

Recent Advances in the Synthesis of Amine Complexes of Chromium(III)

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SUBSTITUTION reactions of amine complexes of chromium(III)* have not been as extensively studied as those of cobalt(III) because of the greater difficulty in the synthesis of the former than the latter complexes. Garner and House¹ reviewed the work done on amine complexes of chromium(III) published up to June, 1969, and they divided the syntheses into eight general methods. Tsuchiya² also reviewed the syntheses of chromium(III) complexes with multidentate ligands, published up to early 1970. During the past six years, many new amine complexes of chromium(III) have been prepared; and many of the methods used were new since 1969. In this review the work done during the past six years will be divided into twelve general methods.

1. *Reactions of anhydrous chromium(III) chloride.* This insoluble salt is infrequently used as the starting material. The only preparations using CrCl_3 in the past six years were by Michelsen³ who obtained α -*cis*- $[\text{CrCl}_2(\text{pcn})_2]\text{Cl}$ by reacting 2-aminomethylpyridine with a suspension of CrCl_3 in dmsO and by Chang⁴ who obtained *cis*- $[\text{CrCl}_2(\text{ophn})_2]\text{Cl}$ and *trans*- $[\text{CrCl}_2(\text{ophn})_2]\text{Cl}$ by refluxing different ratios of CrCl_3 and 1,2-diaminobenzene in 1-butanol.

2. *Reactions of hydrated chromium(III) salts.* Direct reaction of hydrated chromium(III) salts with amines is also infrequently used. Josephsen and Schäffer⁵ prepared di- μ -hydroxobis[bis(2,2'-bipyridine)-chromium(III)] perchlorate and di- μ -hydroxobis[bis(1,10-phenanthroline)chromium(III)] perchlorate by reacting $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with the amine in perchloric acid solution, adding LiOH solution during the reaction. They also prepared *cis*- $[\text{CrCl}_2(\text{phen})_2]\text{Cl}$ by reacting 1,10-phenanthroline hydrochloride hydrate with $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, adding LiOH during the reaction. Vaughn *et al.*⁶ prepared *trans*- $[\text{Cr}(\text{OAc})_2(\text{tmd})_2]\text{Cl}$ by

reacting $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ with glacial acetic acid and the amine, and Vaughn and Marzowski⁷ prepared $[\text{CrF}_2(\text{pn})_2][\text{CrF}_4(\text{pn})]$ by heating $\text{CrF}_3 \cdot 3.5\text{H}_2\text{O}$ with 1,2-propanediamine. Since the displacement of coordinated water molecules in these hydrated chromium(III) salts is difficult, methods have been developed whereby an indirect displacement is used (*vide infra*).

3. *Reactions of hexaacidochromium(III) complexes with amines.* Again this method received little attention. Kaizaki *et al.*⁸ obtained *cis*- and *trans*- $[\text{Cr}(\text{CN})_2(\text{en})_2]\text{ClO}_4$ by reacting $[\text{Cr}(\text{en})_3]\text{Cl}_3$ with NaCN and chromatographing the resulting solution on Dowex 50, eluting the desired complexes with lithium perchlorate, followed by vacuum rotatory evaporation. Khan⁹ prepared many mixed amine-chloro-thiourea complexes of chromium(III) by reacting $[\text{Cr}(\text{tu})_3]\text{Cl}_3$ with the amines in methanol. Botar *et al.*¹⁰ prepared *cis*- $[\text{Cr}(\text{NCSe})_2(\text{en})]$ and *cis*- $[\text{Cr}(\text{NCSe})_2(\text{en})_2]\text{Cl}$ by refluxing $\text{K}_2[\text{Cr}(\text{NCSe})_6]$ with 1,2-ethanediamine by acetonitrile, followed by chromatography on alumina and precipitation with CsCl.

4. *Reactions of $[\text{CrCl}_3(\text{thf})_3]$ with amines.* Although many complexes of the type $[\text{CrCl}_3\text{L}_3]$ (L = py, dmf, dmsO, and thf) have been used as the starting materials¹, this method has received scant attention in the last six years. Only Ferguson and Tobe¹¹ prepared *cis*- and *trans*- $[\text{CrCl}_2(\text{cyclam})]\text{Cl}$ by the reaction of $[\text{CrCl}_3(\text{thf})_3]$ with 1,4,8,11-tetraazacyclotetradecane in dmf.

