Crystal Structure of Hydrogenbis(pyridine *N*-oxide) Tetrachloroaurate(III), revealing a Short Hydrogen Bond †

By **M. Sakhawat Hussain,*** Department of Chemistry, University of Petroleum and Minerals, Dhahran, Saudi Arabia
Elmer O. Schlemper, Department of Chemistry, University of Missouri, Columbia, Missouri 65211, U.S.A.

An *X*-ray diffraction study of the title compound $[H(pyo)_2][AuCl_4]$ (pyo = pyridine *N*-oxide) was done to investigate the dimeric cation $[H(pyo)_2]^+$ with a short hydrogen bond. The compound crystallizes in the triclinic space group $P\bar{1}$ and has lattice parameters a = 7.276(6), b = 8.631(3), c = 6.799(8) Å, α = 105.4(3), β = 96.4(3), and γ = 67.9(2)°. The structure was solved both by the direct method and by the heavy-atom method using a CAD-4 SDP system. The final value for $R(F_o)$ was 0.044 for 1 343 unique reflections. The structure consists of discrete $[AuCl_4]^-$ anions and $[H(pyo)_2]^+$ cations with the gold and the bridging hydrogen atoms located at centres of symmetry. The hydrogen bond is symmetric as a result of crystallographic requirements. Two pyridine *N*-oxide molecules are hydrogen-bonded to form the planar dimeric cation, $[H(pyo)_2]^+$. The $[AuCl_4]^-$ anion has no bonded interaction with any adjacent anion or cation, indicating four-co-ordinated planar gold. The O $\cdots$ O distance [2.41(1) Å] is within the usual range observed for short hydrogen bonds. The structure of this compound, its spectral data, and its comparison with the structures of known compounds having similar dimeric cations are of significance because of the importance of gold complexes in chrysotherapy (gold treatment).

RECENT structural studies have revealed a tendency for neutral Lewis bases to form diadducts of the proton (H^+), analogous to the well known $H_5O_2^+$ ion which exists in aqueous solutions as well as in solids.[1] We have recently reported[2] complete *X*-ray and neutron diffraction studies of one such diadduct, the dimethylacetamide (dma) cation $[H(dma)_2]^+$, which revealed a strong O–H $\cdots$ O hydrogen bond. Another diadduct, the pyridine (py) cation $[H(py)_2]^+$, having a N–H $\cdots$ N hydrogen bond was reported earlier.[3] The hydrogen bond in the cation $[H(py)_2]^+$ is much weaker than that in $[H(dma)_2]^+$ indicating that the strength of the bond is related to the strength of the base and to the type of the donor atom involved, *e.g.* nitrogen compared with oxygen. The present study reports another diadduct cation, $[H(pyo)_2]^+$, formed from pyridine *N*-oxide (pyo).

Another purpose of the present work was to decide between various structural possibilities for the title compound $[H(pyo)_2][AuCl_4]$. The ^1H n.m.r. spectrum was reported[4] to exhibit a signal for the hydrogen-bonded proton with δ(H) — 14 p.p.m. The i.r. spectrum showed bands characteristic of hydrogen bonding in the complex. These spectral data were interpreted on the basis of a six-co-ordinate gold(III) complex as was the case in the related gold(III) adduct of dimethylacetamide.[5] However, the formation of an ionic compound having $[AuCl_4]^-$ anion and a hydrogen-bonded cation, $[C_5H_5N–O–H \cdots O–NC_5H_5]^+$, cannot be excluded on the basis of spectral data. The structure of this complex may also be significant because of the importance of gold complexes in chrysotherapy (gold treatment).[6]

EXPERIMENTAL

Preparation of the Compound, Crystal Growth, and Spectral Data.—The compound was prepared by adding an excess of ethanolic solution of pyridine *N*-oxide to a solution of $HAuCl_4$ in a minimum amount of the same solvent. A crystalline precipitate was obtained on partial removal of the solvent. A prolonged exposure of the solid to air results in reduction of gold(III) to metallic gold. Single crystals were grown by a very slow evaporation of an aqueous solution of the compound in the presence of an excess of the ligand. On evaporation to near dryness, clear orange coloured crystals with uniform morphology were harvested from a mixture of clear and opaque crystals. The density of the compound was determined by filtration in $C_6H_3Br_2NO_2$. Infrared spectra were recorded on a Perkin-Elmer model 180 spectrophotometer using KBr pellets. The ^1H n.m.r. spectra were obtained on a Varian T-60 n.m.r. spectrometer using $[^2H_6]$dimethyl sulphoxide as solvent and $SiMe_4$ as external standard. The u.v. and visible spectra were taken on a Perkin-Elmer model 202 spectrophotometer.

