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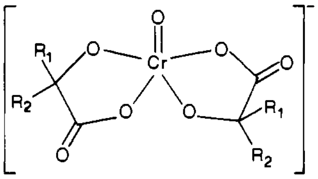
Inorganic Chemistry

Communications

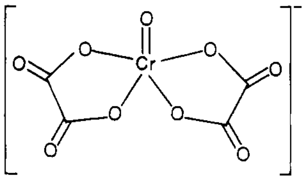
Electrochemistry of Chromium(V) Complexes

Sir:

A recent report on the electrochemistry of the oxochromate(V) complex I[1,2] has prompted us to communicate our results on the electrochemistry of complexes I–III.[1] The unexpected stability of complexes I and II in water[3,4] and also the unusual quasi-reversibility of the Cr(V)/Cr(IV) couple of I at moderate scan rates in cyclic voltammograms in water (pH 3–4)[2] have been reported. However, the electrochemistry of the Cr(V) complexes in nonaqueous solvents has not been studied previously, and the results reported here show a remarkable stability of the rare Cr(IV) oxidation state[5] in certain solvents. In particular, the Cr(V)/Cr(IV) couples of I and II are quasi-reversible in dimethyl sulfoxide and dichloromethane, even at very low scan rates. The Cr(IV) complexes only decompose on a time scale of minutes in dichloromethane at 20 °C. A second feature in the nonaqueous electrochemistry of I and II is the presence of irreversible oxidations (~+0.9 V vs Fc^+/Fc, Table I). In addition to the studies on I and II, the Cr(V)/Cr(IV) redox responses of reactive intermediates formed in the oxidation of organic ligands by Cr(VI) have been examined for the first time. It was found that the Cr(V)/Cr(IV) couples of Cr(V) intermediates are well removed from the reduction processes of the Cr(VI) reactant and Cr(III) products in the Cr(VI) oxidation of oxalic acid.[6] Thus, the rates of formation and decomposition of the rapidly interchanging Cr(V) intermediates, presumed to be III[1] and a six-coordinate intermediate, are monitored readily.



I: $R_1=R_2=Et$
II: $R_1=Me$, $R_2=Et$



III

It has been long recognized that Cr(V) intermediates are produced in the oxidations of various substrates by Cr(VI), and the kinetics of these redox processes have been the subject of extensive investigations.[7-10] However, it has only been in relatively recent times that stable Cr(V) complexes containing organic ligands have been prepared.[3,4,11] The inherently interesting properties of I and II[2,3,12-16] along with our interest in chromium speciation in natural waters and wastewaters prompted us to investigate the electrochemical properties of complexes I–III. Complexes I and II were prepared by standard techniques,[3,4] while

Table I. Electrochemistry of the Cr(V) Complexes at 20 ± 2 °C Using a Glassy-Carbon Working Electrode

compd	couple	rev/ irrev	solvent	potential, V	ref electrode
I	Cr(V)/(IV)	rev	water[a,b]	+0.19	SCE
				+0.06	Fc^+/Fc[c]
		rev	Me_2SO[d,e]	−0.97	Fc^+/Fc[f]
II	Cr(V)/(IV)	rev	water[a]	+0.12	Ag/AgCl/ KCl(satd)
				−0.05	Fc^+/Fc[c]
		rev	acetone[e,g,h]	−0.78	Fc^+/Fc[f]
		rev	DCM[d,e]	−0.99	Fc^+/Fc[f]
	Cr(VI)/(V)	irrev	acetone	+0.92[i]	Fc^+/Fc[f]
		irrev	DCM	+0.89[i]	Fc^+/Fc[f]
III	Cr(V)/(IV)	rev	aqueous acetic acid	+0.93[h,j]	Ag/AgCl/ KCl(satd)
				+0.76	Fc^+/Fc[c]

