An Osmium(II) Complex of a Novel Hexadentate Diphosphinobis(disulfide) Macrocyclic Ligand with Pendant Thiolate Groups

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The complex $[OsCl_2(PPh_3)_3]$ reacts with $P(C_6H_4SH\text{-}2)_3$ to give the neutral osmium(II) complex [OsL], where L has been confirmed by an X-ray crystal structure determination to be a hexadentate ligand formed by the oxidative coupling of two $P(C_6H_4S\text{-}2)_3$ ligands *via* two disulfide bonds.

There has been considerable recent interest in the co-ordination chemistry of thiolate ligands,[1,2] but relatively little of this has been directed towards the platinum group metals. The chemistry of iron with thiolate ligands has received particular attention due to the known involvement of iron–sulfur species in the FeMo–Co cluster of nitrogenase and ferredoxins. Of the other elements in the iron group, the chemistry of ruthenium with polydentate ligands with thiolate and sulfide donors has been explored in some depth,[3–9] but comparatively few of the complexes also involved tertiary phosphine ligands. In view of the predominance of phosphine coligands in the binding and stabilisation of small molecules we have been investigating the co-ordination chemistry of polydentate phosphinothiolate ligands. There have been a few relatively sporadic reports of complexes of phosphinoalkanethiolates,[10–16] and more recently Block and co-workers[17–20] have reported a convenient route to mono-, bis- and tris-2-mercaptophenylphosphine ligands, together with a limited amount of their co-ordination chemistry. We here report on the reactions of tris(2-mercaptophenyl)phosphine and bis(2-mercaptophenyl)phenylphosphine with ruthenium, osmium, rhodium and iridium precursors, the first two giving complexes of a novel hexadentate ligand formed by coupling two $P(C_6H_4S\text{-}2)_3$ moieties *via* disulfide bonds.

The osmium(II) complex $[OsCl_2(PPh_3)_3]$ reacts with $PPh(C_6H_4SH\text{-}2)_2$ to give olive-green $[NHEt_3][Os\{PPh(C_6H_4S\text{-}2)_2\}_2]$.* This complex is poorly soluble in organic solvents, as are the related complexes $[M\{PPh(C_6H_4S\text{-}2)_2\}_2]^-$ (M = Ru, Rh or Ir). However, we believe that these complexes are all monomeric with octahedrally co-ordinated metal ions, with a P_2S_4 set of donor atoms. Reaction of $[OsCl_2(PPh_3)_3]$ with $P(C_6H_4SH\text{-}2)_3$ under similar conditions† gives initially a green anionic complex formulated on the basis of analysis as $[NHEt_3][Os\{P(C_6H_4S\text{-}2)_3\}_2]$. This complex **2** is very unstable in solution, which precluded any NMR spectroscopy in solution, but the similarity in colour to $[Os\{PPh(C_6H_4S\text{-}2)_2\}_2]$ suggests that the two complexes may have similar P_2S_4 co-ordination. On attempted recrystallisation of **2** it is rapidly and completely converted into brown [OsL] **1** in high yield. Elemental analysis suggested the stoichiometry of $Os\{P(C_6H_4S\text{-}2)_3\}_2$ and eight-co-ordinate osmium(VI). Accordingly a single-crystal X-ray diffraction study was undertaken.‡

The structure is shown in Fig. 1, together with the atom labelling scheme. The most significant feature of the structure is the P(2)–S(21)–P(1)–S(12) macrocycle generated by the coupling of two $P(C_6H_4S\text{-}2)_3$ ligands *via* two disulfide bonds S(11)–S(21) and S(12)–S(22). Only two of the disulfide sulfurs are co-ordinated, and the S–S distances are typical for disulfide linkages. The 14-membered macrocycle is co-ordinated so as to leave two *cis* sites which are occupied by thiolato-sulfurs. The metal–disulfide distances [average 2.339(1) Å] are significantly shorter than the metal–thiolate bonds [average 2.440(2) Å]. The bond angles about the osmium atom are relatively close to octahedral values, with the greatest distortion being found for the bite of the five-membered phosphorus–thiolate S and disulfide S units. The crystals also include one molecule of crystallisation of dichloromethane, which was located in the structure determination and also identified by ^1H NMR spectroscopy. The analogous ruthenium complex and the related anionic complexes of Rh and Ir are assumed on the basis of IR and NMR spectroscopy to have structures related to that of complex **1**.

