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Anion Detection Driven by a Surprising Internal Hydrogen-Bonding Association in a Dinuclear Rhenium(I) Complex

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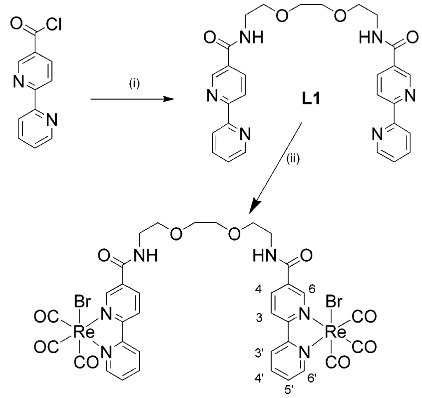
A neutral dinuclear rhenium(I) bipyridinetricarbonyl bromide complex has been investigated with a range of anions, giving a remarkable binding affinity for dihydrogenphosphate. These studies highlight that anion sensing can be achieved with structurally simple species provided that the compound adopts an unconventional conformation, through, for example, intramolecular hydrogen bonding in solution.

Despite being a fairly recent field of research, interest in bipyridylrhenium(I)-based sensors has given rise to some very interesting and potentially useful molecular devices.[1,2] In particular, systems designed to recognize anions have led to some sophisticated and intricate complexes. Elegant examples include the cationic molecular squares of Hupp and co-workers that selectively sense perchlorate,[3] the rotaxane recently reported by the Beer group that shows a selectivity for hydrogensulfate,[4] and the dimetallic diamide complex reported by Sun et al.[5] As a result, we pose the question, is it possible to achieve a good anion selectivity with a structurally simple sensor, without reliance on a preorganized structure? The detection of dihydrogenphosphate is attracting considerable interest because of its environmental impact, resulting in a large variety of intricate structures.[6] Building on the work of Beer, who reported a simple dinuclear neutral rhenium(I) complex with selectivity for dihydrogenphosphate,[7] we describe here an increase in fluorescence upon selective anion binding driven by hydrogen-bond interactions.

Scheme 1[a]



[a] (i) 2,2′-(Ethylenedioxy)diethylamine, NEt_3, dry THF. (ii) $[Re(CO)_5Br]$, dry toluene.

The synthesis of the flexible neutral dinuclear complex $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L1})]$ proved to be relatively straightforward (Scheme 1). Condensation of 5-(chlorocarbonyl)-2,2′-bipyridine[8] with 2,2′-(ethylenedioxy)diethylamine afforded ligand **L1** as a white solid in 93% yield. Reaction of **L1** with a slight excess of $Re(CO)_5Br$ produced the bis(bipyridyl)rhenium(I) tricarbonyl bromide complex $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L1})]$ as an orange solid in 80% yield. The complex was fully characterized, with the NMR spectrum demonstrating the C_2-symmetry of the system in deuterated acetone.

The square-wave voltammetry studies indicate that the reduction of $[\{Re(CO)_3Br\}_2(\mu\text{-}\mathbf{L1})]$ gives first a reversible ligand-centered process at -1.09 V, followed by an irreversible wave assigned as a metal-centered rhenium(I/0) reduction at -1.65 V, and a second ligand-centered process at -1.90 V (relative to a silver wire electrode normalized against ferrocene[9]). Surprisingly, the complex presented two separate oxidation peaks of the same intensity at 1.41 and 1.49 V attributed to a metal-centered rhenium(I/II) process (supplementary Figure 1 in the Supporting Information). This could be explained by the formation of a mixed-valence complex; however, because of the flexible nature of the ligand and the large metal separation, this is extremely unlikely. Consequently, the two metal centers must be in two different environments in solution and so giving two different rhenium(I/II) couples. Surprisingly, this was not apparent in the ^1H NMR spectrum

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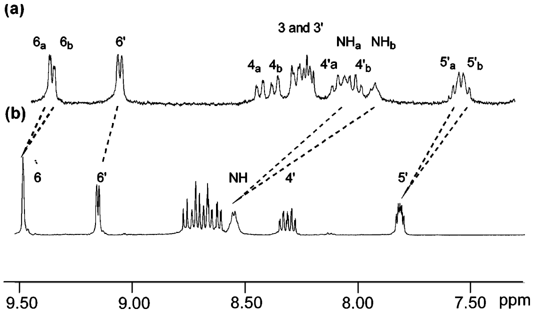


Figure 1. ^{1}H NMR spectra of [{Re(CO)$_3$Br}$_2$(μ-**L1**)]: (a) 300 MHz, CDCl$_3$, 25 °C; (b) 500 MHz, acetone-d_6, 25 °C.

