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Redox Potentials of the Aquo, Cyano and EDTA Complexes of Some Transition Metal Ions by CNDO Calculations

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By using an approximate molecular orbital method standard redox potentials were calculated for the series $M(CN)_6^{4-,5-}$, $M(CN)_6^{3-,4-}$ *(M = Cr, Mn, Fe and Co),* $M(EDTA)^{2-,3-}$, *(M = Cr, Co, Ni and Cu),* $M(H_2O)_6^{2+,+}$ *(M = Cr, Mn, Fe, Co, Ni and Cu) and* $M(H_2O)_6^{3+,2+}$ *(M = Cr, Mn, Fe and Co). Reasonable agreement with experimental values was obtained in the case of the* $M(CN)_6^{3-,4-}$ *couples. From the results for the* $M(CN)_6^{4-,5-}$ *series the redox potentials for the couples* $Cr(CN)_6^{4-,5-}$ *and* $Fe(CN)_6^{4-,5-}$ *were estimated to be −1.7 V and −2.5 V respectively. The agreement with the experimental data is poor for the* $M(H_2O)_6^{3+,2+}$ *couples, both absolute and relative. It is concluded that this discrepancy is caused by the large bond length differences for the* $M(H_2O)_6^{3+,2+}$ *couples. The corresponding energy differences are estimated to be 6–9 eV for the* $M(H_2O)_6^{3+,2+}$ *series. For the* $M(H_2O)_6^{2+,+}$ *series these energy differences may also be large (up to 6 eV for* $Cu^{2+,+}$*), whereas they are smaller for the* $M(EDTA)^{2-,3-}$ *series: about 3–5 eV. For the* $M(CN)_6^{4-,5-}$ *and* $M(CN)_6^{3-,4-}$ *series the energy differences due to relaxation are of the order of 1 eV.*

Introduction

For many redox couples standard redox potentials or half wave potentials are available [1]. There are, however, many systems left unstudied and often it is impossible to obtain a particular redox potential experimentally. An alternative is to calculate the redox potentials by an approximate CNDO or INDO self-consistent molecular orbital method. Recently Yamabe *et al.* reported results on CNDO/2 MO calculations for a series of benzene-1,2-diols [2]. They found a linear correlation between the HOMO energies of the neutral molecules and the experimental redox potentials. In the literature thus far no such calculations have been reported for metal complexes. The principal aim of the present work was to calculate the trend of the redox potentials of the metal EDTA* complexes. The calculations were performed essentially according to the CNDO/S method of Jaffé and co-workers [3], modified to include first-row transition metals analogous to the method of Clack *et al.* [4]. To test the method of calculation, the redox potentials of the hexaquo and hexacyano complexes were also calculated, as for these species experimental redox potentials are available for comparison. The absolute values of the calculated redox potentials and the trends within the series are discussed.

Method of Calculation

Assumptions

We assumed regular octahedral structures for all hexaquo and hexacyano complexes. The values for the bond lengths were taken from X-ray diffraction experiments. If not available, the metal–ligand bond lengths were estimated by comparing the radii of the metal ions [5]. The geometries of the $CuEDTA^{2-}$ and $CoEDTA^{2-}$ complexes were taken from X-ray diffraction experiments. The CNDO method used requires that the bond lengths in the reduced and oxidized state are equal. With this restriction the effect of a small error in the absolute value of the metal–ligand bond length is not large: for the $Mn(H_2O)_6^{2+,+}$ couple the total electronic energy difference increases by 0.03 eV for a bond length increase of 0.002 nm. In the CNDO method the one-centre exchange integrals are neglected. This is not justified for the case of d–d exchange integrals [6]. They were therefore calculated separately from the appropriate expressions given by Gerloch and Slade [7] and the Slater–Condon factors given by Bacon and Zerner [8]. The computed values were added to the calculated total energies.

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*ETA = ethylenediaminetetraacetate.

