A chloro(2-pyridinecarboxalde-hyde)(2,2':6',2''-terpyridine)-ruthenium(II) complex

Eric P. Kelson,[a]* Proma P. Phengsy[a] and Atta M. Arif[b]

[a]Department of Chemistry, California State University Northridge, Northridge, CA 91330-8262, USA, and [b]Department of Chemistry, University of Utah, Salt Lake City, UT 84112-0850, USA
Correspondence e-mail: eric.kelson@csun.edu

The aldehyde moiety in the title complex, chloro(2-pyridinecarboxaldehyde-N,O)(2,2':6',2''-terpyridine-κ^3N)ruthenium(II)–chloro(2-pyridinecarboxylic acid-N,O)(2,2':6',2''-terpyridine-κ^3N)ruthenium(II)–perchlorate–chloroform–water (1.8/0.2/2/1/1), $[RuCl(C_6H_5NO)(C_{15}H_{11}N_3)]_{1.8}[RuCl(C_6H_5NO_2)(C_{15}H_{11}N_3)]_{0.2}(ClO_4)_2 \cdot CHCl_3 \cdot H_2O$, is a structural model of substrate coordination to a transfer hydrogenation catalyst. The title complex features two independent Ru^{II} complex cations that display very similar distorted octahedral coordination provided by the three N atoms of the 2,2':6',2''-terpyridine ligand, the N and O atoms of the 2-pyridine-carboxaldehyde (pyCHO) ligand and a chloride ligand. One of the cation sites is disordered such that the aldehyde group is replaced by a 20 (1)% contribution from a carboxylic acid group (aldehyde H replaced by carboxyl O—H). Notable dimensions in the non-disordered complex cation are Ru—N 2.034 (2) Å and Ru—O 2.079 (2) Å to the pyCHO ligand and O—C 1.239 (4) Å for the pyCHO carbonyl group.

Comment

Metal complexes of aldehydes and ketones have attracted recent attention as possible models for catalytic intermediates in the transfer hydrogenation of ketones by alcohols. Though many ruthenium(II)-based transfer hydrogenation catalysts are known, the specifics of the catalytic process remain a matter of debate. Several mechanistic proposals suggest that the key step involves activation of the coordinated substrate, making ruthenium(II) ketone and aldehyde complexes of structural interest (Yamakawa *et al.*, 2000). Though a few ruthenium(II) ketone and aldehyde complexes have been reported, the coordination environments do not resemble those of known transfer hydrogenation catalysts. As a continuation of our research into the activity of a new class of Ru^{II}(terpy)-based (terpy is 2,2':6',2''-terpyridine) transfer hydrogenation catalysts, the present work is concerned with the crystal structure of the newly synthesized complex obtained from the reaction of Ru^{III}(terpy)Cl_3 with 2-pyridinecarboxaldehyde (pyCHO). This compound, (I), is the first crystallographically characterized ruthenium(II) complex with pyCHO and features a coordinated aldehyde within the ligand set of a transfer hydrogenation catalyst.
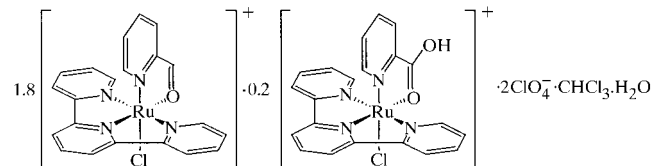
(I)

Our analysis shows that complex (I) consists of two crystallographically independent $[Ru^{II}Cl(pyCHO)(terpy)]^+$ cations and two ClO_4^- anions, together with lattice molecules of chloroform and water. During the refinement process, it became apparent that one of the cation sites (cation A) was disordered, with the aldehyde group being replaced by a 20 (1)% contribution from a carboxylic acid group (aldehyde H replaced by carboxyl O—H); details are provided in the *Experimental* section. The two cations are nonetheless very similar and exhibit the same structural features. In each cation, the Ru atom is surrounded by a distorted octahedral arrangement of one terpy molecule coordinated in a tridentate manner, one pyCHO ligand coordinated through the N and O atoms, and a Cl$^-$ ion placed *trans* with respect to the pyCHO N atom (Fig. 1). Replacement of 20 (1)% of the aldehyde function in cation A with a carboxylic acid function appears to cause little difference to the principal geometry features. The mean Ru—N distances to the terpy ligands are typical of Ru^{II}(terpy) complexes, with values of 2.064 (6) Å to the outer pyridine rings and 1.952 (4) Å to the inner pyridine rings. The mean Ru^{II}—Cl distance of 2.391 (5) Å is also as expected. The Ru—N distances to the pyCHO ligand, 2.042 (2) and 2.034 (2) Å for cations A and B, respectively, are short of the typical range from 2.114 to 2.100 Å for monopyridyl ligands in Ru^{II}(terpy) complexes (Hecker *et al.*, 1991; Rasmussen *et al.*, 1995). Similarly, the Ru—O distances to the pyCHO ligand, 2.071 (2) and 2.079 (2) Å for cations A and B, respectively, are somewhat shorter than the value of 2.11 Å reported for monodentate Ru^{II}–aldehyde complexes (Carmona *et al.*, 1997).

