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Redox Potentials and Related Thermodynamic Parameters of (Diamino polycarboxylato)metal(III/II) Redox Couples

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The formal potentials, reaction entropies, and other thermodynamic parameters have been determined for 23 diamino polycarboxylato complexes of vanadium(III/II), chromium(III/II), iron(III/II), and ruthenium(III/II). The diamino polycarboxylates (L) used in this work are edta^{4-} (ethylenediaminetetraacetate) and its derivatives. The entropy differences of the redox couples are dependent on both the charges of the metal complexes and the kind of the central metal ions. From extensive measurements for chromium(III/II) redox couples, it has been shown that the enthalpy of the reaction $Cr^{III}L + {}^1/_2H_2 \rightleftharpoons Cr^{II}L + H^+$ increases by introducing a methylene group to the diamine moiety, substituting the acetate for propionate arms, or removing one of the acetate arms of edta^{4-} and related ligands.

Introduction

In a previous paper,[2] the formal potentials, reaction entropies, and other thermodynamic parameters were determined for 12 (diamino polycarboxylato)cobalt(III/II) redox couples in aqueous solutions. The systematic study has shown that the magnitude of free energies is governed primarily by the entropy terms rather than the enthalpy terms and that the entropies are dependent on the charges of the complex ions. In this paper, this study has been extended to diamino polycarboxylato complexes of chromium(III/II), vanadium(III/II), iron(III/II), and ruthenium(III/II), in order to understand trends that prevail among the thermodynamic parameters of these redox couples.

Experimental Section

Materials. The solutions of sodium perchlorate and lithium perchlorate were prepared by treating the corresponding carbonate with an equivalent amount of 70% perchloric acid.

Table I shows the structures and abbreviations of ligands (L) used in this work.

Complexes [Cr(Hedta)(H_2O)],[3,4] [Cr(Hpdta)(H_2O)],[5] Na[Cr(trdta)]·$3H_2O$,[6,7] Na[Cr(cydta)]·$4.5H_2O$,[8] K[Cr(eddd)]·$2H_2O$,[9] [Cr(edtra)(H_2O)]·H_2O,[10] [Cr(medtra)(H_2O)]·$1.5H_2O$,[10] [Cr(hedtra)(H_2O)]·H_2O,[10] [Cr(aeedtra)(H_2O)]·$1.5H_2O$,[11] and [Ru(Hedta)(H_2O)]·$3H_2O$[12] were prepared as reported in the literature.

Preparation of Na[Cr(dpot)]. A solution of H_4dpot (0.97 g) in 60 mL of water was neutralized with $NaHCO_3$ (0.74 g). After the addition of $Cr(CH_3CO_2)_3{\cdot}H_2O$ (0.74 g), the solution was heated on a boiling water bath for 3 h. The pH was kept at 4.5 with $NaHCO_3$ during the heating. When the solution was evaporated to a small volume by a rotary evaporator, a violet powder deposited. After filtration, the filtrate was heated on a water bath. Red crystals of Na[Cr(dpot)] deposited; yield 44%. Anal. Calcd for Na[Cr(dpot)]: C, 33.59; H, 3.58; N, 7.12. Found: C, 33.65; H, 3.98; N, 7.20.

Preparation of Na[Cr(*ms*-bdta)]·3H$_2$O. The chromium complex was prepared by a method similar to that for Na[Cr(dpot)]. When a solution containing H_4-*ms*-bdta (0.32 g) and $Cr(CH_3CO_2)_3{\cdot}H_2O$ (0.27 g) at pH 4.5 was heated, violet crystals of Na[Cr(*ms*-bdta)]·$3H_2O$ deposited; yield 55%. Anal. Calcd for Na[Cr(*ms*-bdta)]·$3H_2O$: C, 32.36; H, 4.97; N, 6.29. Found: C, 32.38; H, 5.00; N, 6.41.

