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Bond elongation in the anion radical of coordinated tetrazine ligands: A crystallographic, spectroscopic and computational study of a reduced $\{Re(CO)_3Cl\}$ complex

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The binuclear complex $[(\mu\text{-}Me_2BPTZ)(Re(CO)_3Cl)_2]$ (**1**), where Me_2BPTZ = 3,6-(5-methyl-pyridyl)-1,2,4,5-tetrazine, can be reduced by addition of bis(η^5-pentamethylcyclopentadienyl) iron(II) (decamethylferrocene, Fc*), to obtain a stable radical anion form $\mathbf{1}^{\cdot -}$. A single-crystal X-ray diffraction study of the radical anion $(\mathbf{1}^{\cdot -})(Fc^{*+})$ was conducted and compared with a computational model of the same compound in the neutral and reduced states. As such, this work presents the first structural analysis of a reduced diimine ligand that is coordinated to $\{Re(CO)_3Cl\}$ moieties. Bond-length changes within the tetrazine ring system were consistent with previously reported examples of tetrazine radicals and with calculated structures that show clear elongation of the azo-type N=N bond. Consistently atomic charge calculations indicate that the extra electron in the radical anion resides largely at the tetrazine core. A negligible change in the Re–Cl bond length is observed and computed.

1. Introduction

Tetrazine-based polypyridyl ligands provide access to coordination compounds [1] with rich electronic properties and supramolecular complexes [2] with redox-switchable behaviors [3,4]. These functionalities are derived from an accessible lowest-unoccupied molecular orbital (LUMO) such that facile one-electron reduction generates stable radical anions. Insight into the nature of these anions has been gained from electron paramagnetic resonance (EPR) [5], infrared (IR) [6], Raman [7] and UV–Vis [3,5–7] spectroscopy, whether the anion is formed using outer-sphere electron transfer agents, by electrochemistry, or by a stoichiometrically controlled self-assembly comproportionation [8,9]. The spectra provide insight on how the radical anion is distributed over the ligand and the metal moiety frameworks. Structural changes can also be used to inspect the electron's distribution by the direct observation of bond lengths. However, crystal structures of radical anions are not always readily produced. The binucleating ligand 3,6-(2-pyridyl)-1,2,4,5-tetrazine (BPTZ), which has been studied extensively by Kaim since 1985 [10], has been obtained in the solid state as the radical anion when coordinated with $\{Cu(PPh_3)_2\}^+$ [8] or $\{Cu(AsPh_3)_2\}^+$ [9] moieties. We examine a new addition to these anionic structures where two rhenium(I) tricarbonylchloro moieties, $\{Re(CO)_3Cl\}$, are coordinated to 3,6-(5-methyl-2-pyridyl)-1,2,4,5-tetrazine (**Me_2BPTZ**) to form the binuclear complex $[(\mu\text{-}Me_2BPTZ)(Re(CO)_3Cl)_2]$ (**1**) (Fig. 1) where the anion is generated by reduction with bis(η^5-pentamethylcyclopentadienyl) iron(II) (decamethylferrocene, Fc*). A similar binuclear complex, instead using BPTZ [6], has been prepared and the EPR spectrum of its radical anion analyzed [5]. Line broadening introduced by the $\{Re(CO)_3Cl\}$ moiety, however, hampered a clear picture of the singly-occupied molecular orbital (SOMO). Thus, the crystal structure analysis presented herein can complement solution-phase characterizations. As with the crystal analysis of the radical anion in the copper(I) coordination environments [8,9], the largest bond length changes in the reduced complex $\mathbf{1}^{\cdot -}$ are localized in the azo (N=N) bonds of the tetrazine core.

$Re(CO)_3Cl(NN)$ complexes, where NN is a diimine ligand, e.g., 2,2′-bipyridine, have been studied on account of their attractive photophysical and electrochemical properties. These complexes have also been shown to possess catalytic properties for the reduction of CO_2 to CO [11], a property that is reinvigorating the investigation of these compounds [11g] in the light of increasing concerns over the impact of green-house gases on global warming. The intermediates involved in this catalytic process are proposed to be a singly reduced state where the electron is initially localized on the diimine ligand, i.e., $Re(CO)_3Cl(NN^{\cdot -})$ [11] before leading to the loss of chloride. All the previous work directed at characterizing the reduced forms of these rhenium(I) complexes involved spectroscopic techniques. Herein, we report the first structural

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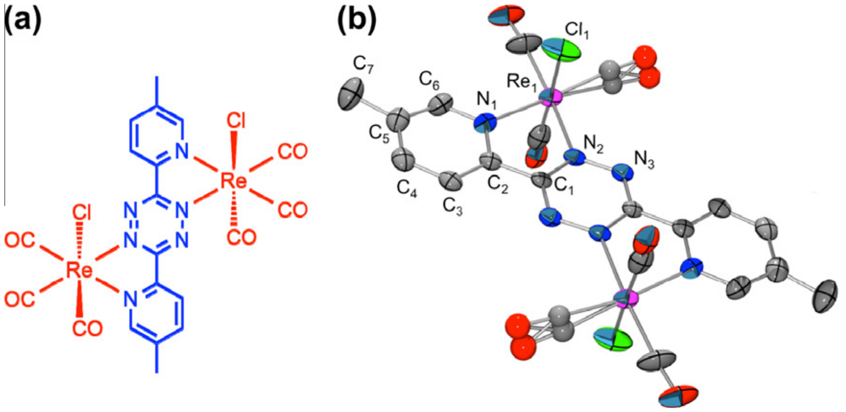