Space Group Determination, Data Collection, and Crystal Data.—A crystal having dimensions 0.3 × 0.2 × 0.1 mm was cut from a large crystalline mass and mounted in a thin-walled glass capillary with the longest dimension approximately parallel to the fibre axis. Preliminary cell dimensions were obtained by use of the Enraf-Nonius program SEARCH to locate 25 independent reflections, 15 of which were used in the program INDEX to obtain an orientation matrix to provide approximate cell dimensions which was improved by the addition of 10 new reflections. The crystal data and lattice constants were determined by the least-squares refinement of the diffraction geometry for 25 centred reflections having $8.5 < \theta < 16.0°$ measured at an ambient temperature of 22 ± 2 °C. $C_{10}H_{11}AuCl_4N_2O_2$, M = 530, Triclinic, a = 7.276(6), b = 8.631(3), c = 6.799(8) Å, α = 105.4(3), β = 96.4(3), γ = 67.9(2)°, U = 381.5(9) Å^3, $F(000)$ = 248, D_m = 2.32, Z = 1, D_c = 2.307 g cm^{-3}, space group $P\bar{1}$, Mo-K_α radiation, λ = 0.7107 Å, μ(Mo-K_α) = 106.5 cm^{-1}.

The mosaicity of the crystal was judged acceptable on the basis of several θ scans. Data were collected on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/E computer using graphite-monochromated Mo-K_α radiation and the θ—2θ scan mode with θ scan range of $(0.65 + 0.35\tan\theta)°$ centre about the calculated Mo-K_α peak position. The scan rate varied from 0.59

---

† Presented at the 12th Congress and General Assembly of the International Union of Crystallography, Ottawa, August 15—25, 1981, held under the sponsorship of the National Research Council of Canada.

to 4.0° 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 2 684 reflections ($\pm h, \pm k, \pm l$) for $1.5 < 2\theta < 55°$ were measured. Three standards, monitored after every 6 000 s of X-ray exposure time, gave some indications of crystal deterioration. The intensity (I) for each reflection is then given by $I = [(FF)/S][P - 2(B_1 + B_2)]$, where P is the number of counts accumulated during the peak scan, B_1 and B_2 are left and right background counts, S is an integer which is inversely proportional to the scan rate, and FF is either unity or a multiplier to account for the occasional attenuation of the diffracted beam. The standard deviations in the intensities, $\sigma(I)$, were computed as $[\sigma(I)^2 = [(FF)^2/S^2][P + 4(B_1 + B_2)]$. Raw intensity data .were corrected for crystal decay using the program CHORTA of the structure determination package.* The decay correction ranged from 0.9771 to 1.3409 with an average of 1.0232. The intensities were also corrected for absorption using the PSI scan method with a transmission factor ranging from 21.24 to 99.72 with an average of 59.83. Lorentz and polarization corrections were made with the ENXDR program. The intensities of equivalent reflections were averaged to obtain 1 343 reflections, all of which were used in the analysis.

Solution and Refinement of the Structure.—All calculations were performed on a PDP11/34 computer using the Enraf-Nonius Structure Determination Package.* Since the intensity distribution statistics did not clearly support a centrosymmetric space group the solution and refinement of the structure was done both in centric and acentric space groups. The co-ordinates of the Au atom and two Cl atoms were obtained from a three-dimensional Patterson synthesis. The same co-ordinates for gold and chlorine atoms, along with the co-ordinates for N and O atoms, were obtained by direct methods using MULTAN. A Fourier map phased on the refined positions of Cl, N, and O atoms with gold at a special position led to the location of all non-hydrogen atoms. Several cycles of anisotropic least-squares refinement followed by a difference-Fourier synthesis revealed the positions of all hydrogen atoms with a strongest peak at ($\frac{1}{2}$,0,0) indicating the hydrogen atom of the hydrogen bond. These positions were in good agreement with the calculated positions. Final refinement of 89 variables including anisotropic thermal parameters for non-hydrogen atoms and fixed positional and isotropic thermal parameters for the hydrogen atoms led to the final residual factors $R = 0.044$ and $R' = 0.062$. The largest shift in any parameter during the final cycle of refinement was 0.15 times its estimated standard deviation. A final difference-Fourier synthesis was virtually featureless with some small residual electron density in the vicinity of the gold atom. Refinement of the structure in the acentric space group using unaveraged data failed to converge, indicating that our original choice of centric space group was correct.

