Synthesis and Characterization of Mercury(II) Complexes with 2,6-Diacetylpyridine Bis[*N*-methyl-*N*-(2′-pyridyl)hydrazone]. *X*-Ray Structure of Chloro{2,6-diacetylpyridine bis[*N*-methyl-*N*-(2′-pyridyl)hydrazone]}-mercury(II)–Hexachlorodimercurate(II)(2/1)†

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The quinquedentate ligand 2,6-diacetylpyridine bis[*N*-methyl-*N*-(2′-pyridyl)hydrazone], (dapmp) reacts in ethanol with $Hg(NO_3)_2 \cdot H_2O$ in the presence of perchlorate ions to give the seven-co-ordinate diaqua complex $[Hg(dapmp)(H_2O)_2][ClO_4]_2$ (**1**), while starting from $HgCl_2$ the species $[Hg(dapmp)Cl] \cdot 0.5[Hg_2Cl_6]$ (**2**) is obtained. The complexes have been characterized by a number of physicochemical measurements including the *X*-ray analysis of (**2**). Crystals of (**2**) are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 12.081(2), b = 10.295(2), c = 21.480(2) Å, β = 93.00(1)°, 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 0.037 for 3 350 observed reflections. The crystal consists of a packing of discrete units of $[Hg(dapmp)Cl]^+$ cations and $[Hg_2Cl_6]^{2-}$ anions in the ratio 2:1. The co-ordination in the cation is approximately pentagonal pyramidal; the five basal positions are occupied by five N atoms of the polydentate ligand with a remarkable helical distortion and the apical position by a Cl atom which makes an angle of 10.3(1)° with the normal to the mean plane passing through the co-ordinated N atoms. The Hg atom lies 0.51 Å over this plane in the Cl direction.

Quinquedentate ligands derived by the condensation of 2,6-diacetylpyridine with diamines, hydrazines, and hydrazides have been shown to be effective in imposing unusual co-ordination geometries on a range of metal ions. A number of seven-co-ordinate pentagonal-bipyramidal complexes have been prepared and characterized mainly by means of *X*-ray structural analysis.[1–11]

Recently we have studied the interaction between mercury(II) salts and 2,6-diacetylpyridine bis(2′-pyridylhydrazone) (H_2-dapp), obtaining a series of charged seven-co-ordinate pentagonal-bipyrimidal complexes in which H_2dapp behaves as a N_5 chelating ligand and the co-ordination is completed by water molecules and/or halogen atoms in the apical positions.[12] In particular, in the $[Hg(H_2dapp)][HgCl_4]$ complex the apical positions are occupied by two Cl atoms belonging to the tetrahedral anions. As an extension of this work we have now prepared the parent N_5 ligand 2,6-diacetylpyridine bis[*N*-methyl-*N*-(2′-pyridyl)hydrazone], (dapmp), and studied its reaction with mercury(II) salts. The results are reported here together with the crystal structure of the complex obtained by reaction of the ligand and $HgCl_2$ under the same experimental conditions as for $[Hg(H_2dapp)][HgCl_4]$.

Experimental

Reagents.—Reagent-grade mercury(II) chloride, mercury(II) nitrate, lithium perchlorate (Alfa products), 2,6-diacetylpyridine, 2-bromopyridine, and *N*-methylhydrazine (Fluka products) were used without further purification. All the solvents used were purified as reported.[13] The solvent for ^1H n.m.r. spectra, $(CD_3)_2SO$, was an Aldrich product with a minimum isotopic purity of 99.9%.

N-*Methyl*-N-(2′-*Pyridyl*)*hydrazine*.—This was prepared as described in the literature[14] by refluxing 2-bromopyridine in *N*-methylhydrazine. Its purity was checked by comparing its ^1H n.m.r. spectrum with that reported.