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Application of Hess' law

Redox potentials were calculated from gas phase ionization energies with Hess' law, the application of which is depicted in Fig. 1 for the $M^{3+,2+}$ couple. An analogous scheme can be given for the other complexes. The individual contributions are the following:

$$\tfrac{1}{2}H_2(aq) \longrightarrow \tfrac{1}{2}H_2(g) + 8.8\ \text{kJ/mol}$$

$$\tfrac{1}{2}H_2(g) \longrightarrow H(g) + 203\ \text{kJ/mol}$$

$$H(g) \longrightarrow H^+(g) + e^- - 1314\ \text{kJ/mol}$$

$$H^+(g) \longrightarrow H^+(aq) + 1090\ \text{kJ/mol}$$

$$M(H_2O)_6{}^{3+}(aq) \longrightarrow M(H_2O)_6{}^{3+}(g) + {} + \Delta G_{hydr}(M(H_2O)_6{}^{3+})$$

$$M(H_2O)_6{}^{3+}(g) + e^- \longrightarrow M(H_2O)_6{}^{2+}(g) + {} + IE(M(H_2O)_6{}^{2+})$$

$$M(H_2O)_6{}^{2+}(g) \longrightarrow M(H_2O)_6{}^{2+}(aq) - \Delta G_{hydr}(M(H_2O)_6{}^{2+})$$

The sum of these contributions gives the standard free enthalpy for process I (see Fig. 1). Expressed in eV one obtains

$$\Delta G_I = -IE(M(H_2O)_6{}^{2+}) + \Delta G_{hydr}(M(H_2O)_6{}^{2+}) - {} - \Delta G_{hydr}(M(H_2O)_6{}^{3+}) + 4.34 \qquad (1)$$

From the CNDO calculations one obtains the ionization energy IE. To obtain the redox potential one also needs to know the difference in hydration-free enthalpies between the oxidized and the reduced complex.

$$\begin{tikzcd}
M(H_2O)_6^{3+}(g) + & \tfrac{1}{2}H_2(g) \arrow[r, "II"] & M(H_2O)_6^{2+}(g) + \arrow[d] & H^+(g) \arrow[d] \\
M(H_2O)_6^{3+}(aq) + \arrow[u] & \tfrac{1}{2}H_2(aq) \arrow[u] \arrow[r, "I"] & M(H_2O)_6^{2+}(aq) + & H^+(aq)
\end{tikzcd}$$

Fig. 1. Application of Hess' law for the calculation of the redox potential of the couple $M_{aq}{}^{3+,2+}$.

Hydration Free Enthalpies

The knowledge of solvation effects, even for a solvent such as water, is still far from accurate (a clarifying discussion of this subject is given in [9]). Therefore one cannot expect that accurate absolute values for the redox potentials can be calculated. On the other hand, if calculated redox potentials within homologous series are compared, it is expected that the errors introduced by the hydration-free enthalpies will cancel out to a large extent.

As a first approximation for the hydration-free enthalpy of an ion Born's equation can be used [10]:

$$G_{hydr} = -\frac{Z^2e^2}{8\pi\epsilon_o r}\left(1 - \frac{1}{\epsilon}\right) \qquad (2)$$

in which Z is the charge of the ion and r its radius. In the derivation of (2) ϵ is taken as being equal to the bulk dielectric constant. This is not justified however, since there is a dielectric saturation effect close to the ion due to the polarization of the water dipoles [11, 12, 13]. As a consequence, (2) gives too large negative values as is known from a comparison with experimental hydration enthalpies. The discrepancy can be as large as 50% for small and/or highly charged ions [11].

Abraham *et al.* performed some model calculations taking into account the polarization effect [12, 13]. They assumed a gradual change of the dielectric constant ϵ as a function of the distance from the ion. The parameters involved can, however, only be roughly estimated so that the model of Abraham *et al.* cannot be applied to our problem.

