Solid-state and Solution Conformation of a New Cobalt Dimer μ-Formamido-bis[penta-amminecobalt(III)] Pentachloride Monohydrate: *X*-Ray and Kinetic Studies

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The crystal and molecular structure of the title compound has been determined by three-dimensional *X*-ray analysis. Crystals are triclinic, space group $P\bar{1}$, with $Z = 2$ in a unit cell of dimensions: $a = 6{\cdot}981(8)$, $b = 14{\cdot}346(8)$, $c = 11{\cdot}992(6)$ Å, $\alpha = 99{\cdot}41(4)$, $\beta = 103{\cdot}68(9)$, $\gamma = 93{\cdot}11(7)°$. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations to *R* 0·082 for 922 observed reflections measured by diffractometer. The crystal structure consists of discrete cations, anions, and water molecules separated by normal distances. In the cation the octahedrally co-ordinated cobalt atoms are linked by the bidentate formamido-ligand which has a *cis*-conformation of the NH and CH groups. Co–N(formamido) is 1·94(2), and the mean of the other Co–N bonds is 1·99(2) Å. Other bond lengths are Co–O 1·92(2), C–O 1·26(3), and C–N 1·34(4) Å.

The cation is shown to have the same *cis*-conformation in solution (from nuclear Overhauser studies) as that found in the solid state. Kinetics of reduction show that the complex is reduced by an initial outer-sphere mechanism.

BINUCLEAR complexes of cobalt(III) have been prepared with a variety of bridging ligands, yielding both single- and double-bridged compounds.[1,2] Recently, interest has centred on the reactions of these binuclear dicobalt complexes,[3] and in particular, on their redox reactions.[4]

We report here the crystal structure, solution conformation, and reactions of a new binuclear dicobalt complex, μ-formamido-bis[penta-aminecobalt(III)] pentachloride monohydrate.

EXPERIMENTAL

The preparation and characterization of the complex has been described previously.[5]

Crystal Data.—$CH_{32}Cl_5Co_2N_{11}O,H_2O$, $M = 527{\cdot}37$, Triclinic, $a = 6{\cdot}981(8)$, $b = 14{\cdot}346(8)$, $c = 11{\cdot}992(6)$ Å, $\alpha = 99{\cdot}41(4)$, $\beta = 103{\cdot}68(9)$, $\gamma = 93{\cdot}11(7)°$, $U = 1145{\cdot}8$ Å^3, $Z = 2$, $D_c = 1{\cdot}53$, $F(000) = 544$. Space group $P\bar{1}$ (C_i^1). Mo-K_α radiation, $\lambda = 0{\cdot}71069$ Å, μ(Mo-K_α) = 15·41 cm^{-1}.

The crystal used was the only suitable one obtained on recrystallization from water, and had dimensions 0·25 × 0·25 × 0·40 mm^3. Preliminary precession and Weissenberg photographs (Cu-K_α radiation) revealed space group $P1$ or $P\bar{1}$; the latter was assumed, and confirmed by the analysis. Accurate cell parameters were obtained by a least-squares refinement of the setting angles of 12 reflections, measured on a Hilger and Watts Y 290 four-circle diffractometer. No density was measured as the only available crystal used for data collection decomposed on irradiation.

Data were collected on the diffractometer by the θ—2θ scan method with Zr-filtered Mo-K_α radiation. A symmetric step scan of 1·2° (0·01° step s^{-1}) was used with stationary-background measurements of 30 s at both sides of the peak. Intensities for one half of the sphere of reflection with $\theta_{max.}$ 15° were collected. The intensities of 3 standard reflections, monitored throughout the data collection, decreased uniformly, and at the termination had decreased by 34%. Data were corrected for decomposition (assumed linear between standards), Lorentz and polarization factors. Of 1079 measured reflections, 922 having intensities $>3\sigma(I)$ were considered observed and used in the structure solution.

