Nucleophilic addition of water to coordinated di-(2-pyridyl)ketone (DPK) in rhenium(V) complexes. Synthesis and crystal structure of the adduct* (DPK·H)$^+$[{ReOCl$_2$(DPK·OH)}$_2$Cl]$^-$

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Abstract

The crystalline adduct of formula (DPK·H)$^+$[{ReOCl$_2$(DPK·OH)}$_2$Cl]$^-$ was prepared by the reaction of *trans*-ReOCl$_3$(PPh$_3$)$_2$ with di-(2-pyridyl)ketone (DPK) in THF or dichloromethane. The compound was characterized by elemental analysis, vibrational, optical and ^{1}H NMR spectroscopy. The evidence suggests that the coordinated DPK ligands have undergone addition of water at the carbonylic carbon atom, and that the (C$_5$H$_4$N)$_2$C(O)(OH) moiety acts as a uninegative, terdentate N,O,N-donor ligand. The X-ray crystal structure of the compound is also reported. Crystal data: $C_{33}H_{27}Cl_5N_6O_7Re_2$, triclinic, space group $P\bar{1}$; $a = 9.483(3)$, $b = 14.399(5)$, $c = 15.413(7)$ Å, $\alpha = 110.68(3)$, $\beta = 104.73(3)$, $\gamma = 92.66(3)°$ and $U = 1879.9(9)$ Å^3 to give $Z = 2$ for $D_{calc} = 2.07$ Mg/m^3.

Key words: Crystal structures; Rhenium complexes; Polydentate ligand complexes; Ketone complexes; Amine complexes; Chelate complexes

Introduction

We recently described [1] the syntheses of rhenium(V) and technetium(V) oxo complexes with the molecule di-(2-pyridyl)ketone (DPK). It was shown that the coordinated DPK ligand had undergone nucleophilic addition of water and ethanol at the carbonylic carbon atom, and the crystal structure of the monomeric neutral complex ReOCl$_2$[(C$_5$H$_4$N)$_2$C(O)(OH)] illustrates that the (C$_5$H$_4$N)$_2$C(O)(OH) moiety acts as a uninegative, terdentate N,O$^-$,N-donor ligand to the rhenium(V), which resides in a distorted octahedral environment [1]. The two *cis* chlorides, along with the nitrogen donors, occupy the equatorial sites, with the oxo ligand *trans* to the diolate oxygen atom.

In efforts to prepare the complex ReOCl$_3$(DPK), in which the ketone group is intact, we reacted *trans*-ReOCl$_3$(PPh$_3$)$_2$ with DPK in the solvents THF and CH$_2$Cl$_2$ under anaerobic conditions. In both instances the species (DPK·H)$^+$[{ReOCl$_2$(DPK·OH)}$_2$Cl]$^-$ was isolated. This report describes the crystal structure and properties of this adduct.

Experimental

All chemicals used were of analytical reagent grade. Di-(2-pyridyl)ketone was obtained commercially (Aldrich), and was recrystallized from diethyl ether. *trans*-ReOCl$_3$(PPh$_3$)$_2$ was prepared according to a literature procedure [2].

Scientific instrumentation used in this study is the same as reported elsewhere [3].

Synthesis of (DPK·H)$^+$[{ReOCl$_2$(DPK·OH)}$_2$Cl]$^-$

To 200 mg (240 μmol) of *trans*-ReOCl$_3$(PPh$_3$)$_2$ in 15 cm^3 of THF was added 90 mg (490 μmol) of DPK in 5 cm^3 THF. The reaction mixture was heated under reflux for 30 min under nitrogen, during which time its colour changed to dark blue. After cooling to room temperature, a violet precipitate was collected by filtration, washed with diethyl ether and dried under vacuum. The product was recrystallized from acetonitrile to give a yield of 108 mg (77%); m.p. 204 °C (dec.).

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*Bis[dichloro(hydroxy-di-2-pyridylmethoxide)oxorhenium(V)]-(di-2-pyridiniumketone)monochloride.

