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Octahedral Cobalt(III) Complexes of the Chloropentammine Type. Part XXXIII. Preparation, Properties and Reactions of *cis*-Chloro(2,2-dialkoxyethylamine)-bis(ethylenediamine)cobalt(III) Complexes

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In a previous publication [1] the preparation of *cis*-chloro (2-methoxyethylamine) bis (ethylenediamine) - cobalt(III) chloride was described, the 2-methoxyethylamine ligand acting as an N-bonded monodentate. As far as we are aware, nothing has been done with 2,2-dimethoxyethylamine which, because of the susceptibility of the acetal group to hydrolysis (acetal → hemi-acetal → aldehyde), should present a more interesting problem, with possible complications arising from the reducing properties of the aminoacetaldehyde ligand, as well as the coordinating power of its carbonyl group.

As in previous preparations, the reaction was carried out with an excess of 2,2-dimethoxyethylamine except that the purification was performed in the absence of hydrochloric acid, the complex isolated being *cis*-chloro(2,2-dimethoxyethylamine)bis(ethylenediamine)cobalt(III) chloride. When this was treated with hydrochloric acid (6 mol dm^{-3}), methanol was liberated and *cis*-chloro(2,2-methoxyhydroxyethylamine)bis(ethylenediamine)cobalt(III) chloride was obtained. At 373 K *in vacuo*, the 2,2-dimethoxyethylamine complex was thermally stable, but the corresponding 2,2-methoxyhydroxyethylamine complex lost water of crystallisation and methanol (as indicated quantitatively by the observed loss in weight), changed colour from pink to green, and formed aminoacetaldehydebis(ethylenediamine)-cobalt(III) chloride, in which the aminoacetaldehyde ligand acts as a bidentate. The above sequence of reactions was also confirmed by similar observations with the 2,2-diethoxyethylamine system.

In aqueous solutions, the visible absorption spectra of both the 2,2-dialkoxyethylamine and 2,2-alkoxyhydroxyethylamine series of complexes all showed maxima at 530 and 368 nm, and minima at 418 and 330 nm. For each cation, the intensities of the longest wavelength absorption peak for both chloride and nitrate were virtually identical, thus establishing the isomeric purity of the complexes. ϵ values (with concentration in mol dm^{-3} and cell length in cm) were in the range of 70–80, indicating a *cis*-configuration, which was also confirmed in the solid state by infra-red observations in four characteristic regions of the cobalt–ethylenediamine ring system, *viz.* NH_2 bend [2], NH_2 wag [3], CH_2 rock [4] and Co–N stretch [5] (Table I). The presence of the alkoxy substituents in these complexes was evidenced by the appearance of a relatively strong and sharp absorption peak at about 1180 cm^{-1}, which may be assigned to the C–O–C anti-symmetric stretching mode. Furthermore, for the 2,2-alkoxyhydroxyethylamine complexes, an absorption band at about 3400 cm^{-1} was also observed, due to OH stretch.

In dilute aqueous solutions at elevated temperatures (330–350 K), *cis*-chloro(2,2-dialkoxyethylamine)bis(ethylenediamine)cobalt(III) cations undergo solvolytic aquation, liberating chloride ions and shifting the longest-wavelength visible absorption peak to 480 nm (d–d transition for the aqua product). The aquation was followed by measuring the increase of free chloride ion concentration in solution and the kinetic data obtained are collected in Table II, where they are compared with the corresponding results determined previously [1] for the *cis*-chloro(2-methoxyethylamine) bis (ethylenediamine) cobalt (III) cation. The similarity in rate constants and activation parameters indicates that the same dissociative mechanism also operates in the present reactions, and the negative entropy of activation is suggestive of a square-pyramidal intermediate, leading to the formation of *cis*-products. On the other hand, the first-order plots for the appearance of chloride ions from the corresponding 2,2-alkoxyhydroxyethylamine cations showed considerable departure from linearity. Furthermore, the visible absorption spectrum of the product solution did not correspond to that expected for the *cis*-aqua(2,2-alkoxyhydroxyethylamine)bis-(ethylenediamine)cobalt(III) cation, but there was a general similarity to the spectrum (measured in the

TABLE I. Frequencies of Absorption Bands in the Four Characteristic Regions for Complexes of the Type *cis*-[Coen$_2$(RNH$_2$)Cl]Cl$_2$.

R	Frequencies (cm^{-1})			
	NH_2 bend	NH_2 wag	CH_2 rock	Co–N stretch
$CH_2CH(OMe)_2$	1580, 1610	1120, 1145	878, 893	508,522,575,588
$CH_2CH(OEt)_2$	1570, 1610	1120, 1145	873, 896	509,523,570,588
$CH_2CH(OMe)(OH)$	1575, 1595	1110, 1142	873, 896	509,523,570,588
$CH_2CH(OEt)(OH)$	1575, 1610	1110, 1140	875, 896	505,515,565,580

TABLE II. Rate Constants (at 333.2 K) and Activation Parameters for the Solvolysis of *cis*-$[Coen_2(RNH_2)Cl]^{2+}$ Cations in Aqueous Solution.

R	10^5 k_1 (s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
CH_2CH_2OMe [1]	3.4	94	−50
$CH_2CH(OMe)_2$	3.9	88	−67
$CH_2CH(OEt)_2$	4.0	87	−69

open atmosphere) of a solution containing cobalt(II) chloride and ethylenediamine in the ratio of 1:2, indicating interference of the solvolytic aquation by redox processes. In view of these complications, the kinetic studies were not pursued further.

