from three dimensional counter data by Patterson and Fourier methods and refined by full-matrix least squares to R 0.040 for 2 654 observed reflections. The packing can be described either as consisting of infinite chains of alternating pentagonal planar [Hg(H_2dapp)]$^{2+}$ cations and tetrahedral [$HgCl_4$]$^{2-}$ anions running along b or as infinite chains of μ-Cl-connected pentagonal bipyramidal (pbp) and tetrahedral Hg complexes. In the pbp co-ordination around the metal atom the five basal positions are occupied by five N atoms of the polydentate ligand and the two apical positions by two Cl atoms belonging to the tetrahedral anions. The five-co-ordinate ligand is not planar, and its general form is that of a flattened helix.

Seven is an unusual co-ordination number for most elements, but in the presence of planar quinquedentate ligands the metal ion can be forced to adopt a pentagonal-bipyramidal (pbp) arrangement. Using this approach in the last few years a number of pbp complexes of the first-row transition elements have been synthesized with a series of quinquedentate chelating ligands derived by the condensation of 2,6-diacetylpyridine with diamines, hydrazines, and hydrazides, and characterized mainly by means of *X*-ray structural analysis.[1–11]

As part of a program of investigation into the metal complexes of quinquedentate hydrazones,[12–14] we have now studied the reactions between Hg^{II} salts and 2,6-diacetylpyridine bis(2′-pyridylhydrazone) (H_2dapp), which has been shown to behave as a *NNNNN* chelating ligand towards Co^{II}, Zn^{II},[15] and the uranyl ion,[2] giving charged and neutral complexes, owing to the possibility of deprotonation of the diazapropenic groups =C=N–NH–. In this paper we report the preparation and physicochemical characterization of the cationic and neutral Hg^{II} complexes obtained, and the *X*-ray crystal structure of the species [Hg(H_2dapp)][$HgCl_4$], which confirm the ability of the H_2dapp ligand to stabilize the pbp geometry.

Experimental

Reagents.—Reagent-grade mercury(II) chloride, mercury(II) nitrate, mercury(II) perchlorate, lithium perchlorate (Alfa products), 2,6-diacetylpyridine, and 2-hydrazinopyridine (Fluka products) were used without further purification. All solvents used were purified as reported.[16] Deuteriated solvents for ^{1}H n.m.r. were Aldrich products with a minimum isotopic purity of 99.9%.

2,6-Diacetylpyridine Bis(2′-pyridylhydrazone) (H_2dapp).—The ligand was prepared as reported[17] and recrystallized from ethanol. Its purity was checked by elemental analysis and comparison of its i.r. spectrum with that reported in the literature.[12]

2,6-Diacetylpyridine Bis(2′-pyridylhydrazone) Dihydrochloride Monohydrate, H_2dapp·2HCl·H_2O.—This was obtained by treating H_2dapp (0.345 g, 1 mmol) dissolved in ethanol (20 cm^3) with concentrated HCl (2 cm^3). The product which precipitated immediately was filtered off, washed with ethanol and diethyl ether, and dried under reduced pressure (0.362 g, 83%).

[2,6-Diacetylpyridine bis(2′-pyridylhydrazone)]mercury(II) *Tetrachloromercurate*(II), [Hg(H_2dapp)][$HgCl_4$] (**1**).—To a warm solution of H_2dapp (0.345 g, 1 mmol) in absolute ethanol (20 cm^3) a suspension of $HgCl_2$ (0.542 g, 2 mmol) in ethanol (5 cm^3) was added at room temperature with stirring. The slow dissolution of the mercury salt was accompanied by rapid formation and precipitation of a yellow product which, after stirring for 1 h, was filtered off, washed with ethanol and diethyl ether, and dried under reduced pressure (0.86 g, 97%). The crude product was crystallized from a concentrated dimethylformamide (dmf)–methanol (30:70, v/v) solution left overnight at −10 °C.

Diaqua[2,6-diacetylpyridine bis(2′-pyridylhydrazone)]mercury(II) *Perchlorate* [Hg(H_2dapp)(H_2O)$_2$][ClO_4]$_2$ (**2**).—A warm solution of H_2dapp (0.345 g, 1 mmol) in ethanol (20 cm^3)

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

Table 1. Analytical and physical data

	Compound	Colour	M.p./°C	Λ_M/Ω^{-1} cm^2 mol^{-1}	Analysis (%)[a] C	H	Cl	N
	H_2dapp	Pale yellow	195 (195—196)[b]		66.2 (66.1)	5.50 (5.55)		28.2 (28.4)
	H_2dapp·2HCl·H_2O	Pale yellow			52.3 (52.3)	5.15 (5.50)	16.7 (16.3)	22.4 (22.5)
(1)	[Hg(H_2dapp)][$HgCl_4$]	Yellow	> 220 (decomp.)	35[c]	25.5 (25.7)	2.10 (2.10)	15.9 (16.0)	10.9 (11.05)
(2)	[Hg(H_2dapp)(H_2O)$_2$][ClO_4]$_2$	Yellow	> 220 (decomp.)	124[d]	29.2 (29.2)	2.45 (2.95)	9.05 (9.10)	12.7 (12.5)
(3)	[Hg(H_2dapp)Cl(H_2O)][ClO_4]	Yellow	> 220 (decomp.)	67[d]	33.0 (32.6)	2.75 (3.00)	10.2 (10.2)	14.5 (14.0)
(4)	[Hg(dapp)]	Red	195—197		41.3 (42.0)	3.05 (3.10)		18.0 (18.0)
(5)	[Zn(H_2dapp)(H_2O)$_2$]Cl_2	Yellow	230 (230)[e]		44.3 (44.1)	4.25 (4.40)	13.5 (13.7)	19.2 (18.9)
(6)	[Zn_2(dapp)$_2$]	Red			55.2 (55.8)	4.30 (4.15)		23.2 (24.0)

[a] Calculated values in parentheses. [b] From ref. 12. [c] In methanol. [d] In dimethylformamide. [e] From ref. 15.