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TABLE 1. Crystal data and data collection

Crystal data	
Empirical formula	$C_{33}H_{27}Cl_5N_6O_7Re_2$
Color: habit	dark violet parallelepipeds
Crystal size	0.4 × 0.2 × 0.1
Crystal system	triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	9.483(3)
b (Å)	14.399(5)
c (Å)	15.413(7)
α (°)	110.68(3)
β (°)	104.73(3)
γ (°)	92.66(3)
Volume (Å^3)	1879.9(9)
Z	2
Formula weight	1169.3
Density (calc.) (Mg/m^3)	2.07
Absorption coefficient (mm^{-1})	6.8
$F(000)$	1116
Data collection	
Diffractometer used	Siemens R3m/V
Radiation, λ (Å)	Mo Kα, 0.71073
Temperature	294
Monochromator	highly oriented graphite crystal
2θ range (°)	4.5–45.0
Scan type	ω–2θ
Scan speed	variable. 2.51 to 14.65°/min in ω
Scan range (ω)	1.25° plus Kα separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 25% of total scan time
Standard reflections	2 measured every 150 reflections
Index ranges	$0 < h < 10$; $-15 < k < 15$, $-16 < l < 15$
Independent reflections	4928
Observed reflections	3594 ($F > 3.0\sigma(F)$)
Absorption correction	empirical (ψ-scans)
Solution and refinement	
System used	Siemens SHELXTL PLUS (Release 4.2) (1990)
Solution	heavy-atom methods
Refinement method	full-matrix least-squares
Quantity minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Hydrogen atoms	riding model, common variable isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0078F^2$
No. parameters refined	479
Final R indices (obs. data) (%)	$R = 3.63$, $R_w = 4.79$
R indices (all data) (%)	$R = 4.95$, $R_w = 5.84$
Goodness-of-fit	0.51
Largest and mean Δ/σ	0.771, 0.146
Data-to-parameter ratio	7.5:1

Anal. Calc. for $C_{33}H_{27}Cl_5N_6O_7Re_2$: C, 33.90; H, 2.33; N, 7.19; Cl, 15.16. Found: C, 34.32; H, 2.52; N, 7.20; Cl, 14.84%. Conductivity (10^{-3} M, DMF): 64 Ω^{-1} cm^2 mol^{-1}. IR data (cm^{-1}, KBr): ν(Re=O) 953; ν(C=O) 1692; ν(py) 1617, 1584; ν(O–H) 3399; ν(Re–Cl) 326; ν(C–O) 1277; ν(NH$^+$) 3074. ^{1}H NMR ($(CD_3)_2SO$): δ (ppm) 8.73 (d, 2H, $H_{5a}H_{11a}$); 8.43 (d, 4H, H_5, H_5', H_{11}, H_{11}'); 8.01–8.13 (m, 12H); 7.83 (ddd, 4H, H_4, H_{10}, H_4', H_{10}'); 7.71 (ddd, 2H, H_{4a}, H_{10a}). Electronic spectrum (DMSO) [λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))]: 635 (500), 352 (5500), 260 (25000), 218 (55400). Solid reflectance spectrum [λ_{max} (nm) (relative intensity)]: 627 (0.66), 375sh (0.95), 350 (1.0), 255 (0.17).

Crystallography

Good quality crystals were grown from the slow evaporation of an acetonitrile solution of the compound. Table 1 contains all relevant information related to the data collection and reduction, along with the structure solution method and refinement procedure results. Final

