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Intramolecular Imine Formation.
Synthesis and Crystal Structure of Chloro(1,2-diaminoethane) [2-(2′-aminoethylimino)-ethylamine]cobalt(III) Chloride Perchlorate Monohydrate

PETER D. FORD, KEVIN B. NOLAN
Department of Chemistry, University of Surrey, Guildford GU2 5XH, U.K.

and DAVID C. POVEY
Sub-department of Chemical Physics, University of Surrey, Guildford GU2 5XH, U.K.

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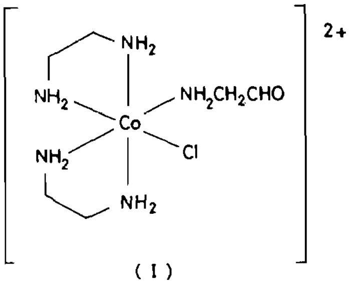
The complex cis-$[Co(en)_2\{NH_2CH_2CH(OCH_3)_2\}Cl]^{2+}$, *en = 1,2-diaminoethane, undergoes hydrolysis in dilute HCl solution to the aminoacetaldehyde complex,* cis-$[Co(en)_2(NH_2CH_2CHO)Cl]^{2+}$, *which was isolated in an equilibrium mixture with its hydrated adduct,* cis-$[Co(en)_2\{NH_2CH_2CH(OH)_2\}Cl]^{2+}$. *In aqueous solution an intramolecular condensation occurs between a 1,2-diaminoethane ligand and the carbaldehyde group, in the aldehyde complex to give the tridentate imine product* $[Co(en)\{NH_2(CH_2)_2N{=}CHCH_2NH_2\}Cl]^{2+}$. *A single crystal X-ray analysis of* $[Co(en)\{NH_2(CH_2)_2N{=}CHCH_2NH_2\}Cl](Cl)(ClO_4)\cdot H_2O$ *showed that of the three amine sites* cis *to the aminoacetaldehyde ligand in* cis-$[Co(en)_2(NH_2CH_2CHO)Cl]^{2+}$, *condensation occurs at an amino group* cis *to* Cl^-, *giving a product in which the tridentate imine ligand adopts a facial arrangement in the coordination octahedron. Spectral and kinetic data for the various complexes are reported.*

Condensation reactions between amines and carbonyl compounds have been widely investigated and many examples of such reactions both in the absence of and in the presence of metal ions have been reported [1]. Metal ions can sometimes promote these reactions by arranging the reactants in a proper geometry, usually as juxtaposed ligands in their co-ordination spheres [2]. On the other hand with substitutionally inert metal complexes imine-forming reactions may be inhibited due to blocking of the lone pair on the amino group by the metal ion* [3], although in such cases a possible reaction pathway is provided by deprotonation of the amine ligand followed by nucleophilic attack on the carbonyl group by the amido conjugate base [2].

In a recent paper Sargeson *et al.* [4], described base catalyzed imine formation in $[Co(NH_3)_5(NH_2CH_2COCH_3)]^{3+}$ and analogous aminoketone complexes. In addition a regio- and stereospecific carbinolamine adduct was observed to form in the complex α-$[Co(trien)(NH_2CH_2CHO)Cl]^{2+}$, resulting from attack on the carbonyl group by the amido conjugate base generated in the position *trans* to Cl^-. Before Sargeson's work was reported we had investigated imine formation in the cation *cis*-$[Co(en)_2(NH_2CH_2XHO)Cl]^{2+}$ (en = 1,2-diaminoethane), I, where as in the above example, a number of possible products could be formed depending on the location of the nucleophilic amido site attacking the carbonyl group. In this paper we report the preparation and properties of this complex, and results of an X-ray crystallographic study on the condensation product.



(I)

Experimental

Preparation of Complexes

(a) cis-$[Co(en)_2\{NH_2CH_2CH(OCH_3)_2\}Cl]Cl_2$

This complex was prepared from *trans*-$[Co(en)_2Cl_2]Cl$ and 2,2-dimethoxyethylamine (Aldrich Ltd.)