Table 2. ^{1}H N.m.r., u.v.–visible band maxima, and selected i.r. absorptions

	^{1}H N.m.r.[a]/p.p.m.	U.v.–visible band maxima[b] (nm)	Selected i.r. absorptions (cm^{-1})
H_2dapp	2.06 (s, 6 H, CH_3), 6.29—7.85 (m, 11 H, py), 9.47 (s, 2 H, NH)	332 252 (sh) 232	3 320, 3 200, 1 598, 1 580, 1 510, 1 505, 1 440, 985, 768, 630
H_2dapp·2HCl·H_2O		396 (12 380) 343 (37 400) 283 (15 220)	3 420, 3 250, 1 645, 1 613, 1 555, 1 488, 1 442, 995, 625
(1)	2.62 (s, 6 H, CH_3), 7.07—8.37 (m, 11 H, py), 11.44 (s, 2 H, NH)	386 (sh) 339 (26 480) 285 (21 260)	3 260, 1 613, 1 580, 1 558, 1 515, 1 485, 1 435, 1 000, 780, 637
(2)	2.77 (s, 6 H, CH_3), 7.21—8.60 (m, 11 H, py), 11.94 (s, 2 H, NH)	386 (sh) 339 (28 000) 285 (22 500)	3 500, 3 270, 1 613, 1 580, 1 555, 1 515, 1 485, 1 440, 1 000, 780, 620
(3)	2.70 (s, 6 H, CH_3), 7.22—8.34 (m, 11 H, py), 11.55 (s, 2 H, NH)	386 (sh) 339 (25 400) 286 (20 460)	3 500, 3 250, 1 613, 1 609, 1 578, 1 555, 1 518, 1 485, 1 435, 998, 780, 620
(4)	2.58 (s, 6 H, CH_3), 6.10—7.57 (m, 11 H, py)	482 436 (sh) 395 (sh) 333 282 (sh)	1 602, 1 578, 1 518, 1 468, 988, 760, 630
(5)	2.60 (s, 6 H, CH_3), 6.96—8.27 (m, 11 H, py), 11.22 (s, 2 H, NH)		3 500, 3 160, 1 615, 1 580, 1 555, 1 518, 1 487, 1 000, 770, 630
(6)	2.78 (s, 6 H, CH_3), 6.11—7.66 (m, 11 H, py)		1 607, 1 582, 1 523, 1 468, 987, 760, 630

[a] H_2dapp, (1)—(3), and (5) in $(CD_3)_2SO$; (4) and (6) in $CDCl_3$; in p.p.m. from $SiMe_4$ as external standard. [b] H_2dapp in MeOH; H_2dapp·2HCl·H_2O, (1)—(3) in water; (4) and (6) in $CHCl_3$; molar absorption coefficient, ε (dm^3 mol^{-1} cm^{-1}) in parentheses.

was mixed with a solution of $Hg(ClO_4)_2·3H_2O$ (0.453 g, 1 mmol) in ethanol (3 cm^3) with stirring. The yellow product which precipitated immediately was filtered off, washed with ethanol and diethyl ether, and dried under reduced pressure (0.68 g, 87%). The same product was obtained starting from equimolar solutions of $Hg(NO_3)_2·2H_2O$ and H_2dapp saturated with $LiClO_4$ in the same solvent.

Aquachloro[2,6-*diacetylpyridine bis*(2′-*pyridylhydrazone*)]-*mercury*(II) *Perchlorate*, [Hg(H_2dapp)Cl(H_2O)][ClO_4] (3).—To a warm solution of H_2dapp (0.345 g, 1 mmol) in absolute ethanol (20 cm^3), saturated with $LiClO_4$, a suspension of $HgCl_2$ (0.271 g, 1 mmol) in ethanol (5 cm^3) was added at room temperature with stirring. The dissolution of the mercury salt was accompanied by a colour change of the mixture from almost colourless to yellow followed by rapid formation of a deep yellow product which, after stirring for 1 h at reflux, was filtered off, washed with ethanol and diethyl ether, and dried under reduced pressure (0.62 g, 89%). Brilliant deep yellow crystals were obtained by slow crystallization from methanol.

[2,6-*Diacetylpyridine bis*(2′-*pyridylhydrazonato*)]*mercury*(II), [Hg(dapp)] (**4**).—A suspension of (**3**) (0.698 g, 1 mmol) in water (50 cm^3) was treated with a concentrated aqueous solution of KOH, until pH 9 was achieved, with stirring at 50 °C, and the deep red solid rapidly formed was extracted with $CHCl_3$ (3 × 20 cm^3). The extract was dried over anhydrous magnesium sulphate and, after cooling and slow evaporation of the solvent, the compound was isolated as red microcrystals (0.33 g, 61%). The product (**4**) can also be obtained starting from compound (**2**), using the same procedure.

