Intra- and Inter-molecular Stacking in Tetracyanoethylene (tcne) Complexes of Platinum Metal Dithio Acids: The Structures and Electrochemistry of $[Os(S_2PR_2)_2(PPh_3)(tcne)]$ (R = Me, Ph)

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The solid-state structure of $[Os(S_2PR_2)_2(PPh_3)(tcne)]$ (R = Me) shows intermolecular stacking of N-bound tetracyanoethylene (tcne) ligands, whereas for R = Ph intramolecular interaction of co-ordinated tcne and a Ph group of a $S_2PPh_2^-$ moiety is observed; electrochemical reduction of $[M(S_2PR_2)_2(PPh_3)(tcne)]$ affords the complex anions $[M(S_2PR_2)_2(PPh_3)(tcne^{\cdot-})]^-$ (M = Ru, Os; R = Me, Ph, OEt).

The study of mixed-salts containing stacked tetracyanoethylene (tcne), tetrathiofulvalene (ttf) and related redox-active molecules has been the subject of much interest recently in relation to the development of materials which show unusual electronic and magnetic properties.[1,2] Charge-transfer species such as $[Fe(C_5Me_5)_2]^+[tcne]^-$ (ref. 2) and related metallocene and organometallic complexes[3] incorporate tcne$^-$ as a non-co-ordinated molecule. We were interested in synthesising metal complexes incorporating tcne bound directly to a redox-active metal centre.

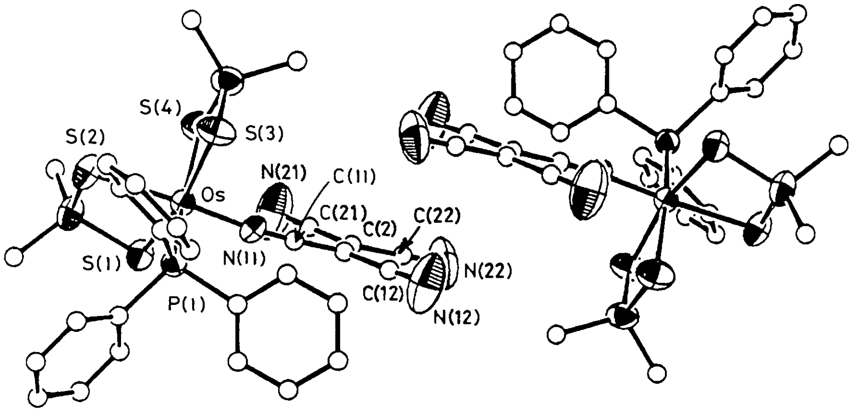

Figure 1. Crystal structure of $[Os(S_2PMe_2)_2(PPh_3)(tcne)]$. H atoms have been omitted for clarity. Os–N(11) 1.899(7), Os–P(1) 2.3249(22), Os–S(1) 2.4590(23), Os–S(2) 2.456(3), Os–S(3) 2.384(3), Os–S(4) 2.522(3), C(1)–C(2) 1.360(13), N(11)–C(11) 1.143(11), N(12)–C(12) 1.142(18), N(21)–C(21) 1.142(17), N(22)–C(22) 1.131(16), C(1)–C(11) 1.410(13), C(1)–C(12) 1.436(15), C(2)–C(21) 1.412(16), C(2)–C(22) 1.445(15) Å.

Reaction of $[M(S_2PR_2)_2(PPh_3)_2]$ (M = Ru, Os; R = Me, Ph, OEt) with an excess of tcne in $CHCl_3$ under N_2 affords the dark green diamagnetic complexes $[M(S_2PR_2)_2(PPh_3)(tcne)]$ in high yield.† The i.r. spectra of these products show bands in the region 2100—2235 and at 1430 cm^{-1} assigned to $C{\equiv}N$ and $C{=}C$ stretching vibrations, $\nu_{C\equiv N}$, and $\nu_{C=C}$, respectively. The shifts of these vibrational bands to lower frequency relative to metal-free tcne[4] are consistent with back-donation of electron density from M to N-bound tcne. Complete electron transfer from metal to co-ordinated tcne in the complexes $[V(C_5H_5)(Br)(tcne)]$[5] and $[Mn(C_5MeR_4)(CO)_2(tcne)]$ (R = H, Me)[6] has been assigned on the basis of the $\nu_{C=C}$ stretching vibration occurring near 1400—1420 cm^{-1} in the i.r. spectrum.

