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FULL PAPER

Synthesis and structure of tris(1,2-benzoquinone diimine)osmium(II) perchlorate, and its redox and spectroelectrochemical series‡

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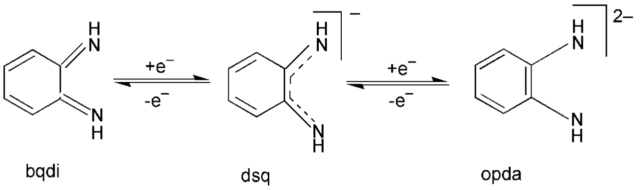
Reaction of $[NH_4]_2[Os^{IV}Br_6]$ with 1,2-diaminobenzene (H_2opda) in aerobic conditions afforded $[Os(bqdi)_3][ClO_4]_2$ (bqdi = 1,2-benzoquinone diimine), a diamagnetic osmium(II) complex containing three redox non-innocent α,α′-diimine ligands. In the crystal structure the relatively long C=N distances together with short Os–N distances indicate the existence of considerable metal(dπ)–ligand(pπ) interactions. Cyclic voltammetry of $[Os(bqdi)_3][ClO_4]_2$ shows one electron redox processes at −0.24, −0.67 and −1.78 V *versus* Fc–Fc$^+$ (Fc = ferrocene) which are assigned as successive reductions of the coordinated bqdi, and an irreversible Os^{II}–Os^{III} couple at +0.99 V. The solution electronic spectra of the mixed-valent (ligand) compounds, generated by electrolysis of $[Os(bqdi)_3]^{2+}$ in an optically transparent thin-layer electrode cell at potentials past the first and the second cathodic responses, show near-IR transitions at 1405 and 1164 nm, respectively, assignable to inter-valence charge transfer between the reduced 1,2-diiminosemiquinone monoanion (dsq) and non-reduced (bqdi) ligands. The spectrum of the triply reduced form is more consistent with the formulation $[Os^{III}(dsq)_2(opda)]^-$ than with the expected formulation $[Os(dsq)_3]^-$, suggesting that an internal redox isomerism has occurred.

Introduction

Metal complexes of the non-innocent dioxolene ligand series (catecholate, semiquinone and quinone) together with their nitrogen analogues (1,2-benzoquinone diimine, bqdi, and the corresponding diiminosemiquinone and diamide forms; Scheme 1) have been the subject of considerable interest because of (i) their exceptionally rich redox and spectroscopic behaviour, and (ii) intramolecular electron transfer and the oxidation state formalism for highly delocalised systems. Both of these phenomena are related to a strong degree of orbital mixing between metal d(π) and ligand p(π) frontier orbitals which can render conventional oxidation-state assignments difficult.[1–5]



Scheme 1 Three possible oxidation states of the ligand bqdi.

Ruthenium complexes of bqdi and its redox partners have been the focus of many recent studies, in part because of their relationship with the much better known ruthenium complexes of 2,2′-bipyridine. The first report of a ruthenium–bqdi complex was by Warren,[3] who described the synthesis, spectral and redox properties of $[Ru(bqdi)_3][PF_6]_2$. Subsequently, Cheng and Peng reported the crystal structure of the ‘mixed-valence’ complex $[Ru(bqdi)_2(H_2opda)][PF_6]_2$ (H_2opda = *o*-phenylenediamine).[4f] There have also been several reports, mainly from Lever's group, on the studies of metal–diimine orbital mixing in mixed-ligand Ru^{II}–bqdi complexes.[5] In comparison, although homoleptic[6] and mixed-ligand[7] osmium–dioxolene complexes have been known for a while, osmium complexes of bqdi and its redox partners are rare. About a decade ago Danopoulos *et al.* reported[8] the formation of *trans*-$[Os^{VIII}O_2(opda)_2]$ from the reaction of OsO_4 with H_2opda, and some of us have reported complexes of the type $OsBr_2L_2$ (L = *N*-aryl-1,2-benzoquinone diimine) which represent the first examples of osmium–bqdi complexes.[9]

As a part of our ongoing work in the areas of (i) metal-catalysed assembly of diimine complexes based on oxidation of aromatic amines,[10] and (ii) redox and spectroelectrochemical properties of complexes of Ru and Os with non-innocent dioxolene-based ligands,[11] we report herein the synthesis, characterisation, crystal structure and UV/VIS/NIR spectroelectrochemical properties of $[Os(bqdi)_3][ClO_4]_2$.