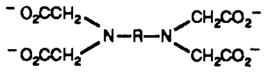
Preparation of [Cr(eedtra)(H$_2$O)]·H$_2$O and [Cr(hpedtra)(H$_2$O)]·1.5H$_2$O. Na_3eedtra and Na_3hpedtra were prepared from *N*-ethylethylenediamine and *N*-(3-hydroxypropyl)ethylenediamine, respectively, by a method similar to that for Na_3medtra by Van Saun and Douglas.[13] The reaction mixtures were used directly for the preparation of the chromium(III) complexes without isolation of the ligands. The chromium(III) complexes were prepared by a method similar to that for [Cr(medtra)(H_2O)]·H_2O reported previously.[10] Yield for [Cr(eedtra)(H_2O)]·H_2O: 43%. Anal. Calcd for [Cr(eedtra)(H_2O)]: C, 34.59; H, 5.51; N, 8.07. Found: C, 34.54; H, 5.89; N, 8.28. Yield for [Cr(hpedtra)(H_2O)]·$1.5H_2O$: 53%. Anal. Calcd for [Cr(hpedtra)(H_2O)]·$1.5H_2O$: C, 34.20; H, 5.74; N, 7.25. Found: C, 34.05; H, 5.71; N, 7.43.

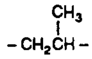
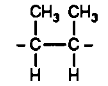
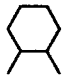
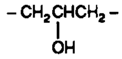
Preparation of [Ru(H$_3$edta)Cl$_2$(H$_2$O)]·2.5H$_2$O. $RuCl_3{\cdot}nH_2O$ containing 44% Ru (3.0 g) was dissolved in 20 mL of 0.6 M HCl solution. The mixture was heated on a water bath and evaporated to a volume of 10 mL. Then the solution was transferred to a flask together with 3.9 g of H_4edta and refluxed for 30 min. When the solution was concentrated at 60 °C, yellow crystals deposited. Yield: 57%. Anal. Calcd for [Ru(H_3edta)Cl_2(H_2O)]·$2.5H_2O$: C, 22.82; H, 4.21; N, 5.32. Found: C, 22.88; H, 4.11; N, 5.37.

Preparation of [Ru(H$_3$pdta)Cl$_2$(H$_2$O)]·3H$_2$O. $RuCl_3{\cdot}nH_2O$ containing 44% Ru (1.0 g) was dissolved in 7 mL of 3 M HCl. H_4pdta (1.3 g) was dissolved in 5 mL of water by adjusting the pH to be 3.7 by adding 6 M NaOH solution. These two solutions were combined, and the mixture was refluxed for 2.5 h. Then the mixture was filtered, and the filtrate was evaporated to almost dryness. The crude crystals deposited were recrystallized from 6 M HCl solution. Yield: 64%. Anal. Calcd for [Ru(H_3pdta)Cl_2(H_2O)]·$3H_2O$: C, 24.05; H, 4.59; N, 5.10. Found: C, 24.01; H, 4.77; N, 5.13.

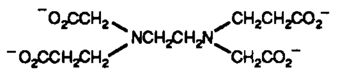
Table I. Structures and Abbreviations of Diamino Polycarboxylates

Tetraacetates

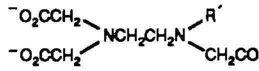


–R–	abbrevn	–R–	abbrevn
$-(CH_2)_2-$	edta	 $-CH_2CH(CH_3)-$	pdta
 $-CH(CH_3)-CH(CH_3)-$	*ms*-bdta	$-(CH_2)_3-$	trdta
	cydta	 $-CH_2CH(OH)CH_2-$	dpot

ethylenediamine-*N*,*N*′-diacetate-*N*,*N*′-dipropionate (abbrevn: eddd)



Triacetates



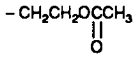
–R′	abbrevn	–R′	abbrevn
–H	edtra	$-CH_3$	medtra
$-C_2H_5$	eedtra	$-(CH_2)_2OH$	hedtra
$-(CH_2)_3OH$	hpedtra	 $-CH_2CH_2OC(=O)CH_3$	aeedtra

