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Hard-to-detect Co^{III}/Co^{II} reduction in a hexacyanocobaltate

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Self-consistent confirmations of a high negative value of the redox potential of the $[Co(CN)_6]^{3-}/[Co(CN)_6]^{4-}$ system are demonstrated, which come from quantum-chemical calculations, electrochemical data and spectroscopic data.

Transition metal cyanoferrates (especially, the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system) can be regarded as convenient model reactants for the elucidation of the kinetics of electron transfer due to their high symmetry and homogeneous charge distribution.[1] At the same time, despite of the important role of Co^{III}/Co^{II} systems,[2] relevant data on the $[Co(CN)_6]^{3-}$ reduction are significantly lacking in literature. At first glance, a value of –0.83 V (NHE) reported for the Co^{III}/Co^{II} redox potential[3] seems suitable for studying both homogeneous and heterogeneous redox reactions. However, this potential is related to $[Co(CN)_6]^{3-}/([Co(CN)_5]^{3-} + CN^-)$ equilibrium,[4] while a special polarographic search for the single electron reduction of $[Co(CN)_6]^{3-}$ was unsuccessful[5] [no current was observed up to –1.8 V (SCE); at more negative potentials, the discharge of K^+ was assumed[5]]. We found that the $[Co(CN)_6]^{3-}$ reduction occurs just at the vicinity of the solvent decomposition on mercury.

No reduction waves were observed in polarographic[†] experiments in 1–10 mmol dm^{-3} $K_3[Co(CN)_6]$ solutions with various additives or without them (Figure 1). The currents at potentials more negative than –1.8 to –1.9 V (SCE) are significantly higher than in supporting electrolyte solutions. However, in this case, the distinct hydrogen evolution and the discharge of supporting cation already start in this potential region, which makes the correction procedure (background current subtraction) less accurate. The corrected curves [(*1*)–(*4*) in Figure 1] can be attributed to the reduction of $[Co(CN)_6]^{3-}$, unlikely to the catalytic hydrogen evolution. Furthermore, these curves demonstrate a typical feature for anions electroreduction at negative electrode charges:[6] the current at a fixed potential increases with supporting electrolyte concentration because of the screening of electrostatic repulsion.

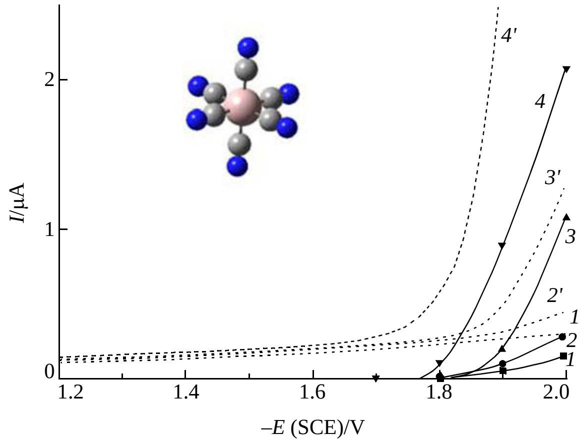

Figure 1 Polarograms measured on a dropping mercury electrode in solutions of various ionic strengths. (*1*)–(*4*) – corrected for background current, (*1'*)–(*4'*) – without background correction. (*1*), (*1'*) $K_3[Co(CN)_6]$ 1 mmol dm^{-3}; (*2*), (*2'*) $K_3[Co(CN)_6]$ 1 mmol dm^{-3} + KCl 10 mmol dm^{-3}; (*3*), (*3'*) $K_3[Co(CN)_6]$ 1 mmol dm^{-3} + KCl 100 mmol dm^{-3}; (*4*), (*4'*) $K_3[Co(CN)_6]$ 1 mmol dm^{-3} + KCl 1 mol dm^{-3}.