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

	x	y	z	U^a
Re	7630(1)	1778(1)	1574(1)	35(1)
Cl(1)	7874(3)	3376(2)	1497(2)	60(1)
Cl(2)	5943(3)	2243(3)	2467(2)	63(1)
O(1)	6560(7)	1047(5)	468(5)	50(3)
O(2)	9314(6)	2162(4)	2731(4)	34(2)
O(3)	11483(6)	1638(5)	3394(4)	45(3)
N(1)	7817(8)	472(6)	1940(5)	35(3)
N(2)	9548(9)	1444(6)	1060(5)	37(3)
C(1)	9208(9)	475(6)	2465(6)	30(3)
C(2)	9558(11)	−294(7)	2762(7)	42(4)
C(3)	8436(12)	−1075(7)	2539(7)	49(5)
C(4)	7038(11)	−1062(7)	2007(7)	44(4)
C(5)	6742(11)	−287(7)	1725(7)	44(4)
C(6)	10219(10)	1410(7)	2646(6)	34(4)
C(7)	10656(10)	1306(7)	1738(6)	33(4)
C(8)	11999(10)	1102(7)	1545(7)	44(4)
C(9)	12186(12)	1081(8)	677(7)	56(5)
C(10)	11050(14)	1249(9)	25(8)	63(5)
C(11)	9740(13)	1425(8)	217(7)	53(5)
Re′	2800(1)	6887(1)	1771(1)	38(1)
Cl(1′)	3157(3)	8523(2)	1785(2)	61(1)
Cl(2′)	1105(3)	7348(3)	2655(2)	69(1)
O(1′)	1700(7)	6232(5)	654(2)	54(3)
O(2′)	4466(6)	7169(5)	2951(4)	39(3)
O(3′)	6446(7)	6452(5)	3590(5)	51(3)
N(1′)	2859(8)	5517(6)	2017(5)	39(3)
N(2′)	4693(8)	6526(6)	1264(5)	39(3)
C(1′)	4204(10)	5439(7)	2528(7)	41(4)
C(2′)	4458(12)	4602(7)	2736(7)	49(5)
C(3′)	3306(12)	3833(8)	2442(8)	57(5)
C(4′)	1945(12)	3911(7)	1939(8)	53(5)
C(5′)	1730(11)	4778(7)	1723(7)	48(4)
C(6′)	5301(10)	6378(7)	2804(6)	37(4)
C(7′)	5772(10)	6311(7)	1905(7)	38(4)
C(8′)	7079(12)	6053(8)	1723(8)	52(5)
C(9′)	7297(13)	6032(9)	852(9)	64(6)
C(10′)	6209(13)	6247(9)	218(8)	60(5)
C(11′)	4916(12)	6482(8)	427(7)	50(5)
Cl(3)	8752(3)	8311(2)	4666(2)	55(1)
O(1a)	5038(9)	6554(6)	5432(7)	78(4)
N(1a)	2502(8)	8245(6)	5170(6)	44(4)
N(2a)	1188(9)	6384(7)	4483(6)	50(4)
C(1a)	3785(11)	7909(7)	5364(7)	45(4)
C(2a)	5097(12)	8580(10)	5741(8)	62(6)
C(3a)	5037(14)	9576(10)	5919(8)	64(6)
C(4a)	3699(14)	9906(9)	5725(8)	64(6)
C(5a)	2431(12)	9226(9)	5355(7)	54(5)
C(6a)	3872(13)	6819(8)	5188(7)	56(5)
C(7a)	2500(12)	6044(8)	4740(6)	48(5)
C(8a)	2546(14)	5058(9)	4621(9)	65(6)
C(9a)	1302(16)	4334(9)	4174(10)	78(7)
C(10a)	25(16)	4656(10)	3874(8)	72(6)
C(11a)	−21(14)	5657(10)	4053(8)	67(6)

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

atomic positional and equivalent isotropic thermal parameters are listed in Table 2, while relevant bond lengths and angles .are reported in Table 3. The SHELXTL-PLUS package of computer programs [4] was employed for the solution and refinement of the structure. See also 'Supplementary material'.

Results and discussion

The title compound was prepared in good yield by the reaction of *trans*-$ReOCl_3(PPh_3)_2$ with DPK in THF under nitrogen (containing 2.0 vpm water) at reflux conditions. The same product was also obtained when dichloromethane was used as solvent, and when the molar excess of DPK was varied from twofold to tenfold. The compound is diamagnetic and is a 1:1 electrolyte in acetonitrile and DMF.

A very intense band in the solid state IR spectrum at 953 cm^{-1} is attributed to the stretching frequency of the Re=O group, since it appears in the range that is normally observed for neutral six-coordinate mono-oxorhenium(V) complexes [5]. A distinct band at 1692 cm^{-1} is assigned to ν(C=O) of the $DPK \cdot H^+$ fraction of the adduct (at 1675 cm^{-1} in uncoordinated DPK). A strong band at 1617 cm^{-1} and one of medium intensity at 1584 cm^{-1} are assigned to the deformation vibrations of the coordinated and uncoordinated pyridine rings, respectively. This increase in ring frequency from 1579 cm^{-1} in the free DPK to 1617 cm^{-1} has previously been related [6] to N,N-chelation of the ligand in which the ketone group of DPK has suffered nucleophilic addition. The compound exhibits a strong band at 1277 cm^{-1}, which is attributed to ν(C−O), and it has an additional broad hydrogen-bonded O−H absorption band at 3400 cm^{-1}.

