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cis-Bis(2,2′-bipyridyl-κ^2N,N')chloro(1-phenyl-4,4′-bipyridinium-$\kappa N^{1'}$)ruthenium(**II**) bis(hexafluorophosphate)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.007 Å
Disorder in solvent or counterion
R factor = 0.060
wR factor = 0.128
Data-to-parameter ratio = 13.1

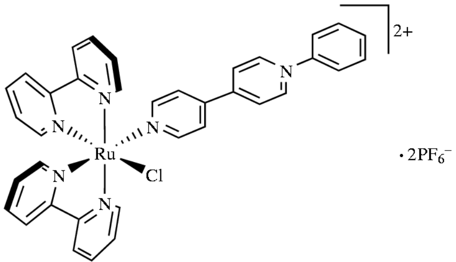
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The crystal structure of the title compound, [RuCl($C_{16}H_{13}N_2$)($C_{10}H_8N_2$)$_2$](PF_6)$_2$, is described. Although related compounds are known to display nonlinear optical (NLO) properties, the present salt crystallizes in the centrosymmetric space group $P2_1/c$, so is not expected to show bulk NLO effects.

Comment

Investigations into new molecular materials having nonlinear optical (NLO) properties are important for the development of emerging optoelectronic and photonic technologies (Bosshard *et al.*, 1995; Nalwa & Miyata, 1997). Recent studies in this field have involved a wide range of organotransition metal complexes, which can show very pronounced NLO effects (Di Bella, 2001; Coe, 2004). Previous studies from our laboratory have included ruthenium(II) ammine complexes of *N*-arylated pyridinium ligands, such as *N*-phenyl-4,4′-bipyridinium (PhQ$^+$; Coe *et al.*, 1998, 2002; Coe, Jones *et al.*, 2003). The creation of potentially useful quadratic NLO materials requires the optimization of both molecular and macroscopic properties. Active chromophores must be arranged non-centrosymmetrically for bulk quadratic NLO effects, such as frequency doubling (second harmonic generation, SHG), to be observed.

We have recently studied a series of complex salts containing *cis*-[Ru(NH_3)$_4$(L)$_2$]$^{4+}$ (L = PhQ$^+$ *etc.*), which have strongly two-dimensional molecular NLO responses (Coe, Harris & Brunschwig, 2003). The investigation of related compounds is clearly of interest, and readily accessible targets include species in which the ammine ligands are replaced by the classical chelating 2,2′-bipyridyl (bpy) ligand. The new compound, (I), was synthesized as an intermediate on the route to *cis*-[Ru(bpy)$_2$(PhQ$^+$)$_2$]$^{4+}$, by the reaction of *cis*-RuCl$_2$(bpy)$_2$·2H_2O (Lay *et al.*, 1986) with [PhQ$^+$]PF_6 (Coe *et al.*, 2000).



(I)

The complex salt, (I), shows an intense broad visible absorption band at λ_{max} = 498 nm in acetonitrile. This absorption is attributable to $d \rightarrow \pi^*$ metal-to-ligand chargetransfer (MLCT) transitions from the Ru-based HOMO to the LUMOs localized on the bpy and PhQ^+ ligands. PhQ^+ is expected to be a stronger electron acceptor than bpy, so it is likely that the low-energy tail of the MLCT band corresponds to Ru→ PhQ^+ excitations. Such low-energy MLCT bands are typically associated with large molecular quadratic NLO responses (Di Bella, 2001; Coe, 2004). Cyclic voltammetric studies reveal a reversible $Ru^{III/II}$ wave at $E_{1/2} = 0.88$ V *versus* Ag–AgCl, together with several irreversible ligand-based reduction processes, the first of which has an E_{pc} value of −0.63 V *versus* Ag–AgCl (most likely attributable to a $PhQ^{+/0}$ process).

