Crystal Structure of Chloro(2,2':6',2''-terpyridine)(2-phenylazopyridine)-ruthenium(II) Chloride

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There is considerable interest in $[\text{Ru}(\text{tpy})(\text{L})\text{Cl}]^{n+}$ type complexes (where tpy = 2,2':6',2''-terpyridine, L = bidentate ligand, $n = 0$ or 1), because they are used as precursors of aquo complexes, which can finally be converted to oxo compounds. Oxo-ruthenium complexes are useful as catalysts in different reactions, particularly in the catalytic oxidation of water to dioxygen.^{1,2} As a part of serial studies on the properties of oxo-ruthenium complexes, we synthesized the title complex, $[\text{Ru}(\text{tpy})(\text{L})\text{Cl}]\text{Cl}$ (where L = 2-(phenylazo)pyridine = azpy).

2-(Phenylazo)pyridine (azpy) and $[\text{Ru}(\text{tpy})\text{Cl}_3]$ were prepared by methods reported in the literatures.^{3,4} $\text{Ru}(\text{tpy})\text{Cl}_3$ (0.2 g) and azpy (0.09 g) were refluxed for 3 h in 25 mL of ethanol-water containing LiCl (0.07 g) and triethylamine (0.06 mL). A hot solution was filtered and the filtrate was allowed to stand for 10 days. Crystals suitable for an X-ray technique were selected from the obtained solid. Details concerning the X-ray structure determination are given in Tables 1–3.

Ru(II) is in a distorted octahedral environment bonded to three nitrogen atoms of the tpy ligand, two nitrogen atoms of the azpy ligand and one chlorine atom. The four nitrogen atoms (N3, N4, N5, N6) define the equatorial plane, whereas the Cl1 and N1 atoms occupy the *trans*-axial sites. The longest bond, Ru–Cl1, is comparable to those in *cis*- $\text{Ru}(\text{azpy})_2\text{Cl}_2$.⁵

It is noted that the N(6)–Ru–N(3) angle is $104.82(16)^\circ$, greater

than that ($99.4(3)^\circ$) in $[\text{Ru}(\text{tpy})(\text{azpy})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$.¹ The bite angle of the azpy ligand, N(3)–Ru–N(1), is $76.70(15)^\circ$, smaller than that in *cis*- $[\text{Ru}(\text{bpy})_2\text{Cl}_2]$.⁶ The Ru–N(azo) ($1.999(4)\text{\AA}$) bond distance is longer compared to the value $1.971(7)\text{\AA}$ in $[\text{Ru}(\text{tpy})(\text{azpy})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$.¹ However, the Ru–N(azo) bond distance is still shorter than that of Ru–N(pyridine), as expected. This is due to the greater π -backbonding, $d(\text{Ru}) \rightarrow \pi^*(\text{azo})$. The tpy ligand is planar with the maximum deviation being $0.086\text{\AA}$ for C13 from the best

Table 1 Crystal and experimental data

Empirical formula:	$\text{C}_{26}\text{H}_{20}\text{Cl}_2\text{N}_6\text{Ru}$
Formula weight	= 588.45
Temperature:	295(2)K
Radiation:	Mo $\text{K}\alpha$
Wavelength:	$0.71073\text{\AA}$
Crystal system:	monoclinic
Space group:	$P2_1/n$
a	= $8.7780(9)\text{\AA}$
b	= $22.607(2)\text{\AA}$
c	= $12.8686(14)\text{\AA}$
β	= $99.755(2)^\circ$
V	= $2516.8(5)\text{\AA}^3$
Z	= 4
D_x	= 1.553 Mg/m^3
$\mu(\text{Mo K}\alpha)$	= 0.862 mm^{-1}
$F(0\ 0\ 0)$	= 1184
Crystal size:	$0.30 \times 0.20 \times 0.20\text{ mm}$
Reflections collected	= 16145
Independent reflections	= 6033 [$R_{\text{int}} = 0.0411$]
Reflections observed ($I > 2\sigma(I)$)	= 4429
No. of parameters	= 327
Goodness-of-fit	= 0.937
Final R indices [$I > 2\sigma(I)$]:	$R = 0.0524$ $wR^2 = 0.1439$
R indices (all data):	$R = 0.0772$ $wR^2 = 0.1575$
$(\Delta\rho)_{\text{max}}$	= $1.492\text{ e}\text{\AA}^{-3}$
$(\Delta\rho)_{\text{min}}$	= $-0.585\text{ e}\text{\AA}^{-3}$
Measurement:	Bruker SMART CCD
Structure determination:	Patterson method (SHELXS97) ⁷
Refinement method:	full-matrix on F^2 (SHELXL97) ⁸
Molecular graphics:	XPMA & ZORTEP ⁹

Fig. 1 Chemical diagram.