2,6-*Diacetylpyridine Bis*[N-*methyl*-N-(2′-*pyridyl*)*hydrazone*] (dapmp).—A solution of *N*-methyl-*N*-(2′-pyridyl)hydrazine (2.46 g, 20 mmol) in ethanol–glacial acetic acid (15:1, v/v; 30 cm^3) was added to a stirred solution of 2,6-diacetylpyridine (1.63 g, 10 mmol) in ethanol (50 cm^3). The resulting solution was refluxed with stirring for 4 h and, after cooling, the yellow crystalline product obtained was filtered off, washed with ethanol and diethyl ether, and dried under reduced pressure (2.0 g, 54%). M.p. 122 °C (Found: C, 67.4; H, 6.25; N, 26.3. $C_{21}H_{23}N_7$ requires C, 67.6; H, 6.15; N, 26.3%). U.v.–visible band maxima (freshly prepared solution in MeOH): 306 (sh) and 352 nm. ^1H N.m.r. $[(CD_3)_2SO–SiMe_4]$: δ 2.57 (s, 6 H, $CH_3C{=}N$), 3.45 (s, 6 H=NCH_3), and 6.79–8.29 (m, 11 H, pyridine rings). Selected i.r. bands (4000–250 cm^{-1}, KBr pellets): 3 060w, 3 020w, 2 980mw, 2 860w, 1 600vs, 1 560vs, 1 470vs, 1 455s, 1 435vs, 1 400s, 985vs, and 775vs cm^{-1}.

2,6-*Diacetylpyridine Bis*[N-*methyl*-N-(2′-*pyridyl*)*hydrazone*] *Mercury*(II) *Perchlorate*, $[Hg(dapmp)(H_2O)_2][ClO_4]_2$ (**1**).—To a warm solution of dapmp (0.373 g, 1 mmol) in absolute ethanol (20 cm^3) saturated with $LiClO_4$ a solution was added of $Hg(NO_3)_2 \cdot H_2O$ (0.342 g, 1 mmol) in ethanol (5 cm^3) at room temperature with stirring. The yellow product which precipitated rapidly was filtered off, washed with ethanol and diethyl

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Crystal data for $[Hg(dapmp)Cl]^+ \cdot 0.5[Hg_2Cl_6]^{2-}$

Formula	$C_{21}H_{23}Hg_2Cl_4N_7$
M	916.44
Crystal size/mm	0.14 × 0.21 × 0.33
Space group	$P2_1/c$
a/Å	12.081(2)
b/Å	10.295(2)
c/Å	21.480(2)
α/°	90
β/°	93.00(1)
γ/°	90
U/Å^3	2667.9(7)
$F(000)$	1 704
Z	4
D_c/g cm^{-3}	2.29
D_m/g cm^{-3}	2.20
μ(Mo-K_α)/cm^{-1}	119.4
Radiation	Mo-K_α
Monochromator	Graphite
$\theta_{min.}$ $\theta_{max.}$/°	2, 27
Standard reflections	3
T/°C	22
Independent reflections	5 805
Reflections with $I > 3\sigma(I)$	3 350
Variables (last cycle)	307
Final $R = \Sigma\|\Delta F_o\|\Sigma\|F_o\|$	0.037
Final $R' = (\Sigma w\|\Delta F_o\|/\Sigma w\|F_o\|^2)^{\frac{1}{2}}$	0.043
Final shift/max. error	0.01
Largest peak in the final difference map (outside Hg co-ordinate sphere)/e Å^{-3}	0.64
Weighting, w	$4F_o^2/[\sigma^2(F_o^2) + 0.04(F_o^2)^2]$
Error in an observation of unit weight	1.32

ether, and dried under reduced pressure (0.78 g, 96%). M.p. > 220 °C (Found: C, 31.05; H, 2.80; Cl, 8.60, N, 12.1. $C_{21}H_{27}Cl_2HgN_7O_{10}$ requires C, 31.2, H, 3.35; Cl, 8.75; N, 12.1%). Conductance of a 1 × 10^{-3} mol dm^{-3} solution in MeCN at 25 °C: 281 ohm^{-1} cm^2 mol^{-1}. U.v.–visible band maxima: 288, 370 (freshly prepared solution in water); 400, 297, and 243 nm (in the solid state). ^{1}H N.m.r. [$(CD_3)_2SO$–$SiMe_4$]: δ 2.81 (s, 6 H, CH_3C=N), 3.32 (s, 4 H, water), 3.73 (s, 6 H, =NCH_3), and 7.11–8.52 (m, 11 H, py rings). Selected i.r. bands (4 000—250 cm^{-1}, KBr pellets): 3 090w, 1 603s, 1 595s, 1 566m, 1 480s, 1 433m, 1 383m, 1 300w, 1 100br, vs, 1 000m, 778s, 741m, 664w, 633m, 623s, and 410w cm^{-1}.