Table 3. Crystal data for $[Hg(H_2dapp)][HgCl_4]$

Formula	$C_{19}H_{19}Cl_4Hg_2N_7$
M	888.40
Crystal size/mm	0.15 × 0.26 × 0.48
Space group	$P2_1/n$
a/Å	12.271(5)
b/Å	15.948(6)
c/Å	12.703(6)
β/°	109.06(3)
U/Å^3	2 350(2)
F(000)	1 640
Z	4
D_c/g cm^{-3}	2.511
D_m/g cm^{-3}	2.45
μ(Mo-K_α)/cm^{-1}	135.35
Radiation	Mo-K_α
Monochromator	Graphite
$\theta_{min.}$—$\theta_{max.}$/°	2—27
Standard reflections	3
T/°C	22
Independent reflections	5 100
Reflections with $I > 3\sigma(I)$	2 654
Variables (last cycle)	289
Final $R = \Sigma\lvert\Delta F_o\rvert/\Sigma\lvert F_o\rvert$	0.040
Final $R' = (\Sigma w\lvert\Delta F_o\rvert/\Sigma w\lvert F_o\rvert^2)^{\frac{1}{2}}$	0.046
Final max. shift/error	0.01
Largest peak in final difference map (outside Hg co-ordination sphere)/e Å^{-3}	0.61
Weighting	$1/w = 1/[\sigma^2(I) + 0.05(I)]$
Error in an observation of unit weight	1.06

Diaqua[2,6-*diacetylpyridine bis*(2′-*pyridylhydrazone*)]*zinc*(II) *Chloride*, $[Zn(H_2dapp)(H_2O)_2]Cl_2$, (**5**), *and Bis*[2,6-*diacetylpyridine bis*(2′-*pyridylhydrazonato*)]*dizinc*(II), $[Zn_2(dapp)_2]$, (**6**).—These were prepared as reported in the literature.[15]

Analytical and some physical data of both the ligand and its complexes are reported in Table 1, while spectroscopic ^1H n.m.r., i.r., and u.v.–visible data are summarized in Table 2.

Physical Measurements.—I.r. spectra (4 000—250 cm^{-1}, KBr discs) were recorded on a Perkin-Elmer 683 spectrophotometer; u.v.–visible spectra (500—200 nm) were measured on Varian-Cary 219 and Perkin-Elmer Lambda 5 spectrophotometers with a 1-cm quartz cell at 25 °C; ^1H n.m.r. spectra were obtained on a Varian FT 80 spectrometer at 34 °C; conductometric measurements were carried out with a CDM 83 Radiometer Copenhagen conductivity meter and CDC 334 immersion electrode at 25 °C.

Crystal-structure Determination.—The intensity data for compound (**1**) were collected on an Enraf-Nonius CAD4 diffractometer with monochromated Mo-K_α radiation and the ω—2θ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 22 centred reflections in the range $9 < \theta < 14°$. Crystal data are reported in Table 3. The intensities of three standard reflections, monitored every 2 h, showed no significant variation during data collection. All data were corrected for Lorentz, polarization, and absorption (minimum transmission factor: 0.468). Scattering factors and anomalous dispersion parameters were taken from ref. 18. The positions of the two Hg atoms were obtained from Patterson synthesis; all Cl atoms and some C atoms were located in the subsequent Fourier map and the other non-H atoms were found from difference Fourier maps. After a few cycles of isotropic refinement, the structure was refined by full-matrix least squares using anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were assigned calculated positions (C–H = 0.95 Å) and fixed isotropic thermal parameters (5 Å^2). Weights for the last cycle were applied according to the scheme given in Table 3. All calculations used the SDP system of programs.[19] Final positional parameters[20] are given in Table 4. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Treatment of stoicheiometric (1:1) amounts of H_2dapp and $HgCl_2$ in ethanol gives, quantitatively, the ionic species (**1**). Compound (**1**) analyzes as a compound with a mol ratio,

Table 4. Positional parameters (× 10^4) with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Hg(1)	1 907.9(4)	220.8(4)	−2 133.0(4)	C(4)	2 500(10)	458(10)	1 569(9)
Hg(2)	1 231.2(4)	−2 614.4(3)	−1 601.7(4)	C(5)	2 535(9)	261(8)	506(8)
Cl(1)	2 476(3)	−2 925(2)	−2 722(3)	C(6)	4 079(9)	−984(8)	−774(9)
Cl(2)	1 925(4)	−2 311(3)	366(3)	C(7)	4 852(11)	−1 524(10)	98(11)
Cl(3)	464(3)	−1 175(2)	−2 558(3)	C(8)	4 119(9)	−981(8)	−1 942(9)
Cl(4)	−372(3)	−3 658(2)	−1 994(3)	C(9)	4 875(10)	−1 458(9)	−2 275(11)
N(1)	1 962(7)	695(7)	−379(7)	C(10)	4 904(9)	−1 369(9)	−3 358(11)
N(2)	3 219(8)	−393(6)	400(7)	C(11)	4 187(9)	−830(8)	−4 061(10)
N(3)	3 328(8)	−481(6)	−624(7)	C(12)	3 421(9)	−370(8)	−3 700(8)
N(4)	3 398(8)	−463(6)	−2 652(7)	C(13)	2 533(10)	195(9)	−4 435(9)
N(5)	1 723(7)	408(6)	−4 042(7)	C(14)	2 576(11)	449(9)	−5 520(10)
N(6)	845(8)	909(7)	−4 627(7)	C(15)	−4(10)	1 122(7)	−4 181(10)
N(7)	130(8)	878(6)	−3 139(8)	C(16)	−955(11)	1 559(9)	−4 819(10)
C(1)	1 358(10)	1 394(8)	−252(9)	C(17)	−1 781(11)	1 788(8)	−4 370(10)
C(2)	1 302(9)	1 607(9)	768(10)	C(18)	−1 643(10)	1 547(9)	−3 280(10)
C(3)	1 884(11)	1 134(10)	1 697(9)	C(19)	−694(10)	1 095(9)	−2 668(9)

Hg:H_2dapp, of 2:1 which can be formulated as $[Hg(H_2dapp)]^{2+}[HgCl_4]^{2-}$, in accord with the fact that after separation of the complex half the H_2dapp initially added can be recovered from the mother solution. The molar conductance of a 2.0×10^{-3} mol dm^{-3} solution in methanol (35 Ω^{-1} cm^2 mol^{-1}) is approximately half the conductance expected for a 1:1 electrolyte (80—115 Ω^{-1} cm^2 mol^{-1}),[21] due to the bulkiness of both the cation and anion which can result in seriously reduced ionic mobilities.