Results and discussion

Synthesis and characterisation

Reaction of $[NH_4]_2[OsBr_6]$ with three equivalents of H_2opda in water–^{t}BuOH (1:1) at room temperature (298 K) produces an intense green solution from which $[Os(bqdi)_3]^{2+}$ was isolated as its perchlorate salt. This reaction occurs only in air, with reduction of Os^{IV} to Os^{II} and concomitant two-electron oxidation of each ligand to the bqdi state. We suggest that, by analogy with the known ruthenium-promoted oxidative dehydrogenation of coordinated aromatic amines,[3,12] and on

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† Royal Society of Chemistry Sir Edward Frankland fellow for 2000/2001.
‡ Electronic supplementary information (ESI) available: ^{1}H NMR spectrum and cyclic voltammogram of $[Os(bqdi)_3][ClO_4]_2$, spectral changes during conversion of $[Os(bqdi)_2(dsq)]^+$. See http://www.rsc.org/suppdata/dt/b0/b006808j/

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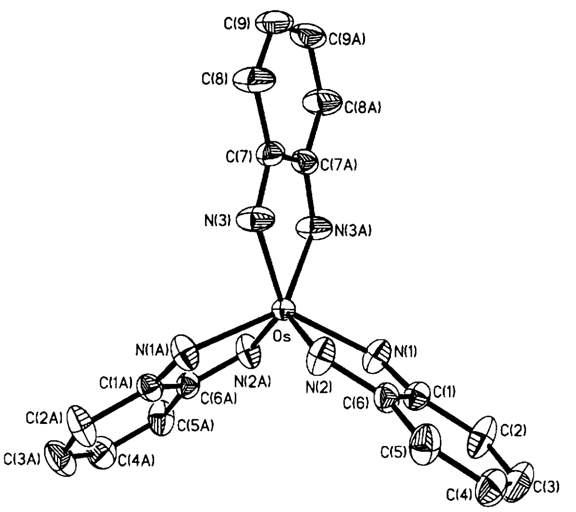

Fig. 1 Molecular structure of $[Os(bqdi)_3]^{2+}$, showing the atom numbering scheme. Selected bond distances (Å): Os–N(1) 1.990(4), Os–N(2) 1.994(3), Os–N(3) 1.980(3), N(1)–C(1) 1.326(5), N(2)–C(6) 1.333(5), C(1)–C(2) 1.416(6), C(2)–C(3) 1.350(7), C(3)–C(4) 1.421(8), C(4)–C(5) 1.350(7), C(5)–C(6) 1.415(6) and C(1)–C(6) 1.413(5).

the basis of other work from us,[6,13] that oxidation of (coordinated) H_2opda to bqdi by atmospheric O_2 likewise is mediated by the osmium centre. For example in 1982 Lay *et al.* reported oxidative dehydrogenation of an osmium(IV)–ethylenediamine complex to the corresponding osmium(II)–diimine.[14]

$[Os(bqdi)_3][ClO_4]_2$ is moderately soluble in water, freely soluble in polar organic solvents (MeCN, DMF, CH_3OH, *etc.*) and diamagnetic. The ^1H NMR spectrum in CD_3CN consists of three resonances: a broad N–H singlet at δ 13.65, and two at δ 7.09 and 7.31 assigned to the two C–H environments of the bqdi ligand ring, consistent with the high symmetry of the complex. This spectrum is very similar to that of $[Ru(bqdi)_3][PF_6]_2$.[3] The IR spectrum of $[Os(bqdi)_3][ClO_4]_2$ shows the expected single N–H stretching band at 3400 cm^{-1}.

The crystal structure (Fig. 1) shows that the central osmium atom has a trigonally distorted octahedral coordination environment, with the chelate bite angles associated with each bqdi ligand being 75.5°; this type of trigonal distortion follows that observed in related iron[4a] and ruthenium[4f] complexes. The short Os–N distances [average, 1.988(3) Å] are comparable to Os^{II}–N(azo) bond distances (1.972–1.978 Å) in complexes where extensive Os–azo π bonding occurs;[15] in contrast, typical Os^{II}–N(pyridyl) distances are in the range 2.032 to 2.072 Å.[15,16] This strong π back bonding from Os^{II} to the bqdi ligand is also reflected in the C–N distances of (average) 1.324(5) Å which are significantly lengthened compared to those of free bqdi due to d(π)–p(π) back bonding.[17] The other C–C bond distances reflect the alternation of localised single (average, 1.416 Å) and double (average, 1.351 Å) bonds that would be expected for the ligand in the bqdi oxidation state. In general the details of the crystal structure confirm the formulation of the complex cation as $[Os(bqdi)_3]^{2+}$ with strong Os–bqdi π bonding.