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*Whereas labile metal-diamine complexes react relatively rapidly with acetone analogous inert metal complexes fail to react.

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by the Meisenheimer method [5] and was recrystallised from a minimum of hot water (50 °C). The mauve crystalline product analyses correctly for [Co(en)$_2${NH$_2$CH$_2$CH(OCH$_3$)$_2$}Cl]Cl$_2$. Found: C, 24.3; H, 7.1; N, 17.9%. $CoC_8H_{27}N_5Cl_3O_2$ requires C, 24.6; H, 7.0; N, 17.9%.

(b) cis-[Co(en)$_2$(NH$_2$CH$_2$CHO)Cl]Cl$_2$·2H$_2$O

Complex (a) (7 g) was dissolved in warm (45 °C) HCl solution (3 mol dm^{-3}, 30 cm^3) and allowed to stand at this temperature for one hour. The solution was evaporated down to a maroon coloured oil under reduced pressure at 45 °C. This was repeated and the oily residue dissolved in a minimum volume of warm HCl solution (3 mol dm^{-3}, 45 °C). After filtration the filtrate was stored at −10 °C for 24 hours, whereupon a mauve crystalline product was obtained. This was washed with acetone and dried over P_2O_5 in an evacuated desiccator. The product analyses correctly for [Co(en)$_2$(NH$_2$CH$_2$CHO)Cl]Cl$_2$·2H$_2$O. Found: C, 19.1; H, 6.2; N, 18.5%. $CoC_6H_{23}N_5Cl_3O_2$ requires C, 18.9; H, 6.6; N, 18.4%.

(c) [Co(en){NH$_2$(CH$_2$)$_2$N=CHCH$_2$NH$_2$}Cl](Cl)(ClO$_4$)·H$_2$O

The pH of a solution of a complex (b) in water (2.5 g, 8 cm^3) was raised to, and maintained in the region of 6.5 by the dropwise addition of dilute sodium hydroxide solution (2 mol dm^{-3}). The solution gradually turned orange brown in colour and was allowed to stand at this pH for about 30 minutes. It was then acidified with concentrated perchloric acid (1.5 cm^3) and cooled overnight at 0 °C whereupon a brown-coloured complex crystallised from solution. The crystals were dried over P_2O_5 is an evacuated desiccator. The product analyses correctly for [Co(en){NH$_2$(CH$_2$)$_2$N=CHCH$_2$NH$_2$}Cl](Cl)(ClO$_4$)·H$_2$O. Found: C, 17.6; H, 5.1; N, 16.7; Cl, 26.2; O, 19.6%. $CoC_6H_{21}N_5Cl_3O_5$ requires C, 17.6; H, 5.2; N, 17.1; Cl, 26.0; O, 19.6%. Alternatively a solution of complex (b) in water (2 g, 10 cm^3) was heated at 50 °C for 30 minutes, sodium perchlorate (4 g) added to the solution, and this then filtered. On cooling the filtrate in a refrigerator (−5 °C) overnight, crystals of complex (c) were obtained. When another solution of complex (b) in water (2 g, 5 cm^3) was treated similarly but additional sodium perchlorate (10 g) added, crystals of the complex [Co(en){NH$_2$(CH$_2$)$_2$N=CHCH$_2$NH$_2$}Cl](ClO$_4$)$_2$·H$_2$O (soluble in acetone) were obtained. Found: C, 15.5; H, 4.2; N, 14.7%. $CoC_6H_{21}N_5Cl_3O_9$ required C, 15.2; H, 4.5; N, 14.8%.

Instrumentation

UV-visible spectra of the complexes were recorded on a Pye Unicam SP 8-100 spectrophotometer. IR spectra were recorded as nujol mulls between sodium chloride plates on a Perkin Elmer 577 grating infrared spectrophotometer. ^{1}H NMR spectra were obtained using a Bruker WH 90 spectrometer. Kinetics of base hydrolysis were followed at 25 ± 0.1 °C using a Radiometer pH Meter 26 linked to a Titrator 11 and a Titrigraph, with the titrant being delivered from an ABU 12 autoburette. Kinetics of Hg^{II}-catalysed acid hydrolysis were investigated spectrophotometrically on a Unicam SP 8-100 spectrophotometer.

