# OCTAHEDRAL COBALT(III) COMPLEXES OF THE CHLOROPENTAMMINE TYPE*

## XII.† THE PREPARATION, PROPERTIES, AND REACTIONS OF THE CHLOROPENTAKISMETHYLAMINECOBALT(III) CATION

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Although chloropentaamminecobalt(III) chloride can be obtained from cobalt(II) chloride, ammonia, ammonium chloride, and hydrogen peroxide by the method of Willard and Hall,[1] attempts to prepare the corresponding pentakismethylamine complex lead to the formation of a blue precipitate. We have now successfully prepared the complex $[CoCl(CH_3NH_2)_5]Cl_2$ by the action of buffered aqueous methylamine on solid *trans*-dichlorotetrakispyridinecobalt(III) chloride hexahydrate. The chloride so obtained can be converted into the nitrate by the action of ammonium nitrate.

However, attempts to extend the method to higher homologous alkylamines were not successful.

Both salts are purple-red in colour, and are more soluble in water than the corresponding chloropentaamminecobalt(III) compounds. In basic and neutral aqueous solutions, the complex cation decomposes completely to yield the brown insoluble cobalt oxide. If, however, it is dissolved in dilute nitric acid, the coordinated chloride is slowly replaced by water. The product is presumably the aquopentakismethylaminecobalt(III) cation, but attempts to prepare salts of this aquo ion have so far proved unsuccessful.

$$[CoCl(CH_3NH_2)_5]^{2+} + H_2O \rightarrow [Co(H_2O)(CH_3NH_2)_5]^{3+} + Cl^-$$
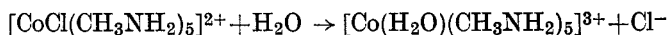
The visible absorption spectrum of a solution of chloropentakismethylaminecobalt(III) nitrate in dilute nitric acid ($\lambda_{max}$ 555 m$\mu$, $\epsilon_{max}$ 63·2 l. mole$^{-1}$ cm$^{-1}$; $\lambda_{max}$ 382 m$\mu$, $\epsilon_{max}$ 65·0 l. mole$^{-1}$ cm$^{-1}$) was virtually identical with that for the corresponding chloride salt, indicating that the conversion of the chloride into nitrate by the action of ammonium nitrate leaves the complex cation intact. Compared with the spectrum of the corresponding pentaammine complex, the first absorption peak (*d–d* band) for the present cation occurs at a longer wavelength (and with a higher extinction coefficient), reflecting the relative strengths of the field produced by the five ammonia and the five methylamine ligands.

The hydrolysis of chloropentakismethylaminecobalt(III) nitrate was studied in dilute nitric acid, and the first-order rate constants obtained (see Experimental)

were independent of acid concentration over the range $0 \cdot 05$–$0 \cdot 20$M. The temperature dependence of these rate constants ($k$) could be satisfactorily expressed by

$$k = 2 \cdot 9 \times 10^{13} \exp(-22000/\mathbf{R}T) \text{ min}^{-1}$$

over a temperature range of 30° (between 30 and 60°). At $25 \cdot 0$°, the rate constant obtained by extrapolation is $2 \cdot 2 \times 10^{-3}$ min$^{-1}$, and this was some 22 times higher than the corresponding value for the chloropentaamminecobalt(III) cation. Comparison of the Arrhenius parameters shows that the greater reactivity of the present complex is reflected almost entirely in its lower (by $1 \cdot 7$ kcal/mole) activation energy of reaction.

TABLE 1

FIRST-ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF CHLOROPENTAKISMETHYLAMINECOBALT(III) NITRATE

| Temp. | [HNO$_3$] | $k$ (min$^{-1}$) | Temp. | [HNO$_3$] | $k$ (min$^{-1}$) |
|---|---|---|---|---|---|
| $30 \cdot 0$° | $0 \cdot 10$ | $3 \cdot 89 \times 10^{-3}$ | $40 \cdot 0$° | $0 \cdot 20$ | $1 \cdot 34 \times 10^{-2}$ |
| $40 \cdot 0$ | $0 \cdot 05$ | $1 \cdot 32 \times 10^{-2}$ | $50 \cdot 0$ | $0 \cdot 10$ | $3 \cdot 90 \times 10^{-2}$ |
| $40 \cdot 0$ | $0 \cdot 10$ | $1 \cdot 33 \times 10^{-2}$ | $60 \cdot 0$ | $0 \cdot 10$ | $1 \cdot 05 \times 10^{-1}$ |

