Redox Chemistry of $[Fe_2(CN)_{10}]^{4-}$. Part 2.[1] Reaction with Thiosulfate

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The oxidation of thiosulfate by the iron(III) dimeric complex $[Fe_2(CN)_{10}]^{4-}$ in acidic aqueous solution at an ionic strength of 1.0 mol dm^{-3} (Na_2SO_4) has been investigated by stopped-flow and conventional spectrophotometry. The overall reaction is quite complicated, occurring in two distinct processes. The first comprises two steps, involving an intermediate, and results in a relatively fast one-electron reduction to $[Fe_2(CN)_{10}]^{5-}$, the rate of which was monitored by the stopped-flow technique; this is followed by a much slower second reaction leading to fission of the cyanide bridges and the formation of the pentacyano(thiosulfato)ferrate-(II) and -(III) complexes. Separate mechanisms are given for each step based on the observed kinetic data.

The di-μ-cyanobis[tetracyanoferrate(III)] ion, $[Fe_2(CN)_{10}]^{4-}$, was first reported around the turn of the century by Hofmann.[2] However it was fifty years later that Emschwiller[3] first recognised the species was dimeric and systematically investigated its chemistry. More recently there has been a new wave of interest in cyano-bridged binuclear complexes arising mainly from their importance[4-7] as intermediates in inner-sphere electron-transfer reactions. If their stabilities and rates of formation from monomeric species are known then a correct assignment of the mechanism can be made in an electron-transfer reaction. Most of these studies refer to species with a single cyanide bridge, those of doubly bridged ones being less extensive. Higginson, Murray and co-workers[8-11] reported several such investigations. Substitution reactions with thiocyanate have been studied by Espenson and Wolenuk,[12] who observed cleavage of the cyanide bridges and formation of $[Fe(CN)_5(SCN)]^{3-}$. A redox reaction with iodide was observed by Stedman *et al.*,[1] with reduction to the mixed-valence compound $[Fe_2(CN)_{10}]^{5-}$. From $E°$ values it is known that the comproportionation constant $[Fe_2(CN)_{10}{}^{5-}]^2/[Fe_2(CN)_{10}{}^{4-}][Fe_2(CN)_{10}{}^{6-}]$ is large. A complex redox/ substitution reaction with nitric and nitrous acids has been reported.[13] The present study concerns reaction of $[Fe_2(CN)_{10}]^{4-}$ with the thiosulfate ion, which is a powerful reducing agent $[E°(S_4O_6{}^{2-} \longrightarrow 2S_2O_3{}^{2-}) = 0.169\ V]$ and also a strong nucleophile. Oxidation reactions of thiosulfate by transition-metal complexes occur by both inner- and outer-sphere mechanisms; in the latter case radical intermediates may be involved. The present work follows on from preliminary work by Leis and Pena.[14]

Experimental

Preparation of $[Fe_2(CN)_{10}]^{4-}$.—The complex $[Fe_2(CN)_{10}]^{4-}$ was prepared by the method of Emschwiller[3] and purified by passage through a column of Sephadex G25. A variation was to use persulfate instead of bromine vapour for the oxidation. Throughout the preparation the temperature was kept below 5 °C to minimise decomposition. The dark purple solution which resulted had λ_{max} at 560 nm and concentrations were calculated using $\varepsilon = 1600$ dm^3 mol^{-1} cm^{-1}.[12] This solution was stored in a refrigerator.

All chemicals used in the preparation were AnalaR grade.