Table 1. IR C═O Band for Complex [{Re(CO)$_3$Br}$_2$(μ-**L1**)]

	carbonyl (cm^{-1})	amide (cm^{-1})
solid state	2022, 1913, 1898	1659
CH$_2$Cl$_2$	2025, 1924, 1902	1673
[(n-C$_4$H$_9$)$_4$]H$_2$PO$_4$	2022, 1917, 1895	1657
[(n-C$_4$H$_9$)$_4$]NO$_3$	2025, 1923, 1902	1669

in deuterated acetone or acetonitrile. However, when the spectrum was recorded in CDCl$_3$, two sets of signals were present for the 2,2′-bipyridine groups (Figure 1).

To account for these differences, there must be a restricted conformation. In a study by Ward et al., elongation in the distance between two metal centers has been observed in a polyglycol chain, driven by a change in the polarity of the solvent.[10] In this case, a similar effect is possible; however, there is also the opportunity to form hydrogen bonds between the amide and one of the carbonyl groups on the rhenium center (Scheme 2). This could give rise to the observed inequivalence of the two coordination spheres.

IR spectra of the complex in the solid-state and a dichloromethane solution were similar; one of the equatorial carbonyl bands and a band of the axial rhenium-coordinated carbonyl groups are virtually identical. However, the second equatorial carbonyl band and the band of the CO amide group are significantly shifted (+11 and +14 cm^{-1}, respectively) in a dichloromethane solution when compared to the solid state, consistent with a change in the orientation of the hydrogen bonds (Table 1). With the addition of 4 equiv of tetra-n-butyl dihydrogenphosphate to the solution, a shift of −16 cm^{-1} for the CO amide stretch and a shift of −7 cm^{-1} for the equatorial rhenium-coordinated CO band were observed, whereas the axial rhenium-coordinated CO stretch is much less affected (−3 cm^{-1}). In comparison, the addition of 4 equiv of tetra-n-butyl nitrate resulted in virtually no change. Dihydrogenphosphate will form strong hydrogen bonds with the amidic protons, while nitrate does not. Hence, the phosphate can break the proposed intramolecular hydrogen bonding in the neutral complex. This supports the argument for a folded conformation in aprotic solvents, consistent with the ^{1}H NMR spectra, and explains the two oxidation waves in the electrochemical study. Consequently, this proposed supramolecular folding could give rise to selectivity for anions depending on their ability to break and form hydrogen bonds.

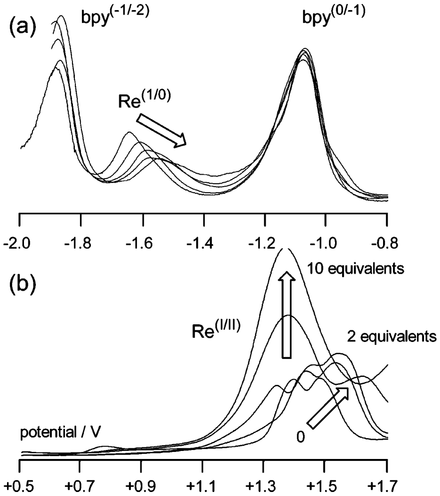
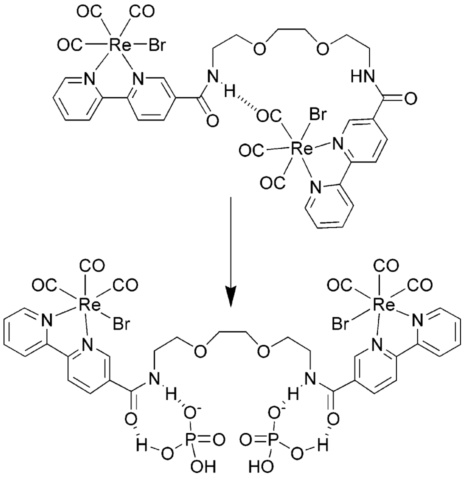


Figure 2. Square-wave electrochemical titration of [{Re(CO)$_3$Br}$_2$(μ-**L1**)] with 0−10 equiv of (a) [(n-C$_4$H$_9$)$_4$]Cl and (b) [(n-C$_4$H$_9$)$_4$]H$_2$PO$_4$ (recorded in acetonitrile, at 1 × 10^{-2} M, against a Ag/Ag$^+$ reference electrode and a 0.1 M [(n-C$_4$H$_9$)$_4$]PF$_6$ base electrolyte solution at 25 °C).