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Table II. Electrochemical and Thermodynamic Data for (Diamino polycarboxylato)chromium(III/II) Complexes at 25 °C and $I = 0.1M$ ($LiClO_4$)

group	ligand	charge of complex	$E°'$/V vs SCE	ΔE[a]/mV	$\Delta S_{rc}°$/J K^{-1} mol^{-1}	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
1	edta	1−/2−	−1.230 ± 0.005[b]	66	−46 ± 8	95.4 ± 0.5	57 ± 3	−130 ± 8
	pdta	1−/2−	−1.208 ± 0.004	70	−38 ± 7	93.3 ± 0.4	57 ± 2	−122 ± 7
	ms-bdta	1−/2−	−1.229 ± 0.003	67	−41 ± 5	95.3 ± 0.3	58 ± 2	−125 ± 5
	cydta	1−/2−	−1.189 ± 0.005[c]	92	−49 ± 9	91.5 ± 0.5	52 ± 3	−133 ± 9
	av		−1.21 ± 0.02		−44 ± 7	94 ± 2	56 ± 3	−128 ± 8
2	trdta	1−/2−	−1.345 ± 0.004	61	−43 ± 7	106.5 ± 0.4	69 ± 2	−127 ± 7
	dpot	1−/2−	−1.301 ± 0.005	83	−35 ± 9	102.3 ± 0.5	67 ± 3	−119 ± 9
	eddd	1−/2−	−1.422 ± 0.007[d]	70	−34 ± 11	113.9 ± 0.7	79 ± 4	−118 ± 11
	av		−1.36 ± 0.05		−37 ± 9	108 ± 5	72 ± 5	−121 ± 9
3	edtra	0/1−	−1.264 ± 0.004	70	10 ± 7	98.7 ± 0.4	77 ± 2	−74 ± 7
	medtra	0/1−	−1.243 ± 0.005	67	−1 ± 9	96.7 ± 0.5	71 ± 3	−85 ± 9
	eedtra	0/1−	−1.228 ± 0.003	68	8 ± 6	95.2 ± 0.3	73 ± 2	−76 ± 6
	aeedtra	0/1−	−1.177 ± 0.003	67	8 ± 6	90.3 ± 0.3	68 ± 2	−76 ± 6
	hpedtra	0/1−	−1.222 ± 0.004	71	−5 ± 7	94.6 ± 0.4	68 ± 2	−89 ± 7
	hedtra	0/1−	−1.186 ± 0.004[e]	65	10 ± 7	91.2 ± 0.4	69 ± 2	−74 ± 7
	av		−1.22 ± 0.04		5 ± 7	94 ± 3	71 ± 4	−79 ± 7

[a] The separation between cathodic and anodic peaks determined at a sweep rate of 50 mV s^{-1}. [b] $E°'$ at 20 °C and $I = 0.1$ M (KCl) was reported to be −1.227 V vs SCE.[16] [c] $E°'$ at 25 °C and $I = 0.5$ M (NaCl) was reported to be −1.22 V vs SCE.[17] [d] $E°'$ at 22 °C and $I = 1.0$ M ($NaClO_4$) was reported to be −1.424 V vs SCE.[18] [e] $E°'$ at 22 °C and $I = 0.2$ M ($NaClO_4$) was reported to be −1.22 V vs SCE.[19]