Chloro{*2,6-diacetylpyridine bis*[N-*methyl*-N-*(2′-pyridyl)-hydrazone*]}*mercury*(II) *Hexachlorodimercurate*(II)(2/1)[Hg(dapmp)Cl]·0.5[Hg_2Cl_6] (**2**).—To a warm solution of dapmp (0.373 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 the rapid formation and precipitation of a yellow product which, after 1 h of stirring, was filtered off, washed with ethanol and diethyl ether, and dried under reduced pressure. The crude product was crystallized from a concentrated dimethylformamide–methanol solution (30:70, v/v) left overnight at −10 °C (0.86 g, 94%). M.p. > 220 °C (Found: C, 27.3; H, 2.50; N, 10.8. $C_{21}H_{23}Cl_4Hg_2N_7$ requires C, 27.5, H, 2.50; N, 10.7%). U.v–visible band maxima: 288, 370 (freshly prepared solution in water); 455, 375, 310, and 245 nm (in the solid state). Selected i.r. bands (4 000—150 cm^{-1}, KBr and polyethylene pellets): 3 080w, 1 595s, 1 563s, 1 549m, 1 473s, 1 435s, 1 178s, 1 016m, 1 000m, 770s, 741m, 660w, 480w, 410w, 292w, 284w, 275w, 262w, 244w, 237w, 225w, and 192w cm^{-1}.

[*2,6-Diacetylpyridine bis(2′-pyridyl)hydrazone*]*mercury*(II) *Tetrachloromercurate*(II), [Hg(H_2dapp)][$HgCl_4$] (**3**).—This was prepared as reported in the literature[12] and its purity checked by elemental analysis and comparison of its i.r. spectrum with that reported. U.v.–visible band maxima (in the solid): 410, 375, 303, and 255 nm. I.r. bands (300–150 cm^{-1}, polyethylene pellets): 252 and 213 cm^{-1}.

Physical Measurements.—I.r. spectra were recorded on Perkin-Elmer 683 (4 000–250 cm^{-1}, KBr pellets) and on 180 (300—150 cm^{-1}, polyethylene pellets) spectrometers, u.v.–visible spectra of solutions and of the solids (500—200 nm) on Varian-Cary 219 and Perkin-Elmer Lambda 5 spectrophotometers with 1-cm quartz cells at 25 °C and as Nujol mulls between quartz discs, respectively, and ^{1}H n.m.r. spectra 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.—Intensity data were collected on a Enraf–Nonius CAD4 diffractometer with monochromated Mo-K_α radiation and ω—2θ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 25 centred reflections in the range 9 ⩽ θ ⩽ 12°. Crystal data are reported in Table 1. Intensities were corrected for Lorentz, polarization, and absorption (minimum transmission factor: 0.59). Scattering factors and anomalous dispersion parameters were taken from ref. 15. The positions of the two Hg atoms were located from Patterson synthesis and all other non-H atoms were found in the subsequent Fourier maps. Hydrogen atoms were assigned calculated positions with C–H bond distances of 0.95 Å and fixed isotropic B values of 5.0 Å^2. 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. Weights for the last cycle were applied according to the scheme given in Table 1. All calculations used the SDP system of programs.[16] Final positional parameters are given in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises the atom co-ordinates and thermal parameters.

Results and Discussion

Treatment of stoicheiometric (1:1) amounts of the quinquedentate N_5 ligand dapmp and $Hg(NO_3)_2 \cdot H_2O$ in the presence of an excess of perchlorate ions, in ethanol, gives the ionic yellow product [Hg(dapmp)(H_2O)$_2$][ClO_4]$_2$ (**1**) in high yield. The molar conductance of a 1 × 10^{-3} mol dm^{-3} solution of (**1**) in MeCN (281 Ω^{-1} cm^2 mol^{-1}) is typical of a 1:2 electrolyte.[17] Accordingly, its solid-state i.r. spectrum shows a strong broad band centred at *ca.* 1 085 cm^{-1} accompanied by a sharp unsplit band at 620 cm^{-1}, both of them due to free perchlorate ion.

