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Electrochemical Generation and Solution Properties of the $[Re_2(O_2CR)_4X_2]^-$ Anions (X = Cl, Br, I)[1]

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The electrochemical reduction of several series of rhenium(III) carboxylate complexes of the type $Re_2(O_2CR)_4X_2$, where R = an alkyl or aryl group and X = Cl, Br, or I, has been investigated by using cyclic voltammetry and coulometry techniques. Dichloromethane solutions of these complexes are reduced to the monoanions $[Re_2(O_2CR)_4X_2]^-$. The reduction potentials show a linear dependence upon the nature of the halogen (becoming more negative in the order I < Br < Cl) and upon the Taft σ^* parameter for R. In the case of the bromide and iodide complexes, release of free halide ion (plus the formation of an unidentified rhenium complex) occurs following electrolysis probably via the reaction of $[Re_2(O_2CR)_4X_2]^-$ with adventitious oxygen. Otherwise, the reduced anions are quite stable and ESR spectral measurements show that they all possess the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ electronic ground-state configuration. There is no obvious correlation between the voltammetric half-wave potentials ($E_{1/2}$) and the energies of the electronic absorption bands ($10^2 < \epsilon < 10^3$) which occur in the spectral region between 400 and 580 nm. The possible consequences of this as regards the assignment of the $\delta \rightarrow \delta^*$ transition are discussed.

Introduction

The redox chemistry of complexes containing metal–metal multiple bonds is currently under study in our laboratory with the object of exploring to what extent these bonds can undergo changes in bond order without metal–metal bond cleavage occurring. Among the many interests in such molecules is their role as 4-electron (or greater) oxidants or reductants. Thus we recently reported[2] that the rhenium(IV) anion $Re_2Cl_9^-$, formally derived from the Re_2^{8+} core and therefore possessing a Re–Re triple bond ($(\sigma)^2(\pi)^4$ ground-state configuration), could be reduced to the rhenium(II) complex $Re_2Cl_4(PEt_3)_4$. The latter species also possesses a Re–Re triple bond, but one which is best considered[3] as $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2$. This reaction is the first example of a 4-electron reduction of a metal dimer which is not accompanied by the disruption of the strong metal–metal bond.

The electrochemical properties of molecules containing metal–metal multiple bonds constitute one important means of exploring their redox characteristics. Our earlier studies[4–6] on the electrochemistry of the $Re_2X_4(PR_3)_4$, $Re_2X_4(dppe)_2$, and $Re_2X_4(arphos)_2$ dimers (X = Cl, Br, I; dppe = 1,2-bis(diphenylphosphino)ethane; arphos = 1-(diphenylphosphino)-2-(diphenylarsino)ethane) led to the discovery of a novel series of coupled electrochemical–chemical reactions and the isolation and characterization of salts of the oxidized paramagnetic cations $[Re_2X_4(PEt_3)_4]^+$ (X = Cl, Br), $[Re_2Cl_4(dppe)_2]^+$, and $[Re_2Cl_4(arphos)_2]^+$. Related electrochemical measurements on the rhenium(III) dimers $Re_2X_6(PR_3)_2$, species which contain a Re–Re quadruple bond, revealed[5] that reduction to paramagnetic $[Re_2X_6(PR_3)_2]^-$ ("isoelectronic" with $[Re_2X_4(PR_3)_4]^+$) was readily accomplished ($E_{1/2}$ values of between +0.06 and −0.13 V vs. the saturated sodium chloride calomel electrode).

More recently, we have chosen to carry out related studies on an extensive series of rhenium(III) carboxylate dimers of the type $Re_2(O_2CR)_4X_2$ with the following objectives: first, to ascertain through cyclic voltammetry the dependence of the $E_{1/2}$ value(s) upon the nature of R and X; second, to establish whether the electronic structures of these complexes are dependent upon R and X by measuring the ESR spectra of any paramagnetic reduction products; finally, to attempt the isolation of salts of the $[Re_2(O_2CR)_4X_2]^-$ anions. Although we were unsuccessful in accomplishing the last objective, we have now completed the electrochemical and ESR spectral studies, and we report herein the significant findings of this work.

Experimental Section

Starting Materials. The complexes $(Bu_4N)_2Re_2X_8$, where X = Cl or Br, were prepared according to the standard method.[7] Tetra-*n*-butylammonium hexafluorophosphate (TBAH) was obtained by reacting tetra-*n*-butylammonium iodide with KPF_6 in hot water. The product was recrystallized from aqueous ethanol and dried in vacuo. Gaseous HBr and HI were obtained from Matheson Gas Products.

Solvents used for electrochemical experiments were of the highest purity commercially available (Fisher Scientific Co.) and were used without further purification. The CH_2Cl_2 used in obtaining the ESR glass spectra was freshly distilled and stored under N_2 in the dark prior to use.

Synthesis of the Rhenium(III) Carboxylates. The alkyl carboxylate complexes of the type $Re_2(O_2CR)_4X_2$, where X = Cl or Br, were prepared from $(Bu_4N)_2Re_2Cl_8$ and $(Bu_4N)_2Re_2Br_8$ by the usual procedure.[8] The related aryl carboxylates were prepared by fusing, under an atmosphere of nitrogen gas, the appropriate aromatic carboxylic acid with the rhenium(III) acetate, $Re_2(O_2CCH_3)_4X_2$, where X = Cl or Br.[8] A sample of $Re_2(O_2CCH_3)_4I_2$ was available from an earlier preparation[9] via the reaction of $(Bu_4N)_2Re_2I_8$ with acetic acid/acetic anhydride.

During the course of the present investigation we discovered that a particularly convenient synthesis of the bromo- and iodorhenium(III) carboxylates was through the reaction of the appropriate chloro complex $Re_2(O_2CR)_4Cl_2$ with HBr(g) or HI(g) as the following procedure indicates. A well-ground sample of $Re_2(O_2CR)_4Cl_2$ (0.30 g) was placed in a large test tube and the reaction tube flushed with nitrogen gas for 20 min. The nitrogen was then replaced by a flow of HX gas for ~15 min and the test tube cooled in a slush bath (acetone/dry ice for HBr, cyclohexanone/dry ice for HI) thereby permitting ~15 mL of HX to condense onto the sample. The reaction tube was *slowly* warmed to room temperature, to evaporate the excess HX, and the system again flushed with nitrogen gas. The solid product was washed twice with 5-mL poritons of ethanol and anhydrous ether and then dried in vacuo. In all instances yields were in the range 80–95%.