In order to confirm the co-ordination mode of the tcne ligand in these complexes, single crystal *X*-ray structural determinations of $[Os(S_2PR_2)_2(PPh_3)(tcne)]$ (R = Me, Ph) were undertaken. The structures of both complexes (Figures 1 and 2)‡ confirm co-ordination of tcne through a terminal N-donor. In each structure, the Os centre is co-ordinated to two bidentate dithiophosphinate ligands, one PPh_3, and to a monodentate N-bound tcne ligand. The diffraction studies of $[Os(S_2PR_2)_2(PPh_3)(tcne)]$ (R = Me, Ph) represent the first fully-refined characterisation of tcne N-bound to a transition metal centre,[5—7] alkenyl binding of tcne to metal centres *via* the $C{=}C$ bond being more common.[8]

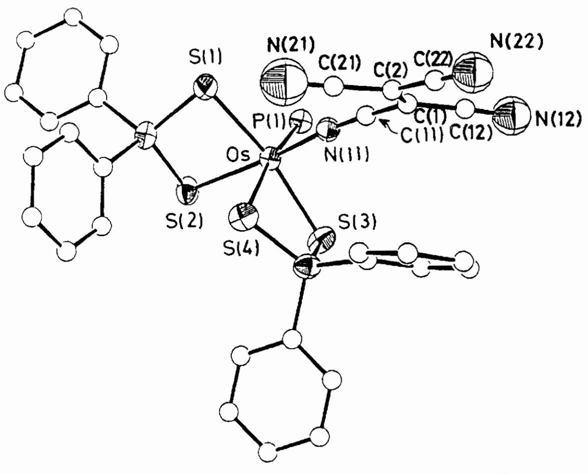

Figure 2. Crystal structure of $[Os(S_2PPh_2)_2(PPh_3)(tcne)]$. H Atoms and Ph rings on PPh_3 have been omitted for clarity. Os–N(11) 1.858(10), Os–P(1) 2.324(3), Os–S(1) 2.455(4), Os–S(2) 2.459(3), Os–S(3) 2.395(3), Os–S(4) 2.516(3), C(1)–C(2) 1.401(19), N(11)–C(11) 1.213(17), N(12)–C(12) 1.153(21), N(21)–C(21) 1.12(3), N(22)–C(22) 1.162(22), C(1)–C(11) 1.379(19), C(1)–C(12) 1.436(19), C(2)–C(21) 1.419(21), C(2)–C(22) 1.407(23) Å.

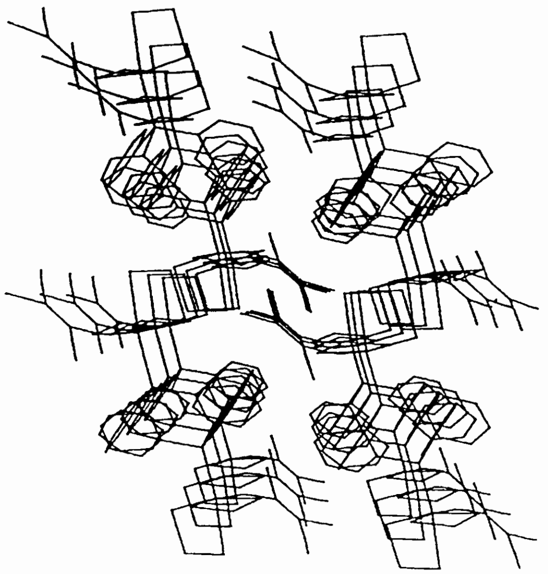

Figure 3. Packing diagram for $[Os(S_2PMe_2)_2(PPh_3)(tcne)]$, viewed perpendicular to the plane of the co-ordinated tcne.