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Table 2 Final coordinates and equivalent displacement parameters (Å)

Atom	x	y	z	U_{eq}
Ru	.7955 (1)	.1658 (1)	.4266 (1)	.022 (1)
Cl (1)	.6479 (1)	.1938 (1)	.2585 (1)	.034 (1)
N (1)	.9125 (4)	.1365 (2)	.5657 (3)	.026 (1)
C (1)	.9915 (6)	.1682 (2)	.6454 (4)	.035 (1)
C (2)	1.0624 (6)	.1431 (3)	.7372 (4)	.042 (1)
C (3)	1.0534 (8)	.0830 (3)	.7507 (5)	.049 (2)
C (4)	.9733 (8)	.0493 (3)	.6704 (5)	.049 (2)
C (5)	.9043 (6)	.0770 (2)	.5780 (4)	.035 (1)
N (2)	.8231 (5)	.0445 (2)	.4957 (3)	.036 (1)
N (3)	.7714 (5)	.0780 (2)	.4154 (3)	.028 (1)
C (6)	.6825 (6)	.0455 (2)	.3303 (4)	.031 (1)
C (7)	.7065 (6)	.0554 (2)	.2284 (4)	.035 (1)
C (8)	.6201 (7)	.0242 (3)	.1463 (4)	.045 (1)
C (9)	.5055 (8)	-.0140 (3)	.1662 (5)	.055 (2)
C (10)	.4787 (9)	-.0218 (3)	.2679 (6)	.062 (2)
C (11)	.5701 (7)	.0058 (3)	.3500 (5)	.048 (2)
N (4)	.6049 (5)	.1828 (2)	.4979 (3)	.029 (1)
C (12)	.5003 (6)	.1437 (2)	.5221 (4)	.038 (1)
C (13)	.3819 (7)	.1588 (3)	.5732 (5)	.046 (1)
C (14)	.3666 (7)	.2179 (3)	.6013 (5)	.049 (2)
C (15)	.4690 (6)	.2589 (3)	.5745 (4)	.038 (1)
C (16)	.5891 (5)	.2404 (2)	.5250 (4)	.027 (1)
N (5)	.8203 (4)	.2519 (2)	.4569 (3)	.026 (1)
C (17)	.7113 (5)	.2798 (2)	.5014 (4)	.029 (1)
C (18)	.7260 (7)	.3401 (2)	.5224 (4)	.037 (1)
C (19)	.8538 (7)	.3695 (2)	.4988 (5)	.046 (1)
C (20)	.9657 (7)	.3402 (2)	.4548 (5)	.043 (1)
C (21)	.9446 (6)	.2804 (2)	.4326 (4)	.031 (1)
N (6)	.9977 (4)	.1838 (2)	.3695 (3)	.027 (1)
C (22)	1.0452 (5)	.2413 (2)	.3817 (4)	.028 (1)
C (23)	1.1805 (6)	.2608 (3)	.3505 (4)	.040 (1)
C (24)	1.2705 (6)	.2208 (3)	.3062 (4)	.043 (1)
C (25)	1.2220 (7)	.1628 (3)	.2935 (5)	.046 (1)
C (26)	1.0851 (6)	.1458 (3)	.3255 (4)	.036 (1)
Cl (2A)*	.8414 (2)	.0946 (1)	.9576 (2)	.042 (1)
Cl (2B)**	.9061 (8)	-.0383 (2)	.8630 (5)	.044 (1)

$$U_{eq} = (1/3) \sum \sum U_{ij} a_i^* a_j^* (a_i \cdot a_j)$$

Occupancy=0.77, ## Occupancy=0.23

plane, whereas the azpy ligand is not planar, because the phenyl ring is twisted with respect to the pyridine ring and the dihedral angle between the two mean planes is 49.47°. This twisting reduces the delocalization throughout the azpy ligand.

During a refinement, the chloride anion was found to be distributed over two positions, C12A and C12B, with a site occupancy ratio of 0.77/0.23. Hydrogen atoms were constrained to ride on the respective carbon (C-H 0.93 Å) with an isotropic displacement parameter equal to 1.2 U_{eq} of their parent atom. The crystal structure is mainly stabilized by van der Waals forces.

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Table 3 Bond lengths (Å) and angles (°)

Ru-N (5)	1.990 (4)	Ru-N (3)	1.999 (4)
Ru-N (1)	2.019 (4)	Ru-N (6)	2.073 (4)
Ru-N (4)	2.076 (4)	Ru-Cl (1)	2.4107 (12)
N (1)-C (1)	1.344 (6)	N (1)-C (5)	1.357 (6)
C (5)-N (2)	1.384 (6)	N (2)-N (3)	1.300 (5)
N (3)-C (6)	1.434 (6)	N (4)-C (12)	1.348 (7)
N (4)-C (16)	1.361 (6)	N (5)-C (21)	1.348 (6)
N (5)-C (17)	1.351 (6)	N (6)-C (26)	1.339 (6)
N (6)-C (22)	1.365 (6)		
N (5)-Ru-N (3)	172.90 (15)	N (5)-Ru-N (1)	97.20 (15)
N (3)-Ru-N (1)	76.70 (15)	N (5)-Ru-N (6)	78.82 (16)
N (3)-Ru-N (6)	104.82 (16)	N (1)-Ru-N (6)	92.37 (15)
N (5)-Ru-N (4)	78.57 (16)	N (3)-Ru-N (4)	97.59 (16)
N (1)-Ru-N (4)	89.76 (15)	N (6)-Ru-N (4)	157.38 (17)
N (5)-Ru-Cl (1)	86.77 (11)	N (3)-Ru-Cl (1)	99.26 (11)
N (1)-Ru-Cl (1)	175.85 (11)	N (6)-Ru-Cl (1)	89.58 (11)
N (4)-Ru-Cl (1)	89.84 (11)	N (3)-N (2)-C (5)	111.3 (4)
N (2)-N (3)-C (6)	112.3 (4)	N (2)-N (3)-Ru	120.2 (3)

Fig. 2 Molecular structure of the cation in [Ru(tpy)(azpy)Cl]Cl with the atom numbering scheme; displacement ellipsoids are drawn at the 50% probability level.

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