Homobinuclear complexes of osmium(IV) with nitrogen-containing π-conjugated bridging units

Andrei Maiboroda and Heinrich Lang*

Lehrstuhl für Anorganische Chemie, Institut für Chemie, Fakultät für Naturwissenschaften,
Technische Universität Chemnitz, Straße der Nationen 62, D-09111 Chemnitz, Germany.
E-mail: heinrich.lang@chemie.tu-chemnitz.de

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The synthesis as well as chemical and physical properties of anionic homobinuclear osmium(IV) complexes of the general type $[AsPh_4]_2[OsCl_5(LL)OsCl_5]$ [LL = pyrazine (**6**), 4,4′-bipyridine (**7**), 1,4-dicyanobenzene (**8**) and 4-cyanopyridine (**9**)] is described. While **6** and **9** exhibit strong (**6**) or weak (**9**) intramolecular electronic communication between the Os(IV) centres, in **7** and **8** the metals can be considered non-interacting.

Since the early work of Creutz and Taube, there has been continuing interest in the synthesis of iron,[1] ruthenium[2] and/or osmium[3]-containing homo- and heterobinuclear complexes in which a π-conjugated organic ligand spans the transition metal centres. In this respect, for example in the mixed-valence Creutz–Taube ion $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ (pyz = pyrazine), an intramolecular electron transfer is observed between the two Ru^{II} and Ru^{III} ions *via* the bridging π-conjugated organic ligand pyz.[2a–c] In contrast, to the best of our knowledge, much less is known about binuclear complexes that contain the $[OsCl_5]^-$ transition metal building block as the sub-unit.[4a]

In view of our earlier studies in this area, where we reported the successful isolation of the novel mononuclear Os(IV) complex $[AsPh_4][OsCl_5(H_2O)]$,[4a] which is a very promising starting material for the synthesis of homo- and/or heterobinuclear transition metal complexes based on $[OsCl_5]^-$ entities,[4b] we set out to synthesise new homobinuclear Os(IV) complexes of the general type $[Cl_5Os(LL)OsCl_5]^{2-}$ (LL = nitrogen-containing bidentate π-conjugated organic ligand). Their electrochemical behaviour is also reported.

Experimental

General

UV-Vis spectra were recorded on a Perkin Elmer Lambda 40 spectrophotometer in dichloromethane solutions and with concentrations in the 1.2–1.5 × 10^{-5} mol dm^{-3} range. The IR spectra were recorded on a Bruker IFS 48 spectrometer as CsI tablets. Melting (decomposition) points were determined with a Gallenkamp MFB 595 010 M melting point apparatus. Electrochemical measurements were performed by cyclic voltammetry in dichloromethane solutions (degassed prior to study with N_2) containing $[N^nBu_4]PF_6$ (0.1 mol dm^{-3}) at 25 °C, using a standard three-electrode Pt | Pt | calomel cell on a Radiometer DEA 101 potentiostat (range of the working electrode: −1.4 to +1.4 V). The scan rate used for all reported results was 60 mV s^{-1}. All potentials are quoted *vs.* the ferrocene/ferrocenium couple. NMR spectra were recorded on a Bruker Avance 250 spectrometer operating in the Fourier transform mode; ^1H NMR spectra were recorded at 250.131 MHz (internal standard $CDCl_3$, δ 7.29); $^{13}C\{^1H\}$ NMR spectra were recorded at 62.902 MHz (internal standard $CDCl_3$, δ 77.5). Dichloromethane was distilled from CaH_2 before use. Microanalyses were performed by the Laboratory of Organic Microanalysis of the Nesmeyanov Institute of Organometallic Compounds (Moscow).

Commercially available pyrazine (pyz) (**2**), 4,4′-bipyridine (bipy) (**3**), 1,4-dicyanobenzene (dcb) (**4**) and 4-cyanopyridine (cpy) (**5**) were used without purification.

