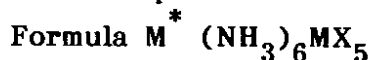


Studies Involving Labile Vitamin B₁ Metal Complexes.

Part III. Preparation and General Mechanism for the Formation of Complexes of the General



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Summary: Reactions of labile Vitamin B₁ metal complexes, thiaminium tetrachloromercurate (II) monohydrate, $\text{Hg(Th)Cl}_4 \cdot \text{H}_2\text{O}$, thiaminium tetrachlorocadmate (II) monohydrate, $\text{Cd(Th)Cl}_4 \cdot \text{H}_2\text{O}$ and thiaminium tetrachlorozincate(II) monohydrate, $\text{Zn(Th)Cl}_4 \cdot \text{H}_2\text{O}$ with hexammineruthenium(III) chloride, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ in aqueous medium (1:1 molar ratio) yielded hexammineruthenium (III) pentachloromercurate(II), $\text{Ru}(\text{NH}_3)_6\text{HgCl}_5$, hexammineruthenium(III) pentachlorocadmate (II), $\text{Ru}(\text{NH}_3)_6\text{CdCl}_5$ and hexammineruthenium(III) pentachlorozincate(II), $\text{Ru}(\text{NH}_3)_6\text{ZnCl}_5$, respectively. These new compounds have been characterized by elemental analyses and infrared spectra. The rationale for the particular geometry assumed by each of the HgCl_5^{3-} , CdCl_5^{3-} and ZnCl_5^{3-} complex ions is discussed.

Introduction

The last fifteen years have witnessed a dramatic increase in the number of authentic five-coordinate transition metal complexes [1,2]. Although attempts have been made to formulate a systematic basis for various factors which favour a given five-coordinate structure, the choice of polydentate ligands [3-7], some of which are capable of imposing their own stereochemistry on the resulting complexes [5,8] made initial attempts rather difficult. This initial difficulty was overcome by studying simple five-coordinated complexes [8-11] where the monodentate ligands exert no specific steric requirements.

Up-to-date, a very limited number of five-coordinated complexes containing only one kind of unidentate ligand have been reported [18-20]. However,

the method employed earlier involved high temperature and the use of concentrated hydrochloric acid which constitutes a great risk. In order to avert such a great risk, an alternative method which does not involve any danger has been worked out in our laboratory. Our interest is two fold (1) to prepare more of the five-coordinated complexes by employing an alternative method which is simple and of general application (2) to propose a mechanism for the formation of the complexes containing the authentic five coordinated structures.

Of particular interest is the wide variety of geometries assumed by these five coordinate species. For example, CdCl_5^{3-} is tetragonal pyramidal while MnCl_5^{2-} prefers square pyramidal

[18,20]. In order to shed more light on the various factors which favour given five-coordinate structures, we report, in the meantime, the synthesis, elemental analyses and infrared spectra of three new compounds, $\text{Ru}(\text{NH}_3)_6\text{HgCl}_5$,

$\text{Ru}(\text{NH}_3)_6\text{CdCl}_5$ and $\text{Ru}(\text{NH}_3)_6\text{ZnCl}_5$.

Experimental

Hexammineruthenium(III) chloride, $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ was used as commercially available while $\text{Hg}(\text{Th})\text{Cl}_4 \cdot \text{H}_2\text{O}$, $\text{Cd}(\text{Th})\text{Cl}_4 \cdot \text{H}_2\text{O}$ and $\text{Zn}(\text{Th})\text{Cl}_4 \cdot \text{H}_2\text{O}$ were prepared as earlier reported [12-15]. In general, slow evaporation of aqueous mixture of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ and each of the labile Vitamin B₁ (thiamine) metal complexes after been individually warmed (< 40°C), filtered and cooled afforded the new complexes, $\text{Ru}(\text{NH}_3)_6\text{HgCl}_5$, $\text{Ru}(\text{NH}_3)_6\text{CdCl}_5$ and $\text{Ru}(\text{NH}_3)_6\text{ZnCl}_5$.

Anal. Calcd. for $\text{Ru}(\text{NH}_3)_6\text{HgCl}_5$ (MW = 580.88): Ru, 17.40; Hg, 34.51, H, 3.01; N, 14.45; Cl, 30.51%. Found: Ru, 17.51; Hg, 34.67; H, 3.03; N, 14.57; Cl, 30.55%.