TABLE 1

Atomic parameters (× 10^4), with standard deviations in parentheses

	x/a	*y/b*	*z/c*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co(1)	1681(6)	7225(3)	4952(4)	209(34)	526(37)	318(35)	90(27)	130(27)	162(27)
Co(2)	−294(6)	7497(3)	577(4)	144(31)	415(34)	273(34)	116(25)	108(25)	163(26)
Cl(1)	758(12)	5092(6)	8076(7)	629(74)	434(66)	463(68)	113(55)	118(57)	146(53)
Cl(2)	4342(12)	2072(7)	7321(8)	255(64)	898(81)	679(75)	214(56)	231(55)	400(62)
Cl(3)	3922(12)	7512(6)	8536(7)	267(63)	838(78)	410(67)	109(54)	91(52)	165(57)
Cl(4)	916(15)	582(6)	1768(9)	126(10)	448(72)	759(85)	203(67)	468(75)	211(62)
Cl(5)	3058(12)	4014(6)	4054(7)	263(65)	824(79)	586(71)	129(56)	163(53)	356(60)

	x/a	*y/b*	*z/c*	*U*		*x/a*	*y/b*	*z/c*	*U*
N(1)	1436(34)	8294(16)	4139(20)	313(76)	N(8)	1923(34)	8448(16)	649(20)	352(76)
N(2)	426(35)	7921(16)	6125(20)	549(87)	N(9)	−2502(35)	6532(18)	505(23)	389(78)
N(3)	−929(33)	6642(15)	4004(19)	359(77)	N(10)	−2080(34)	8526(16)	641(20)	359(77)
N(4)	2983(34)	6505(16)	3831(20)	363(77)	N(11)	−1057(34)	7297(16)	−1137(20)	326(75)
N(5)	4344(34)	7836(16)	5897(20)	467(83)	C(1)	926(41)	8305(22)	2995(30)	263(93)
N(6)	1923(34)	6147(16)	5862(20)	386(78)	O(1)	372(25)	7561(13)	2228(16)	225(57)
N(7)	1598(34)	6462(17)	576(21)	382(78)	O(2)	4359(36)	4894(15)	1788(17)	788(82)

* The anisotropic thermal parameters U_{ij}/Å^2 are the terms in the expression: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

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[1] A. Werner, *Ann. Chem. Liebigs*, 1910, **375**, 1; H. Siebert and H. Feuerhake, *Chem. Ber.*, 1969, **102**, 295; W. P. Schaefer, A. W. Cordes, and R. E. Marsh, *Acta Cryst.*, 1968, **B24**, 283.

[2] B. F. Hoskins, F. D. Whillans, D. H. Dale, and D. C. Hodgkin, *Chem. Comm.*, 1969, 69.

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

[4] M. R. Hyde, K. L. Scott, and A. G. Sykes, *Co-ordination Chem. Rev.*, 1972, **8**, 121.

[5] R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, 1973, **12**, 1438.

Solution and Refinement.—The positions of all the non-hydrogen atoms were obtained by the heavy-atom method. In addition to the atoms of the cation and anions, a further peak was observed in a position, and with an integrated peak density, consistent with it being an oxygen of a water molecule of hydration. The assignment of chemical types to atoms O(1) and N(1) of the formamido-group was made after comparing peak heights in electron-density maps. Confirmation was obtained by refining both O(1) and N(1) with nitrogen scattering factors; this consistently resulted in the thermal parameter for oxygen becoming negative. The atomic parameters were refined by full-matrix least-squares calculations with anomalous dispersion corrections [6] for cobalt and chlorine. The cobalt and chlorine atoms were treated as having anisotropic thermal motion, and the remaining carbon, oxygen, and nitrogen atoms were only refined isotropically. Eight cycles of refinement converged to a conventional residual, R, of 0·082, and to a weighted residual, R', of 0·095 $[R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)]$. The maximum shift-to-error ratio was 0·11. Weights were assigned according to the scheme: $\sqrt{w} = 1$ if $F_o < 45$ and $\sqrt{w} = (45/F_o{}^2)^{\frac{1}{2}}$ if $F_o \geqslant 45$, and gave a satisfactory weighting-scheme analysis. Scattering factors were obtained from ref. 7. Programs used are listed in ref. 8.

Final atomic positional and thermal parameters are listed in Table 1, bond lengths and angles in Table 2, and selected intra- and inter-molecular contacts in Table 3. Observed and calculated structure factors are given in Supplementary Publication SUP 21229 (11 pp., 1 microfiche).*

TABLE 2

(*a*) Bond lengths (Å)

Co(1)–N(1)	1·941(25)	Co(1)–N(4)	1·982(25)
Co(1)–N(2)	1·991(28)	Co(1)–N(5)	2·003(22)
Co(1)–N(3)	1·963(21)	Co(1)–N(6)	2·025(26)
Co(2)–N(7)	2·040(24)	Co(2)–N(11)	1·965(23)
Co(2)–N(8)	1·983(23)	Co(2)–O(1)	1·908(19)
Co(2)–N(9)	1·992(24)	Mean Co–N	1·993
Co(2)–N(10)	1·987(24)		
N(1)–C(1)	1·337(42)	C(1)–O(1)	1·265(32)

