Short Hydrogen Bonds: Diadducts of Substituted Pyridine *N*-Oxides: Synthesis, Spectroscopic Studies, and *X*-Ray Structure†

M. Sakhawat Hussain* **and Saud A. Aziz Al-Hamoud**
Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia

Hydrogen-bonded diadducts of substituted pyridine *N*-oxides, stabilized by $[AuCl_4]^-$, have been prepared and studied by spectroscopic techniques. The presence of a broad absorption around 800 cm^{-1} in the i.r. spectra, and the existence of bands characteristic of the ligands and $[AuCl_4]^-$, in the u.v. spectra, indicate a short $O \cdots H \cdots O$ hydrogen bond. An *X*-ray diffraction study of one of the diadducts, $[H(3Me\text{-}pyo)_2][AuCl_4]$(3Me-pyo = 3-methylpyridine *N*-oxide), revealed an $O \cdots O$ distance of 2.406(9) Å. The complex crystallizes in the triclinic space group $P\bar{1}$, with a = 6.857(4), b = 8.011(1), c = 8.797(2) Å, α = 105.05(2), β = 66.89(3), γ = 89.39(2)°, and Z = 1. The structure was refined to R = 0.063 using 2 339 reflections collected on a CAD4 diffractometer. On the basis of $Au \cdots O$ contacts, an uncommon distorted octahedral environment for Au^{III} may be assumed in the solid state.

The donor properties of pyridine *N*-oxide (pyo) and its substituted derivatives have been the subject of several recent e.s.r.,[1,2] *X*-ray diffraction,[3,4] and synthetic and spectral studies.[5] These heterocyclic *N*-oxides primarily form two types of compounds: (*a*) complexes with the *N*-oxides acting as a bridging or monodentate ligand, co-ordinating to the metal through the N–O oxygen atom[5] and, (*b*) diadducts of the *N*-oxide, analogous to the $[H_5O_2]^+$ ion,[6] which form as a short hydrogen-bonded hydrogen(1+) ion stabilized by a large anion such as $[AuCl_4]^-$ or $[ClO_4]^-$. Several compounds of type (*a*) exhibit Jahn–Teller effects and are interesting systems for spectroscopic and e.s.r. studies. Compounds of type (*b*) exhibit short intramolecular hydrogen bonds and their crystallographic studies are directed to an understanding of the potential functions associated with short hydrogen bonds. Furthermore, both symmetry-free[3] and symmetry-restricted[4,7] dimeric cations in compounds of type (*b*) possess free rotation along the $O \cdots O$ axis and are interesting molecular systems for conformational analysis, leading to theoretical predictions of the most stable orientation of the two heterocycles in solution or the solid state. Gold complexes of the *N*-oxides are significant in their own right too, since they serve as model systems for understanding the chemistry of gold drugs used in chrysotherapy[8–11] and for elucidating the structures of analytical reagents used in the extractive-photometric determination of gold.[12]

As a part of our continuing research programme investigating short hydrogen bonds, we have synthesized several novel $[AuCl_4]^-$ stabilized hydrogen(1+) diadducts of the substituted pyridine *N*-oxides 2-, 3-, and 4-methylpyridine *N*-oxide (2Me-pyo, 3Me-pyo, and 4Me-pyo respectively), 4-nitropyridine *N*-oxide ($4NO_2$-pyo), 2,6-dimethylpyridine *N*-oxide, ($2,6Me_2$-pyo), and *N*-oxopyridine-3-carboxylic acid (opyca). The present paper reports the u.v., ^1H n.m.r., and i.r. spectroscopic studies of these complexes. Since more than one structure could be proposed on the basis of the spectroscopic data, the structure of bis(3-methylpyridine *N*-oxide)hydrogen(1+) tetrachloroaurate(III) was determined by single-crystal *X*-ray diffraction.

Experimental

Chemicals.—All chemicals and deuteriated solvents were obtained from the Fluka Chemical Company and were used without further purification.

