

Low-Temperature Voltammetric Study of $(\text{Bu}_4\text{N})_2[\text{Re}_2(\text{NCS})_8]$. Spectroelectrochemical Characterization of 9-Electron $[\text{Re}_2(\text{NCS})_8]^{3-}$ and 7-Electron $[\text{Re}_2(\text{NCS})_8]^{1-}$ and $[\text{Re}_2\text{Cl}_8]^{1-}$

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Ever since the recognition of metal–metal multiple bonds, the variation in properties with changing electronic occupancy of the orbital manifold has invited attention.^{1,2} For quadruply bonded binuclear octahalide complexes $[\text{M}_2\text{X}_8]^{z-}$ ($\text{M} = \text{Mo}$ or W , $z = 4$; $\text{M} = \text{Tc}$ or Re , $z = 2$) which share the dominant 8e (8-electron) $\sigma^2\pi^4\delta^2$ configuration, such comparisons have been precluded by the unavailability of these materials in alternative oxidation states, with the welcome exception^{3,4} of 9e $[\text{Tc}_2\text{Cl}_8]^{3-}$. In particular, in the even 8e systems direct spectroscopic quantification of the δ/δ^* orbital splitting is beset with massive interference from electron-correlation contributions to the promotion energy.^{5,6} Thus, stabilization of the $^1A_{1g}$ ground state by configurational interaction causes the observed $\delta\delta^* \leftarrow \delta^2$ transitions to occur at energies more than twice the underlying orbital separation as estimated by SCF- $X\alpha$ methods.⁷

We have shown^{8,9} recently that low-temperature electrochemical techniques are a convenient means of manipulating the oxidation state in both 8e $[\text{Re}_2\text{Cl}_8]^{2-}$ and 10e $[\text{Os}_2\text{Cl}_8]^{2-}$. The electro-generated species 9e $[\text{Re}_2\text{Cl}_8]^{3-}$ and 9e $[\text{Os}_2\text{Cl}_8]^{1-}$ were spectroscopically characterized in situ in chilled nonaqueous media revealing the characteristic δ/δ^* bands at 6950 and 4600 cm^{-1} , respectively. We now report parallel studies on $[\text{Re}_2(\text{NCS})_8]^{2-}$ and the characterization of the corresponding 9e $[\text{Re}_2(\text{NCS})_8]^{3-}$ and 7e $[\text{Re}_2(\text{NCS})_8]^{1-}$ species as redox-differentiated odd-electron systems, free of electron correlation complications, together with the first characterization of 7e $[\text{Re}_2\text{Cl}_8]^{1-}$. The $[\text{Re}_2(\text{NCS})_8]^{n-}$ and $[\text{Re}_2\text{Cl}_8]^{n-}$ systems ($n = 1, 2, \text{ or } 3$) constitute the first series of M_2X_8 complexes characterized in three oxidation states, while $[\text{Re}_2(\text{NCS})_8]^{1-}$ and $[\text{Re}_2\text{Cl}_8]^{1-}$ are the first 7e octahalide (or pseudohalide) complexes to be described.

Voltammetry¹⁰ of $(\text{Bu}_4\text{N})_2[\text{Re}_2(\text{NCS})_8]$ in *n*-PrCN at 290 K reveals two reversible one-electron reductions at -0.20 (8e \rightarrow 9e) and -0.90 V (9e \rightarrow 10e) (Figure 1a) and a reversible oxidation

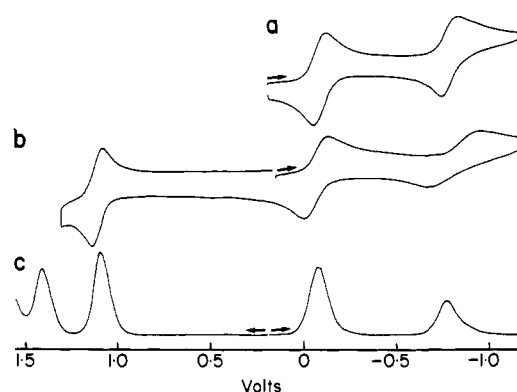


Figure 1. Voltammetry of $(\text{Bu}_4\text{N})_2[\text{Re}_2(\text{NCS})_8]$ in *n*-PrCN. (a) Cyclic dc scan, 290 K, 100 mV/s. (b) Cyclic dc scan, 215 K, 100 mV/s. (c) Linear ac scan, 290 K, 50 mV/s.