(*b*) Bond angles (°)

N(1)–Co(1)–N(2)	89·2(11)	N(7)–Co(2)–N(10)	177·8(11)
N(1)–Co(1)–N(3)	90·5(9)	N(7)–Co(2)–N(11)	92·2(9)
N(1)–Co(1)–N(4)	92·8(11)	N(7)–Co(2)–O(1)	84·6(9)
N(1)–Co(1)–N(5)	88·5(10)	N(8)–Co(2)–N(9)	179·4(10)
N(1)–Co(1)–N(6)	177·5(10)	N(8)–Co(2)–N(10)	89·7(10)
N(2)–Co(1)–N(3)	90·5(10)	N(8)–Co(2)–N(11)	91·5(10)
N(2)–Co(1)–N(4)	177·7(13)	N(8)–Co(2)–O(1)	93·1(9)
N(2)–Co(1)–N(5)	89·8(10)	N(9)–Co(2)–N(10)	90·9(10)
N(2)–Co(1)–N(6)	88·4(11)	N(9)–Co(2)–N(11)	88·5(10)
N(3)–Co(1)–N(4)	90·5(9)	N(9)–Co(2)–O(1)	86·9(9)
N(3)–Co(1)–N(5)	178·9(14)	N(10)–Co(2)–N(11)	89·9(9)
N(3)–Co(1)–N(6)	90·3(9)	N(10)–Co(2)–O(1)	93·4(9)
N(4)–Co(1)–N(5)	89·2(10)	N(11)–Co(2)–O(1)	174·3(9)
N(4)–Co(1)–N(6)	89·5(10)	Co(1)–N(1)–C(1)	129·8(18)
N(5)–Co(1)–N(6)	90·7(10)	N(1)–C(1)–O(1)	123·1(28)
N(7)–Co(2)–N(8)	89·4(10)	C(1)–O(1)–Co(2)	126·3(20)
N(7)–Co(2)–N(9)	90·0(10)		

Kinetic Studies.—Reduction studies were carried out under pseudo-first-order conditions (reductant in 10—20 fold excess over oxidant) at an ionic strength of 1·0M (LiClO$_4$), as described earlier.[9] The disappearance of the Co^{III} dimer peak at 492 nm was monitored. Values of k_{obs} in s^{-1} (k_2 values given in Table 4) were obtained from plots of log $(A_t - A)$ *versus* time, where A_t and A are the absorbance at time t and when the reaction is complete. In general, the plots were linear for >95% of the reaction.

TABLE 3

(*a*) Intramolecular contacts (Å)

N(1) ··· N(2)	2·76(4)	O(1) ··· N(4)	2·99(3)
N(1) ··· N(3)	2·77(3)	O(1) ··· N(7)	2·66(3)
N(1) ··· N(4)	2·84(3)	O(1) ··· N(8)	2·83(3)
N(1) ··· N(5)	2·75(3)	O(1) ··· N(9)	2·68(2)
N(1) ··· O(1)	2·29(3)	O(1) ··· N(10)	2·84(3)
N(2) ··· N(3)	2·81(3)	N(7) ··· N(8)	2·83(3)
N(2) ··· N(5)	2·82(4)	N(7) ··· N(9)	2·85(3)
N(2) ··· N(6)	2·80(3)	N(7) ··· N(11)	2·89(3)
N(3) ··· N(4)	2·80(3)	N(8) ··· N(10)	2·80(3)
N(3) ··· N(6)	2·83(3)	N(8) ··· N(11)	2·83(3)
N(4) ··· N(5)	2·80(3)	N(9) ··· N(10)	2·83(3)
N(4) ··· N(6)	2·82(4)	N(9) ··· N(11)	2·76(4)
N(5) ··· N(6)	2·87(3)	N(10) ··· N(11)	2·79(3)
O(1) ··· N(3)	2·97(3)		

(*b*) Intermolecular contacts (Å)

