A Combined Neutron and *X*-Ray Diffraction Study of Hydrogenbis(*NN*-dimethylacetamide) Tetrachloroaurate(III) revealing a Short Hydrogen Bond

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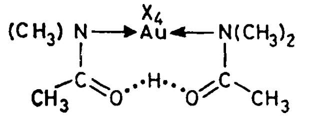
A combined room-temperature neutron and *X*-ray diffraction study of the title compound $[\{(CH_3)_2NC(CH_3)O\}_2H][AuCl_4]$ is reported. The compound crystallizes with two molecules in a monoclinic unit cell of space group $P2_1/a$ with lattice parameters a = 11.597(3), b = 10.404(2), c = 7.657(2) Å, and β = 108.61(1)°. The structure has been solved by the heavy-atom method and the final values for $R(F_0^2)$ were 0.088 for 617 neutron data and 0.082 for 817 *X*-ray data. It consists of distinct $[AuCl_4]^-$ anions and $[(dma)_2H]^+$ cations (dma = dimethylacetamide) with the gold and the bridging hydrogen atoms located at centres of symmetry. The hydrogen bond is 'symmetrical' as a result of crystallographic requirements. The O $\cdots$ O distance is 2.430(16) Å. Thermal-motion analysis of neutron data indicates that methyl groups attached to nitrogen have higher rotational amplitudes resulting in short apparent C–H bond lengths [average 0.96(4) Å] compared with the methyl group attached to carbonyl carbon which has an average C–H bond length of 1.02(2) Å. Other average, uncorrected, neutron-determined bond distances are: Au–Cl 2.265(3); C–O 1.259(8); N–CH_3 1.473(9); N–C 1.299(6); and C–C 1.502(8) Å. The structural analysis clearly indicates that earlier conclusions about the presence of six-co-ordinate gold and nitrogen-co-ordinated dma based upon spectroscopic data are erroneous.

NN-DIMETHYLACETAMIDE (dma) is well known to form complexes with a wide range of metal salts[1-4] and the *X*-ray diffraction studies of a few such complexes[5-8] have been reported. Since the structure of dma is best described as a resonance hybrid of two primary structures,[9] the molecule has two possible centres for co-ordination, *i.e.* either through the oxygen or the nitrogen. Thus, the nature of bonding in dma and other amide complexes has been the subject of some discussion.[1,9]



(I) X = Cl or Br

$[(dma)_2H]^+[AuCl_4]^-$

(II)

On the basis of i.r., ^1H n.m.r., and conductivity evidence dma has been postulated[1-9] to co-ordinate *via* the carbonyl oxygen in all metal complexes except in the case of the dma–decaborane adduct,[10] where bonding through nitrogen was proposed. This was consistent with the thermodynamic calculations of Skinner and Smith[11] and was explained in terms of back co-ordination with boron being more effective with amido-nitrogen than oxygen. Single-crystal diffraction studies[5-8] of dma complexes also indicate bonding through oxygen in all cases so far investigated.

Ziegler *et al.*[12] reported the synthesis of the title compound and proposed co-ordination through nitrogen as shown in structure (I). Since dma is known[1] to form complexes in which the metal ion exhibits its maximum co-ordination number, Ziegler *et al.*[12] proposed six-co-ordinate gold(III) and an intramolecular hydrogen bond of the kind CO $\cdots$ H $\cdots$ OC. Evidence for that structure came mainly from i.r. and ^1H n.m.r. studies which do not exclude an ionic formula of the type (II) having an $[AuCl_4]^-$ anion and a hydrogen-bridged dimeric cation, $[(CH_3)_2NC(CH_3)O \cdots H \cdots O(CH_3)CN(CH_3)_2]^+$. As part of a continuing project dealing with short intramolecular hydrogen bonds, we now report a combined *X*-ray and neutron diffraction study of the title compound which confirms formula (II).

EXPERIMENTAL

Preparation and Crystal Growth of $[(dma)_2H][AuCl_4]$.—The compound was prepared by the general procedure of Ziegler *et al.*[12] Dropwise addition of a slightly greater than stoicheiometric amount of *NN*-dimethylacetamide (Eastman Organic Chemicals) to a concentrated solution of $HAuCl_4$ (Alpha Products) afforded a less soluble yellow crystalline complex. Addition of an excess of dma results in a viscous solution from which crystallization of the complex could not be accomplished even by removal of the excess of dma under vacuum. The i.r. spectrum of the product showed no bands above 3 000 cm^{-1} but two bands centred around 1 660 and 810 cm^{-1}, indicating O–H $\cdots$ O hydrogen bonding in the adduct.