The mean bite angle for the terpy ligands is 79.5 (3)° which is expected for Ru^{II}(terpy) complexes. The mean bite angle for the pyCHO ligands is comparable [78.4 (1)°]. The equatorial planes formed by the Ru atoms, the coordinating terpy N atoms, and the pyCHO O atoms are slightly distorted from planarity, with maximum deviations of 0.011 (1) Å for Ru1A and 0.013 (1) Å for Ru1B toward the apical Cl ligands. The terpy molecules themselves are planar, with maximum deviations of 0.081 (2) Å for N3A and 0.075 (2) Å for N4B, and the dihedral angles between the terpy molecules and the equatorial planes are 2.6 (2) and 3.9 (1)° for cations A and B, respectively, with both terpy planes tipped slightly toward the

metal-organic compounds

Cl ligands likely in response to the steric influence of the axial pyridine ring of pyCHO. The pyCHO ligand is also planar, with a maximum deviation of 0.028 (2) Å for O1*A* and 0.027 (3) Å for C6*B*. The dihedral angles between the mean planes of the terpy and pyCHO ligands are 87.39 (4) and 82.16 (6)° for cations *A* and *B*, respectively, suggesting modest flexibility in the tipping angle of the pyCHO ligand.

Bond distances and angles within the terpy molecule have expected values. The pyCHO carbonyl C6*B*—O1*B* distance of 1.239 (4) Å in the non-disordered cation *B* is significantly longer than 1.22 Å of monodentate Ru^{II}–aldehyde complexes (Carmona *et al.*, 1997). Further, the corresponding pyCHO
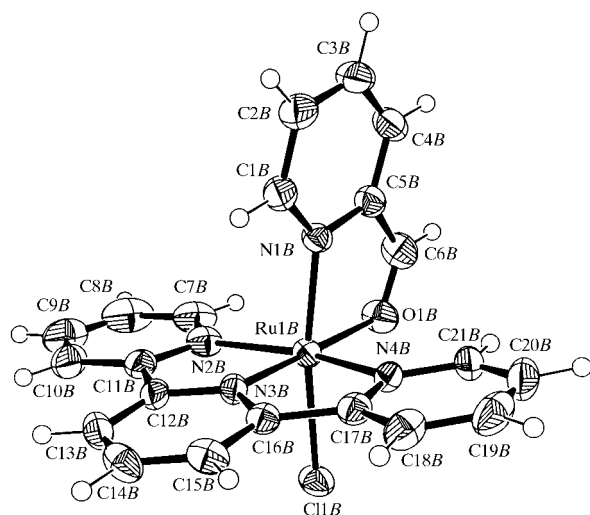

Figure 1
Perspective view of cation *B* of compound (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

ring N1*B*—C5*B* distance of 1.370 (4) Å is longer than the N1*B*—C1*B* distance of 1.345 (4) Å (a typical value for pyridine; Hecker *et al.*, 1991; Rasmussen *et al.*, 1995). The other bond lengths and angles within the pyCHO ligand have expected values. The relatively long carbonyl C6*B*—O1*B* and N1*B*—C5*B* distances taken with the shorter than expected Ru1—N1 and Ru1—O1 distances suggest a modest shift of bond order around the π-system of the Ru–pyCHO metallocycle that weakens the carbonyl bond. An analogous bond order shift is reported for the metallocycle of [(C$_6$-Me$_4$H$_2$)Ru{CH=C(C$_6$H$_4$-*p*-NMe$_2$)CHO}(PPh$_3$)]PF$_6$, which results in an unusually long carbonyl C—O distance [1.260 (5) Å; Pilette *et al.*, 1994]. Compound (I) provides an example of this effect within a hard-donor coordination environment. This mechanism for weakening coordinated carbonyls may have relevance to substrate activation by Ru^{II}– ligand moieties in transfer hydrogenation catalysis.

Hydrogen bonds (see Table 1) from the lattice water molecule to one perchlorate O atom [O6···O5*B* 3.034 (5) Å] and the Cl atom of cation *B* [O6···Cl1*B* 3.300 (3) Å] are evident. There is also a hydrogen bond from the chloroform C—H group to another perchlorate O atom [C22···O3*A* 3.174 (6) Å]. These interactions do not appear to exert a dominant influence on the structure.

