DALTON

Novel triosmium cluster complexes with rod-like molecular geometry. Syntheses and crystal structures of $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH{=}NC_6H_4OC_{16}H_{33})]$ and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NC_5H_3CH{=}NC_6H_4OC_{16}H_{33})]$

Wai-Yeung Wong, Suzanna Chan and Wing-Tak Wong *

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

The reaction of $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ with 1 equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene in the presence of a 10-fold excess of $NC_5H_4(CH{=}NC_6H_4OC_{16}H_{33}\text{-}p)\text{-}4$ in CH_2Cl_2 at room temperature gave $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH{=}NC_6H_4OC_{16}H_{33})]$ **1** in 40% yield. The electronic absorption spectra of **1** in a series of organic solvents show significant negative solvatochromic shifts. Treatment of the activated cluster $[Os_3(CO)_{10}(NCMe)_2]$ with the same Schiff base in CH_2Cl_2 readily afforded the ortho-metallated cluster complex $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NC_5H_3CH{=}NC_6H_4OC_{16}H_{33})]$ **2** in 72% yield. Crystal structure analyses of **1** and **2** revealed that they both exhibit an interesting rod-like molecular geometry.

Transition-metal complexes containing ligands such as 4′-alkyloxy-4-stilbazoles $[NC_5H_4(CH{=}CHC_6H_4OR\text{-}p)\text{-}4]$ and *N*-(4-pyridylbenzylidene)aniline have been the subject of considerable research interest in the preparation of liquid-crystalline materials.[1] Of these, structurally characterized examples are however rare.[2] Besides, to our knowledge, no examples of carbonyl clusters of the iron triad having these kinds of ligands have been encountered. We report herein the syntheses and crystal structures of the first examples of such a system, each containing a long hexadecyl chain on the periphery of a triosmium metal core, and comment on their interesting crystal packings.

Experimental

General procedures

All manipulations were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques and were routinely monitored by solution IR spectroscopy (carbonyl stretching region). Solvents were dried over appropriate reagents according to standard literature procedures[3] and freshly distilled before use. The compounds $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$,[4] $[Os_3(CO)_{10}(NCMe)_2]$[5] and $NC_5H_4(CH{=}NC_6H_4OC_{16}H_{33}\text{-}p)\text{-}4$[1e] were prepared as described previously. Infrared spectra were recorded in solution on a Bio-Rad FTS-7 IR spectrometer, using 0.5 mm CaF_2 solution cells, ^1H NMR spectra on a JEOL GSX-270 FT-NMR spectrometer using CD_2Cl_2 and referenced to $SiMe_4$ (δ 0) and mass spectra on a Finnigan MAT 95 instrument with the fast atom bombardment technique. Elemental analyses were determined by Butterworth Laboratories Ltd., UK. Electronic absorption spectra were obtained on a microprocessor-controlled Perkin-Elmer Lambda 3B UV/VIS spectrometer, thermostatted by a Lauda circulating bath.

Preparations

$[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH{=}NC_6H_4OC_{16}H_{33})]$ 1. Pure $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ (87.3 mg, 0.10 mmol) and the Schiff base $NC_5H_4CH{=}NC_6H_4OC_{16}H_{33}$ (422 mg, 1.00 mmol) were dissolved in CH_2Cl_2 (15 cm^3) and a 1,8-diazabicyclo[5.4.0]-undec-7-ene (dbu)–CH_2Cl_2 solution (15.2 mg, 0.10 mmol) was added dropwise. An immediate colour from almost colourless to dark green was observed. After stirring for 15 min the solution was concentrated to 5 cm^3 *in vacuo*. Purification was accomplished by TLC using hexane–CH_2Cl_2 (60:40, v/v) as eluent to yield the required complex as a brownish red crystalline solid in 40% yield (50.4 mg, 0.04 mmol). IR (CH_2Cl_2, $\tilde{\nu}_{CO}$/cm^{-1}): 2089m, 2055vs, 2024vs, 1983s, 1951m and 1935m. ^1H NMR (CD_2Cl_2): δ 9.67 (d, 2 H, *J* = 7.0, H_α of C_5H_4N), 8.58 (s, 1 H, CH=N), 7.85 (d, 2 H, *J* = 7.0, H_β of C_5H_4N), 7.44 (d, 2 H, *J* = 8.9, C_6H_4), 6.97 (d, 2 H, *J* = 8.9, C_6H_4), 4.01 (t, 2 H, *J* = 6.6, OCH_2), 1.80 (qnt, 2 H, *J* = 6.6 Hz, OCH_2CH_2), 1.54–1.27 [m, 26 H, $(CH_2)_{13}$], 0.88 (m, 3 H, CH_3) and −18.85 (s, 2 H, OsH). FAB mass spectrum (*m*-nitrobenzyl alcohol): *m*/*z* 1260 (M^+) (Found: C, 36.05; H, 3.30; N, 2.15. Calc. for $C_{38}H_{44}N_2O_{10}Os_3$: C, 36.25; H, 3.50; N, 2.20%).

