Spectral Investigation of the Products of Reactions of Cyanide Ion with Oxo-bridged Binuclear Iron(III) Complexes of 1,10-Phenanthroline and 2,2'-Bipyridine [1]

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Reactions of cyanide ion with aqueous solutions of oxo-bridged binuclear complexes of iron(III) and 1,10-phenanthroline or 2,2'-bipyridine, $[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]^{4+}$ (L = phen or bipy), are pH and temperature dependent. In the range 45—50 °C and pH 4·0, the complexes $[Fe^{III}(phen)_2(CN)_2]CN$ and $[Fe^{III}(bipy)_2(CN)_2]CN$ are formed, respectively. At room temperature and pH 1·2—1·5, the reduction products $[Fe^{II}(phen)_2(CN)_2]$ and $[Fe^{II}(bipy)_2(CN)_2]$ are obtained, respectively. Addition of cyanide ion to the binuclear complexes at pH 3·8—4·2 and room temperature results in a green solution, which rapidly becomes yellow. The green solution is believed to be due to the ion $[L_2(CN)Fe\text{-}O\text{-}Fe(CN)L_2]^{2+}$, which in solution may undergo rapid decomposition to $[Fe^{III}L_2(CN)_2]^+$.

THE binuclear complex of empirical formula $Fe(phen)_2(OH)Cl_2$ (phen = 1,10-phenanthroline) was first reported [2] in 1936. Since then considerable attention has been paid to elucidation of its structure. It now seems established [3-6] that this is an oxo-bridged species $[(phen)_2ClFe\text{-}O\text{-}FeCl(phen)_2]Cl_2$. In aqueous media this complex and the corresponding 2,2'-bipyridine (bipy) complex are represented [7] as $[L_2(H_2O)Fe\text{-}O\text{-}Fe(H_2O)L_2]Cl_4$ (L = phen or bipy); water effects rapid and complete replacement of the co-ordinated Cl^- ligands.

Aqueous solutions of the complexes $[Fe_2L_4O]Cl_4$ react with Br^- and SO_4^{2-} ions with complete replacement of chloride ligands or ions,[6,8,9] while reaction with ClO_4^- leads to replacement of only two chloride ions.[6] Reactions with thiocyanate ions are pH dependent; [9] the binuclear complex $[L_2(NCS)Fe\text{-}O\text{-}Fe(NCS)L_2](NCS)_2$ precipitates at pH 3·5—4·0, while rupture of the oxo-bridge is effected at pH 1·2—1·5 to form $[Fe^{III}L_2(NCS)_2]NCS$.

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[1] Presented in part at the XXVth annual meeting of the Brazilian Society for the Progress of Science (SBPC), Rio de Janeiro, July 1973.

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We discuss in this work pH- and temperature-dependent reactions of potassium cyanide with $[L_2(H_2O)Fe{-}O{-}Fe(H_2O)L_2]Cl_4$ complexes in aqueous media.

EXPERIMENTAL

Both 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) (E. Merk) were purified by crystallization from aqueous ethanol, followed by slow vacuum sublimation of the crystals. Dry acetonitrile was obtained by drying the reagent-grade material with CaH_2 followed by distillation over P_2O_5; only the middle 50% of the distillate was used.

Preparation of Complexes.—Binuclear complexes $[Fe_2(phen)_4O]Cl_4$ and $[Fe_2(bipy)_4O]Cl_4$ were prepared by literature procedures.[2,9] Methods of Schilt[10] were used in the preparation of the complexes $[Fe^{III}(phen)_2(CN)_2]NO_3$ and $[Fe^{III}(bipy)_2(CN)_2]NO_3$.

Dicyanobis(1,10-*phenanthroline*)*iron*(II). To an aqueous solution (50 cm³) of $FeCl_3,6H_2O$ (2·03 g, 0·0075 mol) was added phen (2·70 g, 0·015 mol). Enough water was added to redissolve all the precipitate of the complex $[Fe_2(phen)_4O]Cl_4$; the total volume was *ca.* 200 cm³. To this solution was added conc. HCl (2 cm³) followed by potassium cyanide (5 g) dissolved in water (20 cm³). A purple precipitate of complex $[Fe^{II}(phen)_2(CN)_2]$ was formed immediately. This was filtered off under suction, washed with water followed by n-hexane, and dried at room temperature in a vacuum desiccator. *Bis*(2,2′-*bipyridine*)*dicyanoiron*(II) was prepared similarly.