Syntheses

$[AsPh_4]_2[Cl_5Os(pyz)OsCl_5]$ (6). $[AsPh_4][OsCl_5(H_2O)]$ (**1**;[4] 0.3 g, 0.39 mmol) was dissolved in 40 mL of dichloromethane at 25 °C. Pyrazine (pyz, **2**; 15 mg, 0.19 mmol) was added in one portion and the reaction mixture was heated at reflux for 1 h. Afterwards, the reaction mixture was concentrated to 3 mL and passed through a pad of silica gel (column dimension: 1.5 × 15 cm, 25 °C, dichloromethane). The first dark brown fraction was isolated. After removing the solvent under oil pump vacuum, a dark brown solid remained. Yield: 0.26 mg (0.17 mmol, 85% based on **1**). Mp: 265 °C (decomp.). IR: ν(Os–Cl) 307, $\nu(C{=}C)_{pyz}$ 1606 cm^{-1}. ^1H NMR ($CDCl_3$):† δ 7.7–8.0 (m, 40H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$):† δ 121.2 ($^iC/C_6H_5$), 133.7 (CH/C_6H_5), 135.4 (CH/C_6H_5), 136.3 (CH/C_6H_5). UV-Vis (CH_2Cl_2): λ_{max} = 378 nm (ε = 1.53 × 10^4 L cm^{-1} mol^{-1}). Anal. calc. for $C_{52}H_{44}N_2As_2Cl_{10}Os_2$ (1581.72): C, 39.48; H, 2.81%. Found: C, 40.13; H, 3.18%.

$[AsPh_4]_2[Cl_5Os(bipy)OsCl_5]$ (7). In analogy to the preparation of **6**, 0.25 g (0.32 mmol) of **1** were reacted with 25 mg (0.16 mmol) of bipy (bipy = 4,4′-bipyridine, **3**) in 40 mL of dichloromethane for 1 h. After appropriate work-up, 0.23 g (0.14 mmol, 87% based on **1**) of **7** was isolated as a brown solid. Mp: 280 °C (decomp.). IR: ν(Os–Cl) 307, $\nu(C{=}C)_{bipy}$ 1590 cm^{-1}. ^1H NMR ($CDCl_3$):† δ 7.7–8.0 (m, 40H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$):† δ 120.9 ($^iC/C_6H_5$), 132.8 (CH/C_6H_5), 134.3 (CH/C_6H_5), 135.7 (CH/C_6H_5). UV-Vis (CH_2Cl_2): λ_{max} = 369 nm (ε = 1.55 × 10^4 L cm^{-1} mol^{-1}). Anal. calc. for $C_{58}H_{48}N_2As_2Cl_{10}Os_2$ (1657.82): C, 42.02; H, 2.92%. Found: C, 42.16; H, 3.32%.

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† The ^1H- and $^{13}C\{^1H\}$-NMR resonance signals of the bridging ligands pyz, bipy, dcb and cpy could not be detected, owing to the paramagnetism of the osmium(IV) complexes **6**–**9**.

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$[AsPh_4]_2[Cl_5Os(dcb)OsCl_5]$ (8). According to the procedure described for the preparation of **6**, 0.25 g (0.32 mmol) of **1** were reacted with 20 mg (0.16 mmol) of dcb (dcb = 1,4-dicyanobenzene, **4**) in 40 mL of dichloromethane for 1 h in the presence of P_2O_5 (50 mg, 0.45 mmol). After appropriate work-up (*vide supra*), 0.22 g (0.13 mmol, 82% based on **1**) of complex **8** was isolated as a brown solid. Mp: 274 °C (decomp.). IR: ν(Os–Cl) 309, $\nu(C{=}C)_{Ph,\,dcb}$ 1437 (br), $\nu(C{\equiv}N)_{dcb}$ 2267 cm^{-1}. ^1H NMR($CDCl_3$):† δ 7.6–8.0 (m, 40H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$):† δ 121.0 ($^iC/C_6H_5$), 133.3 (CH/C_6H_5), 135.0 (CH/C_6H_5), 135.5 (CH/C_6H_5). UV-Vis (CH_2Cl_2): $\lambda_{max} = 378$ nm ($\varepsilon = 1.46 \times 10^4$ L cm^{-1} mol^{-1}). Anal. calc. for $C_{56}H_{44}N_2As_2Cl_{10}Os_2$ (1629.76): C, 41.27; H, 2.73%. Found: C, 41.52; H, 3.00%.