Table III. Electrochemical and Thermodynamic Data for (Diamino polycarboxylato)metal(III/II) Complexes at 25 °C

complex[a]	$E°'$/V vs SCE	ΔE[b]/mV	$\Delta S_{rc}°$/J K^{-1} mol^{-1}	$\Delta G°$/kJ mol^{-1}	$\Delta H°$/kJ mol^{-1}	$\Delta S°$/J K^{-1} mol^{-1}
Vanadium Complex[c]						
$[V(edta)]^{-/2-}$	−1.250 ± 0.004[d]	69	−1 ± 7	97.3 ± 0.4	72.0 ± 3	−85 ± 7
$[V(pdta)]^{-/2-}$	−1.278 ± 0.005	90	7 ± 9	100.0 ± 0.5	77.0 ± 3	−77 ± 9
$[V(ms\text{-}bdta)]^{-/2-}$	−1.231 ± 0.002	86	−4 ± 4	95.5 ± 0.2	69.3 ± 1	−88 ± 4
Iron Complex[e]						
$[Fe(edta)]^{-/2-}$	−0.121 ± 0.003[f]	65	−8 ± 5[g]	−11.6 ± 0.2	−39 ± 2	−92 ± 5
$[Fe(pdta)]^{-/2-}$	−0.118 ± 0.003[f]	63	−5 ± 5	−11.9 ± 0.3	−38 ± 2	−89 ± 5
$[Fe(cydta)]^{-/2-}$	−0.141 ± 0.005[f]	62	−10 ± 8[g]	−9.7 ± 0.5	−38 ± 5	−94 ± 8
$[Fe(ms\text{-}bdta)]^{-/2-}$	−0.096 ± 0.004	64	0 ± 6	−14.0 ± 0.4	−39 ± 2	−84 ± 6
$[Fe(trdta)]^{-/2-}$	0.023 ± 0.005	64	−83 ± 8	−25.5 ± 0.5	−75 ± 3	−167 ± 8
Ruthenium Complex[e]						
$[Ru(edta)]^{-/2-}$[h]	−0.220 ± 0.006[i]	66	−75 ± 10	−2.0 ± 0.6	−49.9 ± 4	−159 ± 10
$[Ru(pdta)]^{-/2-}$[j]	−0.234 ± 0.010	63	−88 ± 17	−0.7 ± 1.0	−52.0 ± 6	−172 ± 17

[a] The coordinated water molecule, if present, is omitted for simplicity. [b] The separation between cathodic and anodic peaks determined at a sweep rate of 50 mV s^{-1}. [c] $I = 0.10$ M (NaCl). [d] $E°'$ at 20 °C and $I = 0.1M$ (KCl) was reported to be −1.267 V vs SCE.[20] [e] $I = 0.10$ M ($NaClO_4$). [f] $E°'$ values for the EDTA, PDTA, and CyDTA complexes at 25 °C and $I = 0.1M$ (KCl) were reported to be −0.123, −0.123, and −0.153 V vs SCE, respectively.[21] [g] The $\Delta S_{rc}°$ values for the EDTA and CyDTA complexes were reported to be −3.6 and −5.7 eu, respectively.[22] [h] The measurements were made for $[Ru(Hedta)(H_2O)]$. Data obtained from $[Ru(H_3edta)Cl_2(H_2O)]\cdot 2.5H_2O$ were $E°' = -0.220 \pm 0.005$ V vs SCE, $\Delta E = 65$ mV, and $\Delta S_{rc}° = -74 \pm 8$ J K^{-1} mol^{-1}. [i] $E°'$ at 25 °C and $I = 0.1M$ (Ktfms) was reported to be −0.25 V vs SCE.[23] [j] The data were collected by use of $[Ru(H_3pdta)Cl_2(H_2O)]\cdot 3H_2O$.

The solutions of iron(III) complexes were prepared by mixing the solutions of $Fe(ClO_4)_3$ and Na_2H_2L in a molar ratio of 1.2:1. The solutions of vanadium(II) complexes were obtained by mixing solutions of vanadium(II) in hydrochloric acid and Na_2H_2L in a molar ratio of 1:1.2. The vanadium(II) solution was prepared by reducing NH_4VO_3 with zinc amalgam.

