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Short Hydrogen Bond:
Spectral Studies and X-ray Structure of Bis(alpha-picoline N-oxide)-hydronium Tetrachloroaurate(III)

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Spectral and the X-ray diffraction studies of the title compound [H(2-picNO)$_2$][AuCl$_4$] (2-picNO = alpha-picoline N-oxide) were done to investigate the short hydrogen bond in the dimeric cation [H(2-picNO)$_2$]$^+$. The compound exhibits several narrow transmission bands overlaid on a broad continuous absorption characteristic of a short hydrogen bond; it crystallizes with four molecules in a monoclinic unit cell of space group P2$_1$/n with lattice parameters a = *22.376(9),* b = *9.874(6),* c = *7.957(5) Å and β = 94.98(6)°. The structure was solved using 2623 data points collected on a CAD4 to the final value for R(F$_o$) = 0.039. The structure consists of discrete [AuCl$_4$]$^-$ and [H(2-picNO)$_2$]$^+$ ions. Contrary to all known examples, the dimeric cation in this compound has a short hydrogen bond having no symmetry constraints making the present structural analysis unique in this series of compounds. The O---O distance is 2.393(6) Å and the dihedral angle between the two planar 2-picNO moieties in the cation is 44.1°. The [AuCl$_4$]$^-$ anion is planar with an average Au–Cl distance of 2.268(2) Å. The infrared spectrum and the structure of the compound is compared with the related structures.*

Introduction

Fundamental to the chemistry of the heterocyclic N-oxides is the fact that dipolar N-oxide group, $=\overset{+}{N}-\overset{-}{O}-$, is both an electron donor and an electron acceptor by resonance effects, besides being an inductive electron acceptor. In addition to acting as a monodentate [1, 2], bidentate [2] and bridging groups [3], pyridine N-oxide (pyNO) [4] and its substituted derivatives form dimeric cation analogous to the well-known [H$_5$O$_2$]$^+$ ion [5, 6]. The majority of these cations [7, 8] are centrosymmetric *i.e.*, they have Speakman's 'Type A' structures in which the hydrogen atom in the cation is located at a point of crystal symmetry. The shortest O---O bond (2.29(2) Å) reported [9] in [H$_3$O$_2$]$^-$ ion also as $\bar{1}$ site symmetry. The crystallographic restrictions on the bridge hydrogen often obscure the understanding of the potential well in which the hydrogen sits and doubts have been raised [10, 11] as to the centricity of the hydrogen bond in these cases. The symmetry-free open short hydrogen bonds with unambiguously-defined space groups are not very common [7, 12, 13], except in chelate structures [14–17] where compression of the bond may be operative. Two basic salts of α-picoline N-oxide (2-picNO), [H(2-picNO)$_2$]Br and [H(2-picNO)$_2$]Cl·3H$_2$O have been reported [18, 19]. A definitive structure analysis of the first could not be completed because of the crystal being damaged by exposure to X-rays [9], whereas the structure of the second, also called Dunlop's salt, was explained on the basis of a disorder across the twofold axis of the crystal. Nevertheless, in both compounds the cation is bisected by a symmetry element and both have type A structures. The i.r. spectrum of the title compound shows typical spectral manifestation [20] of a short O---O distance. The present structure was done as a part of our programme investigating cations of the type [BHB]$^+$ (B = Lewis base) stabilized by AuX$_4^-$ anions [X = Cl$^-$ and CN$^-$], for understanding the nature of short hydrogen bond in these dimeric species. The compound reported here is also significant in its own right because of the potential importance of similar gold complexes in chrysotherapy (gold treatment) [21] and in the extractive-photometric determination of gold [22].