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* The complex $[OsCl_2(PPh_3)_3]$ (0.5 g, 0.53 mmol), $PPh(C_6H_4SH\text{-}2)_2$ (0.82 g, 2.5 mmol) and NEt_3 (0.5 g, 5 mmol) were heated under reflux in methanol (35 cm^3) under dinitrogen for 3 h. The complex $[NHEt_3][Os\{PPh(C_6H_4S\text{-}2)_2\}_2]$ precipitated analytically pure from the solution on cooling. The ruthenium, rhodium and iridium analogues were prepared in a similar way from $[RuCl_2(PPh_3)_3]$, $[RhCl(PPh_3)_3]$ and $[IrCl_3(PMePh_2)_3]$.

† The complex $[OsCl_2(PPh_3)_3]$ (0.5 g, 0.53 mmol), $P(C_6H_4SH\text{-}2)_3$ (0.89 g, 2.5 mmol) and NEt_3 (0.5 g, 5 mmol) were heated under reflux in methanol (40 cm^3) under dinitrogen for 4 h. Complex **2** precipitated from the solution on cooling in 80% yield. Recrystallisation of it from dichloromethane–methanol gave complex **1** in high yield. The ruthenium analogue was prepared in analogous manner, and the anionic complex $[IrL]^-$ was made in a similar way from $[IrCl_3(PMePh_2)_3]$.

Satisfactory elemental analyses were obtained for all the reported complexes.

‡ *Crystal data.* $C_{37}H_{26}Cl_2OsP_2S_6$, $M = 986.1$, monoclinic, space group $P2_1/n$, $a = 16.398(2)$, $b = 14.428(3)$, $c = 17.014(2)$ Å, $\beta = 113.62(1)°$, $U = 3688$ $Å^3$, $Z = 4$, $D_c = 1.78$ g cm^{-3}, $F(000) = 1936$, $\lambda(Mo\text{-}K_\alpha) = 0.710\,69$ Å. $2\theta_{max} = 50°$, $\mu(Mo\text{-}K\alpha) = 40.5$ cm^{-1}, crystal dimensions 0.11 × 0.16 × 0.67 mm, Enraf–Nonius CAD4 diffractometer, ω–2θ scan, scan width 0.6 + 0.34 tanθ. Structure analysis based on 4410 reflections with $I > 3\sigma(I)$. Osmium atom position by Patterson synthesis, all other atoms located by standard Fourier techniques, Killean and Lawrence weights were used with $w = w_0\exp(15 \sin \theta/\lambda)^2$. Final $R = 0.048$, $R' = 0.040$.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

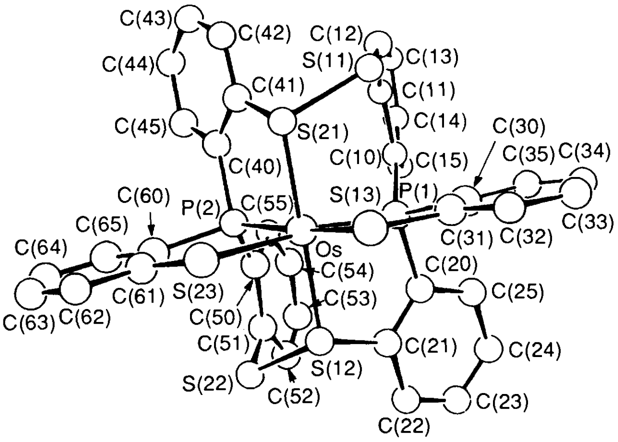
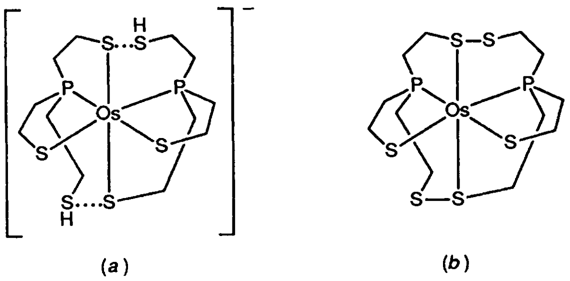