5. *Preparations via dimethylsulfoxide or dimethylformamide complexes.* This method has received a great deal of attention during the past several years. In this method, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is first heated with either dmsO or dmf, in order to drive off the water, before the amine is added; therefore this method is the indirect

* Abbreviations used in this review are as follows: OAc = acetate; ala = alaninate; anth = anthranilate; bpy = 2,2'-bipyridine; bn = 2,3-butanediamine (butylenediamine); chn = *trans*-1,2-cyclohexanediamine; 3-Clpy = 3-chloropyridine; 3-Cp = 3-cyanopyridine; cyclam = 1,4,8,11-tetraazacyclotetradecane; dien = 3-azapentane-1,5-diamine (diethylenetriamine); dma = N,N'-dimethylacetamide; dmf = N,N'-dimethylformamide; dmsO = dimethylsulfoxide; dpt = 4-azapentane-1,7-diamine (dipropylenetriamine); en = 1,2-ethanediamine (ethylenediamine); gly = glycinate; ibn = 1,1-dimethylethane-1,2-diamine (*iso*-butylenediamine); mal = malonate; male = maleate; ophn = 1,2-diaminobenzene (*o*-phenylenediamine); ox = oxalate; pas = *p*-aminosalicylate; phen = 1,10-phenanthroline; pcn = 2-aminomethylpyridine (2-picolyamine); pic = 3-methylpyridine (3-picoline); pn = 1,2-propanediamine (propylenediamine); py = pyridine; succ = succinate; 2,3,2-tet = 3,7-diazanonane-1,9-diamine (1,4,8,11-tetraazaundecane); 3,2,3-tet = 4,7-diazadecane-1,10-diamine (1,5,8,12-tetraazadodecane); tetren = 3,6,9-triazaundecane-1,11-diamine (tetraethylenepentamine); tfac = trifluoroacetate; thf = tetrahydrofuran; tmd = 1,3-propanediamine (trimethylenediamine); tren = tris(2-aminoethyl)amine (triaminotriethylamine); trien = 3,6-diazaoctane-1,8-diamine (triethylenetetramine); tu = thiourea.

displacement of coordinated water molecules. Pedersen¹ prepared the dmsO complex by distilling water off a mixture of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and dimethylsulfoxide. After cooling to ca. 110°C , a viscous violet liquid was obtained; and this liquid was used in all the syntheses. The dmsO complex was not definitely identified, but the crystalline mass obtained by slow cooling is probably $\text{cis-}[\text{CrCl}_2(\text{dmsO})_2]\text{Cl} \cdot \text{dmsO}$. The following compounds were prepared by reacting different amines with the violet liquid: $[\text{Cr}(\text{en})_3]\text{Cl}_3$, $[\text{Cr}(\text{tmd})_3]\text{Cl}_3$, $[\text{Cr}(\text{chn})_3]\text{Cl}_3$, $\text{cis-}[\text{CrCl}_2(\text{en})_2]\text{Cl}$, $\text{cis-}[\text{CrCl}_2(\text{tmd})_2]\text{Cl}$, $\text{cis-}[\text{CrCl}(\text{dmsO})(\text{en})_2]\text{Cl}_2$, $\text{cis-}[\text{CrCl}(\text{dmsO})(\text{chn})_2]\text{Cl}_2$, and $\text{cis-}[\text{CrCl}_3(\text{chn})_2]\text{Cl}$. House¹⁹ used a similar method, but the mixture of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and dimethylsulfoxide was only boiled to expel most of the water before the amine was added. Using this method he prepared $\text{trans-}[\text{CrCl}_2(\text{tmd})_2]\text{ClO}_4$ ¹³, $\text{trans-}[\text{CrCl}_2(\text{en})(\text{tmd})]\text{ClO}_4$ ¹⁴, $[\text{CrCl}(\text{en})(\text{dien})][\text{ZnCl}_4]$, $[\text{CrCl}(\text{tmd})(\text{dien})][\text{ZnCl}_4]$, and $[\text{CrCl}(\text{pn})(\text{dien})][\text{ZnCl}_4]$ ¹⁵. McLean and Maes¹⁶ prepared $\text{cis-}[\text{CrCl}_2(\text{pn})_2]\text{Cl}$ by reacting 1, 2-propanediamine with the chloro-dmsO complex, and Madan¹⁷ used similar method to prepare $[\text{CrCl}_2(\text{tren})]\text{Cl}$.

