REACTIONS OF THE AQUAPENTACYANOFERRATE(II) ION WITH 2-NITROSO-1-NAPHTHOL AND 2-NITROSO-1-NAPHTHOL-4-SULPHONIC ACID

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Abstract—The aqua ligand of the aquapentacyanoferrate(II) ion was replaced by 2-nitroso-1-naphthol and its sulphonate derivative giving the analogous mononuclear nitroso-naptholpentacyanoferrate(II) complex in the first stage of the reaction. In the second stage, a cyano-bridged binuclear product was obtained and characterized as penta-cyanoferrate(II)-μ-cyano-tricyanonitrosonaptholferrate(II). The latter reaction was catalysed by mercury(II) ions. The complexes were characterized on the basis of analytical, IR and UV-vis spectral data and have in the solid state and in solution a predominately quinone oximic structure. The preparation of the tris(2-nitroso-1-naphthol)ferrate(II) complex is also reported.

Like a variety of other nitrogen-containing ligands (amines, nitrogen heterocycles), some aromatic nitroso compounds[1–4] and a number of aliphatic and N-heterocyclic oximes[5–9] are also known to react with the aquapentacyanoferrate(II) ion (AqP). They bind to the $Fe(CN)_5^{3-}$ moiety produced by dissociation of the water molecule from AqP[10] and usually form coloured and water-soluble substituted pentacyanoferrate(II) complexes. If the entering ligand is an actual or a potential bidentate one, an additional replacement of a cyanide group from the iron complex may occur, leading to mononuclear or binuclear tetracyanoferrate(II) species, as in the case of the recently reported reactions of AqP with diamines[11,12] and certain oximes.[13,14] The latter reactions were found to be catalysed by mercury(II) ions.

2-Nitroso-1-naphthol and its water-soluble sulphonate derivative, 2-nitroso-1-naphthol-4-sulphonic acid, are popular reagents in cobalt analysis. Like other naphthols, they are pronounced electron donors and are known to form coloured chelates with a large number of transition metal ions. Since

ortho-substituted nitrosonaphthols are isomeric with oxo-oximes:
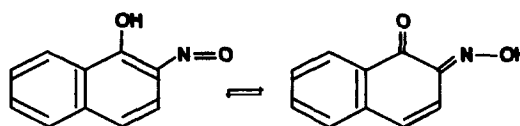
we undertook this investigation to establish if and how they link to the AqP ion in a complex compound.

EXPERIMENTAL

Materials

All the chemicals used were of reagent grade. Redistilled water was used throughout. Britton and Robinson buffers were prepared by mixing 100 cm³ of a phosphoric, boric and acetic acid mixture (all 0.04 M) with different volumes of 0.20 M sodium hydroxide. Solutions of $Na_3[Fe(CN)_5OH_2]$ (AqP) were obtained by aquation of $Na_3[Fe(CN)_5 NH_3] \cdot 3H_2O$ (AmP), dissolving a "Touzart-Matignon" reagent in water 10 min before use. The naphthols were "Fluka" reagents. 2-Nitroso-

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1-naphthol was recrystallized from water (m.p. 142–144°C), while 2-nitroso-1-naphthol-4-sulphonic acid was used as supplied (m.p. 121°C). Their solutions were prepared in ethanol and water, respectively. 1,1′-Bis(pyridinium-4-aldoxime)trimethylene dibromide (TMB-4) and $Fe(ClO_4)_2 \cdot 6H_2O$ were synthesized by known procedures.[15,16] A constant ionic strength of 0.05 M was maintained by sodium chloride. Solutions of mercury(II) ions were prepared by dissolving $HgCl_2$ in water.

The complexes were generated in solution (10% ethanol–water v/v) by mixing buffer (2 cm^3), nitrosonaphthols, sodium chloride, ethanol, AqP and water to produce a volume of 5 cm^3.

Preparations

The nitrosonaphtholpentacyanoferrate(II) complexes were converted to $[Fe(CN)_5(oxime)]^-$ by carrying out a ligand-exchange reaction with a 10-fold molar excess of TMB-4. The quickly formed dark-blue precipitates were filtered off and washed with small portions of ethanol and water. Qualitative analysis showed that the compounds do not contain sodium. Iron was determined as Fe_2O_3. Found: C, 47.2; H, 4.8; N, 24.6; Fe, 11.1 (dealing with 2-nitroso-1-naphthol); C, 47.3; H, 4.6; N, 24.5; Fe, 10.9 (dealing with 2-nitroso-1-naphthol-4-sulphonic acid). Calc. for $H[Fe(CN)_5(C_{15}H_{18}N_4O_2)] \cdot 2H_2O$: C, 47.2; H, 4.5; N, 24.7; Fe, 11.0%.

