Co-ordination Chemistry of Pyridyl and *N*-Methylimidazolyl Ketones. Synthetic and *X*-Ray Structural† Studies of Copper(II), Nickel(II), and Dimethylgold(III) Complexes

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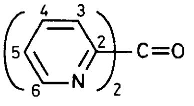
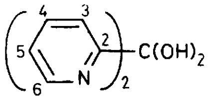
Di-2-pyridyl ketone (dpk) reacts with dimethylgold(III) nitrate in water to form the complex [AuMe$_2$(dpk·H$_2$O)]NO$_3$ in which the ligand has been hydrated to form a geminal diol. The closely related ketones 2-pyridyl *N*-methyl-2-imidazolyl ketone (pik) and di(*N*-methyl-2-imidazolyl) ketone (dik) react with Au^{III}Me$_2$ nitrate to form complexes that do not involve hydration of the ligand, [AuMe$_2$(L)]NO$_3$ (L = pik or dik). They react similarly with copper(II) sulphate and nickel(II) nitrate, forming [Cu(pik)(SO$_4$)]·0.5H$_2$O, [Cu(dik)(SO$_4$)]·2H$_2$O, [Ni(pik)$_2$(NO$_3$)$_2$]·0.5H$_2$O, and [Ni(dik)$_2$(NO$_3$)$_2$]·1.5MeOH; dpk forms [Ni(dpk·H$_2$O)$_2$(NO$_3$)$_2$]·0.5H$_2$O on reaction with nickel(II) nitrate. The crystal structures of [AuMe$_2$(dpk·H$_2$O)]NO$_3$ and [Cu(dik)(SO$_4$)]·2H$_2$O have been determined by single-crystal *X*-ray diffraction at 295 K and refined by least-squares methods to *R* = 0.045 and 0.032 for 2 031 and 4 754 independent 'observed' reflections, respectively. The cation [AuMe$_2$(dpk·H$_2$O)]$^+$ has the ligand *N,N*-chelated with *cis*-square-planar co-ordination for gold(III), with an intramolecular hydroxy group positioned 2.850(8) Å from the gold atom. The complex [Cu(dik)(SO$_4$)]·2H$_2$O has square-pyramidal co-ordination for copper(II), with the *N,N*-chelated ligand in the basal plane together with a water molecule and unidentate sulphate ion, and a water molecule co-ordinated axially. There is an intermolecular Cu ··· O contact of 3.254(2) Å with a ketone oxygen. Possible reasons for different behaviour of the ligands toward hydration are discussed. Crystals of [AuMe$_2$(dpk·H$_2$O)]NO$_3$ are monoclinic, space group $P2_1/c$, a = 9.41(1), b = 7.328(7), c = 22.17(2) Å, β = 97.85(8)°, and Z = 4. Crystals of [Cu(dik)(SO$_4$)]·2H$_2$O are monoclinic, space group $P2_1/n$, a = 11.982(3), b = 13.803(3), c = 8.866(2) Å, β = 107.30(2)°, and Z = 4.

Di-2-pyridyl ketone (dpk) forms complexes with a range of metal ions,[1-10] and under certain conditions undergoes hydration on complex formation to give complexes containing dpk·H$_2$O[2,4-6,9-11] and dpk·OH$^-$.[2,4,11] The hydration reaction has been of particular interest, with two complexes studied by single-crystal *X*-ray diffraction.[9] Several reasons for the hydration behaviour have been presented[2,3,9,11] and the most likely one appears to be that hydration results in a more favourable geometry for the six-membered chelate ring MNCC(OH)$_2$CN than that for the planar ligand in complexes containing MNCC(O)CN.[9,11]

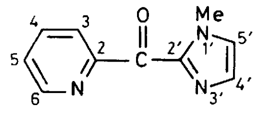
The related ketones 2-pyridyl *N*-methyl-2-imidazolyl ketone (pik) and di(*N*-methyl-2-imidazolyl) ketone (dik) have recently been synthesized.[12,13] Substitution of pyridyl rings by *N*-methylimidazolyl rings may result in subtle changes affecting the tendency toward hydration, in particular the geometry of the chelate rings, and thus an investigation of the co-ordination behaviour of these ketones has been undertaken. As the major aim of the study is further to elucidate reasons for the hydration behaviour, copper(II) sulphate was used under conditions that readily gave the first isolated dpk·H$_2$O complex, [Cu(dpk·H$_2$O)$_2$(SO$_4$)],[2] and dimethylgold(III) nitrate was studied in view of a recent crystallographic characterization of [AuCl$_2$(dpk·H$_2$O)]Cl[9] and our current interest in the co-ordination chemistry of Au^{III}Me$_2$ with multidentate ligands.[14]



