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Weak Metal–Metal Interaction Through the Short, Saturated Bridge in (μ-1,4-dicyanobicyclo[2,2,2]-octane)bis(pentaammineruthenium)$^{5+}$

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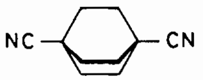
There have been numerous studies involving the use of polyatomic organic bridging ligands to study electron-transfer reactions between metal centers. For example, Nordmeyer and Taube [1] used isonicotinamide (isn) as a bridging ligand to demonstrate remote attack for electron transfer from Cr^{2+} (aq) to the $Co(NH_3)_5isn^{3+}$ center. However, studies on saturated bridging systems have not been common.

There are two fundamental problems inherent to the use of saturated bridging ligands: (1) The formation of the bridged precursor complex must be competitive with outer-sphere electron transfer, and (2) the saturated bridging ligand must maintain a suitable distance between the two metal centers. This latter problem is not limited to saturated systems, since the substitution of nicotinamide (3-pyridinecarboxamide) for isonicotinamide in the Nordmeyer/Taube system results in competitive inner- and outer-sphere electron-transfer processes [1]. The importance of rigidity in the bridging ligand has been demonstrated by Isied and Taube [2] for a similar system. Insertion of a CH_2 group in the isonicotinate bridge between the pyridine ring and the carboxylate group causes the expected rate decrease for electron transfer but not to the extent anticipated. The interpretation [2] is that overlap between the carboxalate and the pyridine π-cloud may allow a short circuit of the π-system.

A third potential problem in studying electron-transfer reactions through saturated bridging ligands is that the 'insulating' σ-system will not effectively couple the metal centers and mediate the electron transfer reaction. This ability to couple metal centers through saturated organic molecules is an important characteristic of many biological electron-transfer reactions. Specific areas in which many model systems have been studied include metallo–proteins [4] as well as long-range electron transfer across rigid, saturated hydrocarbons in models for photosynthesis [5].

We have recently investigated intramolecular electron-transfer reactions of bimetallic complexes involving saturated dinitrile ligands [6]. In such studies it is important to establish by independent experiments the ability of the intervening ligand to act as a nonconducting barrier. Taube *et al.* have shown that electrochemical studies [7], as well as studies of intervalence bands [8], can be used to deduce the ability of a ligand to couple metal atoms. Their studies have involved several types of metal atom binding sites, but of direct relevance to this report are the studies of μ-cyanogenbis(pentaammineruthenium) [9] in which very strong coupling was deduced. In contrast, a variety of conjugated and non-conjugated dinitrilobis(pentaammineruthenium) complexes have been reported in the literature [7b] which show metal/metal coupling ranging from strong to extremely weak (comproportionation constants from 4.5 × 10^4 to 4, respectively).

To investigate metal/metal interactions through a rigid, saturated, organic bridging organic bridging ligand we have prepared the ligand 1,4-dicyanobicyclo[2.2.2]octane(DCBO) and its pentaammineruthenium(III) and bis(pentaammineruthenium(III)) complexes. Preparation and characterization of the ligand and ruthenium(III) complexes will be described herein as well as the electrochemical studies that measure the ability of the metal centers to interact through the saturated bridge.



DCBO

Experimental

Materials

The diethyl succinate, 1,2-dibromoethane, propane, 1,3-dithiol, Raney Nickel catalyst, thionyl chloride, and phosphorus pentoxide used in the preparation of the ligands were analytical reagent grade and used without further purification.

Preparation of 1,4-Dicyanobicyclo[2.2.2]octane

The ligand was prepared by two routes. Most of the material we have used was made by the multistep method of Mauret [10]. The CN stretching frequency (2240 cm^{-1}) and the ^1H NMR spectrum (a single peak at 1.24 ppm *vs.* TMS in benzene) match literature values. The ^{13}C NMR spectrum has peaks at

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123.1 ppm, 28.1 ppm, and 26.2 ppm *vs.* TMS (using a JEOL FX90Q at 22.5 MHz). The mass spectrum shows major peaks at 160.2 and 79.1 m/e with an intensity ratio of 0.947/1.00 (using a Hewlett-Packard 5985 GC/MS system). After recrystallization from benzene/heptane solution, the melting point also matched the literature value.

In a second approach, some material was obtained from the precursor 1,4-dichlorobicyclo[2.2.2]-octane*. In a typical experiment, the diiodo derivative was made by the method of McKinley [11]. The product was crystallized from hexane (mp. 239–241, lit. 240.5–241.5), giving a yield of 1,4-diiodo/bicyclo[2.2.2]octane of 87%. A 200 mg sample of the diiodo species and 800 mg of CuCN were combined in 5 ml of N-methylpyrrolidinone and refluxed under N_2 overnight. The product was extracted with H_2O/CH_2Cl_2, the solvent was evaporated and the product obtained by crystallization from benzene/heptane in 53% yield.