TABLE 1

Analytical data (%)

Complex	Found C	Found H	Found N	Found Fe	Calc. C	Calc. H	Calc. N	Calc. Fe
(I) $[Fe^{II}(phen)_2(CN)_2],H_2O$	64·0	3·6	17·15	11·3	64·2	3·75	17·3	11·5
(II) $[Fe^{II}(bipy)_2(CN)_2],2H_2O$	57·8	4·2	18·3	12·15	57·9	4·45	18·4	12·25
(III) $[Fe^{III}(phen)_2(CN)_2]CN,2H_2O$	61·3	3·95	18·6	10·5	61·15	3·8	18·5	10·55
(IV) $[Fe^{III}(bipy)_2(CN)_2]CN,2H_2O$	57·5	4·3	20·4	11·65	57·25	4·2	20·35	11·6
(V) $[Fe^{III}(phen)_2(CN)_2]NO_3$	58·65	3·1	18·55	10·3	58·9	3·05	18·5	10·55
(VI) $[Fe^{III}(bipy)_2(CN)_2]NO_3,4H_2O$	48·05	4·0	18·1	10·0	47·65	4·35	17·7	10·05

Dicyanobis(1,10-*phenanthroline*)*iron*(III) *cyanide*. A saturated aqueous solution of the complex $[Fe_2(phen)_4O]Cl_4$ (*ca.* 3 g in 100—150 cm³ water) was warmed to 45—50 °C in a water-bath. To this solution was added, with constant stirring, potassium cyanide (10 g) dissolved in water (20 cm³). Scratching the sides of the beaker with a glass rod initiated precipitation of a brown solid. Precipitation was completed by cooling the solution in an ice-bath. The precipitate was then filtered off, washed with ice-cold water followed by n-hexane, and dried at room temperature in a vacuum desiccator. *Bis*(2,2′-*bipyridine*)*dicyanoiron*(III) *cyanide* was prepared similarly.

Iron was determined according to the method of Schilt,[10] water by the loss in weight on heating the given complex under vacuum over phosphorus pentoxide. Quantitative microanalyses for carbon, hydrogen, and nitrogen were undertaken by Alfred Bernhardt Microanalyses Laboratory, Germany. Absorption spectra were measured using a Zeiss RPQ-20A recording spectrophotometer. I.r. spectra were measured as Nujol mulls using Perkin-Elmer 337, Perkin-Elmer 237, or Zeiss–Jena UR-20 spectrophotometers. Mössbauer spectra were obtained using a constant-acceleration doppler-velocity transducer. The source was ^{57}Co-electroplated on Cu and had an initial activity of 5 mCi s^{-1}. The velocity scale of the spectrometer was calibrated using a magnetic iron foil. The absorbers were polycrystalline powders contained in cylindrical acrylic cells of cross-sectional area 2 cm². Magnetic susceptibilities of the solid samples were determined by the Gouy method. Calibration standards were water and solid ammonium iron(II) sulphate. Measurements were made at room temperature (24—26 °C). Conductivities were measured with a Beckman Conductivity Bridge model RC 16B2 and a cell with two platinum electrodes. The cell constant was 0·113. The concentration of the solutions was $5{\cdot}0 \times 10^{-4}$M.

RESULTS AND DISCUSSION

In aqueous media the binuclear oxo-bridged complexes of iron(III) with phen, $[(phen)_2(H_2O)Fe{-}O{-}Fe(H_2O)(phen)_2]Cl_4$, and bipy, $[(bipy)_2(H_2O)Fe{-}O{-}Fe(H_2O)(bipy)_2]Cl_4$, undergo pH- and temperature-dependent reactions with cyanide ion. At pH 1·2—1·5 and room temperature (24—26 °C) CN^- effects rupture of the oxygen bridge and reduction of iron(III) to iron(II). These reactions are instantaneous with 95—98% yield. Electronic, i.r., and Mössbauer spectral data, and magnetic moments of the complexes $[Fe^{II}(phen)_2(CN)_2],H_2O$, (I), and $[Fe^{II}(bipy)_2(CN)_2],2H_2O$, (II) (Tables 2 and 4; Figure 1), are in good agreement with those presented for the complexes prepared according to the method of Schilt.[10,11]

TABLE 2

I.r. spectra (cm^{-1})