The compound is soluble in methylene chloride, chloroform, alcohol, and water. Crystals for *X*-ray and neutron-diffraction studies were obtained by evaporation of a concentrated aqueous solution of the complex at room temperature over 4—6 d. Large crystals suitable for neutron-diffraction studies were obtained along with plenty of small crystals. Single crystals of the compound are somewhat air and *X*-ray sensitive.

Crystal Data.—$C_8H_{19}AuCl_4N_2O_2$, M = 513.8, Monoclinic, a = 11.597(3), b = 10.404(2), c = 7.657(2) Å, β = 108.61(1)°, D_m = 1.95 g cm^{-3} (flotation in CH_2Cl_2–CH_2BrCH_2Br), Z = 2, D_c = 1.949 g cm^{-3}, U = 875.6 Å^3, $F(000)$ = 488, space group $P2_1/a$ based on systematic absences for $h0l$ with h odd and $0k0$ with k odd, Mo-K_α radiation, λ = 0.710 7 Å, μ = 92.59 cm^{-1}.

A crystal having dimensions *ca.* 0.30 × 0.27 × 0.17 mm was sealed in a glass capillary in an arbitrary orientation.

Intensity data were recorded on a Picker diffractometer using Nb-foil-filtered Mo-K_α radiation.

X-Ray Data Collection and Reduction.—*X*-Ray intensity data were collected at room temperature using a θ—2θ scan to a maximum of $2\theta = 60°$. Each scan covered a range from 0.55° below the calculated $K_{\alpha 1}$ position to 0.60° above the calculated $K_{\alpha 2}$ position. All data were collected using a scan rate in 2θ of 1° min^{-1}; stationary background counts for 20 s were measured before and after each scan. A total of 1 381 reflections was measured. The combined intensities of three standard reflections, measured at an interval of 70—80 reflections, showed an almost linear decrease in intensity of *ca.* 11% during the data collection period. The intensities were corrected for this effect, and for background and Lorentz polarization using the usual equations. Absorption corrections based on the crystal dimensions and faces ($1\bar{1}0$, $\bar{1}10$, $0\bar{1}\bar{1}$, 011, $11\bar{1}$, and $\bar{1}\bar{1}1$) were also applied. The range of transmission factors was 0.050—0.263. Equivalent and duplicate measurements were averaged to give 813 independent reflections. The agreement factor $\Sigma|F^2 - F_{av}{}^2|/\Sigma F^2$ was 0.028. The 617 reflections with $F_o{}^2 > 2.0\sigma(F_o{}^2)$ were used for structure solution and refinement.

Determination and Refinement of the Structure.—All computations were performed on the University of Missouri computer system using standard programs.* For structure-factor calculations, scattering factors for all atoms except hydrogen were taken from Cromer and Waber;[13a] hydrogen-atom scattering factors of Stewart *et al.*[13b] were used. Anomalous scattering effects of Au and Cl were included in F_c.[13c]

The space group $P2_1/a$ has four general positions which require that the two molecules per unit cell be constrained at special positions assuming one dma molecule in an asymmetric unit with gold and bridged hydrogen atoms at centres of symmetry. This assumption was readily confirmed by the analysis of the Patterson synthesis from which the positions of the two independent Cl atoms were obtained. Subsequent refinement and difference-Fourier calculations led to the location of all other non-hydrogen atoms. After a few cycles of least-squares refinement with anisotropic temperature factors for all non-hydrogen atoms, the hydrogen atoms were included as a fixed contribution ($B = 6.0$ Å^2) at their idealized locations calculated using a C–H distance of 0.95 Å and consistent with the positions determined by neutron diffraction (see below).

The final model with 80 parameters varied converged to $R(F_o{}^2) = 0.082$ and $R'(F_o{}^2) = 0.155$.† The final value for $R(F)$ was 0.049, and the standard deviation of an observation of unit weight was 2.833. The highest peak on the final difference electron-density map was 1.78 e Å^{-3} in the vicinity of the gold atom. The shifts on all refined parameters in the last cycle were well below a hundredth of their standard deviation. The rather high values for the discrepancy indices are probably due to the large absorption effects which are undoubtedly not perfectly handled.

