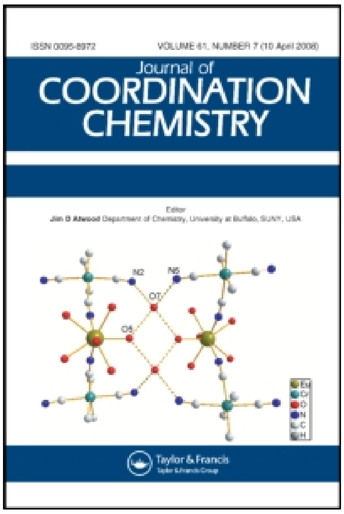

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NUCLEOPHILIC ADDITION OF WATER AND ETHANOL TO COORDINATED DI-(2-PYRIDYL)KETONE IN RHENIUM(V) AND TECHNETIUM(V) COMPLEXES. THE CRYSTAL STRUCTURE OF DICHLORO(HYDROXY-DI-(2-PYRIDYL)METHOXIDE)OXORHENIUM(V)

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NUCLEOPHILIC ADDITION OF WATER AND ETHANOL TO COORDINATED DI-(2-PYRIDYL)KETONE IN RHENIUM(V) AND TECHNETIUM(V) COMPLEXES. THE CRYSTAL STRUCTURE OF DICHLORO(HYDROXY-DI-(2-PYRIDYL)METHOXIDE)OXORHENIUM(V)

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Complexes of general formula $MOCl_2[(C_5H_4N)_2C(O)(OR)]$ (M = Re, Tc; R = H, Et) were prepared by the reaction of *trans*-$ReOCl_3(PPh_3)_2$ and (n-Bu_4N)[$TcOCl_4$] with di-(2-pyridyl)ketone (DPK) in ethanol (R = Et) under nitrogen and in benzene, containing trace amounts of water, in air (R = H). The compounds were characterized by elemental analysis, vibrational, optical and proton nuclear magnetic resonance spectroscopy. The evidence suggests that the coordinated DPK ligand has undergone addition of water and ethanol at the carbonylic carbon atom, and that the $(C_5H_4N)_2C(O)(OR)$ moiety acts as a uninegative, terdentate N,O,N-donor ligand. The X-ray crystal structure of the complex $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$ is also reported. Crystal data: $C_{11}H_9N_2O_3Cl_2Re$, orthorhombic, space group *Pcca*; $a = 14.935(5)$, $b = 11.896(8)$, $c = 14.937(11)$Å, and $U = 2653.8$ (2.7)Å^3 to give $Z = 8$ for $D_{calc} = 2.37$ g cm^{-3}. The structure was solved by Patterson and Fourier methods and refined by least-squares methods to $R = 0.076$. The complex has an Re=O bond distance of 1.67(2)Å, and a deprotonated diolate oxygen of the ligand is coordinated in the position *trans* to the oxo group.

KEY WORDS: Rhenium(V), technetium(V), di-(2-pyridyl)ketone, crystal structure.

INTRODUCTION

The molecule di-(2-pyridyl)ketone (DPK; Figure 1) presents interesting possibilities in the rapidly expanding field of reactions of coordinated ligands. The base may potentially coordinate through both nitrogen atoms (N,N-chelation), or through one pyridyl group together with the carbonyl group (N,O-chelation). DPK also has the ability to undergo metal-promoted addition of various nucleophiles (HX), including

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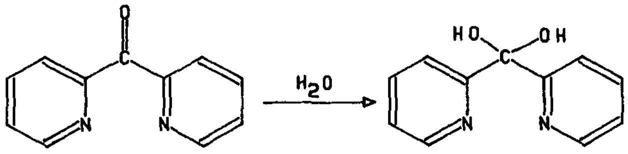

Figure 1 Di-(2-pyridyl)ketone (DPK) and "DPK-hydrate".

water, at the carbon atom of the carbonyl group to produce the corresponding condensation product $(C_5H_4N)_2C(OH)(X)$ after initial coordination to a transition metal ion.[1-4] A consequence of, for example, ketone hydration in N,N-chelated DPK is that one of the two oxygen atoms of the resultant *geminal* diols at the sp^3 hybridized carbon atom will necessarily occupy a position close to one of the octahedral coordination sites at right angles to the MN_2 plane. This would probably lead to steric interaction with any ligand in that position, or alternatively, with steric strain, the oxygen atom in question may coordinate to the metal ion, with the ligand now behaving as a terdentate. It is of course also possible that the deprotonation of a *geminal* diol group may lead to a rearrangement of the binding sites, i.e., from a six-membered N,N-chelate to a five-membered N,O-chelate. These possibilities kindled our interest in the coordination behaviour of DPK.