X-ray Diffraction

[Co(en){NH$_2$(CH$_2$)$_2$N=CHCH$_2$NH$_2$}Cl](Cl)(ClO$_4$)·H$_2$O crystallises with an acircular habit elongated parallel to the x-axis and bounded mainly by the form {011}.

Crystal Data

$CoC_6H_{21}N_5Cl_3O_5$, M = 408.56, Monoclinic, a = 7.618(1), b = 8.819(1), c = 25.024(3) Å, β = 112.65(2)°, μ = 1551.5 Å^3, space group $P2_1/c$, Z = 4, D_c = 1.749 g cm^{-3}, $F(000)$ = 836, μ(Cu-K$_\alpha$) = 175.0 cm^{-1}.

The crystal used for intensity measurement had overall dimensions 0.52 × 0.24 × 0.22 nm. Accurate unit cell dimensions were obtained by a weighted ($\omega = \tan\theta$) least-squares fit to the θ values of 15 reflections for which both $\theta > 45°$ and the $\alpha_1\alpha_2$ peaks were resolved. Intensity data were collected on a Siemens four circle diffractometer (AED). To suppress the fluorescent radiation produced from the cobalt atom in the sample, the detector window was covered with 0.1 mm Al foil. Within the range $0.061 < (\lambda^{-1} \sin\theta) < 0.588$, 2618 symmetry independent reflection intensities were measured; 622 of them for which $I < 2.58\ \sigma(I)$ were classed as 'unobserved', and omitted from the analysis. The intensities were corrected for Lorentz and polarisation effects but not for absorption. The reference reflection varied in intensity by no more than ±2% during the data collection period and the crystal was deemed to have undergone no decomposition.

Structure Analysis and Refinement

The structure was solved by the heavy atom technique; a sharpened Patterson map was used to locate the positions of the cobalt and chlorine atoms. The parameters of these atoms were subjected to four cycles of least squares refinement after an R value of 0.19 was obtained. The positions of the non-hydrogen atoms were located on a difference Fourier synthesis. Refinement was carried out isotropically to R = 0.14. The hydrogen atom positions were then determined from standard molecular geometry. The hydrogen atoms were not refined and were allocated isotropic temperature factors equivalent to the atom to which they were bonded. Anisotropic refinement of all non hydrogen atoms together with the introduction of a weighting scheme ($\omega = 1/(A + |F_o|$

+ $B|F_o|^2$), with A = 22 and B = 0.012 resulted in convergence at $R = 0.089$.

All the computations were performed on the University of London CDC 7600 computer using the X-ray system of crystallographic programs.

Results and Discussion

The reaction between *trans*-$[Co(en)_2Cl_2]^+$ and primary amines, RNH_2, gives products of the type *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$ [5]. Complex (a) has the characteristic features of such a product. The UV visible spectrum of an aqueous solution of (a) has two bands, λ_{max} 527 nm (ϵ, 82.1 dm^3 mol^{-1} cm^{-1}) and 368 nm (ϵ, 89.2 dm^3 mol^{-1} cm^{-1}), the positions of which are indicative of a CoN_5Cl chromophore and the intensities of which suggest a *cis* rather than a *trans* configuration [7, 8]. In acid solutions containing Hg^{II}, complex (a) undergoes Hg^{II}-assisted hydrolysis, rate = $k_2[Hg^{II}]$ [complex (a)] [9], to the corresponding aqua complex (λ_{max} 488, 348 nm) with k_2 (determined spectrophotometrically at 480 nm), equal to 2.10×10^{-2} dm^3 mol^{-1} s^{-1} (T = 25 ± 0.1 °C, $[Hg^{II}] = 0.244$ mol dm^{-3}, $[HClO_4] = 1.0$ mol dm^{-3}). In basic solution complex (a) undergoes base-catalysed hydrolysis, rate = $k_2^1[OH^-]$ [complex (a)] [10], to the corresponding hydroxo complex (λ_{max} 507, 362 nm(, with k_2^1, (determined by the pH stat method), equal to 31.7 dm^3 mol^{-1} s^{-1} at 25.0 ± 0.1 °C, ionic strength 0.1 mol dm^{-3} ($NaClO_4$).

