Inorganica Chimica Acta, *206* (1993) 97–104

Electrochemistry of boron-capped ^{99}Tc–dioxime complexes

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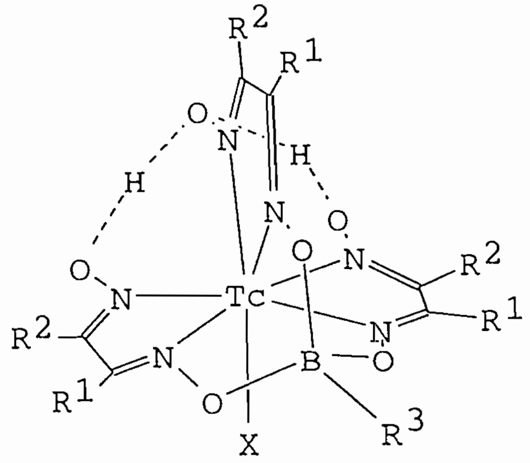
(Received July 31, 1992; revised November 17, 1992)

Abstract

Boron-capped technetium dioxime (BATO) compounds (**1**) have been studied by cyclic voltammetry, d.c. polarography, and controlled-potential coulometry/bulk electrolysis in DMF. Chloro and bromo BATOs undergo an irreversible two-electron reduction at mercury while for hydroxy BATOs two consecutive one-electron reductions are observed. Rhenium analogs to the BATOs exhibit qualitatively similar reduction behaviour, but at more negative potentials. The uncapped tris-dioxime complexes (**2**) also show similar electrochemical behaviour. The two-electron peak potential is more sensitive to changes in the axial ligand and the dioxime than to changes in substituents on the boronic acid capping group. BATO reduction apparently leads to axial ligand loss and yields an air-sensitive, purple species. Both BATO reduction and oxidation appear to be biologically inaccessible.

Introduction

Boronic acid adducts of technetium dioxime (BATO) complexes (**1**) are a new series of compounds, members of which have recently been introduced as myocardial [1] and cerebral [2] perfusion radiopharmaceuticals. These complexes contain three bidendate dioxime ligands capped by a boronic acid moiety, and an anionic 'axial' ligand (X), which occupies a seventh coordination site [3]. Our interest in the electrochemistry of the BATOs was prompted by reports that biological behaviour of metal complexes used for imaging the myocardium may be related to redox potentials [4, 5]. We report here the electrochemical behaviour of several BATO complexes, ^{99}TcX(dioxime)$_3$BR**(X = Cl^-, Br^-, OH^-; dioxime = dimethylglyoxime [DMG], cyclohexanedionedioxime [CDO]; R = OH, Me, Et, Bu^n, Bu^i and Ph) and the uncapped tris-dioxime species, ^{99}TcCl(dioxime)$_3$ (**2**) [6]. The effects of changing dioxime, axial ligand and boronic acid cap substituent on BATO reduction potentials are noted. In addition, the electrochemical behaviour of two rhenium analogs to the BATOs (boronic acid adducts of rhenium dioxime; BAReOs) [7] is reported here.



1

TcX(dioxime)$_3$BR

Axial Ligand:
X = Cl, Br, OH
Dioxime:
DMG; $R^1 = R^2 =$ Me
CDO; $[R^1\text{-}R^2] = [\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}]$
Cap Substituent:
R^3 = Me, Et, Bu^n, Bu^i, Ph, OH

Experimental

Cyclic voltammetry (CV)

CV experiments at a hanging mercury drop electrode employed a Princeton Applied Research (P.A.R.) model

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**The IUPAC name for this family of compounds is quite lengthy and cumbersome. For example, the IUPAC name for the Tc–CDO chloro methyl-capped compound is [bis-[1,2-cyclohexanedione dioximato(1 −)-*O*][1,2-cyclohexanedione dioximato(2 −)-*O*] methylborato(2 −) $N,N',N'',N''',N'''',N'''''$] chlorotechnetium(III). For simplicity, TcCl(CDO)$_3$BMe will be used.

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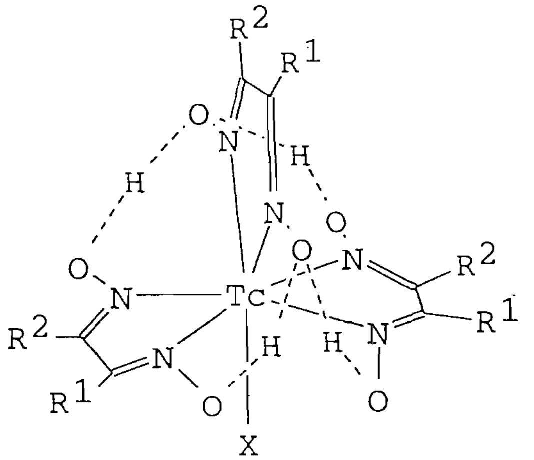

2

TcX(dioxime)$_3$

174A polarographic analyzer with a model 303 static mercury drop electrode and were recorded on a model RE0074 X-Y recorder (all P.A.R.). The reference electrode was Ag/AgNO$_3$ with an acetonitrile filling solution saturated with LiCl and the counter electrode was a platinum wire.