This paper deals with the synthesis and characterization of oxotechnetium(V) and oxorhenium(V) complexes of DPK, in which the ketone group underwent nucleophilic addition of water and ethanol. A crystal structure determination of the complex dichloro(hydroxy-di-(2-pyridyl)methoxide)oxorhenium(V),$ReOCl_2$-$[(C_5H_4N)_2C(O)(OH)]$, shows that $(C_5H_4N)_2C(O)(OH)$ behaves as a uninegative terdentate ligand, with coordination through both pyridyl nitrogen atoms and a deprotonated oxygen of one of the *geminal* diols.

EXPERIMENTAL

Health Precautions

All references to technetium in this paper are to the isotope ^{99}Tc, which is a β-emitter (0.292 MeV) with a half-life of 2.12×10^5 years. Normal glassware gives adequate protection against this weak β-emission if the material is handled in milligram amounts. Secondary bremsstrahlung (X-rays) only presents a health hazard with larger amounts of technetium. Normal radiation safety procedures must be applied at all times, especially with the handling of solid samples, to prevent contamination and inhalation.

Materials

The compounds $(n\text{-}Bu_4N)[TcOCl_4]$[5] and *trans*-$ReOCl_3(PPh_3)_2$[6] were prepared according to literature procedures. DPK was obtained commercially (Aldrich), and was recrystallized from diethylether. All solvents were of analytical grade and were purified and dried by standard methods.[7] All common laboratory chemicals were of analytical grade and were used without further purification.

Apparatus

Scientific instrumentation used in this study is the same as reported elsewhere.[8]

Synthesis of the Complexes

$ReOCl_2[(C_5H_4N)_2C(O)(OEt)]$

To 200 mg (240 μmol) of *trans*-$ReOCl_3(PPh_3)_2$ in 10 cm^3 of ethanol was added 90 mg (490 μmol) of DPK in 5 cm^3 ethanol. The reaction mixture was heated under reflux for 30 min under nitrogen, during which time its colour changed from orange-yellow to blue. After cooling to room temperature, the blue precipitate was collected by filtration, was washed with ethanol, benzene and diethyl ether, and dried under vacuum. It was recrystallized from acetonitrile to give a yield of 73%; mp 275°C. Anal. Calcd. for $C_{13}H_{13}N_2O_3Cl_2Re$: C, 31.08; H, 2.61; N, 5.58; Cl, 14.11%. Found: C, 31.04; H, 2.77; N, 5.56; Cl, 14.24%. Conductivity (10^{-3} M, DMF): 5.7 ohm^{-1} cm^2 mol^{-1}. Infrared data (cm^{-1}, KBr): υ(Re=O) 966; υ(C-O) 1281; υ(py) 1606. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ(ppm) 7.80–8.49 (m, 8H, C_5H_4N); 1.33 (t, 3H, CH_3CH_2O); 3.67 (q, 2H, CH_3CH_2O). Electronic spectrum (DMF) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 385 (2250), 350 (2400), 327sh (1940), 276 (3670).

$ReOCl_2[(C_5H_4N)_2C(O)(OH)]$

A mixture of 200 mg of *trans*-$ReOCl_3(PPh_3)_2$ and 90 mg of DPK was heated under reflux in air for 30 min in 20 cm^3 of benzene containing 0.02% water. After cooling to room temperature, the blue precipitate was collected by filtration, and was washed with benzene and dichloromethane. It was recrystallized from acetonitrile to give a yield of 77%; mp 288°C. Anal. Calc. for $C_{11}H_9N_2O_3Cl_2Re$: C, 27.86; H, 1.91; N, 5.91; Cl, 14.95%. Found: C, 27.80; H, 2.10; N, 5.62; Cl, 14.76%. Conductivity (10^{-3} M, DMF): 12.5 ohm^{-1} cm^2 mol^{-1}. Infrared data (cm^{-1}, KBr): υ(Re=O) 955; υ(C-O) 1304; υ(py) 1616; υ(O-H) 3395. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ(ppm) 7.77–8.45 (m, 8H, C_5H_4N); 9.50 s, 1H, OH). Electronic spectrum (DMF) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 384 (2700), 349 (2700), 321sh (2100), 273 (4800).

