Synthesis, Photophysical Properties and Crystal Structure of Tetra-*n*-butylammonium Bis(maleonitriledithiolato)-nitridoosmate(VI) ‡

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Treatment of [NBu$^n_4$][OsNCl$_4$] with 2 equivalents of Na$_2$(mnt) (mnt = maleonitriledithiolate) gave [NBu$^n_4$][OsN(mnt)$_2$] **1** in good yield. The structure of **1** has been confirmed by an X-ray diffraction analysis, Os≡N being 1.639(8) Å. The complex shows emission from the $^3[(d_{xy})(d_{\pi^*})]$ excited state.

Ditholene (R$_2$C$_2$S$_2$) and related complexes of transition metals are of interest due to their electrochemistry and photochemistry and potential applications as one-dimensional materials.[1] It is also believed that the active site of molybdenum cofactors consists of a oxomolybdenum(VI) complex, which is bonded to molybdopterin *via* the dithiolene linkage.[2] However, there are very few examples of metal dithiolene complexes in relatively high oxidation states presumably because of the strong reducing property of the ligands. By using imide as a stabilising group, stable dithiolene compounds of Cr^V have recently been isolated.[3] As part of our programme to study the chemistry of high-valent metal complexes, we describe herein the synthesis, photophysical properties, and crystal structure of a nitrido-osmium(VI) complex of a dithiolene ligand.

Experimental

All manipulations were carried out under nitrogen by Schlenk techniques. Solvents were dried and distilled prior to use. The UV/VIS spectra were recorded on a Milton Roy Spectronic 3000 diode-array spectrophotometer and steady-state emission spectra on a Spex Fluorolog-2 spectrofluorometer. Lifetime measurements were performed with a Quanta Ray DCR-3 Nd-YAG laser (pulse ouput 355 nm, 8 ns). The absolute emission quantum yield was measured by the method of Demas and Crosby[4] using [Ru(bipy)$_3$]$^{2+}$ (bipy = 2,2′-bipyridine) as standard. Solutions for photochemical experiments were degassed for four freeze–pump–thaw cycles. Infrared spectra (Nujol) were obtained on a Nicolet MAGNA-IR 550 FT-IR spectrophotometer. Elemental analyses were performed by Medac Ltd., Brunel University.

The salts Na$_2$(mnt)[5] (mnt = maleonitriledithiolate) and [NBu$^n_4$][OsNCl$_4$][6] were prepared by the literature methods.

Preparation of [NBu$^n_4$][OsN(mnt)$_2$] **1**.—To a solution of [NBu$^n_4$][OsNCl$_4$] (200 mg) in MeOH (20 cm^3) was added 2 equivalents of Na$_2$(mnt) (126 mg). The reaction mixture was stirred at room temperature overnight. The orange crystals formed were collected, washed with Et$_2$O and recrystallised from MeCN at −10 °C. Yield 70%. UV/VIS (MeCN), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 250 (29 487), 288 (sh) (18 205), 320 (sh) (8947), and 394 (sh) (3333) (Found: C, 39.7; H, 4.9; N, 11.5. C$_{24}$H$_{36}$N$_6$OsS$_4$ requires C, 39.7; H, 5.0; N, 11.6%).

X-Ray Crystallography for Compound **1**.—Crystals were grown from a saturated solution of compound **1** in MeCN at −10 °C.

Crystal data. C$_{24}$H$_{36}$N$_6$OsS$_4$, M = 727.06, triclinic, space group $P\bar{1}$, a = 11.783(2), b = 11.968(2), c = 12.519(2) Å, α = 86.45(1), β = 86.69(1), γ = 60.64(1)°, U = 1534.9(7) Å^3, Z = 2, D_c = 1.573 g cm^{-3}, μ = 42.2 cm^{-1}, F(000) = 724, T = 293 K.