$[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NC_5H_3CH{=}NC_6H_4OC_{16}H_{33})]$ 2. The complex $[Os_3(CO)_{10}(NCMe)_2]$ (60 mg, 0.06 mmol) and $NC_5H_4CH{=}NC_6H_4OC_{16}H_{33}$ (27 mg, 0.06 mmol) were allowed to react in CH_2Cl_2 (20 cm^3) at room temperature for 3 h to give a deep yellow solution. Evaporation to dryness and separation of the residue by TLC using hexane–CH_2Cl_2 (70:30, v/v) gave two yellow bands found to be $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OH)]$ ($R_f \approx 0.8$) and complex **2** ($R_f \approx 0.4$). Complex **2** was isolated as a bright yellow crystalline solid in 72% yield (55 mg, 0.043 mmol) after recrystallization from CH_2Cl_2–MeOH. IR (hexane, $\tilde{\nu}_{CO}$/cm^{-1}): 2104m, 2064vs, 2054vs, 2023vs, 2011vs, 2005s, 1993s and 1977m. ^1H NMR (CD_2Cl_2): δ 8.33 (s, 1 H, CH=N), 8.23 (d, 1 H, *J* = 5.9, H_α of C_5H_3N), 7.65 (d, 1 H, *J* = 2.0, $H_{\beta'}$ of C_5H_3N), 7.28 (d, 2 H, *J* = 8.9, C_6H_4), 7.23 (dd, 1 H, *J* = 5.9, 2.0, H_β of C_5H_3N), 6.92 (d, 2 H, *J* = 8.9, C_6H_4), 3.97 (t, 2 H, *J* = 6.6, OCH_2), 1.78 (qnt, 2 H, *J* = 6.6 Hz, OCH_2CH_2), 1.53–1.27 [m, 26 H, $(CH_2)_{13}$], 0.88 (m, 3 H, CH_3) and −14.75 (s, 1 H, OsH). FAB mass spectrum: *m*/*z* 1274 (M^+) (Found: C, 35.55; H, 3.05; N, 1.95. Calc. for $C_{38}H_{42}N_2O_{11}Os_3$: C, 35.80; H, 3.30; N, 2.20%).

Crystallography

Brownish red crystals of complex **1** suitable for diffraction study were grown by slow evaporation of a solution of it in hexane–CH_2Cl_2 at ambient temperature for 2 d. Bright yellow single crystals of **2** were obtained following crystallization from a $CHCl_3$–MeOH solution at room temperature after 3 d. A rod-shaped crystal of **1** with approximate dimensions 0.23 × 0.33 × 0.44 mm and a crystalline plate of **2** having approximate dimensions 0.24 × 0.36 × 0.40 mm were selected and mounted on glass fibres with epoxy resin. Intensity data for **1** were measured on an Enraf-Nonius CAD4 diffractometer, those for **2** on a Rigaku AFC7R diffractometer, with graphite-monochromated Mo-Kα radiation (λ = 0.710 73Å) using the ω–2θ scan technique. Pertinent crystal data and details of the measurement of diffraction intensities are summarized in Table 1. Intensity data were corrected for Lorentz-polarization effects and semiempirical absorption corrections based on the ψ-scan method were also applied.[6]

The structures were solved by direct methods (MULTAN 82[7] for complex **1**, SIR 88[8] for **2**) and refined by full-matrix least-squares analyses. The osmium atoms were refined anisotropically. Hydrogen atoms on the organic moieties were placed in idealized positions (C–H 0.95 Å). The positions of the metal hydride atoms in both **1** and **2** were estimated by potential-energy calculations.[9] The program packages used were SDP[10] for **1** and TEXSAN[11] for **2**, respectively.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/50.

