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Activation Parameters for Directly Determined First Order Rate Constants for Outer Sphere Electron Transfer Reactions, and Crystal Structure of a Pertinent Pentaammine of Co^{III}

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Abstract

The outer sphere reductions of $Co(NH_3)_5B^{3+}$ by $Fe(CN)_5A^{3-}$ have been studied. The observed pseudo first order rate constants (Co complex in excess) obey the dependence $k_{obs} = K_{os}k_{et}[Co]/(1 + K_{os}[Co])$, as expected for outer sphere electron transfer reactions. Values of the fundamental electron transfer rate constants k_{et} have been determined, along with the equilibrium constant K_{os} for a range of reactions in which A and B are pyridyl ligands of different sizes. The first order electron transfer rate constants vary in a manner that is consistent with adiabatic electron transfer. The outer sphere ion pairing equilibrium constants K_{os} have been calculated: $K_{os} = 8.6 \pm 0.1 \times 10^2\ M^{-1}$ when A and B = pyridine; $K_{os} = 1.07 \pm 0.09 \times 10^3\ M^{-1}$ where A = pyridine, B = 1-phenyl-3-(4-pyridyl)propane; $K_{os} = 1.86 \pm 0.11 \times 10^3\ M^{-1}$ when A = 4,4′-bipyridine, B = pyridine; $K_{os} = 1.27 \pm 0.08 \times 10^3\ M^{-1}$ when A = 4,4′-bipyridine, B = 4-phenylpyridine. Distances of closest approach between the metal centers in the reactive ion pairs are compared, and it is concluded that there is a common mechanism, in which the ammonia side of the cobalt complex approaches the cyano side of the iron complex in each reactive ion pair.

The distance of closest approach between the two metal centers (*a*) was calculated from the experimental values for the ion pairing equilibrium constant K_{os} at 25 °C: 5.2 Å when A = 4,4′-bipyridine, B = pyridine; 5.4 Å when A = 4,4′-bipyridine, B = 4-phenylpyridine; 5.5 Å when A = pyridine, B = 1-phenyl-3-(4-pyridyl)propane; 5.7 Å when A = B = pyridine. These relatively short metal–metal distances, when compared to the X-ray structure of the compound $[Co(NH_3)_5(\text{4-phenylpyridine})]_2[S_2O_6]_3 \cdot 4H_2O$, do not support an ion pair orientation in which the two substituted pyridine ligands A and B are oriented toward each other. [$P2_1/c$, $a = 7.399(3)$, $b = 22.355(10)$, $c = 13.776(4)$ Å, $\beta = 92.02(3)°$, $R = 0.070$.] The crystallographic results show that if the two pseudo-octahedral coordination spheres are oriented in the reactive ion pair so that an ammonia face of the cobalt complex is at hydrogen bonding distance from a cyano face on the iron complex, the metal–metal distance is 5.3 Å, a distance which is in agreement with the kinetic results.

Introduction

As previously reported [1], it is possible to measure the fundamental first order electron transfer rate constants for the reactions shown in eqn. (1)

$$Fe(CN)_5A^{3-} + Co(NH_3)_5B^{3+} + HEDTA^{3-} + 4H^+ \longrightarrow Fe(CN)_5A^{2-} + Co(EDTA)^{2-} + 5NH_4^+ + B \qquad (1)$$

where A and B are derivatives of pyridine. These outer sphere reductions of Co^{III} complexes by Fe^{II} complexes are performed in the presence of $HEDTA^{3-}$, which rapidly sequesters the $Co^{2+}(aq)$ product, preventing formation of a precipitate [2]. A comparison of such directly determined first order rate constants for a series of ligands A and B led to the conclusion [1] that the orientation of these nonspherical ions in the precursor ion pair involved approach of the ammonia side of the cobalt complexes to the cyano side of the iron complexes. Furthermore, it was calculated [1] from the values of ion-pair equilibrium constants that the distance of closest approach between the reactants in the precursor ion pair was uniformly in the range 5.5 to 5.8 Å for any combination of ligands A and B, supporting the proposal for similar reactant orientations in the separate systems. Comparable arguments have been presented [3] for similar reactions.