Metal Complexes

The preparation of trifluoromethanesulfonatopentaammineruthenium(III) trifluoromethanesulfonate, $[Ru(NH_3)_5(CF_3SO_3)](CF_3SO_3)_2$, proceeds as described by Sargeson and coworkers for the analogous cobalt complex [12], with the following exceptions: (1) the ruthenium precursor, $[Ru(NH_3)_5Cl]Cl_2 \cdot 2/3H_2O$, was allowed to react for two h at 95 °C instead of one h, and (2) the product was filtered by equally dividing the reaction mixture into three medium porosity, fritted, filter funnels of 2.5 cm diameter and 10.5 cm height fitted using septum caps and under positive pressure of dry nitrogen gas. Visible spectrum (in anhydrous HCF_3SO_3): λ_{max} = 285 nm, $\epsilon = 890\ M^{-1}\ cm^{-1}$; (in sulfolane) λ_{max} = 284 nm, $\epsilon = 875\ M^{-1}\ cm^{-1}$. *Anal.* for $RuC_3H_{15}N_5F_9O_9S_3$: Calc., C, 5.68%; H, 2.38%; N, 11.05%; F, 26.97%; S, 15.15; O, 22.70; found**, C, 5.56%, H, 2.75%; N, 10.75%; F, 26.79%; S, 14.969; O, 22.91%. This material is stable in a vacuum dessiccator for months.

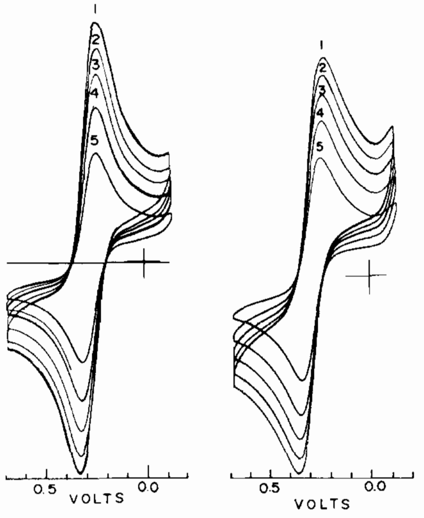
The preparation for the bimetallic complex (μ-1,4-dicyanobicyclo[2.2.2]octanebis(pentaammineruthenium(III)) trifluoromethanesulfonate involves the addition of two mol of the triflate metal complex to one mol of the ligand in a relatively inert solvent. Typical amounts used were 0.100 g of trifluoromethanesulfonatepentaammineruthenium(III) and 0.0126 g of 1,4-dicyanobicyclo[2.2.2]octane in 2.0 ml of doubly-distilled dried sulfolane in the presence of 30 1 of trifluoromethanesulfonic anhydride. The reaction required two h at 60 °C. It was monitored with the aid of cyclic voltammetry. The yield was about 49%. *Anal.* for $Ru_2C_{16}H_{42}N_{12}F_{18}S_6O_{18}$: Calc., C, 13.50%; H, 2.95%; N, 11.81%; found†, C, 13.55%; H, 2.78%; N, 11.34%. Visible-UV spectrum: λ_{max} = 298 nm, $\epsilon = 1367\ M^{-1}\ cm^{-1}$. Infrared spectrum: CN stretch 2300 cm^{-1}. This species appears to be indefinitely stable in the solid state. In aqueous solution, it undergoes slow acid-independent hydrolysis to form the Ru(III)-amido complex ($t_{1/2}$ = 5 h at 25°).

Electrochemistry

The differential pulse and cyclic voltammograms of the complexes are obtained in DMF with 0.10 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. A three electrode system consisting of a platinum wire working and auxiliary electrode and a Ag/AgCl reference electrode was used for the measurements.

Results and Discussion

The cyclic voltammograms of the mono- and bis-(pentaammineruthenium(III)) complexes of 1,4-dicyanobicyclo[2.2.2]octane are illustrated in Fig. 1. The voltammograms of the mono- and bis-systems are similar in peak position and in peak shape. Any appreciable coupling between the ruthenium centers in the Ru(III)–Ru(II) complex, formed by the one electron reduction of the bis-complex, should distort



(a) (b)

Fig. 1. Cyclic voltammograms of: (a) 1,4-dicyanobicyclo[2.2.2]octanepentaammineruthenium(III) trifluoromethanesulfonate and (b) (μ-1,4-dycyanobicyclo[2.2.2]octane)bis(pentaammineruthenium(III)) trifluoromethanesulfonate, at several scan rates (1–250 mV/sec, 2–200 mV/sec, 3–150 mV/sec, 4–100 mV/sec and 5–50 mV/sec). The potential scale is relative to a Ag/AgCl reference electrode.