The most interesting feature of the solid-state structures of these complexes is, however, in the short-range interaction of the ligated tcne ligands. Figure 3 shows a packing diagram of $[Os(S_2PMe_2)_2(PPh_3)(tcne)]$ viewed perpendicular to the plane of the cyano-alkene. The complex exists in the solid state as a structure containing staggered, parallel tcne ligands whose centres, related by the inversion centre at (½, ½, ½), are 4.66 Å apart and whose perpendicular separation is 3.12 Å. In contrast, the structure of $[Os(S_2PPh_2)_2(PPh_3)(tcne)]$ shows no such intermolecular interaction but does show an intramol-

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† The complexes have been characterised by i.r., u.v.–visible, ^1H, ^{31}P n.m.r. spectroscopy, and by elemental analysis.

‡ A green–black crystal of $[Os(S_2PMe_2)_2(PPh_3)(tcne)]$ (0.15 × 0.10 × 0.05 mm) suitable for *X*-ray analysis was obtained by recrystallisation from diethyl ether and light petroleum (b.p. 60—80 °C).

Crystal data: $C_{28}H_{27}N_4OsP_3S_4$, M = 830.9, triclinic, space group $P\bar{1}$, a = 9.675(3), b = 10.698(4), c = 16.711(2) Å, α = 89.72(3), β = 73.39(3), γ = 85.64(3)°, U = 1689.3 Å^3 (from θ values of 12 reflections with θ = 13.0—14.0° measured at ±ω), D_c = 1.633 g cm^{-3}, Z = 2; $F(000)$ = 816, $\bar{\lambda}$(Mo-K_α) = 0.71073 Å, μ = 41.81 cm^{-1}. Of 3700 reflections measured (2.5 < θ < 22.5°, h −10→10, k −12→12, l 0→18), 3044 with $F \geqslant 6\sigma(F)$ were used in all calculations. Initial absorption correction using 72 ψ scans (maximum and minimum transmission factors were 0.129 and 0.097 respectively). No crystal decay was apparent. A Patterson synthesis was used to locate the Os atom; all other non-H atoms were located by iterative rounds of least-squares refinement and difference Fourier synthesis.[11] Os, N, P, and S atoms were refined anisotropically. At isotropic convergence, final correction for absorption was made using DIFABS.[10] All H atoms and C atoms of the phenyl rings were included in fixed, calculated positions (AFIX).[11] The weighting scheme $w^{-1} = \sigma^2(F) + 0.000313F^2$ gave satisfactory agreement analyses. At convergence, R, R_w = 0.032, 0.038 respectively for 185 parameters, S = 1.122. The maximum and minimum residues in the final ΔF synthesis were 0.65 and −0.79 e Å^{-3} respectively.

A green–black crystal of $[Os(S_2PPh_2)_2(PPh_3)(tcne)]$ (0.15 × 0.15 × 0.05 mm) suitable for *X*-ray analysis was obtained by recrystallisation from diethyl ether and light petroleum (b.p. 60—80 °C).

Crystal data: $C_{48}H_{35}N_4OsP_3S_4$, M = 1079.2, monoclinic, space group $P2_1/c$, a = 20.5384(25), b = 9.5578(16), c = 23.730(3) Å, β = 100.13(4)°, U = 4585.6 Å^3 (from θ values of 40 reflections with θ = 15.0—17.0° measured at ±ω), D_c = 1.563 g cm^{-3}, Z = 4; $F(000)$ = 2144, $\bar{\lambda}$(Mo-K_α) = 0.71073 Å, μ = 30.99 cm^{-1}. Of 5220 reflections measured (2.5 < θ < 22.5°, h −22→21, k 0→10, l 0→25), 3905 with $F \geqslant 6\sigma(F)$ were used in all calculations. Initial absorption correction using 72 ψ scans (maximum and minimum transmission factors were 0.861 and 0.513 respectively). No crystal decay was apparent. A Patterson synthesis was used to locate the Os atom; all other non-H atoms were located by iterative rounds of least-squares refinement and difference Fourier synthesis.[11] Os, N, P, and S atoms and C atoms of the tcne ligand were refined anisotropically. At isotropic convergence, final correction for absorption was made using DIFABS.[10] All H atoms and C atoms of the phenyl rings were included in fixed, calculated positions (AFIX).[11] The weighting scheme $w^{-1} = \sigma^2(F) + 0.00061F^2$ gave satisfactory agreement analyses. At convergence, R, R_w = 0.048, 0.059 respectively for 247 parameters, S = 1.135. The maximum and minimum residues in the final ΔF syntheses were 1.06 and −1.00 e Å^{-3} respectively. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ecular interaction between the ligated tcne and a phenyl ring [C(321)–C(326)] of one of the dithiophosphinate ligands. The centres of gravity of these moieties are 3.740 Å apart; their least-squares mean planes make a dihedral angle of 7.72° and have a perpendicular separation of 3.615 Å.