$[AsPh_4]_2[Cl_5Os(cpy)OsCl_5]$ (9). In analogy to the preparation of **6**, 0.25 g (0.32 mmol) of **1** were reacted with 17 mg (0.16 mmol) of cpy (cpy = 4-cyanopyridine, **5**) in the presence of 50 mg (0.45 mmol) of P_2O_5 in 40 mL of dichloromethane for 1 h. After appropriate work-up, 0.23 g (0.14 mmol, 87% based on **1**) of **9** was isolated as a brown solid. Mp: 270 °C (decomp.). IR: ν(Os–Cl) 308, $\nu(C{=}C)_{cpy}$ 1540, $\nu(C{\equiv}N)_{cpy}$ 2267 cm^{-1}. ^1H NMR ($CDCl_3$):† δ 7.6–8.0 (m, 40H, C_6H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$):† δ 121.0 ($^iC/C_6H_5$), 133.6 (CH/C_6H_5), 135.1 (CH/C_6H_5), 136.1 (CH/C_6H_5). UV-Vis (CH_2Cl_2): $\lambda_{max} = 375$ nm ($\varepsilon = 1.48 \times 10^4$ L cm^{-1} mol^{-1}). Anal. calc. for $C_{54}H_{44}N_2As_2Cl_{10}Os_2$ (1605.74): C, 40.39; H, 2.77%. Found: C, 40.97; H, 2.75%.

Results

Synthesis

The homobinuclear Os(IV) complexes $[AsPh_4]_2$-$[OsCl_5(LL)OsCl_5]$ (**6**–**9**) in which two $[OsCl_5]^-$ entities are bridged by the π-conjugated nitrogen-containing organic ligands LL, can be prepared by treatment of 2 equiv. of $[AsPh_4][OsCl_5(H_2O)]$ (**1**)[4] with 1 equiv. of LL [LL = pyrazine (**2**); 4,4′-bipyridine (**3**); 1,4-dicyanobenzene (**4**); 4-cyanopyridine (**5**)] in boiling dichloromethane (Scheme 1). However, in the synthesis of complexes **8** and **9** the addition of P_2O_5 is necessary to adsorb the leaving H_2O ligand. Otherwise, either no reaction between **1** and **4** (synthesis of **8**) or only substitution of the H_2O ligand by the pyridino group of **5** (reaction of **1** with **5**) takes place.

After appropriate work-up, the homobinuclear complexes **6**–**9** were isolated as air-stable brown solids, which are nicely soluble in dichloromethane and carbon tetrachloride. All complexes were fully characterised by elemental analysis, spectroscopic studies (IR, UV-Vis, ^1H, $^{13}C\{^1H\}$ NMR) as well as cyclic voltammetry.

Spectroscopic studies

Complexes **6**–**9** contain as bridging units between the two osmium(IV) centres nitrogen-containing heterocyclic groups; $AsPh_4{}^+$ is present as the counter-ion. For this reason their UV-Vis spectra were studied in dichloromethane solutions. As in the UV-Vis spectrum of the starting material $[AsPh_4][OsCl_5(H_2O)]$ (**1**) [351 nm ($\varepsilon = 7.1 \times 10^3$ L cm^{-1} mol^{-1})],[4] the homobimetallic complexes **6**–**9** also only show one significant absorption band between 370 and 380 nm. By going from mononuclear **1** to the homobinuclear complexes **6**–**9** a very characteristic shift of the corresponding absorption maximum to a higher wavelength is found, due to the exchange of the datively bonded H_2O ligand in **1** by nitrogen-containing groups in **6**–**9**. Similar observations were made for mononuclear osmium complexes that also possess heterocyclic rings, for example complexes $[OsCl_5(py)]^-$ and $[OsCl_4(py)_2]$.[5]