[a] pH 3–4, 1.0 M $LiClO_4$ (I) or 0.5 M $LiClO_4$ (II). [b] Reference 2, +0.43 V vs. the standard hydrogen electrode. [c] Using a value of +0.13 vs. SCE for the Fc^+/Fc couple in water: Sahami, S.; Weaver, M. J. *J. Solution Chem.* **1981**, *10*, 199–208). [d] Quasi-reversible at all scan rates above 10 mV s^{-1} in CV. [e] Nonaqueous solvents contained 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte. [f] The standard ferrocenium/ferrocene redox couple was used as an internal standard in nonaqueous solvents: IUPAC Commission on Electrochemistry (U.K.) *Pure Appl. Chem.* **1984**, *56*, 461–466. [g] Peak potential in differential-pulse voltammetry: pulse amplitude = 50 mV, scan rate = 4 mV s^{-1}, sample width = 20 ms, pulse width = 60 ms, pulse period = 1000 s, and scan direction is negative. [h] Quasi-reversible only at scan rates >100 mV s^{-1} in CV. [i] Peak potential from DPV: scan direction is positive; all other conditions are the same as in footnote *g*. [j] 50% aqueous acetic acid, pH ~1.

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(1) I = bis(2-ethyl-2-hydroxybutanoato(2−))oxochromate(V), II = bis(2-hydroxy-2-methylbutanoato(2−))oxochromate(V), and III = bis(oxalato(2−))oxochromate(V).

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the equilibrium mixture of the Cr(V) complexes believed to be complex III, and a six-coordinate analogue, was generated in situ from the reaction of chromium trioxide (5 mM) with oxalic acid (100 mM) in 50% aqueous acetic acid (0.5 M in $HClO_4$).[6] *Caution.* The results of bacterial mutagenicity tests and in vitro experiments involving cleavage of DNA,[17] indicate that the complexes I and II (and by implication, III) are potentially potent carcinogens. Appropriate precautions should be exercised in handling these complexes.

The Cr(V)/Cr(IV) couples of I and II were examined by differential-pulse voltammetry and cyclic voltammetry (CV). The cyclic voltammograms of acetone solutions of II are irreversible at slow scan rates, but begin to show quasi-reversible behavior at higher scan rates (>100 mV s^{-1}). By contrast, these couples are quasi-reversible at all scan rates (≥10 mV s^{-1}) in dichloromethane and dimethyl sulfoxide. The process was determined to be one electron by controlled-potential electrolysis (in dichloromethane) and from the peak to peak separation of 75 mV at 10 mV s^{-1} in CV, which approaches that expected for a one-electron process. The peak to peak separation increases with scan rate in the manner expected for slow heterogeneous electron-transfer (100% *iR* compensated) such that the peak to peak separation is 265 mV at 10 V s^{-1}. The slow electron transfer may be indicative of large geometric changes in the coordination spheres of the two complexes. The Cr(IV) complex could be partially reoxidized to Cr(V) in the controlled-potential electrolysis experiments, indicating a half-life on a time scale of minutes at room temperature. This stability may enable the Cr(IV) complex to be characterized. The high stability of the Cr(V) complex in dichloromethane (stable for weeks in the absence of light) and the reversibility of the Cr(V)/(IV) couple are probably linked to the poor coordinating properties of this solvent. Indeed, the stabilities of both the Cr(V) and Cr(IV) complexes generally decrease in order of increasing coordinating ability of the solvent (i.e. the order of stability is dichloromethane > acetone > acetonitrile). However, the prolonged stability of both the Cr(V) and Cr(IV) complexes of I in dimethyl sulfoxide indicates that the factors which stabilize both Cr(V) and Cr(IV) are more complex than just the coordinating ability of the solvent.