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Experimental

Preparation and Crystal Growth

The compound was prepared by mixing a methanolic solution of 0.54 g (4.95 mmol) of 2-Picoline N-oxide (Fluka AG) and 0.400 g of $HAUCl_4$ (Fluka AG) dissolved in a minimum amount of water. A yellow colored precipitate was immediately formed. The ppt was dissolved slowly in methanol till the total solution volume was about 30 ml. Another 0.050 g of 2-Picoline N-oxide was added to keep the ligand in excess. The solution was allowed to evaporate under a constant flow of nitrogen in a dry box. A prolonged exposure of the concentrated solution of the complex to air resulted in partial reduction of gold(III) to metallic gold.

Fine, yellow-colored crystals started dropping out when the solution volume was about 15 ml (after about 24 hours). Further reduction in volume to about 10 ml gave the first very well-formed crop of crystals which was filtered out and dried under nitrogen. Elemental analysis of the crystalline product was: Calculated for $C_{12}H_{15}N_2O_2AuCl_4$: C, 25.83; N, 5.02 and H, 2.71. Found: C, 25.58; N, 4.96 and H, 2.77.

Spectroscopic Measurements

Infrared spectra of the compound were obtained on a Perkin Elmer 180 spectrophotometer using KBr pellets. The ^{1}H-NMR spectra of freshly prepared solutions in acetonitrile, nitromethane, methanol and d_6-dimethyl sulfoxide were taken on a Varian T60 using TMS as an external standard. The elemental analysis was carried out on a Carlo Erba (Italy) Elemental Analyzer.

X-Ray Data Collection and Structure Solution

A well-formed, almost equidimensional light yellow crystal (0.16 X 0.15 X 0.16) mm^3 was mounted on a glass fiber in an arbitrary orientation. Lattice constants were obtained by the least-squares refinement of the diffraction geometry of 25 centered reflections having $13 < \theta < 19°$ measured at an ambient temperature of 23 ± 3 °C. $C_{12}H_{15}$-$AuCl_4N_2O_2$, $M = 558$, Monoclinic, $a = 22.376(9)$, $b = 9.874(6)$, $c = 7.957(5)$ Å, $\beta = 94.98(6)°$, $U = 1751.4$ Å^3, F(000) = 1056, $D_m = 2.13$, $Z = 4$, $D_c = 2.12$ g cm^{-3}, Mo-K$_\alpha$ radiation $\lambda = 0.71073$ Å, μ(Mo-k$_\alpha$) = 86.4 cm^{-1}. Space group $P2_1/n$ based on systematic absences for h0l with (h + l) odd and 0k0 with k odd. The density of the compound was measured by floating the crystals in a solution containing 1,3-dibromopropane and bromoform. The density of the solution was determined with a pycnometer. No cell of higher symmetry was found with the lattice transformation program TRACER-II.

The X-ray intensity data were collected on an Enraf-Nonius CAD-4 diffractometer controlled by a PDP8/A computer using graphite-monochromated Mo-K$_\alpha$ radiation and the ZIGZAG method in $\omega-2\theta$ scan mode with a θ scan range of $(1.10 + 0.35 \tan \theta)°$ centered about the calculated Mo-K$_\alpha$ peak positions. The scan rate varied from 1.68 to 5.03° min^{-1}. 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 6320 h, ±k, ±l reflections (twice the amount required) including the standards for $2 < 2\theta < 50°$ were measured. Three standards, monitored every 8000 S of X-ray exposure time, gave no indications of crystal deterioration. The crystal orientation was checked each 50 reflections. The intensities were corrected for background, Lorentz and polarization effects and equivalent and duplicate reflections were averaged ($R_{int} = 0.008$) to obtain 3078 unique reflections, 2623 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. This was later confirmed by excellent convergence in the least squares refinement.

The coordinates for Au and four Cl atoms were obtained using the automatic centrosymmetric direct routine in the SHELX76 [23] program package. A difference Fourier map phased on the refined position of Au and Cl atoms led to the location of all non-hydrogen atoms. Several cycles of isotropic refinement followed by four cycles of anisotropic refinement (R = 4.48%) revealed the positions of most of the hydrogen atoms. These hydrogen positions were refined isotropically while holding all non-hydrogen atoms at fixed positions. Final refinement of 208 variables led to the residual factors R = 0.039 and R_w = 0.036. The value of w was based on counting statistics and was equal to $(1.8502/\sigma^2(F_o) + 0.001|F_o|^2)$. The largest shift in any parameter at the final stage was 0.1 times its estimated standard estimation. The highest peak in the final difference Fourier synthesis was 0.8 e/Å^3.