Results and Discussion

The dbu-initiated reaction[12] between $[Os_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCl)]$ and 10 equivalents of the Schiff base $NC_5H_4CH{=}N\text{-}C_6H_4OC_{16}H_{33}$ gives $[Os_3(\mu\text{-}H)_2(CO)_9(\mu_3\text{-}CNC_5H_4CH{=}N\text{-}C_6H_4OC_{16}H_{33})]$ **1** in the form of a brownish red crystalline solid. On the other hand, reaction of the activated triosmium cluster $[Os_3(CO)_{10}(NCMe)_2]$ with the same base was performed at room temperature, on the basis of the well known orthometallation of pyridine,[13] giving $[Os_3(\mu\text{-}H)(CO)_{10}\text{-}(\mu\text{-}NC_5H_3CH{=}NC_6H_4OC_{16}H_{33})]$ **2** as a major yellow product. The formulae of **1** and **2** were first established by FAB mass, IR and ^1H NMR spectroscopies, and both complexes gave satisfactory elemental analyses. In addition to being soluble in halogenated solvents, **1** and **2** were very soluble in alkanes, probably due to the presence of the highly hydrophobic hexadecyl tails.

Spectroscopic properties

The ν_{CO} IR spectrum of complex **1** is typical of other triosmium alkylidyne clusters with a similar formulation[12] and suggests that the pyridine ligand is bound to the apical carbon atom in an upright geometry without disturbing the symmetry of each molecule. Besides, the similarity of the IR spectra between those of **2** and $[Os_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}NC_5H_4)]$ indicates that **2** almost certainly has a corresponding orthometallated structure.[13] The ^1H NMR spectra of both complexes show proton resonances expected for the ligand and the appropriate bridging hydrides on the cluster frameworks. The signals due to the long alkyloxy chains are assigned as far as possible with the OCH_2 and OCH_2CH_2 methylene groups and the terminal methyl groups giving rise to discernible triplet, quintet and triplet signals respectively. The downfield displacement of the proton resonances of the ligand observed for **1**, in relation to those for the free base, confirms that the pyridyl nitrogen co-ordinates to the electron-withdrawing Os_3C core. Such shifts can be as large as *ca.* 1.0 ppm for H_α. However, there is no such dramatic change in δ for the ligand in **2**. Both the pyridyl and phenyl rings in **1** are analysed as AA'BB' systems, with two pairs of pseudo-doublets of roughly equal intensities.

Crystal structures

The solid-state structure of complex **1** has been ascertained by X-ray crystallography. A perspective view of the molecular geometry is depicted in Fig. 1, together with the atom-numbering scheme. The structure of **1** consists of a triangle of osmium atoms symmetrically capped by the trihapto-ligand $CNC_5H_4CH{=}NC_6H_4OC_{16}H_{33}$. The Os–C (alkylidyne) bond distances are almost equivalent (average 2.09 Å). The Os_3 triangle is essentially isosceles with the two hydrido-bridged Os–Os bonds [Os(1)–Os(2) 2.8724(6), Os(1)–Os(3) 2.8829(7) Å] significantly longer than the remaining unbridged Os–Os bond [Os(2)–Os(3) 2.7626(6) Å]. Each osmium atom is bonded to two equatorial and one axial carbonyl groups. No unusual structural or bonding feature has been encountered in the organic moieties of **1**. The C=N bond length is 1.24(1) Å, 0.11 Å longer than the corresponding value for a ferrocenyl cluster complex reported recently.[14] The two aromatic rings adopt twisted conformations in the solid state and the dihedral angle between them is 11.9°. The overall dimensions of the