Complex	ν (CN)
(I) $[Fe^{II}(phen)_2(CN)_2],H_2O$	2 080, 2 064 s,d
$[Fe^{II}(phen)_2(CN)_2],2H_2O$ *	2 075, 2 062 s,d †
(II) $[Fe^{II}(bipy)_2(CN)_2],2H_2O$	2 080, 2 063 s,d
$[Fe^{II}(bipy)_2(CN)_2],2H_2O$ *	2 074, 2 064 s,d
(III) $[Fe^{III}(phen)_2(CN)_2]CN,2H_2O$	2 130, 2 120 s,d; 2 050w ‡
(IV) $[Fe^{III}(bipy)_2(CN)_2]CN,2H_2O$	2 140s; 2 050w ‡
(V) $[Fe^{III}(phen)_2(CN)_2]NO_3$ *	2 354s, 2 335s,sh
(VI) $[Fe^{III}(bipy)_2(CN)_2]NO_3,4H_2O$ *	2 360s, 2 340s,sh

* Prepared according to the method of Schilt (ref. 10). † Value from ref. 11. ‡ These weak peaks are assigned to ionic cyanide.

s = Strong, d = doublet, sh = shoulder, w = weak.

The reactions of CN^- with the binuclear complexes at pH 3·8—4·0 are more interesting. At 45—50 °C,

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brownish yellow precipitates of the complexes $[Fe^{III}(phen)_2(CN)_2]CN$, (III), and $[Fe^{III}(bipy)_2(CN)_2]CN$, (IV) are formed, respectively. Electronic, i.r., and Mössbauer spectral data, and magnetic moments of these compounds are listed in Tables 2 and 4 and Figure 2. At room temperature (24—26 °C) and pH 3·8—4·0, addition of CN^- to an aqueous solution of the binuclear complexes results in formation of a dark green solution, which rapidly changes colour to brownish yellow. We believe the green solution is probably due to the binuclear complex $[L_2(CN)Fe{-}O{-}Fe(CN)L_2]^{2+}$, which undergoes rupture at the oxo-bridge to form $[Fe^{III}L_2(CN)_2]CN$, or even lower complexes of iron(III) with L (L = phen or bipy).

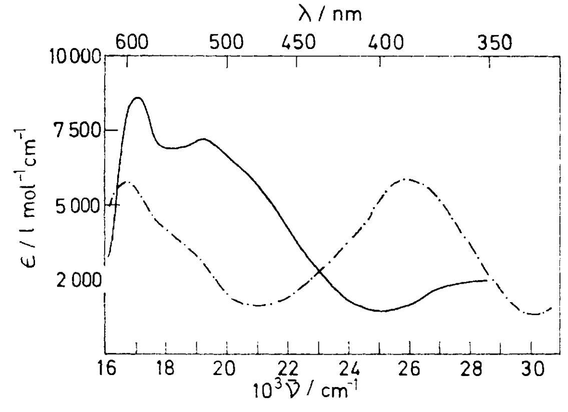

FIGURE 1 Electronic absorption spectra of dicyanobis(1,10-phenanthroline)iron(II), (I) (——), and dicyanobis(2,2′-bipyridine)iron(II), (II) (· — ·), in acetonitrile media

TABLE 3

Molar conductivities

	Complexes	Solvent	Λ/Ω^{-1} cm^2 mol^{-1}
(I)	$[Fe^{II}(phen)_2(CN)_2],H_2O$	$MeCN{-}H_2O$ (50 : 50)	12
	$[Fe^{II}(phen)_2(CN)_2],2H_2O$ *	$MeCN{-}H_2O$ (50 : 50)	13
(II)	$[Fe^{II}(bipy)_2(CN)_2],2H_2O$	$MeCN{-}H_2O$ (50 : 50)	10
	$[Fe^{II}(bipy)_2(CN)_2],2H_2O$ *	$MeCN{-}H_2O$ (50 : 50)	15
(III)	$[Fe^{III}(phen)_2(CN)_2]CN,2H_2O$	H_2O	102
(IV)	$[Fe^{III}(bipy)_2(CN)_2]CN,2H_2O$	H_2O	94
(V)	$[Fe^{III}(phen)_2(CN)_2]NO_3$ *	H_2O	119
(VI)	$[Fe^{III}(bipy)_2(CN)_2]NO_3,4H_2O$ *	H_2O	120

* Prepared according to the method of Schilt (ref. 10).