A more useful method is the one of Bernal and Fowler, extended and improved by Verwey and later by Buckingham [14, 15, 16]. In addition to the Born charging term it involves the ion–dipole and ion–quadrupole interactions of the first hydration layer. There is reasonable agreement with the experimental values. For the alkaline earth series deviations are less than 5%, or 25 kJ/mol [11].

The ion-dipole-quadrupole model was used in the present work for the hexacyano and EDTA complexes, whereas for the hexaquo complexes the Born equation (2) was used [17]. The calculated hydration-free enthalpies are given in Table I.

Results and Discussion

The results of the calculations are given in Table II. The differences in total electronic energies ΔE_T follow directly from the CNDO calculations. Taking into account the differences between the exchange energies EE, one obtains the ionization energies IE. Finally, by taking the hydration free enthalpies into account one finds the calculated standard redox potentials E°.

The Hexacyano Complex

The calculated redox potentials for the $M(CN)_6{}^{3-,4-}$ couples are given in Fig. 2. The Z-dependences of the calculated and measured series are comparable.

From Table II it can be seen that the calculated redox potentials for the hexacyano complexes are far too high when the Born equation (2) is used for the calculation of the hydration free enthalpies. Better agreement with experiment is obtained by calculating the hydration terms with the ion-dipole-quadrupole model. But even here there remain uncertainties. One needs to know the number of water molecules in the first hydration layer [28], and furthermore for a highly charged ion it is doubtful whether the effective charge to be used in the calculation is equal to the formal charge. For this reason, absolute values of the calculated redox potentials cannot be relied upon, but within a series of similar couples the trend should be approximately correct.

The redox potentials of the couples $Cr(CN)_6^{4-,5-}$ and $Fe(CN)_6^{4-,5-}$ can now be estimated by assuming that the CNDO calculations give the correct trend. One thus obtains −1.7 V for the $Cr(CN)_6^{4-,5-}$ couple and −2.5 V for the $Fe(CN)_6^{4-,5-}$ couple. The latter value is close to the redox potential of sodium (−2.714 V), which means that $Fe(CN)_6^{4-}$ is difficult to reduce. Indeed the hydrated electron, a very powerful reducing agent with $E^\circ = -2.86$ V [29], does not react with $Fe(CN)_6^{4-}$ at a measurable

TABLE I. Calculated Hydration Free Enthalpies in eV.

Radius, nm	$\lvert Z \rvert$	Born equation	Ion-dipole model[†]
0.35	1	−2.03	−2.31
	2	−8.12	−7.76
	3	−18.26	−15.74
	4	−32.46	−26.18
	5	−50.72	−39.13
0.33	1	−2.15	−2.53
	2	−8.61	−8.32
	3	−19.37	−16.74
	4	−34.43	−27.76
	5	−53.80	−41.40
0.30	1	−2.37	−2.94
	2	−9.47	−9.38
	3	−21.30	−18.67

[†] The ion-dipole model predicts different hydration free enthalpies for anions and cations of the same size. The values listed are only valid for anions. It is assumed that the first hydration layer consists of six water molecules.

TABLE II. Calculated Redox Potentials. The Standard Redox Potentials E° were calculated using Hydration Free Enthalpies according to Born (A) and to the Ion-dipole Model (B) (see Table I). Radii are 0.30 nm for the Aquo Complexes and 0.35 nm for the Other Complexes.

