Tetranuclear osmium complexes of tetracyanoquinodimethane [TCNQ, 2,2′-(cyclohexa-2,5-diene-1,4-diylidene)bis(propane-1,3-dinitrile)] and 1,2,4,5-tetracyanobenzene (TCNB). Synthesis, spectroelectrochemistry and magnetism †

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The new complexes [(μ₄,η⁴-TCNX){Os(PR₃)₂(CO)(H)Cl}₄], R = isopropyl, TCNX = tetracyanoquinodimethane [TCNQ, 2,2′-(cyclohexa-2,5-diene-1,4-diylidene)bis(propane-1,3-dinitrile)] or 1,2,4,5-tetracyanobenzene (TCNB), were studied by spectroelectrochemistry in the UV/VIS/NIR and IR regions and by EPR spectroscopy. Both compounds are reduced in two reversible steps and oxidized in a two-electron process (reversible for TCNQ, quasi-reversible for TCNB). In all oxidation states studied $(-, 0, 2+)$ the TCNQ complexes exhibited intense long-wavelength absorptions in the near IR region ($\lambda_{max} > 1000$ nm). The EPR spectra of the monoanionic forms exhibit hardly any g anisotropy and thus very little metal participation, suggesting an oxidation state formulation [(TCNX·⁻)(Osᴵᴵ)₄]. The dication of the TCNQ system is formulated as [(TCNQ)(Os²·⁵)₄] with an intervalence transfer transition at $\lambda_{max} = 1245$ nm ($\varepsilon = 50\,000$ м⁻¹ cm⁻¹). In the solid state, the neutral complexes show temperature dependent paramagnetism that could be fitted with a model implying two coupled $S = \frac{1}{2}$ entities.

The TCNX ligands {*e.g.* tetracyanoethene (TCNE), tetracyano-quinodimethane [2,2′-(cyclohexa-2,5-diene-1,4-diylidene)bis-(propane-1,3-dinitrile)] (TCNQ) or 1,2,4,5-tetracyanobenzene (TCNB)} are very unusual[1] because of their variable co-ordination behaviour (σ or π),[1–3] their proven ability to bridge up to four metal centres,[1,4–8] their tendency to form aggregates *via* π–π interaction (stacking[3,9]) and their non-innocence, *i.e.* their facile reduction to the radical anionic or dianionic state.[1,2,10–13] In the course of exploring the electron transfer and oligonucleation behaviour of the TCNX ligand family we have recently extended our previous studies on Group 6 and 7 organometallic[5,13–17] and pentaammineruthenium complexes[6] to organoosmium[18] complexes [(μₙ,ηⁿ-TCNE){Os(PR₃)₂(CO)-(H)Cl}ₙ], $n = 1, 2$ or 4; R = isopropyl.[8] The ability to obtain a tetranuclear compound has prompted us now to study the related systems [(μ₄,η⁴-TCNX){Os(PR₃)₂(CO)(H)Cl}₄], [(TCNX)(Osf)₄], TCNX = TCNQ or TCNB.

The 16 valence electron organoosmium fragments [Osf] = [Os(PR₃)₂(CO)(H)Cl] have been employed in the bind-ing of O₂ or H₂ and in catalysis studies.[19,20] Among the ques-tions posed by the present investigation will be that of the proper oxidation state formulation with respect to the bridging ligand (TCNX⁰ᐟ·⁻ᐟ²⁻) and the four metal centres.[1,6,8] These ques-tions pertain to the neutral state as well as to spectroelectro-chemically accessible oxidized and reduced forms. We also address the magnetism of these materials since other tetra-nuclear complexes of the TCNX ligands with pentaam-mineruthenium or organomanganese fragments have exhibited peculiar and unique magnetic coupling behaviour.[21,22] The observed paramagnetism is of particular interest as it involves heavy and/or organometallic transition-metal centres with

[TCNQ][Osf]₄

[TCNB][Osf]₄
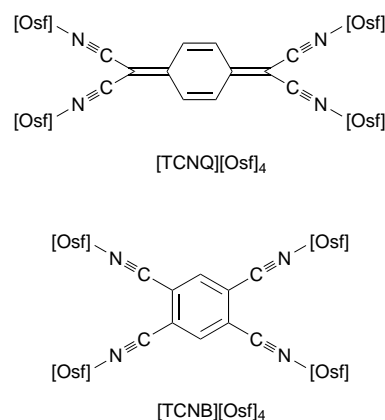
formal 18 valence electron configurations; few such examples are known in the literature.[21–23]