$Zn_3[(CN)_5Fe—NC—Fe(CN)_3(C_{10}H_6O_2N)]$ was prepared in the following way: 7 cm^3 of an ethanolic solution of 0.104 g of 2-nitroso-1-naphthol (0.6 mmol) was added to 18 cm^3 of a buffered (pH 6.06) solution of 0.039 g of AmP (0.12 mmol) under nitrogen. The resulting intensely green-coloured mixture was left firmly closed for 6 days in the dark. The precipitated nitrosonaphthol was then filtered off and the filtrate evaporated under reduced pressure at maximum 40°C till dryness. The obtained dark-green sodium salt of the complex was washed with 150 cm^3 of acetone and dissolved in water. An acetic acid solution of zinc nitrate[17] precipitated from the solution of the pure complex a gelatinous blue–violet precipitate which was filtered off, washed with 100 cm^3 of water and dried *in vacuo*. The yield was 0.02 g. Iron and zinc were determined by atomic absorption spectroscopy. Found: C, 24.7; H, 3.2; N, 15.3; Fe, 12.0; Zn, 21.0. Calc. for $Zn_3[Fe_2(CN)_9(C_{10}H_6O_2N)] \cdot 12H_2O$: C, 24.5; H, 3.2; N, 15.1; Fe, 12.0; Zn, 21.1%. The complex with 2-nitroso-1-naphthol-4-sulphonic acid was prepared in an analogous way. Found: Fe, 11.9; Zn, 22.1. Calc. for $Zn_3[Fe_2(CN)_9(C_{10}H_5NO_5SNa)] \cdot 4H_2O$: Fe, 12.6; Zn, 22.1%.

The preparation of the sodium salt of the complex, $Na_6[(CN)_5Fe—NC—Fe(CN)_3(C_{10}H_6O_2N)]$, was repeated in the presence of $HgCl_2$: 5 cm^3 of an ethanolic solution containing 0.069 g of 2-nitroso-1-naphthol (0.4 mmol) was added to 25 cm^3 of an aqueous solution of 0.021 g of AmP (0.08 mmol). Immediately after mixing, 40 μg of Hg^{2+} ions were added and the mixture was placed firmly closed in the dark for 3 h. It was then evaporated till dryness under reduced pressure at 40°C and the residual dark-green powder recrystallized from cold water. Sodium was determined by flame photometry. Found: C, 25.8; H, 2.6; N, 14.9; Na, 14.7; Fe, 12.3. Calc. for $Na_6[Fe_2(CN)_9(C_{10}H_6O_2N)] \cdot 12H_2O$: C, 26.2; H, 3.5; N, 16.1; Na, 15.8; Fe, 12.8%.

Tris(2-nitroso-1-naphthol)ferrate(II) was prepared by mixing methanolic solutions of 2-nitroso-1-naphthol and $Fe(ClO_4)_2 \cdot 6H_2O$ in a 3:1 molar ratio. The precipitated sparingly soluble green product was washed with water and ethanol and dried *in vacuo*. When prepared in solution it showed a maximum at $\lambda_m = 700$ nm. Found: C, 59.9; H, 3.3; N, 6.8; Fe, 14.4. Calc. for $Fe[Fe(C_{10}H_6O_2N)_3]_2$: C, 60.0; H, 3.0; N, 7.0; Fe, 14.0%.
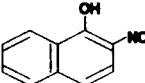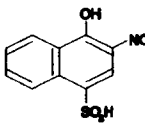
Physical measurements

Spectroscopic measurements were made by a UNICAM SP 600 UV spectrophotometer and 1-cm silica-glass cells. IR spectra were recorded in KBr pellets.