Electrochemical properties

Cyclic voltammetry of $[Os(bqdi)_3][ClO_4]_2$ in dmf showed three fully reversible one-electron redox processes at −0.24, −0.67 and −1.78 V *vs.* Fc–Fc^+, which we assign as successive reductions of the ligands. For all three waves the cathodic and anodic peak currents are equal, with peak–peak separations of 60–70 mV at a scan rate of 100 mV s^{-1}. In principle a coordinated bqdi ligand can undergo two reductions, to give the diiminosemiquinone monoanion (dsq) and then the diamide (opda) dianion,[1c,5c,11c,18] in exactly the same way as for the related dioxolene series quinone/semiquinone/catecholate.[7,11e,19] Given the presence of three reductions it is reasonable to assign one to each ligand, *i.e.* successive reduction of each bqdi ligand to the dsq state. We also examined the complex in MeCN and observed similar electrochemical behaviour, however in this solvent the most negative process was irreversible and resulted in desorption spikes on the return scan. The anodic scan, on the other hand, showed an irreversible anodic response at +0.99 V which we assign to an Os^{II}–Os^{III} process. Similar electrochemical behaviour was observed for the ruthenium congener, $[Ru(bqdi)_3]^{2+}$, for which the redox processes appeared at +1.38 (irreversible), 0.03, −0.31 and −1.08 V *vs.* SCE in MeCN.[3]

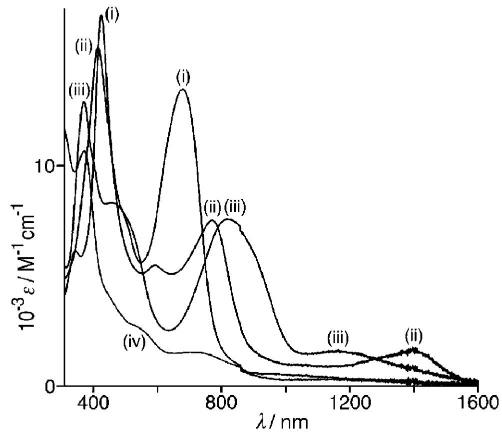

Fig. 2 Electronic spectra of (i) $[Os(bqdi)_3]^{2+}$, (ii) the singly reduced species $[Os(bqdi)_2(dsq)]^+$, (iii) the doubly reduced species $[Os(bqdi)(dsq)_2]$, and (iv) the triply reduced species (see text for formulation) in dmf at 243 K.

The three ligand-centred reductions of the related complex $[Os(bipy)_3]^{2+}$ occur at −1.63, −1.81 and −2.11 V *vs.* Fc–Fc^+ (in MeCN). The much more positive potentials for the reductions of $[Os(bqdi)_3]^{2+}$ are consistent with the expected greater ease of reduction of coordinated bqdi compared to bipy; for example, in $[Ru(bipy)_2(bqdi)]^{2+}$ both reductions of the bqdi ligand (at +0.59 and −0.34 V *vs.* SCE in MeCN) occur before the bipy-centred reductions (−1.72 and −1.96 V *vs.* SCE).[18a] It is clear that bqdi is a considerably better π-acceptor ligand than bipy.[3]

The substantial separation between these ligand-centred reductions ($E_{1/2}$ = 420 mV between the first and second; and 1080 mV between the second and third) is noteworthy, especially when compared to the much smaller separation of typically *ca.* 200 mV between successive reductions of bipyridyl ligands in $[Os(bipy)_3]^{2+}$. This is consistent with the greater degree of metal/ligand orbital mixing that is a characteristic feature of complexes of Ru and Os with non-innocent ligands of this type.[1,18,19] If there is a significant contribution from the central metal ion to the redox orbitals then we would expect a much greater electrostatic interaction between successive added electrons than would occur in a complex with genuinely ligand-localised redox orbitals, where the added electrons would more spatially be isolated.

