Bis(8-quinolinolato-N,O)platinum(II) and its synthetic intermediate, 8-hydroxyquinolinium dichloro-(8-quinolinolato-N,O)platinate(II) tetrahydrate

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Bis(8-quinolinolato-N,O)platinum(II), $[Pt(C_9H_6NO)_2]$, (I), has a centrosymmetric planar structure with *trans* coordination. The molecules form an inclined π stack, with an interplanar spacing of 3.400 (6) Å. 8-Hydroxyquinolinium dichloro(8-quinolinolato-N,O)platinate(II) tetrahydrate, $(C_9H_8NO)[PtCl_2(C_9H_6NO)]\cdot4H_2O$, (II), is soluble in water and is regarded as the synthetic intermediate of the insoluble neutral compound (I). The uncoordinated 8-hydroxyquinolinium cations and the monoquinolinolate complexes form an alternating π stack. The origins of fluorescence and phosphorescence in (II) are assigned to the 8-hydroxyquinolinium cation and the monoquinolinolate–Pt complex, respectively.

Comment

The metal complexes of 8-quinolinol (qH), such as $[Alq_3]$, have attracted much attention recently as luminescent materials. In contrast with $[Alq_3]$, which emits yellow–green fluorescence, bis(8-quinolinolato)platinum(II), $[Ptq_2]$, (I), was reported to emit red phosphorescence with a relatively long lifetime (Ballardini *et al.*, 1986). The origin was deduced to be a ligand-centred excited state on the basis of the similarity of the emission properties to those of the tris(8-quinolinolato)-rhodium(III) and -iridium(III) complexes.

In the course of the synthesis of the red crystal of (I), we found a new orange crystal of (II), which showed both yellow fluorescence and red phosphorescence in solution. The emission maxima are 480 and 600 nm in EtOH–MeOH (1:1 *v/v*) at

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77 K, respectively. The phosphorescence spectrum is similar to that for (I) ($\lambda_{max} = 620$ nm).

Compound (II) is soluble in water, and very soluble in organic solvents such as methanol and dimethyl sulfoxide, while the neutral compound (I) is much less soluble. However, once compound (II) had dissolved, the red crystal (I) crystallized from the solution. Therefore, (II) can be regarded as the synthetic intermediate of the more stable (I).
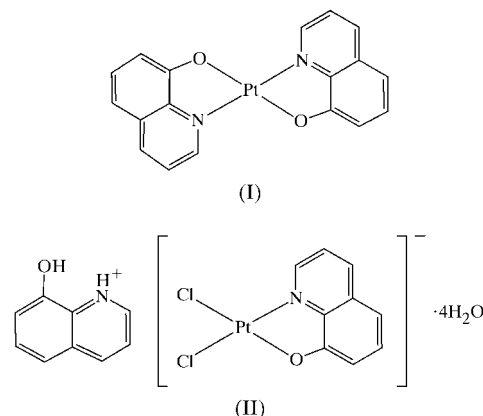
X-ray crystallography proved that (II) is an unexpected composite crystal of an uncoordinated 8-hydroxyquinolinium ion and the monoquinolinolate complex, $(qH_2)[PtCl_2q]\cdot4H_2O$. In addition, the structure of (I) has also been determined, owing to the successful selection of a single crystal from mostly twin crystals.

As shown in Fig. 1, the molecular structure of (I) is planar and the two 8-quinolinolate ligands are coordinated in a *trans* geometry. The Pt atom lies on a crystallographic inversion centre. The deviations of the atoms from the least-squares plane of (I) are within 0.03 Å.