RESULTS

2-Nitroso-1-naphthol reacts with the aquapentacyanoferrate(II) ion in slightly acidic and neutral media by forming a green complex in a few minutes. Its ethanol–water solution exhibits one intense absorption maximum in the visible region located at 710 nm, which is assigned to the iron-to-ligand charge transition. The composition of the complex determined spectrophotometrically was found to be 1:1. After 3 min this complex begins to disintegrate and a new one starts to form in the pH range from 1.5 to 10 ($\lambda_m = 620$ nm). This reaction reaches completion after a few days, when it was found that the complex produced is of a molar ratio 2 AqP:1 nitrosonaphthol (Table 1). Mercury(II) ions catalyse this latter reaction. We assumed that the primarily produced complex is sodium nitrosonaphtholpentacyanoferrate(II) and that the secondary product results from the further labilization of one cyanide group, which is followed by ring closure and the formation of the corresponding tetracyanoferrate(II) species, of binuclear type.

Table 1. Visible absorption spectral data and stability constants K of the complexes with AqP ($I = 0.05$ mol dm^{-3}, $t = 23°C$)

| Ligand	λ_m, nm (ε, M^{-1} cm^{-1})	Reaction time	pH	Composition	log K	
					Ref. 18	Ref. 19
(1-nitroso-2-naphthol structure: OH, NO)	710 (5200)	2–3 min	3–7	1:1	2.64±0.04	2.52±0.02
	620 (2660)	Several days	1.5–10	2AqP:1 ligand	6.60[a]	
(nitrosonaphthol sulfonic acid structure: OH, NO, SO₃H)	690 (4700)	4–6 min	4–6	1:1	2.64±0.07	2.58±0.08
	630 (2370)	Several days	1.5–10	2AqP:1 ligand	8.70[a]	

[a] Approximate value.

The formation of the pentacyanide in the first stage of the reaction was confirmed by carrying out a ligand-exchange reaction with TMB-4. The assumed labile [Fe(CN)$_5$(nitrosonaphthol)]$^{4-}$ instantly reacts with the newly entering ligand and forms the previously defined[9] blue-coloured oximatopentacyanoferrate(II) complex of higher stability (log $K = 4.64$), which, owing to its lower solubility in water, is precipitated. The residual solution lacks the maximum at 710 nm. The secondly formed complex, assumed to be a tetracyanoferrate(II), does not react with TMB-4 since tetracyanoferrates(II) are known to be stable and inert towards substitution. It was isolated from a solution of the aquapentacyanoferrate(II) and a five-fold molar excess of the nitrosonaphthol and analysed in the form of its zinc and sodium salts. Based on this distinct reactivity of cyanoferrate(II) species, different cyano complexes of bidentate diamines were recently effectively separated by the reaction with pyrazinamide and methylpyrazinium.[12]

The UV spectrum of this complex closely resembles that of 2-nitroso-1-naphthol in alkaline medium. Two maxima appear at 276 nm ($\varepsilon = 8100$ M^{-1} cm^{-1}) and 326 nm ($\varepsilon = 4400$ M^{-1} cm^{-1}). The first is a $\pi \to \pi^*$ band characteristic of the o-quinone oxime system.[20] It undergoes a 10 nm hypsochromic shift with increasing polarity of the solvent, in accordance with the behaviour of the conjugation bands in α, β-unsaturated ketones.[21] The second weaker absorption has been compared with the benzenoid band of benzenoid o-benzoquinone oximes[20] and it is also present in the spectra of 1,2-naphthaquinone-1-oxime and of the methyl ether of 1,2-naphthaquinone-2-oxime.[22]

In the visible region a broad band appears around 420 nm ($\varepsilon = 2600$ M^{-1} cm^{-1}). It has been associated[23] with the charge resonance:

(structure: charge resonance representation of nitrosonaphthol tautomers)
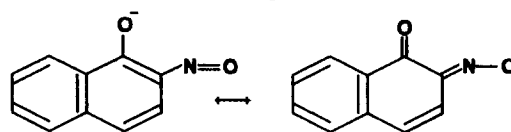
but it probably includes the absorbance contribution of the constituent Fe(CN)$_5$(NC) chromophore in the dimer ($\lambda_m[(CN)_5Fe(NH_3)]^{3-} = 400$ nm, $\varepsilon = 450$ M^{-1} cm^{-1}) assigned to the charge transfer transition from the metal $d(\pi)$ orbitals to the acceptor $p(\pi^*)$ nitrogen orbital of the bridging cyanide group. Finally, the characteristic band of the complex situated at 620 nm is the iron-to-ligand charge transfer transition.

