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An electron transfer series of octahedral chromium complexes containing a redox non-innocent α -diimine ligand†

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An electron-transfer series of octahedral α -diimine complexes $[(^H\text{L}^{\text{Cy}})_3\text{Cr}]^{n+}(\text{BARF})_n$ ($n = 2, 1, 0$) has been synthesized and crystallographically characterized. Cyclic voltammetry indicated additional formation of $[(^H\text{L}^{\text{Cy}})_3\text{Cr}]^{3+}$. The molecular structures suggested that all redox processes were ligand-based. Magnetic moments were consistent with spin ground states of $S = 0$ for $[(^H\text{L}^{\text{Cy}})_3\text{Cr}]^0$, $S = 1/2$ for $[(^H\text{L}^{\text{Cy}})_3\text{Cr}]^{+1}$, and $S = 1$ for $[(^H\text{L}^{\text{Cy}})_3\text{Cr}]^{+2}$. The experimental data is consistent with chromium maintaining the +III oxidation state throughout, while being coordinated by varying numbers of neutral diimines ($^H\text{L}^{\text{Cy}}$) and diimine radical anions ($^H\text{L}^{\text{Cy}\bullet-}$).

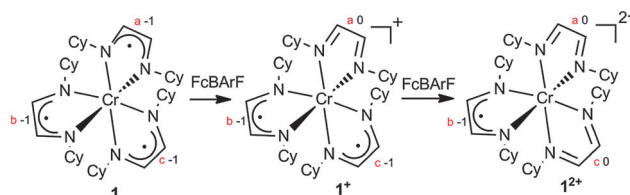
As part of our wide-ranging exploration of open-shell chromium organometallics,¹ we have recently employed α -diimines (aka 1,4-diazadienes) as ancillary ligands.² We were particularly attracted by the redox activity of these ligands, which might be expected to ameliorate the strictures imposed by oxidation state changes during catalytic cycles (e.g. $\text{Cr}^{\text{I}}/\text{Cr}^{\text{III}}$ in the selective oligomerization of ethylene).³ Three oxidation states of the α -diimine ligands have been identified, namely the neutral diimine (L), the radical monoanions ($\text{L}^{\bullet-}$), and the two-electron-reduced enediamide (L^{2-}).⁴ The assignment of ligand oxidation states is informed by their detailed structural parameters, which change in a predictable way; however, spectroscopic and computational techniques are also often employed.

The electronic flexibility of α -diimine ligands enables the preparation of molecules with unusual atomic and electronic structures. A representative example from our laboratory was the serendipitous discovery of dinuclear $[(^H\text{L}^{\text{iPr}})_2\text{Cr}]_2$ ($^H\text{L}^{\text{iPr}} = N,N'$ -bis(2,6-diisopropylphenyl)-1,4-diazadiene),⁵ which features a rather short Cr–Cr quintuple bond between $\text{Cr}(\text{I})$ (d^5) ions

coordinated by two singly reduced bridging α -diimines ($^H\text{L}^{\text{iPr}\bullet-}$) and exhibits notable reactivity with a wide variety of small molecules.⁶ In an extension of this chemistry, we encountered the deceptively simple octahedral complex $(^H\text{L}^{\text{Cy}})_3\text{Cr}$ (**1**, $^H\text{L}^{\text{Cy}} = N,N'$ -bis(cyclohexyl)-1,4-diazadiene). In years past, **1** might have been described as a low-spin $\text{Cr}(\text{0})$ (d^6) complex containing neutral diimine ligands. However, in the age of lost ligand innocence,⁷ all indications are that **1** is best understood as a $\text{Cr}(\text{III})$ (d^3 , $S = 3/2$) complex, with strong antiferromagnetic coupling to three $^H\text{L}^{\text{Cy}\bullet-}$ radical anions ($S = 1/2$).⁸ This description is consistent with that of analogous compounds, *i.e.* those containing ligands such as 2,2'-bipyridine (bpy), 2,2',6',2''-terpyridine (terpy),⁹ dithiolene,¹⁰ α -catecholates,¹¹ and others. Herein we report on the redox chemistry of **1**, which is extensive and appears entirely ligand based.

