Inorganica Chimica Acta, 111 (1986) L33–L34

The Reaction between Sodium Pentacyanoamminoferrate(III) and Para-aminophenol

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Received July 30, 1985

The reaction which occurs between the reagent $Na_2[Fe(CN)_5NH_3]\cdot H_2O$ (**I**) and various aromatic amines and nitrogen heterocycles was originally investigated as a colour reaction for the determination of the organic compounds [1–4]. More recently reports indicated that the end product of the reaction with amino-compounds was a coordinated quinone-imine complex of pentacyanoferrate(II) [5]. During an investigation of reagents capable of producing phenoxy radicals from a number of phenols we have re-examined the reaction of (**I**) with *para*-aminophenol and have detected the initial formation of the *para*-aminophenoxyl radical which itself can coordinate to the pentacyanoferrate(II) moiety.

Experimental

The reagent (**I**) was prepared from sodium nitroprusside via the intermediate $Na_3[Fe(CN)_5NH_3]\cdot 6H_2O$ according to literature procedures [6]. Commercial *para*-aminophenol was purified by chromatography on a column of activated alumina using benzene as eluant. The blue zinc salt of the complex formed from the reaction of (**I**) with the aminophenol was prepared according to the method of Herington [1]. Infra-red spectra were recorded on samples incorporated in KBr discs using a Pye-Unicam SP 2000 spectrophotometer and visible spectral studies were carried out using a Pye-Unicam SP 800 spectrophotometer. Electron spin resonance studies were made at ambient temperature ($\simeq 293$ K) using a Varian E.3 ESR spectrometer working at 9.5 GHz with standard Varian quartz accessories. Hyperfine coupling constants were measured using Frémy's salt as calibrant ($a_N = 1.301$ mT) and g values were measured relative to diphenylpicrylhydrazyl ($g = 2.0036$). Mössbauer spectra were measured with a constant acceleration spectrometer [7] using natural iron as calibrant and ^{57}Co in a rhodium matrix as source. Magnetic susceptibility measurements were carried out by conventional Gouy methods using $HgCo(CNS)_4$ as calibrant.

Results and Discussion

A re-examination of the molecular equilibrium between (**I**) and *para*-aminophenol by the method of 'continuous variation' [8] at $\lambda = 692$ nm confirmed the 1:1 stoichiometry of the reaction and infra-red studies (Table I) on the blue salt gave results comparable to that of previous workers [1]. Microanalysis of the zinc salt confirmed the formula previously reported [1].

TABLE I. Infra-red Data (cm^{-1}) for $Zn_3[Fe(CN)_5H_2N\cdot C_6H_4\cdot O\cdot]_2\cdot 4H_2O$

3620sh	3440br	3210br	2090s	1942w	1633m	1608m	1572sh
1510sh	1400w	1365w	1340sh	1270sh	1172sh	1164w	1121w
868w	844w						

The fingerprint region of the infra-red spectrum of the zinc salt contained several bands characteristic of the organic part of the complex though there was no evidence of a strong absorption characteristic of C=O which one might have expected if there was a quinone-imine present. The presence of a CN stretch at 2090 cm^{-1} is close to that recorded for CN in $Zn_2Fe(CN)_6$ [1].

The ESR spectrum obtained from admixture of solutions of (**I**) in dilute NaOH (pH $\simeq 9$) and the aminophenol in ethanol, both at concentrations of 10^{-3} M and de-aerated for some 30 min, using oxygen-free nitrogen, is given in Fig. 1. There are some seventy or more well resolved hyperfine lines present which analyse in terms of the coupling constants given in Table II and the g value of the centre line is 2.0041.

The Mössbauer spectrum of the zinc salt (Fig. 2) shows a strong quadrupole splitting (Δ) of 0.787 mm s^{-1} with an isomer shift (δ) of 0.00 mm s^{-1}. The magnetic susceptibility measurements on Na_3[Fe-

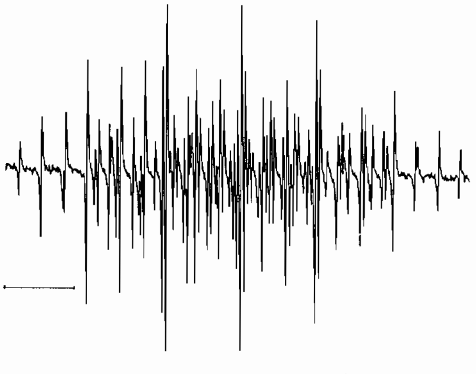

Fig. 1. ESR spectrum of *para*-aminophenoxyl (bar represents 0.5 mT).

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TABLE II. Hyperfine Coupling Constants for *Para*-aminophenoxyl

a_N (mT)	a_{NH} (mT)	a_H (mT)	a_H (mT)	Reference
0.519	0.550	0.313	0.150	This work
0.510	0.510	0.325	0.135	9

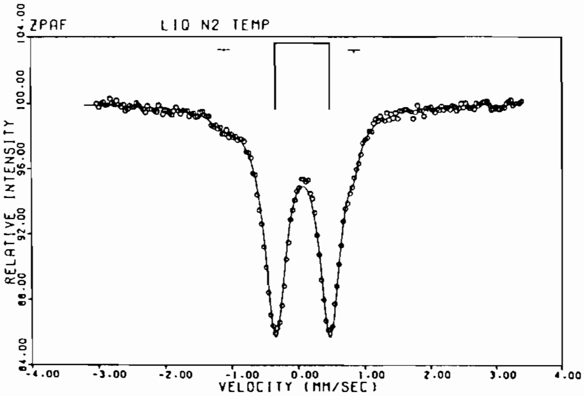

Fig. 2. Mössbauer spectrum of the zinc salt of the complex formed between *para*-aminophenoxyl and pentacyanoferrate(II).

$(CN)_5NH_3]\cdot6H_2O$, $Na_2[Fe(CN)_5NH_3]\cdot H_2O$ and the zinc salt gave magneton numbers of 0.0, 1.84 and 1.7, respectively.

The hyperfine coupling constants derived from the ESR spectrum agree well with those reported in the literature for *para*-aminophenoxyl [9], and indicate that the initial stage of the reaction is a one electron oxidation of the phenol. The earlier suggestion that iron in the blue complex is in the +2 oxidation state is further substantiated by the Mössbauer isomer shift and quadrupole splittings where much larger values are to be expected for Fe(III) with an incomplete electron subshell.

That the zinc salt, however, is paramagnetic with a magneton number of 1.7 indicates the presence of one unpaired electron, which would not be expected for an Fe(II) low-spin complex of C_{4v} symmetry (as indicated from the result for $Na_3[Fe(CN)_5NH_3]\cdot6H_2O$). This leads us to the conclusion that the complex ion in the zinc salt should be formulated as $[Fe(CN)_5\cdot H_2N\cdot C_6H_4\cdot O\cdot]^{3-}$ *i.e.* a coordinated aminophenoxyl. The coordination of free radicals by transition metals ions is not unknown; thus, Co(III) has been shown to coordinate semiquinones [10] and nitroxide radical species of the type $[Co(CN)_5NRO\cdot]^{3-}$ and similar iron complexes have been reported [11–13].

Acknowledgements

We are pleased to acknowledge the assistance of Dr. B. W. Fitzsimmons of Birkbeck College in the recording and interpretation of the Mössbauer spectrum and Dr. E. F. G. Herington for his interest in the work. We are grateful for financial support from the Science Research Council for a grant towards the cost of the ESR spectrometer.

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