*Experimental*

*Chloropentakismethylaminecobalt(III) Chloride*

*trans*-Dichlorotetrakispyridinecobalt(III) chloride hexahydrate[2] ($11 \cdot 8$ g) was ground in a mortar with an ice-cold mixture of 40% aqueous methylamine (10 ml) and methylamine hydrochloride ($4 \cdot 5$ g). Ethanol was added to the resulting red-purple paste, which was then filtered and washed with alcohol and ether. The crude product was purified by dissolving at room temperature in water slightly acidified with hydrochloric acid, filtering, and adding solid ammonium chloride. The ratio of ionic to coordinated chloride in this complex was found to be 2 : 1 (Found: C, $18 \cdot 4$; H, $7 \cdot 8$; Cl, $33 \cdot 0$; Co, $18 \cdot 2$; N,* $21 \cdot 6$. [CoCl(CH$_3$NH$_2$)$_5$]Cl$_2$ requires C, $18 \cdot 7$; H, $7 \cdot 9$; Cl, $33 \cdot 2$; Co, $18 \cdot 4$; N, $21 \cdot 9$%).

*Chloropentakismethylaminecobalt(III) Nitrate*

This salt was prepared by dissolving the chloride in water (slightly acidified), filtering, and adding solid ammonium nitrate. The process was repeated until the resulting crystals were free from ionic chloride (Found: C, $16 \cdot 3$; H, $6 \cdot 8$; Cl, $9 \cdot 4$, $9 \cdot 5$;* Co, $15 \cdot 5$; N, $25 \cdot 6$. [CoCl(CH$_3$NH$_2$)$_5$](NO$_3$)$_2$ requires C, $16 \cdot 1$; H, $6 \cdot 7$; Cl, $9 \cdot 5$; Co, $15 \cdot 8$; N, $26 \cdot 2$%).

*Analyses and Measurements*

Microanalyses of the two salts were by Dr Zimmermann, Australian Microanalytical Service, Melbourne, with the exceptions noted.

Ionic chloride was estimated separately from coordinated chloride by passing a fresh solution containing a known weight of the complex in dilute nitric acid through a cation exchange resin column (Amberlite IR-120; H$^+$ form). The effluent and washings contain the corresponding amount of hydrochloric acid, which was analysed by Volhard's method.

Visible absorption spectra were measured with a Unicam SP800 spectrophotometer, using a slow scan speed.

* Analyses by the Microanalytical Laboratory of the University of Singapore.

[2] Werner, A., and Feenstra, R., *Ber. dt. chem. Ges.*, 1906, **39**, 1538.

*Kinetics*

The progress of the hydrolysis was followed by titrating the chloride ion liberated (Volhard), after the complex cation was removed by a cation exchange resin column. The reaction solutions were made up by dissolving a weighed amount (about 4 mmole/l.) of chloropentakismethylamine-cobalt(III) nitrate in dilute nitric acid previously brought to the temperature of the reaction. Samples were then withdrawn from time to time, cooled, and passed through the resin for analysis.
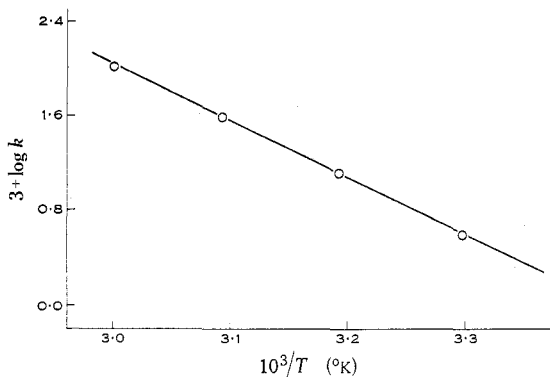


Fig. 1.—Arrhenius plot for the hydrolysis of chloropentakismethylamine-cobalt(III) nitrate in dilute nitric acid.

The resin column was surrounded by ice-water, and continually flushed with water between separations. The first-order rate constants were determined from the slopes of the plots of $\log(V_\infty - V_t)$ against time, where $V_t$ is the titre of silver nitrate consumed at time $t$ and $V_\infty$ is the corresponding value calculated from the weight of complex taken, assuming complete replacement of coordinated chlorine. The results are collected in Table 1, where each entry represents the average of three constants, determined from separate runs, which agree reasonably well. The Arrhenius plot for these data is shown in Figure 1.

The thermostat used was of conventional design capable of holding temperatures constant to $\pm 0 \cdot 05°$. Light was carefully excluded from the reaction mixture as a routine precaution.

*Acknowledgment*