A hybrid bidentate and tridentate ruthenium(II) complex incorporating triazine and polypyridine carbene ligands

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Key indicators

Single-crystal X-ray study
$T = 100$ K
Mean σ(C–C) = 0.004 Å
Disorder in solvent or counterion
R factor = 0.033
wR factor = 0.088
Data-to-parameter ratio = 12.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, (acetonitrile)[4-(4-bromophenyl)-2,6-di-2-pyridyl-1,3,5-triazine](1,3-di-2-pyridyl-2,3-dihydro-1H-imidazolyl)ruthenium(II) bis(hexafluorophosphate) acetonitrile hemisolvate [Ru(C_2H_3N)($C_{19}H_{12}BrN_5$)($C_{13}H_{10}N_4$)]-(PF_6)$_2$·0.5C_2H_3N, was synthesized incorporating a tridentate triazine-based ligand and a bidentate carbene-based polypyridine ligand. Bidentate coordination is favoured due to steric strain enforced by the five-membered ring in the carbene ligand, leaving one uncoordinated pyridyl ring. An acetonitrile molecule completes the distorted octahedral geometry.

Comment

Carbene-based polypyridine ligands were recently shown to improve dramatically the photophysical properties of Ru^{II} polypyridine complexes compared with Ru(tpy)$_2$$^{2+}$ (Son *et al.*, 2004). Carbenes are strong σ-donors and destabilize metal-centred states relative to emissive ^{3}MLCT states, thus prolonging the excited state lifetimes of these complexes. By contrast, electron-deficient triazine ligands also improve the photophysical properties of the complexes through the stabilization of ligand-based orbitals relative to metal orbitals, with a consequential stabilization of ^{3}MLCT emitting states (Polson *et al.*, 2002). It has previously been observed that the combination of a strong σ-donating ligand with a strong π-accepting ligand can favour long excited-state lifetimes associated with the ^{3}MLCT emitting state (Maestri *et al.*, 1995). We present here the crystal structure of an Ru^{II} complex combining a strong σ-donating carbene ligand and a strong π-accepting triazine ligand.
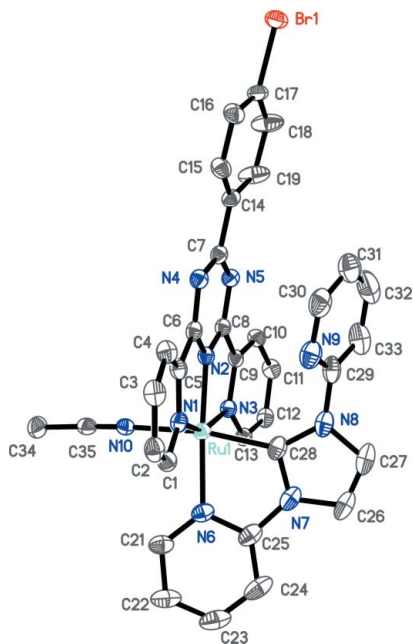

(I)
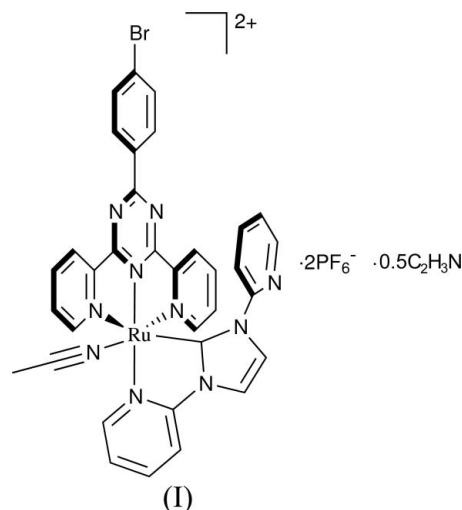
Figure 1
A view of the cation, showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity.

Compound (I) crystallizes in the monoclinic space group $C2/c$ with one cation, two PF_6^- anions and half a molecule of acetonitrile in the asymmetric unit. The complex possesses octahedral geometry with significant distortions due to the bidentate and tridentate nature of the coordinating ligands. Similar configurations have previously been observed for Ru^{II} complexes of the 2,2':6',2''-terpyridine and 2,2'-bipyridine ligands (Rillema *et al.*, 1992; Pyo *et al.*, 1999).

The five-membered carbene ligand cannot overcome the strain associated with tridentate coordination; therefore, bidentate coordination is favoured, with an N—Ru—C bite angle of 78.0 (1)°. The non-coordinated pyridine ring of the carbene ligand is twisted away from the central ring by 68.7 (1)°, enabling it to overlay and π-stack with the triazine ring of the second ligand. The triazine ligand is coordinated in a tridentate manner, with a bite angle of 156.5 (1)°. Its pendant benzene ring is twisted away from a coplanar configuration by 7.30 (13)° with respect to the triazine ring, slightly less than in a Co^{II} complex of the same ligand (13.3°; Medlycott *et al.*, 2005). The Ru—N bond distances are similar to those previously observed for Ru^{II} complexes of triazine ligands (Polson *et al.*, 2002, 2004; Hartshorn *et al.*, 2005), with a shorter bond distance to the central triazine ring [1.955 (2) Å] compared with the adjacent pyridine rings [2.088 (2) and 2.107 (2) Å]. The Ru—N bond distance for the coordinated carbene ligand is 2.098 (2) Å and the Ru—C bond distance is shorter [1.993 (3) Å], as expected because of its superior σ-donating properties. The longest Ru—N bond is observed for the coordinating acetonitrile molecule [2.113 (2) Å] *trans* to the carbene ligand.

