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Spectroelectrochemical Characterization of $[Re_2(\mu\text{-}NCS)_2(NCS)_8]^{z-}$ ($z = 1-4$): Evidence for the Interconversion of an Edge-Shared Bioctahedral and a Direct Metal−Metal-Bonded Structure

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Several studies of halide-bridged edge-shared bioctahedral (ESBO) dirhenium complexes have revealed extensive redox chemistry associated with the predominantly metal-based molecular-orbital (MO) manifold.[1] A related pseudohalide complex is $(^nBu_4N)_3[Re_2(\mu\text{-}NCS)_2(NCS)_8]$ (the anion hereinafter designated $[Re_2(NCS)_{10}]^{3-}$), which was first isolated and characterized by Cotton *et al.* in 1967.[2] Originally misformulated as $(^nBu_4N)_3[Re_2(\mu\text{-}CO)_2(NCS)_{10}]$, the true identity of the complex was later established by X-ray crystallography which revealed it to consist of a distorted ESBO structure with solely N-bound bridging isothiocyanates.[3] The distortion is substantial, as evident from the shortened Re•••Re distance of only 2.613 Å and the Re−N−Re′ and N−Re−N′ bond angles of 77 and 102°, respectively.

We recently investigated the electrochemistry of $[Re_2(NCS)_{10}]^{3-}$, and discovered a variety of redox processes. Spectroelectrochemical studies suggest that the parent edge-shared bioctahedral structure $[Re_2(NCS)_{10}]^{z-}$ is preserved for z = 1, 2, or 4, although $[Re_2(NCS)_{10}]^-$ has only limited stability. Further reduction of $[Re_2(NCS)_{10}]^{4-}$ can be achieved, but significant structural rearrangement accompanies this process. Results presented here provide evidence for the reversible interconversion of an ESBO and a direct metal−metal (M−M) bonded structure.

The cyclic voltammogram (CV) of $(^nBu_4N)_3[Re_2(NCS)_{10}]$ in dichloromethane at room temperature is shown in Figure 1.[4] This complex undergoes two oxidations and two reductions, the first oxidation ($E_{1/2}$ = +0.46 V) and the first reduction ($E_{1/2}$ = 0.00 V) being reversible on the electrochemical time scale. The voltammetric responses of the reversible couples are consistent with diffusion-controlled one-electron processes, and linear sweep voltammetry (LSV) confirms that these processes involve the same number of electrons.[5]

The chemical reversibility of the $[Re_2(NCS)_{10}]^{2-/3-}$ and $[Re_2(NCS)_{10}]^{3-/4-}$ couples at room temperature was established by spectroelectrochemical techniques. The infrared (IR) spectra were collected by electrogeneration in a modified infrared reflection−absorption spectroscopy (IRRAS) cell (Table 1).[6]

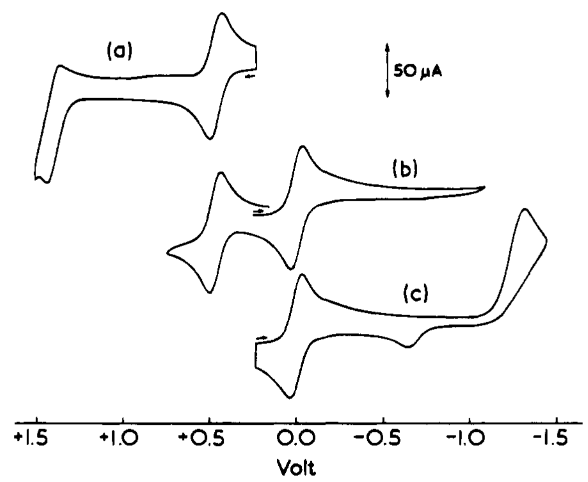

Figure 1. Room-temperature cyclic voltammetry of $(^nBu_4N)_3[Re_2(NCS)_{10}]$ in 0.5 mol dm^{-3} $^nBu_4N[PF_6]$/dichloromethane. Scan rate = 100 mV s^{-1}.