In further studies of reactions of the type shown in eqn. (1), we have directly determined the first order electron transfer rate constants k_{et} at 25 °C and the equilibrium constants K_{os} for a total of four systems featuring different ligands A and B.

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We have been guided in these studies by the expectation that, if the reactive ion pair is oriented as described above, the distance of closest approach between the reductant and oxidant would be the same, despite fairly large changes in the size of the ligands A and B. These results are particularly interesting in view of the current interest in the effect of donor–acceptor distance and orientation upon electron transfer [4].

Experimental

Kinetic Studies

All reagents and materials were prepared as described previously [1]. Satisfactory analyses (C, H, N) were obtained for all cobalt complexes used in this study. Kinetic experiments were performed as described previously [1], at ionic strength 0.08 (adjusted with $LiClO_4$). Pseudo first order rate constants (k_{obs} at each cobalt concentration) were evaluated by linear least-squares analysis of $\ln(A_t - A_\infty)$ *versus* time, and plots were linear for up to four half lives, with minimum correlation coefficients of 0.998.

Values of k_{et} for each different reaction were determined from the intercepts of the reciprocal plots of $1/k_{obs}$ *versus* $1/[Co]$. These plots were linear with minimum correlation coefficients of 0.991. Values of K_{os} were determined from the values of k_{et} and the slopes of the inverse plots.

X-ray Crystallographic Analysis of Pentaammine(4-phenylpyridine)cobalt(III) Dithionate Tetrahydrate

The complex was crystallized by evaporation from aqueous solution. An orange crystal was mounted on a glass fiber. The space group was determined to be $P2_1/c$ from Weissenberg and Buerger precession photographs. Final cell parameters (Table I) were obtained by a least-squares analysis of 15 centered reflections obtained from diffractometer measurements.

Data were collected on a Syntex $P2_1$ four-circle diffractometer with Mo radiation and a highly oriented graphite monochromator. The $2\theta:\theta$ scan technique (bisecting mode) was used to measure 3372 unique reflections ($+h$, $+k$, $\pm l$) to a 2θ limit of 45°, ($\sin\theta/\lambda = 0.5385$), at a variable scan speed (depending upon intensity). Three check reflections measured every 100 reflections showed no decay in intensity. Scan: background time ratio was 0.5. A total of 2162 reflections with $I > 2.5\ \sigma(I)$ (where $\sigma(I)$ were determined from counting statistics) were considered observed and included in further calculations. Values of $\sigma(F)$ were calculated as $\sigma(F) = (F/2)[\sigma^2(I)/(I)^2 + \delta^2]^{1/2}$, where δ (0.02) is an instrumental uncertainty determined from the variation in the intensity of the check reflections. The data were corrected for Lorentz and polarization factors and scaled with a Wilson plot [5a]. A spherical absorption correction was applied.

TABLE I. Crystal Data for Pentaammine(4-phenylpyridine)-Co(III) Dithionate Tetrahydrate

Empirical formula	$CoC_{11}H_{28}N_6O_{11}S_3$
Formula weight	575.504 daltons
$F(000)$	1196 electrons
Space group	$P2_1/c$ (monoclinic) $h0l$, l = odd; $0k0$, k = odd, systematically absent
Z	4
a	7.399(3) Å
b	22.355(10) Å
c	13.776(4) Å
β	92.02(3)°
V	2277(2) $Å^3$
D_X	1.679 g cm^{-3}
D_{meas} (flotation)	1.66 g cm^{-3}
λ (Mo Kα)	0.71069 Å
μ (Mo Kα)	10.175 cm^{-1}
Crystal size	0.18 × 0.17 × 0.35 mm
Temperature	25 °C

The structure was solved by direct methods [5b]. The atomic positions and anisotropic thermal parameters of all non-hydrogen atoms were refined by a full matrix least-squares computer program [5a]. All calculations were performed on a DEC VAX 11/750 computer. The quantity minimized was $\Sigma w[|F_o| - |F_c|]^2$ where the weights, w, were $1/\sigma^2(F)$. Correction for anomalous scattering was applied [5c].

Since the thermal factors of the water oxygen atoms were quite high, the possibility of positional disorder was considered. In that case, the water oxygen positions would be occupied in only a fraction of the unit cells. However, refinement of the occupancy factor for these oxygen atoms confirmed that the occupancy factors should be 1.0, and that there was no positional disorder.