Measurements. Cyclic voltammograms were obtained in solutions of (diamino polycarboxylato)metal(III) except for vanadium(II) complexes. The pHs of the solutions were adjusted to be 4–6, where no pH dependence of the potentials was observed. Acetate buffer solutions containing 1.0×10^{-2} M sodium acetate were used for changing pHs of the solutions.

The procedures for the determination of formal potentials, $E°'$, and the entropy differences between the oxidized and the reduced species, $\Delta S_{rc}°$, were described in the previous paper.[2] The reversibility of the redox waves was further confirmed by the measurements of ΔE (the separation between cathodic and anodic peak) values vs the sweep rate. Cyclic voltammograms were obtained with a Yanaco P-1000 voltammetric analyzer at sweep rates of 0.01–1 V s^{-1}; most voltammograms were obtained at 0.05 V s^{-1}. A hanging-mercury-drop electrode was used as the working electrode.

Results

The complexes reported here show reversible or quasi-reversible cyclic voltammetric behavior, allowing the determination of the formal potentials, $E°'$, and the entropy differences, $\Delta S_{rc}°$. From these values the thermodynamic parameters $\Delta G°$, $\Delta H°$, and $\Delta S°$ of the reaction

$$M^{III}L + \tfrac{1}{2}H_2 \rightleftarrows M^{II}L + H^+ \qquad (1)$$

were calculated.[2,14]

The electrochemical data and thermodynamic parameters for the chromium(III/II) complexes are given in Table II and the corresponding values for vanadium(III/II), iron(III/II), and

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(14) The $\Delta S_{rc}°$ value for the standard hydrogen couple $H^+/{}^1/_2H_2$, 84.0 J K^{-1} mol^{-1}, was used.[15] Hence as stated in the previous paper,[2] the derived parameters ($\Delta G°$, $\Delta H°$, and $\Delta S°$) are neither standard nor formal quantities but, rather, hybrid.

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Table IV. Coordination Number of the Metal–EDTA Complexes Determined by X-ray Crystal Structure Analyses

oxidn state of metal	coord no.				
	V	Cr	Mn	Fe	Co
II			7[a,b]		6[c,d]
III	7[a,e]	6[c,f]	6[c,g]	6,[c,h] 7[a,i]	6[c,j]

[a] Seven-coordinate complex containing a sexidentate $edta^{4-}$ and one water molecule. [b] In $Mn_3(Hedta)_2 \cdot 10H_2O$.[25] [c] Six-coordinate complex containing a sexidentate $edta^{4-}$. [d] In $[Co(H_2O)_4Co(edta)] \cdot 2H_2O$.[26] [e] In $Na[V(edta)(H_2O)] \cdot 3H_2O$.[27] [f] In $K[Cr(edta)] \cdot 2H_2O$.[28] [g] In $K[Mn(edta)] \cdot 2H_2O$.[29] [h] In $Li[Fe(edta)] \cdot 3H_2O$.[30] [i] In $Li[Fe(edta)(H_2O)] \cdot 2H_2O$ and $Rb[Fe(edta)(H_2O)] \cdot H_2O$.[31] [j] In $NH_4[Co(edta)] \cdot 2H_2O$ and $Rb[Co(edta)] \cdot 2H_2O$[24] and $[Co(sarp)(NH_3)_3][Co(edta)] \cdot H_2O$,[32] where $sarp^{2-}$ denotes sarcosinate-*N*-propionate.

ruthenium(III/II) complexes are summarized in Table III. The formal potentials of several (diamino polycarboxylato)metal(III/II) redox couples have been reported also by other workers. The reported values of $E^{\circ\prime}$ are referred to in Tables II and III. Our data are in reasonably good agreement with these values.

Discussion

An X-ray structural analysis of $[Co(edta)]^-$ indicates that the complex is distorted from regular octahedral geometry and the in-plane acetate arms are more strained than the out-of-plane acetate arms.[24] Furthermore, the Co–O(in-plane acetate) bonds are longer than the Co–O(out-of-plane) bonds. Therefore, when the size of a central metal ion increases, the strain of the in-plane acetate arms would increase. The strain of the coordinated $edta^{4-}$ could be released by introducing a methylene group to the diamine moiety, substituting acetate for propionate arms or removing one of the acetate arms of the $edta^{4-}$.