Complex (a) was heated in dilute HCl in the hope of obtaining the N-coordinated aminoacetaldehyde complex, *cis*-$[Co(en)_2(NH_2CH_2CHL)Cl]^{2+}$. The hydrolysis of acetals is an acid catalysed process which occurs *via* carbonium ion and hemiacetal intermediates [11]. However the product obtained was mainly the hydrated aldehyde complex, *cis*-$[Co(en)_2\{NH_2CH_2CH(OH)_2\}Cl]^{2+}$. Hence it showed only a very weak –C=O absorption [12] at 1730 cm^{-1} in its IR spectrum (nujol mull). The ^1H NMR spectra of solutions of the complex in 0.1 mol dm^{-3} DCl (30–120 mg/ml) showed a weak aldehydic, –CHO, signal [13] at 9.60 ppm downfield from DSS, integration of which relative to the $-CH_2$-proton signals of 1,2-diaminoethane showed that the free aldehyde was present to an extent of only about 5% under these conditions. Although it has been shown that aldehydes are appreciably hydrated in aqueous solution [14] generally the adducts are not stable substances and are seldom isolable. However the introduction of electron-withdrawing substituents into the aldehyde molecule may confer stability on the hydrate and aldehydes such as trichloroacetaldehyde, and phenylglyoxal can readily be isolated as stable crystalline hydrates [15]. In the present example, complex (b), although the electron withdrawing metal ion is two atoms removed from the carbonyl centre, the water molecule is nevertheless very tightly held and is extremely difficult to remove. An aqueous solution of complex (b) has a UV-visible spectrum typical of *cis*-$[Co(en)_2(RNH_2)Cl]^{2+}$ complexes, λ_{max} 526 nm (ϵ, 75.9 dm^3 mol^{-1} cm^{-1}), 367 nm (ϵ 87.4 dm^3 mol^{-1} cm^{-1}). In acidic solutions containing Hg^{II}, complex (b) undergoes Hg^{II}-assisted acid hydrolysis to the corresponding aqua complex (λ_{max} 480, 350 nm) with a second order rate constant of 3.87×10^{-2} dm^3 mol^{-1} s^{-1} at 25.0 ± 0.0 °C, $[Hg^{II}] = 0.244$ mol dm^{-3}, $[HClO_4] = 1.0$ mol dm^{-3} (measured spectrophotometrically at 480 nm). Base hydrolysis of complex (b) was complicated by a competing imine forming reaction.

Concentrated aqueous solutions of the aldehyde complex (b) undergo colour changes from mauve to orange brown as imine formation occurs, over a period of time which depends on the pH of the solution. Due to complexities in the system (some reduction to cobalt(II) species as well as competing hydrolysis reactions of complex (b)) our attempts to study the reaction kinetics in order to establish a pH-rate profile proved unsuccessful. However for 0.8 mol dm^{-3} solution raised to pH 6.5 the reaction was complete after about 15 minutes at 25 °C but took 12 hours to reach completion at the ambient pH, 2.5. The increased rate at higher pH is consistent with a mechanism involving pre-equilibrium formation of an amido conjugate base, which subsequently attacks the carbonyl group to give a carbinolamine intermediate, rapid dehydration of which gives the imine product. During these reactions the weak aldehyde signal in the ^1H NMR spectrum of complex (b) disappears and is replaced by a more intense signal at 8.1 ppm downfield from DSS (–CH=N– [13]). The products were isolated as either a mixed chloride perchlorate salt or as a diperchlorate depending on the amount of $NaClO_4$ or $HClO_4$ added to cause crystallisation (see experimental section). The complexes have sharp absorption bands in their IR spectra (nujol mulls) at 1690 cm^{-1} confirming the presence of a –C=N group [12]. The ^{13}C NMR spectra of the complexes (in H_2O, containing dioxane $\delta = 67.39$, as an internal standard) show an imine signal at 181.8 ppm downfield relative to TMS with the remaining carbon signals (5) appearing between 45.7 and 57.1 ppm at positions similar to those reported for a variety of (1,2-diaminoethane)cobalt(III) complexes [16]. The UV-visible spectra of the complexes display relatively intense bands at 469 nm (ϵ, 164 dm^3 mol^{-1} cm^{-1}) and 359 nm (ϵ, 102 dm^3 mol^{-1} cm^{-1}), the former carrying a shoulder at ~520 nm (ϵ, 91 dm^3 mol^{-1} cm^{-1}). The imine complex (c), in aqueous solution undergoes Hg^{II} assisted acid hydrolysis to the corresponding aqua complex (λ_{max} 458, 346 nm) with a second order rate constant of 2.85×10^{-2} dm^3 mol^{-1} s^{-1} at $[Hg^{II}] = 0.244$ mol dm^{-3}, $[HClO_4] = 1.0$ mol

