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Unprecedented Spin Localisation in a Metal-Metal Bonded Dirhenium Complex†

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The molecular and electronic structure of edge-sharing bioctahedral [N(n-Bu)$_4$]$_3$[Re$_2$(mnt)$_5$] is reported here. Despite the short intermetal bond length of 2.6654(2) Å with computed bond order of 1.2, the unpaired electron is localised by the asymmetric ligand distribution, as demonstrated by its remarkable EPR spectrum.

The existence of direct metal-to-metal multiple bonds was first demonstrated with the identification of Re-Re double bonds in the structure of Cs$_3$[Re$_3$Cl$_{12}$].[1] This discovery marked the inception of the field of multicenter transition metal chemistry, which expanded inorganic structural and bonding ideas beyond the traditional Wernian motif of a single metal ion surrounded by a set of ligands. Just a year later came the structural characterization of [N(n-Bu)$_4$]$_2$[Re$_2$Cl$_8$],[2] a species with an unanticipated short Re-Re distance that was quickly interpreted as being due to a metal-metal quadruple bond. This first recognition of a quadruple bond redefined the bond order (b.o.) ceiling – a value previously seen as being limited at three. Since that time, the body of crystallographically characterized multimetallic complexes with multiply bonded metal atoms has grown rapidly and steadily, the number now being in the thousands and involving all but two elements across groups 5 – 10.[3] The eclipsed arrangement of the square planar opposing ReCl$_4$ units is brought about by the strength of the metal-metal bonds. Each Re^{III} ion has one d orbital (d$_{x^2-y^2}$) σ bonded to four Cl$^-$ ligands. The remaining four d orbitals form one σ bond (d$_{z^2}$-d$_{z^2}$), two π bonds (d$_{xz}$-d$_{xz}$, d$_{yz}$-d$_{yz}$), and a δ bond (d$_{xy}$-d$_{xy}$), giving a b.o. of 4. This δ bond contributes to stabilizing the D_{4h}-symmetric eclipsed structure. The chemistry of the quadruple bond has been examined in oxidative additions reactions with various small molecules that have led to a plethora of new edge-sharing bioctahedral (ESBO) M$_2$L$_{10}$ species,[3,4] a commonly encountered motif in molecular and solid state chemistry. The effect upon the Re-Re bond order, now with one d orbital removed from interacting with the other metal by bonding to the new ligands, has been conveniently appraised by X-ray diffraction, or in the absence of suitable crystals, by spectroscopy.
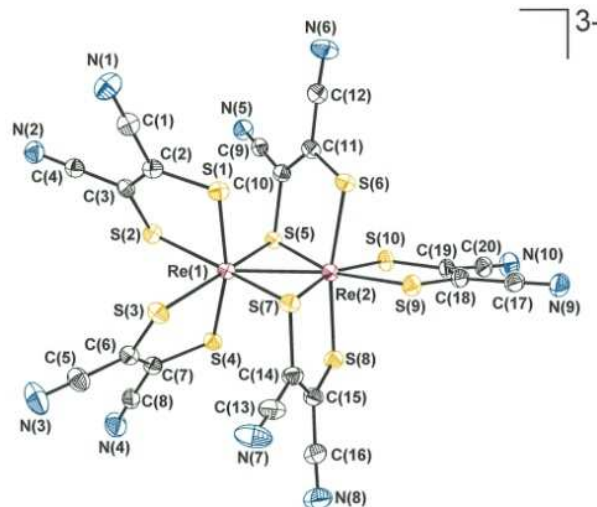

Fig. 1 Structure of the anion in crystals of [N(n-Bu)$_4$]$_3$[Re$_2$(mnt)$_5$]·C$_2$H$_4$Cl$_2$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å): Re(1)−Re(2) 2.6654(2), Re(1)−S(1) 2.3997(9), Re(1)−S(2) 2.4358(9), Re(1)−S(3) 2.4161(9), Re(1)−S(4) 2.3681(9), Re(1)−S(5) 2.4020(9), Re(1)−S(7) 2.3986(9), Re(2)−S(5) 2.3244(8), Re(2)−S(6) 2.3758(9), Re(2)−S(7) 2.3124(9), Re(2)−S(8) 2.3826(9), Re(2)−S(9) 2.4267(9), Re(2)−S(10) 2.4125(9).