The coordination numbers of the metal–EDTA complexes determined by X-ray crystal structure analyses are given in Table IV. According to our recent structural determinations,[27] the formulation of the vanadium(III)–EDTA complex in the solid state was found to be $Na[V(edta)(H_2O)] \cdot 3H_2O$: The vanadium(III) ion is seven-coordinate, the $edta^{4-}$ is sexidentate, and the complex contains one water molecule in the first coordination sphere. $[V^{III}(hedtra)(H_2O)] \cdot 2H_2O$ is also a seven-coordinate complex in which the $hedtra^{3-}$ acts as a sexidentate ligand with the coordinated hydroxyethyl group. A coordination mode similar to that of $Na[V(edta)(H_2O)] \cdot 3H_2O$ has been found for $[Mn(edta)(H_2O)]^{2-}$ in $Mn_3(Hedta)_2 \cdot 10H_2O$.[25] For the chromium(III)–EDTA complex, there have been controversial arguments on the solution structure,[33-38] whether the $edta^{4-}$ ion is quinquedentate with a coordinated water molecule $[Cr(edta)(H_2O)]^-$ or sexidentate without a water molecule $[Cr(edta)]^-$. In the crystal of $K[Cr(edta)] \cdot H_2O$, it has been verified that the complex contains a sexidentate $edta^{4-}$ and does not contain a water molecule in the first coordination sphere.[28] A quinquendentate structure of the $edta^{4-}$ in the chromium(II)–EDTA complex has been proposed by Pecsok et al.[16] $Li[Fe(edta)] \cdot 3H_2O$ complex is six-coordinate.[30] However, the crystal of $Li[Fe(edta)(H_2O)] \cdot 2H_2O$ is also known in which the $edta^{4-}$ is sexidentate and one water molecule occupies an equatorial edge of pentagonal-bipyramidal coordination sites.[31] The ruthenium(III)–EDTA complex has been shown to be $[Ru(edta)(H_2O)]^-$ where the $edta^{4-}$ is a quinquedentate ligand and the sixth coordination site of the ruthenium(III) ion is occupied by a water molecule.[12,23,39] Owing to the electrochemically reversible behavior of the ruthenium(III/II)–EDTA couple, the ruthenium(II)–EDTA complex has been assumed to have the same coordination environment as the ruthenium(III)–EDTA complex.[23] From an equilibrium study, it was reported that the cobalt(II)–EDTA complex is mixture of sexidentate species and quinquedentate species.[40] As a result, when the size of central metal ions increases, seven-coordinate complexes could be formed in which the $edta^{4-}$ acts as a sexidentate ligand and one water molecule occupies the seventh coordination site, or six-coordinate complexes could be formed in which the $edta^{4-}$ acts as a quinquedentate ligand and one water molecule occupies the sixth coordination site.

The parameters given in Table II indicate that the chromium(III) complexes can be classified into three groups: Uninegative complexes with ligands that can form only five-membered chelate rings belong to group 1, their $E^{\circ\prime}$ values being -1.21 ± 0.02 V vs SCE. Group 2 contains uninegative complexes with the ligands that can form both five- and six-membered chelate rings, showing $E^{\circ\prime}$ values at -1.36 ± 0.05 V vs SCE. Uncharged complexes with the quinquedentate ligands that can form only five-membered chelate rings conform to group 3, their $E^{\circ\prime}$ values being -1.22 ± 0.04 V vs SCE. Though the $E^{\circ\prime}$ values of groups 1 and 3 are similar to each other, the ΔS_{rc}° values are quite different: The averaged ΔS_{rc}° value of group 1 is -44 J K^{-1} mol^{-1}, whereas that of group 3 is essentially zero. The ΔS_{rc}° values of group 2 are almost the same as those of group 1. Therefore, the entropy differences are governed primarily by the charges of the complex ions. The same feature as this was observed for the ΔS_{rc}° values of (diamino polycarboxylato)cobalt(III/II) redox couples,[2] though the values for the chromium complexes are more negative than those for the corresponding cobalt complexes.