Neutron Data Collection and Reduction.—A well formed crystal having dimensions *ca.* 1.5 × 0.6 × 3.1 mm was sealed in a quartz capillary and mounted with the *c* axis along ϕ on a locally modified PDP 11/03 computer-controlled Mitsubishi four-circle diffractometer at the University of Missouri Research Reactor. The monochromatic neutron beam was obtained from a Be crystal and the determination of the neutron wavelength (1.058 Å) has been described earlier.[14] One quadrant (*hkl* and *hkl*) of neutron data was measured out to $2\theta = 95°$, using coupled θ—2θ step scans with 0.08° steps and scan ranges of 31 steps. Two sets of data were recorded, the first for the region $2\theta \leqslant 60°$ rejecting extinct reflections and the second set measuring all possible reflections below $2\theta = 95°$. The combined intensities of the three standard reflections measured after every 50 reflections showed a random variation of *ca.* 4% for which no correction was made. A set of $F_o{}^2$ values was obtained after Lorentz and absorption corrections[15] ($\mu = 1.797$ cm^{-1}). ‡ The transmission coefficient range was 0.81—0.89. A total of 2 895 reflections was sorted at this point and merged under $P2_1/a$ symmetry to yield 2 015 unique data, of which 817 having $I > 2.0\sigma(I)$ were used in subsequent calculations. The agreement factor $\Sigma|F^2 - F_{av}{}^2|/\Sigma F^2 \times 100$ for averaged reflections was 6.8%.

Location and Refinement of Hydrogen Atoms.—All hydrogen atoms were located from a difference-Fourier map phased upon isotropically refined *X*-ray positional parameters for nine non-hydrogen atoms. The largest negative peak on this map, corresponding to the bridging hydrogen atom in the O–H $\cdots$ O bond, was found at the centre of symmetry at $x = 0.5$, $y = 0.0$, and $z = 0.50$. Several cycles of anisotropic least-squares refinement of 166 variables including a scale factor converged to the final values of 0.088 for $R(F_o{}^2)$, 0.135 for $R'(F_o{}^2)$, and 1.58 for the goodness of fit. A final difference-Fourier synthesis of nuclear scattering density was virtually featureless. The shifts in all refined parameters in the last cycle were well below one hundredth of their standard deviations.

Positional parameters along with their standard deviations are given in Table 1. The thermal parameters and observed and calculated structure amplitudes are available as Supplementary Publication No. SUP 22694 (15 pp.).§

RESULTS AND DISCUSSION

General Description of the Structure.—The structure consists of $[AuCl_4]^-$ anions, and centrosymmetric dimeric cations $[(dma)_2H]^+$ in which two dma molecules are bridged by a hydrogen bond (Figure 1). One gold atom, two chlorine atoms, and a dma molecule form the crystallographic asymmetric unit having gold and bridging hydrogen atoms located at the centre of symmetry. The spatial relationship of the dma dimer as a whole to the $[AuCl_4]^-$ unit is shown in Figure 2 as a stereoscopic view of the unit cell. The closest atoms to

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* On the Amdahl 470/V7 and IBM 370/158 network using the programs: ANGSET, angle setting; TRACERA, lattice transformation and Delauney reduction, S. L. Lawton; SORTH, sorting, W. C. Hamilton; HORSE, general absorption correction, W. C. Hamilton; FORDAP, Fourier, A. Zalkin; NUCLS, least-squares, R. Doeden and J. A. Iber, a modification of ORFLS, W. Busing and H. Levy; ORFEE, function and error, W. Busing and H. Levy; ORTEP, thermal ellipsoid plot, C. Johnson.

† $R = (\Sigma|F_o{}^2 - kF_c{}^2|/\Sigma F_o{}^2)$, $R' = [\Sigma w(F_o{}^2 - kF_c{}^2)^2/\Sigma w F_o{}^4]^{\frac{1}{2}}$; R(conventional) $= \Sigma|F_o - kF_o|/\Sigma F_o$, goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o = number of independent observations and N_v = number of variable parameters. All refinements were based on the minimization of $\Sigma w(F_o - F_c{}^2)^2$ with individual weights $w = 1/\sigma^2(F_o{}^2)$ and $\sigma^2 = \sigma^2{}_{counting} + (0.05F_o{}^2)^2$. The neutron-scattering amplitudes were $b_{Au} = 0.76$, $b_C = 0.66$, $b_N = 0.94$, $b_O = 0.575$, $b_{Cl} = 0.958$, and $b_H = -0.372$ (all in units 10^{-12} cm) ('International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, p. 270, Tables 2—6).

‡ An incoherent scattering cross-section of 34 for hydrogen was included in the μ value.

§ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

gold are two chlorine atoms at an average distance of 2.265 Å, making a Cl(1)–Au–Cl(2) angle of 89.3°. A centre of symmetry generates the other two chlorine atoms, forming a planar $[AuCl_4]^-$ unit. There are no other close contacts to the gold atom and neither nitrogen nor oxygen of dma is within bonding distance of the gold. The closest atom other than the chlorines is a hydrogen atom which is more than 3.4 Å from the gold atom.