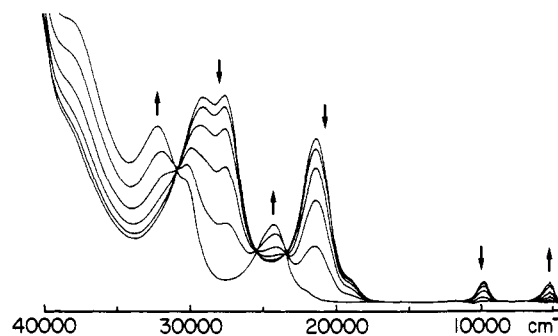


Figure 2. Reversible reduction of $[\text{Re}_2(\text{NCS})_8]^{2-}$ to $[\text{Re}_2(\text{NCS})_8]^{3-}$ in *n*-PrCN, 215 K.

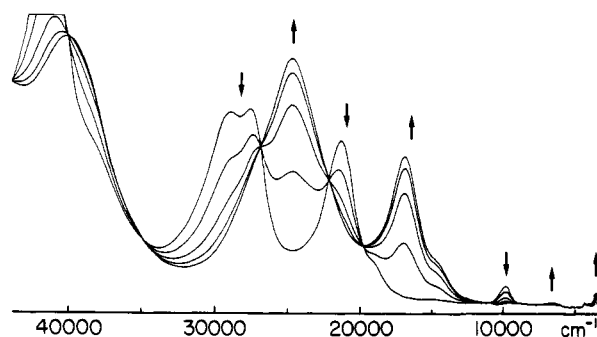


Figure 3. Reversible oxidation of $[\text{Re}_2(\text{NCS})_8]^{2-}$ to $[\text{Re}_2(\text{NCS})_8]^{1-}$ in *n*-PrCN, 215 K.

at 1.10 V (8e \rightarrow 7e), as reported by Walton¹² for CH_2Cl_2 solutions. At 215 K, the reduction at -0.90 V becomes noticeably sluggish, i.e., quasireversible with $E_{\text{P,C}} - E_{\text{P,A}} = 0.27$ V (Figure 1b). In *n*-PrCN, at 1.40 V, a further oxidation (7e \rightarrow 6e) is observed for the first time (Figure 1c).

Spectroelectrochemical characterization from 3200 to 45 000 cm^{-1} of $[\text{Re}_2(\text{NCS})_8]^{3-}$, $[\text{Re}_2(\text{NCS})_8]^{1-}$, and $[\text{Re}_2\text{Cl}_8]^{1-}$ (Figures 2, 3, 4) was achieved using a cryostated Optically Transparent Thin-Layer Electrode (OTTLE) cell, as described elsewhere.¹³ In 0.2 M $[\text{n-Bu}_4\text{N}][\text{BF}_4]/\text{n-PrCN}$ solution at 215 K, the LMCT bands (29 000, 27 500, 21 300 cm^{-1}) of $[\text{Re}_2(\text{NCS})_8]^{2-}$ shift by ca. 3000 cm^{-1} to higher energy upon reduction to $[\text{Re}_2(\text{NCS})_8]^{3-}$ and by ca. 4000 cm^{-1} to lower energy upon oxidation to $[\text{Re}_2(\text{NCS})_8]^{1-}$, while the $\delta\delta^* \leftarrow \delta^2$ transition band (9800 cm^{-1}) is replaced by a $\delta\delta^*2 \leftarrow \delta^2\delta^*$ band (5200 cm^{-1}) for 9e $[\text{Re}_2(\text{NCS})_8]^{3-}$ and by a $\delta^* \leftarrow \delta$ band (3200 cm^{-1}) for 7e $[\text{Re}_2(\text{SCN})_8]^{1-}$. Even though both oxidation and reduction of

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(10) $(\text{Bu}_4\text{N})_2[\text{Re}_2(\text{NCS})_8]$ was prepared according to a literature procedure.¹¹ Solvents were freshly distilled and degassed: 0.4 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ was used as supporting electrolyte; all measurements were carried out with a Princeton Applied Research 170 potentiostat under a dry- N_2 atmosphere versus a Ag/AgCl reference electrode for which the ferrocene/ferrocenium redox couple was measured at 0.55 V.

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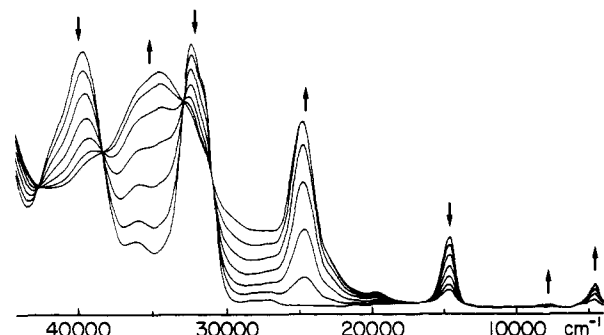


Figure 4. Reversible oxidation of $[\text{Re}_2\text{Cl}_8]^{2-}$ to $[\text{Re}_2\text{Cl}_8]^{1-}$ in (1:1) $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$, 200 K.