Anal. Calcd. for $\text{Ru}(\text{NH}_3)_6\text{CdCl}_5$ (MW = 492.72): Ru, 20.51; Cd, 22.81; H, 3.65; N, 17.05; Cl, 35.97%. Found: Ru, 20.81; Cd, 23.01; H, 3.68; N, 17.51; Cl, 36.03%.

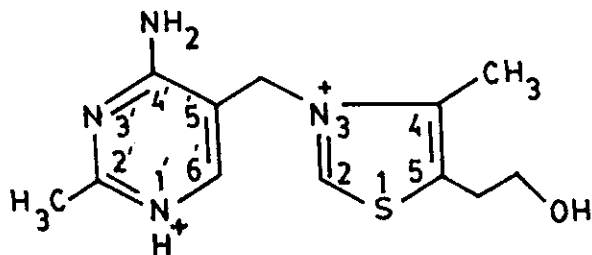
Anal. Calcd. for $\text{Ru}(\text{NH}_3)_6\text{ZnCl}_5$ (MW = 445.70): Ru, 22.68; Zn, 14.66; H, 4.03; N, 18.85; Cl, 39.76%. Found: Ru, 22.59; Zn, 14.53; H, 4.00; N, 18.59; Cl, 39.63%.

Elemental analyses were performed by Atlantic Microlab. Inc., U.S.A.

The infrared spectra of the three compounds were recorded on a Beckman 621 Infrared Grating Spectrometer in KBr pellets.

Results and Discussion

Thiamine (Vitamin B₁) is protonated at N(1') position of the pyrimidine moiety at pH 3 and the same is true of the complexes [12-15] of the general formula $\text{M}(\text{Th})\text{X}_4 \cdot \text{H}_2\text{O}$. This condition should favour the formation of the complexes $\text{M}^+(\text{NH}_3)_6\text{MX}_5$ investigated in this work.



Earlier investigators [16-18] have advanced the possibility of large cation +3 charge being capable of stabilising ZnCl_5^{3-} in $\text{Co}(\text{NH}_3)_6\text{ZnCl}_5$. The chances of ZnCl_5^{3-} being stabilized in $\text{Ru}(\text{NH}_3)_6\text{ZnCl}_5$ should even be greater than in $\text{Co}(\text{NH}_3)_6\text{ZnCl}_5$, Ru^{3+} being larger than Co^{3+} .

In $\text{Co}(\text{NH}_3)_6\text{CuCl}_5$, $\text{Co}(\text{NH}_3)_5\text{OH}_2\text{CuCl}_5$; $\text{Co}(\text{NH}_3)_6\text{CdCl}_5$, $\text{Co}(\text{NH}_3)_6\text{ZnCl}_5$ and $\text{Co}(\text{NH}_3)_6\text{ZnCl}_4(\text{NO}_3)$ compounds reported earlier [19] the pentachloro complex anion is stabilized except in the zinc - containing species. It is therefore not unreasonable to speculate that the stability of these pentachloro complex anion (MX_5^{3-}) depends not only on the size

Table-1: Infrared spectra data (cm⁻¹) of Ru(NH₃)₆HgCl₅
Ru(NH₃)₆CdCl₅ and Ru(NH₃)₆ZnCl₅ compounds

Ru(NH ₃) ₆ HgCl ₅	Ru(NH ₃) ₆ CdCl ₅	Ru(NH ₃) ₆ ZnCl ₅	Assignments
3240-3000s,br	3210-2980s,br	3240-3330s,br	NH str.
1600-1500m, br	1600-1500s, br	1600-1500s,br	NH ₃ degen def.
1375sh	1365w, br	1320 sh	
1310s	1300m	1280s br	
780s,br	1790s, br	778s,br	NH ₃ rock
678sh	690sh		
445m,w	445m,w	450m,w	
325w	328w	328w	M-N
250w	255w	250w	Cl-M-Cl

Abbreviations:

s = strong, br = broad, m = medium w = weak, sh = shoulder, st = stretching sym = symmetric, def. = deformation degen = degeneration

of the trivalent metal ions but also on the size of the divalent metal ions.

