Inorganica Chimica Acta, 36 (1979) 219–222
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Electron Transfer Reactivity of Novel Dirhenium and Dirhodium Tetraazaannulene Complexes

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Received January 29, 1979

The electron transfer reactivities of dirhenium and dirhodium carbonyl complexes of the macrocyclic ligands, 5,7,12,14-tetramethyldibenzo [b, i] [1,4,8,11] tetraaza[14]annulene, (TMTAA), dibenzo [b, i] [1,4,8,11] tetraaza[14]annulene, (TAA), and tetraphenylporphyrin, (TPP) were investigated by cyclic voltammetry and differential pulse polarography. Potentials are reported for the electrochemical generation of π cation and π anion radicals of these complexes in the solvents dichloromethane and dimethylformamide. The potential differences between the π radical reactions of the metallomacrocyclic complexes were compared to the potential differences of the π radical reactions of the free macrocycles.

Introduction

The synthesis and structural characterization of dirhodium [1] and dirhenium [2] carbonyl complexes of the macrocyclic ligand 5,7,12,14-tetramethyldibenzo[b, i] [1,4,8,11] tetraaza [14] annulene, (TMTAA) and dirhenium carbonyl complexes [3] of dibenzo[b, i] [1,4,8,11] tetraaza [14] annulene, (TAA) have recently been completed. These compounds are of interest both in terms of their structural similarity to the natural porphyrins [4] and their potential role in catalysis [5].

Complexes of H_2TAA and H_2TMTAA with a wide variety of +2 and +3 metal ions have been synthesized [6, 7]. The metal(II) or metal(III) ion replaces the two hydrogens from H_2TAA or H_2TMTAA and forms tetradentate N_4-coordinated metal complexes in a manner similar to metalloporphyrins. Resonance Raman studies of M(II)TMTAA (M = Mn, Fe, Co, Ni, Cu or Zn) reveal many similarities between the macrocyclic complexes of the TMTAA ligand and those of the metalloporphyrins [8]. Similarily, electrochemical oxidation of NiTMTAA [9] or $[Mn(III)TMTAA]^+$ [10] yields π cation radicals similar to those observed for metalloporphyrin oxidation [11]. However, to date, all comparisons between the porphyrins and synthetic macrocycles have involved monometallic M(II) and M(III) complexes in which the metal is complexed to all four donor nitrogen atoms. In this study we have investigated the redox properties of four different dimetallic M(I) macrocyclic complexes in which each metal atom is bonded to either two or three nitrogen donor atoms. We have used cyclic voltammetry to probe energy levels of the macrocyclic complexes $[Re(CO)_3]_2$TMTAA and $[Rh(CO)_2]$TMTAA and compared their half wave potentials to those obtained for the oxidation–reduction of $[Re(CO)_3]_2$TAA and the dirhenium complex of tetraphenylporphyrin, $[Re(CO)_3]_2$TPP. The four complexes differ significantly not only in terms of the number of coordinated nitrogens but also in terms of symmetry and degree of metal–metal interactions (see Fig. 1).

Experimental

Chemicals

H_2TAA, $[Re(CO)_3]_2$TAA, $[Re(CO)_3]_2$TMTAA and $[Rh(CO)_2]_2$TMTAA were prepared by literature methods [1–3].

Dichloromethane (CH_2Cl_2) (Fisher, distilled from P_2O_5) and N,N-dimethylformamide (DMF) (Fisher reagent) were used as solvents for electrochemical studies. The supporting electrolyte, tetrabutylammonium fluorborate (TBAT) (Fluka), was recrystallized from methanol and dried under reduced pressure prior to use.