On treating the ligand H_2dapp with mercury(II) perchlorate, or nitrate, in the presence of an excess of perchlorate ions, in ethanol, the yellow product $[Hg(H_2dapp)(H_2O)_2][ClO_4]_2$ (**2**) is obtained. Its molar conductance in dmf (124 Ω^{-1} cm^2 mol^{-1}) is typical of a 1:2 electrolyte and its solid-state i.r. spectrum shows a strong, broad absorption centred at *ca.* 1 100 cm^{-1} due to the free perchlorate ion.

If the reaction is carried out under the same experimental conditions starting from $HgCl_2$ in the presence of an excess of perchlorate ions, the mixed chloro–aqua species $[Hg(H_2dapp)Cl(H_2O)][ClO_4]$ (**3**) is recovered in almost quantitative yield, which accordingly shows a conductance in dmf (67 Ω^{-1} cm^2 mol^{-1}) typical of a 1:1 electrolyte.

Infrared and ^{1}H n.m.r. spectra of the complexes (**1**), (**2**), and (**3**) in the solid state and in deuteriated dimethyl sulphoxide solution respectively (Table 2) suggest symmetric structures and reveal some diagnostic features which define the co-ordination mode.

Co-ordination through the two imino nitrogen atoms, not fully evident by comparison of the i.r. spectra of the complexes and of the free ligand, is confirmed by the downfield shift of the singlet due to the methyl protons of the CH_3–C=N– groups, which experience a deshielding of 0.56, 0.71, and 0.64 p.p.m. respectively, comparable with that (0.54 p.p.m.) observed in the case of $[Zn(H_2dapp)(H_2O)_2]Cl_2$.[22]

Co-ordination of the three pyridine nitrogens to the metal can be assumed by the general deshielding of the ring protons in the ^{1}H n.m.r. spectra of (**1**), (**2**), and (**3**) as compared with that of the free ligand, and by the shift of the i.r. breathing mode of the pyridine residues from 985 cm^{-1} in the free ligand to *ca.* 1 000 cm^{-1} in the solid complexes; an increase which is considered diagnostic of pyridine co-ordination to a metal or a proton.[23] Accordingly, the protonated $H_2dapp{\cdot}2HCl{\cdot}H_2O$ displays this band at 995 cm^{-1}. Other characteristic bands of co-ordinated pyridine residues, with minor shifts or splitting with respect to the free ligand, are present in the i.r. spectra of the complexes in the 1 615—1 440 cm^{-1} range, in accord with assignments for related compounds.[24,25] In particular the pyridine ring vibration which falls at *ca.* 1 600 cm^{-1} in the free ligand is shifted to higher frequency (*ca.* 1 613 cm^{-1}) in the charged complexes.

The more acidic character of the N–H groups induced by co-ordination results in lowering of the relative stretching vibration from 3 320 cm^{-1} in the free ligand to 3 260, 3 270, and 3 250 cm^{-1} for compounds (**1**), (**2**), and (**3**) respectively. This is confirmed in solution by the downfield shift of *ca.* 2 p.p.m. of the hydrazonic protons resonance for the three complexes. Co-ordinated water molecules in compounds (**2**) and (**3**) are responsible for the broad absorption centred at *ca.* 3 500 cm^{-1}, not present in the spectra of both the free ligand and compound (**1**).

The electronic spectra of aqueous solutions of (**1**), (**2**), and (**3**) in the 500—200 nm region show a very similar pattern in that there are two main absorption maxima which fall at the same wavelengths and have similar molar absorption coefficients.

All these results strongly suggest equatorial penta-aza-co-ordination of H_2dapp around the Hg^{II} ion similar to that found in the case of the charged Zn^{II} complex,[15] and a pbp geometry for the complexes achieved by axial co-ordination of two water molecules in (**2**), one water molecule and one chloride in (**3**), and through the $[HgCl_4]^{2-}$ anion in (**1**). The crystal structure of compound (**1**), which is fully discussed later, confirmed the physicochemical findings.

Finally, owing to the possibility of deprotonation of the di-azapropenic sequences =C=N–NH– present in H_2dapp,[12,15,26] compounds (**1**)—(**3**) when treated in water with a base at pH *ca.* 9 are quantitatively transformed into the neutral bis-deprotonated species [Hg(dapp)] (**4**), which can be extracted with chloroform, in which it is moderately soluble, and obtained as red microcrystals. Compound (**4**) is a non-conductor in $CHCl_3$ and MeOH solutions, and does not show any i.r. N–H stretching vibration in the 3 500—3 100 cm^{-1} range. In accord with this no resonance attributable to hydrazonic protons appears in the ^{1}H n.m.r. spectrum. Furthermore there is no indication of the presence of water molecules. It is worth noting that the i.r. spectrum of compound (**4**) is very similar to that of the neutral $[Zn_2(dapp)_2]$ for which an *X*-ray structural analysis revealed a quite uncommon dimeric structure with each Zn atom surrounded by four nitrogens from two different ligands and two nitrogens from the bridging pyridine groups in a distorted octahedral arrangement.[15] On this basis a similar structure for compound (**4**) seems probable.