The crystal structure of (I) is isomorphous with the corresponding Pd[II] complex (Prout & Wheeler, 1966). The bond lengths and angles of (I) are essentially identical to those of
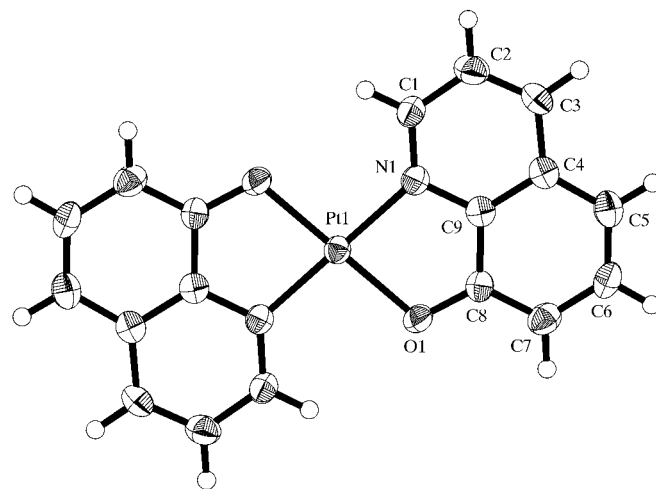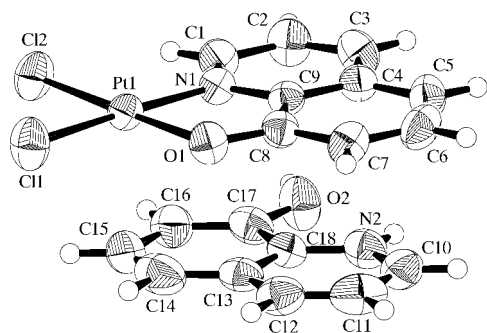

Figure 1
The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids plotted at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

metal-organic compounds

Figure 2
A perspective view of (II), showing the atom-numbering scheme and displacement ellipsoids plotted at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. The hydrate water molecules have been omitted for clarity.

the charge-transfer complex [Ptq$_2$]·TCNQ (TCNQ is 7,7,8,8-tetracyanoquinodimethane; Bergamini *et al.*, 1987). The Pt complexes in (I) are stacked in an inclined fashion, the interplanar spacing of the π–π stack being 3.400 (6) Å. The long Pt···Pt distance of 4.704 (2) Å, which is equal to the cell length of the *b* axis, suggests no Pt—Pt electronic interaction.

Fig. 2 shows a perspective view of (II). The crystal consists of uncoordinated 8-hydroxyquinolinium cations and mono-quinolinolate–Pt complex anions, stacked alternately to form a π stack. The interplanar spacings are found to be typical for π stacks, at 3.44 (1) and 3.47 (1) Å, respectively. The structural features of the integrated stack are similar to those for (ethylenediamine)(α-diimine)platinum(II) complexes and phenanthroline (Kato *et al.*, 2001).

The water molecules in (II) form hydrogen bonds with the Cl$^-$ and quinolinolate ligands in the Pt complex. Differential Fourier synthesis confirmed the existence of the 8-hydroxy-quinolinium cation in (II), showing the peaks of the H atoms bonded to N and O atoms. The geometry of the 8-hydroxy-quinolinium cation is very similar to those of the coordinated quinolinolate ions in (I) and (II).

An additional interesting feature in (II) is the inequality of the coordination angles, in contrast to the symmetrical structure of (I); the Cl2—Pt1—N1 angle is much larger than Cl1—Pt1—O1 (Table 2). This is due to the steric effect of the large Cl atoms and the α-H of the quinolinolate ligand (Cl2···H1 2.70 Å).

On the basis of the structures of (I) and (II), the origin of fluorescence for (II) was assigned to the 8-hydroxy-quinolinium cation, while phosphorescence is due to the monoquinolinolate–Pt complex; the latter would have the same origin as that for (I).

Experimental

To an aqueous solution of K$_2$[PtCl$_4$] adjusted to *ca* pH 10, two equimolar amounts of 8-quinolinol (qH) were added and the solution heated for a few minutes. After cooling to room temperature, a dark-orange precipitate was deposited. This was recrystallized from dimethyl sulfoxide (DMSO) to give red crystals of (I). The filtrate of the reaction solution was allowed to stand for several days at room

temperature to give orange needle crystals of (II). Spectroscopic analysis, ^{1}H NMR (DMSO-d_6, δ, p.p.m.) for (I): 7.00 (*d*, 7H), 7.12 (*d*, 5H), 7.48 (*t*, 6H), 7.71 (*dd*, 3H), 8.65 (*d*, 4H), 8.80 (*d*, 2H); for (II): 7.01 (*d*, 7H^c), 7.17 (*d*, 5H^c), 7.48 (*t*, 6H^c), 7.71 (*dd*, 3H^c), 8.67 (*d*, 4H^c), 9.38 (*d*, 2H^c), 7.30 (*d*, 7H^u), 7.57 (*m*, 5H and 6H^u), 7.79 (*dd*, 3H^u), 8.71 (*d*, 4H^u), 8.95 (*d*, 2H^u), 10.92 (*br*, –OH^u), where *u* and *c* denote the 8-hydroxyquinolinium ion and the coordinated 8-quinolinolate ion, respectively; ESI–MS($-$) for (II): 410 ([*M*]$^-$), 821 ([2*M* + H]$^-$), 843 ([2*M* + Na]$^-$).