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 $R_w[=(\Sigma w|F_o| - F_c||^2/\Sigma wF_o{}^2)^{1/2}]$. All calculations were carried out on the University of Petroleum and Minerals IBM 3033 computer using SHELX76. Atomic scattering factors for non-hydrogen atoms were taken from Cromer and Mann [24], for H atoms from Stewart, Davidson and Simpson [25]. Anomalous dispersion corrections were taken from Cromer and Liberman [26]. The atomic coordinates and thermal parameters (B_{eq}) for all atoms are given in Tables I and II. The anisotropic thermal parameters for non-hydrogen atoms and a list of the observed and calculated structure factors are available as supplementary material.

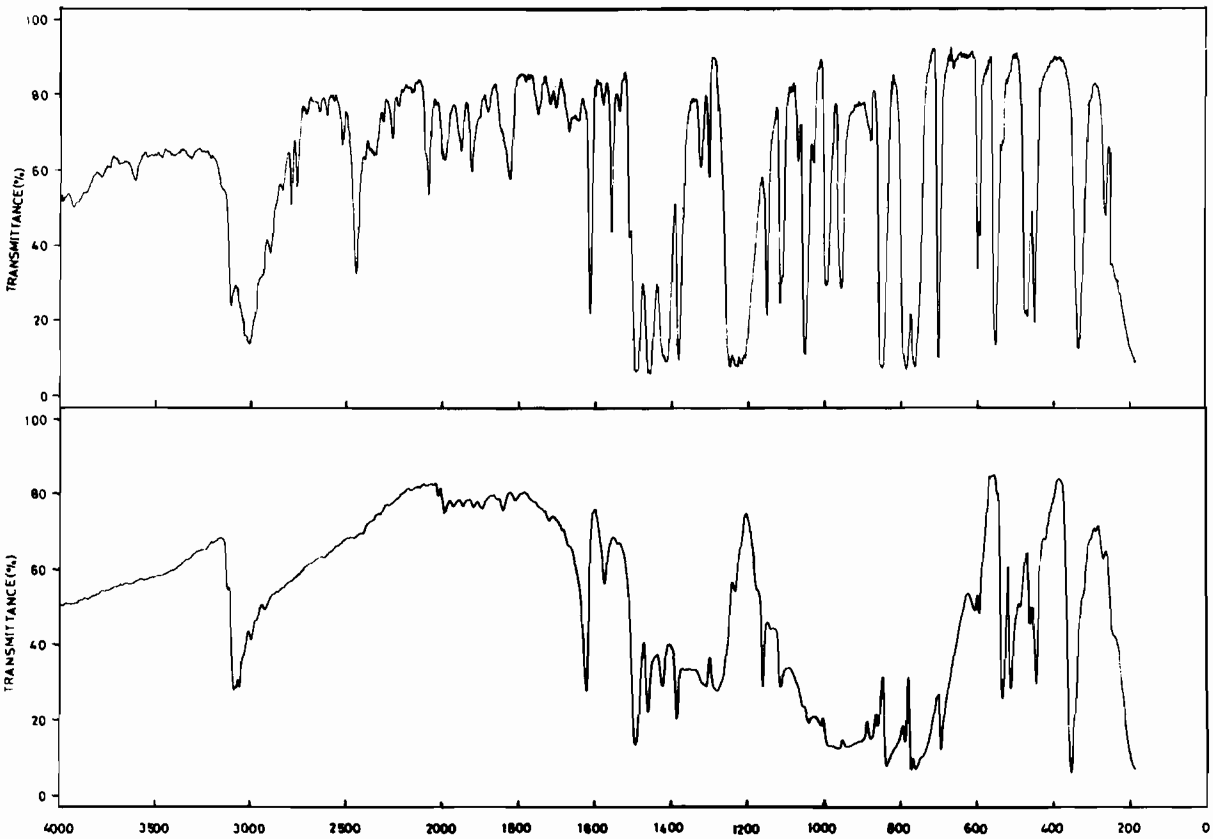

Fig. 1. Infrared spectra of (A) free 2-picoline N-oxide and (B) [H(2-picNO)$_2$] [AuCl$_4$] complex showing Hadzi's Type (ii) spectrum for the symmetry free short O–H–O hydrogen bond.

TABLE I. Positional and Thermal Parameters for Non-hydrogen Atoms.*

Atom	X/a	Y/b	Z/c	B_{eq}*
Au	0.37917(1)	0.31349(3)	0.26822(4)	3.16
Cl(1)	0.4415(1)	0.1346(2)	0.3291(3)	4.85
Cl(2)	0.3055(1)	0.2047(2)	0.3901(4)	5.75
Cl(3)	0.3151(1)	0.4885(2)	0.2092(3)	5.45
Cl(4)	0.4541(1)	0.4263(3)	0.1531(3)	5.90
O(1)	0.8280(3)	0.3365(5)	0.4232(9)	4.98
N(2)	0.8511(3)	0.4605(6)	0.4518(8)	3.59
C(3)	0.9050(3)	0.4886(8)	0.3927(9)	3.40
C(4)	0.9292(4)	0.6131(9)	0.4259(10)	4.17
C(5)	0.8987(5)	0.7103(9)	0.5109(13)	5.08
C(6)	0.8437(5)	0.6771(9)	0.5683(13)	5.28
C(7)	0.8209(4)	0.5494(9)	0.5359(11)	4.60
C(8)	0.9341(4)	0.3784(10)	0.2988(12)	5.03
O(9)	0.7338(3)	0.3705(9)	0.2624(9)	7.06