TABLE I. Fractional Coordinates (×10^4) with Estimated Standard Deviations in Parentheses.

Atom	x	y	z
Co	3586(2)	1836(2)	1066(1)
Cl(1)	2521(5)	−153(3)	1418(1)
Cl(2)	7479(4)	2068(3)	186(1)
Cl(3)	1844(5)	1183(4)	3350(1)
N(1)	1747(13)	3124(11)	1237(4)
C(2)	2438(20)	3313(16)	1871(5)
C(3)	4613(23)	3425(19)	2101(6)
N(4)	5242(14)	2443(11)	1795(4)
C(5)	6967(20)	1912(19)	1993(6)
C(6)	7315(21)	788(23)	1638(7)
N(7)	5711(13)	588(10)	1067(4)
N(8)	1906(13)	1268(10)	303(4)
C(9)	2297(17)	2097(14)	−151(4)
C(10)	2876(20)	3670(13)	90(5)
N(11)	4294(12)	3518(9)	677(4)
O(1)	1480(22)	749(18)	2797(5)
O(2)	278(15)	2099(14)	3332(5)
O(3)	3537(18)	1827(19)	3659(7)
O(4)	1843(20)	−64(17)	3715(6)
O(5)	7880(17)	1291(10)	4086(5)

TABLE II. Interatomic Distances (Å) and Angles (°) with Estimated Standard Deviations in Parentheses.

Co–N(1)	1.974(10)	C(9)–H(9)	1.07
Co–N(4)	1.851(8)	C(9)–H(91)	1.08
Co–N(7)	1.957(10)	C(10–H(10)	1.08
Co–N(8)	1.912(8)	C(10)–H(10)	1.08
Co–N(11)	1.962(9)	N(11)–H(11)	1.04
Co–Cl(1)	2.249(4)	N(11)–H(111)	1.03
N(1)–C(2)	1.47(2)	Co–N(1)–C(2)	108.0(0.8)
C(2)–C(3)	1.53(2)	N(1)–C(2)–C(3)	107.4(1.2)
C(3)–N(4)	1.36(2)	C(2)–C(3)–N(4)	108.1(1.1)
N(4)–C(5)	1.30(1)	C(3)–N(4)–Co	119.0(0.8)
C(5)–C(6)	1.42(2)	C(3)–N(4)–C(5)	122.5(1.0)
C(6)–N(7)	1.49(1)	Co–N(4)–C(5)	118.5(1.0)
N(8)–C(9)	1.47(1)	N(4)–C(5)–C(6)	114.6(1.1)
C(9)–C(10)	1.51(2)	C(5)–C(6)–N(7)	113.6(1.3)
C(10)–N(11)	1.46(1)	C(6)–N(7)–Co	107.8(0.9)
		Co–N(8)–C(9)	112.5(0.6)
N(1)–H(1)	1.03	C(8)–C(9)–C(10)	105.3(0.9)
N(1)–H(11)	1.04	C(9)–C(10)–N(11)	107.9(9.8)
C(2)–H(2)	1.09	C(10)–N(11)–Co	109.4(0.7)
C(2)–H(21)	1.09		
C(3)–H(3)	1.07	N(1)–Co–N(4)	83.8(0.4)
C(3)–H(31)	1.10	N(1)–Co–N(8)	96.3(0.4)
C(5)–H(5)	1.10	N(4)–Co–N(7)	85.0(0.4)
C(6)–H(6)	1.09	N(4)–Co–N(8)	178.0(0.4)
C(6)–H(61)	1.08	N(7)–Co–N(11)	92.3(0.4)
N(7)–H(7)	1.03	N(8)–Co–N(11)	84.7(0.5)
N(7)–H(71)	1.04	N(1)–Co–Cl(1)	88.3(0.3)
N(8)–H(8)	1.02	N(4)–Co–Cl(1)	93.0(0.3)
N(8)–H(81)	1.04	N(7)–Co–Cl(1)	89.1(0.3)
		N(8)–Co–Cl(1)	89.0(0.3)
		N(11)–Co–Cl(1)	173.6(0.2)
O(1)–Cl(3)	1.36(1)	O(1)–Cl(3)–O(2)	106.7(0.8)
O(2)–Cl(3)	1.43(1)	O(1)–Cl(3)–O(3)	118.7(1.0)
O(3)–Cl(3)	1.35(1)	O(2)–Cl(3)–O(4)	104.4(0.9)
O(4)–Cl(3)	1.43(1)	O(3)–Cl(3)–O(4)	101.1(0.9)