$Re_2(O_2CC_2H_5)_4Br_2$. Anal. Calcd for $C_{12}H_{20}Br_2O_8Re_2$: Br, 19.38. Found: Br, 19.80.

$Re_2(O_2CCMe_3)_4Br_2$. Anal. Calcd for $C_{20}H_{36}Br_2O_8Re_2$: Br, 17.06. Found: Br, 17.29.

$Re_2(O_2CCH_2Ph)_4Br_2$. Anal. Calcd for $C_{32}H_{28}Br_2O_8Re_2$: Br, 14.90. Found: Br, 15.55.

$Re_2(O_2CPh)_4Br_2$. Anal. Calcd for $C_{28}H_{20}Br_2O_8Re_2$: Br, 15.72. Found: Br, 16.00.

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[1] This paper is Part 16 of the series "Studies on Metal Carboxylates". For Part 15 see: Glicksman, H. D.; Walton, R. A. *Inorg. Chim. Acta* **1979**, *33*, 255.

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Table I. Electronic Absorption Spectra of Rhenium(III) Carboxylates[a]

complex	abs max,[b] nm						
$Re_2(O_2CCH_3)_4Cl_2$[c,d]	500	420					
$Re_2(O_2CCH_3)_4Br_2$[c,d]	507	(420)					
$Re_2(O_2CCH_3)_4I_2$[c,e]		505					
$Re_2(O_2CCH_2Cl)_4Cl_2$[c]	496	(395)					
$Re_2(O_2CCH_2Br)_4Br_2$[c]	505	(420)					
$Re_2(O_2CC_2H_5)_4Cl_2$	498	403				276	
$Re_2(O_2CC_2H_5)_4Br_2$	500	418		313			
$Re_2(O_2CC_2H_5)_4I_2$	(515)	486	394		302		250
$Re_2(O_2CC_3H_7)_4Cl_2$	498	398				278	
$Re_2(O_2CC_3H_7)_4Br_2$	498	415		315			
$Re_2(O_2CC_3H_7)_4I_2$	(515)	487	394		302		251
$Re_2(O_2CCMe_3)_4Cl_2$	497	402				275	
$Re_2(O_2CCMe_3)_4Br_2$	498	417		314			
$Re_2(O_2CCMe_3)_4I_2$	(510)	485	395		302		251
$Re_2(O_2CCH_2Ph)_4Cl_2$	501	403				276	
$Re_2(O_2CCH_2Ph)_4Br_2$	503	420		318			

complex	abs max,[b] nm							
$Re_2(O_2CCH_2Ph)_4I_2$	(520)	492	401			300		248
$Re_2(O_2CPh)_4Cl_2$	533	(415)		(320)	305		(280)	244
$Re_2(O_2CPh)_4Br_2$	537	(415)			318			245
$Re_2(O_2CPh)_4I_2$	547	(480)	400	(323)	310	(300)		248
$Re_2(O_2CC_6H_4\text{-}p\text{-}CH_3)_4Cl_2$	542	(450)		(324)	312		(275)	253
$Re_2(O_2CC_6H_4\text{-}p\text{-}CH_3)_4Br_2$	545	(420)		(325)	315			258
$Re_2(O_2CC_6H_4\text{-}p\text{-}CH_3)_4I_2$	555	(470)	395	(324)	313	(300)	(~270)[f]	254
$Re_2(O_2CC_6H_4\text{-}p\text{-}OCH_3)_4Cl_2$	561	(457)		332	323		270	
$Re_2(O_2CC_6H_4\text{-}p\text{-}OCH_3)_4Br_2$	555			(332)	318			259
$Re_2(O_2CC_6H_4\text{-}p\text{-}OCH_3)_4I_2$	573	(470)	392	(335)	325	(310)	274	252

[a] All spectra recorded on dichloromethane solutions unless otherwise stated. [b] Shoulders in parentheses. [c] Spectra recorded on the solids (as Nujol mulls or using the diffuse reflectance technique). [d] Data taken from ref 8. [e] Data taken from ref 9. [f] This feature is actually two closely spaced shoulders at 272 and 266 nm.

$Re_2(O_2CC_6H_4\text{-}p\text{-}CH_3)_4Br_2$. Anal. Calcd for $C_{32}H_{28}Br_2O_8Re_2$: Br, 14.90. Found: Br, 15.62.

$Re_2(O_2CC_2H_5)_4I_2$. Anal. Calcd for $C_{12}H_{20}I_2O_8Re_2$: C, 15.69; H, 2.19; I, 27.63. Found: C, 15.86; H, 2.07; I, 27.44.

$Re_2(O_2CC_3H_7)_4I_2$. Anal. Calcd for $C_{16}H_{28}I_2O_8Re_2$: C, 19.72; H, 2.90; I, 26.04. Found: C, 19.79; H, 2.95; I, 26.22.

$Re_2(O_2CCMe_3)_4I_2$. Anal. Calcd for $C_{20}H_{36}I_2O_8Re_2$: I, 24.62. Found: I, 24.57.

$Re_2(O_2CCH_2Ph)_4I_2$. Anal. Calcd for $C_{32}H_{28}I_2O_8Re_2$: C, 32.94; H, 2.42; I, 21.75. Found: C, 32.66; H, 2.37; I, 21.46.

$Re_2(O_2CPh)_4I_2$. Anal. Calcd for $C_{28}H_{20}I_2O_8Re_2$: I, 22.85. Found: I, 23.29.

$Re_2(O_2CC_6H_4\text{-}p\text{-}CH_3)_4I_2$. Anal. Calcd for $C_{32}H_{28}I_2O_8Re_2$: C, 32.94; H, 2.42; I, 21.75. Found: C, 30.93; H, 2.42; I, 22.22.