Structure of $[Hg(H_2dapp)][HgCl_4]$.—An ORTEP view of the content of the asymmetric unit $[Hg(H_2dapp)][HgCl_4]$ is shown in the Figure. Bond distances and angles are reported in Tables 5 and 6.

The packing can be described either as consisting of infinite chains of alternating pentagonal planar $[Hg(H_2dapp)]^{2+}$ cations and tetrahedral $[HgCl_4]^{2-}$ anions running along *b*, or as infinite chains of μ-Cl-connected pentagonal bipyramidal (pbp) and tetrahedral Hg complexes. This second representation seems to be more realistic in view of the general pattern of Hg–Cl distances, as discussed later.

In the pbp co-ordination around the Hg(1) atom the five basal positions are occupied by five N atoms belonging to the polydentate ligand and the two apical positions by two Cl atoms; Cl(3) belonging to the tetrahedral anion of the same asymmetric unit and Cl(1') to the anion displaced at ($\frac{1}{2} - x, \frac{1}{2} + y, -\frac{1}{2} - z$). The five-co-ordinate ligand is not planar, the angles between the least-squares planes through the three

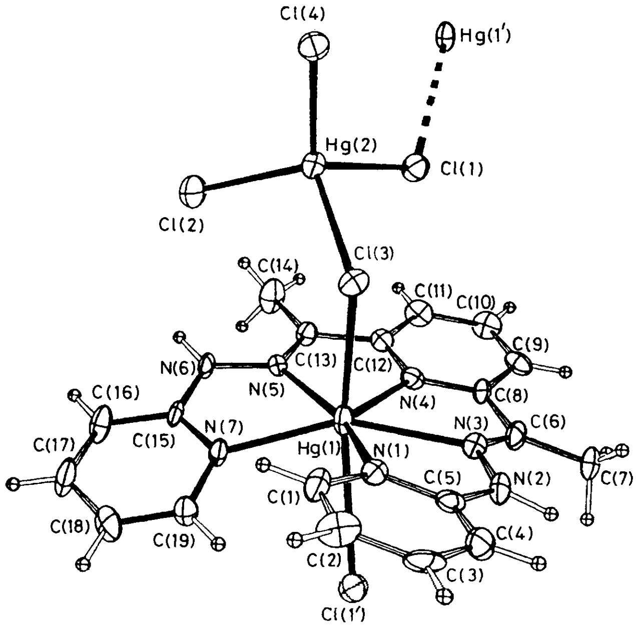


Figure. An ORTEP view of the content of the asymmetric unit $[Hg(H_2dapp)]^{2+}[HgCl_4]^{2-}$ showing the atom labelling scheme

Table 5. Interatomic distances (Å) with e.s.d.s in parentheses

Hg(1)–Cl(3)	2.786(3)	N(6)–C(15)	1.38(2)
Hg(1)–N(1)	2.333(9)	N(7)–C(15)	1.34(2)
Hg(1)–N(3)	2.405(8)	N(7)–C(19)	1.37(2)
Hg(1)–N(4)	2.40(1)	C(1)–C(2)	1.37(2)
Hg(1)–N(5)	2.379(9)	C(2)–C(3)	1.39(2)
Hg(1)–N(7)	2.381(9)	C(3)–C(4)	1.35(2)
Hg(2)–Cl(1)	2.454(4)	C(4)–C(5)	1.40(2)
Hg(2)–Cl(2)	2.412(4)	C(6)–C(7)	1.47(2)
Hg(2)–Cl(3)	2.624(3)	C(6)–C(8)	1.50(2)
Hg(2)–Cl(4)	2.500(3)	C(8)–C(9)	1.37(2)
N(1)–C(1)	1.37(2)	C(9)–C(10)	1.39(2)
N(1)–C(5)	1.31(1)	C(10)–C(11)	1.34(2)
N(2)–N(3)	1.36(1)	C(11)–C(12)	1.38(2)
N(2)–C(5)	1.37(1)	C(12)–C(13)	1.49(1)
N(3)–C(6)	1.28(2)	C(13)–C(14)	1.46(2)
N(4)–C(8)	1.32(1)	C(15)–C(16)	1.37(1)
N(4)–C(12)	1.35(1)	C(16)–C(17)	1.37(2)
N(5)–N(6)	1.35(1)	C(17)–C(18)	1.39(2)
N(5)–C(13)	1.29(2)	C(18)–C(19)	1.37(2)

pyridyl rings, A = N(1), C(1)—C(5), B = N(4), C(8)—C(12), C = N(7), C(15)—C(19), being A—B = 16.4(3), B–C = 14.4(4), and A–C = 30.3(4)°, and its general form is that of a flattened helix with a pitch of *ca.* 1.92 Å and approximate symmetry around a two-fold axis along the C(10)–N(4)–Hg(1) direction. The helical structure has also been observed in the Zn$^{\text{II}}$ and Co$^{\text{II}}$ complexes.[15] Such a distortion of the ligand is attributable to the need to avoid very close contacts between H atoms of the two facing pyridine rings, *i.e.* H(1) and H(19) in the present structure.