Kinetic Measurements.—The initial reaction was followed by stopped-flow spectrophotometry using a Hi-Tech Scientific SF-51 spectrophotometer attached to a Haake D8 water-bath, by observing the disappearance of the peak at 560 nm where the complex has its λ_{max}. The second, slow, reaction was followed at 634 nm on a Phillips PU8800 spectrophotometer. This is the wavelength of maximum absorption for the product $[Fe(CN)_5(S_2O_3)]^{4-}$; the absorbance difference between the iron(II,III) intermediate and the product is of the order of some 0.8 units under our conditions. Measurements in the near-IR region were made on a Pu 8670 VIS/NIR spectrophotometer. A sodium acetate–acetic acid buffer (0.05 mol dm^{-3}) was used to maintain pH at 5.70, measured using an Orion Research EA920 Expandable Ion Analyzer. Ionic strength was maintained at 1.0 mol dm^{-3} using Na_2SO_4.

For the second reaction, the complex was added to a thermostatted solution of the reductant, quickly mixed and transferred to a 1 cm quartz cuvette. This was placed in the constant-temperature cell holder in the spectrophotometer. All kinetic measurements were made under pseudo-first-order conditions with thiosulfate in at least 50-times excess over the complex. Analysis of the biphasic kinetics was carried out using IS-1 rapid kinetics software V1.Oa from Hi-Tech Scientific on a DTK386 series computer. Errors were calculated by a least-squares program. Values of $\Delta S^‡$ have been rounded to the nearest entropy unit.

Results and Discussion

Addition of thiosulfate to a solution of $[Fe_2(CN)_{10}]^{4-}$ results first in the rapid disappearance of the peak at 560 nm, forming a species with a broad maximum in the near IR region. This is followed by a much slower formation of a blue compound with λ_{max} at 634 nm. There are two poorly defined isosbestic points at 430 and 786 nm for this second process. The peak in the near IR region occurred at about 1240 nm which is close to the 1277 nm reported[15] to be λ_{max} for the mixed-valence complex $[Fe_2(CN)_{10}]^{5-}$. Therefore we deduce that initially one of the iron(III) centres in the complex is reduced. The final product, the blue complex with λ_{max} at 634 nm, is thought to be the iron(III) species $[Fe(CN)_5(S_2O_3)]^{4-}$. Leis and Pena[14] found that the product of the reaction of $[Fe(CN)_5(H_2O)]^{2-}$ with thiosulfate absorbed at the same wavelength. Macartney[16] comments that pentacyanoferrate(III) complexes with sulfur-donor ligands show charge-transfer bands in the range 500–700 nm. Thus the blue thiourea complex $[Fe(CN)_5(tu)]^{2-}$ absorbs at 600 nm and $[Fe(CN)_5(SCN)]^{3-}$ absorbs[12] at 590 nm. In confirmation that