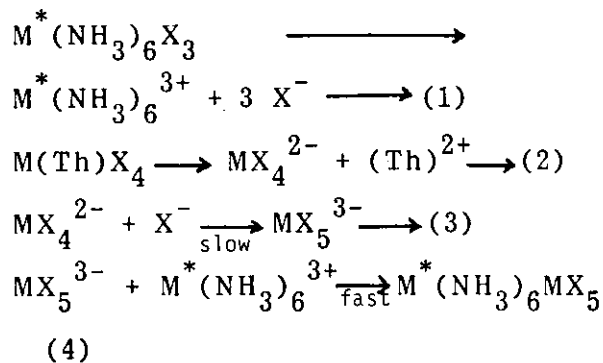
Based on the size of Ru³⁺, it is concluded that the pentachloro complex anions in Ru(NH₃)₆HgCl₅, Ru(NH₃)₆CdCl₅ and Ru(NH₃)₆ZnCl₅ compounds are stabilized. Also assuming that the size of the divalent metal ions is important, one would expect the relative stability of these complex anions to be HgCl₅³⁻ > CdCl₅³⁻ > ZnCl₅³⁻

In Co(NH₃)₆ CdCl₅ compound earlier reported [19], CdCl₅³⁻ anion which contains a d¹⁰ central ion, assumes a trigonal bipyramidal geometry. It is

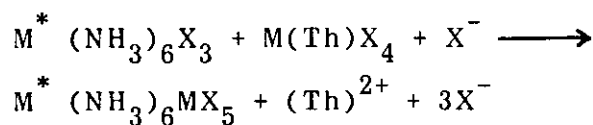
therefore reasonable to expect HgCl₅³⁻ and ZnCl₅³⁻ anions which also contain a d¹⁰ central ion to assume trigonal bipyramidal structure. The identical infrared spectral pattern exhibited by these compounds also lends support to our assumption that they all assume the same geometry. Table 1 lists the infrared spectral data of the three new compounds. The frequency description of the three pentachloro anions is based on the earlier reports [21].

In the absence of any kinetic data but based on mere speculation, the following scheme could be proposed for the formation of the compounds

of the general formula $M^*(NH_3)_6MX_5$ (M^* = trivalent metal ion, M = divalent metal ion, and $X = Cl$), employing the appropriate hexammine and labile vitamin B_1 metal complex of the general formula $M(Th)X_4 \cdot H_2O$.



The overall reaction is thus written as



Summarily, the synthetic approach employed in the present work is very simple and straight forward thus eliminating the hazard imposed by the use of high temperature and concentrated hydrochloric acid in the previous studies [19]. Low temperature ($<40^\circ C$) is employed in the present work so as to prevent the decomposition of the hexammines and vitamin B_1 . In addition, some of these new compounds may find wide application in solid state chemistry. The assumption that the pentachloro anions, $HgCl_5^{3-}$, $CdCl_5^{3-}$ and $ZnCl_5^{3-}$ have a greater chance of being stabilized in $Ru(NH_3)_6HgCl_5$, $Ru(NH_3)_6CdCl_5$ and $Ru(NH_3)_6ZnCl_5$ compounds is based on the size of Ru^+ in very good agreement with earlier studies [19]. Of particular

interest is the zinc - containing compound, $Co(NH_3)_6ZnCl_5$, where the complex anion is $ZnCl_4^{2-}$ rather than the expected $ZnCl_5^{3-}$. Although suitable crystals for X-ray analysis have not been obtained, it is concluded that $ZnCl_5^{3-}$ has a greater chance of being stabilized in $Ru(NH_3)_6ZnCl_5$ than in $Co(NH_3)_6ZnCl_5$ since Ru^{3+} is larger than Co^{3+} . The relative stability of these pentachloro anions could be formulated as $HgCl_5^{3-} > CdCl_5^{3-} > ZnCl_5^{3-}$ based on the relative size of Hg^{2+} , Cd^{2+} and Zn^{2+} . The geometry assumed by $HgCl_5^{3-}$, $CdCl_5^{3-}$ and $ZnCl_5^{3-}$ complex anions is most probably trigonal bipyramid in excellent agreement with $CdCl_5^{3-}$ complex anion found in $Co(NH_3)_6CdCl_5$ compound by X-ray crystallographic method [8,19]. It is also known that the energies of trigonal bipyramidal and that of square pyramidal configurations are similar. It then follows that there exists a possibility of one, two or even all these three pentachloro species to assume square pyramidal structure in preference to the trigonal bipyramidal configuration. It is hoped that X-ray crystallographic method will confirm our assumption.

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