Figure 2 demonstrates another confirmation of the above conclusion. Replacing KCl (curve *1*) by the CsCl (curve *2*) additive we observe a remarkable increase of the current at a minor difference for the background currents in supporting 1 mol dm^{-3} solutions of KCl and CsCl (curves *1'* and *2''* in Figure 2). The reaction enhancement in the presence of Cs$^+$ cations is another well-known feature of anion electroreduction (so-called cationic catalysis).[7]

As can be concluded from Figures 1 and 2, the 'excess' current, which can be related to the $[Co(CN)_6]^{3-}$ reduction, becomes noticeable starting from –1.7 to –1.8 V (SCE). A simple explanation is the occurrence of the $[Co(CN)_6]^{3-}/[Co(CN)_6]^{4-}$ redox reaction with a slow subsequent chemical step (CN$^-$ detachment with formation of $[Co(CN)_5]^{3-}$ or its dimer[8]). It is evident that one cannot exclude kinetic limitations, which make the reduction observable at potentials much more negative as compared to the equilibrium potential. To clarify the problem, we attempted to evaluate the standard potentials of $[Co(CN)_6]^{3-}/[Co(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}/([Co(CN)_5]^{3-} + CN^-)$ redox pairs.

We found[‡] the heat of the following processes, which can occur in an aqueous solution: $[Co(CN)_6]^{4-} = [Co(CN)_5]^{3-} + CN^-$. The heat of the reaction is –0.7 eV. Therefore, the expected standard potential of $[Co(CN)_6]^{3-}/[Co(CN)_6]^{4-}$ is more negative as compared to the experimental value of –0.83 V (NHE).

The calculations of standard redox potentials reckoned from the hydrogen electrode (E_0, Table 1) were performed as follows:

$$E_0 = -zF\Delta\vec{G} - 4.34,$$

where $\Delta\vec{G}$ is the free energy of the reduction process; z is the number of electrons transferred (a value of –4.34 eV refers to the free energy of the reaction[13] $H^+_{(aq)} \rightarrow 1/2H_{2(aq)}$).

The reaction free energy was estimated as difference in the total energies of complexes including the solvation contributions. The corresponding difference between the potentials is 0.70 V. It is easy to see that all the computed values are ~0.2 V more negative than real values, including the value for the reference $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ system [+0.36 V (NHE)]. However,

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[†] Polarograms were measured in a three-electrode cell after the deaeration of solutions with hydrogen. A dropping mercury electrode (flow rate of 0.65 mg s^{-1}; open circuit drop life of 10.1 s) was applied, currents were measured at the end of the drop life time. All potentials were measured *vs.* a saturated calomel electrode (SCE) [0 V (SCE) = 0.245 V (NHE) at room temperature].

[‡] *Quantum-chemical calculations* were performed at the density functional theory (DFT) level with the hybrid functional B3LYP;[9] a basis set of DZ quality (LanL2DZ)[10] was employed to describe the valence electrons of a Co atom. The effect of inner electrons was included in the relativistic effective core potential developed by Hay and Wadt.[10] Several test calculations with larger basis sets of TZ quality have shown the reliability of results obtained using the LanL2DZ basis set. The standard 6-311G basis set augmented by both diffuse (+), and polarization functions (*d* or 2*d*) was used to describe the electrons of N and C atoms. The geometry of complexes for oxidised and reduced forms was optimised with some symmetry restrictions. The solvation effects were treated in the framework of the self-consistent reaction field theory exploiting the polarised continuum model (PCM)[11] with a value of 78 for dielectric constant related to the aqueous solution bulk. The unrestricted formalism was employed to describe the open-shell systems. Pertinent computational details regarding the innersphere contribution (λ_{in}) to the total reorganization energy are described elsewhere.[12]

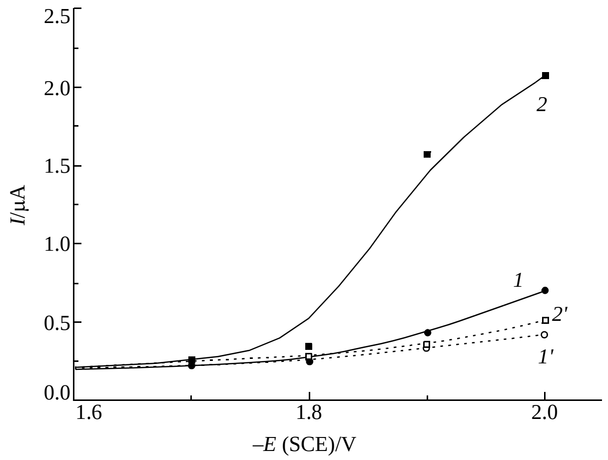

Figure 2 Polarograms measured on a dropping mercury electrode in solutions of various cationic composition. (*1*), (*2*) without correction for background current; (*1′*), (*2′*) background curves. (*1*), (*1′*) $K_3[Co(CN)_6]$ 1 mmol dm^{-3} + KCl 1 mol dm^{-3}; (*2*), (*2′*) $K_3[Co(CN)_6]$ 1 mmol dm^{-3} + CsCl 1 mol dm^{-3}.