Scheme 2. Proposed Mechanism for Conformational Change upon Introduction of [(n-C$_4$H$_9$)$_4$]H$_2$PO$_4$ to [{Re(CO)$_3$Br}$_2$(μ-**L1**)]



The addition of [(n-C$_4$H$_9$)$_4$]Cl to the square-wave voltamogram of [{Re(CO)$_3$Br}$_2$(μ-**L1**)] had little affect on the two ligand-centered reductions, but the rhenium(I/0) couple shifted anodically by over 100 mV (with 10 equiv; Figure 2a). This is consistent with the rupture of a hydrogen bond between the rhenium carbonyl and the amide function, reducing the electronic density on the metal center and making the reduction easier. More extreme effects were observed with the addition of [(n-C$_4$H$_9$)$_4$]H$_2$PO$_4$ to the rhenium(I/0) couple, which is initially slightly shifted to a lower potential with 1 equiv of the anion and then anodically with the addition of further aliquots. In the oxidation processes, the two peaks attributed to the two rhenium(I/II) waves are initially shifted to a higher oxidation potential (Figure 2b), again consistent with the progressive breakage of an intramolecular hydrogen bond being replaced by hydrogen bonds. However, upon further addition, a single new oxidation peak at +1.35 V appears; the two waves coalesce and shift cathodically. We propose that this is consistent with the molecule adopting an unfolded conformation and forming strong hydrogen bonds between

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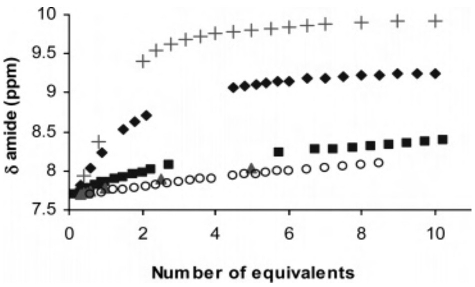

Figure 3. ^{1}H NMR of titration curves of the amide proton of [{Re(CO)$_3$Br}$_2$(μ-**L1**)] (5×10^{-3} M, 300 MHz, CD$_3$CN, 25 °C) with the addition of tetra-*n*-butylammonium salts: (+) $H_2PO_4^-$; (◆) Cl^-; (■) Br^-; (▲) HSO_4^-; (○) NO_3^-. (Note: incomplete curves are due to the overlapping of the amide proton signal with others signals, preventing precise assignment.)

$H_2PO_4^-$ and the amide group and then subsequently with both the rhenium carbonyl and the oxygen atoms of the glycol linkage. As a result, the electronic density on the metal is reduced; therefore, the oxidation potential of the folded species is higher by 60−70 mV in keeping with previous observations.[1,11]

The binding affinity of the complex with a range of anions was investigated by ^{1}H NMR spectroscopy. Because the neutral complex possesses a simple spectrum and does not precipitate with the addition of tetra-*n*-butylammonium salts, titrations were performed in acetonitrile against chloride, bromide, dihydrogenphosphate, and hydrogensulfate. The data show that the signal attributed to the amide proton shifts downfield significantly with all of the anions tested (Figure 3). Similarly, a small change in the peak position was observed for the other bipyridine protons. Dihydrogenphosphate caused the largest interactions (supplementary Figure 2 in the Supporting Information) presumably due to the strong hydrogen-bond interactions discussed previously, with the amidic proton shifting significantly by 2.6 ppm. Smaller, but surprising, upfield shifts are observed for protons 6′ and 5′ by −0.3 ppm. It is also noteworthy that protons 3, 3′, and 4 are observed to be coincident; upon an increase of the concentration of the anion, the three individual protons become discernible. Preliminary inspection of the titrations indicates that the complex interacts strongly with $H_2PO_4^-$, reasonably with Cl^-, but only weakly with Br^-, HSO_4^-, and NO_3^-. The strength of the former two anions gave interactions of sufficient strength to allow determination of the stability constants using EQNMR (using an average of three of the proton signals).[12] The complexation follows a 1:2 model, with the complex showing a much higher affinity for dihydrogenphosphate over chloride (for $H_2PO_4^-$, $\beta_2 = 3.5 \times 10^5$ M^{-1}; for Cl^-, $\beta_2 = 1.5 \times 10^4$ M^{-1}). This selectivity was confirmed by a competition experiment, where, in a 10-fold excess of [(n-C_4H_9)$_4$]Cl, 1 equiv of [(n-C_4H_9)$_4$]H_2PO_4 was added, resulting in a spectrum virtually identical with that observed for H_2PO_4 binding alone.