CV experiments at Pt, Au and glassy carbon working electrodes (B.A.S.) were conducted using a P.A.R. model 173 potentiostat/galvanostat with a model 179 coulometer plug-in module. The CV potential waveform was supplied via a P.A.R. model 175 universal programmer. Data was collected on a Nicolet model 310 digital oscilloscope. The reference electrode (P.A.R.) was saturated calomel (SCE).

All CV solutions were 0.1 M in tetrabutylammonium tetrafluoroborate Bu$_4$NBF$_4$ supporting electrolyte, 0.2–0.7 mM in sample, and thoroughly deoxygenated before analysis. Variations in the reference potential were accounted for by determining the CV of an Ru(acac)$_3$ standard on a daily basis. All measured potentials were corrected according to an absolute peak reduction potential for Ru(acac)$_3$ of -1.210 V versus Ag/AgNO$_3$ at Hg (-0.790 V versus SCE at Pt).

D.c. polarography

D.c. polarography experiments were conducted on the same instrumentation and employed the same electrodes as described above for cyclic voltammetry at mercury. D.c. polarography solutions were prepared as described above for the CV solutions.

Bulk electrolysis/coulometry

Bulk electrolysis/coulometry experiments in DMF employed the P.A.R. model 173 potentiostat/galvanostat with a model 179 coulometry plug-in and a model 377A coulometry cell system. These studies employed a mercury pool working electrode (~ 6 ml). The SCE reference and the Pt mesh counter electrode were each separated from the working compartment by Vycor® glass frits and were immersed in a solution of supporting electrolyte. The electrolysis potential during reductions was at least 0.4 V more negative than the initial peak reduction potential observed in the CV experiments. Sample solutions (prepared as described for CV experiments) were stirred with a magnetic stirring bar. Sample sizes for coulometry measurements were approximately 5×10^{-7} mol in 10 ml of solution.

UV–Vis spectroscopy

UV–Vis spectra were recorded on a Hewlett Packard model 8451A diode array spectrometer. Air-sensitive reduced solutions were analyzed under nitrogen by carefully transferring them via syringe into a N$_2$-flushed spectroscopy cell sealed with a rubber septum.

Reagents

All BATO [3], tris-dioxime [6] and BAReO [7] compounds were prepared according to published procedures and were routinely checked for purity by HPLC. Typical HPLC conditions were 60/40 acetonitrile/0.1 M NH$_4$OAc (aqueous) through a Nucleosil C$_8$ 150×4.6 mm column (flow = 1.5 ml/min). ^{99}Tc is a weak β-emitter (0.29 MeV, half-life 2.12×10^5 years) and should be handled only in laboratories approved for the use of low-level radioactivity. All boronic acids used in these preparations are commercially available except 2-methyl propyl boronic acid, which was prepared in house. Bu$_4$NBF$_4$ (Aldrich) supporting electrolyte was recrystallized twice from MeOH/H$_2$O or acetone/ether, dried, and stored under vacuum. Ru(acac)$_3$ (Strem) and all solvents were used as received.

Results

Cyclic voltammetry

Most CV data were collected at a mercury electrode. Typical cyclic voltammograms for a BATO compound TcX(dioxime)$_3$BR (X = Cl, Br) at Hg in DMF are shown in Fig. 1. Chloro and bromo BATO complexes exhibit three characteristic electrochemical features. An initial irreversible reduction (A) involves two electrons (see polarography and coulometry results below). This reduction remains irreversible at Hg even at fast scan rates (100 V/s). An irreversible re-oxidation peak B clearly involves oxidation of a product of the initial reduction since it is only observed on the return anodic sweep after the initial reduction is traversed. The peak current of B is noticeably smaller than that of A

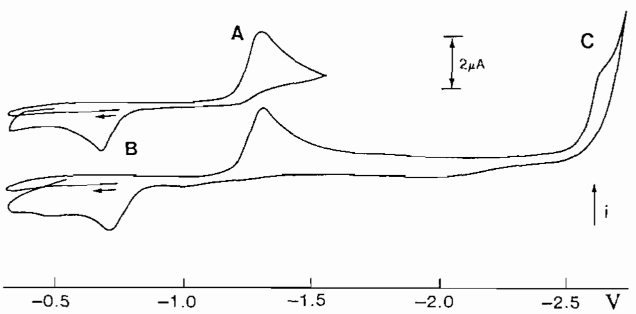

Fig. 1. Cyclic voltammograms in DMF at Hg of $TcCl(DMG)_3BPh$. Scan rate = 100 mV/s. 0.1 M in tetrabutylammonium tetrafluoroborate. Hanging mercury drop working electrode vs. $Ag/AgNO_3$ reference. Sample concentration = 3.08×10^{-4} M.