All but one of the hydrogen atoms in the ammonia ligands were found in the difference Fourier map; the hydrogen atoms in the water molecules were not seen. The final value of $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ was 0.070; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ was 0.067. The highest peak in the final difference Fourier map was 0.051 $Å^{-3}$. Fractional coordinates of the nonhydrogen atoms are given in Table II, and selected bonding distances in Table III. See also 'Supplementary Material'.

Results

Kinetic Studies

In Table IV are listed values for the pseudo-first order rate constants k_{obs} at various cobalt concentrations. The values of k_{et}, the directly determined

TABLE II. Fractional Coordinates and Isotropic Thermal Parameters for Pentaammine(4-phenylpyridine)Co(III) Dithionate Tetrahydrate

Atom	x	y	z	$10B_{iso}$ (Å^2)
Co	0.8950(14)	0.1771(4)	0.5120(7)	21
N(1)	0.8737(8)	0.2647(2)	0.5056(4)	21
N(2)	0.9612(8)	0.1829(3)	0.6523(4)	29
N(3)	1.1573(7)	0.1826(3)	0.4854(4)	27
N(4)	0.8252(8)	0.1688(3)	0.3715(4)	27
N(5)	0.9215(8)	0.0885(2)	0.5199(4)	31
N(6)	0.6335(7)	0.1704(3)	0.5373(4)	27
C(2)	0.9460(10)	0.2970(3)	0.4307(5)	26
C(3)	0.9193(10)	0.3574(3)	0.4202(5)	27
C(4)	0.8151(10)	0.3893(3)	0.4863(5)	23
C(5)	0.7465(10)	0.3565(3)	0.5657(5)	25
C(6)	0.7767(10)	0.2959(3)	0.5706(5)	27
C(7)	0.7776(10)	0.4542(3)	0.4730(5)	28
C(8)	0.7576(13)	0.4782(4)	0.3801(6)	48
C(9)	0.7165(13)	0.5398(4)	0.3696(7)	54
C(10)	0.6964(12)	0.5765(4)	0.4497(7)	48
C(11)	0.7119(12)	0.5510(4)	0.5442(6)	39
C(12)	0.7507(12)	0.4902(3)	0.5572(6)	33
S(1)	0.4539(27)	0.2864(9)	0.3022(13)	27
S(2)	0.3329(27)	0.2131(9)	0.2259(12)	24
S(3)	0.4546(31)	0.0199(9)	0.4332(15)	36
O(1)	0.3273(9)	0.3344(2)	0.2910(5)	60
O(2)	0.6215(8)	0.2963(3)	0.2555(4)	54
O(3)	0.4749(9)	0.2655(3)	0.4009(3)	51
O(4)	0.3216(8)	0.2328(2)	0.1269(3)	42
O(5)	0.4547(8)	0.1640(2)	0.2459(4)	45
O(6)	0.1583(7)	0.2070(3)	0.2673(4)	44
O(7)	0.3834(9)	−0.0444(3)	0.6058(4)	62
O(8)	0.6198(9)	0.0292(3)	0.6224(4)	52
O(9)	0.3244(11)	0.0641(3)	0.4619(5)	77
O(10)	0.2024(10)	0.0683(3)	0.6885(5)	78
O(11)	−0.0068(15)	0.0506(5)	0.3136(7)	137

TABLE III. Selected Bond Distances (Å) for Pentaammine(4-phenylpyridine)Co(III) Dithionate Tetrahydrate

Co–N(1)[a]	1.966(5)
Co–N(2)	1.981(5)
Co–N(3)	1.992(5)
Co–N(4)	1.994(6)
Co–N(5)	1.993(6)
Co–N(6)	1.984(5)
N(1)–C(2)	1.383(9)
N(1)–C(6)	1.360(9)
C(2)–C(3)	1.371(11)
C(3)–C(4)	1.408(10)
C(4)–C(5)	1.425(10)
C(4)–C(7)	1.486(10)
C(5)–C(6)	1.374(10)
C(7)–C(8)	1.392(11)
C(7)–C(12)	1.431(10)
C(8)–C(9)	1.415(13)
C(9)–C(10)	1.388(13)
C(10)–C(11)	1.422(13)
C(11)–C(12)	1.399(11)

[a] N(1) is the 4-phenylpyridine donor atom.