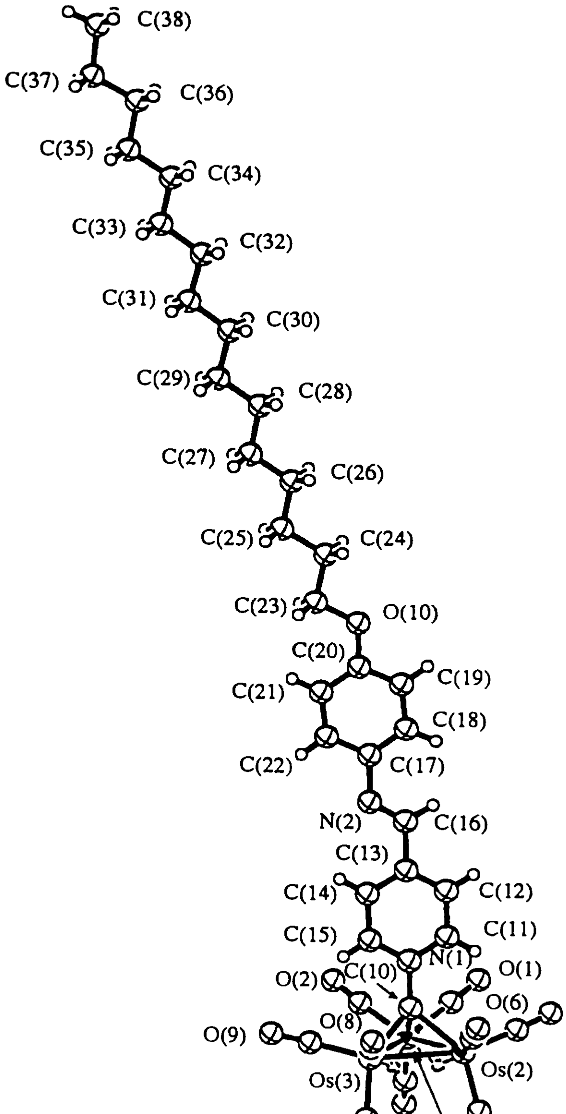

Fig. 1 Molecular structure of complex **1**. Principal bond lengths (Å) and interbond angles (°): Os(1)–Os(2) 2.8724(6), Os(1)–Os(3) 2.8829(7), Os(2)–Os(3) 2.7626(6), Os(1)–C(10) 2.10(2), Os(2)–C(10) 2.091(8), Os(3)–C(10) 2.07(2), N(1)–C(10) 1.47(1), N(2)–C(16) 1.24(1), N(2)–C(17) 1.43(1), C(13)–C(16) 1.51(2) and O(10)–C(20) 1.37(1); Os(2)–Os(1)–Os(3) 57.37(1), Os(1)–Os(2)–Os(3) 61.51(1), Os(1)–Os(3)–Os(2) 61.12(2), Os(1)–C(10)–N(1) 121.7(7), Os(2)–C(10)–N(1) 129.1(6), Os(3)–C(10)–N(1) 133.6(7), N(2)–C(16)–C(13) 119(1), C(16)–N(2)–C(17) 119(1) and C(20)–O(10)–C(23) 118.2(9)

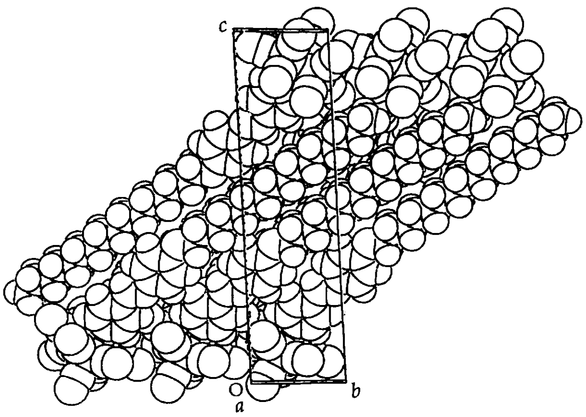

Fig. 2 Molecular packing diagram of the space-filling model of complex **1** (projection down the crystallographic *a* axis)

architecture are noteworthy and the head-to-tail separation is approximately 36.6 Å. The hexadecyl chain adopts an extended, staggered conformation with C–C bond lengths between 1.48(2) and 1.56(2) Å and C–C–C angles between 110(1) and 115(2)°. This long organic side chain is found to bend at atom O(10), with the angle C(20)–O(10)–C(23) being 118.2(9)°. Based on the observed structure, the effective atomic number rule suggests 47 cluster valence electrons (c.v.e.s) for the cluster, which is electron deficient. However, complex **1** can be formulated as a zwitterionic species and this formulation is supported by IR spectroscopic data.[12] A packing diagram viewed down the crystallographic *a* axis is shown in Fig. 2. The rod-like molecules stack with the aliphatic hexadecyl chains pointing towards each other so that a layer of hydrocarbon is sandwiched by two layers of transition-metal cluster core. The crystal is then composed of these sandwich layers stacking along the *c* axis.

