

Short Communication

Preparation and Characterization of Facial Triammine Complexes of Chromium(III)

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Recently a new synthetic route to triammine complexes of Cr(III) was published.¹ The method was based on the successive substitution of the pyridine and fluoride ligands in the complex *mer*-[Cr(py)₃(F)₃] with NH₃ and acido ligands, respectively in almost quantitative yields. Among the synthesized complexes were *fac*-[Cr(NH₃)₃(O₃SCF₃)₃] and *fac*-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃. Further studies have shown that these two complexes were versatile starting materials for the preparation of additional triammine complexes of Cr(III). The syntheses and characterization of a series of novel *fac*-[Cr(NH₃)₃(X)₃] complexes (X = uncharged ligand or acid ligand) are reported here, and the synthetic procedures are outlined in Scheme 1.

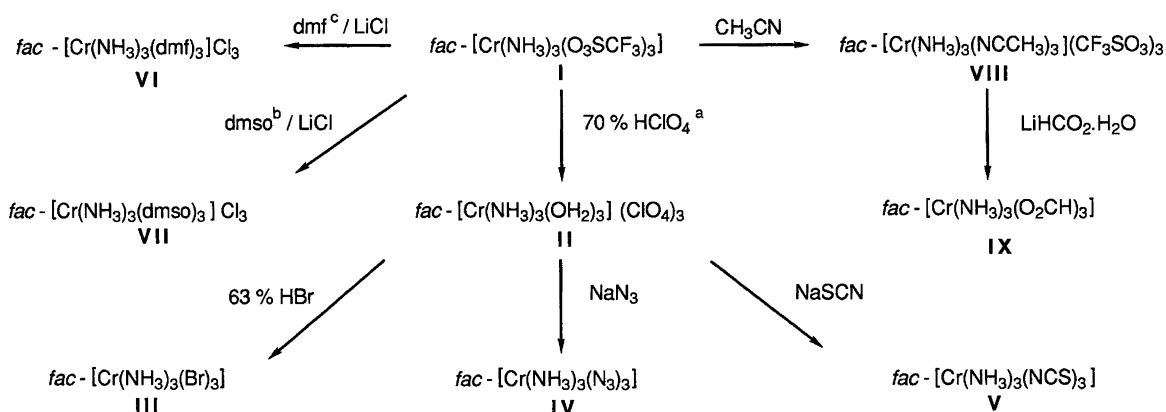
Experimental

Chemicals and chemical analyses. The complexes *fac*-[Cr(NH₃)₃(O₃SCF₃)₃] (I) and *fac*-[Cr(NH₃)₃(OH₂)₃](ClO₄)₃ (II) were prepared by use of literature proce-

dures.¹ The chemicals used were of reagent grade or of a similar or better quality. The synthesized compounds were analyzed on a microscale for C, H, N, Cl, Br and Cr in the microanalytical laboratory at the H. C. Ørsted Institute, University of Copenhagen.

Apparatus. Optical absorption spectra were measured on a Perkin-Elmer Lambda 17 spectrophotometer. The absorption maxima are given for the synthesized complexes (λ/nm, ε/M⁻¹ s⁻¹). Owing to slow solvolysis in some cases, the spectra were recorded within 1 min from dissolution of the complex. The ESR spectra were obtained as previously described¹ with a Bruker ESP 300 instrument on frozen solutions (*N*-methylformamide or 1:1 water/glycerol glass at ca. -190°C) unless otherwise stated.

Warning. *fac*-[Cr(NH₃)₃(N₃)₃] is a potential hazard. It should be prepared only in small quantities and protected from heat and shock. HN₃ is toxic by inhalation, and a well ventilated fume hood should be used.



Scheme 1. The synthetic procedures in the preparations of *fac*-[Cr(NH₃)₃(X)₃] complexes. ^aPrescription given in Ref. 1. ^bdmso = dimethyl sulfoxide. ^cdmf = *N,N*-dimethylformamide.