$Re_2(O_2CC_6H_4\text{-}p\text{-}OCH_3)_4I_2$. Anal. Calcd for $C_{32}H_{28}I_2O_{12}Re_2$: I, 20.62. Found: I, 20.72.

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) were recorded as Nujol mulls on a Beckman IR-12 spectrophotometer. Far-infrared spectra (500–80 cm^{-1}) were recorded as Nujol mulls between polyethylene plates by using a Digilab FTS-20B Fourier transform infrared spectrophotometer. Electronic absorption spectra were recorded as CH_2Cl_2 solutions on Cary 14 and Cary 17B spectrophotometers. A Hewlett-Packard 5950A ESCA spectrometer equipped with monochromated Al $K\alpha_{1,2}$ radiation (1486.6 eV) was used to obtain the X-ray photoelectron spectra (XPS). An electron "flood-gun" was used to reduce the charging effects. The samples were dispersed on gold-plated copper plates and the binding energies were referenced to the C 1s peak at 285.0 eV for contaminant carbon. X-Band ESR spectra of CH_2Cl_2 glasses were recorded at −180 °C with a Varian E-109 spectrometer.

Electrochemical measurements were made on dichloromethane solutions containing 0.2 M tetra-*n*-butylammonium hexaflurophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values (taken as $(E_{p,a} + E_{p,c})/2$) are referenced to the saturated potasssium chloride calomel electrode (SCE) at 22 ± 2 °C and are uncorrected for junction potentials. Cyclic voltammetry experiments were performed by using a BioAnalytical systems Inc. Model CV-1A instrument in conjunction with a Hewlett-Packard Model 7035B x-y recorder. Potential control for coulometric experiments was maintained with a potentiostat purchased from BioAnalytical Systems Inc. Values of *n*, where *n* is the total number of equivalents of electrons transferred in exhaustive electrolyses at constant potentials, were calculated after measuring the total area under current vs. time curves for the complete reactions. The reactions were judged to be complete when the current had fallen below 1% of the initial value. All voltammetric measurments were made at a platinum bead electrode in solutions deaerated in a stream of dry nitrogen.

Analytical Procedures. Elemental microanalyses were performed by Dr. C. S. Yeh of the Purdue University microanalytical laboratory.

Results and Discussion

New Synthetic Procedure. The synthesis of chloro- and bromorhenium(III) carboxylates $Re_2(O_2CR)_4X_2$ has in the past been satisfactorily accomplished via the corresponding octahalodirhenate(III) salts $(Bu_4N)_2Re_2X_8$.[8,10] The only previous reports on related iodo complexes are (1) the isolation of $Re_2(O_2CC_3H_7)_4I_2$ by the reaction of $Re_2(O_2CC_3H_7)_4(H_2O)_2SO_4$ with 55% HI[8] and the related formation of $Re_2(O_2CPh)_4I_2$ (admixed with $Re_2(O_2CPh)_2I_4$) from $Re_2(O_2CPh)_4Cl_2$[11] and (2) the direct conversion of the recently prepared $(Bu_4N)_2Re_2I_8$ to the acetate and pivalate complexes $Re_2(O_2CCH_3)_4I_2$ and $Re_2(O_2CCMe_3)_4I_2$.[9] Our discovery of the very convenient, rapid, and high yield conversion of $Re_2(O_2CR)_4Cl_2$ to $Re_2(O_2CR)_4I_2$ by liquid HI constitutes the first general synthetic route to these derivatives, a procedure which is equally adaptable to the preparation of $Re_2(O_2CR)_4Br_2$ using liquid HBr. Where comparisons are possible, we have found that the complexes prepared by this liquid HX method generally had spectroscopic properties which were identical with those exhibited by samples of the complexes prepared by alternative procedures.[8,9]

In all instances the low-frequency infrared spectra of the iodide complexes exhibit a strong absorption at 118 ± 5 cm^{-1} which is assigned to ν(Re–I). Available evidence[12,13] indicates that the related ν(Re–Cl) and ν(Re–Br) modes of $Re_2(O_2CR)_4Cl_2$ and $Re_2(O_2CR)_4Br_2$ occur in the ranges of 245–220 and 150–134 cm^{-1}, respectively. Further spectral characterizations on $Re_2(O_2CR)_4I_2$ included measurements of XPS core electron binding energies of several such complexes. For the derivatives where R = C_2H_5, CH_2Ph, $C_6H_4\text{-}p\text{-}CH_3$, and $C_6H_4\text{-}p\text{-}OCH_3$, the Re $4f_{7/2}$ binding energies are identical (43.6 ± 0.1 eV) and agree closely with the values of 43.7, 43.8, and 43.4 eV reported previously for the acetate series $Re_2(O_2CCH_3)_4X_2$ (X = Cl, Br, I).[9,14]

Electronic Absorption Spectra of $Re_2(O_2CR)_4X_2$. As a preliminary to our electrochemcial measurements we have made a comparison of the electronic absorption spectra of several series of $Re_2(O_2CR)_4X_2$ (X = Cl, Br, I) complexes. This is the first time that data for the iodide complexes have been available. Our ultimate objective was to ascertain whether any trends in the spectral properties (including the location of the $\delta \rightarrow \delta^*$ transition) could be correlated with the $E_{1/2}$ values which are to be discussed later.

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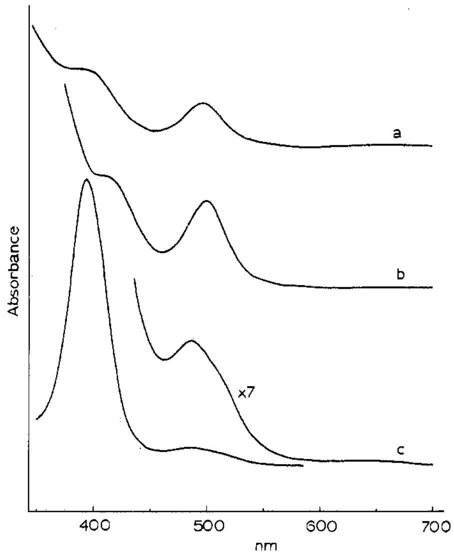

Figure 1. Electronic absorption spectra (350–700 nm) of dichloromethane solutions of $Re_2(O_2CC_2H_5)_4X_2$: (a) X = Cl; (b) X = Br; (c) X = I.

