

Crystal Structures and Nitrosation Reactions of Triamminetriazido Complexes of Chromium(III)

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The reaction between the meridional or the facial isomer of $[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ and NOBF_4 in nitrile solution (RCN , $\text{R}=\text{CH}_3$, CH_3CH_2 or CH_2CH) was investigated. The products of these nitrosation reactions, $[\text{Cr}(\text{NH}_3)_3(\text{NCR})_3](\text{BF}_4)_3$, were isolated and characterized, and the reactions were found to occur stereoretentively. The complex $\text{mer}-[\text{Cr}(\text{NH}_3)_3(\text{NCCH}_3)_3]^{3+}$ was used as a precursor for other chromium(III) complexes such as $\text{mer}-[\text{Cr}(\text{NH}_3)_3(\text{dmf})_3]^{3+}$ ($\text{dmf}=\text{N,N}$ -dimethylformamide) and $\text{mer}-[\text{Cr}(\text{NH}_3)_3\text{Cl}_3]$. The ligand-field parameter Δ_0 in the chromium(III) complexes $[\text{Cr}(\text{NCR})_6]^{3+}$ was calculated to be 19.7×10^3 and $20.0 \times 10^3 \text{ cm}^{-1}$ for $\text{R}=\text{CH}_3\text{CH}_2$ and CH_2CH , respectively. The meridional and facial isomers of $[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ were characterized by single-crystal X-ray crystallography. The crystal structure of $\text{mer}-[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ is triclinic, space group $P\bar{1}$, with $a=7.661(2)$, $b=10.190(3)$, $c=5.807(2)$ Å, $\alpha=93.58(1)$, $\beta=101.37(2)$, $\gamma=81.3(2)^\circ$ with two formula units in the cell. The crystal structure of $\text{fac}-[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ is triclinic, space group $P\bar{1}$, with $a=7.515(1)$, $b=9.759(2)$, $c=6.5665(9)$ Å, $\alpha=96.444(9)$, $\beta=112.496(7)$, $\gamma=88.31(1)^\circ$ with two formula units in the cell.

Recently the preparation and characterization of a series of novel facial triammine complexes of chromium(III), $\text{fac}-[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$ was described¹ and among the complexes prepared was $\text{fac}-[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$. This compound was found to react with NO_2^- in acidic aqueous solution to give the complex $\text{fac}-[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3]^{3+}$, and we have since then studied this type of nitrosation reaction in a non-aqueous medium. Nitrosation in non-aqueous media can be achieved by use of the nitrosonium ion (NO^+) and in this regard the salt NOBF_4 proved useful as a NO^+ source. We report here a study of the nitrosation of the two geometrical isomers of $[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ in various nitriles. The products of the nitrosation, $[\text{Cr}(\text{NH}_3)_3(\text{NCR})_3](\text{BF}_4)_3$, were found to be useful as synthetic precursors for other $[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$ complexes due to the lability of nitrile complexes. As a part of the characterizations single-crystal structure determinations of the facial and meridional isomer of $[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ were carried out.

Experimental

Chemicals and chemical analyses. The complexes $\text{fac}-[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ and $\text{mer}-[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3](\text{ClO}_4)_3$ were prepared as previously described.^{1,2} NOBF_4 was

purchased from Aldrich. The chemicals used were of reagent grade or of a similar or better quality. The synthesized complexes were analyzed for C, Cl, Cr, H and N in the microanalytical laboratory at the H. C. Ørsted Institute, University of Copenhagen.

Warning. The complexes $\text{mer}-[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3](\text{ClO}_4)_3$ and $[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ are potential hazards. They should be prepared only in small quantities and protected from heat and shock. HN_3 is toxic by inhalation, and a well ventilated fume hood should be used.

Preparations.