dtn^{-3}, T = 25.0 ± 0.1 °C (measured spectrophotometrically at 540 nm). Complex (c) also undergoes base hydrolysis to the corresponding hydroxo (λ_{max} 470, 338 nm) with a second order rate constant of 8.4 × 10^{-2} dm^3 mol^{-1} s^{-1} at 25.0 ± 0.1 °C, ionic strength 0.1 mol dm^{-3} $NaClO_4$ (measured by the pH stat method at various pH values in the range 8.0–8.5).

In the complex *cis*-$[Co(en)_2(NH_2CH_2CHO)Cl]^{2+}$, I, there exists the prospect for condensation of the carbonyl group at three amine centres *cis* to the aldehyde ligand (two of these are *cis* to Cl$^-$, the other *trans*). Under the conditions that we have used the reaction appears to be stereospecific yielding, only a single imine product. Hence the reaction solution after sorption onto and elution from a Dowex resin (Na$^+$ form) with 1 *M* NaCl (to separate imine complexes from cobalt(II) species and hydrolysis products of complex (b)) gave only one imine complex, the UV-visible spectrum and kinetic behaviour (base and Hg^{II}-assisted hydrolysis) of which was identical to that of imine complex (c). We decided to investigate the structure of this product by X-ray crystallography to establish the amine site at which condensation occurs. The crystals used for the X-ray investigations were those of $[Co(en)_2\{NH_2(CH_2)_2N{=}CHCH_2NH_2\}Cl](Cl)(ClO_4)\cdot H_2O$.

The fractional coordinates of the non-hydrogen atoms are given in Table I, and the interatomic distances and angles in Table II. The structure of the complex is shown in Fig. 1 together with the atom-

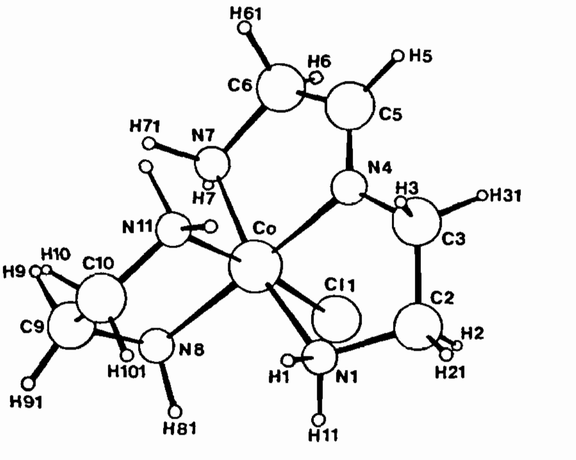

Fig. 1. The stereochemistry of $[Co(en)\{NH_2(CH_2)_2N{-}CHCH_2NH_2\}Cl]^{2+}$, with the atom numbering scheme.