It can easily be calculated that if the ligand were planar with the present Hg–N average distance of 2.38(3) Å, the H(1) $\cdots$ H(19) contact distance would be some 1.34 Å; the helical distortion allows this distance to attain the value of 2.34 Å which is greater than the sum of the van der Waals radii of 2 Å for aromatic hydrogens.[27] That the geometry of the ligand is controlled by the mean M–N distance is shown by the uranyl complex, where this distance is 2.62(3) Å and H$_2$dapp assumes a twisted conformation with such a large distance between the two terminal pyridyls that the in-plane co-ordination of another NO$_3^-$ ligand becomes possible.[12]

With reference to the mean least-squares plane through the N(1), N(3), N(4), N(5), N(7) atoms, the N(4) atom lies almost exactly on it, whereas N(1), N(3), N(5), and N(7) are alternatively displaced above and below the plane by some 0.28 Å and the Hg(1) atom is approximately in the middle of this flattened tetrahedron, at a distance of 0.11 Å from the plane. Bond distances and angles in the ligand match almost perfectly those found in other structures reported above, the C–N and C=N lengths being consistent with single and double bond distances not perturbed by resonance.

The Hg(1)–Cl(3) and Hg(1)–Cl(1′) bonds make angles with the normal to the basal plane of 5.6(2) and 19.5(2)° respectively, the angle between the two bonds being 155.61(9)°. The packing mainly controlled by Hg–Cl–Hg interactions, but there are also the following intermolecular contacts: Cl(3) $\cdots$ H(N6′)–N(6′) $(-x, -y, -z-1)$ [Cl(3) $\cdots$ H(N6′) = 2.66; Cl(3) $\cdots$ N(6′) = 3.43(1) Å; Cl(3) $\cdots$ H(N6′)–N(6′) = 139°], Cl(3) $\cdots$ H(16′)–C(16′) $(-x, -y, -z-1)$ [Cl(3) $\cdots$ H(16′) = 2.82; Cl(3) $\cdots$ C(16′) = 3.62(1) Å, Cl(3) $\cdots$ H(16′)–C(16′) = 143°], and Cl(4) $\cdots$ H(N2′)–N(2′) $(x-\frac{1}{2}, -y-\frac{1}{2}, z-\frac{1}{2})$ [Cl(4) $\cdots$ H(N2′) = 2.62; Cl(4) $\cdots$ N(2′) = 3.54(1) Å; Cl(4) $\cdots$ H(N2′)–N(2′) = 163°], that can be regarded as weak hydrogen bonds.[28]

The concatenation of pbp and tetrahedral Hg polyhedra seems to be the most interesting feature of this structure.

Table 6. Bond angles (°) with e.s.d.s in parentheses

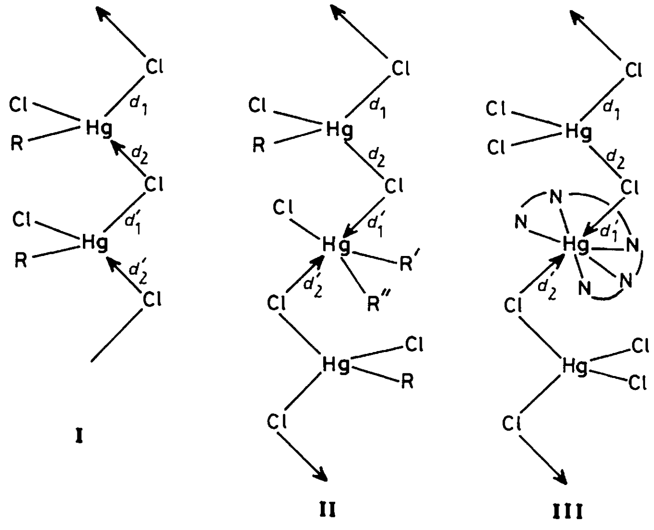
Cl(3)–Hg(1)–N(1)	105.2(2)	N(6)–N(5)–C(13)	121.1(9)
Cl(3)–Hg(1)–N(3)	91.8(2)	N(5)–N(6)–C(15)	119.4(9)
Cl(3)–Hg(1)–N(4)	94.4(2)	Hg(1)–N(7)–C(15)	116.8(8)
Cl(3)–Hg(1)–N(5)	93.4(2)	Hg(1)–N(7)–C(19)	123.4(7)
Cl(3)–Hg(1)–N(7)	80.5(3)	C(15)–N(7)–C(19)	119.3(1.0)
N(1)–Hg(1)–N(3)	66.6(3)	N(1)–C(1)–C(2)	120.6(1.1)
N(1)–Hg(1)–N(4)	128.5(3)	C(1)–C(2)–C(3)	120.0(1.2)
N(1)–Hg(1)–N(5)	153.6(3)	C(2)–C(3)–C(4)	118.9(1.1)
N(1)–Hg(1)–N(7)	96.0(3)	C(3)–C(4)–C(5)	119.4(1.2)
N(3)–Hg(1)–N(4)	65.7(3)	N(1)–C(5)–N(2)	119.4(9)
N(3)–Hg(1)–N(5)	132.4(3)	N(1)–C(5)–C(4)	122.0(1.1)
N(3)–Hg(1)–N(7)	158.6(3)	N(2)–C(5)–C(4)	118.6(1.0)
N(4)–Hg(1)–N(5)	66.7(3)	N(3)–C(6)–C(7)	124.5(1.0)
N(4)–Hg(1)–N(7)	134.4(3)	N(3)–C(6)–C(8)	113.7(1.0)
N(5)–Hg(1)–N(7)	68.4(3)	C(7)–C(6)–C(8)	121.8(1.1)
Cl(1)–Hg(2)–Cl(2)	124.4(2)	N(4)–C(8)–C(6)	116.4(1.0)
Cl(1)–Hg(2)–Cl(3)	96.0(1)	N(4)–C(8)–C(9)	120.1(1.0)
Cl(1)–Hg(2)–Cl(4)	110.4(1)	C(6)–C(8)–C(9)	123.5(1.1)
Cl(2)–Hg(2)–Cl(3)	104.8(1)	C(8)–C(9)–C(10)	119.5(1.2)
Cl(2)–Hg(2)–Cl(4)	109.2(2)	C(9)–C(10)–C(11)	119.7(1.2)
Cl(3)–Hg(2)–Cl(4)	110.5(1)	C(10)–C(11)–C(12)	119.4(1.1)
Hg(1)–Cl(3)–Hg(2)	120.0(1)	N(4)–C(12)–C(11)	120.2(1.0)
Hg(1)–N(1)–C(1)	121.7(7)	N(4)–C(12)–C(13)	116.0(1.0)
Hg(1)–N(1)–C(5)	119.2(8)	C(11)–C(12)–C(13)	123.6(1.0)
C(1)–N(1)–C(5)	119.0(9)	N(5)–C(13)–C(12)	114.6(1.0)
N(3)–N(2)–C(5)	115.3(9)	N(5)–C(13)–C(14)	124.5(1.2)
Hg(1)–N(3)–N(2)	116.3(7)	C(12)–C(13)–C(14)	120.8(1.1)
Hg(1)–N(3)–C(6)	122.8(7)	N(6)–C(15)–N(7)	118.2(1.1)
N(2)–N(3)–C(6)	120.5(9)	N(6)–C(15)–C(16)	119.3(1.1)
Hg(1)–N(4)–C(8)	119.7(7)	N(7)–C(15)–C(16)	122.5(1.2)
Hg(1)–N(4)–C(12)	119.0(7)	C(15)–C(16)–C(17)	119.4(1.2)
C(8)–N(4)–C(12)	121.0(1.0)	C(16)–C(17)–C(18)	118.3(1.2)
Hg(1)–N(5)–N(6)	115.3(6)	C(17)–C(18)–C(19)	120.9(1.2)
Hg(1)–N(5)–C(13)	122.1(7)	N(7)–C(19)–C(18)	119.5(1.1)