Fig. 1. (a) Representation of **1** and (b) the crystal structure (50% ellipsoids) of the reduced bis-rhenium complex $(\mathbf{1}^{\cdot-})(\mathrm{Fc}^{*+})$ (grey = C, blue = N, red = O, green = Cl, pink = Re). The (Fc^{*+}) counterion has been omitted for clarity. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

analysis of a reduced complex where the coordinated diimine ligand is **Me$_2$BPTZ**. The spectroscopic data and the bond length changes of [(μ-Me$_2$BPTZ$^{\cdot-}$)(Re(CO)$_3$Cl)$_2$] concur with the electron distribution computed using density functional theory (DFT) of the SOMO. Although localized on the tetrazine core, the SOMO extends out to the {Re(CO)$_3$Cl} moieties weakening the Re–N bonds and strengthening the Re–CO bonds. There is only a modest population of the Re–Cl σ* orbital as reflected in a Re–Cl bond length for the reduced complex $(\mathbf{1}^{\cdot-})(\mathrm{Fc}^{*+})$ that is relatively unchanged compared to related neutral complexes. This finding is consistent with the enhanced stabilities of the complexes with BPTZ-based anions relative to 2,2′-bipyridine [5,6]. Clearly, the π-acceptor properties of the NN ligands play a role in the catalytic properties of Re(CO)$_3$Cl(NN) complexes.

2. Experimental

2.1. Synthesis

The complex, [(μ-Me$_2$BPTZ)(Re(CO)$_3$Cl)$_2$] (**1**) was synthesized by refluxing two equivalents of rhenium(I) pentacarbonylchloro, Re(CO)$_5$Cl, with the **Me$_2$BPTZ** ligand in a 1:3 mixture of dichloromethane and toluene as reported in the literature [6]. The singly reduced state was obtained by addition of one equivalent of Fc* to the solution of **1** in acetonitrile. Slow diffusion of *n*-pentane into a solution of $(\mathbf{1}^{\cdot-})(\mathrm{Fc}^{*+})$ led to the isolation of single crystals for X-ray diffraction analysis.

2.2. Physical methods

Electrochemistry experiments were performed using a Princeton Applied Research Potentiostat/Galvanostat model 263A, a glassy-carbon solid disc electrode as the working electrode, Ag/AgCl as the pseudoreference electrode and a platinum wire as the counter electrode. Electrochemical grade TBAPF$_6$ obtained from Fluka was recrystallized twice from hot ethanol and dried under vacuum before use. All experiments were conducted in 0.1 M solutions of TBAPF$_6$ in CH$_2$Cl$_2$. The CV experiments were carried out under a blanket of CH$_2$Cl$_2$-saturated Ar gas. The volume of the solution was kept constant by adding CH$_2$Cl$_2$ when required. UV–Vis–NIR experiments were carried out using a Varian Cary 5000 spectrometer using a 1-cm or 1-mm path-length spectrosil quartz cell (Starna). IR spectra were recorded on a Nicolet 510P FTIR spectrometer from solutions in a cell with CaF$_2$ windows.

Table 1
Crystallographic data for $(\mathbf{1}^{\cdot-})(\mathrm{Fc}^{*+})$.

Empirical formula	$C_{20.75}H_{22.25}Cl_1Fe_1N_{3.5}O_3Re_1$
Formula weight	646.18
Crystal system	monoclinic
Space group	*C*2/*c*
T (K)	150
a (Å)	25.2919(12)
b (Å)	9.0451(4)
c (Å)	21.8405(11)
α (°)	90
β (°)	118.6130(10)
γ (°)	90
V (Å^3)	4386.2(4)
Z	8
Density (g cm^{-3})	1.957
μ (mm^{-1})	6.326
θ range (°)	1.834–30.094
Reflections collected	24 589
Completeness (%)	99.5
Number of data/restraints/parameters	6420/135/320
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0806$, $wR_2 = 0.2440$
R indices (all data)	$R_1 = 0.0947$, $wR_2 = 0.2575$
Goodness-of-fit (GOF) on F^2	0.9997
Largest peak difference and hole (e Å^3)	5.87 and −9.25

2.3. Crystallographic details

The data collection (Table 1) was carried out using Mo Kα radiation (graphite monochromator) with a frame time of 10 s and a detector distance of 5.0 cm on an Apex Kappa Duo diffractometer and measured at 150 K. The structure was solved using SIR-92 and refined (full-matrix-least squares) using the Oxford University *Crystals for Windows* system. A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms. All ordered non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms.

The structure of complex $(\mathbf{1}^{\cdot-})(\mathrm{Fc}^{*+})$ exhibits significant disorder in the carbonyl ligands, decamethylferrocenium, and the solvent acetonitrile, all of which were modeled successfully. The disorder was located at the special position and was described with a constraint that the occupancies of the major and minor components sum to 1.0. For acetonitrile, the disorder was found to behave in accordance with the special position; thus, each disordered component of the acetonitrile molecule was modeled so that the disorder atoms have occupancies of 0.5. For the rest of the disordered