The use of dimethylformamide is not as extensive as dimethylsulfoxide, but Madhusudhan and McLean¹⁸ used a method similar to that of Pedersen¹² to prepare $\text{cis-}[\text{CrCl}_2(\text{ibn})_2]\text{ClO}_4$, $\text{cis-}[\text{CrCl}_2(\text{meso-bn})_2]\text{ClO}_4$, and $\text{cis-}[\text{CrCl}_2(\text{dl-bn})_2]\text{ClO}_4$ by first heating $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ with dimethylformamide, followed by the addition of the amines.

6. *Substitution of aqua or acido complexes of chromium(III)*. This method seems to have received the widest applications. This type of reactions has been used not only for the displacement of water molecules or acido groups by amines, it has also been used for displacement of one acido group by another in order to prepare the tetramine complexes which have not been prepared before.

Fee *et al.*¹⁹ used this type of reactions extensively in the preparation of complexes of the type $[\text{CrXY}(\text{en})_3]^{n+}$ (X and Y = Cl^- , Br^- , I^- , ONO^- , NCS^- , and H_2O). $\text{trans-}[\text{CrBr}(\text{ONO})(\text{en})_2]\text{ClO}_4$ was prepared by reacting $\text{trans-}[\text{CrBr}_2(\text{en})_2]\text{Br}$, after aqutation of the latter in the dark, with NaNO_2 and NaClO_4 . $\text{trans-}[\text{CrCl}(\text{ONO})(\text{en})_2]\text{ClO}_4$ was similarly prepared, but chlorine was bubbled through the solution to displace bromide. $\text{cis-}[\text{CrCl}(\text{ONO})(\text{en})_2]\text{ClO}_4$ was prepared by reacting $\text{cis-}[\text{CrCl}(\text{H}_2\text{O})(\text{en})_2]\text{Br}_2$ with NaNO_2 and NaClO_4 . $\text{trans-}[\text{CrBr}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ and $\text{trans-}[\text{CrCl}(\text{H}_2\text{O})(\text{en})_2]^{2+}$ salts were prepared by reacting the nitrito complexes prepared above with HBr and HCl, respectively. $\text{trans-}[\text{CrBrCl}(\text{en})_2]^+$ salts were prepared by the anation of $\text{trans-}[\text{CrCl}(\text{H}_2\text{O})(\text{en})_2]\text{Br}_2$ with HBr, and $\text{trans-}[\text{CrBr}(\text{NCS})(\text{en})_2]\text{ClO}_4$ and $\text{trans-}[\text{CrCl}(\text{NCS})(\text{en})_2]\text{ClO}_4$ were prepared by the anation of trans-aquabromo and trans-aquachloro complexes, respectively, with NaSCN.

There were many other preparations using this method. Nagase and Tanaka²⁰ prepared $\text{trans-}[\text{CrCl}_2(\text{NH}_3)_4]\text{Cl}$ by reacting $[\text{CrCl}_3(\text{NH}_3)_3]$ with 28%