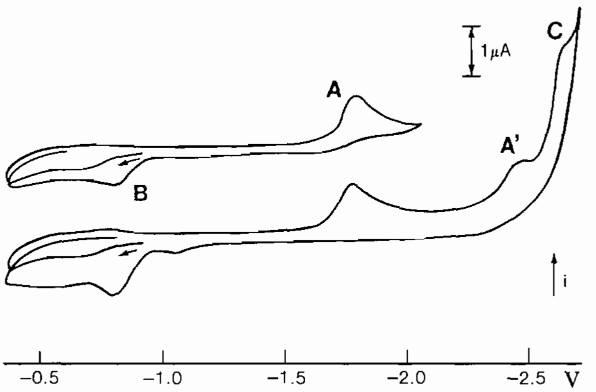

Fig. 2. Cyclic voltammograms in DMF at Hg of $Tc(OH)(CDO)_3BPh$. Scan rate = 100 mV/s. 0.1 M in tetrabutylammonium tetrafluoroborate. Hanging mercury drop working electrode vs. $Ag/AgNO_3$ reference. Sample concentration = 2.86×10^{-4} M.

(typically, $B/A \approx 0.6$), indicating that the reduced species decomposes to electro-inactive products or re-oxidizes in a one-electron step. Extending the negative limits of the experiment also shows an irreversible further reduction (C). Comparison of peak C peak currents to that of A indicates that the peak C reduction also involves two electrons. Peak potential values for a large number of BATOs are tabulated in Table 1.

The hydroxy BATOs studied (X = OH) undergo two-electron reduction in a slightly different manner from the bromo and chloro BATOs: two separate irreversible one-electron processes ($E_1{}^0 > E_2{}^0$) were observed rather than a single two-electron process (Fig. 2). These species also exhibit a re-oxidation peak B and a further reduction peak C. In a CV where only the initial one-electron reduction is traversed, the B/A peak current ratio is approximately 0.6, while in an experiment where both one-electron reductions are encountered, the size of peak B increases to give a new peak ratio B/A (A = initial reduction peak) of ~1.0.

The tris-dioxime complexes (**2**) can be regarded as BATOs without the boronic acid capping group. Two of these species, $TcCl(DMG)_3$ and $TcCl(CDO)_3$, have been studied in DMF and found to show electrochemical features and peak potentials similar to the BATO compounds. Two BAReO complexes, $ReCl(CDO)_3BPh$ and $ReCl(CDO)_3BEt$ (Ph = phenyl, Et = ethyl), were also investigated and found to behave similarly to the BATOs. Results for the tris-dioxime complexes and the BAReOs are also given in Table 1.

We have also studied the electrochemistry of several BATOs at Pt, Au and glassy carbon working electrodes. CVs at these electrodes show qualitatively the same features: an irreversible reduction followed on the return sweep by a re-oxidation process (the further reduction peak C is not seen because the negative limits of the experiment are shortened at these electrode materials). In addition, at the positive extreme of the potential scan, an irreversible oxidation process is observed ($E_{pa} \approx +1.1$ V versus $Ag/AgNO_3$).

D.c. polarography

D.c. polarography experiments show that bromo, chloro and hydroxy BATO compounds undergo reduction at approximately $E_{1/2} = -0.8$, -1.3 and -1.8 V versus $Ag/AgNO_3$ (acetonitrile), respectively. Limiting currents of these reduction processes were compared to that of a one-electron standard, $Ru(acac)_3$ [8], in order to determine the number of electrons transferred. The results indicated that bromo and chloro BATOs undergo two-electron reduction, while hydroxy BATOs accept one electron initially (Table 2)*. These polarography results are corroborated by controlled potential coulometry experiments (vide infra).

Bulk electrolysis/coulometry

As a means of verifying coulometry as an electron-counting method, four samples of the known one-electron standard $Ru(acac)_3$ were bulk electrolyzed in DMF; Q(measured)/Q(theoretical) gave 0.975 ± 0.014 electrons transferred.