The results of ESR experiments on the reduction of Cr(VI) by oxalic acid in aqueous acetic acid have shown the presence of two Cr(V) complexes, which are in rapid equilibrium.[6] These complexes were presumed to be the monochelate and dichelate oxalato complexes of oxochromium(V). However, by analogy with the detailed studies on the stable complexes I and II,[15-17] it is likely that the equilibrium involves the dichelate complex III and a six-coordinate form of III in which the normally vacant axial site is occupied by an aqua, acetato, or monodentate oxalato ligand. This is especially the case since the reactions are performed in excess oxalato ligand, which is unlikely to favor the formation of the monochelate complex. In the electrochemical experiments, a distinct response due to Cr(V) is apparent and it is far removed from the responses due to the Cr(VI) reactants and Cr(III) products. This is illustrated in the differential-pulse voltammograms of Figure 1. Closer examination of the DPV's yields a second weak response with a potential of +1.13 V vs the Ag/AgCl reference electrode. This response appears and decays at a rate similar to that of the major Cr(V) response, but it cannot be stated with certainty whether or not this minor response can be attributed to the second species observed in the ESR spectrum.[6] Figure 2 shows the appearance and disappearance of the major Cr(V)/Cr(IV) couple with time at 20 ● 2 °C, (using differential-pulse voltammetry). The profile obtained by following the variation in the peak heights with time follows closely those obtained by using ESR and UV/vis spectroscopic techniques.[6] The process is identified as a Cr(V)/Cr(IV) couple because a reduction current is observed in the linear sweep voltammograms. At scan rates ≥100 mV s^{-1}, the oxidation wave is apparent in the CV's, showing that the Cr(IV) oxidation state had a lifetime on the order of milliseconds under the reaction conditions. The peak to peak separation of ~120 mV at 100 mV s^{-1} is consistent with the peak to peak separations observed for I[2] and II under the same conditions. The very positive potentials at which the Cr(V)/Cr(IV) couples appear for the Cr(V) intermediates, as compared to I or II (Table I), probably explains the differences in chemical stabilities of the Cr(V) complexes. Thus, the compound presumed to be III is a much stronger oxidant than is Cr(VI) under the same conditions, whereas compounds I and II have oxidizing strengths

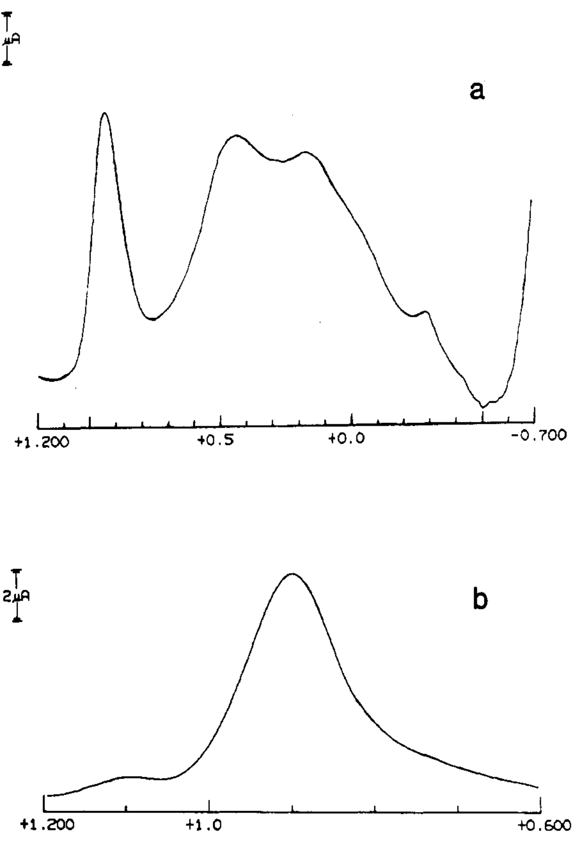

Figure 1. (a) Background-corrected DPV of the products and the reactants of the chromic acid oxidation of oxalic acid after 10 min at 20 ± 2 °C. The Cr(V)/(IV) couple at +0.9 V (vs the Ag/AgCl/saturated KCl reference electrode), is well removed from the complex set of peaks due to the reduction of Cr(VI), at more negative potentials. $[CrO_3]$ = 5 mM; all other experimental conditions are given in the text and Table I. (b) Expansion of the response due to Cr(V) showing the presence of two peaks. $[CrO_3]$ = 6.4 mM; all other conditions are the same as in part a.