Cl(1) ··· N(7^{I})	3·21(2)	Cl(4) ··· N(8^{V})	3·32(2)
Cl(1) ··· O(2^{II})	3·37(3)	Cl(4) ··· N(2^{III})	3·38(3)
Cl(1) ··· N(3^{III})	3·25(2)	Cl(4) ··· N(11^{VI})	3·26(3)
Cl(1) ··· N(9^{III})	3·23(3)		
Cl(2) ··· N(4^{II})	3·36(3)	Cl(5) ··· N(5^{II})	3·30(3)
Cl(2) ··· N(8^{II})	3·33(3)	Cl(5) ··· N(3^{III})	3·27(3)
Cl(2) ··· N(3^{III})	3·35(3)	Cl(5) ··· O(2)	3·46(3)
Cl(3) ··· N(5)	3·35(3)	O(2) ··· N(7)	3·33(3)
Cl(3) ··· N(10^{IV})	3·36(2)	O(2) ··· N(9^{VI})	3·10(3)
Cl(3) ··· N(8^{I})	3·31(3)		

Roman numeral superscripts refer to the following equivalent positions, relative to the reference molecule at x, y, z:

I $x, y, 1 + z$
II $1 - x, 1 - y, 1 - z$
III $-x, 1 - y, 1 - z$
IV $1 + x, y, 1 + z$
V $x, -1 + y, z$
VI $-x, 1 - y, -z$

TABLE 4

Kinetic data for the reduction of μ-formamido-bis-[penta-amminecobalt(III)] by chromium(II) [a,b]

T/°C	[Co^{III}Dimer]/ mol l^{-1}	[Cr^{2+}]/ mol l^{-1}	[H$^+$]/ mol l^{-1}	k_2/ l mol^{-1} s^{-1}
44·6	0·0012	0·0332	0·467	0·011
	0·0012	0·0332	0·052	0·011
	0·0012	0·0332	0·882	0·010
	0·0012	0·0379	0·465	0·012
	0·0012	0·0379	0·880	0·011
	0·0012	0·0623	0·209	0·012
	0·0006	0·0415	0·184	0·011
	0·0012	0·0104	0·147	0·011
	0·0012	0·0415	0·184	0·012
50·2	0·0012	0·0332	0·052	0·016
	0·0012	0·0332	0·467	0·014
	0·0012	0·0332	0·052	0·015
	0·0012	0·0332	0·882	0·015
56·4	0·0012	0·0332	0·882	0·023
	0·0012	0·0332	0·112	0·023

[a] $I = 1{\cdot}0$M (LiClO$_4$); uncertainty in temperature ±0·1 °C.
[b] Concentrations are initial values in molar units.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The cation (Figure 1) is composed of two octahedrally co-ordinated cobalt atoms linked by the formamido-

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 17.

[7] D. T. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] '*X*-Ray' Sytem of Computing Programs, 1972, Computing Science Center, University of Maryland, College Park, Maryland, U.S.A., Report TR 192.

[9] R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, 1970, **92**, 1533.

ligand. The formamido-group is bidentate, bridging through N(1) and O(1).

Comparison of the conformation of the complex in the solid and in solution shows that in the former the ligand NH and CH groups adopt the *cis*-formation (I). An examination of space-filling models of (I) and the *trans*-forms, (II) and (III), indicates that (I) would be preferred on the grounds of minimum intramolecular contacts. Whether (I) is inherently more stable than (II) or (III) is not easy to decide from a crystal-structure analysis alone, because packing effects in the crystal might play a role in determining the molecular conformation. However, the fact that a nuclear Overhauser effect (NOE) was only observed [9] upon irradiation of the set of *cis*-ammines on the *O*-bonded Co(2) atom requires that, in solution, the molecule must adopt the same *cis*-conformation (I) found in the solid state. If the molecule were to adopt a *trans*-conformation (II) in solution, the CH proton would be equidistant from both sets of *cis*-ammines on Co(1) and Co(2); thus, a NOE should be observed upon irradiation of either set of *cis*-ammines. Further, if conformation (III) were correct, a NOE would have been observed for irradiation of the *cis*-ammines on Co(1); none was. Conformation (IV) is sterically impossible.