Data collection and treatment. Diffraction measurements were performed with an Enraf–Nonius CAD4 diffractometer and graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å). Three check reflections were monitored periodically throughout the data collection and showed no significant variations. All intensity data were corrected for Lorentz polarisation effects and an absorption correction by the ψ-scan method was also applied. Transmission coefficients were in the range 0.949–1.000. Calculations were carried out on a MicroVax II computer using the Enraf-Nonius structure determination package.[7]

Structure solution and refinement. The structure was solved by the Patterson method and refined by full-matrix least-squares analysis. All non-hydrogen atoms except carbons of the tetra-*n*-butylammonium cation were refined anisotropically to R = 0.034 and $R' = [(\Sigma w|\Delta F|^2)/\Sigma w F_o^2]^{\frac{1}{2}} = 0.044$, $w = 4F_o^2/[\sigma^2(F_o^2) + 0.04\,(F_o^2)]^2$. The hydrogen atoms were generated in ideal positions (C–H 0.95 Å). Final atomic coordinates are presented in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis.—Interaction of [NBu$^n_4$][OsNCl$_4$] with 2 equivalents of Na$_2$(mnt) in MeOH afforded air-stable [NBu$^n_4$][OsN(mnt)$_2$] **1**, isolated as orange crystals in *ca.* 70% yield [equation (1)]. The infrared spectrum shows an intense peak at

$$[\text{NBu}^n{}_4][\text{OsNCl}_4] + 2\text{Na}_2(\text{mnt}) \longrightarrow \underset{\mathbf{1}}{[\text{NBu}^n{}_4][\text{OsN(mnt)}_2]} + 4\text{NaCl} \quad (1)$$

2218 cm^{-1} assignable to the C≡N stretch of the mnt ligand and ν(Os≡N) at *ca.* 1074 cm^{-1}. In contrast to most metal dithiolene complexes, which display very rich electrochemistry, the cyclic

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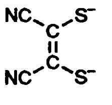
* For general correspondence.

† For correspondence on the crystal structure.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xviii–xxiii.

Table 1 Positional parameters for compound **1** and their estimated standard deviations

Atom	*x*	*y*	*z*
Os	0.106 43(2)	0.178 10(2)	0.426 52(2)
S(1)	0.331 2(2)	0.059 4(2)	0.400 6(2)
S(2)	0.117 1(2)	0.336 2(2)	0.315 3(2)
S(3)	0.146 3(2)	0.067 5(2)	0.591 3(1)
S(4)	−0.065 4(2)	0.348 9(2)	0.512 8(2)
N(1)	0.042 0(5)	0.114 3(6)	0.355 3(5)
N(2)	0.594 3(6)	0.019 3(7)	0.207 9(7)
N(3)	0.318 6(6)	0.365 2(6)	0.088 2(6)
N(4)	−0.289 0(8)	0.407 3(9)	0.750 2(7)
N(5)	−0.010 4(7)	0.058 6(6)	0.849 2(6)
N(6)	0.727 0(4)	0.343 2(4)	0.156 8(4)
C(1)	0.362 5(6)	0.137 0(6)	0.290 2(6)
C(2)	0.271 2(6)	0.254 6(6)	0.253 0(5)
C(3)	0.006 3(6)	0.160 3(6)	0.667 9(5)
C(4)	−0.084 4(6)	0.278 1(6)	0.633 7(6)
C(5)	0.490 4(6)	0.072 2(6)	0.243 2(6)
C(6)	0.297 8(7)	0.316 6(7)	0.160 9(7)
C(7)	−0.199 5(8)	0.352 0(8)	0.697 7(7)
C(8)	−0.005 1(7)	0.104 5(6)	0.769 0(6)
C(1A)	0.667 2(6)	0.487 4(6)	0.173 3(5)
C(1B)	0.729 2(6)	0.519 3(6)	0.262 4(6)
C(1C)	0.650 2(7)	0.663 1(7)	0.278 2(7)
C(1D)	0.711 2(8)	0.701 3(8)	0.365 2(8)
C(2A)	0.872 5(5)	0.279 6(5)	0.129 3(5)
C(2B)	0.909 0(6)	0.331 4(6)	0.025 9(6)
C(2C)	1.056 3(8)	0.257 2(8)	0.011 4(8)
C(2D)	1.102(1)	0.308(1)	−0.091(1)
C(3A)	0.652 1(6)	0.332 1(6)	0.064 2(5)
C(3B)	0.701 3(6)	0.195 5(6)	0.028 5(6)
C(3C)	0.621 4(7)	0.203 3(7)	−0.066 0(7)
C(3D)	0.662(1)	0.071(1)	−0.109 6(9)
C(4A)	0.712 2(6)	0.272 3(5)	0.258 0(5)
C(4B)	0.574 7(7)	0.332 7(6)	0.306 5(6)
C(4C)	0.569 8(7)	0.260 9(7)	0.410 8(7)
C(4D)	0.644 6(9)	0.271 9(9)	0.503 6(9)