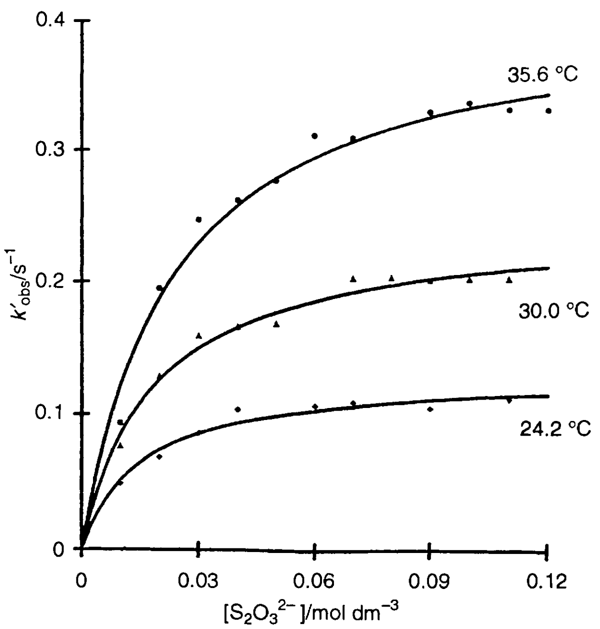


Fig. 1 Plot of k'_{obs} against $[S_2O_3^{2-}]$

we had an iron(III) species, the blue colour rapidly disappeared on reduction with ascorbic acid, similar to the observations of McAuley and Macartney[17] on the reduction of $[Fe(CN)_5(tu)]^{2-}$. Pentacyanoferrate(II) complexes with sulfur ligands absorb[16] around 400–420 nm. These observations establish that the species absorbing at 634 nm is an iron(III) complex. The second stage of the reaction is thus believed to involve ring opening and then a substitution process. This has been confirmed by reducing $[Fe_2(CN)_{10}]^{4-}$ with half an equivalent of ascorbic acid to form $[Fe_2(CN)_{10}]^{5-}$ and then adding thiosulfate. The blue $[Fe(CN)_5(S_2O_3)]^{5-}$ was formed. A similar result was obtained in the iodide reduction of $[Fe(CN)_{10}]^{4-}$ to the iron(II,III) complex. Addition of thiosulfate destroyed the colour of I_3^- and the blue thiosulfate complex was formed.[14] The reaction of $[Fe_2(CN)_{10}]^{4-}$ with thiosulfate therefore occurs in two distinct stages each of which will be considered individually.

Reduction of $[Fe_2(CN)_{10}]^{4-}$ *to* $[Fe_2(CN)_{10}]^{5-}$.—The first process is a one-electron reduction resulting in the formation of the mixed-valence complex $[Fe_2(CN)_{10}]^{5-}$. The kinetic trace (absorbance *versus* time) for this reaction is indicative of a biphasic process with the formation of a transient intermediate. Computer analysis of the absorbance *vs.* time data yielded values of pseudo-first order rate constants k'_{obs} and k''_{obs} for the two stages. Both of these rate constants varied with thiosulfate concentration and typical data are shown in Table 1 and Figs. 1 and 2. The variation of k'_{obs} shows a linear increase at lower $[S_2O_3^{2-}]$ followed by a saturation effect at higher concentrations. Kinetic behaviour of this type is often due to a change in the rate-determining stage of a reaction, and Scheme 1 shows a plausible mechanism involving a ring-opening reaction by fission of a CN–Fe bond to form $[(NC)_4(S_2O_3)Fe\text{–}CN\text{–}Fe(CN)_5]^{6-}$. For such a mechanism equation (1) can be

$$k'_{obs} = \frac{k_1k_2[S_2O_3^{2-}]}{k_{-1} + k_2[S_2O_3^{2-}]} \quad (1)$$

derived. This was checked by a double-reciprocal plot of $1/k'_{obs}$ against $1/[S_2O_3^{2-}]$. Values of k_1 and k_{-1}/k_2 are given in Table 2. The errors on k_{-1}/k_2 are too large to calculate meaningful ΔH values.

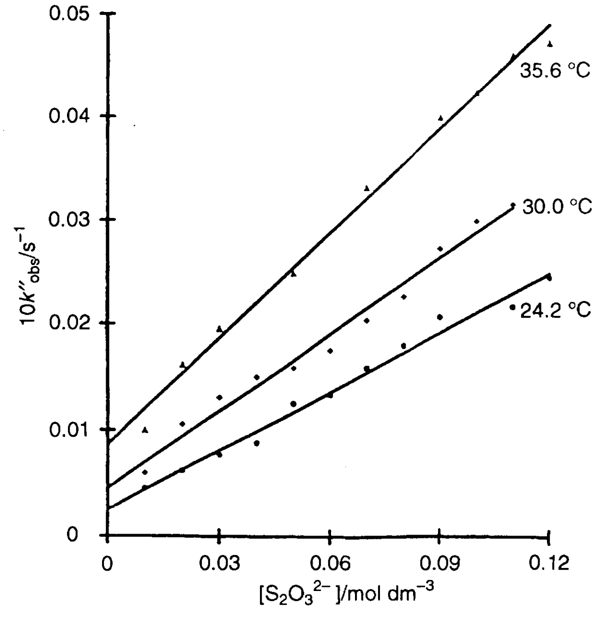


Fig. 2 Plot of k''_{obs} against $[S_2O_3^{2-}]$

Table 1 Pseudo-first-order rate constants for the biphasic reduction of $[Fe_2(CN)_{10}]^{4-}$ to $[Fe_2(CN)_{10}]^{5-}$ by thiosulfate. [Complex] = 0.21 × 10^{-3} mol dm^{-3}; pH 5.70; I = 1.0 mol dm^{-3} (Na_2SO_4); 35.6 °C