Compound (I) is luminescent at room temperature with an emission band centred at 730 nm in acetonitrile. Details of its photophysics will be discussed in a subsequent publication.

Experimental

The complex was synthesized by adapting previously reported procedures (Polson *et al.*, 2004). RuCl$_3$.xH$_2$O (0.27 mmol, 78 mg) was added to an ethanolic solution of the triazine ligand (0.27 mmol, 107 mg) and refluxed for 8 h. The mixture was cooled, filtered and dried to obtain Ru(triazine)Cl$_3$ (100 mg, 61% yield). This intermediate dechlorinated in the presence of three equivalents of AgNO$_3$ (0.51 mmol, 87 mg) for 30 min in refluxing ethanol. The carbene ligand (0.15 mmol, 45 mg) was added to the reaction mixture and refluxing was continued for 14 h. The mixture was filtered over celite to remove AgCl and the complex purified by column chromatography using silica gel with an eluant of 7:1 acetonitrile/KNO$_3$(sat). The complex was isolated as the PF_6^- salt in 85% yield. X-ray quality crystals were obtained by slow diffusion of isopropyl ether into a concentrated solution of the complex in acetonitrile.

Crystal data

[Ru(C$_2$H$_3$N)(C$_{19}$H$_{12}$BrN$_5$)-(C$_{13}$H$_{10}$N$_4$)](PF$_6$)$_2$·0.5C$_2$H$_3$N	D_x = 1.842 Mg m^{-3}
M_r = 1065.09	Cu $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 7159 reflections
a = 37.3866 (4) Å	θ = 3.0–72.6°
b = 13.9391 (2) Å	μ = 6.25 mm^{-1}
c = 15.3229 (2) Å	T = 100 (2) K
β = 105.906 (1)°	Block, orange
V = 7679.57 (17) Å^3	0.45 × 0.40 × 0.25 mm
Z = 8	

Data collection

Bruker SMART 2000 diffractometer	7443 independent reflections
ω scans	7399 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick,1996)	R_{int} = 0.027
T_{min} = 0.110, T_{max} = 0.210	θ_{max} = 72.7°
91815 measured reflections	h = −45 → 42
	k = −17 → 17
	l = −18 → 18

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 23.72P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.033	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.088	$(\Delta/\sigma)_{max}$ = 0.003
S = 1.00	$\Delta\rho_{max}$ = 0.95 e Å^{-3}
7443 reflections	$\Delta\rho_{min}$ = −0.42 e Å^{-3}
604 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ru1—N2	1.955 (2)	Ru1—N6	2.097 (2)
Ru1—C28	1.993 (3)	Ru1—N3	2.107 (2)
Ru1—N1	2.088 (2)	Ru1—N10	2.113 (2)
N2—Ru1—N1	78.44 (8)	N1—Ru1—N3	156.50 (8)
C28—Ru1—N6	77.97 (11)	C28—Ru1—N10	167.91 (10)
N2—Ru1—N3	78.18 (8)	N6—Ru1—N10	92.49 (8)

H atoms were positioned geometrically (C—H = 0.95–0.98Å) and included in the refinement in the riding-model approximation; their displacement parameters were set to 1.5 times U_{eq} of the parent site for methyl H atoms and 1.2 times for others. A final verification of possible voids was performed using the VOID routine of the *PLATON* program (Spek, 2003). Two PF_6^- anions are present for each cation, distributed over three positions. One anion is found on a general position and another one with half occupancy on an inversion

centre. The third anion, again with half occupancy, is disordered around a *C*2 axis, together with the half-occupancy acetonitrile solvent molecule.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *UdMX* (local program).

References

Bruker (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, USA.

Bruker (1999). *SAINT* (Release 6.06) and *SMART* (Release 5.059). Bruker AXS Inc., Madison, Wisconsin, USA.

Hartshorn, R. M., Zibaseresht, R. & Robinson, W. T. (2005). *Acta Cryst.* E**61**, m981–983.

Maestri, M., Armaroli, N., Balzani, V., Constable, E. C. & Thompson, A. M. W. C. (1995). *Inorg. Chem.* **34**, 2759–2767.

Medlycott, E. A., Theobald, I. & Hanan, G. S. (2005). *Eur. J. Inorg. Chem.* pp. 1223–1226.

Polson, M. I. J., Medlycott, E. A., Hanan, G. S., Mikelsons, L., Taylor, N. J., Watanabe, M., Tanaka, Y., Loiseau, F., Passalacqua, R. & Campagna, S. (2004). *Chem. Eur. J.* **10**, 3640–3648.

Polson, M. I. J., Taylor, N. J. & Hanan, G. S. (2002). *Chem. Commun.* pp. 1356–1357.

Pyo, S., Perez-Cordero, E., Bott, S. G. & Echegoyen, L. (1999). *Inorg. Chem.* **38**, 3337–3343.

Rillema, D. P., Jones, D. S., Woods, C. & Levy, H. A. (1992). *Inorg. Chem.* **31**, 2935–2938.

Sheldrick, G. M. (1996). *SADABS*. Bruker AXS Inc., Madison, USA.

Son, S. U., Park, K. U., Lee, Y.-S., Kim, B. Y., Choi, C. H., Lah, M. S., Jang, Y. H., Jang, D.-J. & Chung, Y. K. (2004). *Inorg. Chem.* **43**, 6896–6898.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.