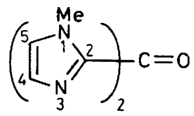
dpk



dpk·H$_2$O



pik



dik

Experimental

The ligand dpk was used as received (Aldrich), and the ligands pik and dik were prepared as described previously.[12] Dimethylgold(III) iodide was prepared from trichloro(pyridine)gold(III),[15] which was obtained from laboratory residues of gold as described previously.[14]

The Au^{III}Me$_2$ complexes were obtained in moderate yield (37—63%) by a similar procedure to that described for other complexes [AuMe$_2$(L)]NO$_3$,[14] involving reaction of equimolar quantities of Au^{III}Me$_2$ nitrate and neutral ligand (L) in water, followed by slow evaporation at ambient temperature, collection of product by filtration, and recrystallization from methanol–water (1:1) (L = dpk·H$_2$O), chloroform–benzene (pik), or chloroform–ethyl acetate (dik).

Green crystals of [Cu(dik)(SO$_4$)]·2H$_2$O were obtained on slow evaporation of an aqueous solution (25 cm^3) containing CuSO$_4$·5H$_2$O (0.504 g, 2 mmol) and dik (1.462 g, 6 mmol), and were recrystallized from water and dried under vacuum over

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† *Supplementary data available* (No. SUP 56161, 8 pp.): H-atom co-ordinates for [AuMe$_2$(dpk·H$_2$O)]NO$_3$, least-squares planes, thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Analytical and spectroscopic data

	Analysis^a (%)					
Complex	C	H	N	$\nu(CO)^{b,c}$/cm^{-1}	$\nu(NO_3)$ or $\nu(SO_4)^b$/cm^{-1}	^{1}H N.m.r. $\delta(AuMe_2)^d$
$[AuMe_2(dpk{\cdot}H_2O)]NO_3$	32.2	3.1	8.6	^{e}	1 395	1.38^f
	(31.8)	(3.3)	(8.6)			
$[AuMe_2(pik)]NO_3$	30.0	3.2	11.7	1 657	1 397	1.29, 1.43^g
	(30.3)	(3.2)	(11.8)			
$[AuMe_2(dik)]NO_3$	27.6	3.1	14.7	1 645	1 395	1.27^h
	(27.6)	(3.4)	(14.6)			
$[Cu(pik)(SO_4)]{\cdot}0.5H_2O$	34.0	2.6	12.0	1 660	1 121	
	(33.8)	(2.8)	(11.8)			
$[Cu(dik)(SO_4)]{\cdot}2H_2O$	27.6	3.3	15.1	1 634	1 119	
	(28.0)	(3.7)	(14.5)			
$[Ni(dpk{\cdot}H_2O)_2(NO_3)_2]{\cdot}0.5H_2O$	43.9	3.7	14.5		1 385	
	(44.3)	(3.6)	(14.1)			
$[Ni(pik)_2(NO_3)_2]{\cdot}0.5H_2O$	42.2	3.0	20.4	1 670	1 414	
	(42.4)	(3.4)	(19.8)			
$[Ni(dik)_2(NO_3)_2]{\cdot}1.5MeOH$	37.9	4.2	22.9	1 641	1 389	
	(38.3)	(4.3)	(22.9)			

[a] Calculated values are given in parentheses. [b] As KBr discs, all strong absorptions. [c] pik has $\nu(CO) = 1\,657$ cm^{-1}, and dik has $\nu(CO) = 1\,631$ cm^{-1}. [d] In D_2O, chemical shift from sodium 4,4-dimethyl-4-silapentanesulphonate, integration appropriate for formulae presented. [e] $\nu(OH)$ for the $dpk{\cdot}H_2O$ group 3 380br cm^{-1}. [f] 7.67 (m), H(4); 8.20 (m), H(3,5); 8.71 (d), H(6); *J*(5,6) *ca.* 6 Hz. [g] 4.06 (s), *N*-Me; 7.53 (s) and 7.77 (s) H(4′,5′); 8.00 (m), H(4); 8.47 (m), H(3,5); 8.90 (d), H(6); *J*(5,6) *ca.* 5 Hz. [h] 4.12 (s), *N*-Me; 7.46 (s) and 7.74 (s) H(4′,5′).

P_2O_5 (0.347 g, 50%). Purple crystals of $[Ni(dpk{\cdot}H_2O)_2(NO_3)_2]{\cdot}0.5H_2O$ were obtained similarly. For the remaining Cu^{II} and Ni^{II} complexes aqueous solutions of copper(II) sulphate or nickel(II) nitrate and ligand were allowed to evaporate to dryness, followed by dissolution in methanol, filtration, and addition of acetone to precipitate the complexes as green $[Cu(pik)(SO_4)]{\cdot}0{\cdot}5H_2O$, purple $[Ni(dik)_2(NO_3)_2]{\cdot}1.5MeOH$. and blue $[Ni(pik)_2(NO_3)_2]{\cdot}0.5H_2O$.