The averaged ΔH° value of group 1 is 56 kJ mol^{-1}, whereas that for group 2 is 72 kJ mol^{-1}; the enthalpy terms are responsible for the more negative $E^{\circ\prime}$ values for group 2. The ligands that belong to group 2 have the enlarging diamine moieties or longer carboxylate arms than EDTA. These changes lead to stabilization of the oxidized form relative to the reduced form. The more negative potential of the EDDD complex than the EDTA complex was noticed by Davies and Earley.[18] The release of the strain by removing an in-plane acetate arm is reflected in the observation that the ΔH° values of the complexes in group 3 are almost identical with those of the complexes in group 2 and larger than those of the complexes in group 1. The $E^{\circ\prime}$ values of group 3 are essentially identical with those of group 1. This must be fortuitous cancellation between the enthalpy and entropy terms. The variation of the ΔH° values for all the cobalt complexes studied previously are surprisingly small; all the ΔH° values span 60–70 kJ mol^{-1}. However, a slightly increased stabilization of the oxidized form was also observed for the TRDTA and DPOT complexes of cobalt(III) ions.[2] The degree of the stabilization is more pronounced for the chromium complexes than for the cobalt complexes, which may be due to the increased ionic radius for the chromium(III) ion relative to the cobalt(III) ion.

The thermodynamic data are summarized in Table III for vanadium, iron, and ruthenium complexes in which the ligands can form only five-membered rings, except $[Fe(trdta)]^-$. These values are almost independent of the nature of the ligands as long as the central metal ions are the same. However, the data of $[Fe(trdta)]^{-/2-}$ are quite different from those of the other iron

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Table V. Formal Redox Potentials and Thermodynamic Parameters for (Ethylenediaminetetraacetato)metal(III/II) Complexes at 25 °C

metal	E_s°[a]/V vs NHE	$E^{\circ\prime}$/V vs NHE	ΔS_{rc}°/J K^{-1} mol^{-1}	log ($K_{M^{III}L}/K_{M^{II}L}$)
V	−0.26[b]	−1.01	−1	12.7
Cr	−0.41[c]	−0.99	−46	9.8
Mn	+1.49[d]	+0.82[e]		11.3[e]
Fe	+0.77[f]	+0.12	−8	11.0
Co	+1.84[g]	+0.37[h]	−28[h]	24.9[h]
Ru	+0.22[i]	+0.02	−75	3.4

[a] Formal redox potential of M_{aq}^{3+}/M_{aq}^{2+}. [b] At 20 °C; from ref 20. [c] At 19 °C; from ref 49. [d] From ref 50. [e] From ref 51. [f] From ref 52. [g] From ref 53. [h] From ref 2. [i] From ref 54.

complexes: Both ΔH° and ΔS° values of the TRDTA complex are large and negative. Such a behavior has not been observed for the corresponding cobalt and chromium complexes. We are unable to offer a good explanation for the unusual behavior of $[Fe(trdta)]^-$.