The full-matrix least-squares refinement was based on F_o, and the function minimized was $\Sigma_w(|F_o| - |F_c|)^2$. Atomic scattering factors were taken from International Tables.[7] The effects of anomalous dispersion were included in F_c by using values from Cromer.[8] Agreement factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = (\Sigma_w(|F_o| - |F_c|)^2/\Sigma_w F_o^2)^{\frac{1}{2}}$. The final positional and thermal parameters for [H(pyo)$_2$][AuCl$_4$] are given in Table 1. Intramolecular bond angles are presented in Table 2. Figure 1 shows a stereoscopic view of the unit cell, while Figures 2 and 3 show the [AuCl$_4$]$^-$ anion and [H(pyo)$_2$]$^+$ cation. A listing of the observed and calculated structure factors and thermal parameters is available as Supplementary Publication No. SUP 23233 (10 pp.).†

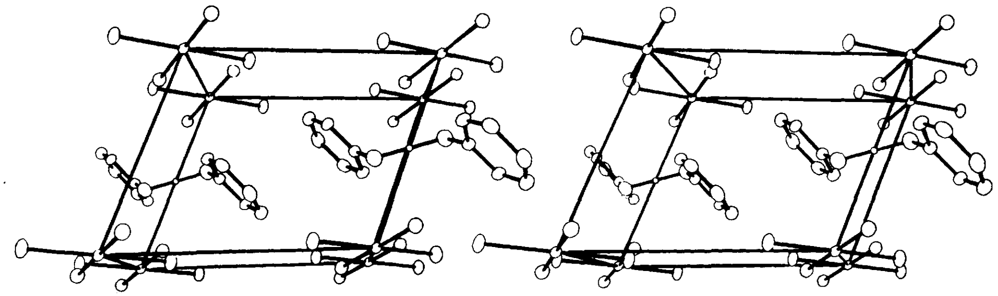

FIGURE 1 Stereoscopic view showing packing of [AuCl$_4$]$^-$ anions and [H(pyo)$_2$]$^+$ cations in the triclinic unit cell. The crystallographic a axis lies along the horizontal direction, the c axis along the vertical direction, and the b axis completes the right-handed co-ordinate system

RESULTS AND DISCUSSION

General Description of the Structure.—As is evident from the packing diagram (Figure 1) the crystal structure consists of well separated [AuCl$_4$]$^-$ anions, and centrosymmetric dimeric [H(pyo)$_2$]$^+$ cations. One gold atom, two chlorine atoms, and a pyo molecule form the crystallographic asymmetric unit with gold and bridging hydrogen atoms located at the centre of symmetry. The metal environment in the complex is square planar with a Cl(1)-Au-Cl(2) angle of 89.94(8)° and two chlorine atoms at an average distance of 2.271(2) Å, similar to the distance observed in [H(dma)$_2$][AuCl$_4$] [2.265(8) Å] but shorter than the corresponding distance in HAuCl$_4$·4H$_2$O.[9] The only interionic distances shorter than 3.5 Å are the Au-O(1) distance of 3.105(7) Å and some chlorine–hydrogen separations listed in Table 2. Pyridine N-oxide has a dipole moment of 4.2 debyes,[10] and the crystal is held together by a combination of van der Waals forces determined by the above interionic contacts and

---

* The programs used were those specificially written for Enraf-Nonius diffraction systems and are explained in SDP User's Guide Revision 3-B, April 1980.

† For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

dipole–dipole interactions. The $[H(pyo)_2]^+$ cation is planar with no atom more than 0.007 Å out of the least-squares plane defined by the atoms in the pyo molecule. The major feature of the structure is the quite loose packing of $[H(pyo)_2]^+$ cations located within the unit cell and $[AuCl_4]^-$ anions at the corners 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. Hydrogen-bonding interaction between adjacent $[H(pyo)_2]^+$ cations or between adjacent $[AuCl_4]^-$ and $[H(pyo)_2]^+$ layers appears to be very weak or absent. The square-planar $[AuCl_4]^-$ units are stacked above one another to form a columnar stacked structure similar to the one observed in the case of $[H(dma)_2][AuCl_4]$ [2] but different from the structures of the nickel, palladium, and platinum complexes of dimethylglyoxime (H_2dmg).[11] The metal–metal separation in the structures of $[H(dma)_2][AuCl_4]$ and $[H(pyo)_2][AuCl_4]$ is quite large compared to the corresponding separation in $[M(Hdmg)_2]$ ($M = Ni^{II}$, Pd^{II}, or Pt^{II}). Any overlap of the metal atom orbital with those of the neighbouring metal atoms in the chain for the former pair of complexes is not possible, whereas such an overlap is possible in $[M(Hdmg)_2]$ with interchain metal–metal distances of 3.245—3.253(3) Å, characteristic of one-dimensional metallic complexes.[12]