$[S_2O_3^{2-}]$/mol dm^{-3}	First step $10k'_{obs}$*/s^{-1}	Second step $10^2k''_{obs}$*/s^{-1}
0.01	0.93	1.00
0.02	1.95	1.62
0.03	2.47	1.96
0.04	2.62	
0.05	2.77	2.49
0.06	3.12	
0.07	3.09	3.32
0.09	3.30	3.99
0.11	3.32	4.59
0.12	3.32	4.71

* Mean value of at least two kinetic measurements at a single thiosulfate concentration.

Table 2 Kinetic and activation parameters for the first stage of the mechanism in Scheme 1

T/°C	k_1/s^{-1}	$10^2(k_{-1}/k_2)$/mol dm^{-3}
24.2	0.138 ± 0.007	1.9 ± 1.3
30.0	0.265 ± 0.012	2.4 ± 1.2
35.6	0.528 ± 0.071	4.3 ± 4.2

$\Delta H_1^{\ddagger}$ = 88.7 ± 2.0 kJ mol^{-1}, $\Delta S_1^{\ddagger}$ = 37 ± 8 J K^{-1} mol^{-1}.

The variation of the other rate constant of the biphasic process, k''_{obs}, with thiosulfate concentration fits equation (2),

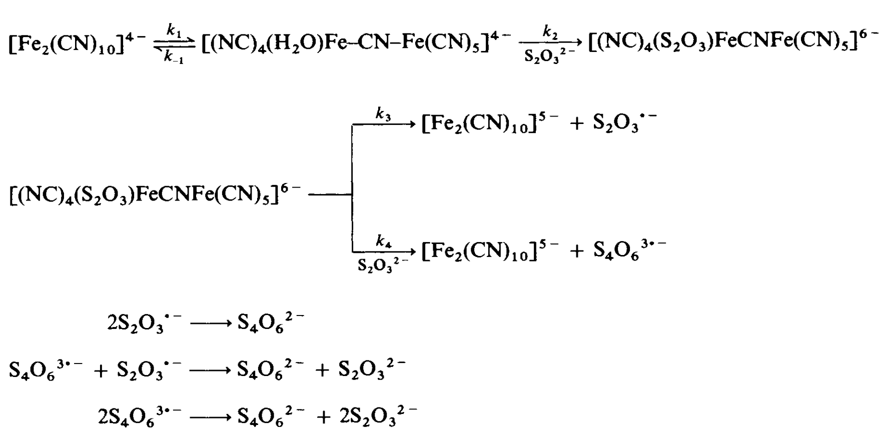
$$k''_{obs} = k_3 + k_4[S_2O_3^{2-}] \quad (2)$$

as shown in Fig. 2. Data on the variation with temperature are given in Table 3.