Spectroelectrochemical studies

$[Os(bqdi)_3][ClO_4]_2$ was subjected to a spectroelectrochemical study in dmf at −30 °C, such that the spectra of all four accessible oxidation states were examined. All three reductions proved to be fully chemically reversible on the slow timescale of the experiment, as shown by complete regeneration of the starting spectrum on reversal of the applied potential at the end of the experiment. We noted however that the third reduction was considerably more sluggish than the first two, requiring much longer to reach completion. The results are summarised in Table 1; see also Fig. 2. We emphasise that these assignments are necessarily tentative. Although spectra of related ruthenium

Table 1 Electronic spectral data of $[Os(bqdi)_3]^{2+}$ and its reduced products[a]

Complex	λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})
$[Os^{II}(bqdi)_3]^{2+}$	680 (14),[b] 429 (17)
$[Os^{II}(bqdi)_2(dsq)]^+$	1405 (1.5),[c] 773 (7.4),[b] 590 (5.3), 418 (15)
$[Os^{II}(bqdi)(dsq)_2]$	1165 (1.5),[c] 820 (7.6),[b] 455 (8.4), 373 (13)
$[Os^{II}(dsq)_3]^-$/$[Os^{III}(dsq)_2(opda)]^-$	715 (1.4), 530 (sh), 373 (10.7)

[a] DMF, 243 K. [b] Os→bqdi MLCT. [c] dsq→bqdi IVCT.

complexes have reliably been assigned with the assistance of ZINDO calculations,[1c,18c] this is not possible for osmium.

For $[Os(bqdi)_3]^{2+}$ in its starting oxidation state, the intense lowest-energy transition at 680 nm is ascribed to an Os[d(π)]→ bqdi(π*) ^{1}MLCT transition by analogy with the assignment of the spectrum of $[Ru(bqdi)_3]^{2+}$.[3] The low energy of this compared to that of $[Os(bipy)_3]^{2+}$ (absorption maxima between 400 and 500 nm)[20] reflects the lower energy of the bqdi π* orbital, which is in turn consistent with the ease of reduction and the strong π-acceptor nature of the bqdi ligands. The transition at 429 nm we ascribe to another MLCT transition involving a higher-energy π* orbital of the bqdi ligand, as it is too low in energy to be a bqdi-centred π→π* transition,[21] even allowing for a substantial red-shift on coordination to Os.[22]

On one-electron reduction of the complex to give $[Os(bqdi)_2(dsq)]^+$ the lowest-energy MLCT transition is red-shifted to 773 nm and reduced in intensity, consistent with its assignment as an Os[d(π)]→bqdi(π*) MLCT process. The higher energy charge-transfer transition is slightly blue-shifted (to 418 nm) and likewise reduced in intensity, although not by so much. In addition a new transition appears in the near-IR region at 1405 nm, which we ascribe to an inter-ligand dsq→bqdi charge transfer.§ This is similar in principle to the more well known IVCT transition between metal centres in different oxidation states.[25] Inter-ligand IVCT transitions have been observed at *ca.* 2200 nm for the singly and doubly reduced forms of $[Ru(bipy)_3]^{2+}$ which contain both bipy and $(bipy^{\bullet -})$ ligands,[23] and related near-IR transitions have been observed by Auburn and Lever[26] and Ward and co-workers[11c] between the reduced and non-reduced diimine termini of mixed-valence bridging ligands in which the valences were localised. Other ligand-to-ligand charge-transfer transitions, *e.g.* from electron-donor catecholate to electron-acceptor bipyridine across a metal centre, are also well known in complexes such as [Pt(bipy)(cat)].[27]

On further reduction to the $[Os(bqdi)(dsq)_2]$ state the two higher-energy transitions show slight shifts in the same sense as before: the lower energy MLCT transition is again red-shifted, to 820 nm, without in this case any significant change in intensity; and the higher-energy transition is again blue-shifted, to 373 nm, and is further slightly reduced in intensity. A new transition appears at 455 nm whose assignment is unclear. The inter-ligand IVCT transition is blue-shifted to 1165 nm but, significantly, is still clearly present (Fig. 2).§

Finally, reducing the complex a third time results in marked spectral changes which help to confirm some of the assignments suggested above. Most significantly, the near-IR inter-ligand IVCT transition has disappeared, which is consistent with formation of the isovalent $[Os(dsq)_3]^-$ state. The weak transition at 715 nm could reasonably be ascribed to an inter-ligand π→π* transition associated with the mono-radical ligands: for example, in complexes where a bipyridyl or related α,α′-diimine ligand coordinated to Ru^{II} is reduced to the radical anion new low-energy π→π* transitions of the $(bipy)^{\bullet -}$ ligand appear in the visible region of the spectrum (*ca.* 500–700 nm).[11c,24]