Infrared spectra (4 000—400 cm^{-1}) of complexes as KBr pellets were recorded with a Digilab FTS.20E Fourier-transform i.r. spectrometer; mass spectra were obtained with a V.G. micromass 7070F spectrometer calibrated with perfluorokerosene; ^{1}H n.m.r. spectra were recorded with a JEOL JNM-4H-100 spectrometer.

Crystallography.—For each complex a unique data set was measured at 295 K with a preset $2\theta_{max.}$ limit determined by the extent of the data; Syntex $P\bar{1}$(Au complex) and $P2_1$(Cu complex) diffractometers fitted with monochromatic Mo-K_α radiation sources ($\lambda = 0.710\,69$ Å) were used in conventional 2θ—θ scan mode, yielding N independent reflections, N_o of these with $I > 2\sigma(I)$ (Au complex) or $I > 3\sigma(I)$ (Cu complex) considered 'observed' and used in the full-matrix least-squares refinement {weights, $w = [\sigma^2(F_o) + 0.0005\ (F_o)^2]^{-1}$} after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were used for the non-hydrogen atoms, for the Au complex hydrogen atom parameters were constrained at idealized estimates; and for the Cu complex ($x, y, z, U_{iso.}$) were also refined for the hydrogen atoms. Residuals quoted for convergence are conventional R and R'. Neutral-atom scattering factors were corrected for anomalous dispersion (f', f'').[16-18]

Computation used the *X*-RAY 76 program system implemented by S. R. Hall on a Perkin-Elmer 3240 computer.[19] The results are given in Tables 2—6 and Figures 1—3.

Table 2. Non-hydrogen atom co-ordinates for $[AuMe_2(dpk{\cdot}H_2O)]NO_3$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Au	0.395 88(4)	0.263 81(5)	0.332 81(2)
C(A)	0.592 8(13)	0.269 4(17)	0.382 6(7)
C(B)	0.472 8(14)	0.452 2(16)	0.277 6(7)
Ligand, ring a			
N(1)	0.186 0(9)	0.253 4(10)	0.282 2(4)
C(2)	0.069 7(11)	0.251 2(12)	0.310 6(4)
C(3)	−0.066 8(12)	0.233 6(14)	0.280 2(5)
C(4)	−0.083 1(15)	0.215 4(15)	0.217 7(6)
C(5)	0.034 8(14)	0.219 2(15)	0.187 4(5)
C(6)	0.166 9(13)	0.238 3(13)	0.220 4(5)
Ligand, ring b			
N(1)	0.315 1(8)	0.069 1(10)	0.390 0(4)
C(2)	0.178 9(11)	0.088 2(13)	0.405 6(5)
C(3)	0.119 9(12)	−0.040 6(15)	0.439 7(5)
C(4)	0.202 9(14)	−0.191 4(16)	0.461 1(5)
C(5)	0.338 4(14)	−0.208 1(15)	0.447 9(6)
C(6)	0.392 5(12)	−0.074 0(15)	0.411 8(5)
Ligand, central atoms			
C	0.098 3(11)	0.258 7(12)	0.380 9(5)
O(1)	−0.031 5(8)	0.267 9(10)	0.404 6(4)
O(2)	0.181 3(8)	0.414 3(9)	0.397 2(3)
Anion			
N	0.245 3(11)	0.167 3(14)	0.049 4(5)
O(3)	0.323 2(9)	0.149 2(13)	0.007 7(4)
O(4)	0.289 7(13)	0.245 0(14)	0.096 7(5)
O(5)	0.121 9(10)	0.103 8(14)	0.040 8(5)

Crystal data for $[AuMe_2(dpk{\cdot}H_2O)]NO_3$. $C_{13}H_{16}AuN_3O_5$, $M = 491.3$, monoclinic, space group $P2_1/c$ (C_{2h}^5, no. 14), $a = 9.41(1)$, $b = 7.328(7)$, $c = 22.17(2)$ Å, $\beta = 97.85(8)°$, $U = 1\,515(2)$ Å^3, $D_m = 2.14(1)$, $Z = 4$, $D_c = 2.15$ g cm^{-3}, $F(000) = 936$. Specimen: $0.30 \times 0.22 \times 0.14$ mm, $\mu(\text{Mo-}K_\alpha) = 97$ cm^{-1}, $2\theta_{max.} = 50°$, $N = 2\,670$, $N_o = 2\,031$ with $I > 2\sigma(I)$, $R = 0.045$, $R' = 0.051$.