N(10)	0.6886(3)	0.3221(7)	0.3464(9)	4.58
C(11)	0.6392(5)	0.3930(9)	0.3511(11)	4.87
C(12)	0.5933(5)	0.3393(11)	0.4338(13)	5.74
C(13)	0.5989(5)	0.2184(13)	0.5053(14)	6.59
C(14)	0.6517(6)	0.1408(13)	0.4943(15)	7.04
C(15)	0.6969(5)	0.1922(10)	0.4184(14)	5.73
C(16)	0.6350(7)	0.5253(11)	0.2711(16)	8.49

*Numbers given in parentheses in this and all subsequent tables are the estimated standard deviations in the last digit(s). $B_{eq} = 8\pi^2 U_{eq}$ (and $U_{eq} = 1/3$ trace $\tilde{U}$).

Results and Discussion

Spectroscopic Evidence of Hydrogen Bonding

The infrared spectrum of the complex (Fig. 1) shows no higher-frequency band associated with the O–H stretch. Instead, as compared to the spectrum of the free 2-picNO, the spectrum of the complex has a broad region of absorption extending over a few hundreds of wavenumber in the range 650–1000 cm^{-1}. This wide background absorption

TABLE II. Positional and Thermal Parameters for Hydrogen Atoms.

Atom	X/a	Y/b	Z/c	B(iso)*
OHO	0.755(5)	0.314(8)	0.316(13)	77
HC4	0.9704(4)	0.6620(9)	0.3988(10)	85
HC5	0.9266(5)	0.7998(9)	0.5161(13)	116
HC6	0.8292(5)	0.7664(9)	0.6318(13)	94
HC7	0.7881(4)	0.6011(9)	0.6046(11)	53
H1C8	0.9763(4)	0.4144(10)	0.2596(12)	68
H2C8	0.9050(4)	0.3500(10)	0.1891(12)	94
H3C8	0.9420(4)	0.2915(10)	0.3801(12)	111
HC15	0.7026(5)	0.0869(10)	0.4504(14)	55
HC14	0.6447(6)	0.0460(13)	0.5575(15)	78
HC13	0.5707(5)	0.1561(13)	0.5771(14)	211
HC12	0.5490(5)	0.3727(11)	0.4585(13)	94
HC16	0.5917(7)	0.5692(11)	0.2869(16)	200
HC16	0.6405(7)	0.5146(11)	0.1382(16)	153
HC16	0.6698(7)	0.5904(11)	0.3286(16)	90