Results and Discussion

Tetranuclear complexes of TCNQ or TCNB have hitherto only been obtained in a few cases.[5–7] For the discrete complexes [(μ₄,η⁴-TCNQ){(C₅Me₅)(CO)₂Mn}₄][5] and [(μ₄,η⁴-TCNX)-{(H₃N)₅Ru}₄]⁸⁺, TCNX = TCNQ or TCNB,[6] it was demon-strated that these addition products of potentially tetradentate TCNX with four d⁶ metal components have a delocalized elec-tronic structure where TCNX has acquired some charge from the electron-rich metals in the ground state.[5,6] The preparation of the new tetranuclear compounds [(μ₄,η⁴-TCNX){Os(PR₃)₂-(CO)(H)Cl}₄], TCNX = TCNQ or TCNB, is similar to that reported for the TCNE analogue.[8] However, the TCNQ and TCNB compounds have greater solubility, thus allowing for spectroelectrochemical characterization (see below). To confirm

Table 1 Proton and ^{31}P NMR spectroscopic data[a]

	^1H NMR						^{31}P NMR
Compound	$\delta(PCHCH_3)$	J(HH)	$\delta(PCHCH_3)$	δ(OsH)	J(PH)	δ(CH)[b]	δ(PR)
[Osf][c]	1.27, 1.20	6.5	2.83	−31.92	14	—	47.3
[(TCNB)(Osf)$_4$][c]	1.35, 1.20	6.9	2.73	−2.44	30	8.27[d]	23.9
TCNB[c]	—	—	—	—	—	8.10	—
[(TCNQ)(Osf)$_4$][e]	1.42, 1.25	6.3	2.75	−2.78	30	7.80[d]	24.0
TCNQ[e]	—	—	—	—	—	7.52	—

[a] Chemical shifts δ in ppm, coupling constants J in Hz. [b] Protons of the TCNX ligand. [c] Solvent C_6D_6. [d] Broad. [e] Solvent CD_2Cl_2.

Table 2 Vibrational data (in cm^{-1}) from IR spectroscopy

Compound	ν(C≡O)	ν(Os−H)	ν(C≡N)
[Osf][a]	1886s	Not observed	—
TCNQ[b]	—	—	2228
TCNQ$^{•−}$[b]	—	—	2197, 2166
TCNQ$^{2−}$[b]	—	—	2164, 2096
[(TCNQ)(Osf)$_4$][b]	1945s, 1892vs	2099w	2180s, 2140s
TCNB[b]	—	—	2245
[(TCNB)(Osf)$_4$][b]	1946s, 1895vs	Not observed	2185s (br)
[(TCNE)(Osf)$_4$][b,c]	1930s, 1905vs	Not observed	2170w, 2110m

[a] Solvent C_6H_6. [b] KBr pellet. [c] From ref. 8.

Table 3 Electrochemical data[a] of ligands and complexes

Compound	$E^{+2/0}$	$E^{0/1−}$	$E^{1−/2−}$
TCNQ	—	−0.29	−0.88
[(TCNQ)(Osf)$_4$]	0.09 (50)	−0.20 (65)	−0.94 (64)
TCNB	—	−1.14	−2.23
[(TCNB)(Osf)$_4$]	0.18 (95)[b]	−1.10 (66)	<−2.3

[a] From cyclic voltammetry in dichloromethane/0.1 M NBu$_4$PF$_6$ at 100 mV s^{-1}. Potentials in V $vs.$ Fe(C$_5$H$_5$)$_2$$^{0/+}$; peak potential differences for complex in mV (in parentheses). [b] Quasi-reversible at 273 K.