Complex	Bond length	Spin mult.	EE	ΔE_T	IE	E°, calc.		E°, exp.
						(A)	(B)	
$Cr(CN)_6^{5-}$	0.208	2	−2.76					
				−11.71	−11.02	+2.90	−2.41	unknown
$Cr(CN)_6^{4-}$	0.208	3	−2.07					
				−5.65	−5.65	+4.21	+0.45	−1.28[b]
$Cr(CN)_6^{3-}$	0.208[a]	4	−2.07					
$Mn(CN)_6^{5-}$	0.200	1	−4.28					
				−11.84	−10.42	+3.50	−1.81	−1.06[c]
$Mn(CN)_6^{4-}$	0.200	2	−2.86					
				−5.78	−5.06	+4.80	+1.04	−0.24[c]
$Mn(CN)_6^{3-}$	0.200[d]	3	−2.14					
$Fe(CN)_6^{5-}$	0.191	2	−5.81					
				−13.64	−11.90	+2.02	−3.29	unknown
$Fe(CN)_6^{4-}$	0.191	1	−4.07					
				−6.24	−4.89	+4.97	+1.21	+0.358[b]
$Fe(CN)_6^{3-}$	0.191[e]	2	−2.72					
$Co(CN)_6^{5-}$	0.1904	3	−9.40					
				−13.09	−10.24	+3.68	−1.63	unknown
$Co(CN)_6^{4-}$	0.1904	2	−6.55					
				−7.14	−5.15	+4.71	+0.95	−0.81[f]
$Co(CN)_6^{3-}$	0.1904[g]	1	−4.56					
$CrEDTA^{3-}$	–[h]	6	−6.34					
				−4.12	−1.59	+4.21	+2.05	unknown
$CrEDTA^{2-}$		5	−3.81					

(continued overleaf)

TABLE II *(continued)*

Complex	Bond length	Spin mult.	EE	ΔE_T	IE	E^0, calc.		E^0, exp.
						(A)	(B)	
$CoEDTA^{3-}$	–[i]	3	−9.40	−3.24	−1.72	+4.08	+1.92	unknown
$CoEDTA^{2-}$		4	−7.88					
$NiEDTA^{3-}$	–[j]	2	−13.47	−3.92	−1.59	+4.21	+2.05	unknown
$NiEDTA^{2-}$		3	−11.14					
$CuEDTA^{3-}$	–[k]	1	−18.21	−1.57	+2.07	+7.87	+5.71	unknown
$CuEDTA^{2-}$		2	−14.57					
$Cr(H_2O)_6^{+}$	0.224	6	−6.34	11.27	13.80	+2.36	–	unknown
$Cr(H_2O)_6^{2+}$	0.224	5	−3.81	19.62	21.36	+5.19	–	−0.407[b]
$Cr(H_2O)_6^{3+}$	0.224	4	−2.07					
$Mn(H_2O)_6^{+}$	0.22	5	−6.57	12.47	12.47	+1.03	–	unknown
$Mn(H_2O)_6^{2+}$	0.22	6	−6.57	20.31	24.74	+8.57	–	+1.5415[b]
$Mn(H_2O)_6^{3+}$	0.22	3	−2.14					
$Fe(H_2O)_6^{+}$	0.209	4	−6.97	10.92	11.60	+0.16	–	unknown
$Fe(H_2O)_6^{2+}$	0.209	5	−6.29	21.48	21.48	+5.31	–	+0.771[b]
$Fe(H_2O)_6^{3+}$	0.209	6	−6.29					
$Co(H_2O)_6^{+}$	0.207	3	−9.40	11.75	13.27	+1.83	–	unknown
$Co(H_2O)_6^{2+}$	0.207	4	−7.88	21.06	24.38	+8.21	–	+1.83[b]
$Co(H_2O)_6^{3+}$	0.207	1	−4.56					
$Ni(H_2O)_6^{+}$	0.205	2	−13.47	11.3	13.63	+2.19	–	unknown
$Ni(H_2O)_6^{2+}$	0.205[l]	3	−11.14					
$Cu(H_2O)_6^{+}$	0.2093	1	−18.21	14.16	17.80	+6.36	–	+0.153[b]
$Cu(H_2O)_6^{2+}$	0.2093[m]	2	−14.5					

[a] Ref. 18. [b] Ref. 1. [c] Ref. 19. [d] Ref. 20. [e] Ref. 21. [f] Ref. 22. [g] Ref. 23. [h] For $CrEDTA^{2-}$ the geometry of $CoEDTA^{2-}$ was used [24]. [i] Ref. 24. [j] For $NiEDTA^{2-}$ the geometry of $CuEDTA^{2-}$ was used [25]. [k] Ref. 25. [l] Ref. 26. [m] Ref. 27.