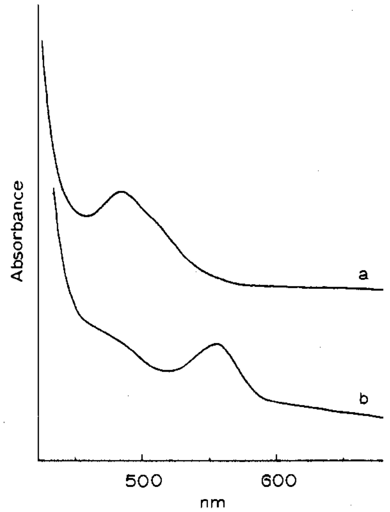

Figure 2. Electronic absorption spectra (430–680 nm) of dichloromethane solutions of (a) $Re_2(O_2CCMe_3)_4I_2$ and (b) $Re_2(O_2CC_6H_4\text{-}p\text{-}CH_3)_4I_2$.

The spectra of dichloromethane solutions of seven groups of such complexes are presented in Table I together with certain solid-state spectral data for the acetate complexes $Re_2(O_2CCH_3)_4X_2$ (X = Cl, Br, I)[8,9] and the haloacetates $Re_2(O_2CCH_2Cl)_4Cl_2$ and $Re_2(O_2CCH_2Br)_4Br_2$. Figures 1 and 2 show the spectral features of a selection of these complexes in the region between 400 and 650 nm. The spectra of several of the chloro and bromo derivatives have been reported previously by Cotton and co-workers[8,10] and the agreement with our data is generally very good. However, in two instances, namely, $Re_2(O_2CCH_2Cl)_4Cl_2$ and $Re_2(O_2CC_3H_7)_4I_2$, we observed spectra which were different from those described in the literature.[8] Since the spectrum we measured for $Re_2(O_2CC_3H_7)_4I_2$ (Table I) is virtually the same as that for the other iodides, we are confident that we have observed the spectrum of the authentic complex. In the case of $Re_2(O_2CCH_2Cl)_4Cl_2$, we obtained a spectrum (λ_{max} at 395 and 496 nm) which is similar to that exhibited by the other alkyl carboxylates $Re_2(O_2CR)_4Cl_2$ in contrast to the results of an earlier investigation (λ_{max} at 418 and 560 nm).[8]

The extinction coefficients of the absorption bands in the spectra of the chlorides and bromides are similar to the values reported previously,[8,10] with $\epsilon \lesssim 200$ for the two lowest energy bands listed in Table I. In the case of the iodide complexes of the alkyl carboxylic acids, the 490-nm absorption, which overlaps another absorption (seen as a shoulder at ~515 nm), has $\epsilon \sim 1500$. In the related aryl carboxylate complexes, these low-energy absorptions no longer overlap to the same extent and, consequently, the value of ϵ decreases to 600–900. The higher energy absorption bands at ~400 and ~250 nm in the spectra of $Re_2(O_2CR)_4I_2$ have ϵ values considerably in excess of 15 000.

The spectra of the chlorides and bromides are remarkably similar, the main differences being a small shift in the band at ~400 nm and, the expected red shift in the higher energy charge-transfer band (presumably halogen (π) → Re)[10] from ~275 nm for the chlorides to ~315 nm for the bromides.

A comparison of the spectra of the alkyl carboxylates $Re_2(O_2CR)_4I_2$ with those of their chloride and bromide analogues reveals some interesting differences. As expected, the intense halogen (π) → Re charge-transfer band shifts to still lower energies in the case of the iodides—the band at 400 nm (Table I) is presumably the counterpart of that at ~315 nm (Br) and ~275 nm (Cl). Also, the two lowest energy bands (Table I) move much closer together, the one at ~515 nm appearing as a shoulder on the more intense absorption at ~490 nm. It thus appears as if all the alkyl carboxylate complexes possess an absorption band close to 500 nm and a second low-energy band which shifts as the halogen atom is varied–400 nm for Cl, 420 nm for Br, and 490 nm for I. Collins et al[10] have suggested that the $\delta \rightarrow \delta^*$ transition may be assignable to the band at ~500 nm (see Table I and Figure 1). This is reasonable in the light of the insensitivity of this absorption band to the nature of the halogen and the results of studies[10] on the temperature dependence of the band shape.

A change from the alkyl to aryl carboxylates is reflected by several systematic changes in the spectra. As expected, the spectra in the region between 350 and 250 nm become more complex with the introduction of the phenyl rings, but it appears that the halogen (π) → Re charge-transfer transitions remain at about the same positions (275 nm for Cl, 315 nm for Br, and 400 nm for I) as for the alkyl carboxylate complexes, although overlap with the internal ligand absorptions of the aryl carboxylate ligands is apparent in the case of the bromides. The most striking difference is the marked decrease in energy of the lowest energy transition (that between 530 and 580 nm) relative to its position in the alkyl carboxylates. For a particular halide the energy of this band decreases in the order Ph > $C_6H_4\text{-}p\text{-}CH_3$ > $C_6H_4\text{-}p\text{-}OCH_3$, whereas for any aryl carboxylate we find (as for the case with the alkyl carboxylates) that the energies of the two lowest bands are as follows, Cl ~ Br > I.

If the lowest energy band is $\delta \rightarrow \delta^*$, as suggested by Collins et al.,[10] then its red shift upon replacing an alkyl by an aryl substituent is in accord with the spectral changes observed in the related spectra of $Mo_2(O_2CR)_4$. The $\delta \rightarrow \delta^*$ transition of $Mo_2(O_2CCH_3)_4$ at 443 nm[15-18] shifts to 520 nm in the benzoate complex $Mo_2(O_2CPh)_4$.[19] These shifts may reflect

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(15) There has been considerable controversy concerning the assignment of the $\delta \rightarrow \delta^*$ transition of $Mo_2(O_2CCH_3)_4$.[16] The weak 440-nm band had been assigned[16] as $\delta \rightarrow \pi^*$ but, more recently,[17] polarized single-crystal spectral studies have led to its interpretation as the $\delta \rightarrow \delta^*$ transition with an inordinately low transition moment. The low-temperature spectra of $Mo_2[(CH_2)_2P(CH_3)_2]_4$ exhibit a well-resolved band at ~500 nm, displaying vibrational structure, which has likewise[18] been attributed to the $\delta \rightarrow \delta^*$ transition.