TABLE IV. Pseudo First Order Rate Constants at 25 °C for the Reduction of $Co(NH_3)_5B^{3+}$ by $Fe(CN)_5A^{3-}$

A	B	[Co] (M × 10^4)	k_{obs}[a] (s^{-1} × 10^4)
Pyridine	pyridine	2.02	10.3 ± 0.9
		3.08	13.9 ± 0.8
		7.01	25.6 ± 0.7
		9.97	29.1 ± 0.7
		14.00	41.6 ± 4.4
		17.82	42.5 ± 2.4
Pyridine	1-phenyl-3-(4-pyridyl)propane	1.99	5.7 ± 0.6
		3.95	9.1 ± 0.6
		6.34	12.1 ± 0.4
		8.11	14.2 ± 0.5
		9.99	17.5 ± 0.3
		12.15	19.3 ± 1.4
		14.05	20.3 ± 0.8
4,4′-Bipyridine	pyridine	1.46	4.5 ± 1.0
		4.70	9.7 ± 0.1
		9.99	13.7 ± 0.1
		17.90	16.0 ± 0.4
4,4′-Bipyridine	4-phenylpyridine	3.53	10.5 ± 0.2
		6.34	15.3 ± 0.1
		10.56	20.3 ± 0.8
		13.26	21.7 ± 0.7
		17.93	22.8 ± 0.9

[a] Observed pseudo first order rate constants at *ca.* $[Fe]_0 = 10^{-5}$ or 10^{-6} M, total ionic strength = 0.08, pH 7.0, [A] = 1.5×10^{-3} M, and [EDTA] = 6.0×10^{-4} M. Errors represent average deviations from the mean for at least two independent determinations of k_{obs} at a particular [Co].

first order rate constants for electron transfer, are listed in Table V, along with the equilibrium constants K_{os}. These k_{et} were determined from the intercepts of the linear reciprocal plots of $1/k_{obs}$ *versus* 1/[Co], because, for these reactions [1], the observed pseudo-first order rate constant (k_{obs}) depends on [Co] according to eqn. (2)

$$k_{obs} = \frac{K_{os}k_{et}[Co]}{1 + K_{os}[Co]} \tag{2}$$

Here K_{os} is the outer sphere ion pairing equilibrium constant, and k_{et} is the first order rate constant for electron transfer within the reactive, or precursor, ion pair.

Crystallographic Studies

Coordination sphere

The six N atoms are coordinated to cobalt in the octahedral geometry typical of Co^{III} complexes (see

TABLE V. First Order Electron Transfer Rate Constants k_{et} (for the Reduction of $Co(NH_3)_5B^{3+}$ by $Fe(CN)_5A^{3-}$), Ion-pairing Equilibrium Constants K_{os}, and Calculated Metal–Metal Distances a in the Ion Pair

	A	B	k_{et} ($s^{-1} \times 10^3$)	K_{os} ($M^{-1} \times 10^{-3}$)	a (Å)
1	pyridine	pyridine	6.8 ± 0.5	0.86 ± 0.10	5.70
2	pyridine	1-phenyl-3-(4-pyridyl)propane	3.2 ± 0.2	1.07 ± 0.09	5.54
3	4,4′-bipyridine	pyridine	2.1 ± 0.1	1.86 ± 0.11	5.16
4	4,4′-bipyridine	4-phenylpyridine	3.4 ± 0.1	1.27 ± 0.08	5.41

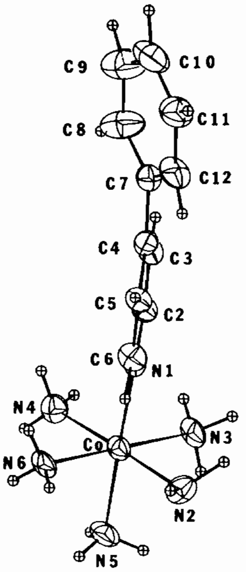

Fig. 1. A perspective view of the pentaammine(4-phenylpyridine)cobalt(III) ion. The thermal ellipsoids represent 50% probability. (One hydrogen atom on N2 was not found, and is not in the drawing.)