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*We have found evidence of adsorption of the reduction product to the mercury electrode in our studies of BATO reduction. D.c. polarograms of hydroxy BATOs show a well-defined prewave. For some BATOs (apparently related to lipophilicity, because CDO > DMG; BPh > BBu > BMe), distortion of both polarographic and cyclic voltammetric waves due to extra current preceding the main wave is noted. Cyclic voltammetric postpeaks associated with the reoxidation peak B have also been noted. The extent of adsorption (i.e. degree of distortion and size of adsorption peaks) in all cases is smaller at lower sample concentration and at faster scan rates, indicating that adsorption is slow relative to the time scale of these experiments (adsorption equilibrium is not attained). We have accordingly adjusted sample concentrations to minimize adsorption, and in d.c. polarography studies where adsorption prewaves are present, the prewave limiting current is included in electron-counting calculations.

TABLE 1. Cyclic voltammetry data for BATO and BAReO compounds MX(dioxime)$_3$BR (M = Tc, Re; dioxime = DMG, CDO) in DMF[a]

X	R	Peak potentials (E_p) (V)					
		DMG			CDO		
		Peak A	Peak B	Peak C	Peak A	Peak B	Peak C
BATOs							
Cl	OH	−1.33	−0.70	−2.66	−1.28	−0.71	−2.66
Cl	Me	−1.35	−0.70	−2.69	−1.29	−0.72	−2.68
Cl	Et	−1.34	−0.71	−2.67			
Cl	Bu	−1.35	−0.70	−2.69	−1.30	−0.71	−2.68
Br	Bu				−0.77	−0.72	−2.68
OH	Bu	−1.84, −2.56[b]	−0.79	−2.68			
Cl	2MP	−1.35	−0.70	−2.67			
OH	2MP	−1.87, < −2.7[c]	−0.82	−2.71			
Cl	Ph	−1.30	−0.69	−2.64	−1.24	−0.69	−2.65
Br	Ph	−0.82	−0.71	−2.64	−0.76	−0.70	−2.69
OH	Ph				−1.76, −2.46[b]	−0.79	−2.64
Cl	uncapped (tris)	−1.38	−0.70	−2.70	−1.34	−0.70	−2.68
BAReOS							
Cl	Et				−1.34	−0.69	−2.58
Cl	Ph				−1.29	−0.68	−2.53

[a] Scan rate = 100 mV/s. All solutions are 0.2–0.7 mM in sample and 0.1 M in tetrabutylammonium tetrafluoroborate. Hanging mercury drop working electrode vs. Ag/AgNO$_3$ reference. Peaks A and C; $E_p = E_{pc}$ = peak potential, cathodic; peak B; $E_p = E_{pa}$ = peak potential, anodic. (R substituents: OH = hydroxy, Me = methyl, Et = ethyl, 2MP = 2-methyl propyl, Bu = butyl, Ph = phenyl). [b] Hydroxy species exhibit two initial reduction peaks; see text. [c] 2nd reduction overlaps with peak C.

TABLE 2. D.c. polarography data in DMF[a]

Compound	Drop time (s)	i_D ratio[b]	Average
TcBr(CDO)$_3$BBu	1	1.83	
	2	1.88	1.89 electrons
	5	1.95	
TcCl(CDO)$_3$BMe	1	2.13	
	2	2.10	2.13 electrons
	5	2.16	
Tc(OH)(DMG)$_3$B2MP	1	0.99	
	2	1.00	1.00 electrons
	5	1.02	

[a] Limiting current ratios for BATO reduction relative to Ru(acac)$_3$ one-electron standard. Hanging mercury drop working electrode vs. Ag/AgNO$_3$ reference. Scan rate = 2, 5 or 10 mV/s. Drop time = 5, 2 or 1 s, respectively. All solutions 0.1 M in tetrabutylammonium tetrafluoroborate. Sample sizes > 13 mg. [b] i_D = limiting current/sample concentration; ratio = i_D[compound]/i_D[Ru(acac)$_3$].

Controlled potential coulometry of TcBr(CDO)$_3$-BBu^n, TcCl(CDO)$_3$BMe, TcCl(DMG)$_3$B2MP (2MP = 2-methyl propyl = Bu^i) and Tc(OH)(DMG)$_3$B2MP at mercury gave 1.59, 2.07, 1.98 and 1.22 electrons transferred, respectively, in the initial reduction processes. Bulk electrolysis of straw yellow bromo or chloro BATO solutions in DMF under N$_2$ yielded bright purple, air-sensitive solutions. The hydroxy species showed no color change after initial reduction, but further reduction at more negative potentials also yielded intensely purple reduced solutions. The purple reduced solutions displayed similar UV–Vis spectra (Fig. 3). In a bulk electrolysis study of TcCl(DMG)$_3$B2MP, it was found that re-oxidation of the reduced solution at the mercury electrode in the absence of air regenerated mostly chloro and hydroxy BATO (as determined by TLC and HPLC). Air re-oxidation of the reduced solution, however, yields a clear brown solution containing several (> 3) polar products.