The IR spectrum of the complex was interpreted according to earlier reports on the spectra of the free ligand[22,24] and its metal complexes.[25] The high degree of hydration is considered to be responsible for the broadness and the intensity of the band at 3440 cm^{-1}. In the cyanide stretching region, the very strong band at 2060 cm^{-1} and the strong shoulder at 2030 cm^{-1} are assigned to the terminal cyanide groups, while the weak band located at 2130 cm^{-1} is associated with the bridging cyanide group. It is well known that the bridge formation causes a shift of cyanide stretching to higher frequencies.[26,27] Below 2000 cm^{-1}, either disappearance or marked attenuation of the numerous bands of the free ligand is observed. The very strong ν(C=O) stretching at 1660 cm^{-1} is weakened and shifted to 1613 cm^{-1}, while the medium band at 1548 cm^{-1} attributed to ν(C=N)$_{oxime}$ almost disappears in the complex, indicating that both the carbonyl and the oxime groups participate in complex formation. The very strong band at 1060 cm^{-1} in the spectrum

of the free ligand has been associated with $\nu(NO)$ stretching,[22,24] which is in accordance with the values found in the spectra of quinone oximes.[28] This band shifts to $1280\,cm^{-1}$ in the complex, which concurs with the $\nu(NO)$ vibration at $1293\,cm^{-1}$ recently found in the spectrum of the tris-(violurate)ruthenium(II) anion,[29] which also exhibits a metal–ketoximato chromophore. Such a high position of the $\nu(NO)$ frequency is based on the fact that the N—O bond order of the deprotonated oxime is appreciably greater than 1 and suggests that the nitrogen atom of the oxime group coordinates to the metal centre.[30]

2-Nitroso-1-naphthol-4-sulphonic acid reacts with the AqP ion in a similar way (Table 1) and shows analogous UV and IR spectra.

DISCUSSION

The nitrosonaphthols examined as polar dyestuffs lead to the formation of cyanoferrate(II) complexes whose electronic spectra are appreciably solvent dependent; hence the spectrophotometric experiments were always performed with solutions of the same ethanol–water composition (2-nitroso-1-naphthol being sparingly soluble in water). As a precaution some preparations of the solid complexes were performed under a nitrogen atmosphere, though no influence of oxygen (air) on the reaction products was observed. The intense green colours of the complexes fade rapidly on addition of hydrogen peroxide, indicating that the iron present is in the bivalent oxidation state.

On the basis of the recorded electronic spectra, it is deduced that the nitrosonaphthols examined are present in solutions of the complexes mainly as oxo-oximes; the high absorption at 276 nm characteristic of the o-quinone oxime system dominated in the UV region, while the band due to the nitroso group at $\lambda_m \sim 700\,nm^{21}$ is absent in the visible region. IR data concur with the above conclusion and are in accordance with the generally accepted statement that 2-nitroso-1-naphthol and its metal complexes have, in the solid state, a quinone oximic structure.[22,24,25]

Since the UV spectra of the complexes closely resemble that of the free nitrosonaphthols in alkaline media,[20,25] it can be deduced that the ligands are bound negatively charged, which is also the case in other metal chelates of these compounds.[25,31] This also agrees with the presented analyses of the isolated sodium and zinc salts of the binuclear tetra-cyanoferrates(II), which show that the charge of the complex anion is -6.

During this work it was found that mercury(II) ions catalyse the second-step reaction of AqP with

the nitrosonaphthols examined. When the ratio of the concentrations of AqP and $HgCl_2$ was greater than 2, the binuclear complexes presented in this paper were formed. When $HgCl_2$ was added in greater amounts, partial or total decomposition of the cyanoferrate(II) species occurred and the corresponding tris(nitrosonaphthol)ferrate(II) was produced, as shown by comparison with the spectrum of the prepared tris(2-nitroso-1-naphthol)-ferrate(II).

Because the uncatalysed reactions take several days to complete, the preparation of the sodium salt of the binuclear tetracyanoferrate(II) with 2-nitroso-1-naphthol was repeated, but with addition of $HgCl_2$. The analysis of the isolated product and its spectral characteristics confirmed that the same complex is formed.

Such an influence of mercury(II) ions agrees with the fact that mercury(II) ions catalyse the reactions of the pentacyanoferrate(II) ion with bidentate ligands such as 2,2'-bipyridyl and 1,10-phen-anthroline,[32] as well as ferrozine[33] and bidentate oximes,[14] and can be explained by the great affinity of Hg^{II} for CN^- and its ability to extract cyanide ligands from the metal centre where the linkage of the bidentate ligands occurs.

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