TABLE 4

Magnetic moments and Mössbauer-effect results at 297 K

	Complexes	μ_{eff}/B.M.	I.s.*/mm s^{-1}	ΔE/mm s^{-1}
(I)	$[Fe^{II}(phen)_2(CN)_2],H_2O$	0·58	+0·21	0·52
	$[Fe^{II}(phen)_2(CN)_2],2H_2O$ †	0·68 [a]	+0·205 [b]	0·52 [b]
		0·55	+0·21	0·52
(II)	$[Fe^{II}(bipy)_2(CN)_2],2H_2O$	0·56	+0·19	0·58
	$[Fe^{II}(bipy)_2(CN)_2],2H_2O$ †	0·61 [a]	+0·195 [b]	0·58 [b]
		0·53	+0·19	0·58
(III)	$[Fe^{III}(phen)_2(CN)_2]CN,2H_2O$	1·85	−0·19	1·06
(IV)	$[Fe^{III}(bipy)_2(CN)_2]CN,2H_2O$	1·92	−0·12	1·25
(V)	$[Fe^{III}(phen)_2(CN)_2]NO_3$	2·34 [a]	+0·025 [b]	1·50 [b]
		2·21		
(VI)	$[Fe^{III}(bipy)_2(CN)_2]NO_3,4H_2O$	2·31 [a]	−0·005 [b]	1·56 [b]
		2·18	−0·02 [c]	1·63 [b]

* Isomer shifts (i.s.) are listed relative to the centre of the spectrum of a natural iron absorber, values from: [a] ref. 10; [b] ref. 15; [c] ref. 14. † Prepared according to the method of Schilt (ref. 10).

Isolation of the brownish yellow complexes $[Fe^{III}L_2(CN)_2]CN$ raises an important question. Schilt[10] reported the preparation of the salts $[Fe^{III}L_2(CN)_2]X$ ($X = NO_3$ or Cl) by oxidation of $[Fe^{II}L_2(CN)_2]$ with nitric acid or chlorine. If these complexes may be represented as $[Fe^{III}L_2(CN)_2]^+$, then the properties of the complexes prepared by Schilt[10] and those prepared in the present work should be identical. We prepared $[Fe^{III}L_2(CN)_2]NO_3$ complexes, (V) and (VI), according to the method of Schilt[10] with a view to comparing their properties with those of $[Fe^{III}L_2(CN)_2]CN$ complexes, (III) and (IV). Comparison of spectral data and magnetic moments for these complexes are presented in

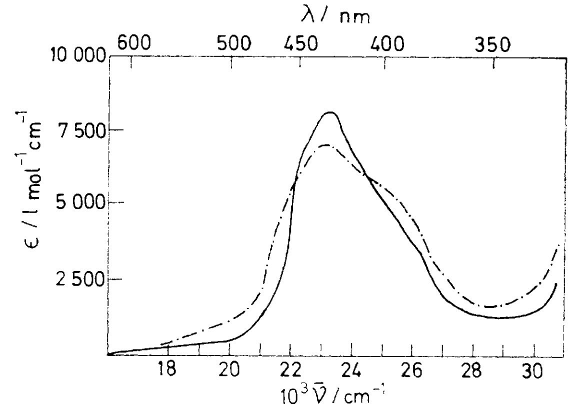

FIGURE 2 Electronic absorption spectra of dicyanobis(1,10-phenanthroline)iron(III) cyanide (——) (III), and dicyanobis-(2,2′-bipyridine)iron(III) cyanide (— · — · —) (IV), in acetonitrile media. Spectra in aqueous media are identical to those in acetonitrile

Figures 2—4 and Tables 2 and 4. Conductivity studies (Table 3) indicate them to be 1 : 1 electrolytes in aqueous media. Magnetic-moment data support a low-spin iron(III) configuration with $S = 1/2$. However, electronic, i.r., and Mössbauer spectral data show that complexes (III) and (IV) are different from (V) and (VI).

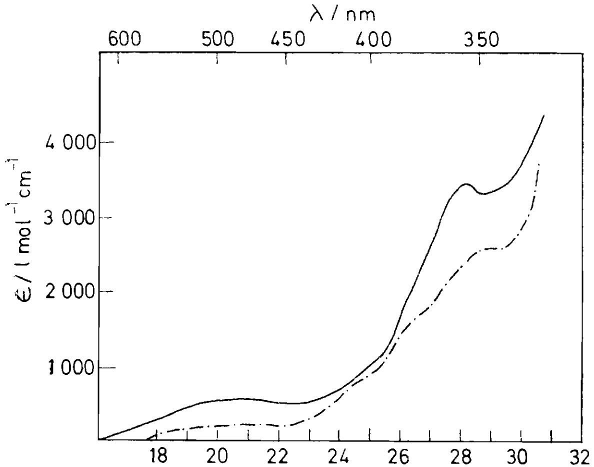

FIGURE 3 Electronic absorption spectra of dicyanobis(1,10-phenanthroline)iron(III) nitrate (——), and dicyanobis(2,2′-bipyridine)iron(III) nitrate (· — ·), in acetonitrile media. Spectra in acetonitrile and aqueous media are identical