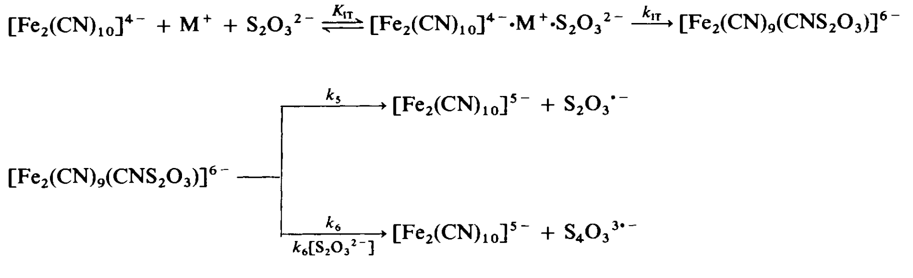
The mechanism postulated in Scheme 1 involves parallel pathways for the decomposition of $[(NC)_4(S_2O_3)Fe\text{–}CN\text{–}Fe(CN)_5]^{6-}$ to $[Fe_2(CN)_{10}]^{5-}$ with the formation of $S_2O_3^{\bullet-}$ and $S_4O_6^{3\bullet-}$. It has been established[18,19] that both these radical anions can exist as transients in aqueous solution. For reaction (3) the forward rate constant has a value 2.5 × 10^6 dm^3 mol^{-1} s^{-1} and equilibrium constant is *ca.* 750 dm^3 mol^{-1}.

$$S_2O_3^{2-} + S_2O_3^{\bullet-} \rightleftharpoons S_4O_6^{3\bullet-} \quad (3)$$

The lower $\Delta H^{\ddagger}$ for the k_4 than for the k_3 path may reflect the greater stability of radical species with several sulfur atoms, and



Scheme 1



Scheme 2

Table 3 Rate constants and activation parameters for the reaction of thiosulfate with the intermediate $[(NC)_4(S_2O_3)Fe–CN–Fe(CN)_5]^{6-}$ in Scheme 1

T/°C	10^3k_3/s^{-1}	k_4/dm^3 mol^{-1} s^{-1}
24.2	2.48 ± 0.53	0.186 ± 0.008
30.0	4.49 ± 0.77	0.243 ± 0.011
35.6	8.65 ± 0.85	0.335 ± 0.011

$\Delta H_3^{\ddagger}$ = 81.0 ± 3.4 kJ mol^{-1}, $\Delta S_3^{\ddagger}$ = −22 ± 10 J K^{-1} mol^{-1}; $\Delta H_4^{\ddagger}$ = 36.8 ± 2.4 kJ mol^{-1}, $\Delta S_4^{\ddagger}$ = −135 ± 10 J K^{-1} mol^{-1}.

the more negative $\Delta S^{\ddagger}$ the difference between a bimolecular (k_4) and a unimolecular path (k_3).

This mechanism is attractive but it is not consistent with the interpretation offered by Higginson and co-workers[20] for their work on the hydrolysis of $[Fe_2(CN)_{10}]^{4-}$ over the range pH 9–11.4. These workers found the reaction to be alkali catalysed and reported k_1/s^{-1} for the bridge cleavage to be 1.9 × 10^{-5} at pH 9.5 and 15 × 10^{-5} at pH 10.3 at 25 °C. Our own limiting rate constant of 1.38 × 10^{-1} s^{-1} at pH 5.75 is far too fast to be consistent with the earlier work. Higginson and co-workers also quote rate constants for 34 °C which are again orders of magnitude lower than our value at 35.6 °C. Thus although the ring-opening hypothesis of Scheme 1 is attractive, it must be rejected.

The arguments above have forced us to turn to alternative interpretations. Saturation effects in kinetics can sometimes be due to a shift in a pre-equilibrium, so that the active form of a reactant changes from being a minor to a major component. Our evidence shows that the rate of reaction is very sensitive to the nature of the alkali-metal cation present, with a reactivity sequence $Cs^+ > NH_4^+ > K^+ > Na^+ > Li^+$. Leis and Pena[14] observed a similar sequence during the course of preliminary studies of this system, and Stedman *et al.*[1] observed similar effects in the oxidation of iodide ion by $[Fe_2(CN)_{10}]^{4-}$. Cation effects of this type are a well known feature of redox reactions between anionic species, and are generally attributed to ion-pairing effects. We suggest that an ion triplet $[Fe_2(CN)_{10}]^{4-}{\cdot}M^+{\cdot}S_2O_3^{2-}$ is the active species, with subsequent attack by the thiosulfate on a cyanide ligand to form an adduct $[Fe_2(CN)_9(CNS_2O_3)]^{6-}$. This mechanism is set out in Scheme 2 from which rate equation (4) can be derived. If at high concentrations of thiosulfate $k_{IT}[S_2O_3^{2-}] \gg 1$ then a saturation effect will be observed with $k'_{obs} = k_{IT}$; at low concentrations $k'_{obs} = k_{IT}K_{IT}[S_2O_3^{2-}]$. Equation (4) clearly will also give a