General Method of Preparation and Crystal Growth.—The ligands were dissolved in the minimum amount of methanol and an aqueous slurry of chloroauric acid added, keeping a gold(III):ligand ratio of 1:2. In most cases a yellow crystalline product immediately formed, which was filtered off and redissolved in an excess of methanol to obtain a clear yellow solution. This solution was allowed to evaporate under nitrogen in a dry box to give yellow crystals which were separated from the solution by decantation. If no residue was formed upon the initial mixing of $HAuCl_4$ and the ligand solution, the resulting solution was filtered and allowed to evaporate slowly under nitrogen until crystals of the product appeared which were harvested. Prolonged exposure of the solution to the atmosphere resulted in the formation of fine particles of metallic gold, which could be prevented by the addition of a few drops of dilute HCl. The compounds which crystallized immediately on mixing could also be prepared by using a HCl solution of $NaAuCl_4$ instead of $HAuCl_4$, and washing the residue twice with a small volume of methanol–water solution to remove any NaCl. The yield from this procedure however was very low. Elemental analyses of the products were performed on a Carlo Erba (Italy) Elemental Analyser. The following compounds with satisfactory elemental analyses were synthesized using the above procedure: $[H(3Me\text{-}pyo)_2][AuCl_4]$, $[H(4Me\text{-}pyo)_2][AuCl_4]$ $[H(4NO_2\text{-}pyo)_2][AuCl_4]$, $[H(opyca)_2][AuCl_4]$, and $[H(2,6Me_2\text{-}pyo)_2][AuCl_4]$. The corresponding complex of 2Me-pyo was reported[3] earlier.

Spectroscopic Measurements.—Infrared spectra of all the compounds were obtained with a Perkin-Elmer IR 180 i.r. spectrophotometer using KBr discs. Proton n.m.r. spectra were obtained at 200 MHz on a Varian XL-200 spectrometer operating in the pulsed Fourier-transform mode. Proton chemical shifts were measured using internal t-butyl alcohol and are reported relative to the methyl proton resonance of sodium 4,4-dimethyl-4-silapentanesulphonate (dss). The methyl resonance of t-butyl alcohol was at 1.23 p.p.m. relative to dss. All ^1H n.m.r. measurements were carried out using $[^2H_6]$dimethyl sulphoxide (dmso) as solvent. Ultraviolet

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† *Supplementary data available* (No. SUP 56147, 6 pp.): thermal parameters, i.r. spectroscopic data of the ligand and the diadducts of substituted pyridine *N*-oxides. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

spectra were obtained in methanol on a Beckman Acta MVII spectrophotometer.

X-Ray Data Collection and Structure Solution.—A well formed almost equidimensional (0.14 × 0.15 × 0.14 mm) crystal of $[H(3Me\text{-}pyo)_2][AuCl_4]$ was mounted on a glass fibre in an arbitrary orientation. Lattice constants were obtained by the least-squares refinement of 25 centred reflections having $20.0 < 2\theta < 28.0°$, located by the SEARCH program of CAD4 software, and measured at an ambient temperature of 23 ± 3 °C.

Crystal data.—$C_{12}H_{15}AuCl_4N_2O_2$, $M = 558$, triclinic, space group $P\bar{1}$, $a = 6.857(4)$, $b = 8.011(1)$, $c = 8.797(2)$ Å, $\alpha = 105.05(2)$, $\beta = 66.89(3)$, $\gamma = 89.39(2)°$, $U = 425.7$ Å^3, $F(000) = 264$, $D_m = 2.17$ g cm^{-3}, $Z = 1$, $D_c = 2.18$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,73$ Å, μ (Mo-K_α) = 89 cm^{-1}.

No cell of higher symmetry was found by Delauney reduction with TRACERII.[13] The density was measured by floating the crystals in a solution containing 1,3-dibromopropane and bromoform. The solution density was determined with a pycnometer. The intensity data were collected on a CAD-4 diffractometer using graphite-monochromated Mo-K_α radiation and the ZIGZAG method in the ω—2θ scan mode, with scan range of $(1.50 + 0.35\tan\theta)°$ centred about the calculated Mo-K_α peak positions. Background counts were measured for half of the total scan time by extending the scan range 25% on either side of the scan limits. A total of 2 568 (h, $\pm k$, $\pm l$) reflections for $1.0 \leqslant 2\theta \leqslant 30.0°$ including standard and extinct reflections was measured. Three standard reflections monitored every 9 000 s of X-ray exposure time gave no indication of crystal deterioration. The crystal orientation was checked each 75 reflections. The intensities were corrected for background, Lorentz and polarization effects. Equivalent and duplicate reflections were averaged ($R_{int.} = 0.008$) to obtain 2 479 unique reflections, 2 339 of which with $I > 3\sigma(I)$ were used in the analysis. Since the crystal was an almost perfect sphere, absorption corrections were not considered necessary. However, at the final stages of this work, absorption effects were checked by carrying out spherical absorption corrections using the TEXRAY230 Stand-Alone[14] system with SDP82 software but no significant improvement in the residual factors was noticed.