NH_4OH . Matts and Moore prepared $\text{trans-}[\text{Cr}(\text{ONO})_2(\text{NH}_3)_4]\text{ClO}_4$ by reacting $\text{trans-}[\text{Cr}(\text{H}_2\text{O})_3(\text{NH}_3)_4](\text{ClO}_4)_3$ with NaNO_2 ²¹, cis- and $\text{trans-}[\text{Cr}(\text{ONO})(\text{H}_2\text{O})(\text{NH}_3)_4]^{2+}$ salts by the aqutation of the dinitrito salts²², and $\text{cis-}[\text{Cr}(\text{NCS})(\text{ONO})(\text{en})_2]\text{ClO}_4$ and $\text{cis-}[\text{Cr}(\text{NCS})(\text{ONO})(\text{NH}_3)_4]\text{ClO}_4$ by reacting the aqua (isothiocyanato) complexes with NaNO_2 ²². Michelsen²³ prepared $\text{trans-}[\text{CrBr}_2(\text{pcn})_2]\text{Br}$ and $\text{trans-}[\text{CrCl}_2(\text{pcn})_2]\text{Cl}$ by reacting $\text{trans-}[\text{Cr}(\text{H}_2\text{O})_2(\text{pcn})_3](\text{NO}_3)_3$ with concentrated HBr and HCl, respectively. Linck *et al.*²⁴ prepared $\text{trans-}[\text{CrBrF}(\text{en})_2]\text{ClO}_4$ and $\text{trans-}[\text{CrClF}(\text{en})_2]\text{ClO}_4$ by reacting $\text{trans-}[\text{CrF}(\text{H}_2\text{O})(\text{en})_2](\text{ClO}_4)_3$ with NH_4Br and NH_4Cl , respectively, in methanol; $\text{trans-}[\text{CrF}_2(\text{NH}_3)_4]\text{ClO}_4$ by reacting $\text{trans-}[\text{CrCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$ with NH_4F in methanol, followed by precipitation with NaClO_4 ; and $\text{trans-}[\text{CrClF}(\text{NH}_3)_4]\text{ClO}_4$ by treating $\text{trans-}[\text{CrF}_2(\text{NH}_3)_4](\text{ClO}_4)_3$ with concentrated HClO_4 , followed by the reaction of the product with NH_4Cl in methanol. Botar *et al.*²⁵ prepared $\text{K}[\text{Cr}(\text{CN})(\text{NCS})_3(\text{en})]$ and $[\text{Cr}(\text{CN})(\text{NCS})(\text{en})_2]\text{SCN}$ by reacting $\text{K}_2[\text{Cr}(\text{CN})(\text{NCS})_5]$ with 1,2-ethanediamine in acetonitrile, followed by chromatography on alumina and precipitation with KSCN. Zipp and Madan¹⁷ prepared $[\text{CrCl}(\text{ClO}_4)(\text{tren})]\text{ClO}_4$, $[\text{CrCl}(\text{HSO}_4)(\text{tren})]\text{HSO}_4$, $[\text{Cr}(\text{ox})(\text{tren})]\text{ClO}_4$, $[\text{CrCl}(\text{NCS})(\text{tren})]\text{Cl}$, $[\text{CrBrCl}(\text{tren})]\text{Br}$, and $[\text{CrCl}(\text{SeCN})(\text{tren})]\text{SeCN}$ by reacting $[\text{CrCl}_2(\text{tren})]\text{Cl}$ with 70% HClO_4 , concentrated H_2SO_4 , $\text{Na}_2\text{C}_2\text{O}_4$, NaSCN, NaBr, and KSeCN, respectively; and $[\text{Cr}(\text{N}_3)_3(\text{tren})]\text{Br}$ by reacting $[\text{CrCl}_2(\text{tren})]\text{Cl}$ with excess NaN_3 , followed by precipitation with NaBr. Recently, Glerup and Schaffer²⁶ prepared $\text{trans-}[\text{CrBr}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Br}_2$, $\text{trans-}[\text{CrCl}(\text{H}_2\text{O})(\text{NH}_3)_4]\text{Cl}_2$, and $\text{trans-}[\text{CrF}(\text{H}_2\text{O})(\text{NH}_3)_4](\text{ClO}_4)_2$ by the aqutation of dibromo-, dichloro-, and difluoro-complexes in HBr, HCl, and HClO_4 , respectively. $\text{trans-}[\text{Cr}(\text{H}_2\text{O})_3(\text{NH}_3)_5](\text{ClO}_4)_3$ was obtained by the treatment of HClO_4 on $\text{trans-}[\text{Cr}(\text{OH})(\text{H}_2\text{O})(\text{NH}_3)_4](\text{ClO}_4)_3$ which was prepared by the aqutation of $\text{trans-}[\text{CrBr}_2(\text{NH}_3)_4]\text{Br}$ in HClO_4 , followed by the addition of pyridine. $\text{trans-}[\text{CrBrF}(\text{NH}_3)_4]\text{ClO}_4$ and $\text{trans-}[\text{CrClF}(\text{NH}_3)_4]\text{ClO}_4$ were obtained by reacting $\text{trans-}[\text{CrBr}_2(\text{NH}_3)_4]\text{NO}_3$ and $\text{trans-}[\text{CrCl}_2(\text{NH}_3)_4]\text{Cl}$, respectively, with HF at -70°C .