Fig. 2 Temperature dependence of the magnetic behaviour of compounds [(TCNX){Os(PR$_3$)$_2$(CO)(H)Cl}$_4$] and simulated responses according to the model described in the text

Fig. 1 Cyclic voltammogram of [(TCNQ){Os(PR$_3$)$_2$(CO)(H)Cl}$_4$] in 1,2-dichloroethane/0.1 M NBu$_4$PF$_6$, 100 mV s^{-1} scan rate
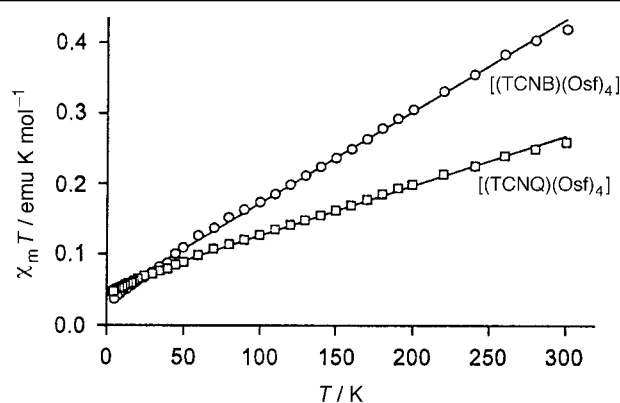
the identity, co-ordination mode and electronic structure of the neutral complexes, we characterized both compounds by ^1H and ^{31}P NMR spectroscopy (Table 1), IR vibrational spectroscopy (nitrile and carbonyl stretching, Table 2), electrochemistry (Table 3), magnetic susceptibility measurements (Table 4), EPR spectroscopy of monoreduced forms (Table 5) and UV/VIS/NIR spectroscopy/spectroelectrochemistry (Table 6). The NMR spectroscopic results (Table 1) show the equivalence of the ^1H and ^{31}P nuclei in the four organoosmium fragments, thus confirming the symmetrically tetranuclear character of the compounds. Whereas the co-ordination of [Osf] causes a slight upfield shift of the ^{31}P resonances after binding to TCNX, the CH protons of the TCNX ligands experience a marginal downfield shift. However, there is also a conspicuous broadening of the H(C) resonances of the co-ordinated TCNQ and TCNB molecules which indicates some degree of paramagnetism. Solid-state susceptibility measurements as described below confirm this interpretation.

Significant effects with regard to intramolecular charge transfer and proper oxidation state formulation[1] are apparent from the vibrational data (Table 2) which also suggest a high symmetry arrangement even on the vibrational time-scale of about 10^{-12} s. There are two low-energy shifted cyanide stretching bands for the TCNQ system which lie in the regions of one- and two-electron reduced TCNQ.[1] Similarly, the broad ν(CN) band of the TCNB complex[6] shows a shift to lower energies.

On the other hand, the carbonyl stretching frequencies within the organoosmium fragment exhibit both a splitting and a high-energy shift, reflecting[5] partial oxidation and vibrational coupling through what appears to be a conjugated tetrametalla π system.[5,6,8]

Cyclic voltammetric measurements of compounds [(μ_4,η^4-TCNX){Os(PR$_3$)$_2$(CO)(H)Cl}$_4$], TCNX = TCNQ or TCNB, gave similar results to those observed for the complex ions [(μ_4,η^4-TCNX){Ru(NH$_3$)$_5$}$_4$]$^{8+}$.[6] There are one (TCNB) or two (TCNQ, Fig. 1) reversible or at least quasi-reversible one-electron reduction steps and one two-electron oxidation wave, the latter occurring at rather low potential for both compounds (Table 3). The reduction potentials are quite close to those of the non-co-ordinated ligands (Table 3), implying an almost full compensation of the σ donor effect (which by itself would facilitate reduction) by the π-back bonding interaction (the effect of which is a cathodic shift).[1,13,14]

Before looking at the nature of the electrogenerated ionic states by EPR and UV/VIS/NIR spectroelectrochemistry we address the small but evident paramagnetism of both compounds. The magnetic moments, μ_{eff}, determined at 300 K are 1.44 μ_B for the TCNQ derivative and 1.83 μ_B for the TCNB analogue. Although this would be formally in agreement with an $S = \frac{1}{2}$ state, the even electron count and the non-saturation behaviour of the magnetic susceptibility suggest otherwise. We therefore undertook a more detailed study.[21,22] The temperature dependence between 5 and 300 K of $\chi_m T$ (χ_m = molar magnetic susceptibility and T = temperature) could be successfully analysed (Fig. 2) employing the model developed recently for

Table 4 Magnetic coupling data* for tetranuclear osmium and ruthenium complexes with TCNX ligands