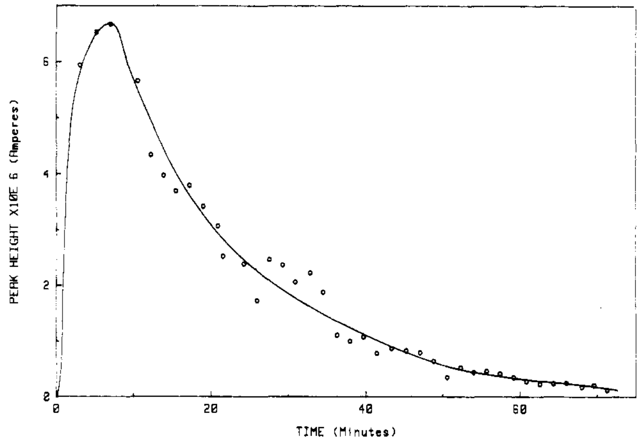

Figure 2. Plot of i_p for the Cr(V)/(IV) couple vs. time in the differential-pulse voltammograms for the Cr(V) intermediate produced in the reduction of Cr(VI) by oxalic acid. Experimental conditions are as described in Table I, with a glassy-carbon working electrode being used.

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[17] Baker, R.; Bonin, T.; Dixon, N. E.; Judd, R. J.; Lay, P. A., submitted for publication.

similar to that of Cr(VI) under the same conditions of pH.

We are continuing to investigate the chemical, electrochemical, and analytical properties of these and related Cr(V) complexes.

Registry No. I^-, 84622-43-5; II^-, 89194-74-1; III^-, 108591-78-2; I^{2-}, 99495-02-0; II^{2-}, 89194-74-1; III^{2-}, 108591-79-3; II, 108591-80-6; acetic acid, 64-19-7.

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Iron-57 Hyperfine Splitting and Rhombic Field Orientation in Low-Spin Ferric Heme Complexes

Sir:

We wish to report the angular orientation of a rhombic crystal field that has been determined for the first time from frozen-solution EPR measurements on ^{57}Fe-substituted low-spin Fe(III) heme complexes, $Fe(TPP)(OMe)_2^-$ and Fe(TPP)(SEt)(MeOH), where TPP is the tetraphenylporphyrin dianion. The analysis of hyperfine (hf) splittings due to the ^{57}Fe nucleus ($I = {}^1/_2$) enables us also to determine the relative orientations of **g** and hf tensors and the sign of the **g** tensor determinant. The rhombic field orientation is closely related to the rotational orientation of axial ligand(s) and, as such, is important in a detailed understanding of structure–reactivity relationships in hemoproteins and their models. Special attention has been drawn to this subject in recent X-ray,[1,2] NMR,[3] EPR,[4] and MO calculation[2] studies.

The second-derivative curves of frozen-solution spectra observed for $^{57}Fe(TPP)(OMe)_2^-$ (**1**) and ^{57}Fe(TPP)(SEt)(MeOH) (**2**) are shown in Figures 1 and 2, respectively. The hf splitting value ($A_{(i)}$) in the g_i absorption peak was obtained by a computer simulation based on the line shape for the corresponding ^{56}Fe species, where g_i and i ($=X, Y, Z$) refer to the principal value and axis of **g** tensor, respectively. The observed values $A_{(i)}$ and $|g_i|$ are summarized in Table I. Remarkable differences in $A_{(X)}$ and $A_{(Y)}$ between **1** and **2** are noticed.

To interpret such observed differences, we have evaluated $A_{(i)}$ theoretically. We assume, in analogy with single-crystal results on low-spin hemoproteins[5] and model complexes,[6] that $|g_Z| > |g_Y| > |g_X|$ and that the Z axis lies along the heme normal. Further, the cubic field is assumed to be much stronger than the low-symmetry field. We then deal with the case in which the axes of the rhombic component field are rotated about the heme normal by an angle φ. It can be shown, according to Oosterhuis and Lang,[7] that the principal axes of **g** and hf tensors rotate about the heme normal by angles φ_g and φ_A, respectively, while the cubic axes (x, y, z) remain fixed to the heme coordinate system (Figure 3). With the lowest Kramers doublet for the $t_2^5\,{}^2T_2$ state,[8] $\Psi^\pm = A(\cos\varphi|\pm{}^1/_2\xi\rangle - \sin\varphi|\pm{}^1/_2\eta\rangle) \pm iB(\sin\varphi|\pm{}^1/_2\xi\rangle + \cos\varphi|\pm{}^1/_2\eta\rangle) \pm C|\mp{}^1/_2\zeta\rangle$, we find that