*B(iso) × 10^3.

is similar to a typical 'D band' of Hadzi's [27] Type (ii) spectrum with various peaks superimposed on the background and a 'negative peak' or 'window' centered about 800 cm^{-1}. The background absorption is overlaid with a number of maxima, some of which correspond to absorptions in 2-picNO itself. The spectrum closely resembles that of crystalline [H(2-picNO)$_2$]Br [7], of Dunlop's salt [19] and of 2,6-dimethylpyridine N-oxide semiperchlorate [28], evidently supporting the presence of a short hydrogen bond in the crystals of the complex. The ν(N–O) absorption observed at 1250 cm^{-1} in the free ligand is shifted to 1225 cm^{-1} in the complex.

The compound is moderately soluble in methanol, nitromethane and acetonitrile, but is very soluble in dimethylsulfoxide. The NMR signals of the bridged proton, even in freshly prepared, highly concentrated solutions of the complex in CH$_3$OH, d$_6$-DMSO or in non-coordinating solvents such as nitromethane could not be detected, presumably because of interionic exchange at room temperature [29]. A sharp singlet for the methyl protons with $\delta(^1H)$ = 2.27 ppm and two multiplets centered at 7.70 and 8.58 ppm with the expected integrated intensities were observed in d$_6$-dimethylsulfoxide. Similar ^{1}H-NMR spectra of the complex were obtained in other solvents and for the free ligand.

Unit Cell and Packing Consideration

In contrast to all known examples (Table III) the present compound crystallizes with four [H(2-pic-

