Mixed Iron–Cobalt Binuclear Complexes. Part I. Identification of Mixed Complexes derived from *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$

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Products from the reactions of the complex *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ (en = ethylenediamine) with the ions $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Co(CN)_6]^{3-}$, and $[Fe(CN)_5NO]^{2-}$ in aqueous solution are μ-cyano-complexes which have been characterised by means of their visible and i.r. spectra.

BINUCLEAR cobalt(III) complexes can be classified either as dicobalt complexes [where both metal centres are cobalt(III)] or as ' mixed ' complexes (where the second centre is a different metal). Whilst the chemistry of the former has been well documented,[1] detailed studies involving mixed binuclear complexes are rare,[2] and yet their importance can be assessed from the fact that they are intermediates in every inner-sphere reaction involving a metal-ion reductant and a cobalt(III) oxidant. In the first of a series of studies, we have utilised the ability of co-ordinated sulphite to labilise the *trans*-position[3] in the complex $[Co(en)_2(H_2O)(SO_3)]^+$ (en = ethylenediamine) in order to generate mixed binuclear complexes.

RESULTS AND DISCUSSION

Visible Spectra.—Figure 1 shows the visible spectrum of *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ and the effect of mixing equimolar solutions of this complex with the ions $[Co(CN)_6]^{3-}$ and $[Fe(CN)_5NO]^{2-}$. Spectra of the new complexes are similar with a peak position at 445 nm compared with that of 465 nm for *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$. Addition of CN^- to the latter to form the complex *trans*-$[Co(en)_2(CN)(SO_3)]$ produced a much larger shift, to 420 nm. Haim and his co-workers have observed the effect of replacing ammonia by isocyanide[4] and cyanide[5] ligands on the spectra of ammine binuclear complexes of this type. They and other workers[6] suggest the order $H_2O < NC^- \sim NH_3 < CN^-$ of increasing ligand-field strength. On this basis the complexes appear to have the formulae $[(NC)_5CoCNCo(en)_2SO_3]^{2-}$ and $[ON(NC)_4FeCNCo(en)_2SO_3]^-$. An equimolar solution (8×10^{-4}M) of $[Co(CN)_6]^{3-}$ and *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ ions had the same spectrum as more concentrated solutions, but with $[Fe(CN)_5NO]^{2-}$

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[1] A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, 1970, **13**, 1.

[2] A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.

[3] R. S. Murray, D. R. Stranks, and J. K. Yandell, *Chem. Comm.*, 1969, 604.

[4] R. A. de Castello, C. P. Mac-Coll, N. B. Egen, and A. Haim, *Inorg. Chem.*, 1969, **8**, 699.

[5] R. A. de Castello, C. P. Mac-Coll, and A. Haim, *Inorg. Chem.*, 1971, **10**, 203.

[6] D. F. Shriver, S. A. Shriver, and S. E. Anderson, *Inorg. Chem.*, 1965, **4**, 725.

changes in the spectrum occurred which suggest incomplete conversion to the binuclear complex at this range of concentrations. From these observations it is estimated that K = *ca.* 10^4 l mol^{-1} [equation (1)].

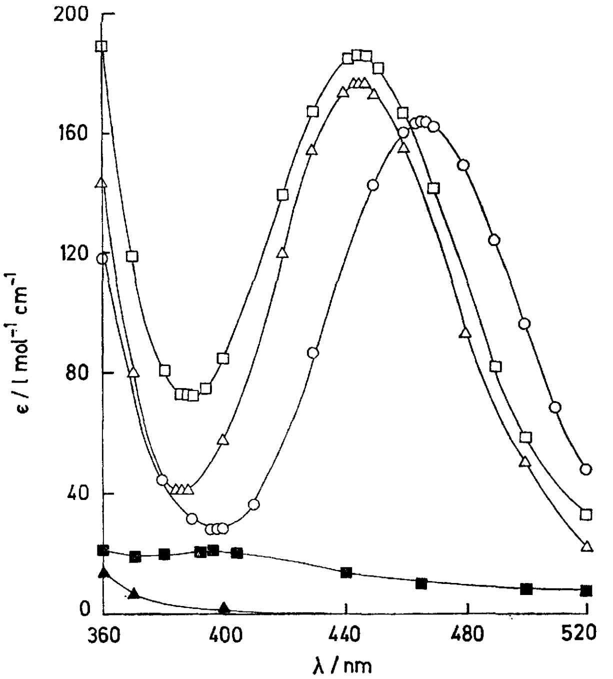

FIGURE 1 Visible absorption spectra of the complexes $[(NC)_5CoCNCo(en)_2SO_3]^{2-}$ (△) and $[ON(NC)_4FeCNCo(en)_2SO_3]^-$ (□) compared with the parent complexes $[H_2OCo(en)_2SO_3]^+$ (○), $[Co(CN)_6]^{3-}$ (▲), and $[Fe(CN)_5NO]^{2-}$ (■) at 25 °C and I = 1·0M ($NaClO_4$)

$$[Fe(CN)_5NO]^{2-} + [Co(en)_2(H_2O)(SO_3)]^+ \xrightleftharpoons{K} [ON(NC)_4FeCNCo(en)_2SO_3]^- \quad (1)$$