Co-ordination through the two imino-nitrogen atoms, not fully evident by comparison of the i.r. spectra of the complex and of the free ligand, is confirmed by the downfield shift of the singlet due to the methyl protons of the CH_3C=N groups, which experience a deshielding of δ 0.24.

Co-ordination of the three pyridine nitrogens to the metal can be analogously assumed by the general deshielding of the ring protons in the ^{1}H n.m.r. spectrum of (**1**) 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} for the free ligand to about 1000 cm^{-1} for the solid complex, an increase which is considered diagnostic of pyridine co-ordination to a metal or a proton.[18]

Co-ordinated water molecules are reasonably responsible for the broad absorption centred at about 3 500 cm^{-1}.

Table 2. Positional parameters (× 10^4) of complex (**2**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hg(1)	106.8(3)	991.3(4)	1 872.4(1)	C(5)	2 507(7)	2 283(9)	1 853(4)
Hg(2)	4 579.9(4)	924.6(5)	4 256.0(3)	C(6)	3 219(8)	1 247(12)	913(6)
Cl(1)	918(3)	−1 220(3)	1 725(1)	C(7)	863(8)	1 742(9)	475(4)
Cl(2)	3 602(3)	226(4)	5 244(2)	C(8)	1 502(9)	1 903(13)	−108(5)
Cl(3)	3 964(5)	−343(4)	3 390(2)	C(9)	−368(7)	1 683(8)	420(4)
Cl(4)	4 928(3)	3 181(3)	4 362(1)	C(10)	−989(9)	1 869(11)	−134(4)
N(1)	1 642(6)	2 269(7)	2 210(3)	C(11)	−2 106(9)	1 931(13)	−143(5)
N(2)	2 339(6)	1 934(8)	1 232(3)	C(12)	−2 604(8)	1 752(11)	378(5)
N(3)	1 250(5)	1 781(7)	1 040(3)	C(13)	−1 998(7)	1 525(9)	941(4)
N(4)	−898(6)	1 499(7)	945(3)	C(14)	−2 529(7)	1 321(8)	1 531(4)
N(5)	−1 866(6)	1 273(7)	2 032(3)	C(15)	−3 752(8)	1 128(11)	1 506(5)
N(6)	−2 216(6)	1 084(8)	2 619(3)	C(16)	−3 157(9)	1 891(13)	2 826(5)
N(7)	−390(6)	431(8)	2 872(3)	C(17)	−1 399(9)	663(9)	3 055(4)
C(1)	1 803(8)	2 637(9)	2 803(4)	C(18)	−1 692(10)	436(11)	3 653(4)
C(2)	2 815(9)	3 006(10)	3 064(4)	C(19)	−886(11)	12(11)	408(4)
C(3)	3 700(8)	3 042(11)	2 672(6)	C(20)	164(11)	−204(10)	3 901(4)
C(4)	3 543(7)	2 699(11)	2 071(5)	C(21)	368(10)	13(10)	3 292(4)

Table 3. Bond distances (Å) with e.s.d.s. in parentheses

Hg(1)–Cl(1)	2.505(3)	N(6)–C(17)	1.394(12)
Hg(1)–N(1)	2.357(7)	N(7)–C(17)	1.322(13)
Hg(1)–N(3)	2.454(6)	N(7)–C(21)	1.323(12)
Hg(1)–N(4)	2.337(6)	C(1)–C(2)	1.372(14)
Hg(1)–N(5)	2.443(7)	C(2)–C(3)	1.396(15)
Hg(1)–N(7)	2.332(7)	C(3)–C(4)	1.342(17)
Hg(2)–Cl(2)	2.584(4)	C(4)–C(5)	1.381(12)
Hg(2)–Cl(3)	2.360(4)	C(7)–C(8)	1.514(14)
Hg(2)–Cl(4)	2.370(3)	C(7)–C(9)	1.487(13)
N(1)–C(1)	1.333(11)	C(9)–C(10)	1.386(12)
N(1)–C(5)	1.328(11)	C(10)–C(11)	1.350(15)
N(2)–N(3)	1.367(9)	C(11)–C(12)	1.311(15)
N(2)–C(5)	1.386(11)	C(12)–C(13)	1.400(13)
N(2)–C(6)	1.475(14)	C(13)–C(14)	1.465(12)
N(3)–C(7)	1.278(11)	C(14)–C(15)	1.489(13)
N(4)–C(9)	1.339(11)	C(17)–C(18)	1.370(13)
N(4)–C(13)	1.329(11)	C(18)–C(19)	1.374(15)
N(5)–N(6)	1.365(10)	C(19)–C(20)	1.363(18)
N(5)–C(14)	1.308(11)	C(20)–C(21)	1.362(13)
N(6)–C(16)	1.494(14)		