TABLE 1

Position parameters for $[H(pyo)_2][AuCl_4]$ *

Atom	*X*	*Y*	*Z*
Au	0.000 0(0)	0.000 0(0)	0.000 0(0)
Cl(1)	−0.071 5(4)	−0.111 5(3)	−0.328 0(4)
Cl(2)	−0.033 1(5)	0.247 9(3)	−0.081 7(5)
O(1)	−0.543(1)	0.873(1)	−0.044(1)
N(1)	−0.473(1)	0.781(1)	−0.234(1)
C(1)	−0.325(2)	0.630(1)	−0.249(2)
C(2)	−0.253(2)	0.533(2)	−0.436(3)
C(3)	−0.335(2)	0.590(2)	−0.608(2)
C(4)	−0.489(2)	0.746(2)	−0.583(2)
C(5)	−0.558(2)	0.841(1)	−0.397(2)
H(C1)	−0.270 8(0)	0.590 0(0)	−0.128 9(0)
H(C2)	−0.144 3(0)	0.424 1(0)	−0.447 4(0)
H(C3)	−0.285 9(0)	0.523 2(0)	−0.740 7(0)
H(C4)	−0.549 4(0)	0.788 0(0)	−0.700 7(0)
H(C5)	−0.666 3(0)	0.949 0(0)	−0.382 6(0)
H(O1)	0.500 0(0)	0.000 0(0)	0.000 0(0)

* Estimated standard deviations are in parentheses in Tables 1—3.

TABLE 2

Bond distances (Å) and angles (°) in $[H(pyo)_2][AuCl_4]$

Au–Cl(1)	2.270(2)	Cl(1)–Au–Cl(2)	89.94(8)
Au–Cl(2)	2.271(2)	O(1)–N(1)–C(1)	117.7(7)
N(1)–O(1)	1.362(8)	O(1)–N(1)–C(5)	119.9(7)
		C(1)–N(1)–C(5)	122.4(7)
N(1)–C(1)	1.33(1)	N(1)–C(1)–C(2)	119.7(8)
N(1)–C(5)	1.34(1)	C(1)–C(2)–C(3)	119.9(9)
C(1)–C(2)	1.35(1)	C(2)–C(3)–C(4)	117.8(8)
C(2)–C(3)	1.38(2)	C(3)–C(4)–C(5)	121.6(8)
C(3)–C(4)	1.38(2)	C(4)–C(5)–N(1)	118.6(8)
C(4)–C(5)	1.34(1)		
O(1) · · · O(1)	2.41(1)		

Interionic distances less than 3.5 Å

Au–O(1)	3.105(7)	Cl(2)–H(Cl)	3.076(2)
Cl(1)–H(C2)	2.691(2)	Cl(2)–H(C3)	3.025(3)
Cl(1)–H(C5)	2.845(2)		

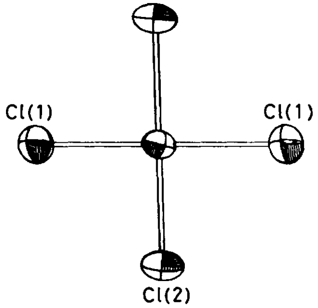

FIGURE 2 ORTEP diagram (15% probability ellipsoids) showing the labelling of atoms in the $[AuCl_4]^-$ anion

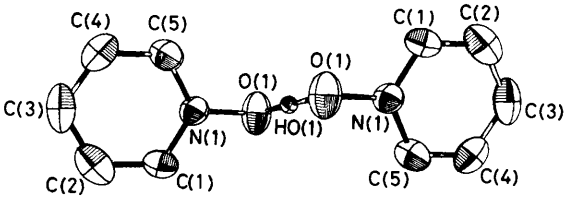

FIGURE 3 ORTEP diagram (15% probability elllipsoids) showing the labelling of atoms in the $[H(pyo)_2]^+$ cation