Crystal data for $[Cu(dik)(SO_4)]{\cdot}2H_2O$. $C_9H_{14}CuN_4O_7S$, $M = 389.9$, monoclinic, space group $P2_1/n$ [C_{2h}^5, no. 14 (variant)], $a = 11.982(3)$, $b = 13.803(3)$, $c = 8.866(2)$ Å, $\beta = 107.30(2)°$, $U = 1\,400.0(5)$ Å^3, $D_m = 1.83(1)$, $Z = 4$, $D_c = 1.83$

Table 3. Atom co-ordinates for $[Cu(dik)(SO_4)]\cdot 2H_2O$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Copper, water, and sulphate groups			
Cu	0.262 73(1)	0.503 85(1)	0.574 13(2)
O(2)	0.189 1(1)	0.388 9(1)	0.701 3(2)
H(21)	0.233(2)	0.339(2)	0.718(3)
H(22)	0.135(2)	0.361(2)	0.647(3)
O(3)	0.126 4(1)	0.519 9(1)	0.380 9(2)
H(31)	0.093(2)	0.572(2)	0.391(3)
H(32)	0.072(3)	0.476(2)	0.336(4)
S	0.097 59(3)	0.666 99(3)	0.652 51(5)
O(4)	0.211 0(1)	0.616 8(1)	0.668 7(2)
O(5)	0.124 1(1)	0.764 0(1)	0.717 3(2)
O(6)	0.031 2(1)	0.613 7(1)	0.739 3(2)
O(7)	0.031 5(1)	0.670 7(1)	0.482 3(2)
Ligand, ring a			
C(1)	0.729 6(1)	0.479 8(2)	0.927 6(3)
C(2)	0.519 7(1)	0.475 9(1)	0.741 9(2)
C(4)	0.448 5(1)	0.598 2(1)	0.837 1(2)
C(5)	0.563 7(1)	0.590 6(1)	0.922 3(2)
N(1)	0.608 1(1)	0.513 9(1)	0.862 6(2)
N(3)	0.420 9(1)	0.526 9(1)	0.725 9(2)
H(4)	0.391(2)	0.641(2)	0.845(3)
H(5)	0.605(2)	0.632(2)	1.012(3)
H(11)	0.777(2)	0.486(2)	0.842(3)
H(12)	0.725(3)	0.413(3)	0.968(4)
H(13)	0.769(3)	0.520(2)	1.001(4)
Ligand, ring b			
C(1)	0.538 7(2)	0.214 9(2)	0.438 4(3)
C(2)	0.435 1(1)	0.360 0(1)	0.517 1(2)
C(4)	0.261 3(1)	0.336 8(2)	0.358 5(2)
C(5)	0.330 8(2)	0.265 4(2)	0.329 5(2)
N(1)	0.440 4(1)	0.280 5(1)	0.429 3(2)
N(3)	0.326 8(1)	0.396 4(1)	0.474 1(2)
H(4)	0.182(2)	0.346(2)	0.314(3)
H(5)	0.316(2)	0.216(2)	0.262(3)
H(11)	0.605(2)	0.256(2)	0.428(3)
H(12)	0.560(3)	0.183(2)	0.551(4)
H(13)	0.513(2)	0.172(2)	0.343(3)
Ligand, central atoms			
C	0.536 3(1)	0.397 3(1)	0.641 5(2)
O	0.633 6(1)	0.363 7(1)	0.656 8(2)

g cm^{-3}, $F(000) = 788$. Specimen: 0.16 × 0.16 × 0.40 mm, $\mu(\text{Mo-}K_\alpha) = 18.1$ cm^{-1}, $2\theta_{\max.} = 65°$, $N = 6\,453$, $N_o = 4\,754$ with $I > 3\sigma(I)$, $R = 0.032$, $R' = 0.043$.

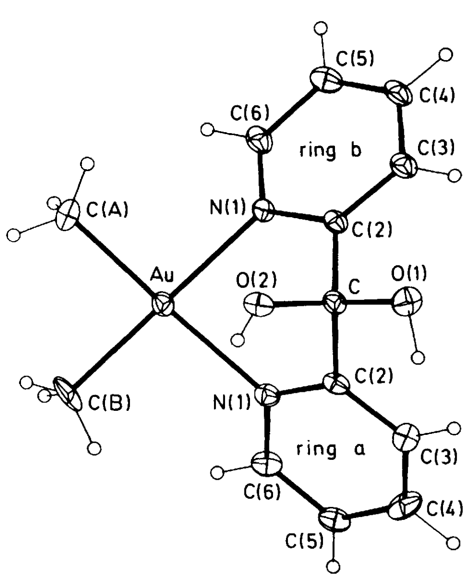

Figure 1. Projection of $[AuMe_2(dpk\cdot H_2O)]NO_3$ normal to the co-ordination plane, showing 20% thermal ellipsoids for the non-hydrogen atoms, and an arbitrary radius of 0.1 Å for the hydrogen atoms