With our continuing investigation into dithiolene chemistry of third row transition metals,[5,6,7,8] we revisited the reaction of [N(n-Bu)$_4$]$_2$[Re$_2$Cl$_8$] with disodium maleonitriledithiolate, Na$_2$mnt,[9] with the intent of determining its molecular structure. The original report by Cotton, Oldham and Walton detailed the isolation of an almost black microcrystalline solid, formulated [AsPh$_4$]$_2$[Re$_2$(mnt)$_4$],[9] although the exact geometry and Re-Re bond order had not been definitively established. A reproduction of this reaction by stirring [N(n-Bu)$_4$]$_2$[Re$_2$Cl$_8$] and Na$_2$mnt in dichloromethane at ambient temperature led to the isolation of [N(n-Bu)$_4$]$_3$[Re$_2$(mnt)$_5$] in modest

yield (38%). The formation of a mixed-valence $Re^{III,IV}$ species appears to arise from the presence of adventitious dioxygen or oxidation by the solvent, dichloromethane. The same reaction performed under aerobic conditions yielded [N(n-Bu)$_4$][ReO(mnt)$_2$],[10] as confirmed by X-ray crystallography (Fig. S1).

Black columns that crystallized in the monoclinic space group $P2_1/c$ showed one [Re$_2$(mnt)$_5$]$^{3-}$ anion, three well separated tetrabutylammonium cations and a 1,2-dichloroethane solvent molecule. The dimetallic complex contains a {Re$_2$S$_{10}$} core with each Re ion possessing approximate octahedral coordination to six sulfur atoms (Fig. 1). This ESBO complex can be viewed as an [Re^{III}(mnt)$_2$]$^{1-}$ unit (Re(1) in Fig. 1) attached to an octahedral [Re^{IV}(mnt)$_3$]$^{2-}$ species (Re(2) in Fig. 1) through sulfur atoms in the cis position, with a C_2 axis along the metal-metal vector. This topology has been observed with dirhenium compounds with di- and tri-thiocarbamate ligands[11] and in one example with 4,5-disulfanyl-1,3-dithiole-2-thionate, (dmit)$^{2-}$.[12] The dimensions of the "Re(mnt)$_3$" component are almost identical to [PPh$_4$]$_2$[Re^{IV}(mnt)$_3$], with the average Re(2)–S bond length at 2.3724(9) Å similar to the monometallic species (2.364(1) Å).[8] It is significant that the average Re(1)–S distance is 0.031 Å longer than for Re(2), which leads to a tentative oxidation state assignment of +III for Re(1). The two chelating (mnt)$^{2-}$ ligands about Re(1) exhibit a noticeable distortion along the S···S vector reducing the fold angle to 159° and resemble the corresponding ligands in [Re$^{IV}_2$(dmit)$_5$]$^{2-}$.[12] All intraligand bond lengths are consistent with the dianionic form of the ligand. The short intermetal separation of 2.6654(2) Å is indicative of metal-metal bonding. This value sits in the range for structurally characterised ESBO complexes containing a {Re$_2$}$^{7+}$ core: [Re$_2$(NCS)$_{10}$]$^{3-}$ (2.613(1) Å),[13] [Re$_2$Cl$_6$(dppm)$_2$]$^{1+}$ (2.682(1) Å; dppm = bis(diphenylphosphino)methane),[14] [Re$_2$OCl$_3$(O$_2$CCH$_2$CH$_3$)$_2$(PPh$_3$)$_2$] (2.514(1) Å),[15] [Re$_2$OCl$_2$(pyt)$_4$]$^{1-}$ (2.5491(4) Å; (pyt)$^{1-}$ = pyridine-2-thiolate).[16]
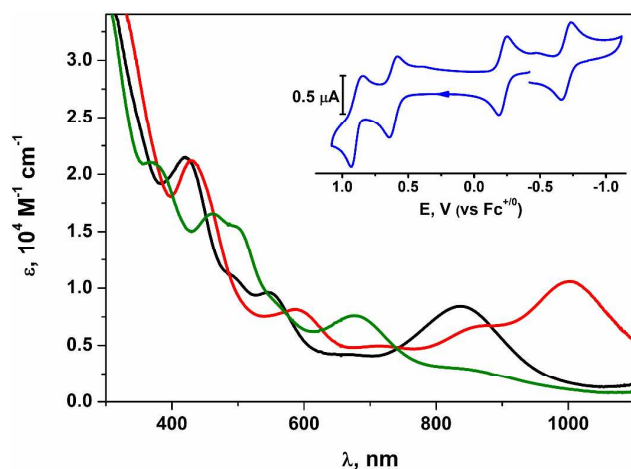
Fig. 2 Electronic spectra of electrochemically generated [Re$_2$(mnt)$_5$]$^{2-}$ (red), [Re$_2$(mnt)$_5$]$^{3-}$ (black), and [Re$_2$(mnt)$_5$]$^{4-}$ (green) species in CH$_2$Cl$_2$ (0.10 M [N(n-Bu)$_4$]PF$_6$) at -25 °C. Inset shows the cyclic voltammogram taken under the same conditions at 100 mV s^{-1} referenced to the Fc$^{+/0}$ couple.