Fig. 1 The molecular structure of complex **1** showing the atom-labelling scheme. Selected bond lengths (Å) and bond angles (°): Os–S(12) 2.323(1), Os–S(13) 2.438(2), Os–S(21) 2.314(1), Os–S(23) 2.442(2), Os–P(1) 2.249(2), Os–P(2) 2.248(2), S(11)–S(21) 2.122(3) and S(12)–S(22) 2.128(3); S(12)–Os–S(13) 94.49(6), S(12)–Os–S(21) 177.54(7), S(12)–Os–S(23) 90.12(7), S(12)–Os–P(1) 85.47(6), S(12)–Os–P(2) 92.48(6), S(13)–Os–S(21) 87.36(6), S(13)–Os–S(23) 89.67(9), S(13)–Os–P(1) 84.33(7), S(13)–Os–P(2) 171.00(6), S(21)–Os–S(23) 91.53(7), S(21)–Os–P(1) 93.09(6), S(21)–Os–P(2) 85.86(6), S(23)–Os–P(1) 172.25(8), S(23)–Os–P(2) 84.61(8) and P(1)–Os–P(2) 101.93(7)



(*a*) (*b*)

Fig. 2 Schematic structures of complexes **1**(*b*) and **2**(*a*) with the phenyl groups omitted for clarity

The anionic intermediate **2** formed en route to **1** is believed to have P_2S_4 co-ordination with pendant SH groups, as shown schematically in Fig. 2(*a*). On attempted recrystallisation in air this complex is rapidly converted into **1** [Fig. 2(*b*)] by oxidative coupling of the free SH groups to ligated thiolate sulfurs with formal reduction of the metal. The proposed structure for **2** is consistent with the absence of any reversible reduction steps in a cyclic voltammogram in CH_2Cl_2 at a platinum electrode, confirming that **1** and **2** have different structures. We have been unable to locate ν(S–H) in the IR spectrum of **2**, but this may be due to strong hydrogen bonding of the hydrogen to the co-ordinated thiolate sulfur. It appears that this reaction may have considerable generality, and we are currently investigating similar examples of macrocycle formation on rhenium, technetium and iron.

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References

1 J. M. Berg and R. H. Holm, *Metal Ions in Biolgoy*, ed. T. G. Spiro, Wiley, New York, 1982, vol. 4, pp. 1–66.
2 P. J. Blower and J. R. Dilworth, *Coord. Chem. Rev.*, 1987, **76**, 121.
3 D. Sellmann, M. Geck, F. Knoch, G. Ritter and J. Dengler, *J. Am. Chem. Soc.*, 1991, **113**, 1819.
4 D. Sellmann, P. Lechner, F. Knoch and M. Moll, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 552.
5 D. Sellmann and I. Barth, *Z. Anorg. Allg. Chem.*, 1989, **577**, 234.
6 D. Sellmann, G. Binker, M. Moll and E. Herdtweck, *J. Organomet. Chem.*, 1987, **327**, 403.
7 D. Sellmann and O. Kaeppler, *Z. Naturforsch., Teil B*, 1987, **42**, 1291.
8 D. Sellmann, G. Binker, M. Moll and C. E. Campana, *Inorg. Chim. Acta*, 1987, **130**, 221.
9 D. Sellmann, U. Reineke, G. Huttner and L. Zsolnai, *J. Organomet. Chem.*, 1986, **310**, 83.
10 V. K. Issleib and W. Gans, *Z. Anorg. Allg. Chem.*, 1982, **491**, 163.
11 V. K. Issleib and D. Weinbeck, *Z. Anorg. Allg. Chem.*, 1978, **440**, 5.
12 M. Savignac, P. Cadiot and F. Mathey, *Inorg. Chim. Acta*, 1980, **45**, L43.
13 V. K. Issleib and W. Gans, *Z. Anorg. Allg. Chem.*, 1981, **475**, 116.
14 P. J. Blower, J. R. Dilworth, G. J. Leigh, B. D. Neaves, F. B. Normanton, J. Hutchinson and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1985, 2647.
15 D. W. Stephan, *Inorg. Chem.*, 1984, **23**, 2207.
16 J. Chatt, J. R. Dilworth, J. A. Schmutz and J. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1979, 1595.
17 E. Block, V. Eswarakrishnan, M. Gernon, G. Ofori-Okai, C. Saha, K. Tang and J. Zubieta, *J. Am. Chem Soc.*, 1989, **111**, 658.
18 E. Block, G. Ofori-Okai and J. Zubieta, *J. Am. Chem. Soc.*, 1989, **11**, 2647.
19 T. Nicholson and J. Zubieta, *Inorg. Chem.*, 1987, **26**, 2094.
20 N. Vries, A. Davison and A. G. Jones, *Inorg. Chim. Acta*, 1989, **165**, 346.

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