The use of fluoro complexes as the starting materials has become very important in the syntheses by this general method. Vaughn *et al.*²⁷ reacted $\text{cis-}[\text{CrF}_2(\text{en})_2]\text{I}$ with concentrated HBr and HCl to obtain $\text{cis-}[\text{CrBr}(\text{H}_2\text{O})(\text{en})_2]\text{Br}_2$ and $\text{cis-}[\text{CrCl}_2(\text{en})_2]\text{I}$, respectively. $\text{trans-}[\text{CrClF}(\text{en})_2]\text{ClO}_4$ was prepared by the reaction of $\text{trans-}[\text{CrF}(\text{H}_2\text{O})(\text{en})_2](\text{ClO}_4)_2$ with NH_4Cl in methanol²⁸. Michelsen²³ prepared $\alpha\text{-cis-}[\text{CrBr}_2(\text{pcn})_2]^-$ and $\alpha\text{-cis-}[\text{CrCl}_2(\text{pcn})_2]^+$ salts by reacting $\alpha\text{-cis-}[\text{CrF}_2(\text{pcn})_3]^+$ salts with concentrated HBr and HCl, respectively, at -16°C . Vaughn and Marzowski¹⁷ prepared $[\text{CrF}_2(\text{H}_2\text{O})_2(\text{pn})]$ I by reacting $[\text{CrF}_2(\text{pn})_2][\text{CrF}_4(\text{pn})]$ with HI; $\text{trans-}[\text{CrF}_2(\text{en})(\text{pn})]\text{Br}$ by refluxing $[\text{CrBrF}_2(\text{H}_2\text{O})(\text{pn})]$ with 1,2-ethanediamine in ethanol; cis- and $\text{trans-}[\text{CrF}_3(\text{pn})_2]\text{Br}$ by refluxing $[\text{CrBrF}_3(\text{H}_2\text{O})(\text{pn})]$ with 1,2-propanediamine in ethanol; $[\text{CrF}_3(\text{pn})(\text{tmd})]\text{Br}$ and $[\text{CrF}_3(\text{pn})(\text{chn})]\text{Br}$ by reacting $[\text{CrBrF}_2(\text{H}_2\text{O})(\text{pn})]$ with 1,3-propanediamine and $\text{trans-1,2-cyclohexanediamine}$, respectively; $\text{trans-}[\text{CrF}(\text{H}_2\text{O})(\text{en})(\text{pn})](\text{ClO}_4)_2$

and *trans*-[CrF(H₂O)(pn)(tmd)](ClO₄)₂ by reacting [CrF₂(en)(pn)]Br and [CrF₂(pn)(tmd)]Br, respectively, with 72% HClO₄; and [Cr(en)₂(pn)]Br₃ by reacting [CrBrF₂(H₂O)(pn)] with excess 1, 2-ethanediamine in ethanol. Zipp and Madan¹⁷ prepared [CrF(H₂O)(tren)](ClO₄)₃ and [CrF(NCS)(tren)]ClO₄ by reacting [CrF₂(tren)]ClO₄ with HClO₄ and NaSCN, respectively; [CrF(OAc)(tren)]ClO₄, [CrF(N₃)(tren)]ClO₄, [CrBrF(tren)]ClO₄, and [CrClF(tren)]ClO₄ by reacting [CrF(H₂O)(tren)](ClO₄)₃ with HOAc, NaN₃, NH₄Br, and NH₄Cl, respectively. Recently, Glerup and Schäffer²⁰ prepared *trans*-[CrBr₂(NH₃)₄]Br and *trans*-[CrCl₂(NH₃)₄]Cl by saturating solutions of *trans*-[CrF₂(NH₃)₄]ClO₄ with HBr and HCl gases, respectively.