A preliminary investigation has been carried out with the aim of finding the typical values of Hg–Cl distances. A total of 96 structures (with *R* factor < 0.10) were retrieved from the Cambridge Crystallographic Database.[29] The histograms of the Hg–Cl distances for terminal single-connected Cl atoms show different distributions for [HgCl$_4$]$^{2-}$ anions (11 cases) and other Hg$^{\text{II}}$ complexes; in the first case the mean *d*(Hg–Cl) distance is 2.47(5) Å, which is systematically longer than in the second case, where it ranges from 2.27 to 2.49 Å for 90% of the structures, with an average value of 2.36(7) Å, which can be taken as the standard Hg–Cl bond distance.

Going back to the present structure, let $d_1 = d$[Hg(2)–Cl(1)], $d_2 = d$[Hg(2)–Cl(3)], $d'_1 = d$[Hg(1)–Cl(3)], $d'_2 = d$[Hg(1)–Cl(1′)], $q_1 = d_2 - d_1$, and $q_2 = d'_2 - d'_1$ (see Table 7) in the infinite chain –Cl(1)–Hg(2)–Cl(3)–Hg(1)–Cl(1′)–. The observed pattern of distances is $d_1 = 2.454$ and $d_2 = 2.624$ Å around the Hg(2) atom, and $d'_1 = 2.786$ and $d'_2 = 3.073$ Å around Hg(1), which are both intermediate between bonding (2.36 Å) and contact (3.25 Å) Hg–Cl distances. It can be interpreted as an electron donation of Cl(3) and Cl(1′) belonging to the two [HgCl$_4$]$^{2-}$ anions to the p_z (or d_{z^2}) orbitals of the sp^2d^2 hybridized Hg(1) atom. The stronger this donation (*i.e.* the shorter is d') the greater is the lengthening of the tetrahedral distance d, with the resultant chain of alternating long-short bonds characterized by differences between adjacent Hg–Cl bonds of $q_1 = 0.17$ and $q_2 = 0.28$ Å. A similar arrangement (with $q_1 = 0.18$ and $q_2 = 0.17$ Å) has been observed only in Hg$_2$Cl$_4$(PR$_3$)$_3$ (**10**) (R = PMe$_2$Et) in Table 7), consisting of [HgCl$_3$(PR$_3$)]$^-$ anions forming infinite chains by electron donation from two tetrahedral Cl atoms to two sp^2 hybridized [HgCl(PR$_3$)$_2$]$^+$ adjacent cations.

In general, infinite linear chains of Cl-bridged Hg atoms are

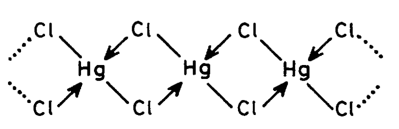
Table 7. Hg–Cl distances (Å) in Hg^{II} complexes forming infinite $-Cl^1 \overset{d_1}{-} Hg \overset{d_2}{-} Cl^2 \overset{d_1'}{-} Hg' \overset{d_2'}{-} Cl^{1'}-$ chains in crystals; $d_1 = d(Cl^1\text{–}Hg)$ or $d(Cl^2\text{–}Hg')$, $d_2 = d(Hg\text{–}Cl^2)$ or $d(Hg'\text{–}Cl^{1'})$; $q_1 = d_2 - d_1$, $q_2 = d_2' - d_1'$, with e.s.d.s in parentheses