The synthesis and characterization of **1** has been described,⁸ it is an air sensitive material that can easily be oxidized (see Scheme 1). Thus treatment of a brown Et_2O solution of **1** with 1.0 equivalent of FcBARF ($\text{Fc}^+ = \text{ferrocenium}$, $\text{BARF}^- = \text{tetrakis[3,5-bis(trifluoromethyl)phenyl]borate}$) yielded a deep purple solution, from which $[(^H\text{L}^{\text{Cy}})_3\text{Cr}][\text{BARF}]$ ($[\text{1}^+]\text{BARF}$) was isolated in 92% yield after recrystallization from $\text{Et}_2\text{O}/\text{toluene}$. In contrast to **1**, solid $[\text{1}^+]\text{BARF}$ appears to be stable in air; its structure has been determined by X-ray diffraction and the result is shown in Fig. 1, with selected bond distances listed in Table 1.

Further oxidation of 1^+ proved feasible. Synthetic access to the green $[(^H\text{L}^{\text{Cy}})_3\text{Cr}][\text{BARF}]_2$ ($[\text{1}^{2+}](\text{BARF})_2$) can be had either by the oxidation of **1** with 2.0 equivalents of FcBARF or by the reaction of $[\text{1}^+]\text{BARF}$ with 1.0 equivalent of FcBARF in Et_2O . Recrystallization from methylene chloride at -30°C afforded



Scheme 1 The electron-transfer series for complexes **1–1²⁺**.

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We note that the Cr–N distances in all three compounds vary within a very narrow range (2.019(3)–2.105(4) Å), without any discernable trend. As higher oxidation states tend to engender shorter metal–ligand distances, this too suggests that the oxidation state of the metal is not changing. For this to be true, successive oxidations must remove electrons from the coordinated diimine radical anions, which should result in systematic changes of the C–C and C–N bond distances of the ligand backbones. Although both 1^+ and 1^{2+} lack threefold crystallographic symmetry, rendering the ligands inequivalent, their metric data do not support the unambiguous identification of one (or two) neutral diimines in 1^+ (or 1^{2+}), respectively. In other words, the C–C and C–N distances of the individual ligands in any given compound do not differ significantly. In principle, this may be due to positional disorder in the crystal, or it might indicate effective delocalization of the available electrons over all three ligands. The present structural data cannot distinguish between these two alternatives. Interestingly, DFT calculations on models for 1^+ and 1^{2+} are consistent with delocalization in the former (Fig. S12, ESI[†]) and localization in the latter (Fig. S13, ESI[†]). In any event, inspection of the average distances (see Table 2, bottom) reveals a gradual lengthening of the C–C bonds and a concomitant foreshortening of the C–N bonds in the order $1 \rightarrow 1^+ \rightarrow 1^{2+}$. Thus, in this order the ligands look on average less like radical anions ($L^{\bullet-}$) and more like neutral diimines (L). To summarize, the structural data are consistent with formulations of 1^+ as $[(L^{\bullet-})_2(L)Cr^{III}]^+$ and 1^{2+} as $[(L^{\bullet-})(L)_2Cr^{III}]^{2+}$.

The electronic spectra are shown in Fig. 3. The intense high energy bands are likely $\pi \rightarrow \pi^*$ transition of the ligands, while the weak transition in the visible region may be attributed to $d \rightarrow d$ transitions of the Cr(III) ion. Most conspicuous are the broad bands in the near IR (1389 nm for 1^+ , 923 and 1006 nm for 1^{2+}), which are absent from the spectrum of 1 ; these are tentatively assigned as ligand-to-ligand intervalence charge-transfer bands associated with the presence of ligands in different redox states on the same metal center.^{9d}

To further characterize the electronic structures of this series of compounds, we have carried out magnetic measurements. The temperature dependencies of the effective magnetic moments of all three complexes are depicted in Fig. 4. Both $[1^+](BARF)$ $[1](BF_4)_2$ are simple paramagnets, whose molar magnetic susceptibilities can be fit with Curie–Weiss expressions.