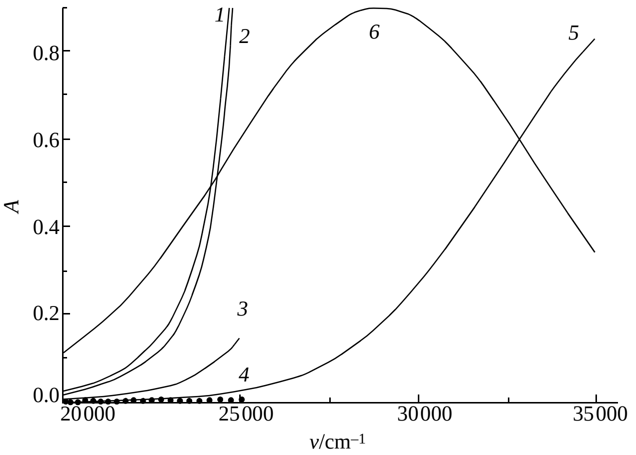

Figure 3 Electronic absorption spectra of the following solutions: (*1*) $K_3[Co(CN)_6]$ 0.3 mol dm^{-3} + $K_4[Fe(CN)_6]$ 0.3 mol dm^{-3}; (*2*) $K_4[Fe(CN)_6]$ 0.3 mol dm^{-3}; (*3*) $K_3[Co(CN)_6]$ 0.3 mol dm^{-3}; (*4*) spectrum obtained by subtraction of *2* and *3* from *1* (solid points); (*5*), (*6*) calculated spectra. $A_{max} = 0.9$, $\nu_{1/2} = 10300$ cm^{-1}; (*5*) $\nu_{max} = 36700$ cm^{-1}; (*6*) $\nu_{max} = 28900$ cm^{-1}.

their differences are in good agreement with experimental data. The shift can result from neglecting the entropy terms (translational, rotational and vibrational contributions).

The solvent effects lead to the appearance of a local energy minimum on the potential energy surface (PES) along the coordinate of the Jahn–Teller distortion of $[Co(CN)_6]^{4-}$, which disappears in a gas phase, where we observed the rupture of two axial Co–CN bonds. Since the heat of the reaction $[Co(CN)_6]^{4-} = [Co(CN)_5]^{3-} + CN^-$ is negative (see above), we can assume an energy barrier on the PES, which separates two minima; this has been confirmed by additional calculations. Therefore, $[Co(CN)_6]^{4-}$ in aqueous solution can be treated as an intermediate state, which may participate in the electron-transfer elementary act.

We found that electron transfer to the anti-binding molecular orbital (E_g) of $[Co(CN)_6]^{3-}$ entails a noticeable reorganization of the inner sheath of a complex reactant. The inner-sphere contribution to reorganization energy λ_{in} was estimated at 0.9 to 1.2 eV, which is much higher than that for $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ (~0.1 eV).[14] Keeping in mind that a smaller value of the dielectric constant ε should be used in the polarised continuum model for concentrated electrolyte solutions or in the vicinity of electrochemical interfaces, we also performed test calculations with an assumed value of 5 for ε. Although we observed a more noticeable Jahn–Teller distortion of the $[Co(CN)_6]^{4-}$, all qualitative conclusions are very similar to those mentioned above.