The interaction and stacking of partially charged tcne molecules is an inherent feature of many solid-state materials showing unusual magnetic and conductivity properties.[1—3] In order to probe the degree of electron transfer from metal to tcne in these complexes, we have undertaken a spectroelectrochemical study of these species. All the complexes $[\mathrm{M(S_2PR_2)_2(PPh_3)(tcne)}]$ (M = Ru, Os; R = Me, Ph, OEt) show a reversible one-electron reduction to afford $[\mathrm{M(S_2PR_2)_2(PPh_3)(tcne)}]^-$. The reduction potentials for this process are dependent upon the metal ion and the dithiolate, and occur at more negative potentials than the corresponding reduction of free tcne ($E_{\frac{1}{2}} = +0.40$ V *vs.* $\mathrm{Ag/Ag^+}$). This is consistent with back donation from M(dπ) to tcne (LUMO) which will increase the electron density on tcne and, therefore, make the co-ordinated tcne more difficult to reduce.[6] The complexes $[\mathrm{M(S_2PR_2)_2(PPh_3)(tcne)}]$ (M = Ru, Os; R = Me, Ph, OEt) show M→tcne charge transfer bands at 11 000—13 000 $\mathrm{cm^{-1}}$. The mono-anions $[\mathrm{M(S_2PR_2)_2(PPh_3)(tcne)}]^-$ can be quantitatively and fully reversibly electrogenerated; coulometry confirms this reduction to be a one-electron process. The electronic spectrum of the reduced species $[\mathrm{Ru(S_2PR_2)_2(PPh_3)(tcne)}]^-$ typically shows charge-transfer bands of reduced intensity and shifted to higher energy, in addition to a broad absorption band near 24 000 $\mathrm{cm^{-1}}$. The new band near 24 000 $\mathrm{cm^{-1}}$ is characteristic of $(\mathrm{tcne}^{\cdot-})$,[9] and is also observed in charge-transfer complexes such as $[\mathrm{Fe(C_5Me_5)_2}]^+[\mathrm{tcne}]^-$ (ref. 2) and $[\mathrm{Mn(C_5MeR_4)(CO)_2(tcne)}]$ (R = H, Me).[6] We therefore assign this first reduction process to be tcne-based to afford $[\mathrm{M(S_2PR_2)_2(PPh_3)(tcne^{\cdot-})}]^-$. The second reductions of these complexes are electrochemically quasi-reversible. Interestingly, only $[\mathrm{Os(S_2PPh_2)_2(PPh_3)(tcne)}]^{2-}$ (assigned as a double-reduction on tcne) can be generated as a stable species. We believe that the stabilisation of the doubly-reduced species may be linked to the interaction of the tcne with a phenyl group of the dithiophosphinate as observed in the crystal structure of this complex. The complexes $[\mathrm{M(S_2PR_2)_2(PPh_3)(tcne)}]$ (M = Ru, Os; R = Me, Ph, OEt) show reversible or quasi-reversible $\mathrm{M^{II}/M^{III}}$ couples near +1.0 V *vs.* $\mathrm{Ag/Ag^+}$ indicating that the parent neutral compounds should be regarded formally as $\mathrm{M^{II}}$–tcne species.

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