However, the other principal feature of the spectrum is less consistent with the description of the triply reduced complex as $[Os(dsq)_3]^-$; *viz.* the single remaining intense transition at 373 nm would have to be assigned to a Os[d(π)]→dsq(SOMO) MLCT transition involving the singly reduced dsq ligands. In other complexes of Ru^{II} and Os^{II} with bqdi (NN donor) or *o*-benzoquinone (analogous OO donor) ligands reduction of the ligand to the semiquinone state always results in a red-shift of the MLCT transition,[11c,18] whereas this one is substantially blue-shifted with respect to the Os[d(π)]→bqdi(π*) transition of $[Os(bqdi)_3]^{2+}$. The high energy of this transition is therefore quite inconsistent with its assignment as Os[d(π)]→dsq(SOMO) MLCT.

An alternative possibility is that an internal rearrangement of electrons occurs to give $[Os^{III}(dsq)_2(opda)]^-$; such 'redox isomerism' is well established in the work of Pierpont with first-row transition-metal complexes with dioxolene-type ligands,[28] and such an assignment is consistent with the known ease of oxidation of Os^{II} to Os^{III}. In this case the complex is still mixed-valence§ and the relatively weak transition at 715 nm can be ascribed to an opda→dsq IVCT.[11c,26] The intense transition at 373 nm would now be an Os^{III}→dsq MLCT whose high energy is consistent with the reduction in energy of the metal orbitals on oxidation to Os^{III}. All of the main features of the spectrum of the triply reduced complex can be accounted for by assuming the formulation $[Os^{III}(dsq)_2(opda)]^-$, although we emphasise again that, due to (i) the absence of similar complexes to compare the spectra with, (ii) the limited value of localised descriptions such as 'MLCT' in a complex where extensive metal–ligand mixing is likely, and (iii) the non-availability of ZINDO spectroscopic parameters for osmium which precludes calculational assistance with our assignments, the above discussion is necessarily tentative.

Conclusion

We have prepared $[Os(bqdi)_3][ClO_4]_2$ which is the first osmium complex with bqdi; the crystal structure and other spectroscopic properties confirm its formulation as an osmium(II) complex with three benzoquinone diimine ligands, albeit with evidence for strong d(π)–p(π) metal–ligand interactions. The complex undergoes three reversible ligand-centred reductions, and all four electrochemically accessible oxidation states have been examined by spectroelectrochemical methods. In the mono- and di-reduced mixed-valence states $[Os(bqdi)_2(dsq)]^+$ and $[Os(bqdi)(dsq)_2]$ inter-ligand IVCT transitions occur in the near-IR region. The spectrum of the triply reduced form is more consistent with the formulation $[Os^{III}(dsq)_2(opda)]^-$ than with the (expected) isovalent formulation, $[Os(dsq)_3]^-$, suggesting that an internal redox isomerism has occurred.

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§ One of the referees pointed out that in mixed-valence complexes such as $[Os(bqdi)_2(dsq)]^+$ and $[Os(bqdi)(dsq)_2]$ the question arises as to whether the mixed-valence states are localised (Robin and Day class 2), or delocalised with all three ligands being equivalent (Robin and Day class 3). Intervalence charge-transfer ('IVCT') transitions could occur in either case. The most extensively studied related complex is $[Ru(bipy)_3]^{2+}$ for which the reduced forms $[Ru(bipy)_2(bipy^{\bullet -})]^+$ and $[Ru(bipy)(bipy^{\bullet -})_2]$ have been described as valence-trapped on the basis of electronic and EPR spectra (refs. 23, 24). In these complexes electronic coupling between reduced $bipy^{\bullet -}$ and non-reduced bipy, which allows the inter-ligand IVCT processes to occur, is mediated by orbitals of the central metal ion and not by direct orbital overlap between ligands which are remote and spatially orthogonal. In $[Os(bqdi)_3]^{2+}$ the metal–ligand orbital mixing is much stronger than in $[Ru(bipy)_3]^{2+}$ (*cf.* the crystallographic and electrochemical results) which means that mixed-valence states such as $[Os(bqdi)_2(dsq)]^+$ are more likely to be delocalised between ligands (class 3 character). However, given the obvious limitations in our assignments of these spectra (see text), compared to the very well understood electronic spectra of $[Ru(bipy)_3]^{2+}$ and its reduction products, we prefer not to speculate on this point but just to note that it is a possibility.