$TcOCl_2[(C_5H_4N)_2C(O)(OEt)]$

To a solution of 100 mg (200 μmol) of (n-Bu_4N)[$TcOCl_4$] in 12 cm^3 of ethanol was added 75 mg (408 μmol) of DPK in 5 cm^3 ethanol. The mixture was heated under reflux for 30 min under nitrogen. After cooling to room temperature, a dark green precipitate was collected from the green solution. The material was washed with ethanol, benzene and diethyl ether, and it was recrystallized from dichloromethane to deliver a yield of 77%; mp 227°C. Anal. Calcd. for $C_{13}H_{13}N_2O_3Cl_2Tc$: C, 37.61; H, 3.16; N, 6.75; Cl, 17.08%. Found: C, 37.65; H, 3.47; N, 6.82; Cl, 16.99%. Conductivity (10^{-3} M, DMF): 4.6 ohm^{-1} cm^2 mol^{-1}. Infrared data (cm^{-1}, KBr): υ(Tc=O) 947; υ(C-O) 1281; υ(py) 1601. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ(ppm) 7.79–8.79 (m, 8H, C_5H_4N); 1.31 (t, 3H, CH_3CH_2O); 3.60 (q, 2H, CH_3CH_2O). Electronic spectrum (DMF) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 315sh (3900), 268 (7800).

$TcOCl_2[(C_5H_4N)_2C(O)(OH)]$

This compound was prepared in a similar way to the rhenium analogue. The green crystalline precipitate was recrystallized from acetonitrile in a yield of 73%; mp 205°C.

Anal. Calcd. for $C_{11}H_9N_2O_3Cl_2Tc$: C, 34.13; H, 2.34; N, 7.24; Cl, 18.32%. Found: C, 34.47; H, 2.12; N, 7.20; Cl, 18.54%. Conductivity (10^{-3} M, DMF): 7.7 ohm^{-1} cm^2 mol^{-1}. Infrared data (cm^{-1}, KBr): ν(Tc=O) 939; ν(C-O) 1281; ν(py) 1609; ν(O-H) 3391. ^{1}H n.m.r. [$(CD_3)_2SO$]: δ(ppm) 7.75–8.75 (m, 8H, C_5H_4N); 9.08 (s, 1H, O*H*). Electronic spectrum (DMF) [λ_{max}, nm (ε, M^{-1} cm^{-1})]: 301sh (4100), 260 (10100).

X-ray analysis of $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$

The reaction mother liquors of $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$ yielded some large blue crystal plates (*ca* 0.40 × 0.40 × 0.08 mm), on which very small fragments firmly adhered. Although the crystals gave only poor quality diffraction and attempts to obtain more suitable crystals from acetonitrile were unsuccessful, it was decided to perform an X-ray analysis in order to find out at least the main features of the coordination geometry around the rhenium atom.

Crystal data

$C_{11}H_9N_2O_3Cl_2Re$, $M = 474.3$, orthorhombic, $a = 14.935(5)$, $b = 11.896(8)$, $c = 14.937(11)$Å, $U = 2653.8(2.7)$Å^3; $Z = 8$, $D_c = 2.37$ g cm^{-3}; space group *Pcca*; μ(Mo-K$_\alpha$) = 9.6 cm^{-1}.

Intensity data were recorded on a fully automatic Siemens Nicolet R3m/V diffractometer (Mo-K$_\alpha$ radiation, $\lambda = 0.71073$Å). A total of 3035 independent reflections was measured within the limit $2\theta \leqslant 55°$. Of these, only 1111 (36.6%) unique reflections were considered observed [$|F_o| > 4\sigma(F_o)$] and were used for the structure analysis.

Structure analysis

The structure was solved by standard heavy-atom methods. In the refinement procedure, to ensure a good observation/variable ratio (1111/103) and, to achieve convergence, only Re, Cl and N atoms were refined anisotropically. Full-matrix least-squares refinement, minimizing the function $\sum w(\Delta F)^2$ ($w = 1$), converged with a reliability index R of 0.076. An empirical absorption correction, based on six reflections at $X \simeq 90°$ for different azimuthal angles (ψ-scan), did not improve the results, which, in any case, are sufficient to clarify, without any doubt, the coordination geometry around Re.

Fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table 1, while bond distances and angles around Re are listed in Table 2. Additional data, including non-essential bond lengths and angles, anisotropic thermal parameters and a listing of the observed/calculated structure factors, are available as supplementary material, from the authors, upon request.