Another general method of displacement of halide from a complex is by reacting the halo complex with silver salts. Fee *et al.*¹⁹ prepared *trans*-[Cr(ONO)(H₂O)(en)₂](ClO₄)₂ and *trans*-[Cr(OH)(ONO)(en)₂]ClO₄ from *trans*-[CrBr(ONO)(en)₂]ClO₄ and AgClO₄ in HClO₄; *trans*-[Cr(ONO)(dmf)(en)₂](ClO₄)₂ and *trans*-[Cr(ONO)(dmsO)(en)₂](ClO₄)₂ from *trans*-[CrBr(ONO)(en)₂]ClO₄ and AgClO₄ in dmf and dmsO, respectively; *cis*- and *trans*-[CrBr(dmf)(en)₂](ClO₄)₂ from *cis*- and *trans*-[CrBr₂(en)₂]ClO₄ and AgClO₄ in dmf; *trans*-[CrBr(dma)(en)₂](ClO₄)₂ from *trans*-[CrBr(en)₂]ClO₄ and AgClO₄ in dma; *trans*-[CrCl(dmsO)(en)₂](ClO₄)₂ and *trans*-[CrCl(dmf)(en)₂](ClO₄)₂ from *trans*-[CrCl(en)₂]ClO₄ and AgClO₄ in dmsO and dmf, respectively; *trans*-[Cr(dmf)₂(en)₂](ClO₄)₃, *trans*-[Cr(dma)₂(en)₂](ClO₄)₃, and *trans*-[Cr(dmsO)₂(en)₂](ClO₄)₃ from *trans*-[CrBr₂(en)₂]ClO₄ and AgClO₄ in dmf, dma, and dmsO, respectively; and *cis*-[Cr(dmf)₂(en)₂](ClO₄)₃ from *cis*-[CrBr₂(en)₂]ClO₄ or *cis*-[CrCl₂(en)₂]ClO₄ and AgClO₄ in dmf. Ferguson and Tobe¹¹ prepared *cis*-[Cr(NO₃)(H₂O)(cyclam)](NO₃)₂ by treating *cis*-[CrCl₂(cyclam)]Cl with AgNO₃, followed by precipitation with LiNO₃ in aceto e. Jordan *et al.*²⁹ prepared [Cr(tfac)(NH₃)₅](ClO₄)₂ by reacting [CrCl(NH₃)₅](ClO₄)₂ with silver trifluoroacetate in dmf. Michelsen prepared α -*cis*-[Cr(OH)(H₂O)(pcn)₂]Cl₂ by reacting α -*cis*-[CrCl₂(pcn)₂]Cl with silver oxide, followed by deprotonation of the resulting diaqua complex with pyridine⁹, and *trans*-[Cr(H₂O)₂(pcn)₂](NO₃)₃ by reacting α -*cis*-[CrCl₂(pcn)₂]Cl with Ag₂O, followed by acidifying the filtrate with concentrated HNO₃²³. Coronas and Casabo³⁰ also used Ag₂O to prepare [Cr(S₂O₈)(NH₃)₅]⁺ salts (S₂O₈²⁻ = dithionate) from [CrCl(NH₃)₅]Cl.