The colour of a freshly prepared aqueous solution of aminoacetaldehydebis(ethylenediamine)cobalt(III) chloride changed from greenish-yellow to orange-yellow at room temperature within about 10 minutes, accompanied by corresponding changes in visible absorption spectrum. Initially a peak at 467 nm was observed, as expected for the d–d transition of cobalt (III) in an octahedral field of five amino nitrogens and one carbonyl group. This peak spontaneously changed to a shoulder and finally disappeared to give the "cobalt(II)" spectrum mentioned at the end of the previous paragraph. In the solid state, the reflectance spectrum with a band at 21,400 cm^{-1} was comparable to that of similar cobalt(III) complexes in the visible region, and the presence of the aminoacetaldehyde ligand was confirmed by the appearance of an infra-red absorption peak at 1675 cm^{-1}. For saturated aliphatic aldehydes, the free C=O stretching vibration is in the region 1740–1720 cm^{-1}, and the observed shift to lower wavenumber indicates reduction of the C=O bond-order arising from coordination to cobalt. There were three chlorine atoms per cobalt atom and so the existence of the blue $[CoCl_4]^{2-}$ anion in the complex appeared unlikely. It may therefore be concluded that aminoacetaldehydebis(ethylenediamine)cobalt(III) chloride undergoes a spontaneous intramolecular redox process in aqueous solution at room temperature by virtue of the reducing properties of its aminoacetaldehyde ligand.

Experimental

Microanalyses (Table III) were carried out by the Australian Microanalytical Service, CSIRO, Melbourne. Visible absorption spectra were measured with a Beckman Acta CIII spectrophotometer using silica cells, and reflectance spectra with a Unicam SP700C spectrophotometer. Infra-red absorption spectra were measured with a Perkin-Elmer 577 spectrophotometer on the solid complex which was mulled with Nujol and placed between KBr plates. Kinetics were measured by standard methods previously described [1].

cis-*Chloro(2,2-dimethoxyethylamine)bis(ethylenediamine)cobalt(III) Chloride*

Finely powdered *trans*-dichlorobis(ethylenediamine)cobalt(III) chloride (9 g) was triturated with 2,2-dimethoxyethylamine (12 cm^3) in a mortar until a red paste was formed. Methanol (70 cm^3) was added slowly with stirring and the crude product was filtered off, washed with methanol and ether and dried in a vacuum desiccator. The salt was purified by dissolution in the minimum amount of water at room temperature. The solution was quickly filtered and the filtrate cooled in ice. Methanol was then slowly stirred into the filtrate and the red crystals obtained were filtered off, washed with methanol and ether and dried at 373 K *in vacuo*.

cis-*Chloro(2,2-methoxyhydroxyethylamine)bis(ethylenediamine)cobalt(III) Chloride*

The dimethoxyethylamine complex (5 g) was dissolved in a minimum amount of 6 mol dm^{-3} hydrochloric acid, and the solution was allowed to stand at room temperature for two hours. Methanol was then slowly stirred into the ice-cold solution and the crystals obtained were filtered off, washed with

TABLE III. Analytical Results.

Compound	Calc. (%)					Found (%)				
	C	H	N	Cl	Co	C	H	N	Cl	Co
$[Coen_2H_2NCH_2CH(OMe)_2Cl]Cl_2$	24.6	6.9	17.9	27.3	15.1	23.4	6.7	17.5	27.1	14.6
$[Coen_2H_2NCH_2CH(OMe)_2Cl](NO_3)_2$	21.6	6.1	22.1	8.0	13.3	20.9	5.9	22.0	8.8	13.3
$[Coen_2H_2NCH_2CH(OEt)_2Cl]Cl_2$	28.7	7.4	16.7	25.4	14.1	27.3	7.2	16.1	23.8	12.6
$[Coen_2H_2NCH_2CH(OEt)_2Cl](NO_3)_2$	25.5	6.6	20.8	7.5	12.5	25.9	6.8	20.6	7.4	11.5
$[Coen_2H_2NCH_2CH(OMe)(OH)Cl]Cl_2 \cdot H_2O$	21.3	6.8	17.7	27.0	15.0	21.4	6.7	17.6	26.8	14.4
$[Coen_2H_2NCH_2CH(OMe)(OH)Cl](NO_3)_2$	19.6	5.8	22.8	8.3	13.7	19.9	5.5	22.5	8.9	12.7
$[Coen_2H_2NCH_2CH(OEt)(OH)Cl]Cl_2$	24.6	6.9	17.9	27.3	15.1	22.8	6.2	17.9	27.3	14.7
$[Coen_2H_2NCH_2CHO]Cl_3$	20.9	6.1	20.3	30.9	17.1	21.5	6.0	20.0	30.8	17.0

methanol and ether, and dried in a vacuum desiccator.

The *nitrate* salts of these two complexes were prepared by passing an ice-cold solution of the chloride salt (3.5 g) in water (25 cm^3) through a column of ion-exchange resin (Amberlite IRA 401; NO_3^- form). Methanol (200 cm^3) was then added slowly with stirring, followed by ether (400 cm^3). The mixture was allowed to stand in an ice-bath and stirred until red crystals appeared. These were filtered off, washed and dried in a vacuum desiccator. Corresponding complexes of the *2,2-diethoxyethylamine* system were prepared by similar methods.

Aminoacetaldehydebis(ethylenediamine)cobalt(III) Chloride

This complex was prepared by heating *cis*-chloro-(2,2-methoxyhydroxyethylamine) bis (ethylenediamine)cobalt(III) chloride at 373 K *in vacuo* until no further loss in weight was observed. The same product was also obtained from the corresponding 2,2-ethoxyhydroxyethylamine complex.

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