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Table II. $E_{1/2}$ Values for the Rhenium(III) Carboxylates, $Re_2(O_2CR)_4X_2$, in Dichloromethane[a]

R	Cl	Br	I
Me_3C	−0.42	−0.35	−0.31
C_2H_5	−0.34	−0.27	−0.20
C_3H_7	−0.34	−0.28	−0.21
$PhCH_2$	−0.24	−0.18	−0.13
p-$CH_3OC_6H_4$	−0.42	−0.35	−0.31
p-$CH_3C_6H_4$	−0.35	−0.29	−0.26
Ph	−0.27	−0.22	−0.18

[a] In volts vs. SCE with a Pt-bead working electrode and 0.2 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte.

different degrees of mixing of symmetry-adapted linear combinations of carboxylate π^* orbitals with the metal–metal δ orbital. Martin et al.[17] have pointed out that one of these combinations is of the same symmetry (B_{2g}) as the δ orbital, thereby providing a mechanism by which the latter may be stabilized, the stabilization of the δ orbital in the aryl carboxylates being less than for the alkyl carboxylate complexes. Although this could explain[17] why the $\delta \rightarrow \delta^*$ transition energy is somewhat greater for $Mo_2(O_2CR)_4$ than for $Mo_2Cl_8^{4-}$, it seems unlikely that this can account for the fact that the $\delta \rightarrow \delta^*$ energies are so much greater for $Re_2(O_2CR)_4X_2$[10] (Table I) than for $Re_2X_8^{2-}$.[9,20] We shall return to the question of the assignment of the $\delta \rightarrow \delta^*$ transition after consideration of the electrochemical results.

Electrochemical Studies on $Re_2(O_2CR)_4X_2$. Voltammetric half-wave potentials vs. SCE for a series of rhenium(III) carboxylate complexes in dichloromethane are presented in Table II. We now have complete data for complexes of the type $Re_2(O_2CR)_4X_2$, where X = Cl, Br, or I, derived from seven carboxylic acids. In all instances, the complexes exhibit a single reduction, $Re_2(O_2CR)_4X_2 + e^- \rightarrow [Re_2(O_2CR)_4X_2]^-$. For sweep rates ($v$) between 50 and 400 mV/s, $i_{p,a}/i_{p,c} \simeq 1$, and the ratio $i_p/v^{1/2}$ was constant for sweep rates between 50 and 200 mV/s in accord with diffusion control. The potential separation between the anodic and cathodic peaks, ΔE_p, was greater than 60 mV and varied with sweep rate, a clear indication of a quasi-reversible electron-transfer process.[21,22] For example, ΔE_p varied between 65 and 85 mV for v between 50 and 400 mV/s in the case of $Re_2(O_2CCH_2Ph)_4Cl_2$ and between 85 and 135 mV for these same scan rates for $Re_2(O_2CC_3H_7)_4I_2$.

In addition to the data in Table II, we have also studied the acetate complex $Re_2(O_2CCH_3)_4I_2$ by cyclic voltammetry (its chloride and bromide analogues are insoluble) and find its $E_{1/2}$ value to be −0.24 V under experimental conditions comparable to those used for the other complexes listed in Table II.

There is one previous literature report dealing with an electrochemical study on a rhenium(III) carboxylate.[23] This describes the use of rotating disk polarography and cyclic voltammetry to elucidate the redox chemistry of the benzoate, $Re_2(O_2CPh)_4Cl_2$. For this complex, $E_{1/2}$ = −0.26 V vs. SCE for acetonitrile solutions and −0.28 V for dichloromethane solutions (with 0.1 M Bu_4NClO_4 as supporting electrolyte),[23] values which are in excellent agreement with our data for this same complex ($E_{1/2}$ = −0.27 V). Comparisons will be made between this earlier study[23] and our results.

The cyclic voltammograms of dichloromethane solutions of the chloride complexes showed no evidence for the presence of free chloride ion which, for dichloromethane solutions of Et_4NCl, is easily identified by its oxidation wave ($E_{p,a} \simeq +1.15$ V, with 0.2 M TBAH as supporting electrolyte). The cyclic voltammogram of $Re_2(O_2CC_2H_5)_4Cl_2$, which is shown in Figure 3a, is typical of the chloride complexes. Cotton and Pedersen[23] had observed a second (irreversible) reduction at approximately −1.1 V vs. SCE for acetonitrile solutions of $Re_2(O_2CPh)_4Cl_2$. We believe that this feature is due to an impurity since it is observed for only a few of the chloride complexes and its presence even then is erratic, depending upon the particular synthetic batch of sample used.

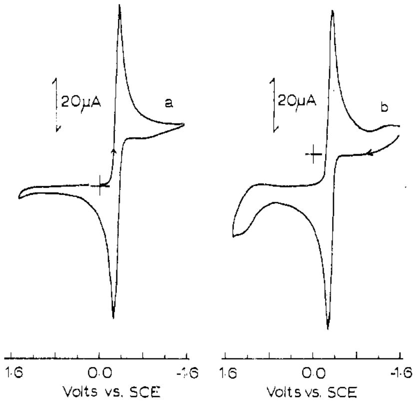

Figure 3. Cyclic voltammograms in 0.2 M TBAH–dichloromethane of $Re_2(O_2CC_2H_5)_4Cl_2$: (a) before and (b) after exhaustive electrolysis at −0.5 V.

Cotton and Pedersen[23] had reported that the addition of an excess of chloride ion to dichloromethane solutions of $Re_2(O_2CPh)_4Cl_2$ inhibits the reduction at −0.27 V (Table II) and leads to a series of irreversible reductions at more negative potentials. In contrast to this, we observed no dependence whatsoever of this reduction upon the concentration of added chloride (Et_4NCl). This was also confirmed by related cyclic voltammetric measurements on $Re_2(O_2CC_3H_7)_4Cl_2$ in the presence of excess chloride. Accordingly, this observation coupled with the absence of "free" chloride ion in the cyclic voltammograms of the chloride complexes shows that the dissociation $Re_2(O_2CR)_4Cl_2 \rightleftarrows [Re_2(O_2CR)_4]^{2+} + 2Cl^-$ does not occur in dichloromethane.