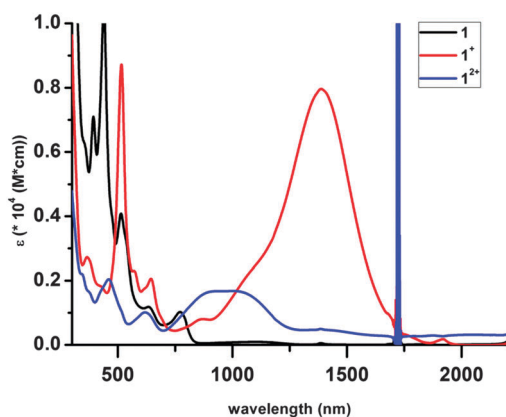


Fig. 3 Electronic spectra of complexes 1 – 1^{2+} in THF.

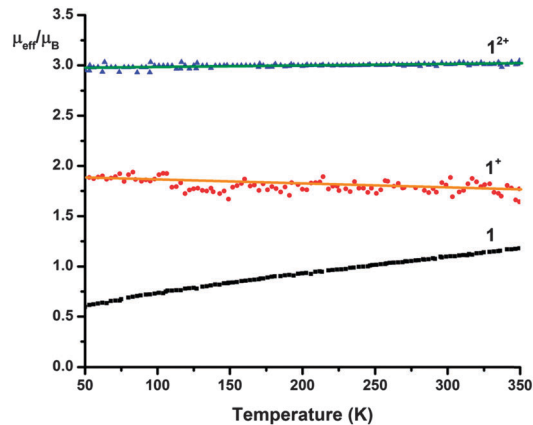


Fig. 4 Temperature dependence of the magnetic moments of 1 – 1^{2+} .

Accordingly, their effective magnetic moments are temperature independent over the whole temperature range of 50–350 K. Their respective values are consistent with spin ground states of $S = 1/2$ for 1^+ and $S = 1$ for 1^{2+} . These presumably result from strong antiferromagnetic coupling between the central Cr(III) ion ($S = 3/2$) and two or one diimine radical anions ($S = 1/2$), respectively. Extending this rationale to 1 would predict diamagnetism (ground state $S = 0$) for this complex. However, as can be seen in Fig. 4, 1 actually exhibits a rather small, and temperature dependent magnetic moment. Indeed, this residual paramagnetism was also evident in the 1H NMR spectrum of 1 . While its resonances were found in the ‘normal’ shift range (δ 1–10 ppm), the room temperature spectrum (in THF- d_6) exhibited a broad resonance at *ca.* 4.7 ppm, which split into two sharp resonances upon cooling. This apparent ‘coalescence phenomenon’ was ultimately traced to significant temperature dependencies of the chemical shifts of the protons on the backbone of the diimine and the cyclohexyl protons adjacent to the nitrogen, which are accidentally isochronous at room temperature (see ESI[†] for more detail). The residual paramagnetism of 1 can be interpreted as a result of antiferromagnetic coupling between the metal and the ligands that is not strong enough to entirely preclude the occupation of the first excited spin state ($S = 1$).^{9d}

We have shown that octahedral tris(diimine) chromium complexes form an extensive electron-transfer series of the composition $[(^HL^{Cy})_3Cr]^{n+}$ ($n = 3, 2, 1, 0$). At least three, and most likely all four of these complexes feature chromium in its highly favored +III oxidation state. The redox processes are wholly ligand based, thus confirming that α -diimines belong to a growing class of non-innocent ligands that extend the redox capacity of metal complexes. This should prove useful in catalytic cycles involving multi-electron redox processes.

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