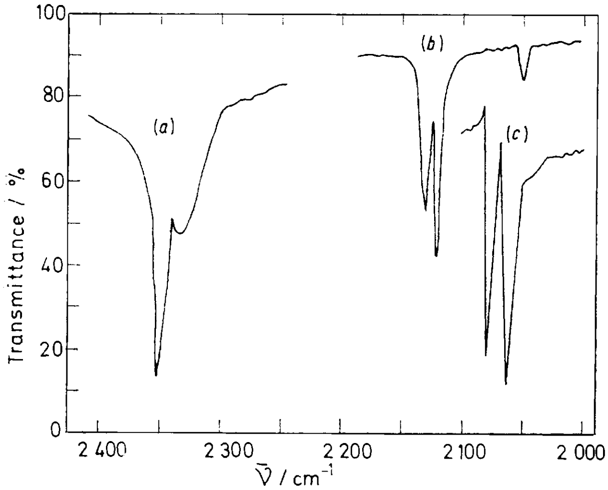

FIGURE 4 Comparison of C≡N stretching bands in the i.r. spectra of the complexes (*a*), $[Fe^{III}(phen)_2(CN)_2]NO_3$, (*b*) $[Fe^{III}(phen)_2(CN)_2]CN$, and (*c*) $[Fe^{II}(phen)_2(CN)_2]$

The C≡N stretching frequencies in the i.r. spectra of complexes (III) and (IV) are in the region expected for a CN^- ligand co-ordinated to iron(III).[12] A large shift in the cyanide-stretching frequency for complexes (V) and (VI) (Figure 4) may indicate the existence of CN^- as a bridging ligand.[12] This suggests that complexes (V) and (VI) are in fact binuclear or even polynuclear, oxidation of $[Fe^{II}(phen)_2(CN)_2]$ and $[Fe^{II}(bipy)_2(CN)_2]$ by nitric acid or chlorine resulting in modification of the CN^- ligands. The exact nature of the ' cyanide bridge ' in these complexes is not clear. The absence of separate stretching modes for bridging and non-bridging cyanide indicates that all the CN^- groups, or modified forms of them, are involved in bridging. This evokes the possibility of eight-co-ordinate iron(III) in these complexes. An alternative is acid-catalysed intermolecular rearrangement of CN^- ligands to form $^-N{\equiv}C{-}C{\equiv}N^-$ which might act as a bridging ligand to form dimeric complexes of the type $[L_2Fe(NCCN)_2FeL_2]^{2+}$, or even polynuclear species. There exists another alternative of octahedral iron(III) with singly bonded (unidentate) phen or bipy ligands. While the entropy consideration or ' chelate effect ' rules out this possibility, the present results do not permit distinction between the other two.

Mössbauer spectral data for the complexes (III)—(VI) are presented in Table 4. Replacing phen or bipy by CN^- ligands normally lowers the isomer shift (i.s.) indicating increased metal-to-ligand π-bonding by virtue of unfilled π-antibonding orbitals of the CN^- ligands, which can accept electrons from the central metal ion.[13] With reference to the system [14] $[Fe(phen)_3]^{2+}$–$[Fe(phen)_2(CN)_2]$, the decrease in i.s. value when one phen is replaced by two CN^- ligands is 0·18 mm s^{-1}. Compared to i.s. values [14] for the complexes $[Fe(phen)_3](ClO_4)_3$ (0·05 mm s^{-1}, with respect to Fe) and $[Fe(bipy)_3](ClO_4)_3$ (0·03 mm s^{-1}, with respect to Fe), the decreases in i.s. for complexes (III) and (IV) are 0·24 and 0·15 mm s^{-1}, respectively, in fair agreement with the expected values. Decreases in quadrupole-splitting (ΔE) values for (III) and (IV) when compared to the corresponding tris-(phen) and -(bipy) complexes [15] are, as expected, due to the increase in distortion from octahedral (O_h) symmetry.

Comparison of i.s. and ΔE values for (V) and (VI) with those for the corresponding tris-(phen) and -(bipy) complexes shows a near equivalence of symmetry and π-bonding capabilities. This may again indicate the absence of linear non-bridged CN^- ligands in the former complexes. Decrease in the π-bonding ability of CN^- ligand may be due to deviation from its linear structure. The exact nature of the ' cyanide-bridge ' in complexes (V) and (VI) is not certain from this work.

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