Compound	J	D	g	TIP	Reference
$[(TCNQ)\{Ru(NH_3)_5\}_4]$	3.2	13.7	1.81	$1.9\cdot10^{-4}$	22
$[(TCNB)\{Ru(NH_3)_5\}_4]$	4.0	9.3	1.47	$2.0\cdot10^{-3}$	22
$[(TCNE)\{Ru(NH_3)_5\}_4]$	8.2	42.1	1.10	$4.4\cdot10^{-4}$	22
$[(TCNQ)(Osf)_4]$	2.6	8.6	0.67	$7.1\cdot10^{-4}$	This work
$[(TCNB)(Osf)_4]$	4.0	8.5	0.59	$1.3\cdot10^{-3}$	This work

* Determined by simulations of experimental $\chi_m T$ vs. T curves. Exchange coupling constants J and zero-field splitting parameters D in cm^{-1}, temperature independent paramagnetism TIP in emu mol^{-1} (1 emu = 10^{-3} A m^2).

the pentaammineruthenium analogues,[22] *i.e.* there is spin–spin coupling between two $S = \frac{1}{2}$ moieties of the molecule, most likely two dimeric $[Os^{2.5}]$ mixed-valent subunits.[22] This model is the most straightforward and reasonable from a chemical and spectroscopic point of view; the best agreement between experiment and calculation was obtained when axial zero-field splitting was added to the isotropic exchange coupling between the two $S = \frac{1}{2}$ spins. The Hamiltonian for this model is shown in equation (1).

$$H = -JS_1S_2 + SDS + \beta SgB \qquad (1)$$

Considering an axial symmetry the eigenvalues E become $E_1^{\parallel} = -(J/4) - [(2/3)D]$, $E_1^{\perp} = -(J/4) - [(3\beta^2/D)g_{\perp}^2B^2]$, $E_2^{\parallel} = -(J/4) - (D/3) - g_{\parallel}\beta B$, $E_2^{\perp} = -(J/4) - (D/3)$, $E_3^{\parallel} = -(J/4) - (D/3) - g_{\parallel}\beta B$, $E_3^{\perp} = -(J/4) - (D/3) + [(3\beta^2/D)g_{\perp}^2B^2]$, $E_4^{\parallel} = -(3/4)J$, $E_4^{\perp} = -(3/4)J$. Combination of these eigenvalues with the Van Vleck equation yields $\chi_m^{\parallel}$ and $\chi_m^{\perp}$ which can be averaged to yield χ_m. Neglecting the g anisotropy ($g_{\perp} = g_{\parallel} = g$) one obtains[22] equation (2) (where TIP is the temperature independ-

$$\chi_m T =$$
$$\frac{2}{3}\frac{N\beta^2}{k}g^2\left[\frac{e^{-D/3kT}}{e^{2D/3kT} + 2e^{-D/3kT} + e^{-J/kT}} + \frac{\frac{6}{D/kT}(1 - e^{-D/3kT})}{1 + 2e^{-D/3kT} + e^{-J/kT}}\right] +$$
$$TIP \times T \quad (2)$$

ent paramagnetism) which was used for curve fitting. The data from this analysis are summarized in Table 4 and compared with the results for the pentaammineruthenium species.[22]

The data from the analysis of the paramagnetism of Ru and Os systems agree with respect to small positive J values and larger D parameters, the numbers for the osmium systems being somewhat smaller in accordance with the diminished paramagnetism of the 5d system. The g values calculated by the fitting procedure are extremely small for the osmium compounds which confirms our previous statement[22] that these numbers reflect unaccounted contributions from the metal spin–orbit coupling. Relative to the TCNQ analogues, the larger J values of the TCNB complexes can be attributed to stronger coupling across this smaller bridging ligand.[22] The smallest J values are thus found for the TCNQ systems, correlating with the largest sum of metal–metal distances.[22] Similar correlations can be drawn using the sum of the numbers of intervening bonds which is largest for TCNQ. Surprisingly, the TCNB ligand fits quite well into such correlations[22] although the free ligand has a distinctly less stabilized π^* acceptor level as compared to TCNQ (Table 2). We therefore do not think it necessary to consider TCNX-based spin in the description of the magnetic behaviour.[21,22]

The positive sign of J is tentatively attributed to the *meta* coupling pattern (TCNB compound) or to a possible deviation from planarity in the TCNQ complex; the barrier towards rotation around exocyclic C–C bonds is strongly diminished in reduced TCNQ.