Bond Distances and Angles.—Bond distances and angles in $[H(pyo)_2][AuCl_4]$ and in some related compounds are given in Tables 2 and 3. Since the scattering of *X*-rays is dominated by the high atomic-number gold atoms, the bond distances and angles involving carbon and nitrogen are less precise than those involving the gold atom. All chemically equivalent bonds in the complex agree within ±2 standard deviations in those bonds. The nitroxide N–O distance of 1.362(8) Å is within the range 1.33(2)—1.37(2) Å reported for the corresponding

TABLE 3

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

Bond	$[H(pyo)_2][AuCl_4]$	pyo	$ONC_5H_4(NO_2)$	$C_5H_4NO{-}H{-}O_2CCCl_3$
N–O	1.362(8)	1.35(2)	1.298(2)	1.39
O–O	2.41(1)			2.411(8)
N–C	1.33(1)	1.34(2)	1.360(3)	1.33
	1.34(1)	1.34(2)	1.364(3)	1.30
C–C	1.35(1)	1.35(2)	1.362(3)	1.38
	1.34(1)	1.37(2)	1.353(3)	1.35
	1.38(2)	1.38(2)	1.380(3)	1.41
	1.38(2)	1.39(2)	1.383(3)	1.45
Method	*X*-Ray	*X*-Ray	Neutron	*X*-Ray
Ref.	This work	13	14	18

distance in the *X*-ray study[13] of pyo. However, this distance differs significantly from the 1.298(2) Å reported[14] for N–O in $O{-}NC_5H_4(NO_2)$ and from the 1.278(1) Å in pyo determined by microwave spectroscopy,[15] and from the 1.290(15) Å obtained from gas-phase electron diffraction studies.[16] A slight elongation in the N–O bond distance observed in the $[H(pyo)_2]^+$ cation may be the result of hydrogen bonding of the polar N ⟶ O bond to produce the short –N–O · · · H · · · O–N– hydrogen-bond system. The C–C bonds parallel to the molecular axis are slightly shorter than other C–C ring bonds, as has been observed in $ONC_5H_4(NO_2)$, indicating a contribution of quinoid resonance structures. The shortening to 1.34(1)—1.35(1) Å is even smaller than reported for $ONC_5H_4(NO_2)$ [1.362(3)—1.353(3) Å], probably indicating the necessity of bond-length correction due to thermal motion. The distance [2.41(1) Å] between intramolecular hydrogen-bonded oxygen atoms is within the range (2.310—2.626 Å) observed for short hydrogen bonds.[1] A similar O–O separation of 2.411(8) Å has been reported in a hydrogen-bonded adduct of pyridine *N*-oxide with trichloroacetic acid.[17] The O–H distance is 1.204 Å with the hydrogen atom symmetrically disposed in the O–H–O bond as a result of crystallographic requirements for the dimeric $[H(pyo)_2]^+$ cation. The O–O distance is significantly longer than the 2.29 Å recently reported[18] for the shortest hydrogen bond in the dihydroxide anion, $H(OH)_2^-$. The $[H(pyo)_2]^+$ cation can be structurally viewed identical to the $H_5O_2^+$ cation free to rotate about the O–H–O axis with the proton being equally shared by the oxygen atoms of the two pyo molecules.

TABLE 4

Spectral data for $[H(pyo)_2][AuCl_4]$ and some related complexes

Spectral region	$[H(pyo)_2][AuCl_4]$	$[H\{ONC_5H_4(NO_2)\}_2][AuCl_4]$	$[H(dma)_2][AuCl_4]$
U.v.–visible $\lambda_{max.}$/nm ($\epsilon_{max.}$/dm^3 mol^{-1} cm^{-1})	207 (1 312) [a] 255 (690)	235 (1 250) [b] 335 (620)	205 (885) [a] 295 (239)
I.r. Bands [c] $\tilde{\nu}$/cm^{-1}	3 430br 1 620w 1 380vs 1 215w 1 100w, br 790s, br	3 440br 1 590w, 1 530s 1 375vs 1 225w 1 100w, br 800w, br	3 440br 1 630br 1 380vs, 1 260s 1 100s, 1 025s 800s

[a] Water as solvent. [b] Ethanol as solvent. [c] KBr pellets; br = broad, w = weak, vs = very strong, s = strong.