Fig. 1). The Co–N distances average 1.985(5) Å, slightly longer than the average Co–N distance of 1.961 Å observed for pentaammineaquacobalt(III) dithionate dihydrate [6]. The small deviations (±3°) of the N–Co–N angles from 90° are assumed to be due to crystal packing forces, since intramolecular hydrogen contacts with the phenylpyridine ligand are actually closer for H(N2) [N(1)–Co–N(2) angle 89.7(2)°] than for H(N4) [N(1)–Co–N(4) angle 91.8(2)°].

Dithionate anion

The S–S bond of one $[S_2O_6]^{2-}$ anion lies on a crystallographic inversion center. The $[S_2O_6]^{2-}$ which lies wholly within the asymmetric unit has oxygen atoms almost perfectly staggered (torsion angles 60° ± 6° and 180° ± 5°). Due to electrostatic repulsion between the oxygen atoms at shorter S–O distance (1.44 Å), the O–S–O angles expand to an average of 114°. The longer S–S bond length (2.126(3) Å) allows the S–S–O angles to shrink to an average of 104°.

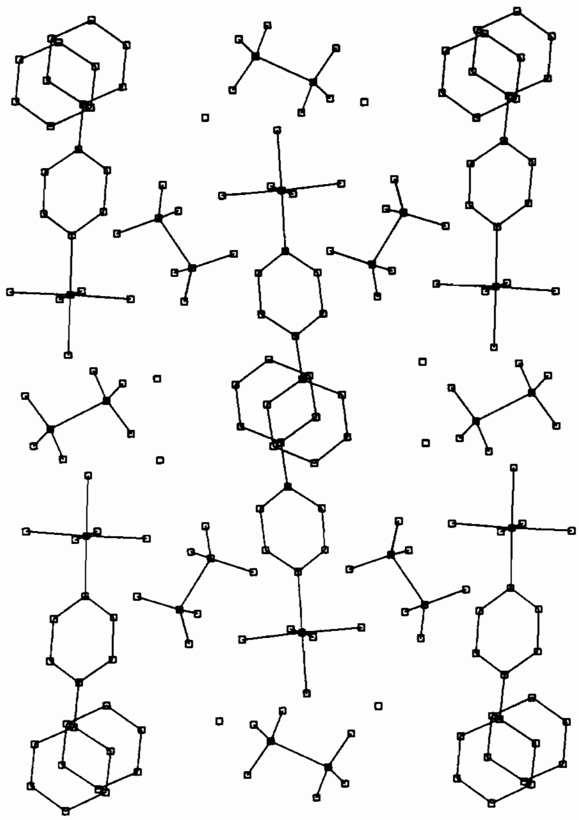

Fig. 2. The packing arrangement in the pentaammine(4-phenylpyridine)cobalt(III) dithionate tetrahydrate crystal, as viewed along the a axis with the c axis horizontal. (Hydrogen atoms omitted for clarity; single squares represent water oxygens.)

4-Phenylpyridine ligand

Both the pyridine ring and the phenyl ring are planar (r.m.s. deviations from the plane are 0.012 and 0.011 Å). The planes of the two rings are at an angle of 32°, quite different from the planar biphenyl molecule found in solid state studies at temperatures above 38 K [7]. However, this value for the inter-ring twist angle is close to the 36° angle common in many crystal structures of biphenyl derivatives [8]. The twisted phenyl rings and the consequent interruption of the π bonding system between the two rings is reflected in the C–C bond lengths: the average C–C distance within the rings is 1.40(1) Å, while the C–C bond between the two rings is 1.49(1) Å. The packing diagram [9] (Fig. 2) shows the stacking of the phenyl rings 3.55 Å apart in the solid, a typical distance for aromatic ring stacking [10].

Hydrogen bonding

There is an extensive network of hydrogen bonding between the ammonia ligands, the dithionate anions and the two water molecules, involving almost every oxygen and hydrogen atom in these groups (see Fig. 2). The average H···O distance is 2.2 Å; the average N–H···O angle is 159°.