Table 5 EPR data*

	298 K	110 K
$[(TCNQ)(Osf)_4]^{\cdot-}$	$g = 2.0124$	$g_{\perp} = 2.0160$
	$\Delta H_{pp} = 1.27$ mT	$g_{\parallel} = 2.0065$
$[(TCNB)(Osf)_4]^{\cdot-}$	$g = 2.0005$	$g_{\perp,\parallel} = 2.0004$
	$\Delta H_{pp} = 0.86$ mT	$\Delta H_{pp} = 1.31$ mT

* Anions generated electrochemically in 1,2-dichloroethane/0.1 M NBu_4PF_6. ΔH_{pp} peak-to-peak linewidth.

Table 6 Absorption maxima[a] of complexes $[TCNX][Osf]_4$ in different oxidation states

Complex	λ_{max}/nm [log $\varepsilon(\varepsilon/M^{-1} cm^{-1})$]
$[(TCNQ)(Osf)_4]^{2+}$	1245 (4.70, $\Delta\nu_{\frac{1}{2}}^{b} = 3800$ cm^{-1})
$[(TCNQ)(Osf)_4]$	1170 (4.46, $\Delta\nu_{\frac{1}{2}}^{b} = 3200$ cm^{-1}), 697 (3.86)
$[(TCNQ)(Osf)_4]^{1-}$	1430 (4.50, $\Delta\nu_{\frac{1}{2}}^{b} = 1700$ cm^{-1}), 1215 (sh), 875 (3.90), 426 (4.31)
$[(TCNB)(Osf)_4]$	673 (4.40, $\Delta\nu_{\frac{1}{2}}^{b} = 4600$ cm^{-1}), 471 (4.23)
$[(TCNB)(Osf)_4]^{1-}$	554 (sh), 461 (4.40)
$[(TCNE)(Osf)_4]$	800[c]

[a] From spectroelectrochemistry in 1,2-dichloroethane/0.1 M NBu_4PF_6. [b] $\Delta\nu_{\frac{1}{2}}$ bandwidth at half height. [c] In 1,2-dichloroethane, from ref. 8.

Summarizing, the analysis of the magnetic data suggests that intramolecular electron transfer can produce a situation which may be described in terms of two strongly coupled mixed-valent sites, *i.e.* dinitrilato-bridged Os^{III}–Os^{II} entities (each with $S_{total} = \frac{1}{2}$) which can couple *via* an essentially diamagnetic bridging ligand.

Whereas the neutral complexes with their even-electron count exhibit 'normal' NMR behaviour but no EPR signals down to 3.5 K despite the apparent paramagnetism, the monoreduced species could be characterized by EPR in fluid and frozen solution (Table 5). The small g anisotropy in the frozen state and the little deviation of g factors from the free electron value of 2.0023 suggests[24] that these species have the unpaired electron in a predominantly ligand-based molecular orbital (MO), hyperfine contributions from TCNX nuclei (^1H or ^{14}N)[6b] or from the metal fragment (^{189}Os or ^{31}P)[24,25] are not observed and must lie within the linewidth (Table 5). In contrast, complexes exhibiting sizeable Os^{III} character are distinguished by rapid relaxation and thus very broad EPR signals as well as by considerable g anisotropy.[26] Summarizing, the anionic states must be formulated with TCNX$^{\cdot-}$ ligands and even-electron osmium(II) centres (5d^6 configuration). The slightly different g_{iso} values reflect the stabilized π^* MO of TCNQ in relation to TCNB. According to a well-established approximation[1,27] the higher g of the TCNQ complex implies the presence of close-lying occupied MOs whereas the low g value of the TCNB analogue reflects the closeness of empty orbitals.