Spectra obtained on mixing equimolar solutions of the complex *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ with the ions $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are far more intense than those obtained with $[Co(CN)_6]^{3-}$ and $[Fe(CN)_5NO]^{2-}$ and involve more than just a simple perturbation of the basic *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ spectrum. Details are given in the Table. The maximum (420 nm) in the spectrum of $[Fe(CN)_6]^{3-}$ is itself very intense (ε 1 030 l mol^{-1} cm^{-1}) which accounts for the apparently enormous enhancement at this position in the binuclear complex. This is not the case with the ion $[Fe(CN)_6]^{4-}$, where there is a very marked enhancement at the 398 nm maximum (ε 770 l mol^{-1} cm^{-1}) compared with the combined absorbances of the reactants (ε 33 l mol^{-1} cm^{-1}). Dilution to 4 × 10^{-4}M revealed no changes of the kind observed in the $[Fe(CN)_5NO]^{2-}$ system [equation (1)]. We conclude that K increases as the charge on the reactant, *i.e.* as $[Fe(CN)_6]^{4-} > [Fe(CN)_6]^{3-} \sim [Co(CN)_6]^{3-} > [Fe(CN)_5NO]^{2-}$ since $[Fe(CN)_6]^{4-}$ displaces all other reactants in preferentially forming the complex $[(NC)_5FeCNCo(en)_2SO_3]^{3-}$, whereas addition of $[Fe(CN)_6]^{3-}$ to solutions of the cyanocobalt(III) binuclear produced incomplete displacement of $[Co(CN)_6]^{3-}$.

Positions (λ/nm) and absorption coefficients (ε/l mol^{-1} cm^{-1}) of maxima (λ_1) and minima (λ_2) in the visible spectra of cyano-bridged complexes at 25 °C and I = 1·0M ($NaClO_4$)

Complex [a]	λ_1	ε_1	λ_2	ε_2
$[H_2OCo(en)_2SO_3]^+$	465	162	398	29
$[(NC)_5CoCNCo(en)_2SO_3]^{2-}$	445	176	387	41
$[ON(NC)_4FeCNCo(en)_2SO_3]^-$	445	186	388	73
$[(NC)_5FeCNCo(en)_2SO_3]^{2-}$	418	1 138	360	590
$[(NC)_5FeCNCo(en)_2SO_3]^{3-}$	398	770	362	670

[a] Ranges of concentration of the complexes are respectively 10^4[Complex] = 100—10; 40—8; 40; 10—4; and 20—4M.

These results relate to the situation where the ratio $[Co(en)_2(H_2O)(SO_3)]^+$: [cyano-complex] = 1·00 : 1. Spectra at ratios <1 : 1 were as expected for a mixture of binuclear complex and unreacted mononuclear cyano-complex. At ratios >1 : 1 further changes in spectra occurred. Figure 2 illustrates this point for the $[Fe(CN)_5NO]^{2-}$ system which is characteristic of all the cases. The linear portion up to a ratio of 1·00 : 1 (formation of binuclear complex) is followed by another region in which a second cobalt(III) complex reacts (formation of trinuclear complex). At higher ratios (broken line) the gradients of the plots assume those expected for the addition of the complex *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ with no reaction. It is not yet possible to say whether a third cobalt(III) complex reacts in the intervening region, or whether this corresponds to saturation of the second equilibrium. From steric considerations we tend to favour the latter.

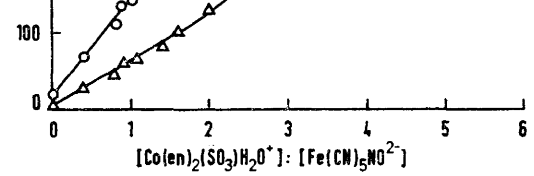

FIGURE 2 Plot of absorption coefficient {ε/l mol^{-1} cm^{-1} per $[Fe(CN)_5NO]^{2-}$} against $[Co(en)_2(SO_3)H_2O^+]$: $[Fe(CN)_5NO^{2-}]$ at 25 °C, I = 1·0M ($NaClO_4$), and $[Fe(CN)_5NO^{2-}]$ = 2·0 × 10^{-3}M: (○), at 420 nm; (△), at 500 nm

Isolation of Solid Samples.—The mixed binuclear complexes so far described are far more soluble than any of the reactants producing them. This proved a difficulty in the isolation of the new complexes as solids so that acceptable analysis figures were only obtained for the complexes $K_2[(NC)_5FeCNCo(en)_2SO_3],3H_2O$ and $K_2[(NC)_5CoCNCo(en)_2SO_3],4H_2O$, which are described in the Experimental section. Visible spectra of these solids were in agreement with those described previously for equimolar mixtures of the reactant solutions.