Preparations

fac- $[Cr(NH_3)_3(Br)_3]$ (**III**). 2.0 g of **II** (4.4 mmol) were added to 5 ml of 63% HBr. The slurry was stirred for two days, at which time a green precipitate formed. The solid was filtered off, washed with water, ethanol and diethyl ether, and air-dried. Yield: 1.3 g of **III** (86%). The total insolubility of the product in any solvent precluded the recording of an optical absorption spectrum. Found: Cr 15.21; H 2.57; N 12.02; Br 69.35. Calc. for $[Cr(NH_3)_3(Br)_3]$: Cr 15.17; H 2.65; N 12.26; Br 69.93.

fac- $[Cr(NH_3)_3(N_3)_3]$ (**IV**). 6.0 g of **II** (13 mmol) and 27 g of NaN_3 (415 mmol) were dissolved in 60 ml of water. Then 18 ml of 70% $HClO_4$ (210 mmol) were added in small portions, and the solution was stirred for 4 h, at which time black-violet crystals began to form. The crystals were filtered off, washed with water, ethanol and diethyl ether, and air-dried. Yield: 1.5 g of **IV** (50%). (λ , ϵ)_{max} (in dmsO): (564, 183), (426, 160). Found: Cr 22.33; H 3.76; N 73.09. Calc. for $[Cr(NH_3)_3(N_3)_3]$: Cr 22.69; H 3.96; N 73.35.

fac- $[Cr(NH_3)_3(NCS)_3]$ (**V**). 2.0 g of **II** (4.4 mmol) were dissolved in 5 ml of a saturated solution of NaSCN in water. The solution was stirred overnight, at which time a red precipitate formed. The solid was filtered off, washed with water, ethanol and diethyl ether, and air-dried. Yield: 1.0 g of **V** (82%). For recrystallization the product was dissolved in a minimum volume of acetone and reprecipitated by addition of diethyl ether. (λ , ϵ)_{max} (in dmsO): (509, 119), (384, 66.6). Found: Cr 18.30; C 12.67; H 3.10; N 29.85. Calc. for $[Cr(NH_3)_3(NCS)_3]$: Cr 18.75; C 12.99; H 3.27; N 30.30.

fac- $[Cr(NH_3)_3(dmf)_3]Cl_3$ (**VI**). 3.0 g of **I** (5.5 mmol) were dissolved in 4 ml of dmf, and the solution was stirred for 2 h, at which time the color changed from violet to red. Then 2 ml of a saturated solution of LiCl in methanol were added in small portions under stirring, and the resulting red-violet solid was filtered off, washed with acetone and diethyl ether, and air-dried. Yield: 1.5 g of **VI** (64%). (λ , ϵ)_{max} (in 1.0 M $NaClO_4$): (517, 73.0), (383, 46.5). Found: Cr 11.94; C 25.02; H 6.89; N 19.75; Cl 24.59. Calc. for $[Cr(NH_3)_3(HC(O)N(CH_3)_2)_3]Cl_3$: Cr 12.13, C 25.21; H 7.05; N 19.60; Cl 24.81.

fac- $[Cr(NH_3)_3(dmsO)_3]Cl_3$ (**VII**). The procedure from the preparation of **VI** was followed. The amounts were 3.0 g of **I**, 9 ml of dmsO and 3 ml of LiCl solution. Yield: 2.3 g (94%) of pinkish **VII**. (λ , ϵ)_{max} (in 1.0 M $NaClO_4$): (537, 68.3), (393, 36.3). Found: Cr 11.91; C 15.98; H 6.33; N 9.61; Cl 23.59. Calc. for $[Cr(NH_3)_3(OS(CH_3)_2)_3]Cl_3$: Cr 11.72; C 16.24; H 6.13; N 9.47; Cl 23.96.

fac- $[Cr(NH_3)_3(NCCH_3)_3](CF_3SO_3)_3$ (**VIII**). 3.0 g of **I** (5.5 mmol) were suspended with 4 ml of CH_3CN for 1 day, at which time an orange-yellow precipitate formed.