Table 1
Selected geometric parameters (Å, °) for (I).

Pt1—O1	2.014 (3)	Pt1—N1	1.992 (4)
O1—Pt1—N1	82.8 (1)	O1—Pt1—N1^i	97.2 (1)

Symmetry code: (i) $-x, -y, -z$.

Compound (I)

Crystal data

[Pt(C$_9$H$_6$NO)$_2$]	D_x = 2.283 Mg m^{-3}
M_r = 483.39	Mo *K*α radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
a = 11.349 (2) Å	reflections
b = 4.704 (2) Å	θ = 14.6–15.0°
c = 13.731 (1) Å	μ = 9.95 mm^{-1}
β = 106.43 (1)°	T = 294.2 K
V = 703.0 (3) Å^3	Plate, red
Z = 2	0.21 × 0.10 × 0.02 mm

Data collection

Rigaku AFC-7*R* diffractometer	R_{int} = 0.015
$\omega/2\theta$ scans	θ_{max} = 27.5°
Absorption correction: analytical	h = 0 → 14
(de Meulenaer & Tompa, 1965)	k = −6 → 0
T_{min} = 0.397, T_{max} = 0.822	l = −17 → 17
1685 measured reflections	3 standard reflections
1607 independent reflections	every 150 reflections
1053 reflections with $I > 2\sigma(I)$	intensity decay: 1.7%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0181P)^2]$
$R(F)$ = 0.018	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.045	$(\Delta/\sigma)_{max}$ = 0.005
S = 0.97	$\Delta\rho_{max}$ = 0.83 e Å^{-3}
1607 reflections	$\Delta\rho_{min}$ = −0.43 e Å^{-3}
107 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	(Sheldrick, 1997)
	Extinction coefficient: 0.0006

Compound (II)

Crystal data

(C$_9$H$_8$NO)[PtCl$_2$(C$_9$H$_6$NO)]·4H$_2$O	Z = 2
M_r = 628.38	D_x = 1.949 Mg m^{-3}
Triclinic, $P\bar{1}$	Mo *K*α radiation
a = 10.665 (3) Å	Cell parameters from 25
b = 14.492 (3) Å	reflections
c = 7.266 (2) Å	θ = 14.7–15.0°
α = 100.46 (2)°	μ = 6.81 mm^{-1}
β = 104.13 (2)°	T = 294.2 K
γ = 85.93 (2)°	Needle, orange
V = 1070.5 (5) Å^3	0.28 × 0.08 × 0.06 mm

Table 2
Selected geometric parameters (Å, °) for (II).

Pt1—Cl1	2.304 (3)	Pt1—O1	2.010 (6)
Pt1—Cl2	2.297 (2)	Pt1—N1	1.999 (7)
Cl1—Pt1—Cl2	91.55 (9)	Cl2—Pt1—O1	178.0 (2)
Cl1—Pt1—O1	90.5 (2)	Cl2—Pt1—N1	95.0 (2)
Cl1—Pt1—N1	173.3 (2)	O1—Pt1—N1	82.9 (3)

Data collection

Rigaku AFC-7R diffractometer	$R_{int} = 0.023$
$\omega/2\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction: ψ scan	$h = -13 \rightarrow 13$
(North *et al.*, 1968)	$k = -18 \rightarrow 18$
$T_{min} = 0.426$, $T_{max} = 0.664$	$l = -9 \rightarrow 1$
5828 measured reflections	3 standard reflections
4929 independent reflections	every 150 reflections
3788 reflections with $I > 2\sigma(I)$	intensity decay: 0.1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0847P)^2$
$R(F) = 0.044$	$+ 1.3493P]$
$wR(F^2) = 0.136$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} = 0.001$
4929 reflections	$\Delta\rho_{max} = 3.46$ e Å^{-3}
262 parameters	$\Delta\rho_{min} = -1.51$ e Å^{-3}
H-atom parameters constrained	

The H atoms of the water molecules in (II) were not included because their positions could not be determined precisely. Other H atoms were treated as riding, with C—H = 0.96–0.98 Å in (I), and C—H = 0.94–0.96, O—H = 1.11 and N—H = 0.88 Å in (II); in both compounds, $U_{iso}(H) = U_{eq}(C)$.

For both compounds, data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku, 1995); cell refinement: *Rigaku/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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