Cyclic voltammograms of reduced DMF solutions of TcCl(DMG)$_3$B2MP are shown in Fig. 4. The purple two-electron reduced solution (Fig. 4(b)) exhibits an initial irreversible oxidation peak at E_{pa} = −0.75 V which corresponds to the re-oxidation peak B in a CV of the

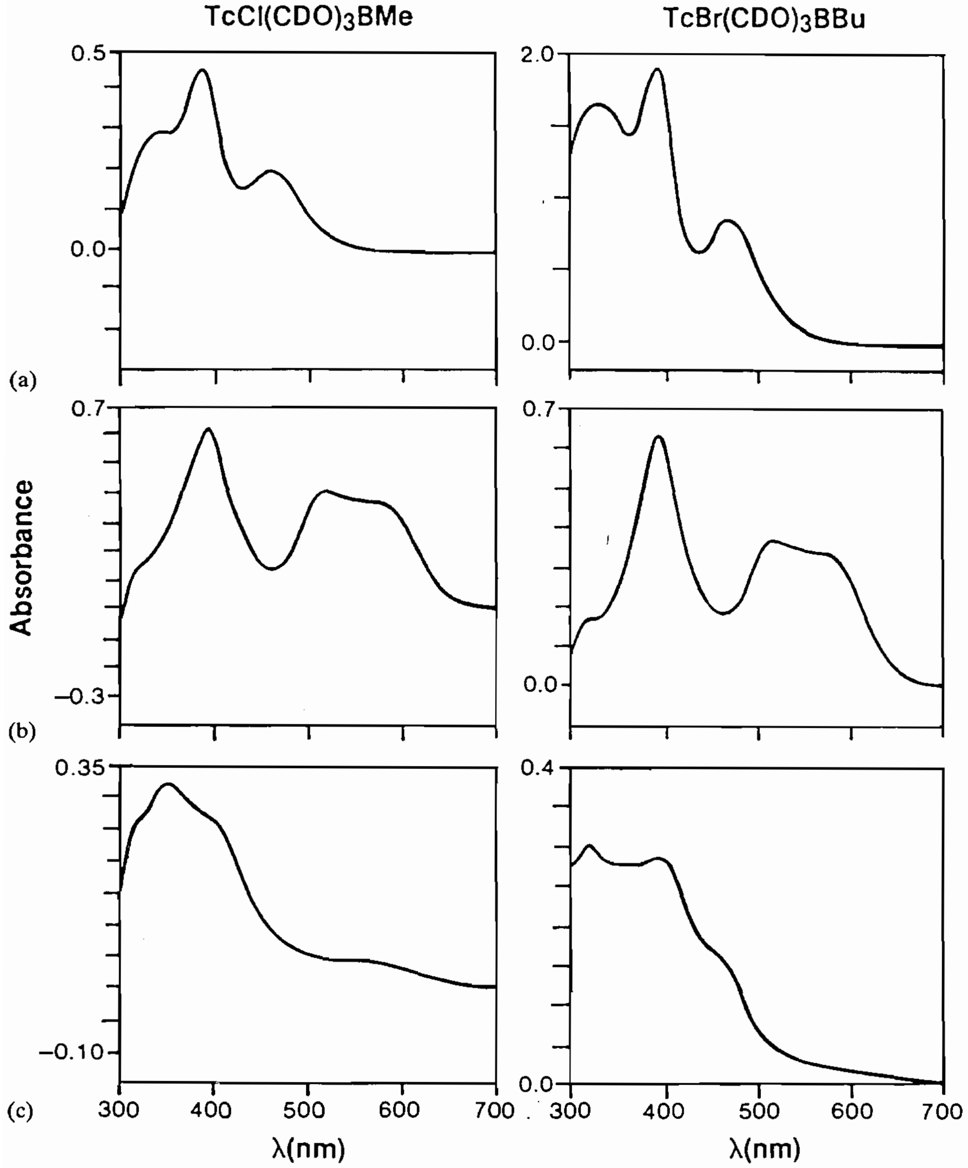

Fig. 3. UV–Vis spectra from bulk electrolysis studies in DMF: comparison of a chloro and a bromo BATO. (a) BATO; (b) BATO reduced by two electrons; (c) BATO reduced and air re-oxidized. Electrolysis performed at Hg (bromo species at −0.8 V; chloro at −1.8 V vs. SCE reference) with 0.1 M TBATfb supporting electrolyte.

unreduced species (Fig. 4(a)). A second oxidation process at $E_{pa} = -0.56$ V with its corresponding re-reduction peak at −0.64 V forms a characteristic distorted redox pair of peaks which by comparison to an authentic sample of LiCl (Fig. 4(d)) can be assigned to oxidation of mercury in the presence of chloride ion [9]. Exposure to air eliminates the −0.75 V peak but leaves behind the chloride ion wave (Fig. 4(c)).