The redox chemistry of [N(n-Bu)$_4$]$_3$[Re$_2$(mnt)$_5$] was probed by electro- and spectroelectrochemistry. The cyclic voltammogram recorded in dichloromethane solution at -25 °C revealed four redox events (Fig. 2 inset): a one-electron reduction at -0.704 V, and three oxidation processes at -0.220, +0.613, and +0.905 V versus Fc$^{+/0}$. By comparison, the corresponding processes for [Re$_2$(dmit)$_5$]$^{2-}$ occur at lower potential: -1.20, -0.86, -0.12, and -0.05 V, respectively.[12] The ease of oxidising the latter underscores the stronger π-donation of

the (dmit)$^{2-}$ ligand, which results in stabilisation of the dirhenium complex as a dianion rather than as a trianion as in [Re$_2$(mnt)$_5$]$^{3-}$. Controlled potential coulometry confirmed the reduction and the first oxidation as fully reversible. Simultaneous measurement of their electronic spectra revealed several isosbestic points during each electrochemical transformation (Figures S2 and S3). The other oxidation waves are not reversible on the timescale of the experiment. In an electrochemical study of the rhenium (mnt)$^{2-}$ species isolated using the original published procedure, McCleverty and co-workers[10] revised the molecular formula as [Re(mnt)$_2$]$_4^{4-}$ to account for the charge per mole of the complex. Their voltammogram revealed this species was reversibly reduced at -0.70 V and oxidized at -0.29 V. Both of these processes are essentially identical to redox features observed for [Re$_2$(mnt)$_5$]$^{3-}$ when corrected for different solvent, electrolyte and reference electrode.[5] It is therefore probable that they had also isolated [N(n-Bu)$_4$]$_3$[Re$_2$(mnt)$_5$].[9] Despite the presence of redox-active dithiolene ligands, all redox processes are defined as metal-centred up to +V, following the trend established for tris(dithiolene) complexes.[5,7,8] Therefore, the five-membered electron transfer series is classified as:

$$[Re_2^{V,V}]^0 \underset{-e}{\overset{+e}{\rightleftharpoons}} [Re_2^{IV,V}]^{1-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [Re_2^{IV,IV}]^{2-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [Re_2^{III,IV}]^{3-} \underset{-e}{\overset{+e}{\rightleftharpoons}} [Re_2^{III,III}]^{4-}$$
$$(S=0) \qquad (S={}^1/_2) \qquad (S=0) \qquad (S={}^1/_2) \qquad (S=0)$$
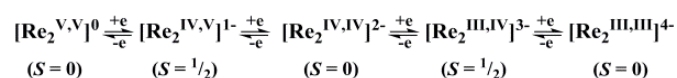
The electronic spectra for the three stable members of the series are overlaid in Fig. 2. The parent complex [N(n-Bu)$_4$]$_3$[Re$_2$(mnt)$_5$] has a significantly intense (ε = 8400 M^{-1} cm^{-1}) peak at 836 nm. It is interesting to note that the electronic spectral data provided in the original report match our spectrum for [N(n-Bu)$_4$]$_3$[Re$_2$(mnt)$_5$].[9] The one-electron reduced tetra-anionic species has a low-energy shoulder at 809 nm and a more prominent band at 675 nm. The spectral profile of the dianionic member of the series is dominated by a peak at 1003 nm (10 600 M^{-1} cm^{-1}) with a shoulder at 876 nm. The prominent low energy band for each complex is too intense to be due to an excitation between molecular orbitals (MO) of the dirhenium unit and is most likely ligand-to-metal charge transfer from filled π MOs to metal-based MOs of π symmetry, such as the vacant π* MO in each member of the series (vide infra).

With an uneven number of valence electrons, the $S = {}^1/_2$ ground state of [N(n-Bu)$_4$]$_3$[Re$_2$(mnt)$_5$] is conveniently probed by EPR spectroscopy. The spectrum presented in Fig. 3 is the most extraordinary of any known dirhenium complex.[17,18] No signal was observed in room temperature or chilled solution. The profile is dominated by six hyperfine lines rather than an anticipated 11-line pattern arising from two Re ions with the ^{185,187}Re isotopes of nuclear spin $I = {}^5/_2$ (100% abundant). This outcome can only arise if the unpaired electron is *localised* on one Re ion, and despite the metal-metal bond, no coupling is observed with the second Re ion. The spectrum was best reproduced with g = (1.878, 1.989, 2.028) and A = (290, 330, 45) × 10^{-4} cm^{-1}, which are similar in magnitude to the only other simulated spectrum of a paramagnetic dirhenium species possessing a {Re$_2$}$^{7+}$ core, [Re$_2$(hpp)$_4$Cl$_2$]$^{1+}$.[18] Successful simulation required the sparingly utilised quadrupolar term (**P**). Spectacularly large quadrupolar couplings were recently found in the EPR spectra of neutral tris(dithiolene)rhenium compounds and their two-electron reduced complex dianions.[7] Similar features can be seen in the spectrum shown in Fig. 3, namely an uneven spacing of the six hyperfine lines and weak quadrupole-allowed transitions in the low field region of the spectrum. The best fit emerged for a rhombic **P** tensor: P = (24, 16, -40) × 10^{-4} cm^{-1},[19] which is parameterised by $P = [P_{zz} - (P_{xx} + P_{yy})/2]/3 = 20 × 10^{-4}$ cm^{-1} and rhombicity, $\eta = (P_{xx} - P_{yy})/2 = 4 × 10^{-4}$ cm^{-1}. This quadrupolar coupling is similar to [Re^{IV}(bdt)$_3$]$^{2-}$ (bdt^{2-} = benzene-1,2-dithiolate),[7] and sits amongst those determined for a variety of Re^{VI} compounds.[20]
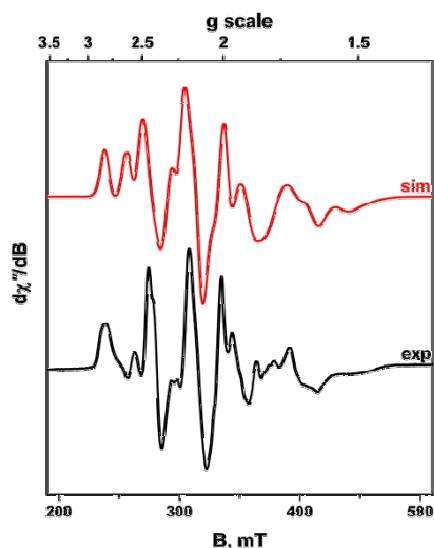
Fig. 3 X-band EPR spectrum of $[N(n\text{-}Bu)_4]_3[Re_2(mnt)_5]$ recorded in CH_2Cl_2/THF solution at 20 K. The simulation is shown in red with the experimental spectrum in black (conditions: frequency, 9.4365 GHz; power, 0.063 mW; modulation, 1.5 mT).