When exhaustive electrolysis was performed on solutions of $Re_2(O_2CR)_4Cl_2$ at approximately −0.5 V, the resulting yellow or green–yellow solutions exhibited cyclic voltammograms (Figure 3b) which were identical with those obtained prior to reduction (Table II and Figure 3a), with the exception that trace amounts of chloride ion ($E_{p,a} \simeq +1.2$ V) could now be detected. For these reductions we obtained n values very close to 1 (e.g., n = 0.97 for $Re_2(O_2CPh)_4Cl_2$ and $Re_2(O_2CCH_2Ph)_4Cl_2$).

One additional observation concerning the cyclic voltammograms of these reduced solutions was the appearance of an irreversible wave close to 0 V ($E_{p,a} \simeq -0.08$ V) on a *second sweep*. We discovered that this product wave appeared only after sweeping through the solvent limit at +1.6 V, an observation which indicates that it arises from the reaction of $[Re_2(O_2CR)_4Cl_2]^-$ with oxidized solvent impurities. The resulting product is strongly adsorbed upon the electrode surface.

The relatively simple and straightforward electrochemical properties which are observed for $Re_2(O_2CR)_4Cl_2$ are also encountered with the related bromide and iodide complexes. As with the chlorides, a one-electron (by coulometry)[24] reduction is observed in all instances (between −0.13 and −0.35 V) and neither the $E_{1/2}$ (Table II) nor ΔE_p values are affected by the addition of excess halide ion (added in the form of Bu_4NBr or Bu_4NI). After completion of the exhaustive electrolysis, cyclic voltammetry on the resultant solutions which

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(20) Preetz, W.; Rudzik, L. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 150.
(21) Murray, R. W.; Reilley, C. N. "Electroanalytical Principles"; Interscience: New York, 1963.
(22) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.
(23) Cotton, F. A.; Pedersen, E. *J. Am. Chem. Soc.* **1975**, *97*, 303.
(24) For example, n = 0.96 for $Re_2(O_2CPh)_4Br_2$ and 0.94 for $Re_2(O_2CPh)_4I_2$.

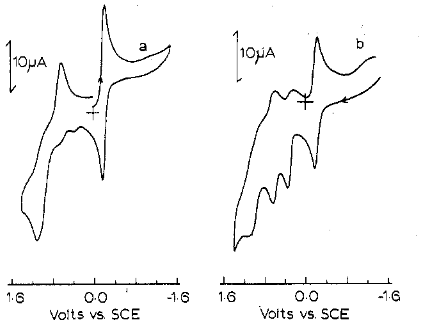

Figure 4. Cyclic voltammograms in 0.2 M TBAH–dichloromethane of $Re(O_2CC_3H_7)_4I_2$: (a) before and (b) after exhaustive electrolysis at −0.5 V.

contain $[Re_2(O_2CR)_4Br_2]^-$ shows that bromide ion is now present since oxidations are seen at approximately +0.8 and +1.1 V (dichloromethane solutions of Bu_4NBr have $E_{p,a}$ at +0.78 and +1.08 V). The amount of bromide released (as measured by peak currents) is dependent upon the particular carboxylate studied. However, we do not observe the growth of any metal-containing product waves which mirror the appearance of bromide ion.

The electrochemistry of the iodide complexes is qualitatively very similar to that of the bromides with the exception that a very small amount of iodide ion ($E_{p,a}$ at approximately + 0.40 and + 0.70 V) is present even in solutions which have not been electrolyzed. However, the amount of iodide ion increases quite dramatically after electrolysis (see Figure 4). Note that in Figure 4a, the cyclic voltammogram of $Re_2(O_2CC_3H_7)_4I_2$ also displays an irreversible oxidation above +0.5 V ($E_{p,a}$ at + 1.10 V and $E_{p,c}$ at +0.62 V). This is probably associated with coordinated iodide in the complex. A similar oxidation is found for all the iodide complexes but for none of the chlorides and bromides within the range of our measurements (+1.4 to −1.4 V).

Once again, the release of halide ion, as with the bromide complexes, is not accompanied by the growth of waves which can be attributed to a metal-containing product such as $[Re_2(O_2CR)_4]^+$. Consequently, we do not believe that the formation of free halide ion in these solutions arises from the dissociation of the monoanion, i.e., $[Re_2(O_2CR)_4X_2]^- \rightleftarrows [Re_2(O_2CR)_4]^+ + 2X^-$, but rather from some other process, specifically the reaction of $[Re_2(O_2CR)_4X_2]^-$ with adventitious oxygen. This leads to the complete disruption of a small portion of the dimers and the formation of perrhenate or some other rhenium species which is not electrochemically active under the conditions of our experiments. Consistent with this conclusion are two experimental observations. First, when attempts are made to rigorously exclude oxygen, the amount of iodide ion released is reduced by a factor of 4 or thereabouts. When this same solution is then deliberately exposed to the atmosphere there is a twofold increase in the amount of iodide ion present. Second, increase in iodide ion is paralleled by a decrease in the amount of $[Re_2(O_2CR)_4I_2]^-$ present (as monitored by the peak currents).

Having discussed the electrochemical results for the individual series of chloride, bromide, and iodide complexes, we are now in a position to consider the trends in $E_{1/2}$ values given in Table II. In all instances, for a particular carboxylic acid the reductions shift progressively to more negative potentials in the sequence I < Br < Cl. In other words, the reduction becomes less favored as the interactions of $Re_2(O_2CR)_4{}^{2+}$ with the halide ligand becomes stronger. This is also consistent with the normal redox characteristics of transition-metal halides,[25] for which the ease of reduction increases in the order Cl < Br < I. The dependence of the redox potential for $Re_2(O_2CR)_4X_2$ upon the axial group is comparable to the related observations of Das, Kadish, and Bear[26] concerning $Rh_2(O_2CR)_4$. They found that the oxidation potential of the rhodium(II) carboxylates varied in a simple fashion with the donor strength of the solvent (the latter can bind to the vacant axial coordination sites of the dimer).