The definitive characterization of **2** as a bridged 2-pyridyl complex came from a single-crystal X-ray diffraction study and Fig. 3 illustrates a perspective drawing of the molecule and the atom-numbering scheme. The structure shows that the pyridyl ring of the Schiff-base ligand is orthometallated and bridges the edge Os(2)–Os(3) of the Os$_3$ triangle to afford a four-membered ring containing Os(2), Os(3), C(11) and N(1). The Os$_3$ triangle makes a dihedral angle of 79.3° with the four-membered ring. The pyridine ring is planar with a mean deviation from the plane of 0.011 Å. The dihedral angle between the pyridine ring and the four-membered osmacycle which shares a common edge N(1)–C(11) is 4.4°. The hydride ligand also bridges the same edge Os(2)–Os(3). The two non-bridged Os–Os bonds are 2.878(2) and 2.895(2) Å in length, while the dibridged Os–Os bond is rather longer, 2.911(2) Å. There are altogether ten carbonyl ligands terminally bonded to the three osmium atoms; four to Os(1) and three each to Os(2) and Os(3). In terms of bonding description, the 2-pyridyl bridging ligand acts as a three-electron donor to form a four-membered ring as in [Os$_3$(μ-H)(CO)$_{10}$(μ-NC$_5$H$_4$)]. The triosmium cluster **2** is thus electron precise and associated with the normal 48 c.v.e.s. The N(2)–C(16) double bond is 1.23(5) Å long and is comparable to the corresponding value observed in **1**. The two aromatic moieties are twisted with respect to each other and the dihedral angle between them is 31.8°. This angle is larger than that observed in **1** by 19.9°. An approximate head-to-tail separation of 35.6 Å is observed. The C–C bonds in the aliphatic hexadecyl chain of the molecule are staggered with C–C bond lengths between 1.43(6) and 1.56(7) Å and C–C–C angles between 111(4) and 119(4)°. All other bond parameters of the molecule are within the expected ranges. An interesting aspect of the structure is the molecular packing in the crystal. Fig. 4 shows the crystal-packing diagram of a unit cell of the molecule of **2**, aligned parallel to each other (view down *b* axis). The unit cell has an exceptionally long crystallographic *a* axis with length of 61.458(8) Å which would favour the alignment of the metal cluster molecules relative to each other in an anisotropic fashion. No abnormally short intermolecular contacts are observed and adjacent molecules are separated by normal van der Waals distances. As in **1**, stacking of the rod-like molecules of compound **2** gives rise to a layer of hydrocarbon sandwiched by two layers of metal cluster core. However, the unit cell of **2** contains two such sandwich layers of organics and metal cluster cores. Stacking of these sandwich layers along the *a* axis then persists throughout the whole crystal lattice. This sort of arrangement is similar to that observed in a recently reported tetradecyl cobalt organometallic complex and is reminiscent of surfactant molecules.[15]

