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NEW SYNTHETIC METHODS OF BIS(ETHYLENEDIAMINE)- AND TETRA-AMMINE-CHROMIUM(III) COMPLEXES USING NON-AQUEOUS SOLVENTS$^{1)2)}$

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New synthetic methods of bis(ethylenediamine)- and tetraammine-chromium(III) complexes using the matrix method in the liquid state are described. The starting materials are $[Cr\ en_3](ClO_4)_3$ and $[Cr(NH_3)_6](ClO_4)_3$. Dimethylsulfoxide and dimethylformamide are used as solvents. The anions (X or L; see text) to be coordinated are added in the form of NH_4X and H_2L (or HL).

The solid state deamination of $[Cr\ en_3]X_3$ has been investigated extensively since Pfeiffer and co-workers first observed it in the chloride and thiocyanate of the complex cation.$^{3)}$ Wendlandt and co-workers studied the deamination of $[Cr\text{-}en_3]X_3$ in the matrix of NH_4X, and established the formation of $[CrX_2en_2]X$ type complexes. This method, which they called the thermal matrix method,$^{4)}$ is however not very convenient, because it must be carried out precisely under the suitable high temperature in vacuo.

The present investigation was undertaken to establish a general and new synthetic procedure of chromium(III) mixed complexes by carring out the matrix method in the liquid state.

The syntheses of bis(ethylenediamine)chromium(III) complexes consist of heating $[Cr\ en_3](ClO_4)_3$ mixed with an equivalent amount of NH_4X or H_2L (or HL) dissolved in dimethylsulfoxide (DMSO) or dimethylformamide (DMF) at 80—140°C for 10—40 min ($X = NCS^-$, F^-, Cl^-, Br^- and I^-, $L = ox^{2-}$, mal^{2-}, $male^{2-}$, $succ^{2-}$, pas^{2-}, $anth^-$, gly^- and ala^-).$^{5)}$ After heating, the solution was evaporated and cooled, and then a few ml of cold water or methanol were added to the syrup with stirring. The precipitate obtained was filtered off, and washed with cold water and methanol and dried over silica gel in a vacuum desiccator. Almost all complexes could be prepared in this way;$^{6)}$ the reaction temperatures and periods are given in Table 1. The tris → bis deamination reaction was followed by spectrophotometry, an example of which is shown in Fig. 1.

For the preparation of tetraammine type complexes, the mixtures consisting of $[Cr(NH_3)_6](ClO_4)_3$ and the matrix of H_2L (or HL) dissolved in DMF were allowed to stand at room temperature for not less than one month. The complexes precipitated were found to be $[Cr(ox)(NH_3)_4]ClO_4$, $[Cr(mal)(NH_3)_4]ClO_4$, $[Cr(male)(NH_3)_4]ClO_4$, $[Cr(succ)(NH_3)_4]ClO_4$, $[Cr(pas)(NH_3)_4]ClO_4$ and $[Cr(ala)(NH_3)_4](ClO_4)_2$.

Table 1. The reaction temperatures and periods for the mixtures consisting of [Cr en_3]$(ClO_4)_3$ and the matrix in non-aqueous solvents

(Table 1-a. In DMSO at 140°C)

Matrix (Ammonium Salt)	Reaction Period (min)
NH_4NCS	20
NH_4F	25 (in DMF)*
NH_4Cl	ca. 20 - 25**
NH_4Br	25 -30
NH_4I	30 -35

* In DMSO, the solution containing NH_4F gives a jelly.

** [Cr en_3]Cl_3 produced is precipitated in the non-aqueous solvent.

(Table 1-b. In DMF at 100°C)

Matrix (Acid)	Reaction Period (min)
oxH_2	ca. 10 - 15 (ppt.)
$malH_2$	ca. 10 - 15 (ppt.)
$maleH_2$	10 - 15
$succH_2$	25 - 30
$pasH_2$	35 - 40
$salH_2$	35 - 40
anthH	25 - 30
glyH	25 - 30
alaH	25 - 30

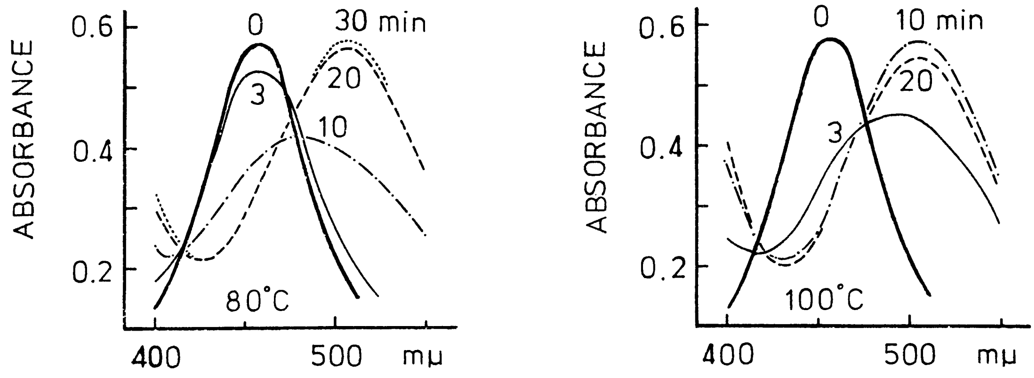

Fig. 1. Changes in the d-d absorption spectra accompanying the decomposition of [Cr en_3]$^{3+}$ to [Cr(male)en_2]$^+$ in DMF.

Footnotes and References

1) For preceding paper of this series, see H. Yoneda, M. Muto and K. Tamaki, Bull. Chem. Soc. Japan, 44, 2863 (1971).

2) Some parts of this study were presented at the 20th Symposium of Coordination Chemistry, Tokyo Toshi Center, October, 1970 and the 26th Anual Meeting of The Chemical Society of Japan, Kansai University, April, 1972.

3) P. Pfeiffer, P. Koch, G. Lando and A. Trieschmann, Ber. Chem. Dtsch. Ges., 37, 4255 (1904).

4) C. H. Stembridge and W. W. Wendlandt, J. Inorg. Nucl. Chem., 27, 569 (1965); idem., ibid., 27, 575 (1965); W. W. Wendlandt and L. K. Sveum, ibid., 28, 293, (1966).

5) ox^{2-}; oxalate, mal^{2-}; malonate, $male^{2-}$; maleate, $succ^{2-}$; succinate, pas^{2-}; p-aminosalicylate, $anth^-$; anthranilate, gly^- ; glycinate, ala^-; alaninate.

6) In any case, a pure complex was obtained from the eluate which was passed through a column containing cation exchange resin (Dowex 50 X8) in hydrogen form. The eluent was 0.5 - 1.0 N aqueous solution of lithim salt (LiCl or LiBr).

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