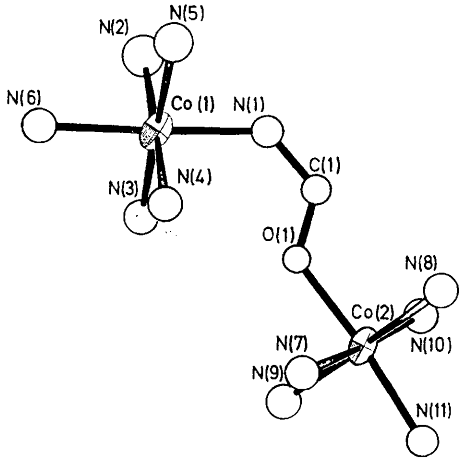


FIGURE 1 A view of the cation showing the conformation found in the solid state

TABLE 5

(*a*) Mean planes * in the cation

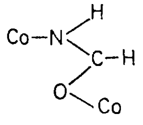
Plane	Atoms	*A*	*B*	*C*	*D*	σ	Distance from Co(1)	Distance from Co(2)
(1)	Co(1), Co(2), C(1), O(1), N(1)	0·99910	−0·02423	−0·03484	−1·18910	0·030	0·015	0·027
(2)	C(1), O(1), N(1)	0·99568	−0·08944	−0·02496	−1·19240	0	0·127	0·064
(3)	N(2)—(5)	−0·00597	0·75274	−0·65829	5·09692	0·031	0·009	
(4)	N(1), N(3), N(5), N(6)	−0·63884	0·49580	0·58827	7·85804	0·026	−0·018	
(5)	N(1), N(2), N(4), N(6)	0·76747	0·41753	0·48647	5·54856	0·001	−0·016	
(6)	N(7)—(10)	−0·01794	0·14039	0·98993	0·25149	0·021		−0·018
(7)	O(1), N(7), N(10), N(11)	0·73110	0·67860	−0·07061	6·52941	0·054		0·032
(8)	O(1), N(8), N(9), N(11)	−0·68433	0·72615	−0·06633	8·37214	0·026		0·032

(*b*) Selected interplanar angles (°) in the cation

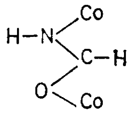
(2)—(3) 86·7, (2)—(4) 45·9, (2)—(5) 44·5, (2)—(6) 86·8, (2)—(7) 48·1, (2)—(8) 41·9, (3)—(4) 89·4, (3)—(5) 89·4, (3)—(6) 56·9, (4)—(5) 89·8, (6)—(7) 89·3, (6)—(8) 87·2, (7)—(8) 89·8

* Equations of the planes are in the form $AX + BY + CZ - D = 0$, and X, Y, and Z are orthogonal (Å) co-ordinates.

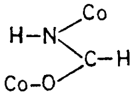
The molecule has approximate *m* symmetry, the approximate mirror plane lying through atoms N(6), Co(1), N(1), C(1), O(1), Co(2), N(11), with the ammine groups N(2) · · · N(5) and N(7) · · · N(10) approximately equidistant from the plane (Table 5). Thus, O(1) is equidistant from N(3) and N(4) [O(1) · · · N(3) 2·97, O(1) · · · N(4) 2·99 Å]. The contacts between O(1) and the equatorial ammine groups bonded to Co(2) fall into two distinct sets: O(1) · · · N(7), O(1) · · · N(9) 2·66 and 2·68 Å, respectively, and O(1) · · · N(8), O(1) · · · N(10), 2·83 and 2·84 Å respectively. These contacts are a consequence of the N(11)–Co(2)–O(1) angle being 5·7° from linearity, implying a repulsion between the C(1)–H group and ammine groups N(8) and N(10) (see Figure 1). There is no correspondingly large bending of the N(1)–Co(1)–N(6) angle from linearity (177·5 ± 1·0°) as a result of interactions between the carbonyl oxygen O(1) and amido-groups N(3) and N(4) on Co(1). Presumably the interaction is not a repulsive one, as the possibility of intramolecular O · · · H–N hydrogen bonding presents itself (but as the hydrogen atoms were not located this cannot be confirmed).



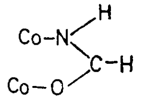
(I)



(II)



(III)



(IV)

The poor quality of the *X*-ray data, caused by the crystal decomposition, precludes a detailed analysis of the formamido-ligand; bearing in mind the standard deviations, the C–O [1·20(3)] and C–N [1·34(4) Å] bond lengths are not significantly different. However the i.r.

data have been interpreted in favour of a delocalized formamido-ligand.[10]

The Co–N(1) bond length [1·94(2) Å] is slightly shorter than the mean of the other Co–N bonds in the complex [1·99(2) Å] but is in good agreement with the value (1·92 Å) [2] found for the similar Co–N bond in the dinitrosyl complex $[(NH_3)_5CoN_2O_2Co(NH_3)_5]$. The Co–O bond length [1·91(2) Å], is within 2σ of that (1·87 Å) for the N_2O_2 complex.