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the voltammogram observed in 1(b). This is not observed and qualitatively indicates very weak coupling between ruthenium centers [13].

A change in the scan rate in the cyclic voltammetry experiment does change the peak-to-peak separation in both the bis-complex and, to a much lesser degree, the mono-complex. A decrease in scan rate decreases the splitting and can be ascribed to slow heterogeneous electron transfer between the complex and the electrode. The heterogeneous electron-transfer rate constant can be calculated from a procedure outlined by Nicholson [14] and approximates 1.5×10^{-3} cm/s^{-1} for the bis complex.

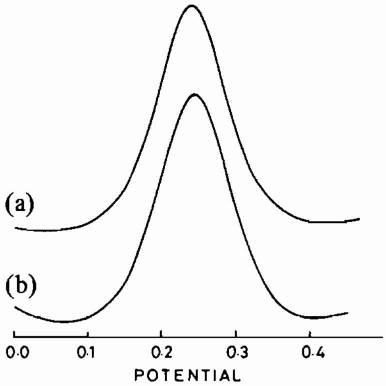

Fig. 2. Differential pulse voltammograms of: (a) 1,4-dicyanobicyclo[2.2.2]octanepentaammineruthenium(III) trifluoromethanesulfonate and (b) (μ-1,4-dicyanobicyclo[2.2.2]-octane)bis(pentaammineruthenium(III)) trifluoromethanesulfonate. The potential scale is relative to the Ag/AgCl reference electrode in DMF with 0.10 M TBAP.

The differential pulse voltammograms (Fig. 2) were obtained for the mono and bis(pentaammineruthenium(III)) complexes of 1,4-dicyanobicyclo-[2.2.2]octane as well as for pentaammineruthenium-(III) complexes of cyanobenzene and 1-adamantylcarbonitrile. The full width of half height for the bimetallic complex (107 mV) is only 15–25 mV greater than those of the various monometallic complexes. Since a Ru(II)–Ru(III) species with no appreciable coupling would be expected to have a FWHM about 37 mV greater for a bimetallic complex than for a corresponding monometallic complex [7], these results provide evidence for very restricted interaction of the Ru(II) and Ru(III) moieties. From the width of the differential pulse voltammogram [7a], $E_{1/2}$ corresponds to 50 mV which leads to $E_{1/2}{}^1$ and $E_{1/2}{}^2$ values of 0.267 and 0.217 v *vs.* Ag^+/AgCl, respectively.

$$\underset{\{3,3\}}{[(NH_3)_5Ru]_2(DCBO)^{6+}} \underset{E_{1/2}{}^{1}}{\overset{+e^-}{\rightleftharpoons}} \underset{\{2,3\}}{[(NH_3)_5Ru]_2(DCBO)^{5+}} \qquad (1)$$

$$\underset{\{2,3\}}{[(NH_3)_5Ru]_2(DCBO)^{5+}} \underset{E_{1/2}{}^{2}}{\overset{+e^-}{\rightleftharpoons}} \underset{\{2,2\}}{[(NH_3)_5Ru]_2(DCBO)^{4+}} \qquad (2)$$

From the $E_{1/2}$ value of 50 mV, a comproportionation constant, K_c, can be calculation for eqn. (3).

$$\{2,2\} + \{3,3\} \overset{K_c}{\rightleftharpoons} 2\{2,3\} \qquad (3)$$

The value for K_c is 7, which is close to the statistical value of 4 expected if there is not inherent stability of the mixed-valence species, {2, 3}.

The electrochemical results indicate very weak coupling of ruthenium atoms across DCBO, supporting the use of this ligand as a barrier to electron transfer in kinetics studies. Hammerskoi and Taube [15] have found in an independent study that the intervalence band for the 5+ bimetallic complex is of relatively high energy (680 nm) and of low absorptivity ($\epsilon \simeq 3$ M^{-1} cm^{-1}), consistent with relatively weak coupling. For the analogous *trans*-1,2-bis(4-pyridyl)ethylene, the molar extinction coefficient is 200 M^{-1} cm^{-1} at a λ_{max} = 925 nm [16].

Saturated bridging ligands, such as the bicyclooctane derivative described here and adamantane derivatives currently under study [17], are short, rigid groups which weakly couple the metal centers which are bound to them. Mechanistically, the weak coupling between metal centers makes these ligands ideally suited for studying the inner-sphere, electron-transfer reactions where the rate determining step is the actual electron transfer [18]. Practically, the ability to remove (or add) more than one electron at roughly the same potential generates a very useful class of multi-electron, redox metallopolymers [17].

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