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ScienceDirect
Mendeleev Commun., 2005, 15(3), 95–96

Mendeleev
Communications

Diquat hexacyanoferrate as a double redox probe for monitoring polymer-modified electrode surfaces

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DOI: 10.1070/MC2005v015n03ABEH002063

$Dq_2[Fe(CN)_6]\cdot 6H_2O$ was used for monitoring the state of electrode surfaces modified by organic films.

Diquat hexacyanoferrate $Dq_2[Fe(CN)_6]\cdot 6H_2O$ **1**[†] was obtained by the reaction of aqueous solutions of potassium hexacyanoferrate and 6,7-dihydrodipyrido[1,2-*a*:2′,1′-*c*]pyrazine-5,8-di-ium[1] (diquat, Dq^{2+}) dibromide at 277 K.[†] This compound is composed of hexacyanoferrate anions, organic cations that are 2,2′-bipyridyl derivatives and water molecules (Figure 1). The shortest distances from the iron atom to the nitrogen atoms of the pyridine ring in compound **1** are Fe(1)···N(4A) 5.02 Å and Fe(1)···N(5) 5.28 Å. The shortest distance from the iron atom to the centre of the pyridine ring is 5.62 Å. These distances are similar to the contact distances between the hexacyanoferrate anions and the cationic amino complexes of transition metals.[4]

The cyclic voltammograms[‡] of a 1 mmol dm^{-3} aqueous solution of compound **1** showed peaks (Figure 2) corresponding to the quasi-reversible (under experimental conditions) one-electron reduction of diquat and the one-electron oxidation of the hexacyanoferrate anion, respectively. The heights of the current peaks are proportional to $v^{1/2}$; this fact allows one to attribute these

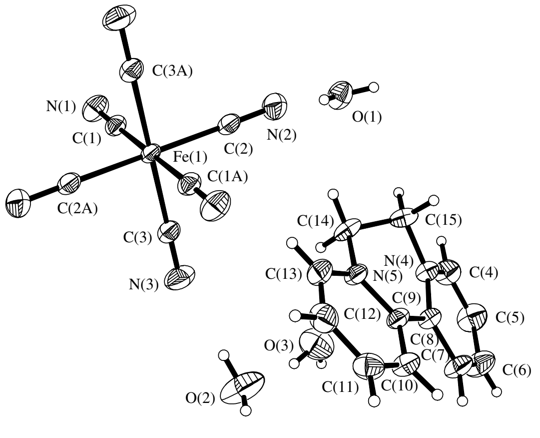

Figure 1 A fragment of the $Dq_2[Fe(CN)_6]\cdot 6H_2O$ structure.

[†] *Crystallographic data for* $Dq_2[Fe(CN)_6]\cdot 6H_2O$, $M = 688.54$, triclinic, space group $P\bar{1}$ (no. 2), $a = 8.5168(7)$, $b = 9.6356(6)$, $c = 10.2568(11)$ Å, $\alpha = 99.62(2)°$, $\beta = 92.76(2)°$, $\gamma = 107.99(2)°$, $V = 784.83(12)$ Å^3, $Z = 1$, $d_{calc} = 1.457$ g cm^{-3}, $F(000) = 360$. The crystal size was 0.3×0.2×0.2 mm. Experiments were performed at 296 K using an Enraf Nonius CAD-4 diffractometer and MoKα radiation ($\lambda = 0.71073$ Å). No decay correction (standards decay –2.8%) and no absorption correction ($\mu = 0.541$ cm^{-1}) were applied. The intensities of 5136 reflections in the range $2.03 < \theta < 27.96°$ were measured ($\omega/2\theta$ scan technique); 3779 of the unique reflections ($R_{int} = 0.0126$) were used for the structure analysis. The structure was solved by a direct method with refinement by the full-matrix least-squares technique in an anisotropic-isotropic (H atoms) approximation. The highest peak in the final difference Fourier was 0.41 eÅ^{-3} (near the Fe atom). The final refinement parameters were as follows: $wR_2 = 0.0898$, $R_1 = 0.0384$ (all reflections), $wR_2 = 0.0869$, $R_1 = 0.0325$ [3429 reflections with $I > 2\sigma(I)$], GOF = 1.042 (286 refinement parameters). All calculations were performed using the SHELXS-97 and SHELXL-97 programs.[2,3]

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 270418. For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2005.