Experimental

General details

The starting compound $[NH_4]_2[OsBr_6]$ was prepared following a reported procedure.[29] 1,2-Diaminobenzene (H_2opda) was obtained from Sigma Chemical Company, USA. Solvents and other chemicals used for synthesis were of analytical grade. **CAUTION**: perchlorate salts of metal complexes can be explosive. Although no detonation tendencies have been observed, care is advised and handling of only small quantities recommended.

The IR spectrum was obtained with a Perkin-Elmer 783 spectrophotometer, and the ^{1}H NMR spectrum with a Bruker Avance DPX 300 spectrometer using $SiMe_4$ as an internal standard. A Perkin-Elmer 240C elemental analyser was used to collect microanalytical data (C, H, N). Electrochemical measurements were made using a PC-controlled EG&G/PAR-273A potentiostat. A conventional three-electrode configuration was used, consisting of platinum-wire working and auxiliary electrodes and an SCE reference. Ferrocene was added at the end of each measurement as an internal standard, and all potentials are quoted *vs.* the ferrocene–ferrocenium couple. UV/VIS-NIR spectroelectrochemical measurements were performed in DMF at 243 K using a home-built OTTLE (optically transparent thin-layer electrode) cell in a Perkin-Elmer Lambda-19 spectrophotometer, as described previously.[30]

Synthesis of tris(1,2-benzoquinone diimine)osmium(II) perchlorate, $[Os(bqdi)_3][ClO_4]_2$

A mixture of $[NH_4]_2[OsBr_6]$ (0.10 g, 0.14 mmol) and 1,2-diaminobenzene (0.050 g, 0.46 mmol) was stirred at room temperature in *tert*-butyl alcohol–water (50 cm^3, 1 : 1 v/v) for 90 minutes. An intense green solution resulted. The solution was filtered, and slow evaporation of the filtrate in air afforded a green precipitate. This precipitate was dissolved in acetonitrile and an aqueous solution of $NaClO_4$ added to precipitate crystalline $[Os(bqdi)_3][ClO_4]_2$. Repeated crystallisation of this from acetonitrile–water mixtures produced needle shaped dark green crystals in 65% yield. ^{1}H NMR (CD_3CN): δ 13.65 (N–H), 7.09, 7.31 (C–H). IR data (selected bands, cm^{-1} in KBr): 3400 (N–H), 3050 (C–H), 1100, 620 (ClO_4). $\Lambda_M = 250\ \Omega^{-1}\ cm^2\ mol^{-1}$ (1×10^{-3} M in MeCN). $E_{1/2}$/V *vs.* Fc–Fc$^+$ (in DMF): 0.99 (E_{pa}, irreversible), −0.24, −0.67 and −1.78. Found: C, 29.9; H, 2.3; N, 11.8%. Calc. for $C_{18}H_{18}Cl_2N_6O_8Os$: C, 30.6; H; 2.4; N,11.9%.

Crystallography

An X-ray quality crystal of $[Os(bqdi)_3][ClO_4]_2\cdot 4H_2O$ was obtained by slow evaporation of a solution of the compound in 1 : 1 MeCN–water. Relevant crystallographic data are collected in Table 2. Intensity data were measured on a Siemens SMART diffractometer, equipped with graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å. Data were corrected for Lorentz-polarisation effects. A total of 9882 reflections were collected of which 3116 were unique and 2841 satisfied the $I > 2\sigma(I)$ criterion and were used in the subsequent analysis. The structure was solved by employing the SHELXS 86 program package[31] and refined by full-matrix least squares based on F^2.[32] All hydrogen atoms of the ligands were located in calculated positions.

CCDC reference number 186/2273.

See http://www.rsc.org/suppdata/dt/b0/b006808j/ for crystallographic files in .cif format.