7. *Substitution reactions in non-aqueous solvents.* Some substitution reactions conducted in non-aqueous solvents are already listed above in the reaction of halo-complexes with silver salts. Jordan *et al.*²⁹ prepared [Cr(tfac)(NH₃)₅](ClO₄)₂ by adding a slight excess of trifluoroacetic anhydride to a solution of [Cr(H₂O)(NH₃)₅](ClO₄)₃ in dmf in the presence of excess N, N-dimethylbenzylamine. [Cr(male)(NH₃)₅](ClO₄)₂ was similarly prepared²¹. Chang *et al.*³² prepared 2-, 3-, and 4-cyanopyridine complexes of chromium(III) in butanol solutions. Muto³³ prepared bis(1, 2-ethanediamine) complexes by heating [Cr(en)₃](ClO₄)₃

with equivalent amount of NH₄X or H₂L in dmsO and tetraammine complexes by reacting [Cr(NH₃)₆](ClO₄)₃ with H₂L in dmf (X = NCS⁻, F⁻, Cl⁻, Br⁻, and I⁻; L = ox²⁻, mal²⁻, male²⁻, succ²⁻, pas²⁻, anth⁻, gly⁻, and ala⁻).

8. *Preparation via pyridine complexes.* Schäffer *et al.*³⁴ prepared many bis(diamine) complexes by the substitution of pyridine by the diamines from *trans*-[CrF₂(py)₄]ClO₄. The method generally involved refluxing the diamines with *trans*-[CrF₂(py)₄]ClO₄ in 2-methoxyethanol whereby the products precipitated. Using this general method, they prepared *trans*-[CrF₂(en)₂]ClO₄, *trans*-[CrF₂(tmd)₂]ClO₄, *trans*-[CrF₂(pn)₂]ClO₄, *trans*-[CrF₂(chn)₂]ClO₄, *cis*-[CrF₂(tren)]ClO₄, *cis*-[CrF₂(trien)]ClO₄, *trans*-[CrF₂(2, 3, 2-tet)]ClO₄, *trans*-[CrF₂(3, 2, 3-tet)]ClO₄, *cis*-[CrF₂(bipy)₂]ClO₄, and *cis*-[CrF₂(phen)₂]ClO₄. A series of tetrakis(monoamine) chromium(III) complexes were also prepared by heating *trans*-[CrF₂(py)₄]I with the amines in an autoclave. The complexes prepared are *trans*-[CrF₂(MeNH₂)₄]I, *trans*-[CrF₂(EtNH₂)₄]I, *trans*-[CrF₂(PrNH₂)₄]I, and *trans*-[CrF₂(C₃H₇NH₂)₄]I, (C₃H₇NH₂ = allylamine). Glerup and Schäffer²⁰ also prepared *trans*-[CrF₂(NH₃)₄]I₃ by reacting *trans*-[CrF₂(py)₄]I with liquid ammonia in an autoclave at 100°C. Using *trans*-[CrBr₂(py)]I, Michelsen³⁵ prepared α -[Cr(pcn)₃]I₃ by reacting the pyridine complex with 2-aminomethylpyridine in a mixture of 2-methoxyethanol and ethanol. β -[Cr(pcn)₃]Br₃ was prepared by reacting *trans*-[CrBr₂(py)₄]Cl with 2-aminomethylpyridine in a mixture of pyridine and ethanol. Michelsen³⁵ also prepared α -*cis*-[CrF₂(pcn)₂]⁺ salts by reacting *trans*-[CrF₂(py)₄]⁺ salts with 2-aminomethylpyridine in 2-methoxyethanol.

9. *Preparation using liquid ammonia.* Chromium(III) complexes of the *trans*-tetraammine series have not been successfully prepared until Glerup and Schäffer recently²⁶ prepared *trans*-[CrF₂(NH₃)₄]I by reacting *trans*-[CrF₂(py)]I with liquid ammonia in a steel autoclave at 100°C. Using *trans*-[CrF₂(NH₃)₄]I as the starting material, they prepared many complexes of this series (*vide supra*). Previously, Kirk and Kelly³⁶ have prepared *trans*-[Cr(NCS)(NH₃)(en)₂](SCN)₃ by reacting *trans*-[CrBr(NCS)(en)₂]SCN with slightly acidic anhydrous ammonia. Wong and Kirk³⁷ prepared *cis*- and *trans*-[CrF(NH₃)(en)₂](ClO₄)₂ by reacting *trans*-[CrBrF(en)₂]ClO₄ with liquid ammonia in a sealed Carius tube. They also prepared *trans*-[Cr(H₂O)(NH₃)(en)₂]Br₃ by reacting *trans*- μ -hydroxobis[chlorobis(1, 2-ethanediamine)chromium(III)] perchlorate with liquid ammonia, containing a trace of LiNH₂, followed by precipitation with concentrated HCl.