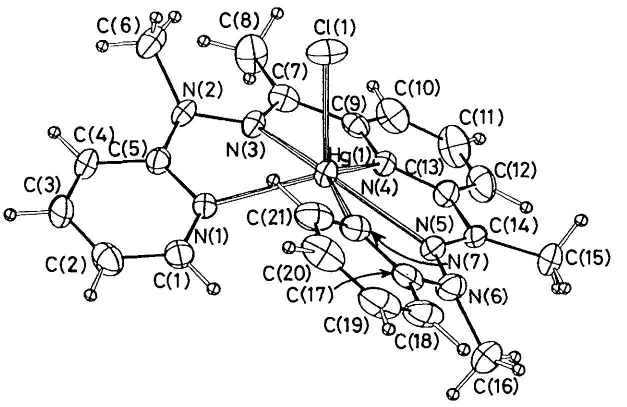

Figure 1. An ORTEP view of the $[Hg(dapmp)Cl]^+$ cation with the atom-labelling scheme. The thermal ellipsoids are drawn at the 30% probability level

All these results strongly suggest equatorial N_5 co-ordination of dapmp around the mercury ion similar to that found in the case of the charged complexes of Zn^{II},[19] Co^{II},[19] and Hg^{II}[12] with H_2dapp, and a pentagonal bipyrimidal geometry for the complex achieved by axial co-ordination of two water molecules.

When stoicheiometric (1:2) amounts of dapmp and $HgCl_2$ are allowed to react in absolute ethanol a slightly soluble species (**2**) is obtained in an almost quantitative yield, which analyses with a mol ratio, dapmp: Hg:Cl, of 1:2:4. The same molar ratio had been previously found for the ionic complex $[Hg(H_2dapp)][HgCl_4]$ (**3**) obtained from $HgCl_2$ and the strictly related quinquedentate ligand 2,6-diacetylpyridine bis(2′-pyridylhydrazone) (H_2dapp), under the same experimental conditions;[12] its structure has been shown to consist of infinite chains of chloride-bridged pentagonal bipyramidal and tetrahedral mercury complexes, with the five basal positions of the cationic part occupied by five N atoms belonging to the polydentate ligand and the two apical positions by two Cl atoms belonging to the tetrahedral anion $HgCl_4^{2-}$.[12] However, the i.r. spectrum of complex (**2**) in the region of Hg–Cl vibrations (400—150 cm^{-1}) is quite different from that of compound (**3**). Furthermore, while compound (**3**) is stable in a number of non-aqueous solvents, *e.g.* dimethyl sulphoxide (dmso), MeCN, and dimethyl formamide (dmf), compound (**2**) rapidly decomposes on releasing the ligand, as shown from a comparison of its ^1H n.m.r. spectrum in deuteriated dmso with that of the ligand in the same solvent. Extensive investigations in solution thus being prevented, the nature of (**2**) was ascertained by determining its crystal structure.

Structure of $[Hg(dapmp)Cl]^+ \cdot 0.5[Hg_2Cl_6]^{2-}$.—Bond distances and angles are reported in Tables 3 and 4 respectively. The crystal consists of discrete units of $[Hg(dapmp)Cl]^+$ cations and $[Hg_2Cl_6]^{2-}$ anions in the ratio 2:1 packed together by means of van der Waals and dipolar interactions. There are a few Cl $\cdots$ H contact distances slightly shorter than the sum of the van der Waals radii, see Table 5. Separate ORTEP[20] views of the two ions are shown in Figures 1 and 2.