Cyclic Voltammetry

Cyclic voltammograms were obtained either with a PAR 174 polarographic analyzer, in conjunction with a Houston Instruments 2000 X–Y recorder, or

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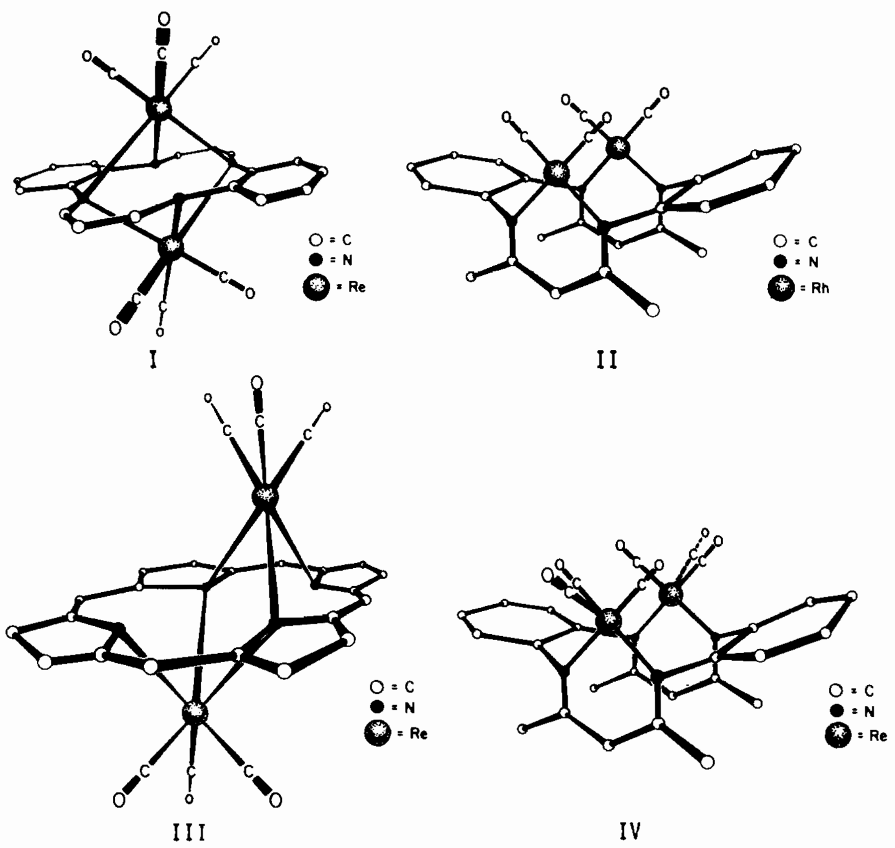

Fig. 1. Schematic pictures of $[Re(CO)_3]_2TAA$ (I), $[Rh(CO)_2]_2TMTAA$ (II), $[Re(CO)_3]_2TPP$ (III), and $[Re(CO)_3]_2TMTAA$ (IV).

a PAR 173 potentiostat and 175 Universal Programmer on an oscilloscope. A three-electrode system was used, consisting of platinum working and counter electrodes and a commercial saturated lithium calomel electrode (SLCE) that was separated from the bulk of the solution by a bridge filled with solvent and supporting electrolyte. Solutions in the bridge were changed periodically to avoid aqueous contamination from entering the cell via the SLCE. All solutions were purged of oxygen by passing purified nitrogen through them for 10 min immediately prior to running cyclic voltammograms. For dichloromethane solutions, the nitrogen was solvent saturated prior to entering the cell. After degassing, a blanket of nitrogen was maintained over the solution.

For reversible electrode reactions, the $E_{1/2}$ values were measured as that potential lying midway between the oxidation and reduction peak for a given couple. For several oxidations in DMF, no reverse cathodic peak was obtained. In these instances the potentials reported are the anodic peak potentials, E_p, recorded at 1 V/sec. These potentials were scan rate dependent and shifted anodically by approximately 30/n mV for each tenfold increase in scan rate.

Results and Discussion

Figure 2 illustrates a typical cyclic voltammogram of H_2TAA in DMF. At fast sweep rates, the half wave potentials were independent of scan rate and $i_p/v^{1/2}$ was constant as expected for a diffusion controlled oxidation–reduction. At slow sweep rates, no reverse peak was observed and E_p shifted along the potential axis by 30–40 mV per tenfold increase in scan rate. These criteria are indications of an electron transfer followed by a chemical reaction (EC) [12]. This mechanism was further confirmed by the invariant peak potential shapes of $E_p - E_{p/2} = 60 \pm 5$ mV (Fig. 2). Peak heights were approximately equal for the oxidation and the reduction processes, confirming the hypothesis that equal numbers of electrons were transferred in each reaction.