Since the intensity distribution statistics did not clearly support a centrosymmetric space group, the initial solution and refinement of the structure was done both in centric and acentric space groups. All results reported here were obtained using the SHELX 76 package.[15] The co-ordinates of the Au and the two Cl atoms were obtained from a three-dimensional Patterson synthesis. A Fourier map, phased on the Au atom at special position 0,0,0 and the Cl atoms at isotropically refined positions, revealed all the non-hydrogen atoms. Several cycles of anisotropic least-squares refinement followed by a difference-Fourier synthesis revealed the positions of most of the hydrogen atoms, which were in good agreement with the calculated positions. The H-bonded hydrogen, H(01), was fixed at the symmetry position 0.5,0,0. Final least-squares refinement of 126 variables, including positional and anisotropic thermal parameters for the non-hydrogen atoms and positional co-ordinates for the hydrogen atoms, with Au and H(01) at special positions, led to the final value of $R = 0.063$ and $R' = 0.066$. The largest shift in any parameter in the final cycle of refinement was 0.181 times its estimated standard deviation. A final difference-Fourier map was virtually featureless with a small (*ca.* 1.2 e Å^{-3}) residual electron density in the vicinity of the gold atom. Refinement of the structure in the acentric space group failed to converge indicating that our choice of centric space group was correct. The whole structure solution was repeated, with the same final results, on TEXRAY230 using SDP82 software which became available in our laboratory at the final stages of work on this compound.

Table 1. Atomic co-ordinates* for $[H(3Me\text{-}pyo)_2][AuCl_4]$

Atom	X/a	Y/b	Z/c
Au	0.000 0	0.000 0	0.000 0
Cl(1)	0.222 2(7)	−0.053 5(5)	−1.283 6(4)
Cl(2)	−0.025 8(7)	0.292 1(4)	−0.972 3(5)
O(1)	0.349 3(14)	0.005 0(11)	−0.868 3(12)
N(2)	0.320 6(14)	0.160 3(11)	−0.747 9(12)
C(3)	0.371 7(15)	0.301 5(13)	−0.799 9(13)
C(4)	0.340 8(15)	0.463 2(13)	−0.677 3(13)
C(5)	0.248 7(15)	0.467 2(14)	−0.504 4(13)
C(6)	0.197 2(15)	0.317 5(14)	−0.455 1(13)
C(7)	0.234 4(15)	0.160 5(14)	−0.582 2(13)
C(8)	0.400 5(17)	0.620 5(14)	−0.740 2(15)
H(O1)	0.500 0	0.000 0	0.000 0
H(C3)	0.435 2(15)	0.292 4(13)	−0.936 8(13)
H(C5)	0.215 7(15)	0.589 2(14)	−0.407 8(13)
H(C6)	0.129 0(15)	0.321 2(14)	−0.319 6(13)
H(C7)	0.197 4(15)	0.041 4(14)	−0.547 0(13)
H(1C8)	0.366 8(17)	0.733 7(14)	−0.633 3(15)
H(2C8)	0.307 7(17)	0.639 6(14)	−0.811 3(15)
H(3C8)	0.566 5(17)	0.600 4(14)	−0.826 3(15)

* Values given in parentheses in this and in all subsequent tables are the estimated standard deviations (e.s.d.s) in the last digit(s) of the number.