The proton nuclear magnetic resonance spectrum of the compound in $(CD_3)_2SO$ shows the presence of the 24 protons of the six pyridyl rings in the range δ7.67–8.75 ppm (Fig. 1). It illustrates the magnetic equivalence

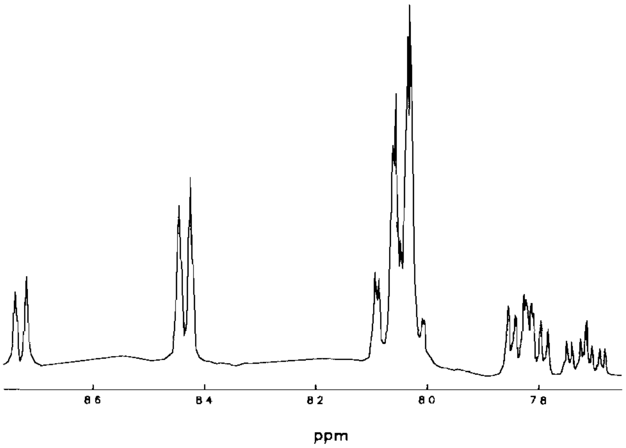

Fig. 1. ^1H NMR spectrum of $(DPK \cdot H)^+[\{ReOCl_2(DPK \cdot OH)\}_2Cl]^-$ in $(CD_3)_2SO$.

TABLE 3. Relevant bond lengths (Å) and angles (°)

	Molecule A		Molecule B		
Re–Cl(1)	2.349(3)		2.356(3)		
Re–Cl(2)	2.338(4)		2.336(4)		
Re–O(1)	1.672(6)		1.670(6)		
Re–O(2)	1.951(5)		1.981(5)		
Re–N(1)	2.148(9)		2.138(9)		
Re–N(2)	2.171(9)		2.148(9)		
O(2)–C(6)	1.40(1)		1.40(1)		
N(1)–C(1)	1.36(1)		1.35(1)		
N(1)–C(5)	1.35(1)		1.34(1)		
C(1)–C(6)	1.51(1)		1.53(1)		
O(3)–C(6)	1.37(1)		1 37(1)		
C(6)–C(7)	1.52(1)		1.53(1)		
N(2)–C(7)	1.36(1)		1.36(1)		
N(2)–C(11)	1.35(1)		1.34(1)		
N(1a)–C(1a)	1.33(1)	C(6a)–C(7a)	1.51(1)	C(1a)–C(2a)	1.39(1)
C(7a)–C(8a)	1.37(2)	C(1a)–C(6a)	1.50(2)	N(2a)–C(7a)	1.37(1)
N(1a)–C(5a)	1.35(1)	N(2a)–C(11a)	1.36(1)	O(1a)–C(6a)	1.20(1)
Cl(1)–Re–Cl(2)	90.5(1)		90.3(1)		
Cl(1)–Re–O(1)	103.6(3)		103.1(3)		
Cl(1)–Re–O(2)	92.8(2)		94.0(2)		
Cl(1)–Re–N(1)	166.9(2)		168 2(2)		
Cl(1)–Re–N(2)	90.6(2)		91.3(3)		
Cl(2)–Re–O(1)	103.3(3)		102.0(3)		
Cl(2)–Re–O(2)	93.3(2)		92.9(2)		
Cl(2)–Re–N(1)	89.6(2)		90.4(3)		
Cl(2)–Re–N(2)	167.3(2)		167.4(2)		
O(1)–Re–O(2)	156.3(3)		157.0(3)		
O(1)–Re–N(1)	89.1(3)		88.3(3)		
O(1)–Re–N(2)	88.8(3)		89.8(3)		
O(2)–Re–N(1)	74.1(3)		74.2(3)		
O(2)–Re–N(2)	74.0(3)		74.5(3)		
N(1)–Re–N(2)	86.4(3)		85 5(3)		
Re–N(1)–C(1)	112.3(6)		113.2(6)		
Re–N(2)–C(7)	111.3(7)		112.7(7)		
Re–O(2)–C(6)	110.7(4)		109.6(4)		
O(2)–C(6)–O(3)	115.2(6)		115.6(6)		
C(1)–C(6)–C(7)	109.8(6)		107.8(7)		
N(1a)–C(1a)–C(2a)	120(1)	O(1a)–C(6a)–C(7a)	118(1)	C(1a)–C(6a)–C(7a)	121(1)
N(2a)–C(7a)–C(6a)	116(1)	O(1a)–C(6a)–C(1a)	120.3(9)		