Additional information on the electronic structures of the compounds can be obtained from UV/VIS/NIR spectroelectrochemistry. Fig. 3 shows the result of one such experiment. Table 6 summarizes the data. A first conspicuous result is that all available states of the TCNQ complex exhibit very intense bands in the near infrared region, $\lambda_{max} > 1000$ nm. The neutral and monoanionic forms of the TCNB complexes, on the other hand, show their long-wavelength absorptions only at much higher energies (Table 6). For the neutral species this result is simply a consequence of the much closer lying highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively) in the case of the TCNQ system; the corresponding differences between redox potentials $E_{ox} - E_{red}$ are 0.29 V for the TCNQ and 1.28 V for the TCNB analogue (0.99 V difference, Table 3). The pertinent absorption maxima at 1170 nm = 1.06 eV and at 673 nm = 1.84 eV, respectively, exhibit an approximately similar difference of 0.78 eV, suggesting com-
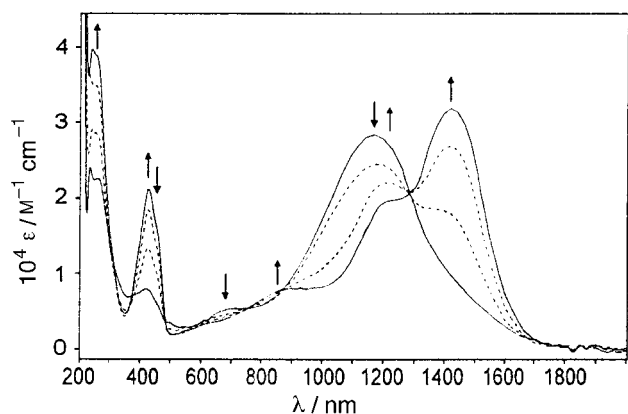
Fig. 3 Spectroelectrochemical response for the reduction of [(TCNQ)-{Os(PR$_3$)$_2$(CO)(H)Cl}$_4$] to the monoanion in 1,2-dichloroethane/0.1 M NBu$_4$PF$_6$

parably large Franck–Condon contributions from intra- and inter-molecular reorganization.[28] On one-electron reduction of the TCNQ compound there is a new spectrum with a high-intensity ($\varepsilon = 32\,000$ M^{-1} cm^{-1}) and vibrationally structured ($\Delta\nu = 1230$ cm^{-1}) transition at very low energy (1430 nm = 0.87 eV) which can be identified as the bathochromically shifted long-wavelength band of TCNQ$^{\cdot-}$ (TCNQ$^{\cdot-}$: $\lambda_{max} = 842$ nm and $\varepsilon = 43\,300$ M^{-1} cm^{-1}; first vibrational spacing 1260 cm^{-1}).[29] Also, a band at 426 nm intensifies which may be associated with the 420 nm feature of free TCNQ$^{\cdot-}$ ($\varepsilon = 24\,300$ M^{-1} cm^{-1}).[29] Obviously, the electronic absorption features confirm the [(TCNQ^{-1})(Os^{II})$_4$] oxidation state formulation that had been deduced from EPR. We similarly attribute the spectrum of the reduced TCNB analogue to a [(TCNB^{-1})(Os^{II})$_4$] state and assume a TCNX ligand-based π^* orbital as the LUMO of the neutral complexes.

As to access of the HOMO we have to take into account the two-electron nature of the electrochemical oxidation which, first of all, suggests a small interaction between the two sites involved.[6] This observation is in agreement with metal-centred processes, as was also suggested by the analysis of the weak spin–spin coupling. Unfortunately, the oxidation of the TCNB complex was not sufficiently reversible on the spectroelectrochemical time-scale of a few minutes. On two-electron oxidation of [(TCNQ){Os(PR$_3$)$_2$(CO)(H)Cl}$_4$] the NIR band intensifies ($\varepsilon = 50\,000$ M^{-1} cm^{-1}) and shifts to lower energies (Table 6). No other significant bands are observed above 350 nm. Since we assume a non-reduced state for the bridging ligand in such a highly charged ion we have to invoke a delocalized mixed-valent formulation [(TCNQ^0)(Os$^{2.5}$)$_4$] to account for the observed high intensity NIR transition. Such very intense features have been reported previously for efficiently coupled dinuclear Os^{III}–Os^{II} systems, bridged by 1,2-diacylhydrazide-(2−).[26a] This interpretation would also explain the two-electron nature of the oxidation (weak coupling across the benzo rings), the NIR absorption of, in effect, malonodinitrilato-bridged[5,6,30] mixed-valent [Os$^{2.5}$]$_2$ systems, and the metal to ligand charge-transfer (MLCT) character of the long-wavelength transitions in the neutral complexes. The peculiar paramagnetism of even-electron species with formally 18 valence electron 5d metal centres merits further investigation, especially since both complexes, the one with the very strong (TCNQ) and the other with the less pronounced π acceptor ligand (TCNB) display rather similar behaviour.