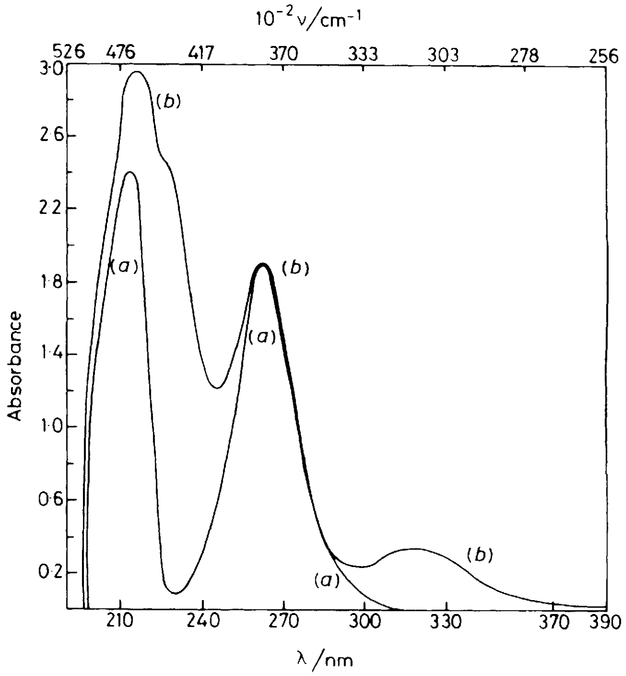

Figure 1. The electronic absorption spectra of: (*a*) 3Me-pyo and (*b*) $[H(3Me\text{-}pyo)_2][AuCl_4]$

The full-matrix least-squares refinement was based on F_o, and the function minimized was $\Sigma\, w[(|F_o| - |F_c|)^2]$. Agreement factors are defined as $R = \Sigma|F_o| - |F_c|/\Sigma F_o$ and $R = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2]^{\frac{1}{2}}$. All calculations and ORTEP drawings were done at the Data Processing Centre of the University of Petroleum and Minerals using an IBM 3033 computer. Atomic scattering factors for the non-hydrogen atoms were taken from Cromer and Mann[16] and for the H atoms from Stewart *et al.*[17] Anomalous dispersion corrections

Table 2. Electronic absorption spectral data for heterocyclic *N*-oxides and their gold(III) complexes*

Compound	λ/nm	ν/cm^{-1}	$10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1}
2Me-pyo	210	47 620	1.48
	259	38 610	1.10
[H(2Me-pyo)$_2$][AuCl$_4$]	213	46 950	17.5
	(229)	43 700	10.1
	257	38 910	7.98
	321	31 150	1.29
3Me-pyo	213	46 950	1.40
	262	38 170	1.10
[H(3Me-pyo)$_2$][AuCl$_4$]	220	45 460	4.71
	(227)	44 050	3.43
	262	38 170	2.71
	320	31 250	4.86
4Me-pyo	207	48 310	1.29
	264	37 880	1.02
[H(4Me-pyo)$_2$][AuCl$_4$]	218	45 870	3.57
	(227)	44 050	2.36
	264	37 880	1.92
	320	31 250	3.21
4NO$_2$-pyo	216	46 300	0.697
	232	43 100	0.723
[H(4NO$_2$-pyo)$_2$][AuCl$_4$]	217	46 080	5.26
	226	44 250	5.30
	324	30 864	3.51
opyca	224	44 640	5.62
	266	37 590	1.03
[H(opyca)$_2$][AuCl$_4$]	224	44 640	5.62
	(230)	43 480	4.75
	266	37 590	2.21
	318	31 450	0.752
2,6Me$_2$-pyo	215	46 500	0.534
	220	45 450	0.842
	256	39 050	0.104
[H(2,6Me$_2$-pyo)$_2$][AuCl$_4$]	222	45 050	4.82
	(234)	42 740	3.77
	255	39 215	3.11
	320	31 25	0.641

* Values for the shoulders are given in parentheses.

were taken from Cromer and Liberman.[18] The final atomic co-ordinates for the heavy atoms and calculated positions for the hydrogen atoms are listed in Table 1.