The molecular structure of the complex cation in (I) is as indicated by ^{1}NMR spectroscopy, with an approximately octahedral metal centre and a *cis* arrangement of the bpy ligands (Fig. 1). The PhQ^+ ligand is highly twisted, with a dihedral angle of 37.5 (3)° defined by the ring planes N1/C1–C5 and N2/C9/C10/C6–C8, and an angle of 47.0 (3)° between the planes N2/C9/C10/C6–C8 and C11–C16. Smaller twists between the pyridyl and pyridinium rings of PhQ^+ have been observed in the compounds *trans*-[Ru(NH$_3$)$_4$(PTZ)(PhQ^+)]-(PF$_6$)$_3$·Et$_2$O (PTZ = S-coordinated phenothiazine; Coe *et al.*, 1998) and *trans*-[RuCl(pdma)$_2$(PhQ^+)](PF$_6$)$_3$·MeCN [pdma = 1,2-phenylenebis(dimethylarsine); Coe *et al.*, 2000], whilst *fac*-[Re(CO)$_3$(*L–L*)(PhQ^+)](PF$_6$)$_2$ (*L–L* = *N*,*N*′-bis-isopropyl-1,4-diazabutadiene) also shows a highly twisted ligand structure (Busby *et al.*, 2004).

The crystal packing of (I) is of interest with regard to quadratic NLO properties. Unfortunately, (I) adopts the centrosymmetric space group $P2_1/c$ and is therefore not expected to display bulk NLO effects. Nevertheless, it is quite possible that metathesis of the hexafluorophosphate counter-anions may cause the complex cations to adopt a more favourable crystal structure.

Experimental

A solution of *cis*-RuCl$_2$(bpy)$_2$·2H$_2$O (100 mg. 0.192 mmol) and [PhQ^+]PF$_6$ (280 mg, 0.740 mmol) in degassed 2:1 ethanol/acetone (60 ml) was heated at reflux in the dark under Ar for 2.5 h. The resulting red–purple solution was reduced in volume on a rotary evaporator, and addition of aqueous NH$_4$PF$_6$ produced a purple precipitate, which was filtered off, washed with water and dried. Excess [PhQ^+]PF$_6$ was removed by washing several times with methanol to afford a dark-purple solid. Yield 102 mg (55%). The product (29 mg) was further purified by vapour diffusion of diethyl ether into a concentrated acetone solution, giving 22 mg of dark-purple crystals. Analysis calculated for $C_{36}H_{29}ClF_{12}N_6P_2Ru$: C 44.48, H 3.01, N 8.65%; found: C 44.50, H 2.86, N 8.51%. ^{1}H NMR (300 MHz, CD$_3$COCD$_3$, p.p.m.): 10.10 (1H, *d*, *J* = 5.7 Hz, bpy H^6), 9.52 (2H, *d*, *J* = 7.0 Hz, C$_5$H$_4$N), 9.11 (2H, *br s*, C$_5$H$_4$N), 8.80 (4H, *d*, *J* = 6.9 Hz, C$_5$H$_4$N), 8.73 (1H, *d*, *J* = 8.2 Hz, bpy H^3), 8.67 (1H, *d*, *J* = 7.8 Hz, bpy H^3), 8.64 (1H, *d*, *J* = 7.8 Hz, bpy H^3), 8.26 (2H, *m*, bpy H^4 and H^3), 8.18 (1H, *d*, *J* = 5.1 Hz, bpy H^6), 8.08–7.94 (7H, *m*, 2 Ph, 3bpy H^4 and 2bpy H^6), 7.84 (4H, *m*, 3 Ph and bpy H^5), 7.76 (1H, *m*, *J* = 1.5, 5.8 and 7.5 Hz, bpy H^5), 7.45 (1H, *m*, *J* = 1.5, 5.9 and 7.1 Hz, bpy H^5), 7.37 (1H, *m*, *J* = 1.3, 5.9 and 7.6 Hz, bpy H^5). ES–MS *m*/*z* = 995 ({*M* + Na$^+$}$^+$), 827 ({*M* − PF$_6^-$}$^+$). Crystals were obtained by slow diffusion of diethyl ether vapour into an acetone solution at 277 K.