of the corresponding protons in the four coordinated pyridyl rings (see Fig. 2), as is evidenced by a four-proton doublet (at δ8.43 ppm) and a four-proton doublet of doublet of doublets (ddd) at δ7.83 ppm. The chemical shift of the two equivalent protons H_{5a} and H_{11a} appears as a doublet, the furthest downfield at δ8.73 ppm, while the chemical shifts of H_{4a} and H_{10a} appear as a doublet of a doublet of doublets, the furthest upfield at δ7.71 ppm.

The title compound is a typical example of a crystalline adduct; in fact, two molecules (from now on referred to as A and B) of the known compound [1] $ReOCl_2[(C_5H_4N)_2C(O)(OH)]$, i.e. dichloro(hydroxy-di-2-pyridylmethoxide)oxorhenium(V) and a single molecule of (di-2-pyridiniumketone)monochloride exist in the asymmetric unit (Fig. 2). Molecules A and B are perfectly superimposable (r.m.s. of 0.02 Å) (Fig. 3), with their equatorial coordination planes Cl_2N_2 being virtually parallel (dihedral angle of 4.1°). They also interact symmetrically with the chloride ion via the O(3) (at $1-x$, $1-y$, $1-z$) and the O(3′) (at x, y, z) atoms of the hydrated ketone, giving place to interactions of 3.029 and 3.028 Å, respectively, and defining an angle O(3)- - -Cl(3)- - -O(3′) of 91.6° (Fig. 4). Hence, three molecules of DPK are present in the asymmetric unit; two of them are magnetically equivalent and modified in such a way that the dipyridylketone hydrate acts as a uninegative, tridentate N,O,N-donor ligand to the pertinent rhenium atom, while the third molecule maintains its ketonic form, as is confirmed by the IR spectra. This last molecule merely undergoes protonation at the N(1a) or N(2a) atom, and the two pyridyl rings are