The rate constant for the following chemical reaction was largest in the absence of a metal ion. For the slow chemical reactions, reversible cyclic voltammograms could be obtained at rapid scan rates. However, in both CH_2Cl_2 and DMF the follow-up chemical reactions of $[H_2TAA]^+$ and $[H_2TMTAA]^+$ were so rapid that even at scan rates of 100 V/sec, no reverse reduction peaks were obtained. No attempt was made to ascertain the nature of the chemical reaction.

TABLE I. Half Wave Potentials of Cation and Anion Radical Formation in DMF.

Compound	$E_{1/2}$(ox) (V *vs.* SLCE)	$E_{1/2}$(red) (V *vs.* SLCE)	$\lvert E_{1/2}(ox) - E_{1/2}(red) \rvert$ (V)
H_2TPP	1.25	−0.90	2.15
H_2TAA	0.85^a	−1.80	2.60
H_2TMTAA	0.96^a	<−2.20	>3.16
$[Re(CO)_3]_2TPP^b$	1.16	−0.66	1.82
$[Re(CO)_3]_2$TAA	1.28^a	−1.09	2.37
$[Re(CO)_3]_2$TMTAA	0.80	<−2.20	>3.00
$[Rh(CO)_2]_2$TMTAA	0.61	<−2.20	>2.81

^{a}Anodic peak potential measured at a scan rate of 1.0 V/s. ^{b}Taken from reference 22 where potentials were obtained in DMF containing 0.1 *M* TBAP and are reported *vs.* SCE.

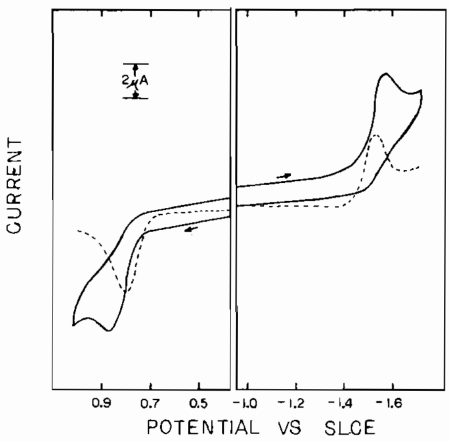

Fig. 2. Cyclic voltammogram (solid line) and differential pulse polarogram (dashed line) showing cation and anion radical formation reactions of 1.8 × 10^{-3} *M* H_2TAA in DMF, 0.1 *M* TBAT. Scan rate = 0.2 V/sec for cyclic voltammogram, 0.01 V/sec for differential pulse polarogram.

Potentials for the electrode reactions of each ligand in DMF and its corresponding dirhenium or dirhodium carbonyl complexes are listed in Table I, while Table II lists the reversible potentials of the dirhodium and dirhenium complexes in CH_2Cl_2. Changing the ligand from H_2TPP to H_2TAA has little effect on the oxidation process to yield cation radicals. In contrast, formation of the anion radical is favored by 0.90 V when the ligand is H_2TPP compared to H_2TAA and by over 1.3 V when compared to H_2TMTAA. A similar shift in reduction potential is observed on going from $[Re(CO)_3]_2$TPP ($E_{1/2}$ = −0.66 V) to $[Rh(CO)_3]_2$ TMTAA ($E_{1/2}$ > −2.20 V).

Most metal complexes with H_2TMTAA are 'saddle shaped' [4, 8, 13] (the only known exception is the palladium complex of the H_2TMTAA ligand [14]) with the *o*-phenylene rings and diiminate framework displaced in opposite directions from the plane of the four nitrogens. This saddle shape configuration allows the two Re(I) or Rh(I) atoms to sit atop the complex with both atoms in close proximity. The dimetallic complexes of TMTAA are thus symmetrical molecules where the metal atoms are each bound to two of the four adjacent donor nitrogen atoms. The metal ions reside in approximately the same plane as the pentane-diiminato chelate ring containing the two coordinated nitrogen atoms. Structural characterization of these complexes show a Rh–Rh separation of 3.086 Å [1] and a Re–Re separation of 4.11 Å [2]. The latter complex contains a water molecule between the two Re(I) atoms. In contrast, $[Re(CO)_3]_2$TPP and $[Re(CO)_3]_2$TAA contain rhenium atoms above and below the donor plane but off the S_2 axis normal to the plane. X-Ray diffraction analysis have shown them to be centrosymmetric, having two metal atoms bound to three adjacent nitrogen atoms, one above and one below the plane of the macrocyclic ligand [2, 15]. The Re–Re separation is 3.345 Å for the $[Re(CO)_3]_2$TAA complex [2] and 3.126 Å for $[Re(CO)_3]_2$TPP [15]. These distances are too long for a formal bond but still allow some metal-metal interaction. [The $[Re(CO)_3]_2$TAA complex, unlike the only other TAA complex, NiTAA [16], studied by X-ray diffraction is non planar [3]. The degree of twisting or distortion in the TAA framework of $[Re(CO)_3]_2$TAA is similar to that of the $[Re(CO)_3]_2$ TPP compound. Also, the bond distances in the 2,4-pentanediiminato side chain clearly show the nondelocalization of the macrocycle with alternating single and double bonds in the struc-