$\text{mer}-[\text{Cr}(\text{NH}_3)_3(\text{N}_3)_3]$ (I). 6.0 g of $\text{mer}-[\text{Cr}(\text{NH}_3)_3(\text{OH}_2)_3](\text{ClO}_4)_3$ (13 mmol) and 27 g of NaN_3 (420 mmol) were dissolved in 60 ml of water. Then 18 ml of 70% HClO_4 were added (210 mmol). Crystals separated out after 4 h. These were washed with water, ethanol and diethyl ether. Yield 1.8 g (60%). $(\lambda, \epsilon)_{\text{max}}$ (in dmsO): (565, 170), (427, 154). Calc. for $\text{CrH}_9\text{N}_{12}$: Cr 22.69; H 3.76; N 73.09. Found: Cr 22.91; H 3.80; N 73.10.

$\text{mer}-[\text{Cr}(\text{NH}_3)_3(\text{NCCH}_3)_3](\text{BF}_4)_3$ (II). To a mixture of 0.9 g of NOBF_4 (7.70 mmol) and 2 ml of CH_3CN was added 0.58 g of I (2.53 mmol) in small portions with stirring and cooling. Drop-wise addition of diethyl ether into the solution yielded a yellow–orange precipitate which was filtered off, washed with ethanol and diethyl

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ether and dried *in vacuo*. Yield: 1.05 g (85%). (λ , ϵ)_{max} (in CH₃CN): (477, 33.9), (355, 34.3). Calc. for B₃C₆CrF₁₂H₁₈N₆: C 14.81; Cr 10.68; H 3.73; N 17.27. Found: C 14.62; Cr 10.47; H 3.88; N 17.18. IR (KBr, ν/cm^{-1}) 2307 (C \equiv N).

mer-[Cr(NH₃)₃(NCCH₂CH₃)₃](BF₄)₃ (III). Made as II using propionitrile and hexane instead of acetonitrile and diethyl ether. Yield 75% of a red–orange product. (λ , ϵ)_{max} (in CH₃CH₂CN): (483, 38.2), (355, 47.0). Calc. for B₃C₉CrF₁₂H₂₄N₆: C 20.44; Cr 9.83; H 4.57; N 15.89. Found: C 20.12; Cr 9.77; H 4.72; N 15.65. (KBr, ν/cm^{-1}) 2306 (C \equiv N).

mer-[Cr(NH₃)₃(NCCHCH₂)₃](BF₄)₃ (IV). Made as III using acrylonitrile instead of propionitrile. Yield 80% of a red–orange product. (λ , ϵ)_{max} (in CH₂CHCN): (480, 35.1), (353, 47.9). Anal. Calc. for B₃C₉CrF₁₂H₁₈N₆: C 20.68; Cr 9.95; H 3.47; N 16.08. Found: C 20.53; Cr 9.90; H 3.69; N 15.99. (KBr, ν/cm^{-1}) 2282 (C \equiv N).

mer-[Cr(NH₃)₃(dmf)₃](BF₄)₃ (V). 200 mg of II (0.41 mmol) was dissolved in 2 ml of *N,N*-dimethyl-

formamide (dmf). The solution was stirred for 2 h during which the color changed from orange to red–violet. Then 5 ml of diethyl ether was added. A red oil separated out and the mother liquor was decanted off. The oil was then redissolved in 3 ml acetone, and the product was reprecipitated as a pink powder after the addition of 5 ml diethyl ether. The product was washed with diethyl ether and air-dried. Yield 180 mg (75%). (λ , ϵ)_{max} (in 1.0 M NaClO₄): (522, 45.7), (385, 47.2). Calc. for B₃C₉CrF₁₂H₃₀N₆O₃: C 18.55; Cr 8.92; H 5.19; N 14.42. Found: C 17.72; Cr 8.86; H 4.90; N 14.21.

mer-[Cr(NH₃)₃Cl₃] (VI). 200 mg of II (0.41 mmol) was added to 4 ml of ethanol and 270 mg of LiCl. The mixture was stirred and heated on a water-bath for ca. 15 min during which a green precipitate of mer-[Cr(NH₃)₃Cl₃] formed. This was filtered off, washed with ethanol and acetone and finally air-dried. Yield 80 mg (93%). Calc. for Cl₃CrH₉N₃: Cl 50.55; Cr 24.83; H 4.22; N 20.06. Found: Cl 50.68; Cr 24.99; H 4.39; N 19.90.

Table 1. Crystallographic data for mer- and fac-[Cr(NH₃)₃(N₃)₃].