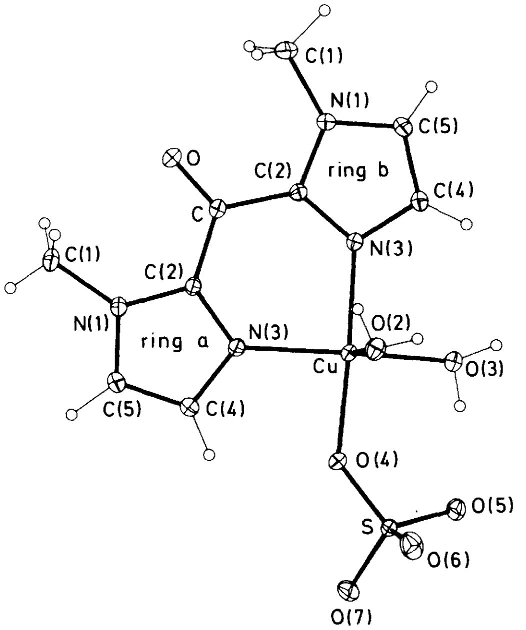

Figure 2. Projection of $[Cu(dik)(SO_4)]\cdot 2H_2O$ normal to the co-ordination plane; see caption to Figure 1

Results

Preparation and Characterization of Complexes.—The complexes $[AuMe_2(L)]NO_3$ (L = dpk·H_2O, pik, or dik), $[Ni(dpk\cdot H_2O)_2(NO_3)_2]\cdot 0.5H_2O$, and $[Cu(dik)(SO_4)]\cdot 2H_2O$ were obtained from addition reactions in water, using metal:ligand ratios of 1:1, 1:2, and 1:3 respectively. The $Au^{III}Me_2$ complexes were recrystallized from non-aqueous solvents, with i.r. absorption unchanged by recrystallization. The remaining Cu^{II} and Ni^{II} complexes were obtained on evaporation of aqueous solutions of metal salt and ligand to dryness, followed by recrystallization from methanol–acetone. The crude products from aqueous solution have i.r. spectra with absorptions characteristic of the complexes after recrystallization. Drying over P_2O_5 also does not alter the i.r. absorptions, indicating that $[Cu(dik)(SO_4)]\cdot 2H_2O$ and those complexes formulated as hemihydrates have firmly bound water, presumably co-ordinated and/or hydrogen bonded.

For the Cu^{II} and Ni^{II} complexes microanalyses are consistent with metal:ligand ratios 1:1 and 1:2, respectively (Table 1), with solvate formation required to account for microanalyses, and confirmed by the presence of ν(OH) absorption in i.r. spectra, a high-resolution mass spectrum of $[Ni(dik)_2(NO_3)_2]\cdot 1.5$ MeOH exhibiting an ion with *m/e* 31.0183 corresponding to CH_3O^+, and the *X*-ray structural analysis for $[Cu(dik)(SO_4)]\cdot 2H_2O$.

Infrared spectra of the complexes exhibit absorptions for the ligand shifted from those of the free ligand. The $Au^{III}Me_2$ and