The SHELXTL-PLUS package[9] of computer programs was employed for the solution and refinement of the structure.

RESULTS AND DISCUSSION

Synthesis and Characterization

Complexes of general formula $MOCl_2[(C_5H_4N)_2C(O)(OR)]$ (M = Re, Tc; R = H, Et) were prepared in good yield by the reaction of *trans*-$ReOCl_3(PPh_3)_2$ and (n-Bu_4N)[$TcOCl_4$] with DPK in ethanol under nitrogen (R = Et) and in benzene, containing 0.02% water, in air (R = H). The complexes with R = H could also be

Table 1 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}*
Re	1313(1)	2556(2)	494(1)	49(1)
Cl(1)	1125(6)	909(13)	−297(5)	78(5)
Cl(2)	−51(6)	3169(12)	−57(6)	76(4)
O(1)	2013(15)	3323(23)	−128(16)	51(6)
O(2)	769(13)	1901(19)	1601(13)	33(5)
O(3)	1028(15)	1659(22)	3119(15)	49(6)
N(1)	1327(16)	3809(25)	1512(16)	39(9)
N(2)	2404(15)	1842(38)	1225(15)	90(16)
C(1)	1319(20)	3476(27)	2332(18)	34(6)
C(2)	1325(26)	4074(34)	3094(24)	56(9)
C(3)	1290(27)	5213(39)	2938(27)	70(11)
C(4)	1274(27)	5898(37)	2044(27)	61(11)
C(5)	1314(24)	4893(37)	1385(24)	55(9)
C(6)	1304(17)	2100(22)	2359(16)	22(5)
C(7)	2256(18)	1754(30)	2122(19)	34(7)
C(8)	2864(21)	1420(32)	2694(22)	45(8)
C(9)	3718(21)	924(28)	2340(21)	38(7)
C(10)	3865(19)	1081(29)	1483(21)	39(8)
C(11)	3195(21)	1400(30)	872(21)	40(8)

*Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2 Bond lengths (Å) and angles (°) in the inner coordination sphere

	Re-Cl(1)	2.305(4)	
	Re-Cl(2)	2.315(10)	
	Re-O(1)	1.67(2)	
	Re-O(2)	2.00(2)	
	Re-N(1)	2.13(3)	
	Re-N(2)	2.14(3)	
Cl(1)-Re-Cl(2)	88.8(4)	Cl(2)-Re-O(2)	93.4(6)
Cl(1)-Re-N(1)	164.2(8)	N(1)-Re-N(2)	84.6(1.2)
Cl(1)-Re-N(2)	90.9(1.1)	N(1)-Re-O(1)	90.5(1.1)
Cl(1)-Re-O(1)	104.8(9)	N(1)-Re-O(2)	71.8(9)
Cl(1)-Re-O(2)	92.5(7)	N(2)-Re-O(1)	91.4(1.2)
Cl(2)-Re-N(1)	92.4(7)	N(2)-Re-O(2)	74.5(9)
Cl(2)-Re-N(2)	167.9(8)	O(1)-Re-O(2)	158.0(1.0)
Cl(2)-Re-O(1)	100.4(9)		

prepared by using the solvents acetonitrile and dichloromethane, containing trace amounts of water, as reaction media in air. These compounds are diamagnetic, and are non-electrolytes in acetonitrile and DMF. They are weakly soluble in common polar organic solvents, in which they dissolve to give green (M = Tc) and blue solutions (M = Re), which are stable for days. They are stable in the solid state for weeks.

Very intense bands in the solid state infrared spectra of the complexes around 960 and 940 cm^{-1} for the rhenium and technetium compounds respectively are attributed to the stretching frequencies of the M = O group. These frequencies occur in the range normally observed for neutral six-coordinate monooxometalate (M = Re, Tc) complexes.[10] The difference of about 20 cm^{-1} between analogous Re(V) and Tc(V) complexes has been previously observed.[10] Only one distinct band is displayed by the complexes in the range 1600–1616 cm^{-1}, and it is ascribed to the deformation vibrations of the pyridine rings. This increase in the ring frequency from 1579 cm^{-1} in the free DPK ligand has previously been related[1] to N,N-chelation of the ligand in which the ketone group has suffered nucleophilic addition, and which have also been observed in several complexes of DPK-hydrate.[3] The absence of peaks assignable to v(CO) in the infrared spectra (at 1675 cm^{-1} in uncoordinated DPK) of the complexes indicates that, in all cases, the ketone group had undergone reaction. All the complexes exhibit a strong band in the range 1280–1305 cm^{-1}, which we attribute to v(C-O), and the complexes with R = H have an additional broad hydrogen-bonded O-H absorption band at ~3400 cm^{-1}.