Experimental

Materials

Tetracyanoquinodimethane (TCNQ) and 1,2,4,5-tetracyano-benzene (TCNB) were used as commercially available. The

compound Os(PPr$^i_3$)$_2$(CO)(H)Cl was prepared according to the literature procedure.[31] All syntheses and spectroscopic manipulations were carried out under an argon atmosphere using dried and redistilled solvents.

Synthesis

[(μ$_4$,η^4-TCNQ){Os(PPr$^i_3$)$_2$(CO)(H)Cl}$_4$]. A solution of TCNQ (24 mg, 0.12 mmol) in toluene (25 cm^3) was added slowly to Os(PPr$^i_3$)$_2$(CO)(H)Cl (325 mg, 0.52 mmol), also dissolved in toluene (15 cm^3). After stirring for about 12 h 20 cm^3 of the solvent were evaporated. Addition of *n*-pentane (10 cm^3), cooling to −28 °C, washing with toluene and *n*-pentane and vacuum drying yielded 185 mg (62%) of the green product (Found: C, 42.94; H, 7.14; N, 2.16. C$_{88}$H$_{176}$Cl$_4$N$_4$O$_4$Os$_4$P$_8$ requires C, 42.20; H, 7.08; N, 2.24%).

[(μ$_4$,η^4-TCNB){Os(PPr$^i_3$)$_2$(CO)(H)Cl}$_4$]. A solution of TCNB (8 mg, 0.04 mmol) in toluene (10 cm^3) was added slowly to Os(PPr$^i_3$)$_2$(CO)(H)Cl (111 mg, 0.19 mmol), also dissolved in toluene (5 cm^3). After stirring for about 12 h 5 cm^3 of the solvent were evaporated. Addition of *n*-pentane (5 cm^3), cooling to −28 °C, washing with toluene and *n*-pentane and vacuum drying yielded 57 mg (53%) of the dark purple product (Found: C, 41.89; H, 7.11; N, 1.98. C$_{86}$H$_{174}$Cl$_4$N$_4$O$_4$Os$_4$P$_8$ requires C, 41.64; H, 7.08; N, 2.26%).

Instrumentation

The EPR spectra were recorded in the X-band on a Bruker System ESP 300, equipped with a Bruker ER035M gaussmeter and a HP 5350B microwave counter; NMR spectra were recorded on a Bruker AC 250 spectrometer, infrared spectra on a Fourier-transform IR spectrometer Paragon 1000 PC. Absorption spectra in the UV/VIS/NIR regions were measured with a Bruins Instruments Omega 10 spectrometer. Cyclic voltammetry was carried out in 0.1 M NBu$_4$PF$_6$ in 1,2-dichloroethane (DCE) using a PAR M273 potentiostat and function generator and a three-electrode configuration (glassy carbon working electrode, platinum wire counter electrode, Ag–AgCl reference electrode). The ferrocene–ferrocenium couple served as an internal standard for the calibration of the redox potential.

Spectroelectrochemical measurements were carried out using an optically transparent thin-layer electrolytic (OTTLE) cell,[32] composed of CaF$_2$ plates, an Ag reference, Pt working and counter electrodes. In all experiments described as reversible the spectral features of the initial state could be regenerated.

Magnetic susceptibility measurements were performed using a Quantum Design SQUID magnetometer, equipped with a Quantum Design controller MPS 1822 and a digital bridge 1802, operating at 0.5 T magnetic field strength and variable temperature (5–300 K). Magnetization studies were carried out between 0.1 and 1 T at 6 K to determine the most suitable field (*i.e.* non-saturation conditions). Typical samples involved 15–25 mg of the compound; all data are corrected for effects from the sample holder and diamagnetic contributions. Simulations were performed on an IBM personal computer using the programs Microsoft Excel 4.0 and Microsoft Excel Solver. Non-linear minimization of R yielded the values of g, J, D and *TIP* given in equation (3). Different sets of starting values were used

$$R = \frac{\Sigma_i[(\chi_m T)_i^{\text{exp}} - (\chi_m T)_i^{\text{calc}}]^2}{\Sigma_i[(\chi_m T)_i^{\text{exp}}]^2} \qquad (3)$$

to avoid local minima. Being largely independent of the number of data points and the absolute values, R allows a comparison of the quality of fit between compounds with widely differing magnetic susceptibilities.[22,33]

Acknowledgements

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