rate ($k < 10^5$ M^{-1} s^{-1}), whereas it reacts very fast with all the other cyano complexes ($k > 3 \times 10^9$ M^{-1} s^{-1}) [30]. It must be noted that the calculated redox potential of the couple $Co(CN)_6^{4-,5-}$ is of theoretical interest only, as the stable oxidized species in water is $Co(CN)_5^{3-}$ instead of $Co(CN)_6^{4-}$ [31].

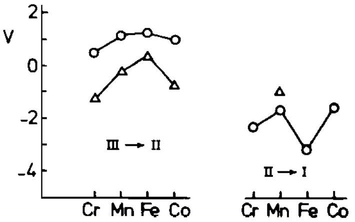

Fig. 2. Calculated (o) and experimental (Δ) redox potentials for the hexacyano couples.

The EDTA Complexes

For the EDTA series no experimental redox potentials are available. From the fact that $CuEDTA^{2-}$ is a stable complex in aqueous solution it can be deduced that the calculated E^0 values are 4 to 5 V too high. This can at least be partly attributed to the uncertainties in the hydration-free enthalpies, as is the case for the hexacyano complexes.

The Hexaquo Complexes

The calculated redox potentials for the hexaquo couples are also too high. There is, however, an important difference with the hexacyano and the EDTA series. For the hexaquo series the hydration free enthalpies were calculated with equation (2), since the ion-dipole-quadrupole model cannot be used. As was explained above, equation (2) gives too large negative values. Improvement of this calculation would lead to smaller values for the hydration-free enthalpies and thus to even higher redox potentials. It must be concluded that the CNDO calculations give too large positive ionization potentials (see below).

The Z-dependence of the calculated values is given in Figs. 3 and 4. For the $M(H_2O)_6^{3+,2+}$ couples the trend is not in agreement with the experimental redox potentials. For the $M(H_2O)_6^{2+,+}$ couples the most striking feature is the relatively high value of the calculated ionization potential for $Cu(H_2O)_6^+$. By using copper as a reference, the E^0 values of the other couples can be estimated from the Z-dependence to be $\leqslant -3.85$ V. This means that the monovalent ions Cr^+, Mn^+, Fe^+, Co^+ and Ni^+ are unstable in aqueous solution. This is in accordance with the fact that no experimental redox potentials are known [1].

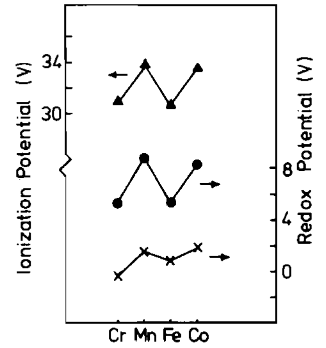

Fig. 3. Calculated redox potentials for the $M_{aq}^{3+,2+}$ couples (o) compared with redox potentials (x) and experimental ionization potentials (Δ).

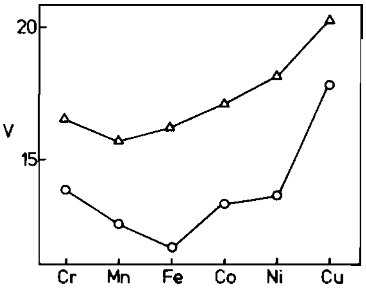

Fig. 4. Calculated ionization potentials for the ions $M(H_2O)_6^+$ (o) compared with the experimental ionization potentials for the ions $M^+(g)$ (Δ).