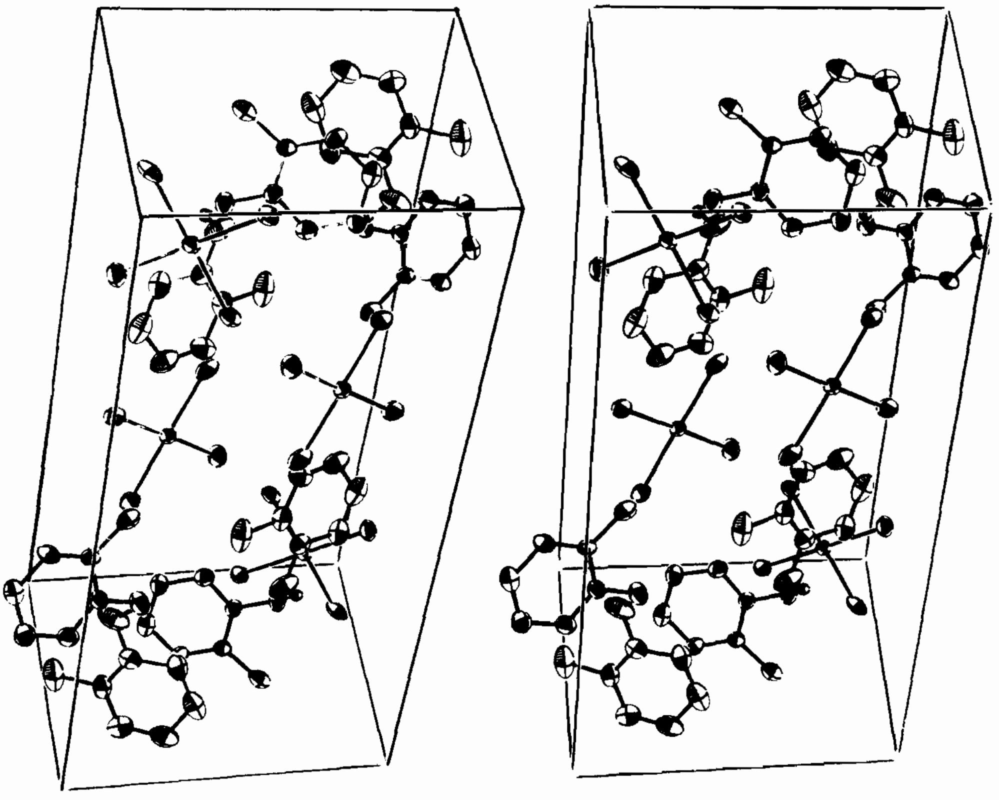

Fig. 2. Stereoscopic view showing packing of [AuCl$_4$]$^-$ and [H-(2-picNO)$_2$]$^+$ ions in the unit cell.

TABLE III. Comparison of the Crystallographic Symmetry and Short Hydrogen Bond in the Related Dimeric Cations.

Compound	Space Group	Molecules per cell	Symmetry of dimeric cation	O- - -O Distance	Ref.
$[H(Ph_3PO)_2][AuCl_4]$	C2/c	4	$\bar{1}$	2.39	32
$[H(PyN\text{-}O)_2][AuCl_4]$	$P\bar{1}$	1	$\bar{1}$	2.41(1)	4
$[H(dma)_2][AuCl_4]$	$P2_1/c$	2	$\bar{1}$	2.46(5) 2.43(2)	8
$[H(H_2O)_2][Au(CN)_2]$	$P2_1/c$	2	$\bar{1}$	2.47(2)	33
$[H(H_2O)\cdot 2H_2O][AuCl_4]$	C2/m	2	2/m	2.57(1)	34
$[H(CH_3)_2PyN\text{-}O)_2]ClO_4$	Cccm	4	2/m	2.345(13)	28
$[H(2\text{-}picNO)_2]Cl\cdot 3H_2O$	Pccn	4	$\bar{1}$	2.414(3)	19
$[\{H(Ph_3As\text{-}O)_2\}]Hg_2Br_6$	C2/c	4	None	2.40(3)	12
$(H(2\text{-}PicNO)_2][AuCl_4]$	$P2_1/n$	4	None	2.393(6)	This work

TABLE IV. Bond Lengths (Å) and Angles (°) in $[H(2\text{-}PicNO)_2][AuCl_4]$.*

(a) Intramolecular bonding distances

Au–Cl(1)	2.277(2)	Au–Cl(2)	2.256(2)
Au–Cl(3)	2.268(2)	Au–Cl(4)	2.271(2)
O(1)–N(2)	1.341(7)	O(9)–N(10)	1.348(9)
N(2)–C(3)	1.361(9)	N(10)–C(11)	1.311(12)
N(2)–C(7)	1.324(10)	N(10)–C(15)	1.404(11)
C(3)–C(4)	1.359(11)	C(11)–C(12)	1.373(14)
C(4)–C(5)	1.387(13)	C(12)–C(13)	1.323(15)
C(5)–C(6)	1.390(14)	C(13)–C(14)	1.417(17)
C(6)–C(7)	1.376(12)	C(14)–C(15)	1.333(16)
C(3)–C(8)	1.500(11)	C(11)–C(16)	1.453(13)
O(1)–OHO	1.42(11)	O(9)–OHO	1.15(10)