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voltammogram of **1** in MeCN only shows an irreversible reduction wave at −1.64 V *vs.* ferrocene–ferrocenium, which is tentatively assigned to the reduction of Os^{VI} to Os^{V}.[8]

The structure of compound **1** was unambiguously confirmed by an X-ray diffraction study. Fig. 1 shows a perspective view of the $[OsN(mnt)_2]^-$ anion. Selected bond lengths and angles are given in Table 2. The geometry around Os is best described as square pyramidal with the nitride ligand at the axial position and the osmium atom slightly displaced above the S_4 plane by 0.651 Å. The Os–N distance of 1.639(8) Å is normal by comparison with those in other osmium(VI) nitrido compounds.[9] The average Os–S bond length of 2.32 Å is comparable to those found in $[OsN(SCH_2CH_2CO_2)_2]$,[10] $[OsN(CH_2SiMe_3)_2(WS_4)]^{2-}$ and $[Os_2N_2(CH_2SiMe_3)_4(WS_4)]$.[11] The C(1)–C(2) bond distance is 1.359(8) Å, suggesting that the mnt ligand is best formulated as an enedithiolate **I**.

Table 2 Selected bond lengths (Å) and angles (°) for compound **1**

Os–N(1)	1.639(8)	C(1)–C(2)	1.359(8)
Os–S(1)	2.325(2)	C(1)–C(5)	1.423(9)
Os–S(2)	2.328(2)	C(2)–C(6)	1.44(1)
Os–S(3)	2.323(2)	C(3)–C(4)	1.346(8)
Os–S(4)	2.325(2)	C(4)–C(7)	1.43(1)
S(1)–C(1)	1.740(8)	N(2)–C(5)	1.143(9)
S(2)–C(2)	1.747(6)	N(3)–C(6)	1.14(1)
S(3)–C(3)	1.740(7)	N(4)–C(7)	1.13(2)
S(4)–C(4)	1.746(8)	N(5)–C(8)	1.13(1)
S(1)–Os–S(2)	86.43(6)	Os–S(1)–C(1)	103.4(2)
S(1)–Os–S(3)	84.04(6)	Os–S(2)–C(2)	103.2(2)
S(1)–Os–S(4)	146.04(8)	Os–S(3)–C(3)	103.6(2)
S(2)–Os–S(3)	148.88(9)	Os–S(4)–C(4)	103.1(2)
S(2)–Os–S(4)	84.92(7)	S(1)–C(1)–C(2)	121.8(5)
S(3)–Os–S(4)	86.63(6)	S(1)–C(1)–C(5)	116.2(5)
S(1)–Os–N(1)	107.2(2)	S(2)–C(2)–C(1)	121.5(6)
S(2)–Os–N(1)	105.7(2)	S(2)–C(2)–C(6)	117.4(5)
S(3)–Os–N(1)	105.4(2)	S(3)–C(3)–C(4)	121.8(5)
S(4)–Os–N(1)	106.7(2)	S(3)–C(3)–C(8)	115.8(4)
C(2)–C(1)–C(5)	122.0(7)	S(4)–C(4)–C(3)	122.0(6)
C(1)–C(2)–C(6)	121.1(6)	S(4)–C(4)–C(7)	117.4(5)
C(4)–C(3)–C(8)	122.4(6)	N(2)–C(5)–C(1)	178.4(8)
C(3)–C(4)–C(7)	120.7(7)	N(3)–C(6)–C(2)	181(2)
		N(4)–C(7)–C(4)	178(1)
		N(5)–C(8)–C(3)	178.1(8)