The crystal structure is stabilized by normal van der Waals non-bonded interactions between chlorine atoms of the $[AuCl_4]^-$ ions and methyl hydrogen atoms of the dma molecule. The shortest interionic contacts, involving hydrogen atoms that are less than the sum of the van der Waals radii (*i.e.* 3.0 Å),[16] are 2.90(2) [Cl(2) · · · 1H(3)] and 2.87(2) Å [Cl(1) · · · 3H(3)], and the angles around these hydrogens are over 155°. Such interactions may either be described as a type of very weak hydrogen bond or they may simply be manifestations of ionic packing in the crystal. The dma molecule is essentially planar. The deviations of the atoms from the plane are not significant as was observed when dma was present as solvent of crystallization [17] and in the case of acetamide.[18]

TABLE 1

Positional parameters for $[(dma)_2H][AuCl_4]$

	Neutron-diffraction data		
Atom	*x*	*y*	*z*
Au	0.0	0.0	0.0
Cl(1)	0.046 0(3)	0.000 7(4)	0.310 6(4)
Cl(2)	0.042 5(3)	0.212 7(3)	0.009 4(6)
O	0.437 4(6)	0.016 2(7)	0.598 8(10)
N	0.299 0(3)	0.129 5(3)	0.670 6(6)
C(1)	0.365 1(4)	0.110 0(5)	0.564 5(7)
C(2)	0.212 8(7)	0.237 0(8)	0.645 8(15)
C(3)	0.355 1(7)	0.197 4(8)	0.404 2(10)
C(4)	0.309 8(8)	0.043 1(9)	0.827 6(12)
H(00)	0.500 0	0.0	0.500 0
1H(2)	0.180 3(29)	0.265 3(30)	0.521 1(43)
2H(2)	0.143 3(21)	0.209 4(22)	0.677 8(45)
3H(2)	0.252 0(22)	0.306 4(28)	0.718 2(55)
1H(3)	0.267 0(16)	0.197 9(21)	0.315 4(21)
2H(3)	0.415 6(16)	0.167 7(19)	0.337 6(23)
3H(3)	0.377 7(18)	0.287 2(18)	0.442 1(25)
1H(4)	0.328 0(38)	0.088 0(25)	0.940 3(27)
2H(4)	0.230 3(22)	0.001 0(27)	0.812 6(31)
3H(4)	0.364 9(27)	−0.028 3(27)	0.834 6(35)

	X-Ray diffraction data		
Atom	*x*	*y*	*z*
Au	0.0	0.0	0.0
Cl(1)	0.042 5(8)	−0.000 2(5)	0.309 1(10)
Cl(2)	0.043 0(7)	0.213 4(7)	0.009 2(8)
O	0.439 8(21)	0.016 6(17)	0.604 4(33)
N	0.298 5(17)	0.127 8(21)	0.668 6(31)
C(1)	0.364 1(26)	0.109 5(26)	0.564 4(40)
C(2)	0.215 0(21)	0.235 7(25)	0.642 8(35)
C(3)	0.357 8(25)	0.195 9(27)	0.400 2(39)
C(4)	0.307 6(29)	0.044 1(33)	0.821 8(52)
H(00)	0.500 0	0.0	0.500 0
1H(2)	0.241 6	0.265 7	0.524 5
2H(2)	0.134 5	0.204 7	0.677 8
3H(2)	0.217 9	0.304 7	0.728 8
1H(3)	0.278 3	0.190 8	0.388 9
2H(3)	0.415 6	0.171 9	0.286 4
3H(3)	0.372 3	0.283 9	0.424 7
1H(4)	0.319 6	0.101 7	0.920 8
2H(4)	0.231 5	0.004 4	0.873 8
3H(4)	0.372 0	−0.011 1	0.787 4

A major feature of the structure is its quite loose packing of almost planar $[(dma)_2H]^+$ cations within the unit cell and $[AuCl_4]^-$ anions located at the corners or faces of the unit cell. As a result of such a packing enough open space is available for solvent (such as water) molecules, although no solvent of crystallization is present in the compound. Packing considerations suggest that the $[AuCl_4]^-$ groups are stacked along the *b* axis with interleaved layers of $[(dma)_2H]^+$ cations. Hydrogen-bonding interactions between adjacent $[(dma)_2H]^+$ cations or between adjacent $[AuCl_4]^-$ and $[(dma)_2H]^+$ layers appear to be weak or absent.