	Meridional	Facial
Chemical formula	H ₉ CrN ₁₂	H ₉ CrN ₁₂
FW/g mol ⁻¹	229.18	229.18
Space group	<i>P</i> 1	<i>P</i> $\bar{1}$
Cell parameters (298 K)		
<i>a</i> /Å	7.661(2)	7.515(1)
<i>b</i> /Å	10.190(3)	9.759(2)
<i>c</i> /Å	5.807(2)	6.5665(9)
α /°	93.58(1)	96.444(9)
β /°	101.37(2)	112.496(7)
γ /°	81.3(2)	88.31(1)
<i>V</i> /Å ³	439.5(2)	442.1(1)
No. of reflections centred	41	26
2 θ range/°	3.639–14.665	10.076–13.939
Calculated density (298 K)/g cm ⁻³	1.731	1.721
Formula units per cell	2	2
Crystal size/mm ³	0.625 × 0.425 × 0.275	0.900 × 0.325 × 0.013
Development forms	110, 100, 001	1–11, 11–1, 010
Radiation (Mo K α), λ /Å	0.71073	0.71073
Monochromator	Graphite	Graphite
Linear abs. coefficient, μ/cm^{-1}	0.1252	0.1245
Range of transmission factors	0.522–0.711	0.6652–0.8502
Scan type	$\theta/2\theta$	$\theta/2\theta$
ω -Scan width, $\Delta\theta$ /°	1.0 + 0.346 tan θ	1.2 + 0.346 tan θ
No. of steps/s	50	50
Time per step/s	1	1
θ -Limits/°	2.02–29.95	2.10–29.99
Octants collected	+ <i>h</i> + <i>k</i> ± <i>l</i>	+ <i>h</i> + <i>k</i> ± <i>l</i>
Standard reflections	222, 1–30	13–3, –13–1
Intensity decay	none	none
No. of unique data	2740	2589
No. of data with $I/\sigma(I) > 3$	2559	2073
No. of variables	233	154
Weights, $w^{-1} = [\sigma_{\text{cs}}(F^2) + 1.03F^2]^{1/2} - F $		
$R = \Sigma(F_o - F_c)/\Sigma F_o $	0.054	0.040
$R_w = (\Sigma w(F_o - F_c)^2/\Sigma w F_o ^2)^{1/2}$	0.067	0.051
<i>S</i>	4.11	1.371
$\Delta/\sigma_{\text{max}}$	0.071	0.106
$\Delta\rho_{\text{max}}/e \text{ \AA}^{-3}$	1.0(2)	1.0(1)

fac-[Cr(NH₃)₃(NCCH₃)₃](BF₄)₃ (VII). Made as II using *fac*-[Cr(NH₃)₃(N₃)₃] as the starting material. The absorption spectrum is identical to that of *fac*-[Cr(NH₃)₃(NCCH₃)₃](CF₃SO₃)₃.¹ Calc. for B₃C₆CrF₁₂H₁₈N₆: C 14.81; Cr 10.68; H 3.73; N 17.27. Found: C 14.50; Cr 10.67; H 3.55; N 17.08. IR (KBr, v/cm⁻¹) 2302 (C≡N).

fac-[Cr(NH₃)₃(NCCH₂CH₃)₃](BF₄)₃ (VIII). Made as III using *fac*-[Cr(NH₃)₃(N₃)₃] as the starting material. Yield 68% of an orange product. (λ, ε)_{max} (in CH₃CH₂CN): (484, 40.3), (357, 43.3). Calc. for B₃C₉CrF₁₂H₂₄N₆: C 20.44; Cr 9.83; H 4.57; N 15.89. Found: C 20.31; Cr 9.64; H 4.70; N 15.80. (KBr, v/cm⁻¹) 2280 (C≡N).

fac-[Cr(NH₃)₃(NCCHCH₂)₃](BF₄)₃ (IX). Made as IV using *fac*-[Cr(NH₃)₃(N₃)₃] as the starting material. Yield 77% of an orange product. (λ, ε)_{max} (in CH₂CHCN): (480, 38.4), (354, 45.6). Calc. for B₃C₉CrF₁₂H₁₈N₆: C 20.68; Cr 9.95; H 3.47; N 16.08. Found: C 20.52; Cr 9.81; H 3.63; N 15.82. (KBr, v/cm⁻¹) 2307 (C≡N).