$[\text{Re}_2(\text{NCS})_8]^{2-}$ are reversible at 290 K on the voltammetric time scale, low temperature was required for bulk electrogeneration. In 0.4 M $[n\text{-Bu}_4\text{N}][\text{ClO}_4]/(1:1) \text{CH}_2\text{Cl}_2:\text{CH}_3\text{CN}$ solution at 200 K, the strong bands (39 700, 32 300 cm^{-1}) of $[\text{Re}_2\text{Cl}_8]^{2-}$ shift to lower energy (34 400, 24 800 cm^{-1}) upon oxidation to $[\text{Re}_2\text{Cl}_8]^{1-}$, while the $\delta\delta^* \leftarrow \delta^2$ transition band (14 700 cm^{-1}) gives way to a $\delta^* \leftarrow \delta$ band (4650 cm^{-1}). In addition, both $[\text{Re}_2(\text{NCS})_8]^{1-}$ and $[\text{Re}_2\text{Cl}_8]^{1-}$ possess a weak, broad band at 6500 and 8000 cm^{-1} , respectively, tentatively assigned to promotion to the singly occupied δ -orbital.

Our earlier failure⁸ to stabilize solutions of electrogenerated $[\text{Re}_2\text{Cl}_8]^{1-}$ was linked to the choice of $[\text{R}_4\text{N}][\text{PF}_6]$ or $[\text{R}_4\text{N}][\text{BF}_4]$ electrolytes. Under the conditions required for one-electron oxidation of $[\text{Re}_2\text{Cl}_8]^{2-}$ (1.60 V vs Ag/AgCl), such fluoro anions are not innocent as they promote the oxidative transformation of $[\text{Re}_2\text{Cl}_8]^{1-}$ to $[\text{Re}_2\text{Cl}_8]^{2-}$, along with the formation of unidentified Re-F species. In the alternative perchlorate electrolyte, $[\text{Re}_2\text{Cl}_8]^{1-}$ is stable in solution at 200 K for short periods, though this highly reactive species decomposes rapidly at higher temperature.

The characteristic vibrational fine structure of the near-infrared bands of $[\text{Re}_2(\text{NCS})_8]^{3-}$, $[\text{Re}_2(\text{NCS})_8]^{1-}$, and $[\text{Re}_2\text{Cl}_8]^{1-}$ allows their unequivocal assignment as δ/δ^* transitions.¹⁴ The mere presence of this band indicates that the complexes retain, or approach, the eclipsed geometry required for the existence of a δ -bond, while for such odd-electron species the band energy corresponds well to the δ/δ^* orbital energy gap. One-electron oxidation and reduction of the Re_2^{6+} core both decrease the formal bond order to 3.5 but have opposite effects on overall bond strength. Reduction actually strengthens the bond, as judged by the Re-Re stretching vibration (and confirmed crystallographically^{3,4} for $[\text{Tc}_2\text{Cl}_8]^{2-}$), and this is attributed to d-orbital expansion in the lower oxidation state.¹⁵ Similarly, d-orbital contraction should contribute to diminished metal-metal interaction in higher oxidation state Re_2^{7+} . Accordingly, the δ/δ^* transition energies of $[\text{Re}_2(\text{NCS})_8]^{1-}$ and $[\text{Re}_2(\text{NCS})_8]^{3-}$, 3200 and 5200 cm^{-1} , respectively, must flank the δ/δ^* orbital separation in $[\text{Re}_2(\text{NCS})_8]^{2-}$, now seen by simple interpolation to be approximately 4200 cm^{-1} . Likewise, the observed δ/δ^* bands of the Re_2^{7+} and Re_2^{5+} octachlorides must bracket the corresponding frontier orbital gap in $8e [\text{Re}_2\text{Cl}_8]^{2-}$, and their mean is 4930 cm^{-1} . (In this low frequency region, it becomes important to consider band origins rather than maxima; here $\nu_{0-0}(\delta/\delta^*) = 3800 \text{ cm}^{-1}$ for $[\text{Re}_2(\text{NCS})_8]^{1-}$ and 6060 cm^{-1} for $[\text{Re}_2\text{Cl}_8]^{1-}$.) In comparison, there is an earlier SCF- $X\alpha$ estimate⁷ of 7000 cm^{-1} for this orbital gap, but for the reasons noted above the $\delta\delta^* \leftarrow \delta^2$ band falls much higher in $[\text{Re}_2\text{Cl}_8]^{2-}$, at 14 700 cm^{-1} . Crystallographic data are not available for $[\text{Re}_2(\text{NCS})_8]^{n-}$, but the lower δ/δ^* transition energies of $[\text{Re}_2(\text{NCS})_8]^{n-}$ compared to $[\text{Re}_2\text{Cl}_8]^{n-}$ (in each oxidation state) indicate quantifiably weaker Re-Re multiple bonding in the octaithiocyanate, as suggested qualitatively by