The solid was filtered off, washed with diethyl ether, and air-dried. Yield: 2.0 g of **VIII** (54%). For recrystallization the product was dissolved in a minimum volume of dry CH_3CN preheated to 40–50°C. The solution was filtered and the product reprecipitated by addition of diethyl ether. (λ , ϵ)_{max} (in dry CH_3CN): (482, 48.2), (360, 49.2). Found: Cr 7.58; C 15.81; H 2.51; N 12.19. Calc. for $[Cr(NH_3)_3(NCCH_3)_3](CF_3SO_3)_3$: Cr 7.72; C 16.05; H 2.69; N 12.48.

fac- $[Cr(NH_3)_3(O_2CH)_3]$ (**IX**). 1.0 g of **VIII** (1.5 mmol) and 0.7 g of $LiHCO_2 \cdot H_2O$ (10 mmol) were stirred in 4 ml of ethanol for 1 h. The resulting red-violet precipitate was filtered off, washed with ethanol and diethyl ether, and air-dried. Yield: 0.25 g of **IX** (70%). (λ , ϵ)_{max} (in 1.0 M $NaClO_4$): (521, 77.3), (386, 34.0). Found: Cr 21.78; C 15.19; H 5.24; N 16.99. Calc. for $[Cr(NH_3)_3(O_2CH)_3]$: Cr 21.83; C 15.13; H 5.08; N 17.65.

Results and discussion

Configurational assignment. It has previously been shown¹ that ESR spectroscopy unambiguously assigns the configuration of the $[Cr(NH_3)_3(X)_3]$ complexes. The ESR spectra of the facial isomers are characterized by a relatively narrow transition at a field corresponding to $g = 2$ as the main feature, almost identical to the ESR spectra of the cations $[Cr(NH_3)_6]^{3+}$ and $[Cr(OH_2)_6]^{3+}$. This is in contrast to the ESR spectra of the meridional isomers, which are more complicated and display several bands. The ESR spectra of frozen solutions of **IV–IX** and of **III** in the solid state at $-190^\circ C$ show the configuration to be facial.

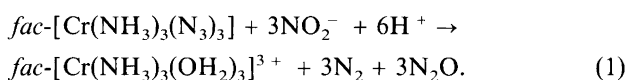
Syntheses. The poor coordinating ability of the $CF_3SO_3^-$ (triflate) ligand has led to the use of triflate complexes as synthetic intermediates as demonstrated by Dixon *et al.*² The very labile triflate complexes readily undergo solvolysis in coordinating solvents, which is illustrated in the syntheses of **VI–VIII**. For $X = dmf$ and dmsO the complexes $[Cr(NH_3)_3(X)]^{3+}$ and *cis*- and *trans*- $[Cr(NH_3)_4(X)_2]^{3+}$ have been prepared,^{3–7} and the X ligands were shown to be O-bonded. Based on the optical absorption spectra (see later) the same is concluded for **VI** and **VII**. Complex **II** also proved to be a useful starting material, as illustrated in the syntheses of **III–V**. To prevent the loss of the ammonia ligands that takes place in basic aqueous solution, acid was added in the case of the basic N_3^- anion, and in the case of the basic HCO_2^- anion ethanol was used as solvent with **VIII** as the starting material. From the absorption spectrum of **V** it was concluded that the thiocyanate ligand is N-bonded. S-Bonded thiocyanate has been found to be close to Br^- in the spectrochemical series,⁸ and the S-bonded isomer of **V** would therefore be green (as **III**). Heating $[Cr(NH_3)_5(NCS)](SCN)_2$ in the solid state has been reported⁹ to give $[Cr(NH_3)_3(NCS)_3]$. An ESR spectrum of

Table 1. Optical absorption maxima of $[\text{Cr}(\text{X})_6]$ and $\text{fac-}[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$ complexes.^a