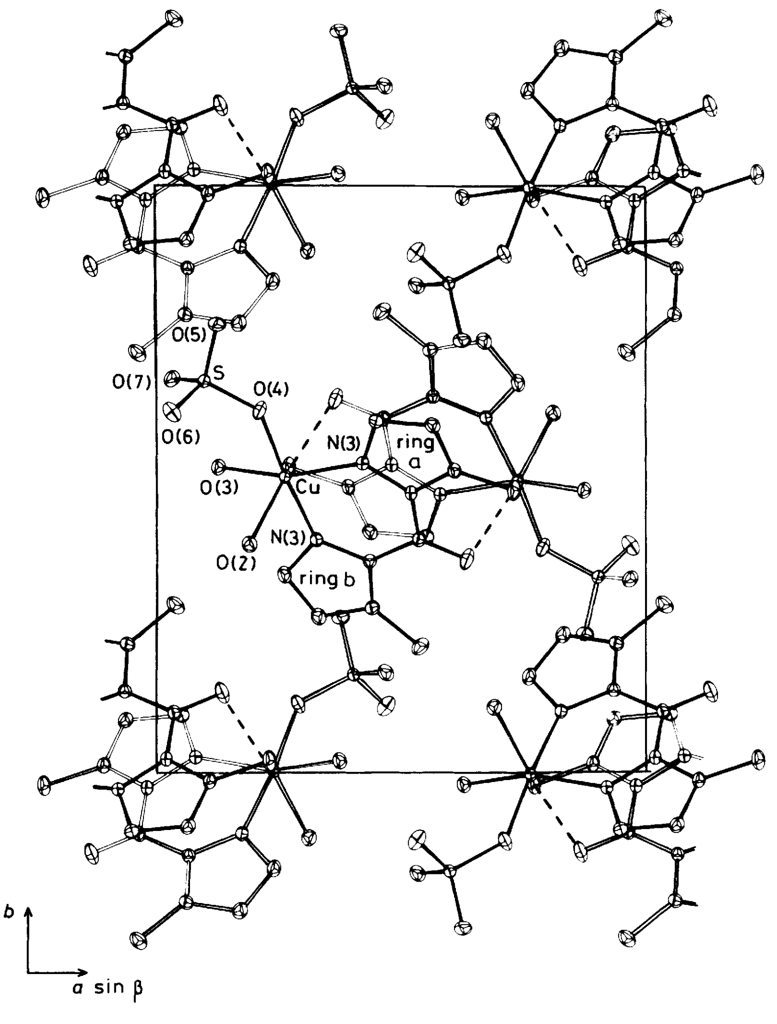

Figure 3. Unit-cell contents of $[Cu(dik)(SO_4)]\cdot 2H_2O$, showing a different view of the co-ordination geometry of the copper atom, and weak Cu $\cdots$ O(ketone) interactions linking the complexes into centrosymmetric dimeric units; see caption to Figure 1

Ni^{II} complexes formed on reaction with dpk have the ligands present as the geminal diol: $[AuMe_2(dpk\cdot H_2O)]NO_3$ and $[Ni(dpk\cdot H_2O)_2(NO_3)_2]\cdot 0.5H_2O$. Thus, they do not exhibit i.r. bands in the region expected for ν(C=O) absorption (1 682 cm^{-1} for dpk), with the nearest i.r. absorptions at 1 605 and 1 607 cm^{-1}, respectively, assigned as a pyridine mode raised from 1 582 cm^{-1} on co-ordination, as observed earlier on complex formation involving hydration of dpk.[2,3,6,10] In contrast, for the six complexes involving reactions of pik and dik an absorption attributable to ν(C=O) occurs in the range 1 641—1 670 cm^{-1}, with absorption frequency increased 3—13 cm^{-1} from the values for the free ligands, except for $[AuMe_2(pik)]NO_3$ which has ν(C=O) unaltered (Table 1).

Proton n.m.r. spectra for the Au^{III}Me$_2$ complexes have appropriate integration for the presence of ions $[AuMe_2(L)]^+$ with *N,N*-chelated ligands (Table 1). Thus, the complex $[AuMe_2(pik)]NO_3$ has two environments for the methyl groups bonded to gold (1.29 and 1.43 p.p.m.), one of these is *trans* to a pyridyl donor group with a similar chemical shift to $[AuMe_2(dpk\cdot H_2O)]NO_3$ (1.38 p.p.m.) and the other *trans* to an *N*-methylimidazolyl group with a similar chemical shift to $[AuMe_2(dik)]NO_3$ (1.27 p.p.m.).

Structures of $[AuMe_2(dpk\cdot H_2O)]NO_3$ *and* $[Cu(dik)(SO_4)]\cdot 2H_2O$ *in the Solid State*.—Aspects of the molecular geometry of the complexes are given in Tables 4 and 5, and views of the structures in Figures 1—3.

The Au^{III}Me$_2$ complex is composed of cations $[AuMe_2(dpk\cdot H_2O)]^+$ and regular (within 2σ in bond lengths and angles) nitrate ions which are well removed from the gold atom (shortest Au $\cdots$ O distance for a nitrate oxygen is 4.08 Å). The square-planar 'AuC_2N_2' kernel has bond lengths and angles within 1σ of those for the closely related tri-2-pyridylmethane (tpm) complex $[AuMe_2(tpm)]NO_3\cdot 2H_2O$ where the ligand is also *N,N*-chelated, with one unco-ordinated pyridyl group.[14] The $AuNC_3N$ ring has a boat conformation essentially identical to that for $[AuCl_2(dpk\cdot H_2O)]Cl$. A hydroxy group of the geminal diol ligand is situated near the gold atom, with Au $\cdots$ O(2) 2.850(8) Å, slightly longer than in the Au^{III}Cl$_2$ complex, 2.77(1) Å.[9] This may represent a weak co-ordination interaction, although the hydroxy group may be constrained in this position by the most favourable conformation of the $AuNC_3N$ ring. The planar pyridyl rings (maximum deviation 0.02 Å from mean planes) form dihedral angles of 44.9° (ring a) and 41.5° (ring b) with the mean AuC_2N_2 plane.