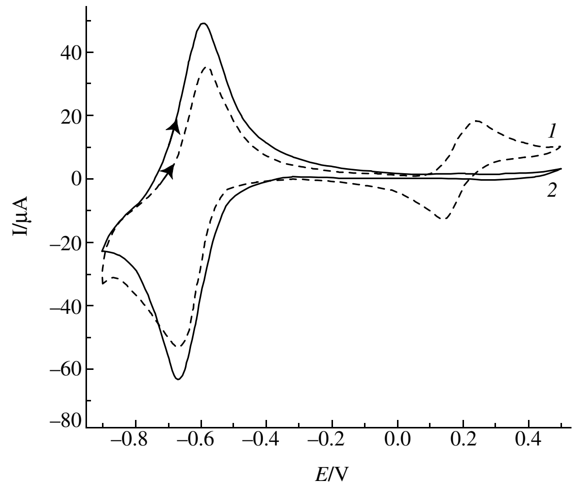

Figure 2 Cyclic voltammograms of 1.0 mmol dm^{-3} $Dq_2[Fe(CN)_6]$ (pH 7.0, 0.1 mol dm^{-3} KCl) (*1*) on a non-modified glassy-carbon electrode and (*2*) after 15 modification cycles in a pyrogallol solution. The potential scan rate is 50 mV s^{-1}.

currents to diffusion-controlled processes. The considerable difference between the formal potentials of the two observed processes (–0.62 and +0.19 V, SCE) and the comparable sizes of the cations make it possible to propose probe **1** for monitoring the state of electrode surfaces during their modification by organic films (where the completeness of coverage of an electrode surface by the film and the sorption of electroactive compounds by the film are monitored parameters) instead of the two redox probes used conventionally, *i.e.*, the hexacyanoferrate ion and the hexaammineruthenium ion.[5]

A film electrode obtained by the electrochemical modification of the surface of a glassy-carbon electrode in a pyrogallol solution was used as the test electrode.[6] Electrodes of this type are promising as electrochemical sensors for the determination of antimony and tin by stripping voltammetry.[7,8] The modification was carried out by the repeated application of potential cycled from –0.20 V to +1.20 V at a rate of 50 mV s^{-1} in a medium containing 1.0 mmol dm^{-3} of pyrogallol (pH 7.0, 0.1 mol dm^{-3} KCl).

Figure 2 shows a cyclic voltammogram of a 1 mmol dm^{-3} aqueous solution of compound **1** after 15 cyclic potential sweeps on a glassy-carbon electrode in the pyrogallol solution. The peak heights are proportional to $v^{1/2}$. The positions of the anodic and cathodic peaks of diquat do not depend on either the potential scan rate or the number of electrode surface modification cycles. Figure 3 shows the cathodic current peaks for ions incorporated in compound **1** on the number of the potential cycle in the pyrogallol-containing medium. The adjusted current values were found after the standard procedure of subtracting the background signal obtained on the modified electrode. The appearance of cyclic voltammograms until about the tenth cycle agrees with the formation of a hydroxyl-containing aromatic compound on the electrode surface; this film hinders the redox transformations of the anionic electroactive probe. The subsequent changes in the cyclic current–voltage curves involve an increase in the current in the region of the redox conversion of diquat. The increase in the current in this region equals the current values recorded during the first subsequent cycling of the modified electrode in a reference electrolyte solution (pH 7.0, 0.1 mol dm^{-3} KCl) in the absence of compound **1**. This allows one to relate the observed changes to the adsorption of the diquat cation into the film. The subsequent cycling of the modified electrode in the reference electrolyte solution results in the fast washout of diquat. An increase in the concentration of the reference solution to 2 mol dm^{-3} resulted in the virtual disappearance of the adsorption of diquat on the modified film electrode.

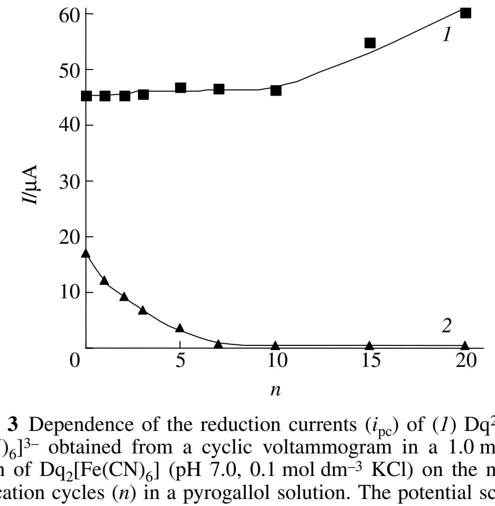

Figure 3 Dependence of the reduction currents (i_{pc}) of (*1*) Dq^{2+} and (*2*) $[Fe(CN)_6]^{3-}$ obtained from a cyclic voltammogram in a 1.0 mmol dm^{-3} solution of $Dq_2[Fe(CN)_6]$ (pH 7.0, 0.1 mol dm^{-3} KCl) on the number of modification cycles (*n*) in a pyrogallol solution. The potential scan rate is 50 mV s^{-1}.

Thus, aqueous solutions of compound **1** can be used as test solutions for monitoring the surfaces of electrodes modified by organic films.

We are grateful to Professor G. A. Tsirlina for valuable discussions of this study.

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Received: 14th October 2004; Com. 04/2388

[‡] The cyclic voltammograms were measured using an Ekotest-VA voltammetric analyser (Russia). The measurements were carried out in a three-electrode 50 ml cell using a glassy-carbon electrode made of a rod 4 mm in diameter and a visible surface of 30 mm^2 and an auxiliary platinum wire electrode. All potentials were measured *versus* a saturated calomel electrode (SCE).