

Highly luminescent neutral *cis*-dicyano osmium(II) complexes

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Two highly luminescent neutral *cis*-dicyanoosmium(II) complexes are prepared by photoinduced oxygen atom transfer reactions of *trans*-[OsO₂(CN)₂(dpphen)] with PPh₃ and Me₂SO; their MLCT excited states are emissive with long lifetimes (0.20–1.99 μs) and high quantum yields [(40–1.8) × 10^{−2}] and the emission maxima show pronounced solvatochromism.

Luminescent metal complexes with high emission quantum yields and which could function as molecular building blocks for polynuclear metal complexes find useful applications in supramolecular chemistry and photocatalysis.¹ However, examples of these complexes are sparse in literature. In this context, we were attracted to the wide applications of [RuL₂(CN)₂]² (L = 2,2′-bipyridine or 1,10-phenanthroline) as building blocks for polynuclear cyano-bridged metal complexes and the striking luminescent properties of [Os^{III}L_x(P–P)_{3–x}]²⁺ (P–P = diphosphine, *x* = 1 or 2).³ Herein is described the formation of highly luminescent neutral cyanoosmium(II) complexes which have the combined features and properties of both [RuL₂(CN)₂] and [Os^{III}L_x(P–P)_{3–x}]²⁺. These complexes are anticipated to provide a new entry to supramolecular photochemistry.

[OsO₂(CN)₂(dpphen)] **1** (dpphen = 4,7-diphenyl-1,10-phenanthroline) was prepared from dpphen and [OsO₂(C–N)₂(OH)₂]^{2–} following the reported literature method.⁴ As with other dioxoosmium(VI) complexes,^{4,5} it has a long-lived and emissive excited state [lifetime 1 μs; quantum yield 5 × 10^{−4}; λ_{max,em} 650 nm].

Under UV irradiation, complex **1** oxidizes PPh₃ and Me₂SO to give OPPh₃ and Me₂SO₂, respectively. For the photoreaction of **1** in neat Me₂SO, removal of the solvent after photolysis gave an orange solid, which was recrystallized from MeOH–Et₂O to give [Os(CN)₂(Me₂SO)₂(dpphen)]·2H₂O **2**. Similar photoreaction with PPh₃ gave [Os(CN)₂(PPh₃)₂(dpphen)] **3**.†

Fig. 1 shows a perspective view of **2**.‡ The structure features a rare example of Os^{II}–CN and Os^{II}–Me₂SO complexes. The

coordination geometry of the Os atom is slightly distorted octahedral with the cyanide ligands *cis* to each other. The Os–C bond of 2.00(1) Å is comparable to that of 2.023 Å in [AsPh₄]₂–[Os(PPh₃)₂(CN)₄]·2MeCN·2H₂O.⁶ The two Me₂SO ligands are S-bonded to the Os atom. They are *trans* to each other with S–Os–S angle of 174.1(2)°. The Os–S distance of 2.293(3) Å is similar to the related distances of 2.31(2) Å in [Os(S₇)(PMe₃)₃]⁷ and 2.261 Å in [Ru(Me₂SO)₃Cl₃][–] (S-coordinated).⁸ To our knowledge, no X-ray structure of an Os^{II}–Me₂SO complex has been reported in the literature. [Os(Me₂SO)₃Cl₃]⁹ has been proposed to be O- and S-coordinated while the structure of [Os(bpy)₂(Me₂SO)₂]²⁺ is unknown.^{3b}

Complexes **2** and **3** are luminescent in the solid state and in solution with emission maxima ranging from 710 to 564 nm. The spectral data are listed in Table 1. The two complexes display a strong absorption band in the UV region (λ_{max} ca. 300 nm, ε > 10⁵ dm³ mol^{−1} cm^{−1}) and a moderate intense absorption band at the visible region (λ_{max} ca. 440 nm, ε > 10³ dm³ mol^{−1} cm^{−1}) with a tailing at 500–600 nm, the latter is ascribed to the Os d_π–π* MLCT transition.¹⁰ Both the absorption and emission spectra are strongly affected by the solvent and both the emission lifetime and quantum yield decrease as the solvent polarity decreases.