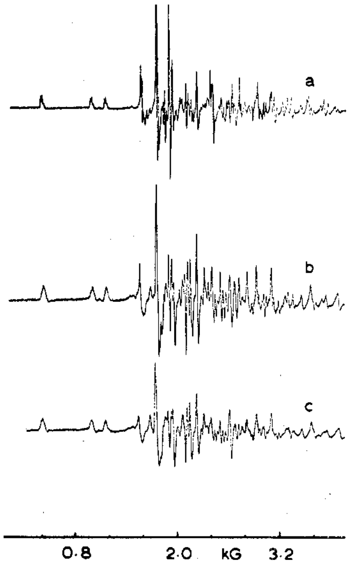

Figure 5. X-Band ESR spectra of CH_2Cl_2 glasses (−180 °C) of the series $Re_2(O_2CC_6H_4\text{-}p\text{-}OCH_3)_4X_2$: (a) X = Cl; (b) = Br; (c) X = I.

In addition to the fairly substantial shift in the reduction (~0.1 V) upon varying the halide ligand, the half-wave potentials are also dependent on R. For the alkyl carboxylates, plots of $E_{1/2}$ vs. the Taft σ^* parameter[27] (a good measure of the inductive effect of the substituents) are linear, or close to it. The value of $E_{1/2}$ becomes more positive as σ^* becomes more positive (i.e., R less electron donating). Thus electron-donating substituents on the carboxylate ligands destabilize the lower oxidation state of the metal dimer. A similar correlation is observed between $E_{1/2}$ and the σ^* parameter[27] for the aryl carboxylates.

ESR Spectra of the $[Re_2(O_2CR)_4X_2]^-$ Anions. During their studies on the benzoate complex $Re_2(O_2CPh)_4Cl_2$, Cotton and Pedersen[23] noted that the yellow or green-yellow solutions which are formed upon bulk electrolysis exhibit considerable air stability. This has permitted the spectral characterization of the solutions.[28] Freshly reduced dichloromethane solutions of 12 complexes comprising the series $Re_2(O_2CR)_4X_2$, where X = Cl, Br, or I and R = CH_2Ph, Ph, or $C_6H_4\text{-}p\text{-}OCH_3$, and

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(25) Walton, R. A. *Prog. Inorg. Chem.* **1972**, *16*, 1.

(26) Das, K.; Kadish, K. M.; Bear, J. L. *Inorg. Chem.* **1978**, *17*, 4.

(27) See: Hine, J. "Physical Organic Chemistry"; McGraw-Hill: New York, 1962; pp 96–8.

(28) We have recorded the electronic absorption solution spectra of freshly prepared $[Re_2(O_2CR)_4X_2]^-$, where X = Cl, Br, or I and R = CH_2Ph, Ph, or $C_6H_4\text{-}p\text{-}OCH_3$, within 5 min of the completion of the electrochemical reduction. In all instances one or two fairly intense absorption bands ($\epsilon > 10^2$) were observed in the region between 700 and 950 nm. However, since we do not understand either the intensity or the wavelength variations which occur as a function of changing X and R, we have not presented a discussion of these results herein (for full experimental data see: Srinivasan, V. Ph.D. Thesis, Purdue University, 1979). We note that the presence of low-energy bands in the electronic absorption spectra of species containing the $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$ electronic configuration is a feature common to all complexes of this type.[5,16,29,30] However, there are two features of our results which are unusual. First, two bands are observed for several of these complexes (rather than the expected one),[30] and second, the absorptions occur at much higher energies than those encountered in isoelectronic molecules such as $Re_2X_4(PR_3)_4{}^+$, $Re_2X_5(PR_3)_3$, and $Tc_2Cl_8{}^{3-}$.[5,29,30]

(29) Ebner, J. R.; Walton, R. A. *Inorg. Chim. Acta* **1975**, *14*, L45.

(30) Cotton, F. A.; Fanwick, P. E.; Gage, L. D.; Kalbacher, B.; Martin, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 5642.

$Re_2(O_2CR)_4Cl_2$, where R = C_2H_5, C_3H_7, or C_6H_4-*p*-CH_3, were quickly frozen in liquid nitrogen and their X-band ESR spectra recorded. These are so similar to one another (Figure 5) and to that reported previously[23] for a dichloromethane solution of $[Re_2(O_2CPh)_4Cl_2]^-$ (see Figure 3 of ref 23) that the complexes must possess the same electronic ground state. In fact, the ESR spectra of the six chloride complexes so far measured are indistinguishable. The bromide and iodide complexes possess spectra which are somewhat less well resolved (Figure 5). This may reflect a small contribution to the HOMO by the halogen. Since Cotton and Pedersen[23] have already published a detailed analysis of the ESR of $[Re_2(O_2CPh)_4Cl_2]^-$, we will not pursue this further at the present time. Suffice it to say that the X-band spectra are best interpreted[23] in terms of hyperfine coupling to two equivalent rhenium nuclei with the unpaired electron residing in the metal–metal δ^* antibonding orbital.

Warming the dichloromethane–$Re_2(O_2CCH_2Ph)_4X_2$ glasses to room temperature (without exclusion of air) and then freezing in liquid nitrogen led to decreases in the ESR signal intensity. The rate at which this occurred (to afford a brown-green species) was I > Br > Cl, reflecting the greater instability of the reduced iodide complex. This observation is in accord with the results of cyclic voltammetric studies discussed in the previous section (vide supra), which revealed that the decomposition of $[Re_2(O_2CR)_4X_2]^-$ was more pronounced in the case of the iodides.