Bond Distances and Angles.—Intramolecular bond distances and angles derived from neutron and *X*-ray data are given in Table 2. The observed differences between the two sets of results are not significant and to a great extent reflect the uncertainty in these parameters. The errors derived from the neutron-diffraction data are almost an order of magnitude smaller. Since the scattering of *X*-rays is dominated by the high atomic number gold atoms, *X*-ray determined bond distances and angles involving carbon and oxygen are less precise than those involving gold only. On the other hand, since the neutron scattering lengths for gold, carbon, and oxygen (as well as for hydrogen) are of comparable magnitude, all neutron-determined bond distances and angles are of comparable precision. All neutron-determined values are within ±1 standard deviation of the values determined by *X*-ray diffractometry. Agreement between chemically equivalent bonds in the complex is excellent. The average Au–Cl distance [2.265(3) Å] is significantly shorter than the corresponding distance (2.285 Å) observed in the neutron-diffraction study [19] of $HAuCl_4 \cdot 4H_2O$. The longer Au–Cl distance in $HAuCl_4 \cdot 4H_2O$ may be the consequence of chlorine atom disorder observed in this compound and/or the hydrogen bonds to the water molecules.

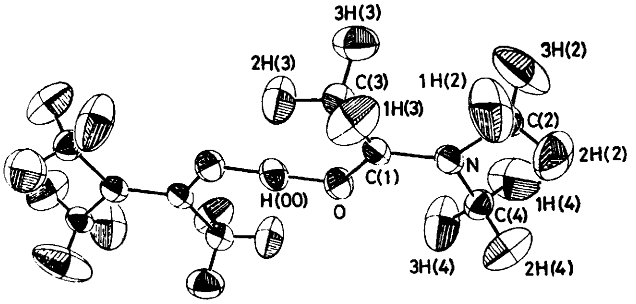

FIGURE 1 Labelling of atoms in the dimeric cation, $[(dma)_2H]^+$ (ORTEP diagram, 15% probability ellipsoids)

The distance [2.430(16) Å] between intramolecular hydrogen-bonded oxygen atoms is within the 2.31—2.626 Å range [14,20] for short hydrogen bonds. The O–H distance is 1.215(8) Å and the hydrogen atom is symmetrically disposed in the O–H · · · O bond as a result of crystallographic requirements for the dimeric $[(dma)_2H]^+$ cation. The O · · · O distance is essentially the same as that [2.442(2) or 2.431(2) Å] observed [21,22] for symmetry-

TABLE 2

Bond distances (Å) and angles (°) in $[(dma)_2H][AuCl_4]$

(*a*) Distances	Neutron diffraction	*X*-Ray diffraction		Neutron diffraction
O–O *	2.430(16)	2.46(5)	O–H(00)	1.215(8)
Au–Cl(1)	2.266(3)	2.258(7)	C(2)–1H(2)	0.95(4)
Au–Cl(2)	2.263(3)	2.272(8)	C(2)–2H(2)	0.96(3)
C(1)–O	1.259(8)	1.28(3)	C(2)–3H(2)	0.94(3)
N–C(1)	1.299(6)	1.28(3)	C(3)–1H(3)	1.03(2)
N–C(2)	1.472(8)	1.45(3)	C(3)–2H(3)	1.04(2)
N–C(4)	1.474(9)	1.44(4)	C(3)–3H(3)	0.99(3)
C(1)–C(3)	1.502(8)	1.53(3)	C(4)–1H(4)	0.94(3)
			C(4)–2H(4)	0.99(3)
			C(4)–3H(4)	0.97(3)
(*b*) Angles				
Cl(1)–Au–Cl(2)	89.3(2)	89.8(2)	1H(2)–C(2)–3H(2)	109(3)
Cl(1)–Au–Cl(2) *	90.7(2)	90.2(2)	2H(2)–C(2)–3H(2)	112(3)
Cl(1)–N–C(2)	123.4(6)	122(2)	1H(2)–C(2)–2H(2)	105(2)
C(1)–N–C(4)	120.2(5)	121(2)	1H(3)–C(3)–2H(3)	111(2)
C(2)–N–C(4)	116.5(7)	117(2)	2H(3)–C(3)–3H(3)	106(2)
C(3)–C(1)–O	120.8(6)	119(3)	1H(3)–C(3)–3H(3)	108(2)
O–C(1)–N	118.5(6)	118(3)	1H(4)–C(4)–2H(4)	105(2)
C(3)–C(1)–N	120.7(5)	120(3)	1H(4)–C(4)–2H(4)	112(2)
			2H(4)–C(4)–3H(4)	104(2)

*At position $\bar{x},\bar{y},\bar{z}$.