Discussion

Substituent effects on peak A E_{pc}

It is evident from Table 1 that whereas peaks B and C remain relatively fixed, there is considerable variation in the position of peak A (the major irreversible reduction). In general we find that the peak A E_{pc} is sensitive to changes in the axial ligand or the dioxime, but insensitive to changes in the capping boronic acid group.

Changing the axial ligand has a large effect on the peak A E_{pc}. Bromo-substituted BATO peak potentials are more positive than the chloro potentials ($\Delta E_{pc} \sim$ 0.5 V) while hydroxy-substituted values are ~1.0 V more negative. Changing the dioxime ligand has some effect on the peak A E_{pc}. CDO complexes in general reduce at a potential that is 60–90 mV more positive than the analogous DMG species. Changing the boronic acid cap has a relatively small effect on the peak A

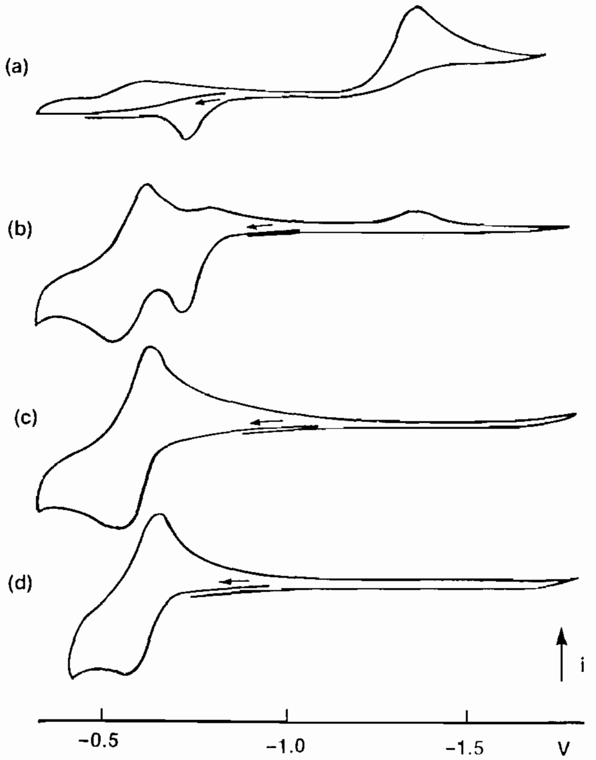

Fig. 4. Cyclic voltammograms in DMF at Hg of reduced TcCl(DMG)$_3$B2MP and LiCl. (a) BATO; (b) BATO reduced by two electrons; (c) BATO reduced and air re-oxidized; (d) LiCl. Scan rate = 100 mV/s. 0.1 M in tetrabutylammonium tetrafluoroborate. Hanging mercury drop working electrode vs. Ag/AgNO$_3$ reference. BATO sample concentration = 2.27×10^{-4} M.

E_{pc}. Compared to shifts in the axial and dioxime ligands, peak potentials vary only a small amount (~10–20 mV) as the capping substituent R is varied, however the aryl-substituted complexes exhibit slightly more positive values than the alkyl substituents. Removing the boronic acid cap also has little effect. The uncapped (tris-dioxime) complexes (**2**) possess peak potentials which are within ~30–40 mV of the corresponding BATOs (not including the aryl-capped species). Since the peak potential values for the uncapped compounds are the most negative of those studied, the net effect of capping is apparently to shift the BATO reduction E_{pc} more positive.

In an electrochemical study of bis-capped iron(II) clathrochelates Fe(dioxime)$_3$(BR)$_2$, it was found that electronic effects of the boron cap substituents (as estimated by Hammett σ_p values) were correlated to the redox potential ($E_{pa}+E_{pc}/2$) of the Fe(II)/Fe(III) couple [10]. The capping substituents divided into two groups; group 1 (R = Cl, Br, F, OH, OCH$_3$) contained atoms with non-bonded electron pairs; group 2 (R = H, CH$_3$, n-C$_4$H$_9$, C$_6$H$_5$) consisted of hydrocarbon moieties. Because of the structural similarity of these compounds to the BATOs, we were interested in doing a similar analysis of the BATO reduction potentials. The iron(II) clathrochelate data is shown in Fig. 5, along with E_{pc} data* for TcCl(DMG)$_3$BR. The results indicate that like the Fe(dioxime)$_3$(BR)$_2$ data, the non-bonded electron pair-containing substituent (−OH) lies on a separate line from the hydrocarbon substituents.