On the Question of the $\delta \rightarrow \delta^*$ Electronic Transition in $Re_2(O_2CR)_4X_2$. There is now no doubt that the ground-state electronic configuration for complexes of the type $Re_2(O_2CR)_4X_2$ is $(\sigma)^2(\pi)^4(\delta)^2$ and for the related monoanions $(\sigma)^2(\pi)^4(\delta)^2(\delta^*)^1$. This being the case, we had questioned whether there might be a correlation between the $E_{1/2}$ values (Table II), which reflect changes in the δ^* orbital energy, and the suspected[10] $\delta \rightarrow \delta^*$ transition in the electronic absorption spectra of $Re_2(O_2CR)_4X_2$ (Table I). As can be seen from a comparison between the two sets of data, no such correlation exists. For example, the chloro complexes of pivalic and *p*-methoxybenzoic acid possess the same $E_{1/2}$ value (−0.42 V) but quite different electronic absorption spectra, with the lowest energy absorption band shifting from 497 to 561 nm. On the other hand, while the $E_{1/2}$ values range from −0.42 to −0.24 V for the series of alkyl carboxylates $Re_2(O_2CR)_4Cl_2$ (Table II), there is very little variation in their electronic absorption spectra (Table I).

The above observations seem to lead to one of two important conclusions. Either the systematic changes in the energy of the δ^* orbital are not paralleled by changes in the δ orbital and, therefore, our expectation of a simple correlation is unjustified or the $\delta \rightarrow \delta^*$ transition has not yet been correctly identified. Remembering that the $\delta \rightarrow \delta^*$ transition of $Mo_2(O_2CCH_3)_4$ has an unexpectedly low intensity,[15–18] an analogous property for the $Re_2(O_2CR)_4X_2$ systems is not out of the question. Of particular interest in this regard is our observation that concentrated solutions of many of the complexes (particularly the bromides and iodides) display a very weak broad feature (usually as a shoulder between 580 and 650 nm) to the low-energy side of this band. Figure 1c shows this low-energy absorption at 640 nm in the spectrum of $Re_2(O_2CC_2H_5)_4I_2$. The question of whether this is the $\delta \rightarrow \delta^*$ transition or, perhaps, is associated with a triplet state[31] is important to a full understanding of the electronic structure of $Re_2(O_2CR)_4X_2$. Hopefully, this important spectral assignment can be firmly established through low-temperature single-crystal studies.[32]

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Registry No. $Re_2(O_2CC_2H_5)_4Br_2$, 15293-25-1; $Re_2(O_2CCMe_3)_4Br_2$, 69897-16-1; $Re_2(O_2CCH_2Ph)_4Br_2$, 73274-53-0; $Re_2(O_2CPh)_4Br_2$, 15654-35-0; $Re_2(O_2CC_6H_4$-*p*-$CH_3)_4Br_2$, 15663-73-7; $Re_2(O_2CC_2H_5)_4I_2$, 73274-54-1; $Re_2(O_2CC_3H_7)_4I_2$, 15654-32-7; $Re_2(O_2CCMe_3)_4I_2$, 67815-35-4; $Re_2(O_2CCH_2Ph)_4I_2$, 73274-55-2; $Re_2(O_2CPh)_4I_2$, 73274-56-3; $Re_2(O_2CC_6H_4$-*p*-$Me)_4I_2$, 73274-57-4; $Re_2(O_2CC_6H_4$-*p*-$OMe)_4I_2$, 73274-58-5; $Re_2(O_2CCH_2Cl)_4Cl_2$, 15663-76-0; $Re_2(O_2CCH_2Br)_4Br_2$, 53097-07-7; $Re_2(O_2CC_2H_5)_4Cl_2$, 15225-81-7; $Re_2(O_2CC_3H_7)_4Cl_2$, 15654-30-5; $Re_2(O_2CC_3H_7)_4Br_2$, 15654-31-6; $Re_2(O_2CCMe_3)_4Cl_2$, 15654-33-8; $Re_2(O_2CCH_2Ph)_4Cl_2$, 15663-75-9; $Re_2(O_2CPh)_4Cl_2$, 15654-34-9; $Re_2(O_2CC_6H_4$-*p*-$Me)_4Cl_2$, 15663-73-7; $Re_2(O_2CC_6H_4$-*p*-$OMe)_4Cl_2$, 33540-83-9; $Re_2(O_2CC_6H_4$-*p*-$OMe)_4Br_2$, 33700-35-5; $[Re_2(O_2CCMe_3)_4Cl_2]^-$, 73360-30-2; $[Re_2(O_2CC_2H_5)_4Cl_2]^-$, 73360-23-3; $[Re_2(O_2CC_3H_7)_4Cl_2]^-$, 73360-22-2; $[Re_2(O_2CCH_2Ph)_4Cl_2]^-$, 73360-40-4; $[Re_2(O_2CC_6H_4$-*p*-$OMe)_4Cl_2]^-$, 73360-42-6; $[Re_2(O_2CC_6H_4$-*p*-$Me)_4Cl_2]^-$, 73360-41-5; $[Re_2(O_2CPh)_4Cl_2]^-$, 73360-33-5; $[Re_2(O_2CCMe_3)_4Br_2]^-$, 73360-32-4; $[Re_2(O_2CC_2H_5)_4Br_2]^-$, 73360-25-5; $[Re_2(O_2CC_3H_7)_4Br_2]^-$, 73360-24-4; $[Re_2(O_2CCH_2Ph)_4Br_2]^-$, 73360-37-9; $[Re_2(O_2CC_6H_4$-*p*-$OMe)_4Br_2]^-$, 73360-39-1; $[Re_2(O_2CC_6H_4$-*p*-$Me)_4Br_2]^-$, 73360-38-0; $[Re_2(O_2CPh)_4Br_2]^-$, 73360-31-3; $[Re_2(O_2CCMe_3)_4I_2]^-$, 73360-28-8; $[Re_2(O_2CC_2H_5)_4I_2]^-$, 73360-27-7; $[Re_2(O_2CC_3H_7)_4I_2]^-$, 73360-26-6; $[Re_2(O_2CCH_2Ph)_4I_2]^-$, 73360-34-6; $[Re_2(O_2CC_6H_4$-*p*-$OMe)_4I_2]^-$, 73360-36-8; $[Re_2(O_2CC_6H_4$-*p*-$Me)_4I_2]^-$, 73360-35-7; $[Re_2(O_2CPh)_4I_2]^-$, 73360-29-9.

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(31) This possibility was suggested by a referee.

(32) Such studies are now underway (unpublished information presented in ref 10).