I.r. Spectra.—The cyanide stretching frequencies of the solid binuclear complexes (KCl discs) were determined in the range 2 000—2 300 cm^{-1}, with reference to the vibration–rotation spectrum of carbon monoxide using a 10 cm path length, 100 mmHg pressure, and a scan rate of 100 cm^{-1} min^{-1}. Haim and his co-workers [4,5,7] have shown that the effect of bridging in cyano-complexes is to increase ν(C≡N). For the complex $K_2[(NC)_5FeCNCo(en)_2SO_3],3H_2O$ stretching wavenumbers were observed at 2 154m, 2 109s, and 2 032m cm^{-1} and for $K_2[(NC)_5CoCNCo(en)_2SO_3],4H_2O$ at 2 171m, 2 143sh, and 2 121s cm^{-1}. The values are accurate to ±1 cm^{-1} by this method. Comparison with the main cyanide stretching frequencies of the ions $[Fe(CN)_6]^{3-}$ (2 120 cm^{-1}) and $[Co(CN)_6]^{3-}$ (2 128 cm^{-1}) shows that an increase was observed in the binuclear complexes consistent with cyanide bridging.

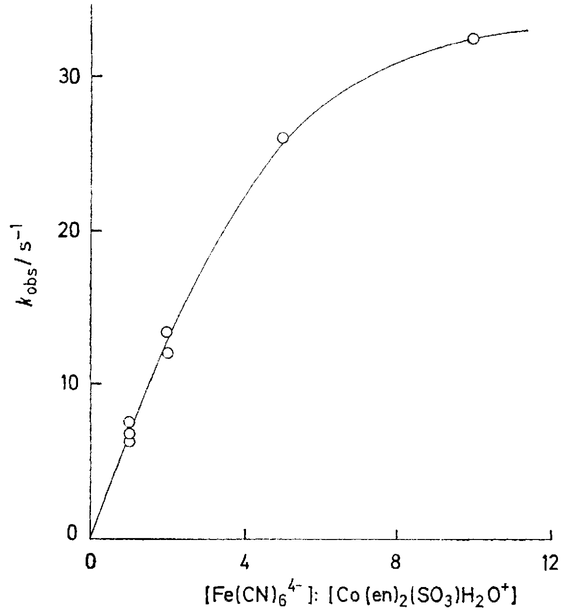

FIGURE 3 Dependence of k_{obs} on $[Fe(CN)_6^{4-}]$ for the reaction of the complex *trans*-$[Co(en)_2(SO_3)H_2O]^+$ ($1{\cdot}0 \times 10^{-3}$M) with $[Fe(CN)_6]^{4-}$ at 25 °C and $I = 1{\cdot}0$M (NaCl)

Kinetic Studies.—As further evidence that new inner-sphere complexes are indeed formed in the systems described (as opposed to ion-pairs) we include some preliminary results from an investigation into the detailed kinetics of these systems. The reaction of the ions $[Fe(CN)_6]^{4-}$ and *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ has been studied under conditions where the only significant product is the binuclear complex $[(NC)_5FeCNCo(en)_2SO_3]^{3-}$; formation is essentially complete over the range pH 3—10. Formation of the binuclear complex at pH 6·5 was monitored at 400 nm by the stopped-flow method and plots of log ($OD_\infty - OD_t$) were linear to >85% completion. The results are shown in Figure 3. An analogous reaction involving substitution by SO_3^{2-} has been studied by Stranks and Yandell.[8] At 25 °C and $I = 1{\cdot}0$M ($NaClO_4$), the rate constant $k = 13{\cdot}4$ s^{-1} was deduced for S_N1 (limiting) loss of water. The k_{obs} value for substitution by the ion $[Fe(CN)_6]^{4-}$ exceeds this value at high concentrations of $[Fe(CN)_6]^{4-}$. This may reflect some contribution from an associative mechanism to the overall rate or to the effect of the high negative charge on the ion-pair. We note however the observed first-order kinetics under conditions where $[Fe(CN)_6^{4-}]$ = [*trans*-$Co(en)_2(H_2O)(SO_3)^+$]. This cannot be due to virtually complete ion-pairing of reactants since this would require a formation constant $>10^5$ l mol^{-1}.