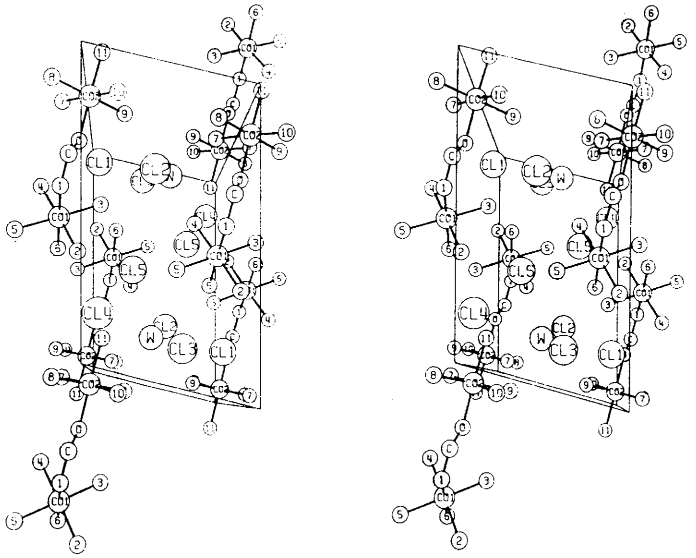


FIGURE 2 A stereopair showing the crystal structure of the complex. The water molecule is indicated by W. The origin of the cell is at the bottom left-hand corner nearer the viewer, with *a* horizontal, *c* vertical, and *b* into the page

The cations are located in layers parallel to [010] with $y/b \approx 0$ (Figure 2) and the chloride ions surround the cations. The water of solvation is located (Table 3) near Cl(1), Cl(5), N(7), and N(9), in a position ideally suited for hydrogen-bond formation; in addition the numerous $N \cdots Cl^-$ contacts could also be explained by a three-dimensional hydrogen-bond network.

The reduction of the dimer by chromium(II) ion has also been studied.[11] Investigation of the stoicheiometry showed that two moles of chromium(II) were consumed per mole of oxidant. The kinetic results were treated according to the rate law $k_{obs} = k_2[Cr^{2+}]$ and no evidence for a two-term rate law was obtained.[12] Data are collected in Table 4. At 25 °C, the specific rate constant is 0·0033 l mol^{-1} s^{-1} and the enthalpy and entropy of activation are 44·7 ± 8·0 kJ mol^{-1} and −142 ± 25 J K^{-1} mol^{-1} respectively. The kinetic parameters obtained are similar to those determined[12] for the chromium(II) reduction of μ-amido-μ-formato-bis[tetra-amminecobalt(III)] and μ-amido-μ-acetato-bis[tetra-amminecobalt(III)]. On this basis, and also because suitable sites for attack of reductant are unavailable, it seems reasonable that the initial step in the reduction of the present complex is an outer-sphere reduction which produces the conjugate base of nitrogen-bonded formamide, $[(NH_3)_5CoNHCHO]^{2+}$ [reaction (1)].

$$[(NH_3)_5Co{\cdot}NH{\cdot}CH{\cdot}O{\cdot}Co(NH_3)_5]^{5+} + Cr^{2+} \xrightarrow{H^+} Co^{2+} + 5NH_4^+ + [(NH_3)_5Co{\cdot}NH{\cdot}CHO]^{2+} \quad (1)$$

$$[(NH_3)_5Co{\cdot}NH{\cdot}CHO]^{2+} + Cr^{2+} \xrightarrow[\text{fast}]{H^+} Co^{2+} + 5NH_4^+ + [(OH_2)_5CrO{\because}CH{\cdot}NH_2]^{3+} \quad (2)$$

This complex is then rapidly reduced, presumably by an inner-sphere process [equation (2)].[9] This type of mechanism for the reduction of dinuclear complexes of cobalt(III) has been well documented.[4] Furthermore, the rate constant and activation parameters for the reduction[9] of $[(NH_3)_5CoOCHNH_2]^{3+}$ ($k^{25°} = 0{\cdot}0085$ l mol^{-1} s^{-1}, $\Delta H^\ddagger = 44{\cdot}7$ kJ mol^{-1}, $\Delta S^\ddagger = -134$ J K^{-1} mol^{-1}) which also proceeds by an outer-sphere mechanism lend support to our suggested mechanism.

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[10] R. J. Balahura, Ph.D. Thesis, 1971, University of Alberta, Edmonton.

[11] R. J. Balahura and R. B. Jordan, unpublished observations.

[12] See *e.g.* K. L. Scott and A. G. Sykes, *J.C.S. Dalton*, 1972, 1833.