Relaxation

Electron transfer is generally followed by a change in the metal-ligand bond length. Standard redox potentials are obtained at equilibrium and thus contain this relaxation effect. The assumption of equal bond lengths in oxidized and reduced states therefore introduces an error in the CNDO results. It appears from our results that this error is large in the case of the $M(H_2O)_6^{3+,2+}$ couples, whereas it seems to be much smaller in the case of the hexacyano couples. For some of the complexes bond lengths have been measured (Table III). It is plausible that the large deviations in the CNDO results for the $M(H_2O)_6^{3+,2+}$ couples are correlated with the large bond length differences. It can be estimated from these errors that the energy changes originating from relaxation are about 6–9 eV for the $M(H_2O)_6^{3+,2+}$ couples. It is interesting to note that the trend of the calculated redox potentials follows the trend of the experimental ionization potentials instead of the experimental redox potentials (Fig. 3). This must be attributed the assumption $\Delta r_{redox} = 0$ used in the CNDO calculations; the differences in radii, for instance 0.073 mm for V^{2+} and 0.090 nm for Mn^{2+}, can be attributted by 90% to the crystal field effect [36], whereas the difference in trends of the experimental ionization and redox potentials is also correlated with the crystal field effect.

The better CNDO results for the $M(CN)_6^{3-,4-}$ couples can be explained by the much smaller relaxation energies, which are in the order of 1 eV. This is supported by the small experimental bond length differences reported for the couples $Mn(CN)_6^{3-,4-}$ and $Fe(CN)_6^{3-,4-}$.

Generally, however, the relaxation effect makes redox potential calculations with the relatively simple, parameterized CNDO method unreliable.

TABLE III. Bond Lengths of some Oxidized and Reduced Metal Complexes.

Oxidized complex	Bond length (nm)	Ref.	Reduced complex	Bond length (nm)	Ref.	Matrix
$Fe(H_2O)_6^{3+}$	0.197	33	$Fe(H_2O)_6^{2+}$	0.214	34	crystal
				0.212	35	crystal
$Fe(H_2O)_6^{3+}$	0.197	32	$Fe(H_2O)_6^{2+}$	0.210	32	solution
$Fe(CN)_6^{3-}$	0.195	23	$Fe(CN)_6^{4-}$	0.191	21	crystal
$Fe(CN)_6^{3-}$	0.188	32	$Fe(CN)_6^{4-}$	0.188	32	solution
$Mn(CN)_6^{3-}$	0.200	20	$Mn(CN)_6^{4-}$	0.195	21	crystal
$Cr(H_2O)_6^{3+}$	0.198	32	$Cr(H_2O)_6^{2+}$	0.207	32	solution
$Ru(H_2O)_6^{3+}$	0.203	32	$Ru(H_2O)_6^{2+}$	0.211	32	solution

Separate bond length optimizations for the oxidized and reduced states are required to solve this problem. Recently Bhattacharyya reported optimum bond lengths of the octahedral complexes $V(H_2O)_6^{2+}$, $Cr(H_2O)_6^{3+}$, $Fe(H_2O)_6^{3+}$, $Co(H_2O)_6^{2+}$ and $Ni(H_2O)_6^{2+}$ calculated by a CNDO method developed from the CNDO/2 method of Pople *et al.* [6]. The calculated bond lengths are too small by about 0.05 nm compared with the experimental values [37]. Clack *et al.* reported some optimum bond lengths calculated with CNDO for the systems TiO^+, NiF_6^{4-} and CrF_6^{3-} [38], and $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ [39]: TiO^+: calculated 0.158 nm, experimental 0.162 nm; NiF_6^{4-}: calculated 0.200 nm, experimental 0.200 nm; CrF_6^{3-}: calculated 0.213 nm, experimental 0.193 nm; $Fe(CN)_6^{4-}$: calculated 0.187 nm, experimental 0.191 nm; $Fe(CN)_6^{3-}$: calculated 0.188 nm, experimental 0.195 nm.

It appears that bond length optimization is a major problem of CNDO calculations involving metals. Only if this problem is solved can reliable trends of redox potentials be calculated with an approximate molecular orbital method.

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