restricted hydrogen bonds in the $[H_5O_2]^+$ cation. A similar O · · · O distance [2.436(2) Å] was observed[23] for the $[H_5O_2]^+$ cation in $[H_5O_2][C_6H_4(NO_2)_3SO_3]\cdot 2H_2O$ where the hydrogen atom is not symmetry restricted and the two O–H distances are 1.128(4) and 1.310(4) Å. In the case of $HAuCl_4\cdot 4H_2O$[19] the O · · · O bond distance in the $[H_5O_2]^+$ ion is considerably longer (2.57 Å) and this is probably associated with disorder of the central H atom where the two half-hydrogen atoms are separated by as much as 0.62 Å across the centre of the O · · · O bond (site symmetry 2/*m*). The corresponding distance in $[H_5O_2][Au(CN)_4]$[24] where no disorder was observed and the $[H_5O_2]^+$ ion is centred in the cell across the $\bar{1}$ site at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ is 2.47(2) Å.

An examination of the shape of the ellipsoids of the O and H atoms (Figure 1) for the hydrogen bond suggests that the vibration of the hydrogen in the direction of the bond is significantly greater than that perpendicular to the bond. When rigid-body thermal parameters[25] (neglecting the screw motion) were subtracted from the thermal parameters for the individual atoms in the O · · · H–O bridge, the root-mean-square (r.m.s.) amplitude of the difference ellipsoid of the hydrogen atom was 0.044(15) Å along the hydrogen-bond axis. The average values in the two directions perpendicular to the O–H · · · O axis were close to zero, and the nuclear thermal difference ellipsoids for the O atom along the hydrogen-bond axis had a r.m.s. amplitude of 0.037(15) Å². As a result, the most plausible picture of the potential well for the intramolecular bond is one in which the H atom lies in a single broad and probably symmetric energy well. However, since the two halves of the $[(dma)_2H]^+$ ion are related by a centre of symmetry at the midpoint of the O · · · O bond and the ellipsoid representing the thermal

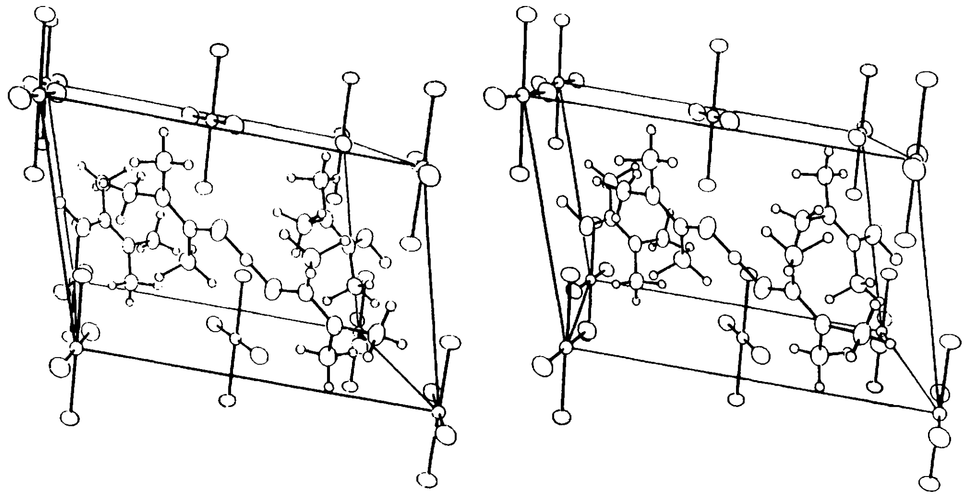

FIGURE 2 Stereoscopic view showing packing of $[AuCl_4]^-$ anions and $[(dma)_2H]^+$ cations in the monoclinic unit cell. The crystallographic *a* axis lies along the horizontal direction, the *c* axis on the vertical direction, and the *b* axis completes the right-handed co-ordinate system

motion of the central H atom is markedly elongated in the bond direction, it is practically impossible to differentiate, on the basis of room-temperature diffraction data alone, between two overlapping disordered hydrogen peaks and a truly single central peak.

The C–H distances range from 0.94(3) to 1.04(3) Å before the thermal motion corrections (Table 2). An average uncorrected C–H distance of 1.02(3) Å was observed for the C(3) methyl group which is attached to the sp^2 carbon, while the average for the methyl groups attached to nitrogen is 0.96(4) Å. After thermal motion correction (Table 3) the average C–H distance for the C(3) carbon increases to 1.092 Å while that for the C(2) and C(4) atoms is 1.115 Å. The average H–C–H angle (108°) is very close to the tetrahedral angle.