The electronic absorption spectrum of [{Re(CO)$_3$Br}$_2$(μ-**L1**)] gives the characteristic ligand-centered (LC) absorption at 296 nm ($\epsilon = 49\,100$ dm^{-3} mol^{-1} cm^{-1}) and a shoulder at 320 nm, as well as a metal-to-ligand charge-transfer (MLCT) at 383 nm ($\epsilon = 7360$ dm^{-3} mol^{-1} cm^{-1}). These transitions are red-shifted in comparison to [Re(CO)$_3$Br(bipy)] (LC = 288 nm; MLCT = 372 nm) because of the electron-withdrawing nature of the amide group. The addition of anions to an acetonitrile solution of the complex, however, resulted in no significant change in the absorption spectra. The complex [{Re(CO)$_3$Br}$_2$(μ-**L1**)] exhibited only a weak luminescence at 632 nm (approximately 10% of that observed for [Re(CO)$_3$Br(bipy)]) when excited at 400 nm in acetonitrile. The effect of the addition of chloride resulted in a slight decrease of the emission, compatible with a dilution effect. However, the addition of dihydrogenphosphate gave rise to a large increase in the emission (Figure 4) and a concomitant blue shift of 10 nm, related to the energy increase of the MLCT state. This dramatic behavior is reminiscent of the ruthenium complexes previously reported by Beer et al.[13] However, the rhenium complex under investigation is neutral and does not rely upon electrostatic ion-pairing interactions prevalent in the analogous ruthenium(II) complexes. This increase in the emission can be attributed to the unfolding of the structure as hydrogen bonds are broken between the amide and rhenium carbonyl as described earlier. With the removal of a strong hydrogen bond to a carbonyl directly attached to the fluorophore, a blue shift in the emission would be anticipated. Interestingly, the addition of a large quantity of a variety of other anions did not cause a significant increase in fluorescence.

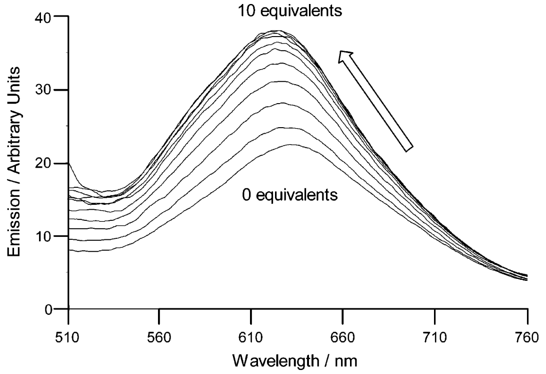

Figure 4. Increase in the emission of [{Re(CO)$_3$Br}$_2$(μ-**L1**)] (5×10^{-3} M, 300 MHz, CD$_3$CN, 25 °C) with the addition of [(n-C_4H_9)$_4$]H_2PO_4.

In summary, a new type of selective fluorescent sensing of dihydrogenphosphate has been observed in an aprotic solvent by an uncharged rhenium complex. This appears to be as a result of a conformational change driven by the breaking of intramolecular hydrogen bonds in a flexible linkage between two metal centers. At the current time, further studies are in progress to compare these complexes with the charged ruthenium(II) bipyridine analogues.

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Supporting Information Available: Experimental details and figures of various titrations. This material is available free of charge via the Internet at http://pubs.acs.org.

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