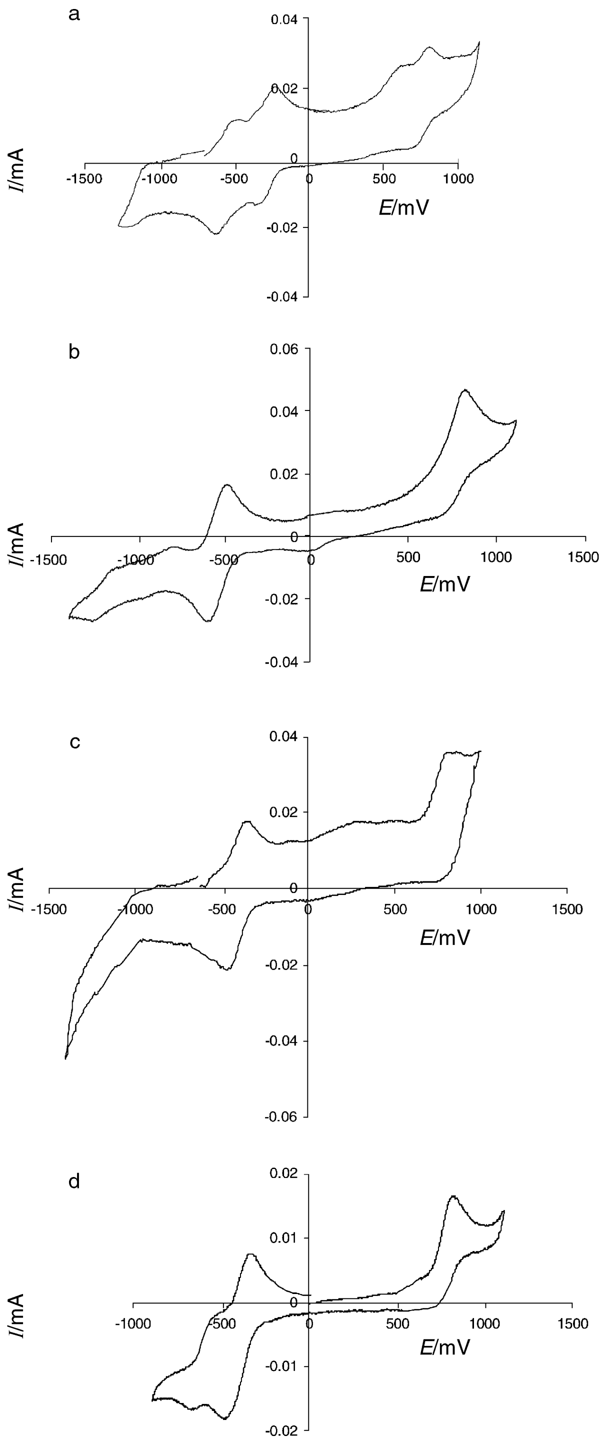


Fig. 1 Cyclic voltammograms of complexes **6** (a), **7** (b), **8** (c) and **9** (d).

IR spectroscopic studies of complexes **6**–**9** clearly reveal that the presence of nitrogen-containing ligands does not significantly influence the Os–Cl stretching vibrations. Typical Os–Cl absorptions are observed in a very narrow window between 305 to 310 cm^{-1}, which is characteristic for this type of species.[6] The $\nu_{C=C}$ stretching vibrations of the N-ligated sites in the homodinuclear complexes **6**, **7** and **9** are found at 1606 (**6**), 1590 (**7**) and 1540 (**9**) cm^{-1}, respectively, while the corresponding *non*-coordinated organic starting materials show this vibration at 1610 (**2**), 1595 (**3**) or 1543 (**5**) cm^{-1}.[7a] This only slight shift to lower wavenumbers upon coordination of **2**, **3** and **5** to a metal centre (as in **6**, **7** and **9**) is most common for transition metal complexes containing pyridine and related ligands.[7b]

In contrast, the C≡N stretching vibration, which is observed in the *non*-coordinated species **4** and **5** at 2238 and 2231 cm^{-1}, respectively, is shifted to higher values in complexes **8** and **9** (2267 cm^{-1}). This can nicely be used as a criterion for the formation of complexes **8** and **9** in which a 1,4-cyanobenzene (**8**) or 4-cyanopyridine (**9**) group spans the two osmium(IV) centres. This shift is typical for datively bonded cyano groups and is also found in nitrile-stabilised metal dichloride complexes of the general type $MCl_2(N{\equiv}CR)_2$ [M = Pd(II), Pt(II); R = CH_3, Ph].[8]

The ^1H NMR spectra of complexes **6**–**9** exhibit a multiplet in the region of 7.6–8.0 ppm, due to the aromatic protons of the $AsPh_4^+$ counter-ion. In their $^{13}C\{^1H\}$ NMR spectra typical resonance signals for the carbon atoms of the $AsPh_4^+$ counter-ion at *ca.* 121 ppm for the *ipso* carbon atom and three additional resonance signals for the hydrogen-bearing carbon atoms between 133 and 136 ppm are observed. However, due to the paramagnetism of the osmium(IV) complexes **6**–**9**, in the ^1H- as well as in the $^{13}C\{^1H\}$-NMR spectra the resonance signals of the corresponding nitrogen-containing bridging units, pyz, bipy, dcb and cpy, could not be detected (see Experimental).