TABLE 3

Thermal-motion analysis of the methyl groups of the cation $[(\mathrm{dma})_2\mathrm{H}]^+$

	C(2)	C(3)	C(4)
U_{11}' [a]	16 (8)	23 (14)	23 (21)
U_{22}'	339 (93)	155 (52)	307 (111)
U_{33}'	59 (34)	19 (18)	51 (37)
r(C–H)/Å [b]	0.9492	1.0191	0.9696
$\langle\theta\rangle$/° [c]	31.5	21.1	29.7
r(C–H)$(\cos\langle\theta\rangle)^{-1}$/Å [b]	1.1133	1.0923	1.1162
V_0/kcal mol^{-1} [d]	0.387	0.846	0.427
ω/cm^{-1} [e]	79	118	82

[a] The U' values are mean-square amplitudes, $(U_{\text{expt.}} - U_{\text{rigid body}}) \times 10^{-3}/\text{Å}^2$. [b] r(C–H) is the uncorrected average C–H bond distance; $r(\text{C–H})/\cos\langle\theta\rangle$ is the corrected C–H bond distance. [c] $\langle\theta\rangle$ is the r.m.s. amplitude of rotation calculated by $\tan\langle\theta\rangle = (U_{22})^{\frac{1}{2}}/r(\text{C–H})$. [d] V_0 (barrier height) $= 0.0040T/U_{22}'n^2$ where $T = 295$ K (*i.e.* room temperature) and $n = 3$. [e] $\omega = 76.8n\,(V_0/I)^{\frac{1}{2}}$ where $n = 3$, $I = \Sigma(m_i r_i^2)$ a.m.u. Å^{-2}, $m_{\mathrm{H}} = 1.008$ a.m.u., and $r = r(\text{C–H})$ (corrected) cos 19.5.

TABLE 4

Comparison of average bond distances (Å) and angles (°) with values for related structures

Compound	C–O	C–N	C–CH$_3$	N–CH$_3$	C–C–O	N–C–O	C–C–N	C–N–C	Ref.
$(\mathrm{CH_3})\mathrm{NHC(CH_3)O}$	1.236(12)	1.290(13)	1.536(16)	1.465(13)	120.5	123	116.5	120.5	18
$\mathrm{C_{24}H_8PdS_2}\cdot$dma	1.27(2)	1.60(2)	1.46(2)	1.46(2)	116(2)	128(3)	115(2)	117(2)	17
$[\mathrm{ZnCl_2(dma)_2}]$	1.256(13)	1.517(17)	1.469(16)	1.469(16)	120.4(10)	120.0(11)	119.7(11)	119.9(11)	5
$[\mathrm{CoCl_2(dma)_2}]$	1.254(7)	1.509(10)	1.484(10)	1.484(10)	120.6(5)	119.0(4)	120.3(5)	119.9(5)	6
$[(\mathrm{dma})_2\mathrm{H}][\mathrm{AuCl_4}]$	1.259(8)	1.502(8)	1.473(8)	1.473(8)	120.8(6)	118.5(6)	120.7(5)	120.0(6)	neutron data
	1.275(29)	1.528(31)	1.495(45)	1.445(45)	119(3)	118(3)	120(3)	120(2)	*X*-ray data

Using the approach suggested by Brown and Shannon,[26a] calculations of the bond strength of the hydrogen atom in the hydrogen bond gave an S_t value of 0.945 compared to the expected value of about 1.0. Similar calculations of the bond summation for the carbonyl oxygen atom using all O–H contacts less than 3.00 Å gave a value of 2.78 for S_t using the empirical relationship [26] $S = S'(R/R')^{-N}$, where $S'(\text{C–O}) = 1.333$, $S'(\text{O–H}) = 0.5$, $R'(\text{O–H}) = 1.184$, $R'(\text{C–O}) = 1.378$, $N(\text{O–H}) = 2.2$, and $N(\text{C–O}) = 4.065$.* The corresponding values in deuteriated imidazolium hydrogen maleate [27] are 2.55 and 2.54 for S_t of the two carbonyl oxygens.

Thermal-motion Analysis.—The r.m.s. components of thermal motion along principal axes and their directions are available as SUP22694 and the directions of vibration can be observed in Figure 1. As would be expected, the methyl-group hydrogen atoms have larger amplitudes of vibration which led to a treatment [25] of thermal motion in which the terminal methyl groups are regarded as hindered rotors.