TABLE II. Half Wave Potentials for Oxidation of Several Dirhenium and Dirhodium Carbonyl Complexes in CH_2Cl_2.

Compound	$E_{1/2}$ (volt *vs.* SLCE)
$[Rh(CO)_2]_2$TMTAA	0.50
$[Re(CO)_3]_2$TMTAA	0.69
$[Re(CO)_3]_2$TAA	1.11
$[Re(CO)_3]_2$TPP	1.01

ture of $[Re(CO)_3]_2TAA$. NiTAA on the other hand, shows a delocalized side chain. These factors lend structural uniqueness to $[Re(CO)_3]_2TAA$ as a TAA compound.

It has been reported for octaethylporphyrin complexes [17], and verified with other metalloporphyrin complexes [18–21], that the potential difference between cation and anion radical formation, $|E_{1/2}(ox) - E_{1/2}(red)|$, is equal to 2.25 ± 0.15 V. With several exceptions, this value is independent of metal ion electron transfers and holds true for a number of different natural and synthetic porphyrins containing metals of +2, +3 or +4 oxidation state. Recently Gross and Jordan [22] showed that this potential difference decreased to 1.82 V for $[Re(CO)_3]_2TPP$ oxidation–reduction and that the change was due almost entirely to changes associated with the lowest unoccupied molecular orbital (LUMO). Our results with H_2TMTAA, $[Re(CO)_3]_2TMTAA$ and $[Rh(CO)_2]_2TMTAA$ also indicate a change in the LUMO but in this case, in a direction opposite to that observed for the porphyrin complexes. Surprisingly $[Re(CO)_3]_2TAA$ behaves very similarly to most metalloporphyrins [11] in regards to the potential separation between the π radical reactions. The oxidation potential of 1.11 Volt in CH_2Cl_2 is almost identical to that for $[Re(CO)_3]_2TPP$ and when combined with the $E_{1/2}(red) = -1.09$ in DMF yields an $|E_{1/2}(ox) - E_{1/2}\ red| = 2.20$ V.

Of special interest is a comparison of the $[Rh(CO)_2]_2TMTAA$ with the $[Re(CO)_3]_2TMTAA$. Both compounds are more easily oxidized than the uncomplexed ligand. However, the reversible half wave potential for oxidation of $[Rh(CO)_2]_2$ TMTAA is anodic of $[Re(CO)_3]_2TMTAA$ by 0.19 V. This is opposite that predicted from the electronegativities of the two metal ions. For a series of M(II) to M(IV) metallooctaethylporphyrins, the difficulty of porphyrin ring oxidation is directly proportional to the negative charge on the porphyrin ligand, and for a given metal oxidation state, half wave potentials for cation radical formation can be linearly related to the electronegativities of the central metal [17]. Since the trend in potentials is reversed for the tricarbonyl rhenium(I) and dicarbonyl rhodium(I), this would imply that between the two complexes differences in metal–metal interaction exist and that the interactions of the metal orbitals with those of the macrocyclic ring differ. Electrochemical studies of other mono and dimetallic complexes of H_2TMTAA are now underway to see if similar trends exist between oxidation potentials and degree of metal–metal interaction.

Acknowledgements

Support from the Robert A. Welch Foundation (K.M.K.) and the Office of Naval Research (M.T.) is gratefully acknowledged.

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