Table 1. IR and UV/Vis Spectroscopic Data

complex	IR max ν_{CN}/cm^{-1} [a]	electronic max/nm [b]
$[Re_2(NCS)_{10}]^-$	1970, 1825	*c*
$[Re_2(NCS)_{10}]^{2-}$	2062, 2022, 1876	463 (87 900), ~500 (sh), 695 (12 800)
$[Re_2(NCS)_{10}]^{3-}$	2078, 2058, 1922, 1885	428 (62 900), ~475 (sh), ~660 (sh)
$[Re_2(NCS)_{10}]^{4-}$	2099, 2087, 1933	333 (29 700), 388 (43 400), 564 (8 300)

[a] Collected in an IRRAS cell at 253 K, in 0.5 mol dm^{-3} $^nBu_4N[PF_6]/CH_2Cl_2$. In the same electrolyte/solvent mixture, ν_{CN} for free NCS$^-$ occurs at 2056 cm^{-1}. [b] Collected in an OTTLE cell at 253 K, in 0.5 mol dm^{-3} $^nBu_4N[PF_6]/CH_2Cl_2$ over the range 225−900 nm. sh = shoulder. ϵ_{max}/M^{-1} cm^{-1} are given in parentheses. [c] The $[Re_2(NCS)_{10}]^-$ species proved to be insufficiently stable for electrogeneration in an OTTLE cell.

Isosbestic points were observed with each oxidation or reduction, each spectrum being regenerated without loss of intensity of any of its features, thus permitting definitive characterization of the $[Re_2(NCS)_{10}]^{z-}$ species in three oxidation levels, z = 2−4.

In describing the solution IR spectrum of $[Re_2(NCS)_{10}]^{3-}$ (Figure 2b), Cotton *et al.* attributed the two bands at 2078 and 2058 cm^{-1} to ν_{CN} from the terminal NCS$^-$ groups and those at 1922 and 1885 cm^{-1} to ν_{CN} from the bridging NCS$^-$ groups.[3] The observation of two ν_{CN} bands from the bridging NCS$^-$ groups is unexpected for an ion of D_{2h} symmetry. Upon either one-electron oxidation or reduction, the two bridging ν_{CN} bands collapse to yield a single band in each case, at 1876 and 1933 cm^{-1}, respectively (Figure 2a,c). Both the terminal and bridging ν_{CN} bands move progressively to lower wavenumber upon oxidation, consistent with the behavior expected of σ/π donor ligands. The wavenumber and intensity patterns of the bands in the ν_{CN} region of the spectra of $[Re_2(NCS)_{10}]^{z-}$ (z = 2, 4),

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(4) Voltammetric experiments were performed in a conventional one-compartment, three-electrode cell. The electrodes used were a Pt bead working electrode, a Pt bar counter electrode, and a AgCl/Ag reference electrode, which was calibrated against the ferrocenium/ferrocene couple (+0.55 V).

(5) For $[Re_2(NCS)_{10}]^{3-/2-}$ and $[Re_2(NCS)_{10}]^{3-/4-}$ at room temperature, ΔE_p = 65−70 mV and was constant for scan rates of 50−1000 mV s^{-1}, while i_{pa}/i_{pc} = 1. For ferrocene/ferrocenium obtained under identical conditions, ΔE_p = 60 mV.

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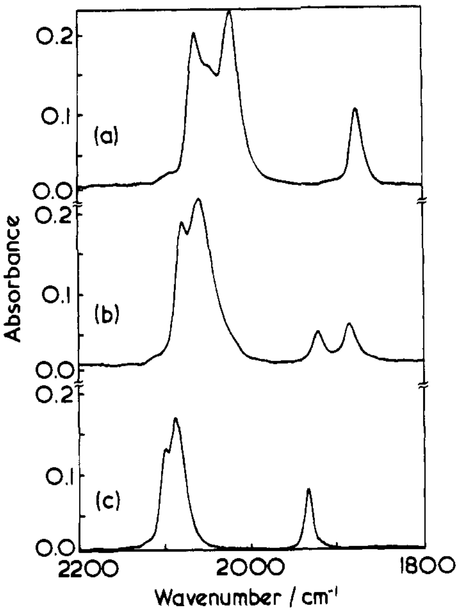

Figure 2. Single-scan (resolution 1.0 cm^{-1}) infrared spectra of $[Re_2(NCS)_{10}]^{z-}$ complexes collected in an IRRAS cell, in 0.5 mol dm^{-3} $^nBu_4N[PF_6]$/dichloromethane at 253 K: (a) $z = 2$, (b) $z = 3$, (c) $z = 4$.

are consistent with the retention of the ESBO structure for these ions. The $[Re_2(NCS)_{10}]^{2-}$ species is particularly interesting in that it is one of the few Re^{IV}_2 complexes possessing an ESBO structure.[7] The ultraviolet/visible (UV/vis) spectra for $[Re_2(NCS)_{10}]^{z-}$ (z = 2, 4) were obtained at room temperature by electrogeneration in an optically transparent thin-layer electrolysis (OTTLE) cell (Table 1)[8] and will be discussed elsewhere.