10. *Preparation by solid-state thermal decomposition or dehydration.* This method is not widely used because the products of thermal decomposition are often mixtures which are sometimes difficult to separate. Fee *et al.*¹⁹ used this method to prepare *trans*-[CrBr(NO₃)(en)₂]⁺ and *trans*-[CrCl(NO₃)(en)₂]⁺ salts from *trans*-[CrBr(H₂O)(en)₂](NO₃)₃ and *trans*-[CrCl(H₂O)(en)₂](NO₃)₃, respectively; *trans*-[CrBrI

(en)₂⁺ and *trans*-[CrCl(en)₂]⁺ salts from *trans*-[CrBr(H₂O)(en)₂]₂I₂ and *trans*-[CrCl(H₂O)(en)₂]₂I₂, respectively; and *cis*-[CrBrCl(en)₂]⁺ salts from *cis*-[CrCl(H₂O)(en)₂]₂Br₂. McLean and Gorman³⁶ prepared *trans*-[CrBr₂(pn)₂]Br by the thermal decomposition of [Cr(pn)₃]Br₃, and Wong and Kirk³⁷ obtained *trans*-[CrCl(NH₃)(en)₂]Br₂ by the thermal dehydration of *trans*-[Cr(H₂O)(NH₃)₂(en)₂]Cl₃, followed by precipitation with acetone from HBr solution.

11. *Preparation via reduction of peroxo complexes.* Garner, House, and coworkers prepared a large number of amine complexes of chromium(III) by the reduction of diperoxo chromium(IV) amines with acids¹. Recently, Orhanovic and coworkers^{39,40} used a similar method to prepare [Cr(H₂O)₅(pic)]³⁺, [Cr(H₂O)₅(3-Cp)]³⁺, and [Cr(H₂O)₅(3-Cly)]³⁺ salts by first reacting chromium(VI) oxide with the amine and 30% H₂O₂, followed by reduction of the peroxo complexes with iron(II) perchlorate in perchloric acid and cation-exchange chromatography on Dowex 50.

12. *Preparations using chromium(II) compounds.* This method is still not much used since the review of Garner and House¹, probably for the reason stated therein. Michelsen⁸ prepared *β-cis*-[CrBr₂(pcn)₂]I and *β-cis*-[CrCl₂(pcn)₂]I by reacting CrBr₂ and CrCl₂, respectively, with 2-aminomethylpyridine, adding slowly a solution of iodine in pyridine. Weschler and Deutsch⁴¹ prepared [Cr(en)₂(SCH₂CH₂NH₂)₂]²⁺ and [Cr(en)(SCH₂CH₂NH₂)₂]⁺ salts by reacting Cr(II) perchlorate with solutions of 1, 2-ethanediamine and 2-aminoethanethiol dihydrochloride, followed by cation-exchange on Dowex 50 or fractional crystallization of the perchlorate salts. In both preparations above, the Cr(II) compounds were used *in situ*. Soignet and Hargis⁴² prepared Cr(II) acetate under argon atmosphere in a specially constructed apparatus and used the Cr(OAc)₂ to react with 2, 2'-bipyridine under inert atmosphere to prepare [Cr(bipy)₂](ClO₄)₂. Banerjee, Roy, and Sarkar⁴³ prepared [Cr(phen)₃](NO₃)₃ by refluxing Cr(III) nitrate and 1, 10-phenanthroline in the presence of a trace of zinc dust. This method probably involved a Cr(II) intermediate.

In this review, the synthesis of amine complexes of chromium(III) is classified into twelve general methods. It can be seen that a large variety of new complexes have been prepared during the past six years, making it possible to study substitution reactions of the amine complexes of chromium(III), especially those of the tetramine type.

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