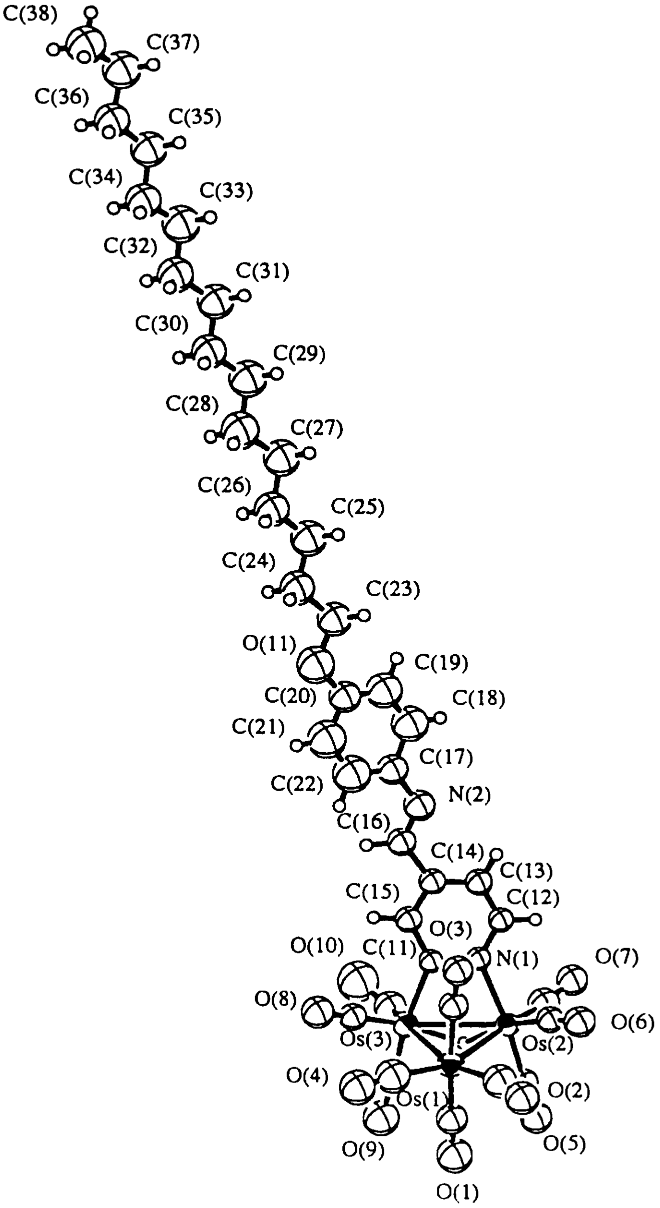

Fig. 3 Molecular structure of complex **2**. Principal bond lengths (Å) and interbond angles (°): Os(1)–Os(2) 2.878(2), Os(1)–Os(3) 2.895(2), Os(2)–Os(3) 2.911(2), Os(2)–N(1) 2.14(3), Os(3)–C(11) 2.09(3), N(1)–C(11) 1.36(4), N(1)–C(12) 1.33(4), N(2)–C(16) 1.23(5), N(2)–C(17) 1.44(5), C(14)–C(16) 1.51(5) and O(11)–C(20) 1.36(5); Os(2)–Os(1)–Os(3) 60.57(6), Os(1)–Os(2)–Os(3) 60.00(6), Os(1)–Os(3)–Os(2) 59.43(6), Os(3)–Os(2)–N(1) 68.4(8), Os(2)–Os(3)–C(11) 68.3(10), Os(2)–N(1)–C(11) 109(2), Os(3)–C(11)–N(1) 113(2), N(2)–C(16)–C(14) 121(3), C(16)–N(2)–C(17) 123(4) and C(20)–O(11)–C(23) 113(4)

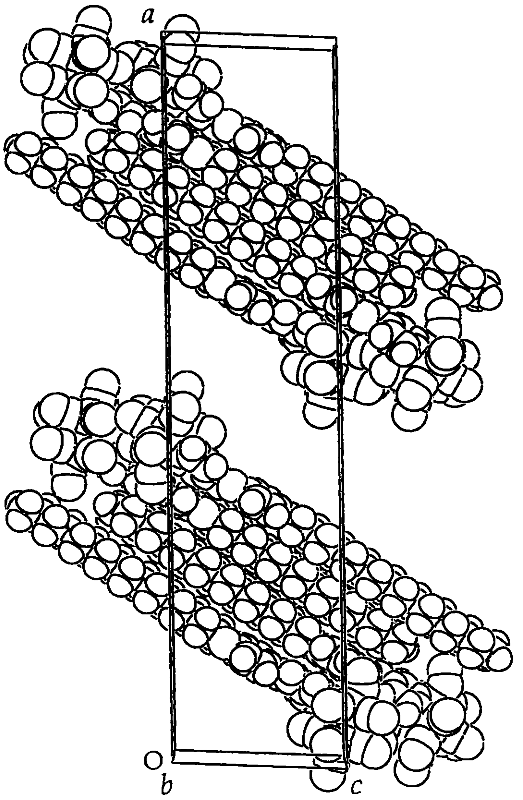

Fig. 4 Molecular-packing diagram of the space-filling model of complex **2** (projection down crystallographic *b* axis)