Ruthenium(III)–EDTA complexes having various compositions have been reported to be formed depending on the synthetic conditions.[12,41,42] In our work, $[Ru(H_3edta)Cl_2(H_2O)]\cdot 2.5H_2O$ was obtained as described in the Experimental Section. An alternative formulation is possible for the complex: e.g. $H[Ru(H_2edta)Cl(H_2O)]Cl\cdot 2.5H_2O$, $H[Ru(H_2edta)Cl_2]\cdot 3.5H_2O$, etc.[43] However, the complex shows almost the same electrochemical behavior as $[Ru(edta)(H_2O)]^-$. Ezerskaya and Solovykh reported that $[Ru(Hedta)Cl]^-$ and $[Ru(H_2edta)Cl_2]^-$ liberate chloride ions rapidly in dilute aqueous solutions.[41] Matsubara and Creutz[23] and Yoshino et al.[44,45] reported that $[Ru(edta)(H_2O)]^-$ undergoes unusually rapid substitution by various ligands X to form $[Ru(edta)X]^{n-}$. From these observations, it was assumed, in this study, that when $[Ru(H_3edta)Cl_2(H_2O)]\cdot 2.5H_2O$ is dissolved in an aqueous solution at pH 4–6, $[Ru(edta)(H_2O)]^-$ is formed relatively rapidly. The electrochemical data obtained from $[Ru(H_3pdta)Cl_2(H_2O)]\cdot 3H_2O$ were regarded as being those for $[Ru(pdta)(H_2O)]^-$. The electrochemical and thermodynamic data of $[Ru(H_3pdta)Cl_2(H_2O)]\cdot 3H_2O$ were almost identical with those of $[Ru(edta)(H_2O)]^-$.

In Table V, the redox potentials and thermodynamic parameters of metal–EDTA complexes are summarized. In the previous paper,[2] we reported that the estimation of ΔS_{rc}° values of cobalt(III/II) complexes by the classical Born equation explains the trend observed experimentally, but the calculated values are different from the found values numerically. The entropy differences of the redox couples (ΔS_{rc}°) studied in this work depend also primarily on the charges of the complex ions for the given metal ions. However, the large variations of the values are seen to be depending on the nature of the central metal ions. The values of the $[M(edta)]^{-/2-}$ couples decrease in the order V ≥ Fe > Co > Cr > Ru. Youngblood and Margerum reported that the change of the number of coordinated water molecules accompanying redox reactions exerts an important influence on ΔS_{rc}° values.[46] This may explain the large variations of the ΔS_{rc}° values depending on the nature of central metal ions. As mentioned above, extensive studies have been carried out on the solution structures of metal complexes containing EDTA and its analogues. However, the dentate number of the complexes and hence the presence of the coordinated water molecule(s) are uncertain for most complexes and may differ between the oxidized and reduced forms. Hupp and Weaver determined ΔS_{rc}° for various M(III/II) redox couples (M = Ru, Fe, Os, Cr) where all complexes are substitution-inert.[47] The values of ΔS_{rc}° were found to correlate well with $1/r$, where r denotes the effective radius of the redox couple defined by Brown and Sutin.[48] The large variations of ΔS_{rc}° values observed in our work cannot be correlated with $1/r$. Hupp and Weaver noted that the correlations of ΔS_{rc}° values with $1/r$ are not observed for complexes containing water molecules due to ligand–solvent hydrogen bonding. This finding may be associated with the absence of the correlation between the ΔS_{rc}° values and $1/r$ for the present system.

The redox potentials of metal(III/II)–EDTA couples ($E^{\circ\prime}$) always shift to the negative side compared with those of the M_{aq}^{3+}/M_{aq}^{2+} couples (E_s°). In particular, the magnitude of the shift is significant in the cobalt system: the potentials differ by 1.5 V. Although the ruthenium system shows the smallest potential difference between $E^{\circ\prime}$ and E_s°, the potential still shifts to the negative side on coordination of EDTA. In Table V, the potential differences are given also by an alternative way, i.e. the ratios of the stability constants of metal(III)–EDTA complexes and the corresponding metal(II)–EDTA complexes. The values were calculated from eq 2, where $K_{M^{III}L}$ and $K_{M^{II}L}$ are the stability constants of M(III)–EDTA and M(II)–EDTA, respectively.

$$E^{\circ\prime} - E_s^{\circ} = -\frac{RT}{F}\ln\frac{K_{M^{II}L}}{K_{M^{III}L}} \qquad (2)$$

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