Plots of ln *k*_{nr} vs. *E*_{em} for complexes **2** and **3** in various solvents are shown in Fig. 2. Except for the data of **2** in protic solvents, a linear correlation between ln *k*_{nr} and *E*_{em} values is observed suggesting that the non-radiative decay is governed by the energy-gap law.¹¹ The slope of −6.8 eV^{−1} and intercept of

Table 1 Spectroscopic data for complexes **2** and **3**

	Solvent (AN ^a)	λ _{max,em} (λ _{max,abs}) ^{b/} nm	Lifetime/μs (quantum yield)
2	C ₆ H ₆ (8.2)	629 (377)	1.12 (0.24)
	C ₆ H ₅ Me (8.2)	630 (375)	1.09 (0.23)
	Me ₂ CO (12.5)	635 (369)	0.92 (0.17)
	dmf (16.0)	630 (359)	0.95 (0.17)
	C ₂ H ₄ Cl ₂ (16.7)	616 (361)	1.45 (0.39)
	Me ₂ SO (19.3)	630 (364)	1.04 (0.20)
	MeCN (19.3)	625 (359)	1.10 (0.18)
	CH ₂ Cl ₂ (20.4)	613 (359)	1.45 (0.34)
	CHCl ₃ (23.1)	597 (357)	1.99 (0.49)
	EtOH (37.1)	600 (344)	1.42 (0.28)
	HCONH ₂ (39.8)	594 (341)	1.43 (0.34)
	MeOH (41.3)	595 (340)	1.34 (0.25)
	MeOH–H ₂ O	575 (332)	1.62 (0.04)
	H ₂ O (54.8)	564 (327)	1.37 (0.08)
	C ₆ H ₆ (8.2)	710 (438)	0.33 (0.03)
3	Me ₂ CO (12.5)	700 (420)	0.42 (0.04)
	Py (14.2)	681 (420)	0.48 (0.06)
	dmf (16.0)	675 (418)	0.55 (0.09)
	Me ₂ SO (19.3)	673 (414)	0.57 (0.08)
	MeCN (19.3)	660 (409)	1.39 (0.05)
	CH ₂ Cl ₂ (20.4)	672 (418)	0.62 (0.09)
	CHCl ₃ (23.1)	595 (379)	3.72 (0.33)
	EtOH (37.1)	645 (399)	0.79 (0.13)
	HCONH ₂ (39.8)	632 (387)	1.09 (0.17)
	MeOH (41.3)	639 (396)	0.94 (0.11)

^a Gutmann's solvent acceptor number.^{14b} Measurements at room temperature. ^b Spin-allowed MLCT absorption maximum.

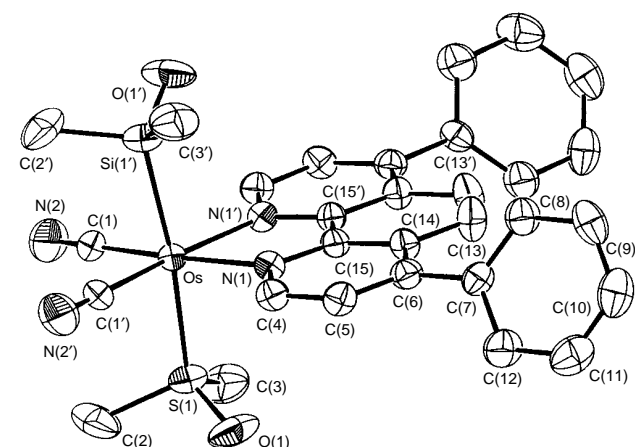


Fig. 1 A perspective view of **2** (40% probability ellipsoids): Os–S(1) 2.293(3), Os–N(1) 2.111(8), Os–C(1) 2.00(1); S(1)–Os–S(1′) 174.1(2), S(1)–Os–C(1) 87.7(3), S(1)–Os–N(1) 91.1(2), N(1)–Os–C(1) 94.5(4), C(1)–Os–C(1′) 94.6(6)

27 agree with similar values of *ca.* -7.5 eV^{-1} (slope) and 28–30 (intercept) of complexes $[\text{OsX}_4\text{L}]$ and $[\text{OsX}_2\text{L}_2]$ ($\text{X} \neq \text{CO}$) in which cases the non-radiative decay is dominated by the ligand-based C–C vibrational stretch modes (*ca.* 1350 cm^{-1}).¹² Complex **2** shows deviation from the linear correlation in protic solvents. Presumably, a change of dominant acceptor vibration for non-radiative decay is attributed to the hydrogen-bonding interaction between the solvent and Me_2SO .^{2c}

For both complexes, the plots of absorption and emission energy *versus* Gutmann's solvent acceptor number, AN, are shown in Fig. 3. Good linear relationship is observed in each case. The absorption and emission spectra shift to higher energy with increasing AN. This implies the donor–acceptor interaction between the solvent and the complexes. The donor–acceptor interaction results in decrease of the σ -donating ability of the cyanide ligand (and/or Me_2SO ligand).