The **g** and **A** matrices, and **P** tensor were all assumed to be coaxial in this simulation. It should be noted that this may not be a unique solution, and additional data are required to resolve the potentially complicated tensor orientations inherent to low symmetry complexes. A mixture of g- and A-strain was employed to model the spectral linewidth, which presumably stems from structural heterogeneity in the frozen glass. Based on the homogeneous linewidth, coupling to the second Re ion can be limited to a maximum value of 20×10^{-4} cm^{-1}. However, there is no evidence to support the existence of this interaction.

The electronic structure for this electron transfer series has been determined by DFT calculations. The optimized structure for the trianion has average Re(1)–S and Re(2)–S bond lengths of 2.422 and 2.395 Å, respectively (Table S2). These values are ~0.02 Å longer than the experimental data, which is typical of the B3LYP functional. The Re–Re distance at 2.736 Å is substantially overestimated (by 0.07 Å), and the two terminal dithiolene ligands on Re(1) retain a noticeable fold angle of ~170° (cf. 159° experimentally). In a simple ligand field description, the available d orbitals for each metal ion in an ESBO form three metal-metal bonds:[4] one σ bond between $d_{x^2-y^2}$ orbitals; one π bond between d_{xz} orbitals, and a δ bond between d_{yz} orbitals, where the x-axis is parallel to the metal-metal vector (Fig. 4b). The MO manifold calculated for $[Re_2(mnt)_5]^{3-}$ shows a bona fide σ bond. However, the strong interaction between the π orbital of the single terminal $(mnt)^{2-}$ ligand of Re(2) stabilises the d orbital manifold and disrupts the overlap with the corresponding orbital on Re(1). The consequence is attenuation of the Re-Re π bond and complete destruction of the δ bond, leading to an unambiguous assignment of a d^3 electron count for Re(2) and d^4 for Re(1). An identical solution resulted from broken symmetry calculations, such that the electronic structure cannot be viewed as the consequence of strong antiferromagnetic coupling between S = 1 and S = $^1/_2$ ions, which is highly unlikely for 5d metals. The Mulliken spin population analysis reveals one unpaired electron at Re(1) with a minor polarization of the metal-metal bond depositing some spin density at the second ion (Fig. 4a). The structural, spectroscopic and computational data support the assignment as a Class I valence localized {Re^{III}Re^{IV}} compound.[21] The calculated bond order (Löwdin) of 1.2 is in keeping with the experimental intermetal bond distance when compared to similar