The $[Hg_2Cl_6]^{2-}$ anion lies on a crystallographic centre of symmetry at ($\frac{1}{2}$, 0, $\frac{1}{2}$) and displays typical bond distances, with the terminal Hg–Cl bond lengths in the range 2.36–2.37 Å, and the bridging ones longer by some 0.20–0.30 Å. The observed bond distances are in perfect agreement with those found by other authors.[21–23]

In the $[Hg(dapmp)Cl]^+$ cation the co-ordination of the central mercury atom is approximately pentagonal pyramidal with the Cl atom at the apical position. The Hg(1)–Cl(1) distances of 2.505(3) Å is somewhat longer than those of the terminal Hg-Cl bonds in the anion, which could be connected with the increased co-ordination number. The five basal co-ordination positions are occupied by five N atoms of the dapmp

Table 4. Bond angles (°) with e.s.d.s in parentheses

Cl(1)–Hg(1)–N(1)	103.8(2)	Cl(3)–Hg(2)–Cl(4)	131.7(1)	Hg(1)–N(7)–C(21)	120.4(6)	C(11)–C(12)–C(13)	121.2(9)
Cl(1)–Hg(1)–N(3)	88.3(2)	Hg(1)–N(1)–C(1)	121.7(6)	C(17)–N(7)–C(21)	118.2(7)	N(4)–C(13)–C(12)	119.1(8)
Cl(1)–Hg(1)–N(4)	106.5(2)	Hg(1)–N(1)–C(5)	117.3(6)	N(1)–C(1)–O(2)	123.5(8)	N(4)–C(13)–C(14)	118.3(7)
Cl(1)–Hg(1)–N(5)	121.1(2)	C(1)–N(1)–C(5)	117.9(8)	C(1)–C(2)–C(3)	117.1(9)	C(12)–C(13)–C(14)	122.6(8)
Cl(1)–Hg(1)–N(7)	90.7(2)	N(3)–N(2)–C(5)	114.2(7)	C(2)–C(3)–C(4)	119.9(9)	N(5)–C(14)–C(13)	116.1(8)
N(1)–Hg(1)–N(3)	64.9(2)	N(3)–N(2)–C(6)	120.7(8)	C(3)–C(4)–C(5)	119.2(9)	N(5)–C(14)–C(15)	126.0(8)
N(1)–Hg(1)–N(4)	120.2(2)	C(5)–N(2)–C(6)	119.9(7)	N(1)–C(5)–N(2)	118.2(7)	C(13)–C(14)–C(15)	126.0(8)
N(1)–Hg(1)–N(5)	130.4(2)	Hg(1)–N(3)–N(2)	112.8(4)	N(1)–C(5)–C(4)	122.3(8)	N(6)–C(17)–N(7)	119.2(8)
N(1)–Hg(1)–N(7)	95.2(2)	Hg(1)–N(3)–C(7)	119.3(6)	N(2)–C(5)–C(4)	119.4(8)	N(6)–C(17)–C(18)	118.3(9)
N(3)–Hg(1)–N(4)	65.9(2)	N(2)–N(3)–C(7)	126.0(7)	N(3)–C(7)–C(8)	127.2(8)	N(7)–C(17)–C(18)	122.4(9)
N(3)–Hg(1)–N(5)	130.8(2)	Hg(1)–N(4)–C(9)	120.0(6)	N(3)–C(7)–C(9)	113.0(7)	C(17)–C(18)–C(19)	118.1(10)
N(3)–Hg(1)–N(7)	159.1(2)	Hg(1)–N(4)–C(13)	119.0(5)	C(8)–C(7)–C(9)	119.3(8)	Hg(1)–N(5)–C(14)	116.7(6)
N(4)–Hg(1)–N(5)	68.0(2)	C(9)–N(4)–C(13)	120.9(7)	N(4)–C(9)–C(7)	117.3(8)	N(6)–N(5)–C(14)	124.0(7)
N(4)–Hg(1)–N(7)	133.9(2)	Hg(1)–N(5)–N(6)	117.7(5)	N(4)–C(9)–C(10)	118.8(8)	N(5)–N(6)–C(16)	118.2(7)
N(5)–Hg(1)–N(7)	66.4(2)	N(5)–N(6)–C(17)	115.0(7)	C(7)–C(9)–C(10)	123.8(8)	C(18)–C(19)–C(20)	120.1(8)
Cl(2)–Hg(2)–Cl(3)	110.8(2)	C(16)–N(6)–C(17)	119.7(7)	C(9)–C(10)–C(11)	121.0(8)	C(19)–C(20)–C(21)	117.5(11)
Cl(2)–Hg(2)–Cl(4)	106.3(1)	Hg(1)–N(7)–C(17)	121.0(6)	C(10)–C(11)–C(12)	119.0(10)	N(7)–C(21)–C(20)	123.7(11)