On the basis of a simple metal-orbital-based bonding scheme for the ESBO $[Re_2(NCS)_{10}]^{z-}$ system ($\sigma < \pi < \delta < \delta^* < \pi^* < \sigma^*$),[9] the formal M−M bond order (BO) increases from 2.0 (z = 4) to 2.5 (z = 3) to 3.0 (z = 2). Theoretical studies have shown that, however, in cases where the bridging ligands have orbitals of suitable symmetry to interact with the metal d orbitals, re-ordering of the molecular orbital scheme may occur.[10] In particular, the ordering of the $\delta\delta^*$ orbitals has often been shown to be reversed, and should this occur in the present system, then the M−M BO varies from 2.0 (z = 4) to 1.5 (z = 3) to 1.0 (z = 2). This latter variation of BO with z is intuitively what may be expected for the variation in Re−Re bond strength in complexes of the type $[M_2X_{10}]^{z-}$ (where X = σ/π donor). Thus on oxidation of the metal centers, spatial contraction of the d orbitals may be expected, in addition to increased electrostatic repulsion between the highly charged metal ions.

In dichloromethane, $[Re_2(NCS)_{10}]^{2-}$ undergoes a further oxidation ($E_{1/2}$ = +1.38 V),[11] although this process is at best only partially reversible, even at low temperatures. In accordance with the cyclic voltammetry, IR spectroelectrochemistry reveals that $[Re_2(NCS)_{10}]^-$ has only limited stability. On oxidation at +1.40 V in the IRRAS cell, bands grow at 1970 and 1825 cm^{-1} at the expense of those from $[Re_2(NCS)_{10}]^{2-}$. The oxidation proceeds to approximately 50% completion before the decomposition of $[Re_2(NCS)_{10}]^-$ occurs, as shown by the breakdown of isosbestic points and the failure to regenerate quantitatively the starting spectrum.

The further reduction of $[Re_2(NCS)_{10}]^{4-}$ ($E_{1/2}$ = −1.22 V)[11] is irreversible in dichloromethane. Accompanying this reduction, which has been shown by coulometry to involve overall two electrons, a very rapid reaction takes place forming another species, which is detected on the return scan, E_{pa}= −0.64 V (Figure 1b,c). Cooling the solution to 213 K does not improve the reversibility of this further reduction, although the product wave does become very broad and ill defined. It should be noted that the $[Re_2(NCS)_8]^{3-/4-}$ reduction ($E_{1/2}$ = −0.69 V) occurs at the same potential as that at which the species produced at the electrode is detected, and this reduction shows similar broadening at low temperature.[12]

Significant changes in the IR spectrum are observed upon reduction of $[Re_2(NCS)_{10}]^{4-}$. The bands characteristic of $[Re_2(NCS)_{10}]^{4-}$ give way to a comparatively simple spectrum, which consists of an intense band at 2077 cm^{-1} and a shoulder in the region 2055−8 cm^{-1}. No bands attributable to υ_{CN} of either solely N-bound or N- and S-bound bridging thiocyanate are observed. The shift of the υ_{CN} bands and the absence of isosbestic points accompanying the reduction are consistent with major structural rearrangement. Accordingly, oxidative currents are not observed until a potential of −0.5 V is applied, whereupon a series of slow spectral changes culminate in the quantitative re-formation of $[Re_2(NCS)_{10}]^{4-}$.

The voltammetric and spectroelectrochemical results noted above are consistent with the formation of a direct M−M-bonded species with very weakly ligated NCS^- groups occupying the axial positions, *i.e.* $\{[Re_2(NCS)_8](NCS)_2\}^{6-}$.[13] Although υ_{CN} for free NCS^- in this medium occurs at 2056 cm^{-1}, the shoulder (2055−8 cm^{-1}) is not so attributed because, for cases where the axial NCS^- ligands are displaced (*e.g.* by acetonitrile), the resulting free NCS^- groups give rise to a much more intense (10×) band at 2056 cm^{-1} than that observed. In the absence of other potential ligands, the existence of axially coordinated NCS^- (albeit very weakly) seems likely. Solution studies of $[Re_2(NCS)_8]^{2-}$ have shown that the energy of the δ−δ^* transition is dependent upon the identity of the solvent.[14] This solvent dependence has been attributed to axial coordination. The tendency of $[Re_2(NCS)_8]^{2-}$ to bind ligands in the axial positions is further evidenced by X-ray structural data.[14] The two single-crystal structure determinations of $[Re_2(NCS)_8]^{2-}$ published to date have both revealed the presence of weakly bound solvent molecules in the axial positions.

Work is continuing on this system, and on the related $[Re_2(NCS)_8]^{z-}$ [2,14] and $[Re_2X_{10}]^{2-}$ (X = Cl, Br) ions.

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(9) Note that for an ESBO structure only one M−M π-bond is possible, whereas in the case of the direct M−M-bonded structure two are possible.

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