Results and Discussion

Spectroscopic Evidence of the Dimeric Cationic Species.—The u.v. spectrum of [H(3Me-pyo)$_2$][AuCl$_4$] is shown in Figure 1 and the electronic absorption spectral data for the heterocyclic *N*-oxides and their metal complexes in the range 190—750 nm are given in Table 2. All the ligands have two relatively intense bands, with molar absorptivities of *ca.* 10^4 or greater, around 215 and 260 nm in the u.v. region. Both bands for the free ligands tail towards the visible region without any peak appearing in this region. In the corresponding gold(III) complexes the higher-energy band is further intensified, with the appearance of a shoulder around 225 nm between the two ligand bands, and a broad absorption of medium intensity around 315 nm, indicative of the [AuCl$_4$]$^-$ anion.[19] A methanolic solution of HAuCl$_4$ has a medium intensity absorption centred at 320 nm and a very weak broad band with $\lambda_{max.}$ at *ca.* 410 nm. The u.v. spectra of the complexes clearly indicate the existence of heterocyclic *N*-oxides and [AuCl$_4$]$^-$ anions in all the complexes. Such spectra were, in fact, used for identification of the complex species in solution.

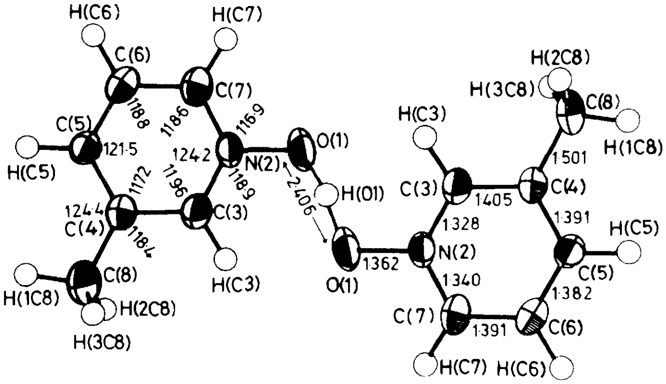

Figure 2. The atom-labelling and bonded distances and angles in the dimeric cation [H(3Me-pyo)$_2$]$^+$. The e.s.d.s for the C–N, N–O, C–C, and O · · · O bonds are 0.004, 0.004, 0.009, and 0.009 Å, respectively. The e.s.d.s for the ONC, NCC, and CCC angles are 0.8, 0.9, and 0.9° respectively.

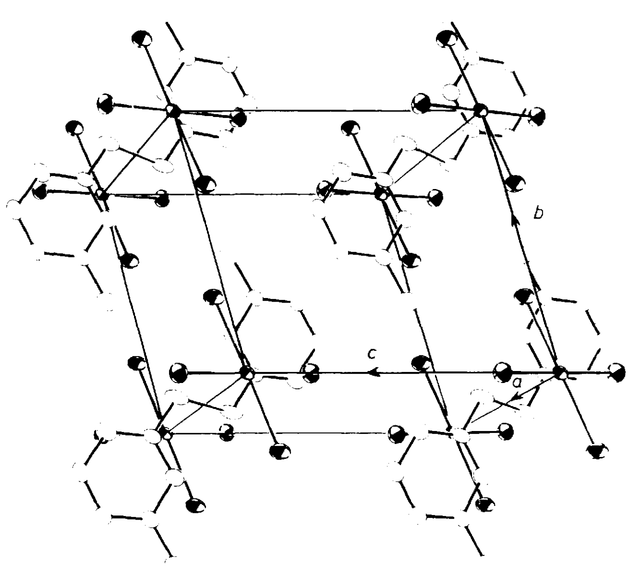

Figure 3. Molecular packing of [H(3Me-pyo)$_2$][AuCl$_4$] in the unit cell viewed along the *a* axis

Infrared absorption frequencies of the free ligands and of all the complexes are listed in SUP 56147. The i.r. spectra of all the complexes have a broad region of absorption extending through the range 600—1 000 cm^{-1}. This wide background absorption, which is overlaid with a number of maxima corresponding to the free heterocyclic *N*-oxides, was also observed in the gold(III) complexes of pyo and 2Me-pyo.[3,4] No absorptions in this region are present in pure chloroauric acid. The existence of a strong and broad background absorption and the absence of any peaks around 3 200 cm^{-1} associated with an O–H stretch are indicative of a short hydrogen bond[3,20,21] in these diadducts irrespective of the nature and position of substituents on the pyo ring. The broad absorption bands in the O–H stretching region present in the free *N*-oxides disappear in the spectra of the complexes. Similarly, the strong N–O stretching bands, around 1 250 cm^{-1} in the free bases do not appear in the spectra of the diadducts. The spectral features mentioned above are similar to those exhibited by substances with symmetrical hydrogen bonds.[21b] The ν(N–O) frequency is shifted by *ca.* 40 cm^{-1} to lower frequency in metal complexes[5b] having monodentate pyo with oxygen–metal co-ordination.