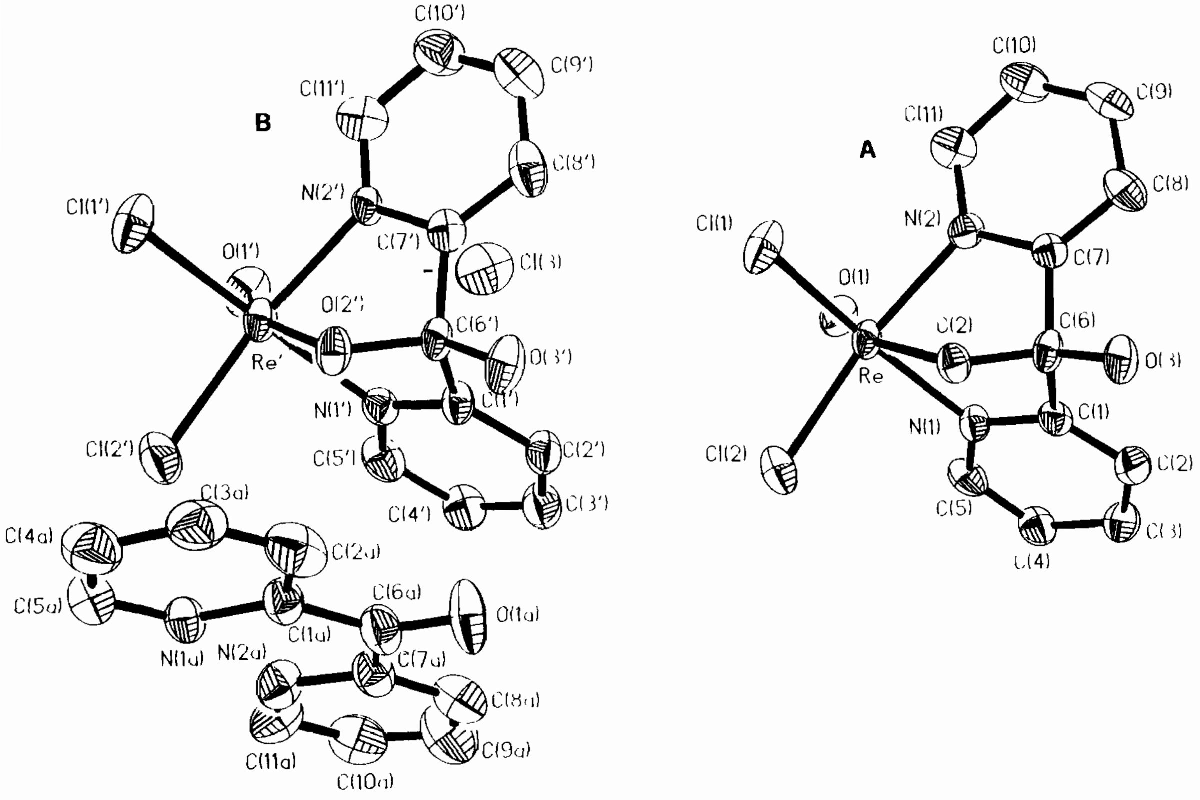

Fig. 2. ORTEP drawing of the asymmetric unit, showing the atom labelling scheme; the thermal ellipsoids are drawn at 40% probability level.

nearly coplanar (dihedral angle of 6.2°); this circumstance makes impossible the simultaneous protonation of the two nitrogen atoms. In a model, in fact, the hypothetical two hydrogens would be separated by an unrealistic H(1a)- - -H(2a) distance of 1.08 Å. In any case, the environment of the cation does not give any information with respect to the most probable position of the proton. The geometry of the neutral complex confirms that found in the already published structure [1], even in the smallest details. In particular, the Re atom is displaced from the mean plane of the Cl_2N_2 equatorial donor set by 0.25 and 0.28 Å in A and B, respectively, towards the oxo-O(1) atom (0.27 Å in the first determination). In the $Cl_2N_2O_2$ coordination polyhedron the Re atom is +0.96 and +0.98 Å (in A and B, respectively) far from the Cl(2)Cl(1)O(1) plane, and −1.43 Å (both in A and B) from the N(1)N(2)O(2) plane, the angles between the two triangular faces being 11.7 and 12.6° in A and B, respectively. The corresponding values from the first determination are +0.98, −1.44 Å and 11.5°.

Bond lengths and angles within the 'inner core' show no unusual features, being within the range expected from the comparison of other six-coordinate monooxorhenium(V) complexes containing multidentate ligands [7].

The driving force for the metal-promoted hydration of the carbonyl group of DPK may be ascribed to the need to relieve angular strain in the molecule. The formation of a planar six-membered ring between the metal and the N,N-chelated DPK would be difficult to achieve, and would create considerable angular strain. The relief of this strain may be achieved by the rehybridization of the keto-carbon from sp^2 to sp^3 and the subsequent formation of the 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. 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 will be facilitated.

A consequence of the ketone hydration 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 the octahedral coordination site *trans* to the rhenyl oxo group (at right angles to the ReN_2 plane). It would lead to steric interaction with any ligand in that position, and this, coupled with the high *trans* effect of the oxo group which labilizes the *trans* chloride, will favour the formation of the chelated product.

Terdentate coordination of the uninegative $[(C_5H_4N)_2C(O)(OH)]$ ligand has previously been es-