Table 5. Intermolecular contacts (Å) less than the accepted sum of van der Waals radii of 2.95 Å (A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441)

		Distance	Translation vector
Cl(1) ··· H(10)	I	2.701	0,0,0
Cl(1) ··· H(1)	II	2.834	0,−1,0
Cl(1) ··· H(163)	II	2.677	0.−1.0
Cl(2) ··· H(18)	I	2.708	0,0,1
Cl(4) ··· H(153)	II	2.854	0,0,0
Cl(4) ··· H(12)	III	2.886	1,0,0

I $-x, -y, -z$; II, $x, \frac{1}{2} + y, \frac{1}{2} - z$; III, $x, \frac{1}{2} - y, \frac{1}{2} + z$.

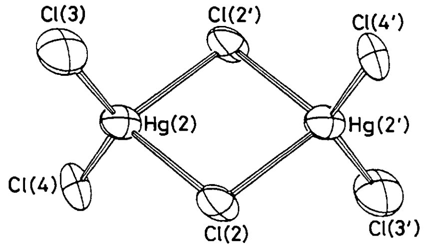

Figure 2. An ORTEP view of the $[Hg_2Cl_6]^{2-}$ anion

Table 6. Selected geometrical parameters (Å)

Compound	Co-ordination number	M–N/Å		$\langle\Delta^2\rangle^{\frac{1}{2}a}$	$\lvert\Delta\rvert_M{}^b$	Ref.
		pyridine	imine			
$[Hg(dapmp)Cl]^+\cdot 0.5[Hg_2Cl_6]^{2-}$	5 + 1	2.357(7) 2.337(6) 2.332(7)	2.454(6) 2.443(7)	0.398	0.507	This work
$[Hg(H_2dapp)]^{2+}\cdot[HgCl_4]^{2-}$	5 + 2	2.333(9) 2.400(10) 2.381(9)	2.405(8) 2.379(9)	0.265	0.110	12
$[Zn(H_2dapp)(H_2O)_2]^{2+}2Cl^-$	5 + 2	2.251(4) 2.305(4) 2.288(4)	2.314(4) 2.286(4)	0.263	0.000	19
$[Co(H_2dapp)(H_2O)_2]^{2+}2Cl^-$	5 + 2	2.207(4) 2.268(4) 2.258(4)	2.248(8) 2.242(4)	0.283	0.003	19

[a] Root mean square displacement of the five N atoms co-ordinated in the basal plane. [b] Displacement of the central metal atom from the least-squares plane through the co-ordinated nitrogens.

ligand. The Hg–N bond distances can be grouped in two different sets, the three Hg–N(pyridine) being 2.357(7), 2.332(7), and 2.337(6) Å, whereas the Hg–N (imine) are 2.454(6) and 2.443(7) Å.

The five-co-ordinated ligand is not planar. First, the whole dapmp molecule has an helical distortion (Figure 1) in which the H atom connected to C(21) is on an upper level compared with the one connected to C(1). Such a distortion has the obvious function of avoiding the clashing of the two hydrogens (present H ··· H distance 2.88 Å). A similar helical distortion has been observed also in the seven-co-ordinate complexes of Zn^{II},[19] Co^{II},[19] and Hg^{II}[12] with 2,6-diacetylpyridine bis(2′-pyridylhydrazone) (H_2dapp), but not in that of $UO_2{}^{2+}$,[24] where the U–N distances are so long (average 2.62 Å) that a further nitrate group can be accommodated in the basal plane.