$$k'_{obs} = \frac{k_{IT}K_{IT}[S_2O_3^{2-}]}{1 + K_{IT}[S_2O_3^{2-}]} \qquad (4)$$

double-reciprocal plot. In this interpretation the values of k_1 in Table 2 correspond to k_{IT} and k_{-1}/k_2 corresponds to K_{IT}.

Murray[21] has produced evidence for the formation of an intermediate in the reduction of $[Fe(CN)_6]^{3-}$ by SO_3^{2-} in which the sulfite ion adds to a cyanide ligand to form $[Fe(CN)_5(CNSO_3)]^{5-}$, and we suggest that our transient intermediate is a similar adduct. We have no evidence to indicate whether a bridging or a terminal cyanide ligand is involved. As we do not see bridge cleavage, it seems more likely that addition occurs to a terminal cyanide. The second stage, involving the breakdown of the intermediate to $[Fe_2(CN)_{10}]^{5-}$ by parallel pathways, is shown in Scheme 2. The rate constants k_5 and k_6 correspond to the values listed under k_3 and k_4 respectively in Table 3.

Reaction of $[Fe_2(CN)_{10}]^{5-}$ *with* $S_2O_3^{2-}$.—This is a much slower process leading to the formation of $[Fe(CN)_5(S_2O_3)]^{4-}$ and $[Fe(CN)_5(S_2O_3)]^{5-}$. The kinetics is monophasic and yields pseudo-first-order rate constants k_{obs} which increase linearly with $[S_2O_3^{2-}]$ at low thiosulfate concentrations, but show a saturation effect at higher concentrations. Data are given in Table 4. In this case we know from the products that ring cleavage has occurred, and our postulated mechanism involves

$$[Fe_2(CN)_{10}]^{5-} \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [(NC)_5Fe^{III}\text{–}NC\text{–}Fe^{II}(CN)_4(H_2O)]^{5-} \xrightarrow{k_8} [(NC)_5Fe^{III}\text{–}NC\text{–}Fe^{II}(CN)_4(S_2O_3)]^{7-}$$

Scheme 3

Table 4 Pseudo-first-order rate constants for the reaction of $[Fe_2(CN)_{10}]^{5-}$ with thiosulfate. [Complex] = 0.21×10^{-3} mol dm^{-3}; pH 5.67; I = 1.0 mol dm^{-3} (Na_2SO_4); 35.5 °C

$[S_2O_3{}^{2-}]$/mol dm^{-3}	$10^4 k_{obs}$*/s^{-1}
0.02	2.9
0.03	9.2
0.05	9.7
0.06	10.7
0.08	13.5
0.12	16.2
0.14	18.8
0.16	23.2
0.22	28.3
0.26	31.5
0.27	33.1
0.28	33.3
0.29	33.3

* Mean value of at least three kinetic measurements at a single thiosulfate concentration.