{Re$_2$}$^{7+}$ units with b.o. ~ 1.5 (vide supra). The molecular and electronic structures of the di- and tetra-anionic members of the electron transfer series were similarly computed (Figures S5-S8). Both are diamagnetic as shown by the absence of an EPR signal on samples generated by bulk electrolysis.
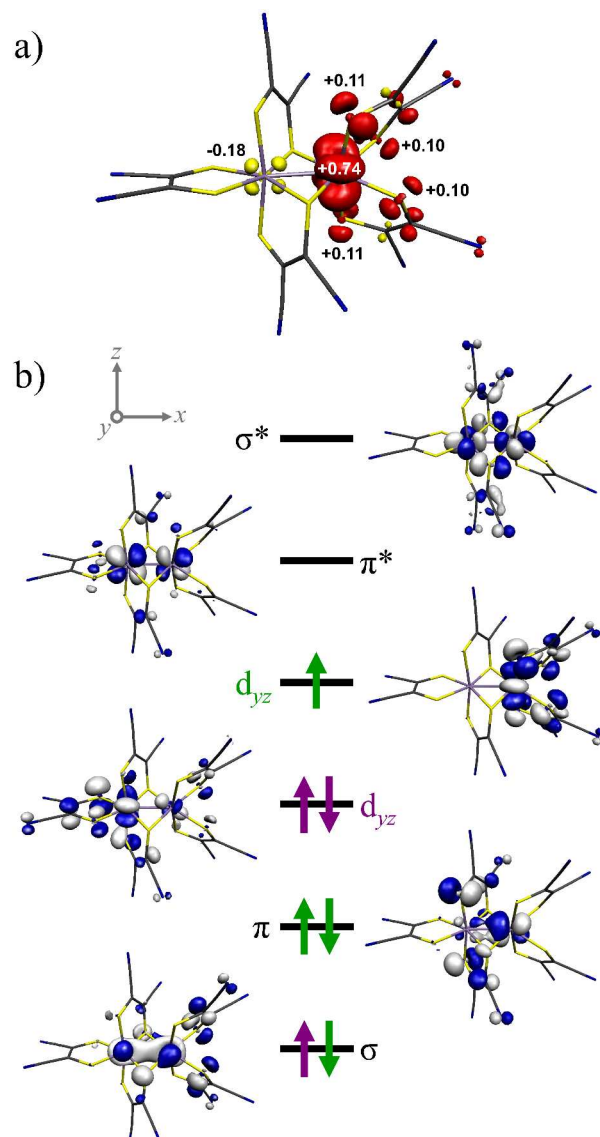

Fig. 4 (a) Mulliken spin population analysis for $[Re_2(mnt)_5]^{3-}$ from spin unrestricted DFT calculations (red: α-spin, yellow: β-spin). (b) Qualitative MO scheme depicting the ordering of the Kohn-Sham orbitals (β-spin) for the {Re$_2$}$^{7+}$ unit in $[Re_2(mnt)_5]^{3-}$.

The intermetal separation diminishes with decreasing metal oxidation state (Table S2). One-electron oxidation to $[Re_2(mnt)_5]^{2-}$ gives a Re-Re bond distance of 2.794 Å. After correcting for the DFT overestimation of 0.07 Å (vide supra), this bond length is similar to the 2.721(2) Å Re-Re distance in $[Re_2(dmit)_5]^{2-}$, which also possesses a C_2 symmetric {Re$_2$}$^{8+}$ core.[12] The one-electron reduced species has an intermetal separation of 2.705 Å from a starting position of 2.736 Å in $[Re_2(mnt)_5]^{3-}$. This distance is still longer than the intermetal separation of 2.573(2) Å in $[Re_2(\mu\text{-}S_3CNMe_2)_2(S_2CNMe_2)_3]^{1+}$ with a C_2 symmetric {Re$_2$}$^{6+}$ core, which stems from the monoanionic charge and reduced bite angle of its di- and tri-thiocarbamate ligands.[11] The short distance results from a better energy match between adjacent d_{xz} orbitals strengthening the

Re-Re π in the tetra-anionic complex (Fig. S8). The $(mnt)^{2-}$ π^*-d_{yz} interaction stabilises this orbital relative to the Re-Re π bonding MO. In contrast, the Re-Re π bond is completely absent in $[Re_2(mnt)_5]^{2-}$ (Fig. S7), where the high positive charge on adjacent ions leads to an elongation of the Re-Re bond, as reflected in a computed bond order approaching unity (Table S2).

The valence localised electronic structure of $[Re_2(mnt)_5]^{3-}$ is driven by strong metal-ligand bonds that override the intermetal interaction, unlike in the archetypal octachlorodirhenate.[2] The highly covalent bonding between soft sulfur-donor dithiolenes and transition metal ions renders these chelates unsuitable for forming paddle-wheel or lantern structures where higher bond orders would be anticipated. A detailed understanding of the inherent physical properties of third row metals such as rhenium will enable their exploitation in new magnetic and spintronic materials. The work is supported by PRF grant 45685-G3 and NSF grant CHE-0845829, and start-up funds from the University of Glasgow.

Notes and references

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