Proton n.m.r. spectra in [$^2H_6$]dmso revealed all the expected resonances with correct integrated intensities except for the H-

Table 3. Comparison of bond distances (Å) in some related gold(III) complexes

Compound	N–O	O···O	Au···O	Ref.
$[H(pyo)_2][AuCl_4]$	1.362(8)	2.41(1)	3.105(7)	4
$[H(2,6Me_2\text{-}pyo)_2][ClO_4]$	1.34(1)	2.345(13)		21
$[H(2Me\text{-}pyo)_2][AuCl_4]$	1.345(8)	2.393(6)	3.240(3)	3
$[H(4Me\text{-}pyo)_2][AuCl_4]$	1.341(9)	2.442(9)	3.200(5)	*
$[H(3Me\text{-}pyo)_2][AuCl_4]$	1.362(4)	2.406(9)	3.040(3)	This work

* M. S. Hussain, unpublished work.

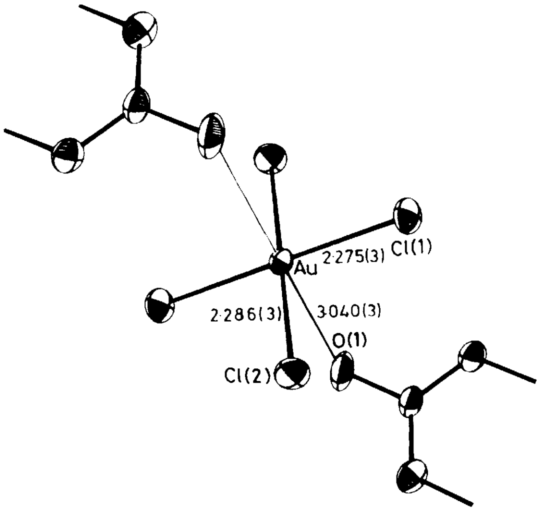

Figure 4. The environment of gold(III) in the crystal lattice depicting six-co-ordination around the metal atom

bonded proton resonance which could not be detected even in freshly prepared, highly concentrated solutions of the complexes in $[^2H_6]$dmso or in nitromethane. The failure to observe an n.m.r. signal might be due to the smallest trace of water in the solvents which would effectively eliminate the signal by exchange. This is inconsistent with the solid-state i.r. spectra and the crystal structure, which clearly revealed a short hydrogen bond. It is also contrary to the n.m.r. spectra of the chelated complexes of α-amine dioximes in which the resonance for the intramolecular short hydrogen-bonded proton was easily observed around 18.5 p.p.m. in $[^2H_6]$dmso.[22,23]

On the basis of the above analytical and spectroscopic results, gold(III) complexes of heterocyclic *N*-oxides could be assumed to possess one of the following two structures: (*a*) four-co-ordinate gold(III) as the $[AuCl_4]^-$ anion and a hydrogen-bridged dimeric cation as in the complex $[H(3Me\text{-}pyo)_2][AuCl_4]$, or (*b*) a very unlikely six-co-ordinate complex, *e.g.* $H[AuCl_4(3Me\text{-}pyo)_2]$, with gold(III) bonded to four Cl^- anions and two *N*-oxide molecules. The second possibility may exist in solution if the absence of the n.m.r. resonance for the bridged proton is considered real and not a result of solvent or interionic exchange at room temperature.[24] The solid-state structures[3,4,7] of dimeric cations involving heterocyclic *N*-oxides are consistent with four-co-ordinate gold(III) with very weak interactions, if any, of the oxygen atoms of the *N*-oxides resulting in an uncommon distorted octahedral environment for gold(III) complexes (see later).