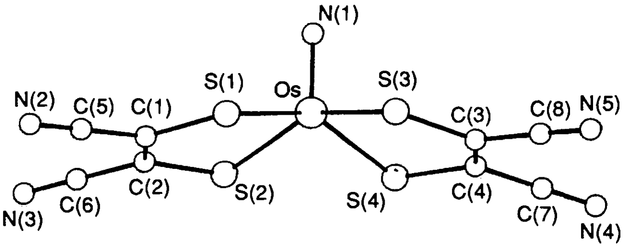

Fig. 1 Perspective view of the $[OsN(mnt)_2]^-$ anion

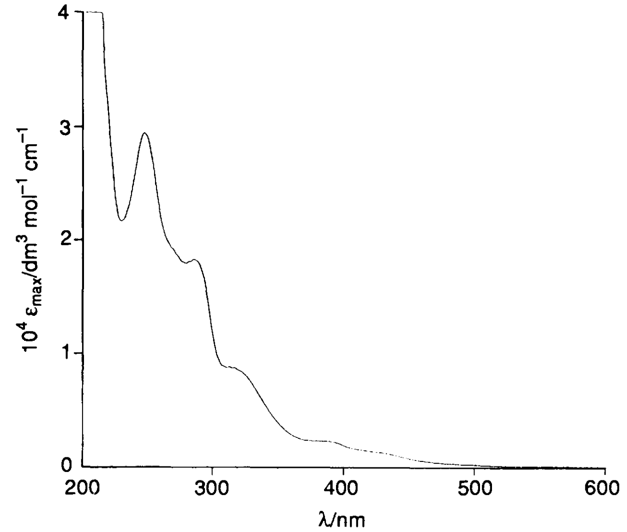

Fig. 2 The UV/VIS absorption spectrum of compound **1** in MeCN

Photophysical Properties.—Previous studies have established that $Os^{VI}{=}O$ and $Os^{VI}{\equiv}N$ complexes of amines, cyanides, aromatic diimines and arsines possess long-lived and emissive $^3[(d_{xy})^1(d_{\pi^*})^1]$ excited states [here π^* refers to (d_{xz}, d_{yz}) and is antibonding due to $Os{\equiv}N$ π-bonding interaction] in fluid solutions at room temperature.[12] The UV/VIS absorption spectra of $[OsNX_4]^-$ have also been studied by Gray and co-workers.[13] These complexes show weak absorptions at 400–600 nm, which are due to the $d_{xy}{\rightarrow}d_{\pi^*}$ transitions. The UV/VIS absorption spectrum of $[OsN(mnt)_2]^-$ is shown in Fig. 2. There are intense absorptions at 394 and 320 nm. From the ε_{max} values, the band at 394 nm is dipole-allowed and hence charge transfer in nature. Assignment of it to $p_\pi(N^{3-}){\rightarrow}Os^{VI}$ is unlikely