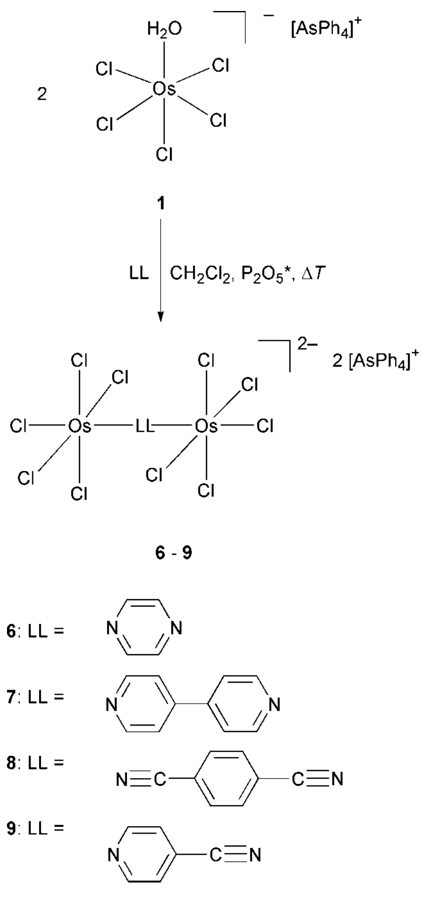
Electrochemical studies

Cyclic voltammetry measurements were carried out on complexes **6**–**9** to get some insight into the metal–metal interaction in these species. The voltammograms are depicted in Fig. 1. The values of the $E_{1/2}$ potentials are summarised in Table 1.

The cyclic voltammogram of homobimetallic **6** [Fig. 1(a)] displays two distinct reversible one-electron reduction processes at $E^1_{1/2} = -0.28$ V and $E^2_{1/2} = -0.59$ V. The intermediate formation of *in situ* generated $[Cl_5Os(pyz)OsCl_5]^{3-}$ can be considered as the product of the first reduction process. This complex anion is formally a mixed-valence Os(IV)–Os(III) species in which the two osmium centres are bridged by the π-conjugated organic pyrazine unit. As expected, further reduction of this mixed-valence species takes place at a more negative potential and results in the formation of the Os(III)–Os(III) complex anion $[Cl_5Os(pyz)OsCl_5]^{4-}$. The cyclic voltammetry data allows us to calculate the comproportionation constant K_c for **6**, that is the equilibrium constant for the reaction shown in eqn. (1).

$$[Cl_5Os(LL)OsCl_5]^{2-} + [Cl_5Os(LL)OsCl_5]^{4-} \rightleftharpoons 2[Cl_5Os(LL)OsCl_5]^{3-} \quad (1)$$

This constant, which describes the stability against disproportionation and gives evidence for the *in situ* formation of a mixed-valence complex, was calculated according to the method developed by Richardson and Taube[9] [eqn. (2)].



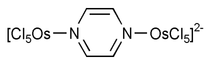
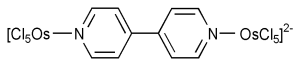
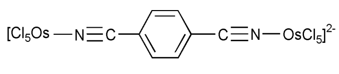
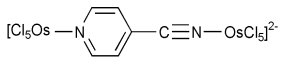
Scheme 1 Synthesis of complexes **6**–**9**.* P_2O_5 was additionally used for the synthesis of **8** and **9**.

$$K_C = \frac{[Os^{III}Os^{IV}]}{[Os^{IV}Os^{IV}][Os^{III}Os^{III}]} = \exp\frac{\Delta E_{1/2}F}{RT} \quad (2)$$

For $T = 298$ K, this equation simplifies to $K_c = \exp(\Delta E/25.69)$, where ΔE is given in mV. Thus for complex **6**, the comproportionation constant can be calculated using the latter equation to give $K_c = 1.74 \times 10^5$. In addition, complex **6** exhibits two oxidation processes at $E^{ox} = +0.59$ and $+0.77$ V (Table 1), due to Os(IV)/Os(V) electron-transfer steps of which the first one is irreversible and the second one reversible, indicating that the electron-transfer reaction is rapidly followed by a chemical reaction; therefore, the second observed oxidation peak is not due to the original complex, rather it may belong to a product species.