Also the first co-ordination sphere is heavily deformed; with reference to the mean least-squares plane through N(1), N(3), N(4), N(5), and N(7), N(4) lies on it (Δ = 0.04 Å) and N(1), N(3), N(5), and N(7) undergo a tetrahedral distortion being displaced by −0.45, 0.31, −0.37, and 0.59 Å, respectively. The Hg atom lies 0.51 Å over the plane, in the Cl direction. The Hg–Cl bond makes an angle of 10.3(1)° with the normal to the same plane.

The only structures strictly comparable to the present one are those of $[Hg(H_2dapp)]^{2+}\cdot[HgCl_4]^{2-}$ [12] and of the complexes of Zn^{II} and Co^{II} of formula $[M(H_2dapp)(H_2O)_2]^{2+}\cdot 2Cl^-$ [19] (Table 6). In the last cases the co-ordination is pentagonal bipyramidal with the two water molecules bonded in the apical positions. The mercury(II) complex is in between pentagonal pyrimidal and pentagonal bipyrimidal co-ordination with two

Cl atoms belonging to $[HgCl_4]^{2-}$ anions co-ordinated in apical positions at very long [3.073(3) Å] or intermediate [2.786(3) Å] distances. In all these compounds the first co-ordination polyhedron is remarkably more flattened and less helically distorted than in the present case, in agreement with the expected differences between pentagonal pyrimidal and pentagonal bipyrimidal co-ordinations. In a similar way the central metal atom lies almost exactly on the mean plane of the five co-ordinated nitrogens, whereas in the present structure it is remarkably displaced from it (Table 6).

It may be of interest that only in the present case M–N distances are arranged in two different sets according to whether they concern pyridine or imine nitrogens. This fact could be well due to not clarified constraints in the geometry of this rather complicated ligand; however, an alternative explanation can be given in terms of hard and soft acid and base concepts.[25] The present $ClHg^+$ cation is quite similar to the $MeHg^+$ cation which is considered a reference soft acid and is known to give preferentially strong bonds with easily polarizable soft bases. As the extended π-conjugated system makes pyridine of higher polarizability than the imino group, this fact could rationalize the observed trend in Hg–N bond distances in spite of the not very different strengths of the two bases.

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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. Chessa, G. Marangoni, B. Pitteri, V. Bertolasi, V. Ferretti, and G. Gilli, *J. Chem. Soc., Dalton Trans.*, 1988, 1479.
13 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' 2nd edn., Pergamon, Oxford, 1980.
14 M. A. Baldo, G. Chessa, G. Marangoni, and B. Pitteri, *Synthesis*, 1987, 720.
15 D. T. Cromer and J. T. Waber, 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2 A.
16 B. A. Frenz, 'Computing in Crystallography,' eds. H. Schenk, R. Olthof-Hazekamp, H. VanKoningsveld, and G. C. Bassi, Delft University Press, Delft, 1978, p. 44.
17 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
18 N. S. Gill, R. H. Nutall, D. E. Scaife, and D. W. A. Sharp, *J. Inorg. Nucl. Chem.*, 1961, **18**, 79.
19 D. Wester and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 755.
20 C. K. Johnson, ORTEP, Report ORNL-5138 (Third Revision), Oak Ridge National Laboratory, Oak Ridge Tennessee, 1976.
21 P. L. Goggin, P. King, M. McEwan, G. E. Taylor, P. Woodward, and M. Sandstrom, *J. Chem. Soc., Dalton Trans.*, 1982, 875.
22 T. J. Kistenmacher, M. Rossi, C. C. Chiang, R. P. Van Duyne, and A. R. Siedle, *Inorg. Chem.*, 1980, **19**, 3604.
23 R. P. Shibaeva and L. P. Rozemberg, *Kristallografiya*, 1981, **26**, 1224.
24 G. Paolucci, G. Marangoni, G. Bandoli, and D. A. Clemente, *J. Chem. Soc., Dalton Trans.*, 1980, 459.
25 R. G. Pearson, *J. Am. Chem. Soc.*, 1963, **85**, 3533.

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