EXPERIMENTAL

The preparation of the complex *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ has been described by Baldwin.[9] Our method involved the addition of ethanol to precipitate the crude *trans*-$[Co(en)_2(Cl)(SO_3)],H_2O$ complex which was stored in the dark. The perchlorate salt used in these studies was prepared as described by Baldwin, but then recrystallised from a liberal amount of water by addition of sodium perchlorate crystals. Dark brown needles were obtained by this method {Found: C, 12·15; H, 5·15; Cl, 8·95; H_2O, 9·2; N, 14·15; S, 8·40. *trans*-$[Co(en)_2(H_2O)(SO_3)]ClO_4,H_2O$ requires C, 12·15; H, 5·05; Cl, 9·00; H_2O, 9·1; N, 14·2; S, 8·10%}.

Preparations.—$K_2[(NC)_5FeCNCo(en)_2SO_3],3H_2O$. The complex *trans*-$[Co(en)_2(H_2O)(SO_3)]ClO_4,H_2O$ (1·00 g) was added slowly with stirring to a solution of $K_3[Fe(CN)_6]$ (AnalaR, 0·833 g) in water (10 cm^3). The deep brown solution was kept on ice for 15 min and potassium perchlorate filtered off. The filtrate was evaporated under reduced pressure at 40 °C to *ca.* 1 cm^3 and any remaining potassium perchlorate was again filtered off. The remaining water was removed from the filtrate, first by evaporating under reduced pressure and then by setting aside overnight in a desiccator over P_2O_5. The *solid*, which is a blue-black glassy material, was then chipped from the flask and left exposed to the atmosphere for 24 h. Yield 1 g {Found: C, 19·5; H, 3·85; H_2O, 9·1; N, 22·9; S, 5·10. $K_2[(NC)_5FeCNCo(en)_2SO_3],3H_2O$ requires C, 19·9; H, 3·65; H_2O, 9·0; N, 23·2; S, 5·30%}.

$K_2[(NC)_5CoCNCo(en)_2SO_3],4H_2O$. The complex *trans*-$[Co(en)_2(H_2O)(SO_3)]ClO_4,H_2O$ (1·975 g) was added slowly with stirring to a solution of $K_3[Co(CN)_6]$ (1·66 g) in water (*ca.* 5 cm^3) and filtered to remove $KClO_4$. The filtrate was concentrated to *ca.* 1 cm^3 by evaporation under reduced pressure and poured into ethanol (50 cm^3). A yellow-brown product was obtained by stirring the oily liquid produced, and was filtered off and washed with ethanol. An attempt was made to purify the product by dissolving it in water (1 cm^3) and passing the solution down a column of Sephadex G-25 resin. The resulting solution was again concentrated to 1 cm^3, poured into ethanol, and collected as before. Yield 1·2 g {Found: C, 19·4; H, 4·10; N, 22·3; S, 5·30. $K_2[(NC)_5CoCNCo(en)_2SO_3],4H_2O$

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[7] D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 33.

[8] D. R. Stranks and J. K. Yandell, *Inorg. Chem.*, 1970, **9**, 751.

[9] M. E. Baldwin, *J. Chem. Soc.*, 1961, 3123.

requires C, 19·2; H, 3·90; N, 22·4; S, 5·10%}. Dehydration gave 8·5% loss in weight (calc. for $3H_2O$, 8·7%).

The complexes $K_3[Fe(CN)_6]$, $Na_2[Fe(CN)_5NO],2H_2O$, and $K_4[Fe(CN)_6],3H_2O$ were of AnalaR grade purity. Sodium hexacyanoferrate(II) (B.D.H., Reagent grade), used in spectroscopic studies, was recrystallised from water and determined to be $Na_4[Fe(CN)_6],9{\cdot}5H_2O$. The complex $K_3[Co(CN)_6]$ (Hopkin and Williams, Reagent grade) was used without further purification. In studies relating to visible spectra, solutions of the complex *trans*-$[Co(en)_2(H_2O)(SO_3)]^+$ were added to solutions of the cyano-complex so that the latter was present in excess, and readings performed within 10 min.

Visible spectra were recorded on a Hilger Uvispek spectrophotometer and i.r. spectra on a Perkin-Elmer 457 grating spectrophotometer. Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn. Hydration numbers were determined by measuring the loss in weight of powdered samples over P_2O_5 in a desiccator for 2 weeks and by the subsequent gain in weight of the anhydrous sample on exposure to the atmosphere.

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