TABLE III. Fractional Coordinates ($\times 10^3$) for the Hydrogen Atoms.

Atom	x	y	z
H(1)	161	417	104
H(11)	40	263	108
H(2)	199	236	206
H(21)	181	433	198
H(3)	499	458	207
H(31)	516	314	256
H(5)	806	231	240
H(6)	756	–29	187
H(61)	859	107	157
H(7)	531	–54	99
H(71)	612	92	73
H(8)	201	13	25
H(81)	52	150	25
H(9)	341	155	–24
H(91)	104	214	–55
H(10)	344	429	–17
H(101)	167	428	10
H(11)	562	331	66
H(111)	441	452	90

Anisotropic Thermal Parameters for the Non-Hydrogen Atoms

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	0.039	0.028	0.029	–0.002	0.009	–0.001
Cl(1)	0.062	0.029	0.043	–0.005	0.028	0.006
Cl(2)	0.037	0.029	0.041	–0.000	0.017	–0.003
Cl(3)	0.048	0.060	0.030	0.015	0.005	0.000
N(1)	0.044	0.033	0.031	0.001	0.016	–0.001
C(2)	0.075	0.058	0.037	0.015	0.029	–0.012
C(3)	0.076	0.082	0.035	–0.029	0.007	–0.014
N(4)	0.049	0.036	0.026	0.006	0.007	0.007
C(5)	0.053	0.066	0.047	–0.011	–0.012	0.009
C(6)	0.053	0.117	0.054	0.037	0.013	0.028
N(7)	0.036	0.030	0.045	0.005	0.020	0.010
N(8)	0.041	0.023	0.032	–0.002	0.017	–0.006
C(9)	0.057	0.045	0.012	0.003	0.003	–0.001
C(10)	0.077	0.022	0.035	–0.001	0.017	0.006
N(11)	0.030	0.024	0.030	–0.004	0.007	–0.000
O(1)	0.174	0.156	0.052	0.074	0.048	0.031
O(2)	0.065	0.091	0.092	0.039	0.022	–0.003
O(3)	0.065	0.130	0.154	0.002	–0.002	–0.010
O(4)	0.115	0.124	0.119	0.051	0.050	0.066
O(5)	0.101	0.024	0.126	0.002	0.048	0.111

labelling scheme used. The coordination about the cobalt ion is best described as tetragonally distorted with the chloride ion, the two primary amino groups of the tridentate imine ligand, N(1) and N(7), and the amino group of the 1,2-diaminoethane ligand, N(11), defining the equatorial plane. Bond lengths and angles are not unusual with the exception of the bond C(3)–N(4) which is shorter than expected. Previous work on complexes of imines (–C=N–C–) indicate that –C=N bond distances lie typically in the range 1.25–1.31 Å while C–N bond lengths generally lie between 1.44 and 1.53 Å [17]. The N(4)–C(5) distance of 1.30 Å reported herein falls within the expected range but the C(3)–N(4) bond is shorter than anticipated.

The structure of the imine complex shows that condensation has occurred between the carbaldehyde group in complex (I) and an amino group *cis* to Cl^-, so that the tridentate imine ligand in the product adopts a facial arrangement in the coordination octahedron. The π isomer of the series $[Co(en)(dien)Cl]^{2+}$ is the product of imine reduction in the complex described herein [18] (κ[Co(en)(dien)Cl]$^{2+}$ is the reduced product of the imine formed if condensation has occurred at the other amino group *cis* to Cl^- in complex (I)). The choice of the amine condensation site is surprising in the light of previous results. In the complex ion α-$[Co(trien)(NH_2CH_2CHO)Cl]^{2+}$ a carbinolamine adduct results from attack on the carbonyl group by the deprotonated secondary amine center *trans* to Cl^- [4]. Also in the related amidine formation reaction in *cis*-$[Co(en)_2(NH_2CH_2CN)Cl]^{2+}$ it is the amido center generated *trans* to Cl^- which attacks the nitrile groups [19].

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