Most osmium(ii) polypyridine complexes are known to be stable towards photosubstitution reaction. However, it has been noted that the $[\text{Os}(\text{bpy})_2(\text{Me}_2\text{SO})_2]^{2+}$ complex is photochemically unstable and this has been ascribed to its MLCT and

low-lying d–d states being close in energy.^{3b} Complexes **2** and **3** were found to be stable even after photolysis in acetonitrile for 2 days. Presumably, the $\text{Os}^{\text{II}} \rightarrow \text{CN}$ π -back bonding increases the d–d state energy relative to the MLCT emitting state.¹³

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Footnotes

† ^1H NMR (CDCl_3) δ 10.01 (d, 2H), 8.06 (s, 2H), 7.84 (d, 2H), 7.67–7.59 (m, 10H), 3.39 (s, 12H, OSMe_2). UV–VIS (MeCN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 269 (34721), 287 (32589), 359 (10457), 405 (sh) (6498), 450 (sh) (1427). (H_2O): 257 (18400), 287 (33098), 327 (13814), 385 (sh) (5697). **3** ^1H NMR (CDCl_3) δ 8.34 (d, 2H), 8.17 (d, 2H), 7.62–7.58 (m, 4H), 7.50–7.41 (m, 18H), 7.17–7.04 (m, 18H), 6.72 (dd, 2H). UV–VIS (MeCN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): 282 (36590), 410 (7454), 440 (6445), 515 (sh) (1185).

‡ *Crystal data*: $[\text{OsS}_2\text{O}_2\text{N}_4\text{C}_{30}\text{H}_{28}\cdot 2\text{H}_2\text{O}]$, $M_r = 766.93$, monoclinic, space group $\text{C}2/c$ (no. 15), $a = 19.180(5)$, $b = 19.902(5)$, $c = 9.471(3)$ Å, $\beta = 118.18(3)^\circ$, $U = 3186(1)$ Å³, $Z = 4$, $D_c = 1.598 \text{ g cm}^{-3}$, $\mu = 41.69 \text{ cm}^{-1}$, $F(000) = 1520$, $T = 301 \text{ K}$. An orange–brown crystal of dimensions $0.15 \times 0.10 \times 0.25 \text{ mm}$, was used for data collection on a Rigaku AFC7R diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å). 2905 unique reflections measured, 2117 of which [$I > 3\sigma(I)$] were considered observed. The structure was solved by the Patterson method and refined by full-matrix least-squares. Convergence for 186 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma(F_o^2)$ where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.014F_o^2)^2]$ for 2117 unique reflections was reached at $R = 0.040$, $R_w = 0.057$, G.O.F. = 1.89. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.38 and -0.81 e Å^{-3} respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/370.

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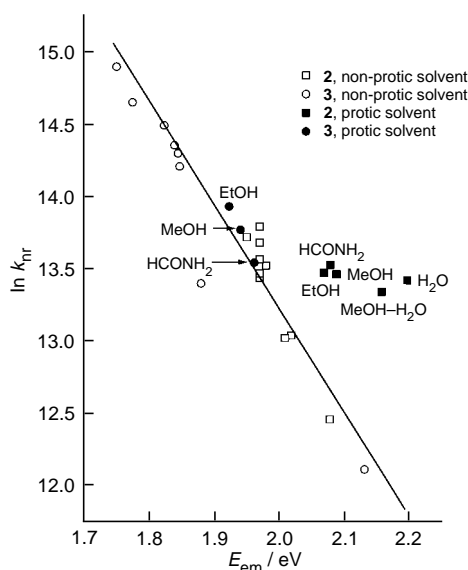


Fig. 2 A plot of $\ln k_{\text{nr}}$ vs. E_{em} for complexes **2** and **3**

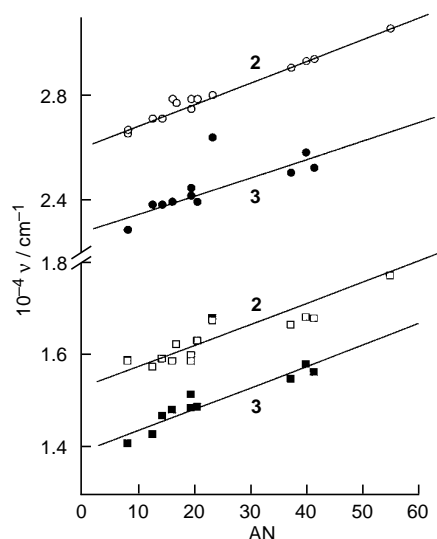


Fig. 3 Plots of ν_{abs} (circles) and ν_{em} (squares) vs. Gutmann's acceptor number (AN) for complexes **2** and **3**