Discussion

The values for k_{et}, like those reported elsewhere [3] for similar outer sphere and inner sphere electron transfer systems, fall within the expected adiabatic regime for reactant charge types 3+/3–. The values of K_{os} can therefore be used to calculate the apparent distances of closest approach, *a*, between the metal centers in the precursor ion pairs, and these are also presented in Table V. In the previous report [1] on this work the distance of closest approach for the metal ion reactants was calculated to fall in the range 5.5 to 5.8 Å (with the 4-phenylpyridine ligand coordinated to cobalt and the 4,4′-bipyridine or 1,2-bis(4-pyridyl)ethane ligands coordinated to iron). Distances calculated from the experimentally determined ion pair equilibrium constants in the present work range from 5.2 to 5.7 Å.

These metal–metal distances can now be compared with the distances obtained from the crystallographic study reported here of the cobalt complex $[Co(NH_3)_5NC_5H_4{-}C_6H_5]^{3+}$ and form the reported structure of a hexacyanoferrate(III) complex [11], in order to draw some conclusions about the orientation of the two complexes in the reactive ion pair. If the electron transfer occurs via the π system of the unsaturated 4,4′-bipyridine and the 4-phenylpyridine ligands, the transfer distance would be more than 21 Å. The two metal centers would be at least 15.4 Å apart if the electron transfer pathway involves a cyano ligand and the 4-phenylpyridine ligand. Even if the electron transfer pathway occurs via the shortest ligands bound to each metal, the cyano ligand on the iron and the ammonia ligand on the cobalt, the transfer distance must be at least 7.4 Å*. These distances are significantly different from the 5.4 Å distance obtained from the experimental ion pair equilibrium constant (K_{os}, Table V).

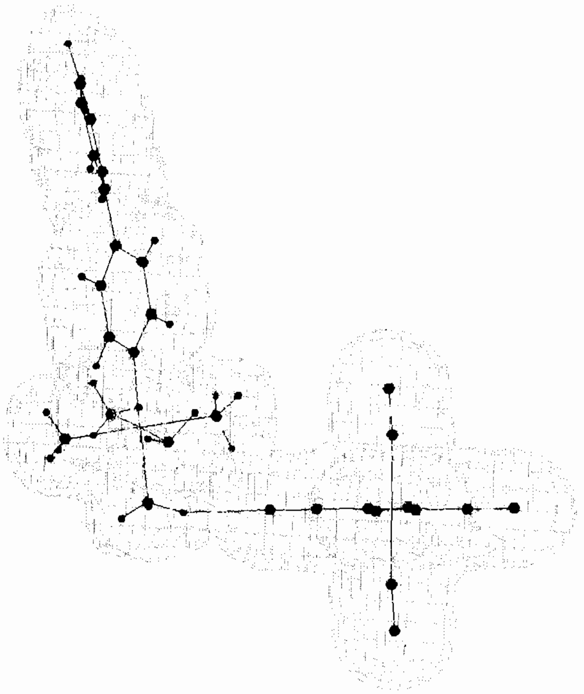

Fig. 3. The van der Waals surface of a hydrogen-bonded ion pair consisting of pentaammine(4-phenylpyridine)cobalt(III) and hexacyanoferrate(III). Crystallographic coordinates from this work and ref. 11. The N–H···N≡C distance is 2.2 Å and the N–H···N angle is 160°, parameters which are consistent with the crystallographic results. The Co–Fe distance in the ion pair is 6.6 Å. The contour lines of the van der Waals surface cross every 0.5 Å.

The much shorter metal–metal distance determined from kinetic measurements supports an ion pair with the metal centers as close to each other as possible, and suggests that the transfer pathway could involve either solvent molecules [4b, 4d] or direct metal–metal overlap [4a] rather than the ligand-mediated pathway. Friedman and Newton [12] have proposed a staggered face-to-face model for the ion pair in aqueous Fe^{2+}–Fe^{3+} electron exchange, where the kinetic results indicated a very short transfer distance. Crystallographic data were used to draw [9] Fig. 3, in which the two octahedral complexes approach each other vertex-to-vertex so that a hydrogen bond** can form between an ammonia hydrogen and a cyano nitrogen. Because the typical hydrogen bond angle is about 160° [13], the distance for direct metal–metal electron transfer can be shorter, 6.6 Å, than the 7.4 Å distance along the ligand pathway. If the two octahedra

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*The distance from the cobalt to the ammonia hydrogens 180° away from the phenylpyridine ligand (Co–H(N5) distance) is 2.5 Å; the Fe–N distance in hexacyanoferrate(III) is 3.1 Å [11]; the ligands are presumed to be at H···N hydrogen bonding distance, 2.2 Å.