Several years ago Deutsch *et al.* suggested that a requirement for a successful heart imaging agent may be a monovalent positive charge [11]. In subsequent studies of cationic metal diphosphine compounds $[MD_2X_2]^+$ (M = Tc, Re; D = tertiary phosphine, X = Cl, Br) they observed faster washout from the heart for the technetium species relative to the rhenium analogs, and attributed this result to their easy reduction *in vivo* [4, 5]. Electrochemical studies showed that the $[TcD_2X_2]^+$ compounds in general are reduced more readily than $[ReD_2X_2]^+$ to neutral complexes, which are expected to be more freely diffusable in the body. Hence, technetium diphosphine complexes are reduced *in vivo* and wash out of the myocardium in some species, while the rhenium analogs apparently fall outside of the biologically accessible range of potentials, and are retained. In order to compare Deutsch's reduction potential data to our own, we conducted cyclic voltammetry on an authentic sample of $[Tc(dmpe)_2Cl_2]^+$ under our conditions. This provided a conversion factor of ~500 mV (Table 3), and indicated that the rhenium III/II diphosphine reduction potential ought to fall at approximately −0.9 V, some 0.4 V more positive than typical chloro BATO peak potentials. Hence BATO reduction is more difficult than the 'inaccessible' $[ReD_2X_2]^+$ reduction, indicating that *in vivo* reduction of the BATOs is unlikely.

Cyclic voltammetry studies at Pt, Au and glassy carbon working electrodes allow for investigation of more positive potentials. The large, irreversible BATO oxidation process ($E_{pa} \approx +1.1$ V) is observed near the anodic experimental limits and is probably also inaccessible *in vivo*.

In the chloro BATO CVs, peak B is some 650 mV removed from peak A, indicating that the initial reduction is not reversible [12] and that the species responsible for peak B is a chemically changed BATO. The existence of a chemically changed BATO is in accordance with the observation of a single, irreversible two-electron reduction wave for the chloro and bromo BATOs. A two-electron reduction requires that the standard potential for the second electron transfer be

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*A comparison of this nature must be made with caution because in an irreversible system, E_{pc} is dependent upon a number of other factors (chemical rate constant k, electron transfer rate constant k_s, $E_2{}^0$), and therefore may not be as accurate a reflection of the formal reduction potential $E_1{}^0$ as $E_{pa}+E_{pc}/2$ from a reversible system. It is assumed that within a given class of compounds, these other factors have a similar contribution.

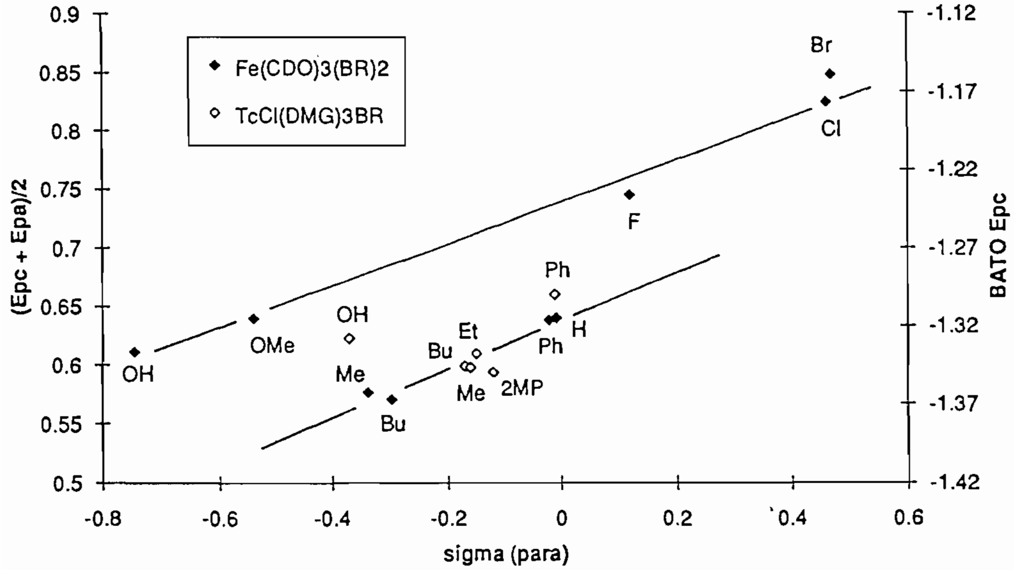

Fig. 5. Substituent effects on reduction potential in clathrochelate complexes. (◆) Fe(II) oxidation in $Fe(CDO)_3(BR)_2$ (data taken from ref. 7); left value axis; (◇) BATO reduction in $TcCl(DMG)_3BR$, right value axis. Lines are best fit to the $Fe(CDO)_3(BR)_2$ data. $Fe(CDO)_3(BR)_2$ sigma (para) values are doubled to account for two substituents.