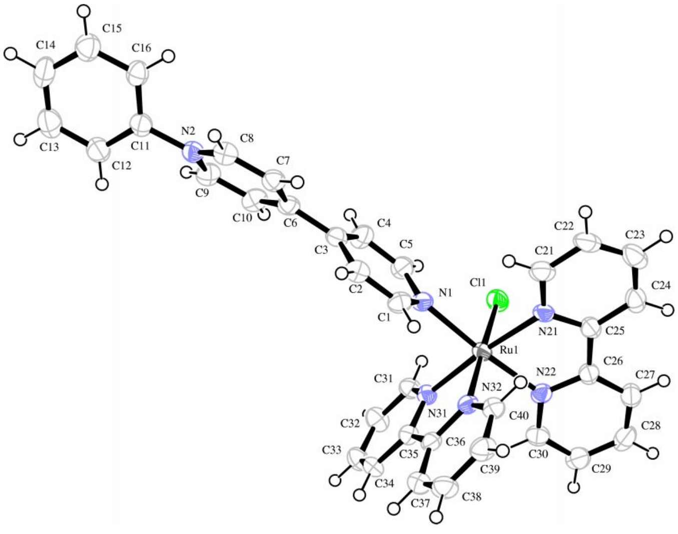


Figure 1
View of the complex cation in salt (I) (35% probability displacement ellipsoids).

Crystal data

[RuCl($C_{16}H_{13}N_2$)($C_{10}H_8N_2$)$_2$](PF$_6$)$_2$	D_x = 1.735 Mg m^{-3}
M_r = 972.11	Mo *Kα* radiation
Monoclinic, $P2_1/c$	Cell parameters from 8598 reflections
a = 12.687 (3) Å	*θ* = 2.9–27.5°
b = 23.424 (17) Å	*μ* = 0.68 mm^{-1}
c = 12.956 (8) Å	*T* = 120 (2) K
β = 104.80 (4)°	Plate, dark purple
V = 3722 (4) Å^3	0.38 × 0.22 × 0.03 mm
Z = 4	

Data collection

Nonius KappaCCD area-detector diffractometer	8537 independent reflections
φ and *ω* scans	5485 reflections with *I* > 2*σ*(*I*)
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995, 1997)	R_{int} = 0.097
T_{min} = 0.783, T_{max} = 0.980	θ_{max} = 27.5°
50 477 measured reflections	*h* = −16 → 15
	k = −30 → 30
	l = −16 → 16

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0483P)^2 + 5.3619P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.060	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.128	$\Delta\rho_{max}$ = 1.40 e Å^{-3}
S = 1.03	$\Delta\rho_{min}$ = −0.49 e Å^{-3}
8537 reflections	
651 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ru1—N32	2.029 (3)	Ru1—N31	2.057 (3)
Ru1—N22	2.038 (3)	Ru1—N1	2.125 (3)
Ru1—N21	2.053 (3)	Ru1—Cl1	2.4059 (16)
N32—Ru1—N22	91.32 (13)	N21—Ru1—N1	97.65 (13)
N32—Ru1—N21	98.91 (14)	N31—Ru1—N1	87.81 (13)
N22—Ru1—N21	78.99 (14)	N32—Ru1—Cl1	173.48 (10)
N32—Ru1—N31	79.60 (15)	N22—Ru1—Cl1	84.68 (10)
N22—Ru1—N31	95.61 (13)	N21—Ru1—Cl1	85.41 (11)
N21—Ru1—N31	174.40 (13)	N31—Ru1—Cl1	95.63 (11)
N32—Ru1—N1	92.09 (13)	N1—Ru1—Cl1	92.18 (10)
N22—Ru1—N1	175.56 (13)		

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The two hexafluorophosphate anions were both disordered over two main sites [site-occupancy factors: (i) PF_6 0.45 (2):0.55 (2) P1:P101; (ii) PF_6 0.581 (5):0.419 (2) P11:P111]. To simplify the modelling, the P—F bonds were restrained to be similar in length, with angles close to 90°. These restraints have resulted in some closer contacts than expected. All H atoms were included in idealized positions, with C—H = 0.95 Å and $U_{iso}(H)$ values set at $1.2U_{eq}(C)$. The maximum electron-density peak is 2.23 Å from atom H39.

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

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