Table 1 Crystallographic data for complexes **1** and **2**

	1	**2**
Empirical formula	$C_{38}H_{44}N_2O_{10}Os_3$	$C_{38}H_{42}N_2O_{11}Os_3$
M	1258.6	1273.4
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
a/Å	8.377(1)	61.458(8)
b/Å	8.832(1)	9.366(7)
c/Å	30.518(5)	14.435(6)
α/°	91.49(2)	
β/°	91.58(2)	92.36(4)
γ/°	114.65(2)	
U/Å^3	2049.6(6)	8301(6)
Z	2	8
D_c/g cm^{-3}	2.039	2.038
F(000)	1188	4800
μ(Mo-Kα)/cm^{-1}	152.16	92.13
2θ range/°	2–45	2–45
No. reflections measured	5779	5899
No. unique reflections	5335	5833
No. observed reflections	4479	3189
No. variables	228	224
Residuals: R^a, R'^b	0.040, 0.056	0.079, 0.091

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $w = 4F_o^2/[\sigma^2(F_o^2) + 0.004(F_o^2)^2]$.

Solvatochromic properties

Table 2 presents data for the electronic absorption spectra of complexes **1** and **2** in the range 300–750 nm. The lowest-energy feature in the visible region for **1** is extremely solvent sensitive and displays marked negative solvatochromism which spans a wide visible range.[16] Fenske–Hall molecular orbital calculations of **1** indicated that the highest occupied molecular orbital (HOMO) is largely metal-based, whereas the lowest unoccupied molecular orbital (LUMO) is mostly dominated by the organic moiety.[17] The calculations suggest that this transition is attributed to metal-to-ligand charge-transfer (m.l.c.t.) character.

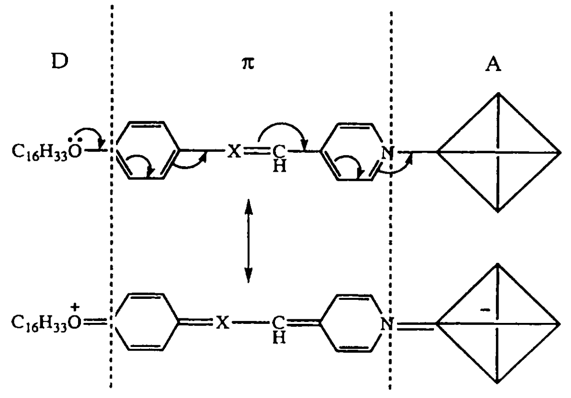

Fig. 5 Zwitterionic formulations of complex **1** showing the donor–π-acceptor structural motif

Table 2 The UV/VIS excitation maxima for complexes **1** and **2**

	λ_{max}/nm (10^{-3} ε/dm^3 mol^{-1} cm^{-1})			
Compound	Hexane	CCl_4	CH_2Cl_2	Me_2CO
1	625 (8.9)	617 (8.4)	577 (10.8)	537 (8.7)
	495 (7.5)	495 (7.4)	427 (12.8)	409 (11.2)
	417 (10.0)	417 (10.0)		
2	372 (8.4)	—	376 (9.2)	374 (7.3)
	294 (7.4)		294 (7.5)	330 (sh) (5.6)

sh = Shoulder.

In contrast, the higher-energy absorptions of **1** are relatively insensitive to variation of solvent polarities. The phenomenon of significant solvent-induced shifts in the low-energy bands of **1** is fully consistent with a zwitterionic formulation of this species in the ground state due to the spontaneous inter-component electron-transfer process and this complex is best regarded as possessing a highly polarizable donor–π-acceptor structural motif as depicted in Fig. 5. Based on this charge separation, a less-polar excited state is produced upon m.l.c.t. excitation. It then becomes obvious that the ground-state molecule is much stabilized by solvents of increasing polarity and hence the transition energy is expected to increase in a more polar solvent. However, with the orthometallated complex **2** no evidence of a solvatochromic shift for the electronic absorptions is obtained. The UV/VIS spectrum of **2** in CH_2Cl_2 shows an intense band in the UV region at 294 nm and another intense absorption in the visible region at 376 nm. Specific assignment is not possible since bands in these regions are also observed for the free Schiff base.