The complex $[Cu(dik)(SO_4)]\cdot 2H_2O$ has a square-pyramidal co-ordination geometry, with the ligand *N,N*-chelated [Cu–N 1.995(1), 1.997(2) Å] together with a unidentate sulphate group [Cu–O(4) 1.957(2) Å] and a water molecule [Cu–O(3) 1.997(1)

Table 4. Non-hydrogen geometries for $[AuMe_2(dpk{\cdot}H_2O)]NO_3$, with estimated standard deviations in parentheses

Co-ordination geometry

Au–C(A)	2.02(1)	C(A)–Au–C(B)	86.5(5)
Au–C(B)	2.04(1)	C(A)–Au–N(b1)	93.7(4)
Au–N(a1)	2.136(9)	C(B)–Au–N(a1)	95.0(4)
Au–N(b1)	2.118(8)	N(a1)–Au–N(b1)	84.7(3)
Au · · · O(2)	2.850(8)	C(A)–Au–N(a1)	178.4(6)
		C(B)–Au–N(b1)	179.7(4)

Ligand geometry

C–O(1)	1.40(1)	O(1)–C–O(2)	110.4(8)
C–O(2)	1.40(1)	C(a2)–C–C(b2)	110.1(8)

	Ring a	Ring b
C(2)–N(1)	1.34(1)	1.38(1)
C(2)–C(3)	1.37(1)	1.37(1)
C(3)–C(4)	1.38(2)	1.40(2)
C(4)–C(5)	1.37(2)	1.35(2)
C(5)–C(6)	1.36(2)	1.41(2)
C(6)–N(1)	1.36(1)	1.33(1)
C–C(2)	1.55(1)	1.52(1)
Au–N(1)–C(2)	120.8(7)	120.3(6)
Au–N(1)–C(6)	121.1(8)	121.7(7)
C(2)–N(1)–C(6)	118.0(9)	118.1(9)
N(1)–C(2)–C(3)	122.9(9)	121.9(9)
N(1)–C(2)–C	115.7(8)	115.2(8)
C(3)–C(2)–C	121.3(10)	122.9(10)
C(2)–C(3)–C(4)	118.0(11)	118.7(11)
C(3)–C(4)–C(5)	120.2(11)	119.9(11)
C(4)–C(5)–C(6)	118.6(11)	119.1(11)
C(5)–C(6)–N(1)	122.3(11)	122.3(11)
C(2)–C–O(1)	109.9(8)	108.8(8)
C(2)–C–O(2)	107.7(8)	109.9(8)

Anion

N–O(3)	1.26(1)	O(3)–N–O(4)	121(1)
N–O(4)	1.22(1)	O(3)–N–O(5)	118(1)
N–O(5)	1.24(1)	O(4)–N–O(5)	121(1)

Å] forming the basal plane, CuN_2O_2, with maximum deviation from the mean plane occurring for N(a3), 0.19 Å. Angles within the square plane are within the range 86.70(6)—91.50(6)°, with the ligand forming a N–Cu–N angle of 90.25(5)°. A more weakly bound axial water molecule [Cu–O(2) 2.271(1) Å] completes the square-pyramidal geometry, although a very weak interaction with the oxygen atom of a ketone group in a neighbouring complex, also axial [Cu · · · O 3.254(2) Å], links the complexes into centrosymmetric dimeric units (Figure 3). There is also a complex hydrogen-bonding network, linking water molecules, sulphate groups, and ketone oxygen atoms.

The imidazolyl rings are planar, and the copper atom lies only −0.047 and −0.180 Å from the mean planes of ring a and b, respectively. The CuN_2O_2 square plane forms dihedral angles of 9.5 and 12.1° with rings a and b, respectively. The ketone ligand is planar as the imidazolyl rings form a dihedral angle of only 3.1°, the ketone carbon atom lies 0.106 and −0.045 Å from rings a and b, and the ketone oxygen atom is 0.256 and 0.098 Å from these ring planes, respectively.

With one axially bonded water molecule and the sulphate group bonded within the square plane, $[Cu(dik)(SO_4)]{\cdot}2H_2O$ differs from related Cu^{II} complexes with bidentate nitrogen donor ligands $[Cu(L)(SO_4)]{\cdot}2H_2O$ (L = 2,2′-bipyridyl,[20] ethylenediamine,[21] or 1,10-phenanthroline[22]), as these complexes have both water molecules bonded within the square plane with bridging sulphate groups bonded axially to give a polymeric and distorted-octahedral geometry for Cu^{II}.

Table 5. Non-hydrogen geometries for $[Cu(dik)(SO_4)]{\cdot}2H_2O$, with estimated standard deviations in parentheses

Co-ordination geometry

Cu–N(a3)	1.997(2)	N(a3)–Cu–N(b3)	90.25(5)
Cu–N(b3)	1.995(1)	N(a3)–Cu–O(2)	101.98(6)
Cu–O(2)	2.271(2)	N(a3)–Cu–O(3)	158.56(5)
Cu–O(3)	1.997(1)	N(a3)–Cu–O(4)	86.70(6)
Cu–O(4)	1.957(2)	N(b3)–Cu–O(2)	87.65(6)
		N(b3)–Cu–O(3)	91.50(6)
		N(b3)–Cu–O(4)	174.75(7)
		O(2)–Cu–O(3)	99.44(5)
		O(2)–Cu–O(4)	97.16(6)
		O(3)–Cu–O(4)	89.79(6)