Spectral Data and Comparison with Related Structures.—The u.v.-visible (190—750 nm) and i.r. spectral bands for $[H(pyo)_2][AuCl_4]$ and some related gold(III) complexes are given in Table 4. Ultraviolet–visible spectra consist of relatively intense charge-transfer bands in the u.v. which tail towards the visible without any strong peak in the blue region. An aqueous solution of $[H(dma)_2][AuCl_4]$ showed absorptions at 205 and 295 nm with no other peak below 750 nm. Similarly, only two strong absorptions below 400 nm were observed for $[H(pyo)_2][AuCl_4]$ and $[H\{ONC_5H_4(NO_2)\}_2][AuCl_4]$. This does not agree with the spectra of other gold(III) compounds. For example, a single-crystal study[19] of $Na[AuCl_4]$ showed absorptions (above 400 nm) at 410 and 480 nm, with another at 312 nm. Similarly, in a KCl disc, the complex $[Au(py)Cl_3]$ gave a peak at 480 nm besides three other absorptions below 400 nm.[20] The solution spectra of $[H(dma)_2][AuCl_4]$, $[H(pyo)_2][AuCl_4]$, and $[H\{ONC_5H_4(NO_2)\}_2][AuCl_4]$ are difficult to interpret since unless the excess of the ligands is maintained the complexes are decomposed and gold(0) deposits with the formation of other gold complexes.

The i.r. spectra of the solids $[H(pyo)_2][AuCl_4]$ and $[H\{ONC_5H_4(NO_2)\}_2][AuCl_4]$ in KBr showed ν(NO) at 1 215 and 1 225 cm^{-1} compared to the corresponding band at 1 243 cm^{-1} in pure pyridine *N*-oxide. The broad bands centred around 800 cm^{-1} were observed in all three compounds indicating the presence of the O–H–O hydrogen bond. A weak, broad band at 3 430 cm^{-1} observed in all three compounds is probably due to moisture.

Some help from Mr. Martin Dawson in obtaining spectral data is acknowledged. Financial support from the National Science Foundation (Grant CHE-77-08325) and from the University of Petroleum and Minerals is gratefully acknowledged.

[1/1454 *Received, 17th September*, 1981]

REFERENCES

[1] J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91 and references therein.

[2] M. S. Hussain and E. O. Schlemper, *J. Chem. Soc., Dalton Trans.*, 1980, 750.

[3] B. E. Villarreal-Salinas and E. O. Schlemper, *J. Cryst. Mol. Struct.*, 1978, **8**, 217.

[4] M. Ziegler and G. Stephan, *Mikrochim. Acta*, 1970, 628.

[5] M. Ziegler, P. Barth, and H. Winkler, *Angew. Chem. Int. Edn.*, 1969, **8**, 980.

[6] (*a*) D. H. Brown and W. E. Smith, *Chem. Soc. Rev.*, 1980, **9**, 217; (*b*) W. S. Preston, W. D. Block, and R. H. Freyberg, *Proc. Soc. Exp. Biol. Med.*, 1942, **50**, 253.

[7] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, Table 2.2B.

[8] D. T. Cromer, *Acta Crystallogr.*, 1965, **18**, 17.

[9] P. Schuster, G. Zundel, and C. Sandorfy, 'The Hydrogen Bond,' 1976, vol. 2, pp. 501, 502; J. M. Williams and J. W. Peterson, *J. Am. Chem. Soc.*, 1969, **91**, 776.

[10] A. N. Sharpe and S. Walker, *J. Chem. Soc.*, 1961, 2974.

[11] M. S. Hussain, B. E. V. Salinas, and E. O. Schlemper, *Acta Crystallogr., Sect. B*, 1979, **35**, 628.

[12] A. E. Underhill and D. M. Watkins, *Chem. Soc. Rev.*, 1980, **9**, 429.

[13] D. Uklu, B. P. Huddle, and J. C. Morrow, *Acta Crystallogr., Sect. B*, 1971, **27**, 432.

[14] Y. Wang, R. H. Blessing, F. K. Ross, and P. Coppens, *Acta Crystallogr., Sect. B*, 1976, **32**, 572.

[15] O. Snerling, C. J. Nielsen, L. Nygaard, E. J. Pedersen, and G. O. Sorensen, *J. Mol. Struct.*, 1975, **27**, 205.

[16] J. F. Chang, *J. Chem. Phys.*, 1974, **61**, 1280.

[17] L. Golic, D. Hadzi, and F. Lazarini, *Chem. Commun.*, 1971, 860.

[18] K. Abu-Dari, K. N. Raymond, and D. P. Freyberg, *J. Am. Chem. Soc.*, 1979, **101**, 3688.

[19] D. H. Brown and W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1976, 848.

[20] D. H. Brown, G. McKinlay, and W. E. Smith, *J. Chem. Soc., Dalton Trans.*, 1978, 199.