The proton nuclear magnetic resonance spectra of the complexes in $(CD_3)_2SO$ show the presence of the eight protons of the pyridine rings in the range δ7.75–8.80 ppm, and illustrate the magnetic equivalence of the corresponding protons in the two pyridine rings in each complex. The spectra in this range consists of two doublets (at ~δ7.9 and 8.8 ppm) and two triplets (at ~δ7.7 and 8.3 ppm). The presence of an ethoxide group in the complexes with R = Et is illustrated by a triplet at ~δ1.3 ppm and a quartet at ~δ3.6 ppm. The complexes at R = H have a broad singlet at δ9.50 and 9.08 ppm for the Re and Tc complex respectively, and illustrate the presence of an enolic proton of the OH group.

Structure of $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$

The structure of $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$ contains discrete, monomeric, neutral monooxorhenium(V) complex units. The $(C_5H_4N)_2C(O)(OH)$ moiety acts as a uninegative, terdentate N,O,N-donor ligand to the rhenium atom, which resides in a highly distorted octahedral environment (Figure 2). The two *cis* chlorides, along with the nitrogen donors, occupy the equatorial sites, with the O(1) oxo ligand *trans* to the O(2) diolate atom. The metal is displaced from the mean plane of the Cl_2N_2 donor set by 0.27Å, towards the oxo-O(1) atom. In the $Cl_2N_2O_2$ coordination polyhedron the Re atom is +0.98Å from the Cl(2)Cl(1)O(1) plane and −1.44Å from the N(1)N(2)O(2) one, the angle between the two triangular faces being 11.5°.

As appears in Figure 2, the Re-O(2)-C(6) plane is virtually normal (dihedral angle of 91.5°) to the equatorial mean plane, while the two pyridine rings are inclined at dihedral angles of 124.7° and 126.2°, respectively, to the equatorial plane, and make an angle of 65.9° with respect to each other. Distortion from an ideal rhenium-centred octahedron mainly results in a non-linear O(2)-Re = O axis of 158.0°, accomplished by Cl(1)-Re-N(1) and Cl(2)-Re-N(2) angles of 164.2° and 167.9°, respectively.

Bond lengths and angles within the "inner core" show no unusual features, being within the range expected from the comparison of 21 other six-coordinate monooxo complexes of Re(V).[11]

Interatomic contacts in the molecular packing have been observed only between O(2) and O(3) atoms (at x, y, $\frac{1}{2}$-z) (2.73Å), having the appropriate geometrical orientation for the setting of possible hydrogen bonding.

The driving force for the addition of protic molecules to the carbonyl group of DPK after coordination to a metal was earlier explained on the basis of the relief of non-bonding interactions between hydrogen atoms adjacent to the pyridine nitrogens of *trans* ligands in 1:2 metal:DPK complexes.[1,3] Since hydration or alcoholization