Table 2 Crystallographic data and details of refinement of $[Os(bqdi)_3][ClO_4]_2\cdot 4H_2O$

Chemical formula	$C_{18}H_{26}Cl_2N_6O_{12}Os$
Formula weight	779.55
T/K	295(2)
Crystal system	Monoclinic
Space group	$C2/c$
a/Å	18.5600(1)
b/Å	9.3076(1)
c/Å	15.9116(2)
β/°	100.416(1)
V/Å^3	2703.42(5)
Z	4
μ/mm^{-1}	4.984
Reflections collected/unique	9882/3116 [$R_{int} = 0.0402$]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0285$, $wR2 = 0.0626$

Acknowledgements

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References

1 (*a*) C. G. Pierpont and C. W. Lange, *Prog. Inorg. Chem.*, 1994, **41**, 331; (*b*) A. B. P. Lever, H. Masui, R. A. Metcalfe, D. J. Stufkens, E. S. Dodsworth and P. R. Auburn, *Coord. Chem. Rev.*, 1993, **125**, 317; (*c*) S. I. Gorelsky, E. S. Dodsworth, A. B. P. Lever and A. A. Vlcek, *Coord. Chem. Rev.*, 1998, **174**, 469.

2 A. Vogler and H. Kunkely, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 221.

3 L. F. Warren, *Inorg. Chem.*, 1977, **16**, 2814.

4 (*a*) S.-M. Peng, C. Chen, D.-S. Liaw, C.-I. Chen and Y. Wang, *Inorg. Chim. Acta*, 1985, **101**, L31; (*b*) S.-M. Peng, K. Peters, E. Peters and A. Simon, *Inorg. Chim. Acta*, 1985, **101**, L35; (*c*) D. Liaw and S.-M. Peng, *Inorg. Chim. Acta*, 1986, **113**, L11; (*d*) M. Hsieh, M. Cheng and S.-M. Peng, *Inorg. Chim. Acta*, 1988, **145**, 1; (*e*) P.-H. Cheng, H.-Y. Cheng, C.-C. Lin and S.-M. Peng, *Inorg. Chim. Acta*, 1990, **169**, 19; (*f*) H.-Y. Cheng and S.-M. Peng, *Inorg. Chim. Acta*, 1990, **169**, 23.

5 (*a*) R. A. Metcalfe and A. B. P. Lever, *Inorg. Chem.*, 1997, **36**, 4762 and references therein; (*b*) C. J. Cunha, S. S. Fielder, D. V. Stynes, H. Masui, P. R. Auburn and A. B. P. Lever, *Inorg. Chim. Acta*, 1996, **242**, 293; (*c*) R. A. Metcalfe, L. C. G. Vasconcellos, H. Mirza, D. W. Franco and A. B. P. Lever, *J. Chem. Soc., Dalton Trans.*, 1999, 2653; (*d*) R. A. Metcalfe, E. S. Dodsworth, S. S. Fielder, D. J. Stufkens, A. B. P. Lever and W. J. Pietro, *Inorg. Chem.*, 1996, **35**, 7741; (*e*) C. J. Cunha, E. S. Dodsworth, M. A. Monteiro and A. B. P. Lever, *Inorg. Chem.*, 1999, **38**, 5399; (*f*) H. Masui, A. L. Freda, M. C. Zerner and A. B. P. Lever, *Inorg. Chem.*, 2000, **39**, 141.

6 A. J. Nielson and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1978, 1501.

7 M. Haga, K. Isobe, S. R. Boone and C. G. Pierpont, *Inorg. Chem.*, 1990, **29**, 3795.

8 A. A. Danopoulos, A. C. C. Wong, G. Wilkinson, M. B. Hursthouse and B. Hussain, *J. Chem. Soc., Dalton Trans.*, 1990, 315.

9 K. N. Mitra and S. Goswami, *Chem. Commun.*, 1997, 49.

10 K. N. Mitra, P. Majumdar, S.-M. Peng, A. Castiñeiras and S. Goswami, *Chem. Commun.*, 1997, 1267; K. N. Mitra, S.-M. Peng and S. Goswami, *Chem. Commun.*, 1998, 1685; K. N. Mitra, S. Choudhury, A. Castiñeiras and S. Goswami, *J. Chem. Soc., Dalton Trans.*, 1998, 2901; K. N. Mitra and S. Goswami, *Proc. Indian Acad. Sci.* (*Chem. Sci.*), 1999, **111**, 461; A. K. Ghosh, K. N. Mitra, G. Mostafa and S. Goswami, *Eur. J. Inorg. Chem.*, 2000, 1961.