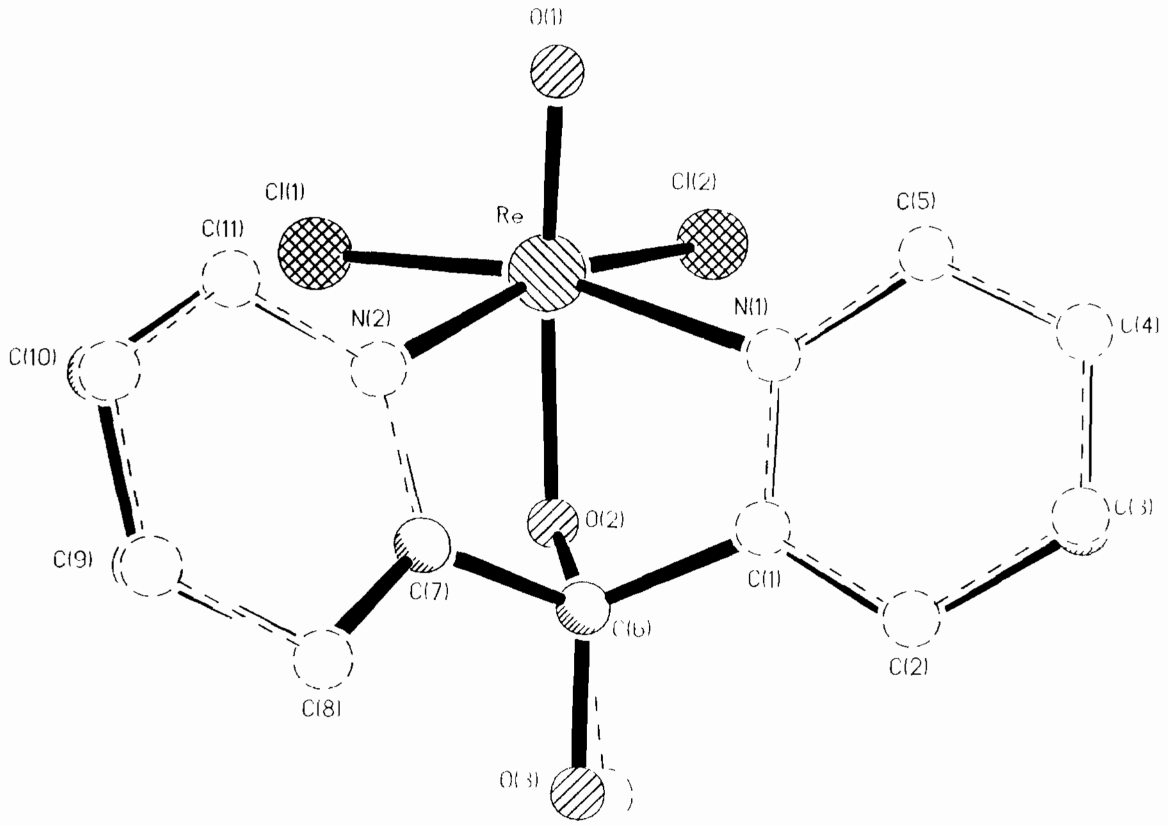

Fig. 3. Superimposition of the two independent A (full line) and B (dashed line) molecules.

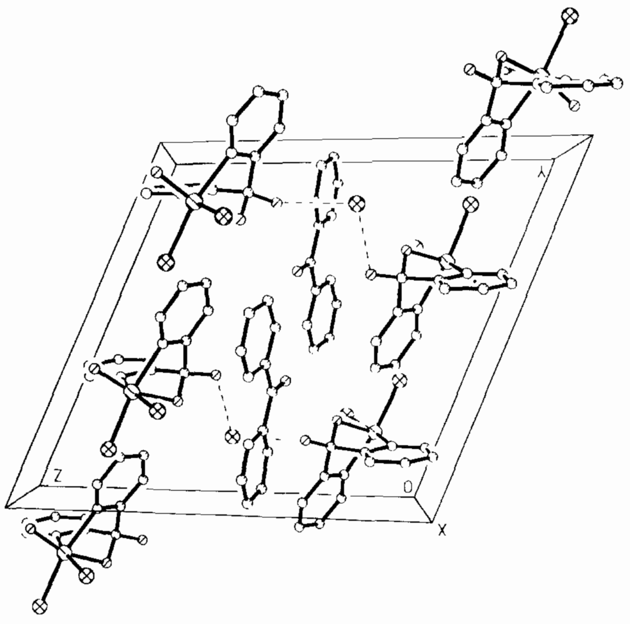

Fig. 4. Packing of the content in the unit cell Hydrogen bonds are drawn in dashed lines.

tablished [8] in the complexes $[Cr(DPK \cdot OH)_2]^+$ and $Ru(DPK \cdot OH)_2$.

Supplementary material

Anisotropic thermal parameters (Table A), complete listing of bond lengths (Table B) and angles (Table C), hydrogen positional parameters (Table D) and a table of observed and calculated structure factors (Table E) are available from the authors on request.

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