Ligand geometry

C–O	1.224(2)	C(a2)–C–C(b2)	119.2(1)

	Ring a	Ring b
C(1)–N(1)	1.475(2)	1.469(3)
C(2)–N(1)	1.367(2)	1.358(2)
C(2)–N(3)	1.348(2)	1.337(2)
C(4)–N(3)	1.363(2)	1.366(2)
C(4)–C(5)	1.366(2)	1.364(3)
C(5)–N(1)	1.360(3)	1.364(2)
C(2)–C	1.455(3)	1.468(2)
Cu–N(3)–C(2)	128.0(1)	128.5(1)
Cu–N(3)–C(4)	125.5(1)	124.7(1)
C(2)–N(3)–C(4)	106.5(1)	106.3(1)
C–C(2)–N(1)	123.4(1)	123.0(1)
C–C(2)–N(3)	127.0(1)	126.7(2)
N(1)–C(2)–N(3)	109.5(2)	110.3(1)
C(1)–N(1)–C(2)	128.9(2)	129.8(1)
C(1)–N(1)–C(5)	123.4(2)	122.9(2)
C(2)–N(1)–C(5)	107.6(1)	107.2(1)
N(3)–C(4)–C(5)	109.4(2)	109.2(2)
C(4)–C(5)–N(1)	107.0(2)	106.9(2)
C(2)–C–O	120.9(1)	119.8(2)

Sulphate group

S–O(4)	1.493(1)	Cu–O(4)–S	136.37(8)
S–O(5)	1.455(2)	O(4)–S–O(5)	107.68(8)
S–O(6)	1.460(2)	O(4)–S–O(6)	109.76(9)
S–O(7)	1.482(1)	O(4)–S–O(7)	108.03(9)
		O(5)–S–O(6)	110.19(11)
		O(5)–S–O(7)	110.99(8)
		O(6)–S–O(7)	110.13(9)

Hydrogen bonding (O · · · H <2.4 Å)

O(4) · · · H(a4)	2.28(2)	O(7) · · · H(31)	1.85(3)
O(6) · · · $H(32^{i})$	1.73(3)	O(7) · · · $H(22^{i})$	2.03(3)
O(5) · · · $H(21^{ii})$	1.94(3)	O · · · $H(b5^{iii})$	2.38(2)
O(5) · · · $H(a5^{iv})$	2.28(2)		

i ($\bar{x}$, $1 - y$, $1 - z$); ii ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $1\frac{1}{2} - z$); iii ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$); iv ($x - \frac{1}{2}$, $1\frac{1}{2} - y$, $z - \frac{1}{2}$).

Discussion

Di-2-pyridyl ketone reacts with $Au^{III}Me_2$ and nickel(II) nitrate in water to form complexes involving hydration of dpk and co-ordination as $dpk{\cdot}H_2O$. However, the ketones containing imidazolyl rings (pik and dik) react with $Au^{III}Me_2$, copper(II) and nickel(II) nitrate under identical conditions to form complexes of the ketones without hydration.

These results are consistent with the proposal that dpk readily hydrates so that a six-membered chelate ring $\overline{\text{MNCC(OH)}_2\text{CN}}$ with a conventional and stable boat conformation can be obtained, rather than that expected for dpk co-ordination where typical M–N distances of *ca.* 2.0 Å require either disruption of planarity of the ketone with loss of carbonyl conjugation[9,11] or retention of planarity with poor overlap of nitrogen lone pairs with metal orbitals. Replacement of pyridyl rings with imidazolyl rings, having smaller angles within the ring, is expected to increase the distance between the nitrogen-donor atoms, and to give direction of nitrogen lone pairs more consistent with M–N distances of *ca.* 2.0 Å and N–M–N angles of *ca.* 90°. Thus, in $[Cu(dik)(SO_4)]\cdot 2H_2O$, the ketone is planar with N–Cu–N 90.25(5)° and the lone pairs are directed toward the copper atom with similar Cu–N(3)–C(2,4) angles of 124.7(1)—128.5(1)°. Although the results of this investigation are consistent with this view, and thus support previous suggestions regarding the reason for hydrolysis of dpk on complex formation, other factors may be important in this study. In particular, replacement of pyridyl groups by imidazolyl groups may affect the properties of the ketones obtained in other ways, *e.g.* alteration in the extent of conjugation. In addition, dpk does form many complexes where hydration does not occur, *e.g.* palladium(II) chloride forms both $[PdCl_2(dpk\cdot H_2O)]$ and $[PdCl_2(dpk)]$,[9] and zinc(II) bromide forms 1:1 complexes with both dpk[7] and bis(4,5-di-isopropyl-*N*-methyl-2-imidazolyl) ketone.[23] The latter complex has N–Zn–N 91.3(4)°,[23] similar to that of the copper(II) complex of dik, 90.25(5)°.

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