**The mean hydrogen bonding angle in this work was found to be 159°; in a general study of 1357 intermolecular N–H···O=C hydrogen bonds the mean angle was 161.2(3)° [13].

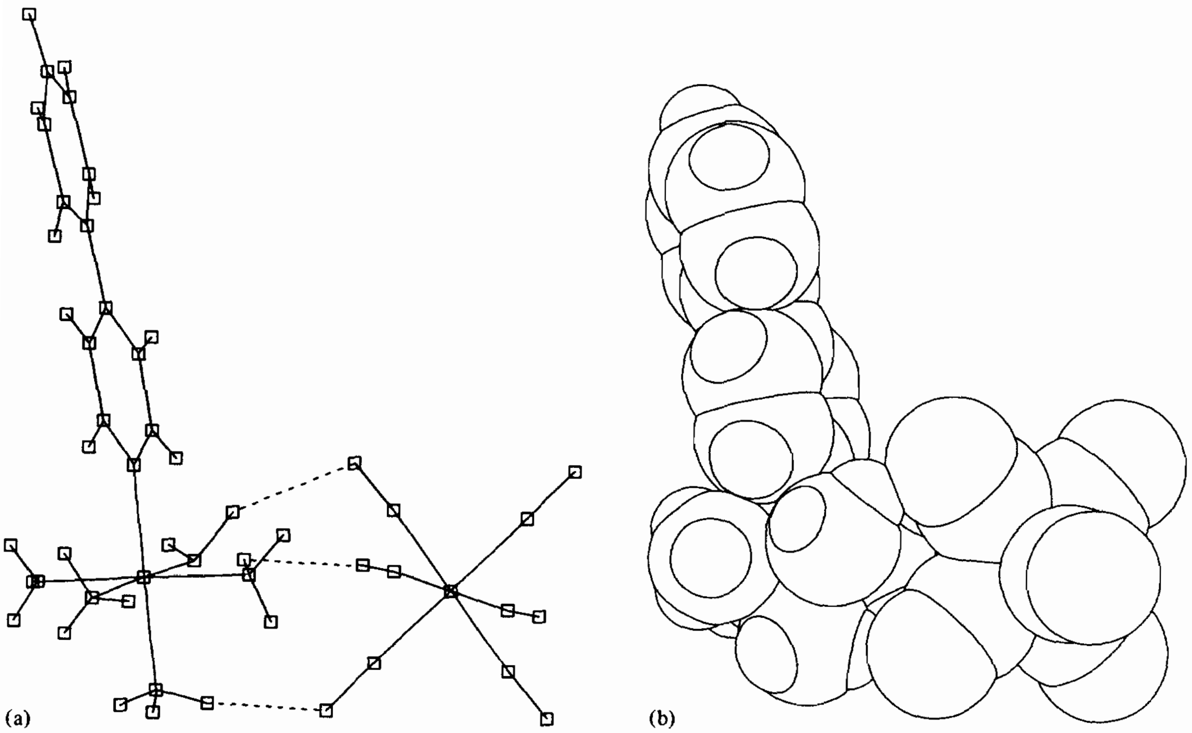

Fig. 4. Face-to-face hydrogen-bonded model for reactive ion pair consisting of pentaammine(4-phenylpyridine)cobalt(III) and hexacyanoferrate(III). The H•••N distances are 2.2 Å, the N–H•••N angles are 160°, the C≡N•••H angles are 100°, 107°, 120°. In (b) the van der Waals radii of the atoms are shown. The Co–Fe distance is 5.3 Å.

approach each other edge-to-edge, or face-to-face, various metal–metal distances ranging from 5.0 to 5.8 Å are possible; these distances are consistent with the range of experimentally determined transfer distances (5.2 to 5.7 Å) reported in Table V. Shown in Fig. 4 is a hydrogen-bonded model in which the metal–metal distance is 5.3 Å, in close agreement with the 5.4 Å transfer distance obtained from the kinetic data.

Supplementary Material

Hydrogen atom parameters, anisotropic thermal parameters, and structure factor tables are available from the authors on request.

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