The amplitudes of vibration of the methyl H atoms were corrected for the rigid-body motion obtained in terms of translation (***T***) and libration (***L***) tensors. The interaction (***S***) tensor was neglected because of the small size of the screw components. The resulting ΔU value $(U_{\text{expt.}} - U_{\text{rigid body}})$ were analyzed in terms of hindered rotation to derive r.m.s. amplitudes of hindered rotation ($\langle\theta\rangle$), estimated vibrational frequencies (ω), and corresponding barrier heights (V_0), which are given in Table 3. In all cases the largest amplitude of the difference ellipsoid was in the direction of axis 2 which corresponds to the hindered rotation of the methyl group. From this analysis it is clear that the methyl groups attached to the nitrogen atoms, *i.e.* the C(2) and C(4) methyl groups, have higher amplitudes and lower frequencies than the methyl group attached to the carbonyl carbon atom. The barrier heights, V_0, for the C(2) and C(4) methyl groups are therefore significantly smaller than that for the other methyl group.

Spectroscopic Evidence and Comparison with Related Structures.—A comparison of average bond distances and angles with closely related structures is given in Table 4. Most of the observed parameters are generally in much better agreement with corresponding values in related complexes having co-ordinated dma molecules than with those in the free ligand. For example, the distances and angles involving C–O, N–CH$_3$, N–C, and C–CH$_3$ bonds are within one standard deviation of the corresponding values observed for $[\mathrm{ZnCl_2(dma)_2}]$ and $[\mathrm{CoCl_2(dma)_2}]$ complexes,[5,6] but differ significantly from the similar parameters in methylacetamide,[28] acetamide,[18] and from those in a palladium complex ($\mathrm{C_{28}H_{27}N_9PdS_2}$) having dma as the solvent of crystallization.[17] The above mentioned similarity is probably indicative of a similar stretching of the C=O bond upon co-ordination with a metal atom or upon hydrogen-bond formation. The overall effect on the absorption frequency of the carbonyl group in the i.r. spectrum of the hydrogen bonded dma dimer would not be as pronounced as in the case of dma complexes where a decrease in the stretching force constant would result in lowering of the absorption

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* S,S' are the strengths or orders of bonds of lengths R,R' (no units); S_t is that for a particular atom (no units; R is the actual bond length, and R' is that which gives a bond strength or order of S' (both in Å); N is the empirical exponential constant for each atom pair (no units).

frequency of the carbonyl group. The i.r. spectrum of $[(dma)_2H][AuCl_4]$ shows a broad (width *ca.* 50 cm^{-1}) weak band at *ca.* 1 660 cm^{-1} as compared to a very sharp strong peak at 1 665 cm^{-1} in pure dma for the C=O absorption. In addition, a broadened band (width up to *ca.* 150 cm^{-1}) centred around 810 cm^{-1} was observed for hydrogen bonding of the kind $CO \cdots H\text{-}OC$ in the $[(dma)_2H][AuCl_4]$ complex and no bands were registered above 3 000 cm^{-1}. These i.r. peaks and the ^1H n.m.r. signals with a $\delta(H)$ value of -17.45 p.p.m. observed by Ziegler *et al.*[12] conclusively prove the existence of a hydrogen-bonded proton in the $[(dma)_2H][AuCl_4]$ complex, but not necessarily confirm the structure (I). In fact, the present single-crystal structural analysis clearly indicates that dma is nowhere close to the gold atom and the assumption of nitrogen co-ordination in the $[(dma)_2H][AuCl_4]$ based upon spectroscopic evidence was erroneous. The spectral and n.m.r. data can very well be explained on the basis of formula (II), where gold is four-co-ordinated and two dma molecules are dimerized through an intramolecular hydrogen bond. The latter structure will certainly give i.r. and ^1H n.m.r. spectra identical to those observed by Ziegler *et al.* Similar hydrogen-bonded dimeric species may also exist in other $[AuCl_4]^-$ compounds such as in hydrogen tetrahalogenobis(pyridine *N*-oxide)aurate(III) [29] since the ^1H n.m.r. of this compound also gave a signal for the hydrogen-bonded proton with $\delta(H) = -14$ p.p.m. In the case of the tetrahydrofuran (thf) adduct of $[AuCl_4]^-$ the ionic structure $[Hthf][AuCl_4]$ proposed by Ziegler and Winkler [30] is appropriate. In all these ionic $[AuCl_4]^-$ compounds gold is four- and not six-co-ordinated as erroneously assumed in earlier work.[12,29] Furthermore, dma is not bonded to the gold atom, and the observed signals in the i.r. and ^1H n.m.r. are the results of hydrogen-bonded dimer formation rather than co-ordination to the metal atom through the nitrogen of the dma.

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