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the smaller separation of its successive electrochemical couples (6e/7e, 7e/8e, 8e/9e).⁸

The unexpected absence of an observable 9e/10e redox couple from the electrochemistry of $[\text{Tc}_2\text{Cl}_8]^{n-}$ and $[\text{Re}_2\text{X}_8]^{n-}$ (X = Cl, Br) has been noted.^{9,16,17} This is particularly challenging as the 8e/9e and 9e/10e couples are separated⁹ by only 0.70 V in $[\text{Os}_2\text{Cl}_8]^{n-}$ and as the second reduction occurs only 0.7–1.3 V more negative than the 8e/9e couple for a variety of substituted analogues, $\text{Re}_2\text{X}_6\text{L}_2$ and $\text{Re}_2\text{X}_4\text{L}_4$, where X = halide and L = PR_3 .¹⁸

For $[\text{Re}_2(\text{NCS})_8]^{n-}$ the chemically reversible 9e/10e couple is readily observable at 290 K and becomes sluggish at low temperature. The behavior of the $[\text{Re}_2(\text{NCS})_8]^{3-/4-}$ couple is consistent with a structural change with an activation energy which is easily overcome at 290 K but is significant at 215 K. To account for this we propose a rotation around the Re-Re axis, interconverting the 9e-eclipsed and 10e-staggered geometries. Further cooling will retard the process even more (flatten the cyclic voltammogram) until it becomes unobservable. Addition of a tenth electron to the M_2X_8 metal-metal orbital manifold disrupts the δ -bond, eliminating the requirement for eclipsed geometry. The 10e $\text{Os}_2\text{Cl}_8^{2-}$ complex has been crystallographically characterized in both the eclipsed and staggered configurations.¹⁹ Similarly, we suggest that the $[\text{Re}_2\text{X}_8]^{3-/4-}$ couple has been rendered unobservable at accessible temperatures through unfavorable electrode kinetics, possibly due to a structural rearrangement such as rotation around the stronger octahalide Re-Re bond. (A rotation should also be associated with 6e/7e $[\text{Re}_2\text{X}_8]^{0/1-}$ (X = Cl, NCS), processes. Electrochemical manifestation of such structural changes has not been observed under similar conditions in those cases or in the $[\text{Os}_2\text{Cl}_8]^{1-/2-}$ process. This can be attributed to weaker metal-metal bonding, associated with the higher oxidation state.)

Vibrational fine structure corresponding to the M-M symmetric stretch is typically observed in δ/δ^* bands when the δ -orbitals involved are rich in metal character. A spectacular Franck-Condon progression was seen⁸ in the $\delta\delta^* \leftarrow \delta^2$ band of $[\text{Re}_2\text{Cl}_8]^{3-}$ in solution but is just observable in the $\delta^* \leftarrow \delta$ band of $[\text{Re}_2\text{Cl}_8]^{1-}$. This is consistent with an increase in the Cl orbital mixing with the Re δ orbitals which is expected to accompany the dirhenium core oxidation from 5+ to 7+ and the consequent Re-Cl bond contraction.

Finally, both 7e $[\text{Re}_2\text{Cl}_8]^{1-}$ and $[\text{Re}_2(\text{NCS})_8]^{1-}$ show a weak band $\sim 3300 \text{ cm}^{-1}$ above their δ/δ^* bands which can be assigned to a π/δ transition. In $[\text{Re}_2\text{Cl}_8]^{2-}$, where both these orbitals are full, a 9600- cm^{-1} separation has been calculated,⁷ comparing reasonably with the measured transition energy of 8000 cm^{-1} for newly available $[\text{Re}_2\text{Cl}_8]^{1-}$.

Our work in the electrogeneration and in situ spectroscopic characterization of M_2X_8 complexes in unfamiliar oxidation states is providing valuable insight into periodic trends in the electronic properties of these multiply bonded systems as well as identifying the conditions—solvent, temperature, and potential window—under which such unstable species can be isolated or examined further.^{8,9,17}

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