Configurationally Chiral Dirhenium Complexes with Triple and Quadruple Re–Re Bonds: Preparation and Circular Dichroism of $[Re_2Cl_4(S,S\text{-dppb})_2]$† and $[Re_2Cl_4(S,S\text{-dppb})_2]^{2+}$

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The first configurationally chiral dirhenium complexes have been prepared and spectroscopically characterised; the c.d. spectrum of the quadruply bonded $[Re_2Cl_4(S,S\text{-dppb})_2]^{2+}$ implies that the complex has the Λ absolute configuration with a twist of less than 45°.

$[Re_2Cl_4(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] (**1**) has the $\sigma^2\pi^4\delta^2\delta^{*2}$ electron configuration and so a Re–Re triple bond. The complex, which has bridging dppe ligands, has a staggered geometry[1] (Figure 1) with a twist of 51° between the two ReP_2Cl_2 units. Compounds containing a Re–Re triple bond are electron rich and may be oxidised[2—4] to the mono- or di-cations which have Re–Re bond orders of 3.5 and 4 respectively. The redox potentials of (**1**) in MeCN have been measured by cyclic voltammetry[3] [$E_{\frac{1}{2}}(1) = +0.23$ V, $E_{\frac{1}{2}}(2) = +1.06$ V *vs.* S.S.C.E.†] and (**1**) has been oxidised to the monocation by $[NO][PF_6]$ ($E_{\frac{1}{2}} = +0.85$ V *vs.* Ag/Ag^+, + 1.18 V *vs.* S.S.C.E.).[5,6] We report that both (**1**) and the novel chiral dirhenium complex $[Re_2Cl_4(S,S\text{-dppb})_2]$† (**2**) may be oxidised to the respective dications by $[NO][PF_6]$ in MeCN or CH_2Cl_2 solution. These are the first examples of twisted dirhenium complexes with a formal quadruple Re–Re bond and (**2**) and $(\mathbf{2})^{2+}$ are the first configurationally chiral dirhenium complexes to be reported.

$[Re_2Cl_4L_2]$
(**1**) L = dppe ($Ph_2PCH_2CH_2PPh_2$)
(**2**) L = *S,S*-dppb (*S,S*-$Ph_2PCHMeCHMePPh_2$)

Addition of $[NO][PF_6]$ to CH_2Cl_2 solutions or MeCN suspensions of (**1**) or (**2**) produces olive-green solutions of the dications $(\mathbf{1})^{2+}$ or $(\mathbf{2})^{2+}$ which are isolated as the $[PF_6]^-$ salts by removal of solvent *in vacuo*. The absorption spectra of (**2**) and $(\mathbf{2})^{2+}$ are shown in Figure 2; the absorption spectra of (**1**) and $(\mathbf{1})^{2+}$ are similar. Evidence that we have synthesised the dications is furnished by the presence of a band at 950 nm in the electronic spectrum of $(\mathbf{2})^{2+}$ which is assigned to the $\delta \rightarrow \delta^*$ transition [$(\mathbf{2})^{2+}$ having the $\delta^2\pi^4\delta^2$ configuration]. This transition is necessarily absent (Figure 2) for the neutral complexes which have the δ^* orbital doubly occupied and occurs at around 1500 nm in the monocations.‡ The red shift in the energy of the $\delta \rightarrow \delta^*$ transition of the staggered complex $(\mathbf{2})^{2+}$ compared to its position in eclipsed $[Re_2Cl_4(PMe_2Ph)_4]^{2+}$ (10.5 and 13.8×10^3 cm^{-1} respectively) is similar to that found in the analogous dimolybdenum complexes.[7,8] The c.d. of the $\delta \rightarrow \delta^*$ transition of $(\mathbf{2})^{2+}$ has the same sign and a comparable dissymmetry factor ($\Delta A/A$) to that of $[Mo_2Cl_4(S,S\text{-dppb})_2]$.[7] The latter complex has the Λ absolute configuration with a twist of 23° about the Mo–Mo bond.[7] The dirhenium complex is predicted to have a similar structure, the *S,S*-dppb ligands dictating the Λ absolute configuration and the c.d. indicating[7,9] a twist of less than 45°.

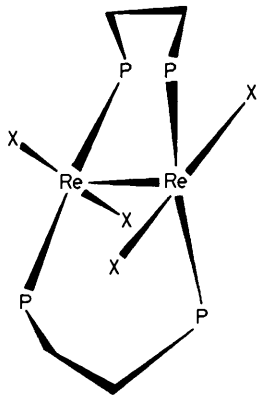

Figure 1. Schematic structure of (**1**).

The dications have different chemical behaviour in CH_2Cl_2 and MeCN solution. The CH_2Cl_2 solutions slowly turn pink to give an unidentified product which cannot be reoxidised. In MeCN, however, the green solutions of $(\mathbf{1})^{2+}$ and $(\mathbf{2})^{2+}$ slowly turn purple giving the monocations $(\mathbf{1})^+$ and $(\mathbf{2})^+$ (identified by their absorption spectra). The reaction is reversible and the solutions of $(\mathbf{1})^+$ and $(\mathbf{2})^+$ may be reoxidised by more $[NO][PF_6]$. The conversions (**1**), (**2**) $\rightleftharpoons$ $(\mathbf{1})^+$, $(\mathbf{2})^+$ $\rightleftharpoons$ $(\mathbf{1})^{2+}$, $(\mathbf{2})^{2+}$ can also be effected electrochemically using an optically

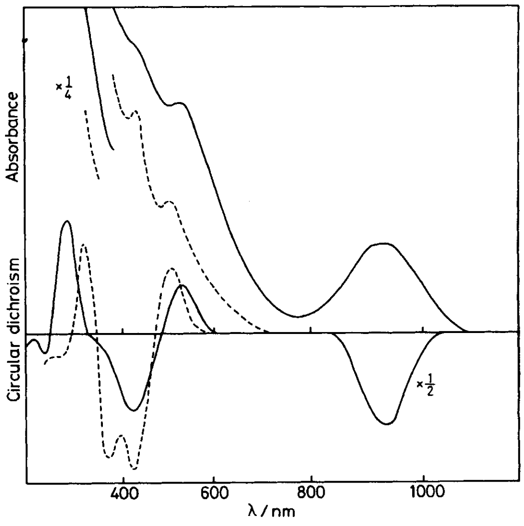

Figure 2. Absorption and c.d. spectra of (**2**) (dashed line) and $(\mathbf{2})^{2+}$ (full line) in CH_2Cl_2 solution.

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† dppb = 2,3-bis(diphenylphosphino)butane; S.S.C.E. = standard sodium chloride calomel electrode.

‡ The $\delta \rightarrow \delta^*$ transition is found at 1360 nm in $[Re_2Cl_4(PMe_2Ph)_2]^+$ (ref. 4). It has not been located in the spectra of the monocations of twisted dirhenium complexes, such as $(\mathbf{1})^+$, presumably because it is too weak.

transparent electrode and the absorption and c.d. spectra thus obtained are identical to those of the chemically produced species.

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8 The $\delta \rightarrow \delta^*$ transition occurs at 17.0×10^3 cm^{-1} in [Mo_2Cl_4-($PBu^n{}_3)_4$] (V. M. Minkowski, R. A. Goldbeck, D. S. Kliger, and H. B. Gray, *Inorg. Chem.*, 1979, **18**, 86) and at 13.7×10^3 cm^{-1} in [$Mo_2Cl_4(S,S\text{-dppb})_2$] (ref. 7).
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