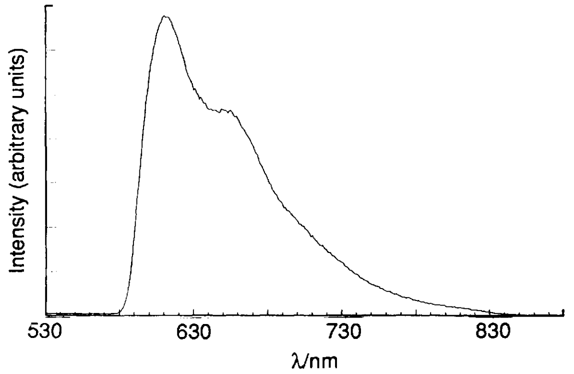

Fig. 3 Emission spectrum of compound **1** in a *n*-butyronitrile glass at 77 K

since a similar intense absorption band is not exhibited by $[OsN(NH_3)_4][CF_3SO_3]_3$.[12d] The transition energy is too low to be due to the intraligand transition of the co-ordinated mnt. We therefore tentatively assign the absorption at 394 nm as due to a S(mnt)$\rightarrow$Os^{VI} charge-transfer transition. Weak absorptions ranging from 400 to 550 nm are also observed. With reference to previous works, these are tentatively assigned to the $d_{xy} \rightarrow d_{\pi^*}$ transition. Room-temperature emission is observed upon photoexcitation of the complex with UV and visible light. In acetonitrile the complex shows a broad emission at 653 nm. Not unexpectedly, the excitation spectrum is quite similar to the absorption spectrum. The emission lifetime and quantum yield are 0.097 μs and 3.0×10^{-4}, respectively. Changing the solvent from acetonitrile to dichloromethane does not alter the emission properties. However, the emission is blue shifted to 610 nm and vibronically resolved in a *n*-butyronitrile glass at 77 K, as shown in Fig. 3. The observed vibrational spacing of about 1070 cm^{-1} is characteristic of the ν(Os≡N) stretch in the ground state. This provides support for the assignment of the emissive excited state as $^3[(d_{xy})^1(d_{\pi^*})^1]$.

Acknowledgements

We thank the Hong Kong University of Science and Technology, the University of Hong Kong, and the Hong Kong Research Grants Council for support.

References

1 See, for example, J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **4**, 49; G. N. Schrauzer, *Acc. Chem. Res.*, 1969, **2**, 72; R. E. Eisenberg, *Prog. Inorg. Chem.*, 1970, **12**, 295; R. H. Holm and M. J. O'Connor, *Prog. Inorg. Chem.*, 1971, **14**, 241; *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, J. A. McCleverty and R. D. Gillard, Pergamon, Oxford, 1987, vol. 2, p. 595.

2 C. G. Young and A. G. Wedd, *ACS Symp. Ser.*, 1993, **535**, 70; R. S. Pilato, K. Eriksen, M. A. Greaney, Y. Gea, E. C. Taylor, S. Goswami, L. Kilpatrick, T. G. Spiro, A. L. Rheingold and E. I. Stiefel, *ACS Symp. Ser.*, 1993, **535**, 84 and refs. therein.

3 W. H. Leung, A. A. Danopolous, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 205.

4 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.

5 A. Davison and R. H. Holm, *Inorg. Synth.*, 1967, **10**, 8.

6 G. W. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.*, 1973, 1315.

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

8 W. H. Leung, M. C. Wu and K. Y. Wong, unpublished work.

9 W. A. Nugent and J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, 1988, p. 112.

10 J. J. Schwab, E. C. Wilkinson, R. S. Wilson and P. A. Shapley, *J. Am. Chem. Soc.*, 1991, **113**, 6124.

11 P. A. Shapley, Z. Gebeyehu, N. Zhang and R. W. Scott, *Inorg. Chem.*, 1993, **32**, 5646.

12 (*a*) C. M. Che, H. W. Lam and T. C. W. Mak, *J. Chem. Soc., Chem. Commun.*, 1989, 1529; (*b*) C. M. Che, H. W. Lam, W. F. Tong, T. F. Lai and T. C. Lau, *J. Chem. Soc., Chem. Commun.*, 1989, 1883; (*c*) H. W. Lam, C. M. Che and K. Y. Wong, *J. Chem. Soc., Dalton Trans.*, 1992, 1411; (*d*) C. M. Che, K. Y. Wong, H. W. Lam, K. F. Chin, Z. Y. Zhou and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1993, 857; (*e*) H. W. Lam, K. F. Chin, C. M. Che, R. J. Wang and T. C. W. Mak, *Inorg. Chim. Acta*, 1993, **204**, 133.

13 C. D. Cowan, W. C. Troggler, K. R. Mann, C. K. Poon and H. B. Gray, *Inorg. Chem.*, 1976, **15**, 1747.

Received 1*st March* 1994; *Paper* 4/01244E