Experimental

The title compound was prepared by refluxing Ru^{III}(terpy)Cl$_3$ (0.12 g) with 2-pyridinecarbinol (0.5 ml) in ethanol (7.5 ml) under an argon atmosphere followed by crystallization with HClO$_4$ (70% *w/w*) (0.5 ml). Elemental analysis: C 43.53, H 2.97, N 9.58%; expected for [Ru^{II}Cl(pyCHO)(terpy)](ClO$_4$): C 43.76, H 2.80, N 9.72%. Vapor diffusion of chloroform into an acetone solution of the product at room temperature over 3 d afforded dark-red prisms of the title compound.

Crystal data

[RuCl(C$_6$H$_5$NO)(C$_{15}$H$_{11}$N$_3$)]$_{1.8}$	$V = 2432.23$ (9) Å^3
[RuCl(C$_6$H$_5$NO$_2$)(C$_{15}$H$_{11}$N$_3$)]$_{0.2}$	$Z = 2$
(ClO$_4$)$_2$·CHCl$_3$·H$_2$O	$D_x = 1.766$ Mg m^{-3}
$M_r = 1293.11$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 21 341
$a = 10.8871$ (2) Å	reflections
$b = 13.4187$ (3) Å	$\theta = 2.14$–32.60°
$c = 17.9641$ (4) Å	$\mu = 1.074$ mm^{-1}
$\alpha = 68.7915$ (12)°	$T = 200$ (2) K
$\beta = 83.8241$ (10)°	Prism, dark red
$\gamma = 87.0651$ (11)°	0.28 × 0.20 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer	11 021 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.030$
Absorption correction: multi-scan	$\theta_{max} = 32.60°$
(*DENZO-SMN*; Otwinowski &	$h = -16 \rightarrow 16$
Minor, 1997)	$k = -19 \rightarrow 18$
$T_{min} = 0.753$, $T_{max} = 0.919$	$l = -19 \rightarrow 27$
21 341 measured reflections	Intensity decay: <2.0%
16 021 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0395P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.049$	$+ 2.2430P]$
$wR(F^2) = 0.116$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.017$	$(\Delta/\sigma)_{max} = 0.001$
16 021 reflections	$\Delta\rho_{max} = 0.89$ e Å^{-3}
652 parameters	$\Delta\rho_{min} = -0.89$ e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	(Sheldrick, 1997)
	Extinction coefficient: 0.0019 (3)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O6—H61···O5*B*	0.93 (3)	2.13 (4)	3.034 (5)	161 (5)
O6—H62···Cl1*B*	0.93 (3)	2.37 (4)	3.300 (3)	175 (5)
C22—H22···O3*A*	1.00	2.25	3.174 (6)	153

The H atoms bound to carbon were positioned with idealized geometry (Csp^2—H = 0.95 Å and chloroform Csp^3—H = 1.00 Å), assigned isotropic displacement parameters equal to 1.2U_{eq} of the parent atom and refined with a riding model. The H atoms of the lattice water molecule were found in a difference Fourier synthesis and were refined with a restrained O—H distance. During the refinement calculations, a large electon-density peak (approximately 2 e Å^{-3}) appeared about 1.32 Å from the aldehyde carbon of cation *A* adjacent to the aldehyde H-atom site. In the final refinement, the additional site was allowed for as a partially occupied O atom (O1*A*2)

with an isotropic displacement parameter; the occupancy parameter refined to 0.201 (10) [aldehyde C—H = 0.799 (10)] and physically corresponds with the aldehyde H atom being replaced in 20% of the sites by a carboxylic acid O—H group. The additional partial O atom so introduced is approximately 2.88 (2) Å from an adjacent perchlorate O atom [O2B(1 + x, 1 + y, z)], a distance consistent with O—H···O hydrogen bonding.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *WinGX* (Farrugia, 1999) and *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97 and IUCr *SHELXL*97 template.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1610). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacavazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1997). *J. Appl. Cryst.* **32**, 115–119.

Carmona, D., Cativiela, C., Elipe, S., Lahoz, F. J., Lamata, M. P., López-Ram de Víu, M. P., Oro, L. A., Vega, C. & Viguri, F. (1997). *J. Chem. Soc. Chem. Commun.* pp. 2351–2352.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Hecker, C. R., Fanwick, R. E. & McMillin, D. R. (1991). *Inorg. Chem.* **30**, 659–666.

Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Pilette, D., Moreau, S., Le Bozec, H., Dixneuf, P. H., Corrigan, J. F. & Carty, A. J. (1994). *J. Chem. Soc. Chem. Commun.* pp. 409–410.

Rasmussen, S. C., Ronco, S. E., Mlsna, D. A., Billadeau, M. A., Pennington, W. T., Kolis, J. W. & Petersen, J. D. (1995). *Inorg. Chem.* **34**, 821–829.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. Release 97-2. University of Göttingen, Germany.

Yamakawa, M., Ito, H. & Noyari, R. (2000). *J. Am. Chem. Soc.* **122**, 1466–1478.