Molecular Packing and X-Ray Structure of $[H(3Me\text{-}pyo)_2][AuCl_4]$.—The atom-labelling scheme corresponding to Table 1, together with distances and angles for $[H(3Me\text{-}pyo)_2][AuCl_4]$ are given in Figure 2. The molecular packing of the $[H(3Me\text{-}pyo)_2]^+$ cations and $[AuCl_4]^-$ anions in the unit cell is shown in Figure 3. The crystallographic asymmetric unit constitutes half a gold atom, two chlorine atoms, and one 3-methylpyridine *N*-oxide molecule. The unit-cell packing in this compound differs from that of the analogous diadduct of 2Me-pyo, $[H(2Me\text{-}pyo)_2][AuCl_4]$,[3] but resembles that of other similar compounds of pyridine *N*-oxide and substituted pyridine *N*-oxides such as $[H(pyo)_2][AuCl_4]$,[4] $[H(2Me\text{-}pyo)_2]Cl\cdot3H_2O$,[20] $[H(2,6Me_2\text{-}pyo)_2][ClO_4]$,[21] and $[H(dma)_2][AuCl_4]$ (dma = dimethylacetamide),[7] all of which have a symmetry-restricted short hydrogen bond. The square planar $[AuCl_4]^-$ units are stacked above one another but the distance between the adjacent metal atoms is quite large forbidding any metal–metal interactions, characteristic of superconducting metallic complexes[25] such as $[Ni(dmg)_2]$, $[Pd(dmg)_2]$ (dmg = dimethylglyoximate), *etc.* The immediate metal environment may be considered square planar with chlorine atoms at an average distance of 2.280(3) Å and a Cl(1)–Au–Cl(2) angle of 89.8(1)°. The oxygen atoms of N–O lie 3.040(3) Å from Au, completing a distorted octahedron (Table 3 and Figure 4) around the metal atom. Gold(III) will have an uncommon six-co-ordinate geometry if Au ··· O(1) interactions are considered real and not a manifestation of the packing forces in the unit cell. The Au ··· O contacts in this compound and other similar contacts of 3.105(7) and 3.240(3) Å in $[H(pyo)_2][AuCl_4]$ and $[H(2Me\text{-}pyo)_2][AuCl_4]$[3,4] are close to 3.20 Å, the sum of the van der Waals radii[26] of the interacting atoms. Heterocyclic *N*-oxides have high dipole moments. A combination of dipole–dipole interactions and the above van der Waals interionic contacts should be the most dominant factors in the packing of the crystal lattice in which gold(III) is in a distorted octahedral environment. The two planar 3Me-pyo moieties in the dimeric cation $[H(3Me\text{-}pyo)_2]^+$ are related by an inversion symmetry with a symmetry-restricted hydrogen bond. No atom in 3Me-pyo is more than 0.014(10) Å out of the least-squares plane defined by all the non-hydrogen atoms in the molecule. The unit-cell packing allows enough space for solvent molecules although no solvent of crystallization was present. There are no significant hydrogen-bonding interactions between adjacent $[AuCl_4]^-$ and $[H(3Me\text{-}pyo)_2]^+$ ions.

Comparison of Bond Distances and Angles with Related Structures.—Some relevant distances and non-bonded contacts in similar compounds are listed in Table 3. The geometry of 3Me-pyo is normal, with internal bond angles varying from 124.2 to 117.2°. The N–O bond length of 1.362(4) Å agrees well with the corresponding distance of 1.358(2) Å in the hydrogen-bonded diadduct, $[H(2Me\text{-}pyo)_2]Cl\cdot3H_2O$[20] or 1.352(9) Å in $[Zn(4Me\text{-}pyo)_6][ClO_4]_2$[2] which has a monodentate *N*-oxide. The position of the electron-donating $-CH_3$ group on the pyo ring does not appear to make any significant difference to the N–O or O ··· O separation. The average lengths for CH_3–C, C–C, and C–N bonds, and angles involving these bonds, are in agreement with the corresponding values in other similar complexes.

The inversion symmetry-related hydrogen bond in the dimeric cation, $[H(3Me\text{-}pyo)_2]^+$, is 'very short' with an O ··· O separation of 2.406(9) Å, close to the shortest O ··· O distance of 2.29(2) Å reported[27] in the $[H_3O]^+$ ion which also has an inversion symmetry. The intramolecular hydrogen-bonding distance is within the range, 2.310—2.626 Å, considered[28] for short hydrogen bonds. Since the exact location of the hydrogen atoms in the presence of heavy atoms such as Au and Cl is not possible from the *X*-ray data, the O–H bond length and other distances involving hydrogen atoms are not specified.

Acknowledgments

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