TABLE 3. $[M(dmpe)_2Cl_2]^+$ reduction potential values; $(E_{pc}+E_{pa})/2$ values from cyclic voltammetry results in DMF

	$(E_{pc}+E_{pa})/2$ vs. Ag/AgCl aqueous[a]	$(E_{pc}+E_{pa})/2$ vs. $Ag/AgNO_3$ ACN[b]	Difference
Tc(III/II)	−0.21 V	−0.66 V	0.45 V
Tc(II/I)	−1.37 V	−1.91 V	0.54 V
Re(III/II)	−0.40 V		
BATO E_{pc}		~ −1.3 V	

[a]Data from ref. 11. [b]Data from this study.

more positive than (or equal to) that of the first, and this is most often ascribed to a structural change associated with the first electron transfer [13].

If the structural change is slow relative to the first electron transfer, a 'chemical step' is discerned between electron transfer steps (an ECE mechanism) [14]. Alternatively, if the electrode process is kinetically controlled by slow initial charge transfer, the chemical step is described as being concerted with electron transfer in an EE mechanism. Analysis of the peak shift versus ln scan rate for $TcCl(DMG)_3B2MP$ over a wide range of scan rates at Hg (50 mV/s to 10 V/s) gave a best-fit line with a slope of −20.3 mV ($y=-20.329x-1412.498$; $R=0.997$)*. This indicates that the EE mechanism is occurring with a transfer coefficient for the first electron transfer $\alpha=0.62$ [15] (Scheme 1).

$$\mathrm{BATO} \xrightarrow[-\mathrm{X}]{+e^-} {*\mathrm{BATO}^-} \qquad \text{electrochemical}$$

$$*\mathrm{BATO}^- \xrightarrow{+e^-} {*\mathrm{BATO}^{2-}} \qquad \text{electrochemical}$$

Scheme 1. EE mechanism; asterisk (*) signifies chemically changed species.

The exact nature of the structural change associated with reduction of the BATOs is unknown, but it is apparent that it involves axial ligand dissociation. The presence of free chloride ion (as detected by CV) in bulk electrolyzed DMF solutions of $TcCl(DMG)_3B2MP$ confirms that the axial ligand is lost upon reduction. In the absence of air, this ligand dissociation process is at least partially reversible, as re-oxidation at the mercury electrode regenerates the original BATO. The other re-oxidation product, $Tc(OH)(DMG)_3B2MP$, probably results from axial coordination of trace amounts of water found in the DMF. Reaction of the reduced BATO with air generates new species which do not contain chloride, as the size of the Cl^- wave in the CV is undiminished.

Axial ligand dissociation following BATO reduction is not unexpected. Ligand dissociation upon reduction,

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*In these experiments, E_{pc} values were corrected for iR drop, with R computed from the separation of $Ru(acac)_3$ cathodic and anodic peak values at a range of scan rates.

coupled with a second reduction step, is a well-known process for metal complexes [16]. It is also known that the axial ligand is labile in the non-reduced BATOs [17]. A chemical step such as this helps to explain the unusual consistency in peak B potentials. As the axial ligand is changed from Cl to Br to OH, there is a large variation in the peak A reduction potential. Peak B, however, remains relatively constant. Axial ligand dissociation would create an equivalent coordinatively unsaturated species for each of these BATOs, and presumably it would have its own unique re-oxidation peak potential.

Our findings that peak potentials are more sensitive to changes in the axial ligand than to changes in the dioxime or the boronic acid cap indicate that the initial BATO reduction is metal-centered. If both electrons are removed from the metal center during BATO reduction, the reduced BATO species would be Tc(I). It is also possible that a one-electron reduction of the metal center to Tc(II) is involved, with an associated reduction of the ligand. Since most Tc(I) complexes are d^6 spin-paired and colorless, the observed purple color of the two-electron reduced BATO species would support the formation of Tc(II). Deeply colored Tc(I) N-donor ligand (bipyridine) complexes have been reported, however [18], with absorption in the visible region attributed to $d\pi(\text{Tc}) \rightarrow \pi^*(\text{bpy})$ metal-to-ligand charge-transfer (MLCT) transitions. The dioxime ligands of d^6 metal clathrochelate complexes very similar to the BATOs also exhibit MLCT, leading to colored complexes [19]. The intensity of the absorption bands ($\epsilon > 6000\ \text{M}^{-1}\ \text{cm}^{-1}$) in the reduced BATO electronic spectrum is indicative of charge transfer transitions. For these reasons, we believe that a Tc(I) reduced BATO exhibiting MLCT transitions is also plausible.

Acknowledgement

We thank Dr P. Rieger (Brown University) for reading the manuscript and providing helpful comments.

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