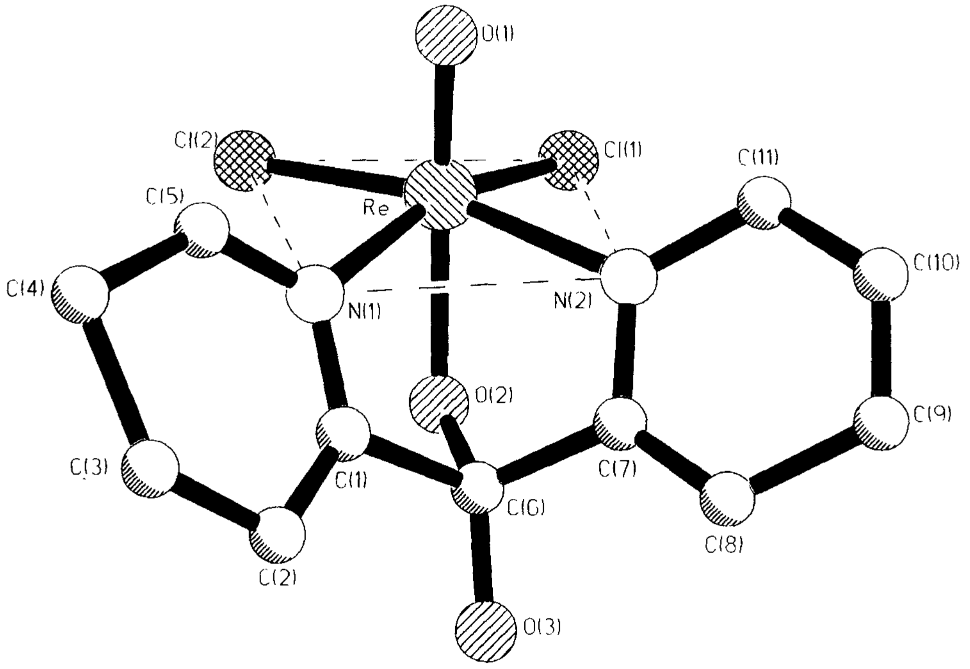

Figure 2 PLUTO drawing (W.D.S. Motherwell and W. Clegg, PLUTO 78, Program for Plotting Molecular and Crystal Structures, University of Cambridge, 1978) of $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$ showing the structure and atom-labelling scheme.

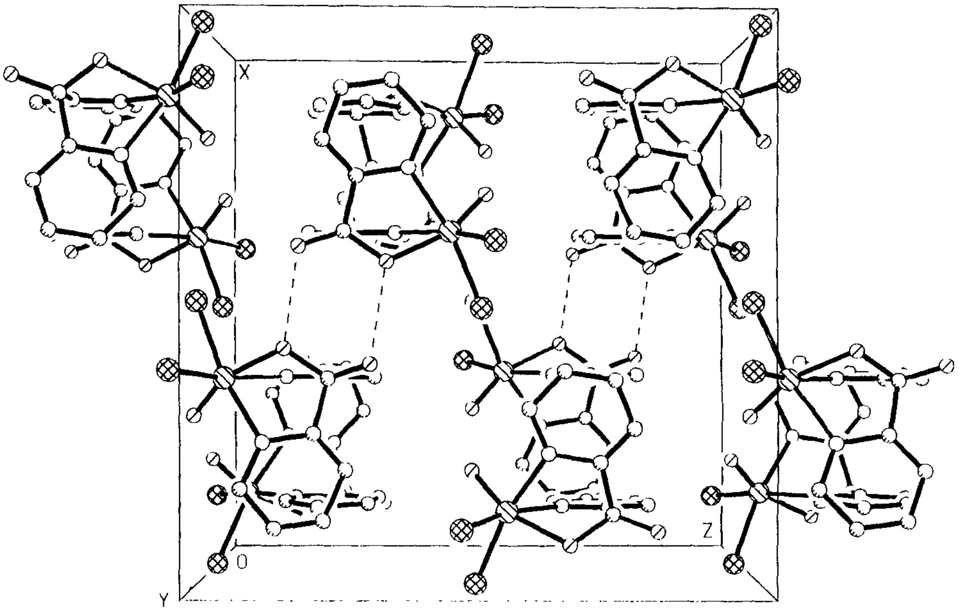

Figure 3 Packing of the molecules in the unit cell. Hydrogen bonds are denoted by a dashed line.

also occurs in 1:1 complexes, where no such steric interaction is present, an alternative explanation was that the formation of a planar six-membered ring between the metal and DPK is difficult, and that the formation of a chelate in the boat form with the metal and the carbonyl carbon above the plane of the two nitrogens and two 2-carbon atoms of the pyridine rings will be easier achieved.[12] In the latter case the coplanarity of the ligand and the conjugation over the carbonyl group would be destroyed, and as a result the nucleophilic attack of the keto-group would be facilitated. An additional driving force for the metal-promoted hydration/alcoholization was ascribed[4] to the possible coordination of one of the *gem*-diols to the metal, as was found in complexes of metal ions which form octahedral complexes.

Terdentate coordination of the neutral diol group $[(C_5H_4N)_2C(OH)_2](HL)$, with one of the hydroxyl groups coordinated to the metal, has been established crystallographically in the complexes $[M(HL)_2]^{2+}$ (M = Ni, Cu),[13] and in the complexes $[Cr(L)_2]^+$ and $Ru(L)_2$ one of the *gem*-diols of each ligand is deprotonated,[14] with the ligand behaving as a uninegative terdentate chelate. In the complexes $PdCl_2(HL)$ and $[AuCl_2(HL)]^+$, crystal structure determinations[4] have shown that the neutral ligand HL only acts as a chelating N,N-donor ligand.

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