Table 5 Kinetic and activation parameters for the reaction of $[Fe_2(CN)_{10}]^{5-}$ with thiosulfate

T/°C	$10^3 k_7$/s^{-1}	(k_{-7}/k_8)/mol dm^{-3}
25.2	2.25	0.186
30.2	3.74	0.165
35.5	6.56	0.304

$\Delta H_7{}^{\ddagger} = 77.0 \pm 1.7$ kJ mol^{-1}, $\Delta S_7{}^{\ddagger} = -38 \pm 6$ J K^{-1} mol^{-1}.

fission of one of the bridging cyanide links. The details are set out in Scheme 3 from which equation (5) can be derived.

$$k_{obs} = \frac{k_7 k_8 [Fe_2(CN)_{10}{}^{5-}][S_2O_3{}^{2-}]}{k_{-7} + k_8[S_2O_3{}^{2-}]} \quad (5)$$

Data on temperature variation are given in Table 5. The limiting rate constant at high thiosulfate concentration is $k_1 = 2.25 \times 10^{-3}$ s^{-1} at 25 °C. An independent study by Greasley and Stedman[22] on the reaction between $[Fe_2(CN)_{10}]^{4-}$ and thiourea shows many parallels to the present study. Reaction proceeds by an initial reduction to $[Fe_2(CN)_{10}]^{5-}$, followed by a reaction with thiourea to form $[Fe(CN)_5(tu)]^{3-}$ + $[Fe(CN)_5(tu)]^{2-}$. This second reaction is also first order with respect to $[(NH_2)_2CS]$ at low concentration of thiourea, but shows a saturation effect at high concentration with a limiting rate constant of 2×10^{-3} s^{-1} at 25 °C. This is consistent with a common rate-determining stage for both thiosulfate and thiourea reactions with $[Fe_2(CN)_{10}]^{5-}$.

Cleavage could occur at either the Fe^{III}–NC or the Fe^{II}–NC bond. In general pentacyanoferrate(II) complexes are much more labile than their iron(III) analogues, so we think cleavage of the Fe^{II}–NC link is more likely. It may be noted that James and Murray quote[23] a value of 1.25×10^{-3} s^{-1} for the rate constant for cleavage of the first cyanide bridge in the iron(II,II) species $[Fe_2(CN)_{10}]^{6-}$, which again involves fission of a Fe^{II}–NC bond.

In the ring-opening reaction a cyanide bridge is being converted into a normal Fe–CN bond, which is presumably more stable, and this may be reflected in the relatively modest $\Delta H^{\ddagger}$ of 77 kJ mol^{-1} for k_7. The mechanism shown in Scheme 3 suggests that the intermediate is trapped as $[(NC)_5Fe^{III}\text{–}NC\text{–}Fe^{II}(CN)_4(S_2O_3)]^{7-}$. Electron transfer through the bridge followed by fission of the Fe–NC bond could lead to $[Fe^{II}(CN)_5(H_2O)]^{3-}$ + $[Fe^{III}(CN)_5(S_2O_3)]^{4-}$, with the former reacting with thiosulfate to give $[Fe^{II}(CN)_5(S_2O_3)]^{5-}$. Alternatively the intermediate could cleave to $[Fe^{II}(CN)_5(S_2O_3)]^{5-}$ and $[Fe^{III}(CN)_5(H_2O)]^{2-}$ and the latter could undergo substitution by thiosulfate to give the observed product, $[Fe^{III}(CN)_5(S_2O_3)]^{4-}$.

Just as there were two explanations for the saturation effect for the formation of $[Fe_2(CN)_{10}]^{5-}$, so there are two explanations for the next stage. In addition to the ring-opening hypothesis, an alternative is that a cation-stabilised ion triplet is formed, $[Fe_2(CN)_{10}]^{5-}\cdot M^+\cdot S_2O_3{}^{2-}$, which becomes the bulk component at high thiosulfate concentrations, and the rate-determining step is the breakdown of this triplet to form $[Fe(CN)_5(S_2O_3)]^{4-}$ + $[Fe(CN)_5(H_2O)]^{3-}$ possibly in several stages. This would account for the cation effect but it would be somewhat surprising if the reaction of thiourea with $[Fe_2(CN)_{10}]^{5-}$ gave the same limiting rate as for thiosulfate, and so we prefer the ring-opening mechanism.

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