The electrochemical studies on complexes **7** and **8** nicely demonstrate that the two Os(IV) metal centres in these molecules are isolated from each other. The only reversible

Table 1 Redox potentials of the homobinuclear osmium complexes **6**–**9**

		$E^{red}_{1/2}$/V (ΔE/mV)[a]	E^{ox}/V (ΔE/mV)[a]
	(**6**)	−0.28 (100)	+0.59[b] (irr.)
		−0.59 (90)	+0.77[b] (110)
	(**7**)	−0.55 (150)	+0.82 (irr.)
	(**8**)	−0.40 (170)	+0.85 (irr.)
	(**9**)	−0.41 (140)	+0.83 (irr.)
		−0.62 (100)	

[a] ΔE = peak separation. [b] $E^{ox}_{1/2}$.

reduction process was observed at $E_{1/2} = -0.55$ V for **7** and at $E_{1/2} = -0.40$ V for **8**. The half-wave potential for the Os(IV)/Os(III) couple in **7** and **8** is in agreement with the values determined for the mononuclear complexes $[OsCl_5(py)]^-$ and $[OsCl_5(N{\equiv}CPh)]^-$, for example.[10]

Nevertheless, complex **9** exhibits—as does complex **6**—two reversible reduction waves at $E^1_{1/2} = -0.42$ V and $E^2_{1/2} = -0.62$ V. This electrochemical behaviour can be attributed to two different effects: on the one hand, the 4-cyanopyridine bridged bimetallic complex **9** contains two osmium centres in which the transition metal atoms possess different environments, provided by the pyridino and cyano units. On the other hand, 4-cyanopyridine allows electronic communication between the two metal centres.[2e] Exact attribution of the experimental data to one of these two effects is difficult, as was shown earlier for homobinuclear ruthenium amino complexes featuring similar π-conjugated bridging moieties.[2e] The comproportionation constant K_c for **9** was calculated to be 2.40×10^3.

The cyclic voltammograms of **7**–**9** in the cathodic region look very similar to each other. The irreversible oxidation processes ($E^{ox} = +0.82$ to $+0.85$ V) can be attributed to the Os(IV)/Os(V) oxidation.

Discussion

Treatment of $[AsPh_4][OsCl_5(H_2O)]$ (**1**) with nitrogen-containing heterocyclic molecules, such as pyrazine (**2**) or 4,4′-bipyridine (**3**), leads to the selective substitution of the H_2O ligand in **1** by the corresponding nitrogen-containing group and the homobinuclear complexes **6** and **7** are formed in quantitative yield. At the same time, the cyano entities, which are present in dicyanobenzene (**4**) and 4-cyanopyridine (**5**), possess only weak donating properties, which make them able to substitute for the H_2O ligand in **1** only in the presence of the water-absorbing reagent P_2O_5. Otherwise, no reaction takes place (as in the reaction of **1** with **4**) or else the H_2O ligand is replaced by the pyridino group (as in the reaction of **1** with **5**). The newly synthesised complexes **8** and **9** are stable for an extended time as solids as well as solutions (dry dichloromethane) in air.