(b) Intramolecular bonding angles

Cl(1)–Au–Cl(2)	89.8(1)	Cl(3)–Au–Cl(4)	91.0(1)
Cl(2)–Au–Cl(3)	88.8(1)	Cl(4)–Au–Cl(1)	90.4(1)
O(1)–N(2)–C(3)	117.9(6)	O(9)–N(10)–C(11)	119.7(8)
O(1)–N(2)–C(7)	119.0(7)	O(9)–N(10)–C(15)	116.2(8)
C(3)–N(2)–C(7)	123.1(7)	C(11)–N(10)–C(15)	124.0(8)
N(2)–C(3)–C(4)	117.8(7)	N(10)–C(11)–C(12)	118.3(8)
C(8)–C(3)–N(2)	117.4(7)	C(16)–C(11)–N(10)	119.0(1)
C(8)–C(3)–C(4)	124.8(7)	C(16)–C(11)–C(12)	122.0(1)
C(3)–C(4)–C(5)	121.2(8)	C(11)–C(12)–C(13)	120.5(1.0)
C(4)–C(5)–C(6)	118.9(8)	C(12)–C(13)–C(14)	120.6(1.1)
C(5)–C(6)–C(7)	118.6(8)	C(13)–C(14)–C(15)	119.5(1.1)
C(6)–C(7)–N(2)	120.3(8)	C(14)–C(15)–N(10)	116.9(1.0)

(c) Non-bonding distances and angles

O(1)- - -O(9)	2.393(6)	O(1)- -OHO- -O(9)	137(7)
Cl(1)- - -Cl(2)	3.200(3)	Cl(1)- -Au- - -Cl(3)	178.6(1)
Cl(2)- - -Cl(3)	3.166(4)	Cl(2)- -AuA- -Cl(4)	178.3(1)
Cl(3)- - -Cl(4)	3.238(4)		
Cl(4)- - -Cl(1)	3.226(4)		

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*Chemically equivalent distances in the two 2-picNO moieties are shown against each other.

TABLE V. Least-squares Planes and Dihedral Angles.

Plane 1: $AuCl_4^-$ anion
$-0.218X - 0.412Y - 0.885Z + 4.977 = 0$

Au	0.0110(3)	Cl(3)	0.017(2)
Cl(1)	0.017(2)	Cl(4)	−0.022(3)
Cl(2)	−0.023(3)		

Plane 2: Two picoline N-oxide (Molecule I)
$-0.392X + 0.328Y - 0.860Z + 8.927 = 0$

O(1)	−0.010(7)	C(5)	0.005(10)
N(2)	0.001(6)	C(6)	0.004(10)
C(3)	0.006(7)	C(7)	0.002(9)
C(4)	−0.020(8)	C(8)	0.009(9)

Plane 3: Two picoline N-oxide (Molecule II)
$-0.312X - 0.420Y - 0.853Z + 8.382 = 0$

O(9)	0.013(7)	C(13)	−0.005(11)
N(10)	−0.020(7)	C(14)	0.019(12)
C(11)	−0.000(9)	C(15)	−0.011(11)
C(12)	0.000(11)	C(16)	0.004(13)

Dihedral Angles

Plane I	Plane II	Angle (°)
1	2	44.7
1	3	5.7
2	3	44.1

NO)$_2$] [AuCl$_4$] units per cell in a monoclinic space group P2$_1$/n (order four) exhibiting a 'pseudo-Type A' structure with a symmetry-free short hydrogen bond rendering the cation free to assume a configuration not obscured by symmetry. One each of a well-defined, discrete dimeric cation, [H(2-picNO)$_2$]$^+$, and $AuCl_4^-$ anion constitute an asymmetric unit. The crystallographic packing of the ions in the unit cell is shown in Fig. 2. There being four formula units in the cell, the implications of the space group are that the cation and anion both be on general positions. This makes the structure unique since it differs from the known structures of similar dimeric salts [4, 8] and also from the structure of Dunlop's salt [19] in which [(2-picNO)$_2$H]$^+$ lies across a centre of symmetry and [ClHCl]$^-$ across a twofold axis.

There are no unusual non-bonding interactions among the ions and the packing in the crystal lattice is primarily electrostatic in nature.

Bond Distances and Angles

The atom-numbering system, corresponding to Table I, is shown in Fig. 3. The principal bond-lengths and angles including some intermolecular non-bonded data, are listed in Table IV. The least-squares-plane data are summarized in Table V.