A remarkable difference between the E_0 values characterising cyanoferrate and cyanocobaltate redox pairs can be understood bearing in mind that five electrons occupy the highest three binding molecular orbitals (T_{2g}) of $[Fe(CN)_6]^{3-}$ in the ground state. In other words, an electron is transferred at reduction to the binding orbital forming the electronic structure T^6_{2g}. Therefore, for the case of $[Fe(CN)_6]^{3-}$ reduced state is more favourable than $[Co(CN)_6]^{3-}$ and, in turn, reducing the $[Fe(CN)_6]^{3-}$ complex must be more easy in comparison with inert hexacyano cobaltates. Note that, for the iron and cobalt aqua complexes, a difference between the E_0 values is also very high; however, their signs are positive and opposite of those for the cyano complexes. Such a drastic difference for certain redox couples containing aqua and cyano ligands can also be inferred from some features of the molecular orbital structure characterising the oxidised and reduced states of complexes. It is well known that the energy split (Δ) between the T_{2g} and E_g orbitals is much higher for the cyano complexes than for the aqua complexes. This favours, in turn, the high-spin electronic configurations for the case of $[Co(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$ ($T^4_{2g}E^2_g$ and $T^3_{2g}E^2_g$, respectively) in contrast to the low-spin structure, which is more preferable for the cyano complexes. In the electrode reactions, electron is transferred to the T_{2g} binding MO of the aqua complexes, which explains the positive sign of E_0 in this case. At the same time, the Δ value for $[Co(H_2O)_6]^{3+}$ is higher in comparison with $[Fe(H_2O)_6]^{3+}$. This can elucidate a more positive E_0 value observed for the Co^{3+}/Co^{2+} redox pair in aqueous solution than for the case of Fe^{3+}/Fe^{2+}.

Table 1 Standard electrode potentials computed for redox pairs.

Redox pair	E_0/V (NHE)
$[Co(CN)_6]^{3-}$/$[Co(CN)_6]^{4-}$	–1.8
$[Co(CN)_6]^{3-}$/$[Co(CN)_5]^{3-} + CN^-$	–1.1
$[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$	+0.19[a]

[a] The unrestricted B3LYP formalism was employed for the single-point calculation of the complex in an oxidised state.

An additional indirect test of the self-consistency of potential values discussed above comes from the electronic absorption spectra. The electron transfer in ionic associates results in the appearance of bands in the near-infrared region (this phenomenon was studied in detail for the $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ system[15]). For $[Co(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$, a similar band related to the reaction

$$[Co(CN)_6]^{3-}, nK^+, [Fe(CN)_6]^{4-} \xrightarrow{h\nu} [Co(CN)_6]^{4-}, nK^+, [Fe(CN)_6]^{3-}$$

is also expected. The position of the band maximum (ν_{max}) depends on two key factors, namely, the values of standard redox potentials for $[Co(CN)_6]^{3-}$/$[Co(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ and the total reorganization energy (λ, the sum of the inner-sphere solvent contributions). The difference spectrum[§] presented in Figure 3 (curve *4*) demonstrates a minor additional absorption in the UV region, in which the specific absorption of ionic components dominates, leaving no chance to determine the position of a maximum directly. One can judge the ion interaction effects only from a comparison of experimental spectra with model absorption calculations.

We have chosen $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ as a reference system.[15] The constant of ionic association (which determines the concentration of associated species), the solvent reorganization energy and the energy of ionic atmosphere reorganization are assumed to be equal for $[Fe(CN)_6]^{3-}$/$[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$/$[Fe(CN)^6]^{4-}$ due to a minor difference in the geometry and charge distributions in both of the systems. Using the above values of E_0 and λ_{in} and taking into account that the ratio of the absorption coefficients of associates becomes 5–10 times higher when switching from d^5 complexes to the relative d^6 complexes (like for ionic associates with amino complexes[16]), we simulated a model spectrum (curve *5* in Figure 3). The experimentally found absence of additional absorption in

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[§] Spectra were measured on a Specord 50 PC instrument in 1 cm quartz cells at room temperature.

the region below 25000 cm^{-1} agrees with the model spectrum based on our estimates of the reorganization energy and redox potential. If the value of –0.83 V (NHE) for the standard redox potential of $[Co(CN)_6]^{3-}/[Co(CN)_6]^{4-}$ pair is used instead of the computed one [–1.8 V (NHE)], the red shift of bands for *ca*. 8000 cm^{-1}. This leads to a difference between the experimental and calculated absorbance values in the region 20000–25000 cm^{-1}, which exceeds one order of magnitude (curve *6* in Figure 3).

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