	Complex	Structure	Hg co-ordination no.		Distance to bridging Cl				
			Hg	Hg′	d_1	d_2	q_1	q_2	Ref.
(**7**)	$[N(CH_3)_4][HgCl_3]$	I	4	4	2.421(8) 2.425(9)	2.901(8) 2.922(8)	0.48	0.50	*a*
(**8**)	$HgCl_2[P(CH_2CH_2CN)_3]$	I	4		2.714(7)	2.780(2)	0.07	(= q_1)	*b*
(**9**)	$HgCl_2(guo)^c$	I	4		2.659(7)	2.761(7)	0.10	(= q_1)	*d*
(**10**)	$Hg_2Cl_4(PMe_2Et)_3$	II	4	5	2.62(1) 3.07(1)	2.45(1) 3.25(1)	0.18	0.17	*e*
(**11**)	$HgCl_2(deimdt)^f$	I	4		2.58(2)	2.70(2)	0.12	(= q_1)	*g*
(**1**)	$[Hg(H_2dapp)][HgCl_4]$	III	4	7	2.454(4) 2.786(3)	2.624(3) 3.073(3)	0.17	0.28	This work

[a] M. Sikirica, D. Grdenic, and I. Vickvic, *Cryst. Struct. Commun.*, 1982, **11**, 1299. [b] N. A. Bell, M. Goldstein, L. A. March, and I. W. Nowell, *J. Chem. Soc., Dalton Trans.*, 1984, 1621. [c] guo = guanosine. [d] M. Authier-Martin, J. Hubert, R. Rivest, and A. L. Beauchamp, *Acta Crystallogr., Sect. B*, 1978, **34**, 273. [e] N. A. Bell, M. Goldstein, T. Jones, and I. W. Nowell, *Acta Crystallogr., Sect. B*, 1980, **36**, 708. [f] deimdt = *N,N′*-diethylimidazoline-2-thione. [g] M. Cannas, F. A. Devillanova, G. Marongiu, and G. Verani, *J. Inorg. Nucl. Chem.*, 1981, **43**, 2383.

uncommon and, of the 96 crystal structures of Hg complexes from the literature, it has only been observed in four other cases [(**7**), (**8**), (**9**), (**11**) in Table 7]. All refer to chemically identical Hg atoms of stoicheiometry $[HgCl_3]_n^-$ (**7**) or $[Hg_2Cl_2R]_n$ [(**8**), (**9**), (**11**) in Table 7], as the stoicheiometry $HgCl_2$ would have given rise to infinite ribbons of the type shown below.



Though the difference, *q*, between adjacent *d* or *d′* distances can be rather different in the six compounds of Table 7, these are joined together by the alternation of short and long bonds along the chain which can be rationalized in terms of consecutive three centre-four electron bonds of the type Cl–Hg–Cl and Hg–Cl–Hg where two Cl atoms compete for one Hg and two Hg for one Cl atom.

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References

1 M. G. B. Drew, A. Hamid bin Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 438.
2 D. H. Cook, D. E. Fenton, M. G. B. Drew, S. G. McFall, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 446.
3 G. J. Palenik and D. Wester, *J. Am. Chem. Soc.*, 1973, **95**, 6505.
4 D. Wester and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 1975, 74.
5 G. J. Palenik, D. W. Wester, U. Rychlewska, and R. C. Palenik, *Inorg. Chem.*, 1976, **15**, 1815.
6 G. J. Palenik and D. Wester, *J. Am. Chem. Soc.*, 1974, **96**, 7565.
7 C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1980, 1970.
8 C. Pelizzi, G. Pelizzi, G. Predieri, and S. Resola, *J. Chem. Soc., Dalton Trans.*, 1982, 1349.
9 C. Lorenzini, C. Pelizzi, G. Pelizzi, and G. Predieri, *J. Chem. Soc., Dalton Trans.*, 1983, 721.
10 C. Lorenzini, C. Pelizzi, G. Pelizzi, and G. Predieri, *J. Chem. Soc., Dalton Trans.*, 1983, 2155.
11 T. J. Giordano, G. J. Palenik, R. C. Palenik, and D. A. Sullivan, *Inorg. Chem.*, 1979, **18**, 2445.
12 G. Paolucci, G. Marangoni, G. Bandoli, and D. A. Clemente, *J. Chem. Soc., Dalton Trans.*, 1980, 459.
13 G. Paolucci, G. Marangoni, G. Bandoli, and D. A. Clemente, *J. Chem. Soc., Dalton Trans.*, 1980, 1304.
14 G. Marangoni and G. Paolucci, *J. Chem. Soc., Dalton Trans.*, 1981, 357.
15 D. Wester and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 755.
16 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' 2nd edn., Pergamon, Oxford, 1980.

17 J. D. Curry, M. A. Robinson, and D. H. Busch, *Inorg. Chem.*, 1967, **6**, 1570.

18 D. T. Cromer and J. T. Waber, 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2 A.

19 B. A. Frenz, 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. Van Koningsveld, and G. C. Bassi, Delft University Press, Delft, 1978, p. 44.

20 W. C. Hamilton, *Acta Crystallogr.*, 1959, **12**, 609.

21 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

22 S. Stelluto, Doctor in Chemistry Thesis, University of Venice, 1982–1983.

23 N. S. Gill, R. H. Nuttall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, 1961, **18**, 79.

24 C. F. Bell and D. R. Rose, *Inorg. Chem.*, 1968, **7**, 325.

25 A. Mangia, C. Pelizzi, and G. Pelizzi, *Acta Crystallogr., Sect. B*, 1974, **30**, 2146.

26 R. Lions, *Rev. Pure Appl. Chem.*, 1969, **19**, 177.

27 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

28 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.

29 F. H. Allen, S. Bellard, M. D. Brice, B. A. Cartwraight, A. Doubleday, H. Higgs, B. G. Hummelink-Peters, O. Kennard, W. D. S. Motherwell, J. R. Rogers, and D. G. Watson, *Acta Crystallogr., Sect. B*, 1979, **35**, 2331.

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