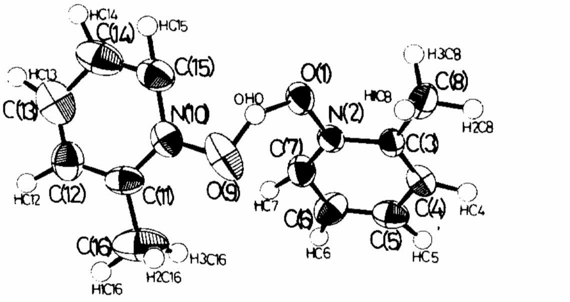

Fig. 3. ORTEP diagram (45% probability ellipsoids) showing relative orientation of 2-picNO moieties and labelling of atoms in the [H(2-picNO)$_2$]$^+$ cation.

The two 2-picNO moieties in the cation are crystallographically non-equivalent but their dimensions hardly differ. Because of the absence of symmetry in the present compound, nearly twice as many dimensions need to be listed. The average values of CH_3–C, C–C and C–N bonds and angles involving these bonds are in agreement in the two 2-picNO moieties in the complex as well as with the corresponding values in other similar structures [19, 28]. The average N–O distance 1.345(8) Å is slightly shorter than the corresponding distance of 1.362(8) Å in [(pyNO)$_2$–H] [AuCl$_4$] and of 1.358(2) Å in Dunlop's salt [19]. The least-squares plane defined by the oxygen atom, methyl carbon and the six atoms of the pyridine ring for the two 2-picNO moieties are given in Table V. Deviations from these planes are very small and the dihedral angle between the normals to the two rings is 44.1°. A similar non-linear arrangement having a dihedral angle of 86.6° was observed [30] for the two planar pyridine rings of [(C_5H_5)$_2$H]$^+$ cation in [(C_6H_5)$_2$H] [ZnBr$_{3/2}$Cl$_{3/2}$-(C_5H_5N)] salt. When no symmetry constraints are involved, it appears that the two rings in the cations adopt an orientation dictated by packing considerations in the unit cell which are influenced by the steric requirements of the base and the large size of the anion. A change in the anion or a base having different steric requirements may result in an altogether different relative arrangement of the base moieties in the dimeric cation [8, 19].

Despite the lack of symmetry constraints, the hydrogen bond in the dimeric cation, [(2-picNO)$_2$–H]$^+$ is 'very short' with O- - -O distance of 2.393(6) Å close to the mean value of 2.445(2) Å observed in Type A salts of monocarboxylic acids [7]. The most reasonable position of the proton obtained from the difference map is somewhat off-centre, its distances from O-atoms being 1.416(11) and 1.148(10) Å. Such a difference fits the idea of a shallow potential energy well, perhaps non-parabolic in shape for the short hydrogen-bond, and may be explained on the basis of environmental differences of the two oxygen atoms. There was no indication of a second hydrogen position near O(1) as might be expected for a double minimum potential of sufficient barrier height [13] and the occupancy of the OHO atom refined closed to unity. However, conclusions about bridge hydrogen should be considered with caution because the X-ray analysis is unlikely to locate an H-atom accurately in the presence of heavy atoms such as Au and Cl, even if the convergence during least-squares refinement was excellent (R = 3.90%).

The $AuCl_4^-$ ion is square-planar with the four Au–Cl distances rather variable. The average Au–Cl distance of 2.268(2) Å is equal to the value of 2.27(1) Å reported [21b] as the most accurate value for the Au–Cl bond. The Au and four Cl atoms are coplanar (Plane 1: Table V) but the formal crystallographic symmetry of the ion is lower than the ideal 4/mm. The closest atoms to the Au other than Cl atoms are the O(1) atom at 3.240 Å and the N(2) atom at 3.712 Å, excluding any possibilities of coordination of these atoms to the gold atom. The distances involving hydrogen atoms are quite normal without any intermolecular hydrogen bonds. The present compound is an example of a dimeric cation having an isolated 'open symmetry-free' short O--H--O hydrogen bond without any intermolecular and/or chelate constraints.

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