11 (*a*) A. M. Barthram, Z. R. Reeves, J. C. Jeffery and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 2000, 3162; (*b*) A. M. Barthram and M. D. Ward, *New J. Chem.*, 2000, **24**, 501; (*c*) N. C. Fletcher, T. C. Robinson, A. Behrendt, J. C. Jeffery, Z. R. Reeves and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1999, 2999; (*d*) A. M. Barthram, R. L. Cleary, R. Kowallick and M. D. Ward, *Chem. Commun.*, 1998, 2695; (*e*) L. F. Joulié, E. Schatz, M. D. Ward, F. Weber and L. J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, 1994, 799.

12 S. E. Diamond, G. M. Tom and H. Taube, *J. Am. Chem. Soc.*, 1975, **97**, 2661; F. R. Keene, D. J. Salmon and T. J. Meyer, *J. Am. Chem. Soc.*, 1976, **98**, 1884.

13 K. N. Mitra and S. Goswami, *Inorg. Chem.*, 1997, **36**, 1322.
14 P. A. Lay, A. M. Sargeson, B. W. Skelton and A. H. White, *J. Am. Chem. Soc.*, 1982, **104**, 6161.
15 B. K. Ghosh, A. Mukhopadhyay, S. Goswami, S. Ray and A. Chakravorty, *Inorg. Chem.*, 1984, **23**, 4633.
16 F. Basuli, S.-M. Peng and S. Bhattacharya, *Polyhedron*, 1999, **18**, 391; A. Das, S.-M. Peng and S. Bhattacharya, *Polyhedron*, 2000, **19**, 1227.
17 O. Carugo, K. Djinovic, M. Rizzi and C. N. Castellani, *J. Chem. Soc., Dalton Trans.*, 1991, 1551.
18 (*a*) H. Masui, A. B. P. Lever and P. R. Auburn, *Inorg. Chem.*, 1991, **30**, 2404; (*b*) H. Masui, A. B. P. Lever and E. S. Dodsworth, *Inorg. Chem.*, 1993, **32**, 258; (*c*) R. A. Metcalfe, L. C. G. Vasconcellos, H. Minza, D. W. Franco and A. B. P. Lever, *J. Chem. Soc., Dalton Trans.*, 1999, 2653.
19 M. Haga, E. S. Dodsworth and A. B. P. Lever, *Inorg. Chem.*, 1986, **25**, 447.
20 S. Decurtins, F. Felix, J. Ferguson, H. U. Güdel and A. Ludi, *J. Am. Chem. Soc.*, 1980, **102**, 4102.
21 T. Nogami, T. Hishida, M. Yamada, H. Mikawa and Y. Shirota, *Bull. Chem. Soc. Jpn.*, 1975, **48**, 3709.
22 G. M. Bryant, J. E. Fergusson and H. K. J. Powell, *Aust. J. Chem.*, 1971, **24**, 257.
23 G. A. Heath, L. J. Yellowlees and P. S. Braterman, *Chem. Phys. Lett.*, 1982, **92**, 646.
24 G. A. Heath, L. J. Yellowlees and P. S. Braterman, *J. Chem. Soc., Chem. Commun.*, 1981, 287; P. Bugnon and R. E. Hester, *Chem. Phys. Lett.*, 1983, **102**, 537.
25 M. D. Ward, *Chem. Soc. Rev.*, 1995, **24**, 121.
26 P. R. Auburn and A. B. P. Lever, *Inorg. Chem.*, 1990, **29**, 2551.
27 K. H. Puthraya and T. S. Srivastava, *Polyhedron*, 1985, **4**, 1579; S. S. Kamath, V. Uma and T. Srivastava, *Inorg. Chim. Acta*, 1989, **166**, 91.
28 A. S. Attia and C. G. Pierpont, *Inorg. Chem.*, 1998, **37**, 3051; O. S. Jong, D. H. Jo, Y. A. Lee, B. J. Conklin and C. G. Pierpont, *Inorg. Chem.*, 1997, **36**, 19; O. S. Jong, D. H. Jo, Y. A. Lee, Y. S. Sohn and C. G. Pierpont, *Inorg. Chem.*, 1998, **37**, 5875.
29 F. P. Dwyer and J. W. Hogarth, *Inorg. Synth.*, 1957, **5**, 204.
30 S.-M. Lee, R. Kowallick, M. Marcaccio, J. A. McCleverty and M. D. Ward, *J. Chem. Soc., Dalton Trans.*, 1998, 3443.
31 G. M. Sheldrick, SHELXS 86, Program for the solution of crystal structures, University of Göttingen, 1986.
32 G. M. Sheldrick, SHELXL 93, Program for the solution of crystal structures, University of Göttingen, 1993.