$$\varphi_g = -\varphi \qquad (1)$$

and

$$\tan 2\varphi_A = -(E - F)\tan 2\varphi/(E + F) \qquad (2)$$

together with the expressions for g_i and $A_{(i)}$ given as

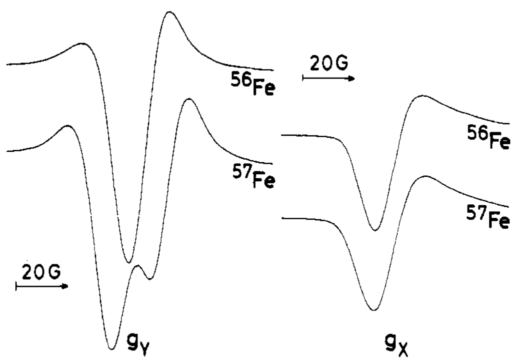

Figure 1. ^{57}Fe hf splittings observed for $Fe(TPP)(OMe)_2^-$ (**1**) in CH_2Cl_2–CD_3OD (1:1 v/v) at 20 K. The second-derivative curves of the g_X and g_Y absorption peaks are compared between the ^{57}Fe (95.15% enriched) and ^{56}Fe (in natural abundance) species. The scale is adjusted so that the two curves have the same height. The sample solution was prepared in situ by adding 50 equiv of CD_3ONa to 1.4 mM solution of ^{57}Fe- or ^{56}Fe(TPP)Cl in CH_2Cl_2–CD_3OD. The deuterium substitution resulted in a slight narrowing of the line width.

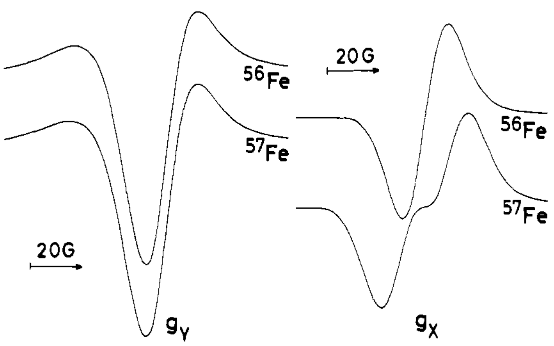

Figure 2. ^{57}Fe hf splittings observed for Fe(TPP)(SEt)(MeOH) (**2**) in CH_2Cl_2–MeOH (3:1 v/v) at 20 K. The second-derivative curves of the g_X and g_Y absorption peaks are compared between the ^{57}Fe (95.15% enriched) and ^{56}Fe (in natural abundance) species. The scale is adjusted so that the two curves have the same height. The sample solution was prepared in situ by adding 15 equiv of EtSH to 1.4 mM solution of ^{57}Fe- or ^{56}Fe(TPP)(OMe) in CH_2Cl_2–MeOH. **2** is formed according to Fe(TPP)(OMe) + EtSH → Fe(TPP)(SEt) + MeOH → **2**. The deuterium substitution was not undertaken.

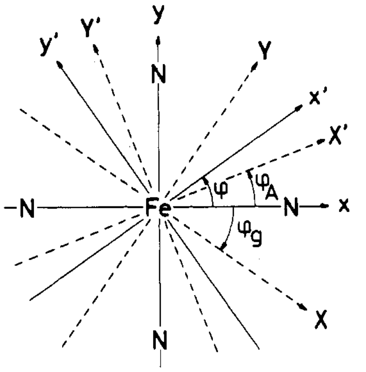

Figure 3. Angular orientation of the principal axes of the **g** tensor (X, Y, Z), hf tensor (X', Y', Z'), and low-symmetry field (x', y', z') with respect to the cubic field axes (x, y, z), which remain fixed to the heme coordinate system.

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(8) $|\pm{}^1/_2\gamma\rangle = |t_2^5\,{}^2T_2 \pm {}^1/_2\gamma\rangle$ ($\gamma = \xi, \eta, \zeta$). Note that the transformation properties of γ are defined in the x, y, z coordinate system, while $\pm{}^1/_2$ refer to the spin functions for S_X, S_Y, S_Z.

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