To conclude, both compounds **1** and **2** possess interesting structural properties, but importantly they also serve as potential molecular precursors for metal-based liquid crystalline materials. Besides, the solvatochromic and donor–acceptor properties of **1** make it an important candidate in the field of non-linear optics.[18] It may thus be possible to obtain liquid crystals with non-linear optical properties.

Acknowledgements

We thank the Hong Kong Research Grants Council and the University of Hong Kong for support of this work. W.-Y.W. and S. C. acknowledge the receipts of Scholarships administered by the Croucher Foundation.

References

1 (*a*) M. A. Esteruelas, E. Sola, L. A. Oro, M. B. Ros, M. Marcos and J. L. Serrano, *J. Organomet. Chem.*, 1990, **387**, 103; (*b*) M. A. Esteruelas, L. A. Oro, E. Sola, M. B. Ros and J. L. Serrano, *J. Chem. Soc., Chem. Commun.* 1989, 55; (*c*) C. Bertram, D. W. Bruce, D. A.

Dunmur, S. E. Hunt, P. M. Maitlis and M. McCann, *J. Chem. Soc., Chem. Commun.*, 1991, 69; (*d*) D. W. Bruce and S. A. Hudson, *J. Mater. Chem.*, 1994, **4**, 479; (*e*) M. Marcos, M. B. Ros, J. L. Serrano, M. A. Esteruelas, E. Sola and L. A. Oro, *Chem. Mater.*, 1990, **2**, 748; (*f*) J. P. Rourke, F. P. Fanizzi, N. J. S. Salt, D. W. Bruce, D. A. Dunmur and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1990, 229.

2 F. J. Lahoz, A. Martin, M. A. Esteruelas, E. Sola, J. L. Serrano and L. A. Oro, *Organometallics*, 1991, **10**, 1794; H. Adams, N. A. Bailey, D. W. Bruce, S. C. Davis, D. A. Dunmur, P. D. Hempstead, S. A. Hudson and S. J. Thorpe, *J. Mater. Chem.*, 1992, **2**, 395.

3 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, Oxford, 1980.

4 J. B. Keister and T. L. Horling, *Inorg. Chem.*, 1980, **19**, 2304.

5 J. N. Nicholls and M. D. Vargas, *Reagents for Transition Metal Complex and Organometallic Syntheses, Inorganic Syntheses*, ed. R. J. Angelici, Wiley, New York, 1990, vol. 28, p. 289.

6 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.

7 P. Mains, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq and M. M. Woolfson, MULTAN 82, A System of Computer Programs for the Automatic Solution of Crystal Structures, Universities of York and Louvain, 1991.

8 M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Crystallogr.*, 1989, **22**, 389.

9 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

10 SDP Structure Determination Package, Enraf-Nonius, Delft, 1985.

11 TEXSAN; Crystal Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

12 B. F. G. Johnson, F. J. Lahoz, J. Lewis, N. D. Prior, P. R. Raithby and W. T. Wong, *J. Chem. Soc., Dalton Trans.*, 1992, 1701; S. Chan, W. Y. Wong and W. T. Wong, *J. Organomet. Chem.*, 1994, **474**, C30; W. Y. Wong, S. Chan and W. T. Wong, *J. Organomet. Chem.*, 1995, **493**, 229.

13 C. C. Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1975, 2091; A. J. Deeming, R. Peters, M. B. Hursthouse and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1982, 787.

14 W. Y. Wong, W. T. Wong and K. K. Cheung, *J. Chem. Soc., Dalton Trans.*, 1995, 1379.

15 E. J. Starr, S. A. Bourne, M. R. Caira and J. R. Moss, *J. Organomet. Chem.*, 1995, **490**, C20.

16 E. Buncel and S. Rajagopal, *Acc. Chem. Res.*, 1990, **23**, 226; D. M. Manuta and A. J. Lees, *Inorg. Chem.*, 1986, **25**, 3212.

17 C. E. Housecroft, personal communication.

18 N. J. Long, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 21 and refs. therein; S. R. Marder, *Inorganic Materials*, eds. D. W. Bruce and D. O'Hare, Wiley, Chichester, 1992, p. 115.

Received 15*th January* 1996; *Paper* 6/00286B