The electrochemical behaviour of the homobimetallic Os(IV) complexes **6**–**9** is in accordance with the experimentally observed data for other transition-metal complexes that feature similar π-conjugated organic bridging entities.[1,2] In general, these bridging groups give rise to metal–metal interactions in the binuclear complexes. Consequently, intramolecular electronic communication occurs when relatively small symmetric organic bridging ligands, such as dinitrogen,[1e] dicyanogen,[11] pyrazine[1b] or imidazole,[12] span the transition metal centres. In contrast, complexes containing larger aromatic ligands, such as 2,2′-, 4,2′- or 4,4′-functionalized bipyridines[13] or saturated molecules, such as dithiane[14] or dicyanocyclopropane,[2e] exhibit only weak metal–metal interactions. Cyclic voltammetry studies carried out on complex **6** clearly show that the two Os(IV) centres linked by the pyrazine bridge are dependent on each other. Addition of one electron to $[Cl_5Os(pyz)OsCl_5]^{2-}$ (**6**) results in the formation of a mixed-valence Os(III)–Os(IV) species; the charge delocalisation in this intermediate causes the second reduction step $E^2_{1/2}$ to be at a more negative potential than the first one. The comproportionation constant K_c allows us to neatly classify species **6** as a homobinuclear species with a strong metal–metal interaction. The value of K_c found for **6** (1.74×10^5) is close to the value obtained for $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{6+}$ (4.0×10^6),[2a,b] but at the same time significantly smaller than the K_c found for the isostructural osmium complex $[(NH_3)_5Os(pyz)Os(NH_3)_5]^{6+}$ (7.0×10^{12}).[15] The less pronounced interaction between the osmium metal centres in **6**, when compared with $[(NH_3)_5Os(pyz)Os(NH_3)_5]^{6+}$, can be attributed to the different ligand environments: a strong π-donor group such as NH_3 *vs.* a weaker π-donating Cl^- ligand.

Complexes **7** and **8** show physical properties similar to those of homobinuclear amine complexes of Ru(III) with identical bridging ligands.[13] For example, the homobimetallic complexes $[(NH_3)_5Ru(bipy)Ru(NH_3)_5]^{6+}$ and $[(NH_3)_5Ru(dcb)Ru(NH_3)_5]^{6+}$ exhibit comproportionation constants K_c of 20 and 23, respectively, which clearly show that in these species the ruthenium centres are only weakly interacting with each other.[13] These values are close to the smallest value of K_c (*i.e.* 4) that can be experimentally determined.[9] Complexes **7** and **8** show electrochemical properties that correspond to those found in mononuclear $[OsCl_5(py)]^-$ and $[OsCl_5(N{\equiv}CPh)]^-$.[10] This points to very weak site–site interactions, so they could not be observed electrochemically. $E^1_{1/2}$ and $E^2_{1/2}$ can be directly measured by cyclic voltammetry only when ΔE is sufficiently large (>120 mV).[9] However, for the homobinuclear systems **7** and **8** the ΔE values are probably smaller than this, which makes the observation of two different one-electron steps in the cyclic voltammogram impossible. This is attributed to the significantly long distances between the corresponding osmium centres in **7** and **8**, resulting in a weak metal–metal interaction only. A further explanation is given by the fact that 4,4′-bipyridine can adopt a tilted configuration,[16] which significantly reduces π-conjugation between the two aromatic rings of the bipy ligand.

The comproportionation constant K_c calculated from the electrochemical data for complex **9** has a value of 2.4×10^5. However, this does not allow us to affirm that a strong site–site interaction takes place in this complex. For homobinuclear ruthenium complexes containing 3- and 4-cyanopyridine (3-cpy, 4-cpy) ligands it was found that the observed potential difference is mainly determined by the difference in the microscopic potentials of the metal centres.[2e] The Os(IV)/Os(III) redox potentials of the mononuclear complexes $[OsCl_5(py)]^-$ ($E_{1/2} = -0.54$ V)[10] and $[OsCl_5(N{\equiv}CPh)]^-$ ($E_{1/2} = -0.40$ V)[10] can be considered as the microscopic potentials for the $[RC_5H_4N \rightarrow OsCl_5]^-$ and $[ArC{\equiv}N \rightarrow OsCl_5]^-$ fragments (R = singly bonded organic or inorganic group, Ar = aryl). Whereas the first Os(IV)/Os(III) redox process for **9** is observed at almost the same potential as for $[OsCl_5(N{\equiv}CPh)]^-$,[10] the potential of the second reduction step is slightly shifted to a more negative value in comparison with the $E_{1/2}$ observed for $[OsCl_5(py)]^-$.[10] This observation points to the fact that a site–site interaction takes place in the mixed-valence intermediate $[Cl_5Os(cpy)OsCl_5]^{3-}$.

In conclusion, in the newly synthesised complexes **6**–**9** only homobimetallic **6**, containing pyrazine as a π-conjugated bridging group, exhibits strong intramolecular electronic communication between the two osmium centres. In contrast, complex **9** shows only a weak interaction between the corresponding metal centres, while in complexes **7** and **8** the metals can be considered as *non*-interacting.

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