X	$[\text{Cr}(\text{X})_6]$		$\text{fac-}[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$	
	$\nu_{1(\text{obs})}/10^3 \text{ cm}^{-1}$	Ref.	$\nu_{1(\text{obs})}/10^3 \text{ cm}^{-1}$	$\nu_{1(\text{calc})}/10^3 \text{ cm}^{-1}$ ^b
NH_3	21.65	14		
NCCH_3	^c		20.75	^c
NCS^-	17.73	15	19.65	19.69
OH_2	17.42	16	19.49 ^d	19.54
O_2CH^-	17.15	17	19.19	19.40
dmf	16.92	18	19.34	19.29
dmsO	15.77	19	18.62	18.71
O_3SCF_3^-	^c		18.35 ^d	^c
N_3^-	15.00	20	17.73	18.33
F^-	14.95	21	17.99 ^d	18.30

^a Charge omitted. ^b Eqn. (2). ^c $[\text{Cr}(\text{X})_6]$ not known. ^d Ref. 1.

the product prepared by that procedure showed the configuration to be meridional. An interesting reaction is the stereoretentive nitrosation of **IV**. Reaction with nitrite in acidic solution [eqn. (1)] yielded the cation of **II** as shown by an absorption spectrum of the resulting solution. A



similar reaction of the complex $[\text{Co}(\text{NH}_3)_5(\text{N}_3)]^{2+}$ has been described by Haim and Taube.¹⁰ The complex **IV** has previously been reported¹¹ as a green compound (insoluble in any solvent) obtained by boiling an aqueous solution of NaN_3 and $[\text{Cr}(\text{NH}_3)_6](\text{ClO}_4)_3$. The product is more likely to be a mixture of several compounds and/or a polymeric product.

Optical absorption spectra. In a d^3 -complex with O_h symmetry the energy (ν_1) of the first spin-allowed ligand field transition (${}^4\text{A}_{2g} \rightarrow {}^4\text{T}_{2g}$) is equal to the ligand field splitting parameter Δ_o , the one-electron energy difference between the t_{2g} and e_g orbitals.¹² In the complexes $\text{fac-}[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$, having holohedrized symmetry O_h , the value for ν_1 should therefore be close to the average ligand field splitting [eqn. (2)], in accordance with the principle of transferability of ligand field parameters.¹³

$$\nu_1[\text{Cr}(\text{NH}_3)_3(\text{X})_3]_{\text{calc}} = \{\nu_1[\text{Cr}(\text{NH}_3)_6]_{\text{obs}} + \nu_1[\text{Cr}(\text{X})_6]_{\text{obs}}\}/2 \quad (2)$$

Literature values of ν_1 in $[\text{Cr}(\text{X})_6]$ complexes are collected in Table 1, along with calculated and observed values of ν_1 in the $\text{fac-}[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$ complexes. The good agreement between observed and calculated values is another piece of evidence for the facial configuration and for O -bonded dmsO and dmf. A slight tendency for better agreement if X is an uncharged ligand is, however, noted. Effects resulting from change in the overall charge of the complex are absent in these cases. With negatively charged ligands the π -donation from the X ligands is expected to increase going from $[\text{Cr}(\text{X})_6]^{3-}$ to $[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$ owing to the less negative charge on the

metal center. This should result in a decrease in $\nu_{1(\text{obs})}$ compared to $\nu_{1(\text{calc})}$, and this is in agreement with the observed deviation. Furthermore, in the F^- case it is well known²² that absorption spectra of fluoro complexes of Cr(III) are solvent-dependent because of hydrogen-bond formation between solvent and coordinated fluoride, thereby influencing the σ -donor and/or π -donor properties of the fluoro ligand. In the N_3^- case solvent dependence of the Cr–N–N angle could for the same reason explain the deviation. By use of eqn. (2) the ligand field parameters Δ_o for the hypothetical complexes $[\text{Cr}(\text{O}_3\text{SCF}_3)_6]^{3-}$ and $[\text{Cr}(\text{NCCH}_3)_6]^{3+}$ can then be estimated to be 15.1×10^3 and $19.9 \times 10^3 \text{ cm}^{-1}$, respectively. Comparing these with the values in Table 1 it is noted that the CF_3SO_3^- ligand is close to the N_3^- ligand in the spectrochemical series, thereby placing it lowest among O -donor ligands.

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