X-Ray crystallography. The crystals that separated out in the syntheses of the two isomers of [Cr(NH₃)₃(N₃)₃] were suitable for a structure determination. The crystals were mounted on a Huber four-circle diffractometer. Cell dimensions were determined from reflexions measured at ±2θ. Intensities were measured at room temperature and two standard reflexions were monitored every 50 reflexions. Crystal data are given in Table 1. Data were corrected for dead-time, background, Lorentz and polarization effects and absorption. The structures were solved using SIR92³ and subsequent electron density maps. The meridional isomer has two molecules in the unit cell and

the space group is clearly *P1* with no hint of symmetry. Structures were refined by the least-squares minimization of Σw(|F_{obs}| - |F_{calc}|)² using a modification of ORLFS.⁴ All non-hydrogen atoms were refined with anisotropic displacement parameters. Some of the hydrogen atoms were determined from difference electron-density maps, and the rest of the hydrogen atoms were calculated.

Other physical measurements. Optical absorption spectra were recorded on a Perkin-Elmer Lambda 17 spectrophotometer. The absorption spectra are given for the synthesized compounds (λ/nm, ε/M⁻¹ cm⁻¹). IR spectra were recorded on a Perkin Elmer 1600 FTIR instrument.

Results and discussion

Description of the structures. The structures turned out to be *mer*- and *fac*-[Cr(NH₃)₃(N₃)₃] as expected; the molecular structure of the meridional isomer is shown in Fig. 1 and that of the facial isomer in Fig. 2.⁵ In both structures the Cr atoms are octahedrally coordinated to three azide and three ammonia ligands. The Cr-N-N angles fall in the range 119.5–131.7° and the azide N-N-N angles are all close to the ideal 180°. In the meridional isomer the Cr1-Cr2 distance is 5.95 Å and in the facial isomer the nearest Cr-Cr distance is 5.56 Å. None of the structures has hydrogen bonds. The fractional atomic coordinates and the equivalent isotropic displacement parameters are listed in Tables 2 and 3, and selected geometric parameters in Tables 4 and 5. An inspection of Table 4 shows only minor differences between the two molecules in the unit cell of *mer*-[Cr(NH₃)₃(N₃)₃] in the bond lengths and angles. It is also noted that the bond lengths Cr-N(ammonia) and

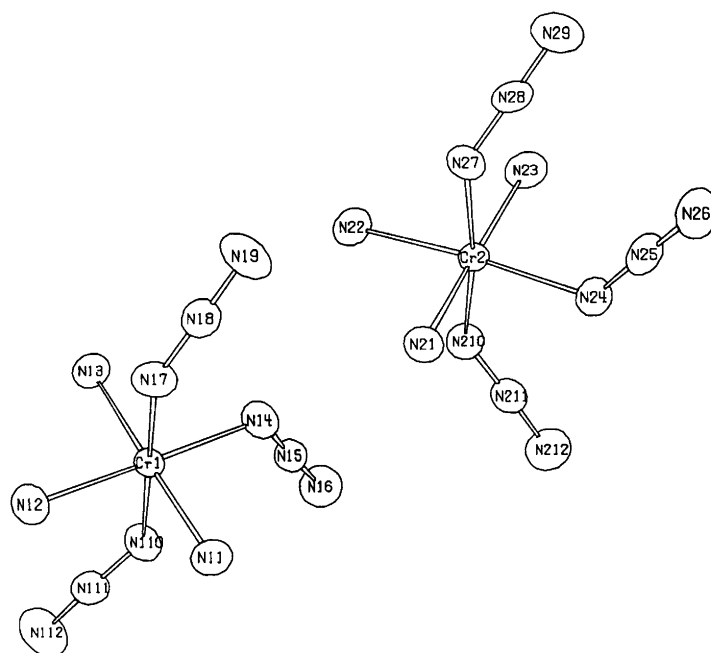
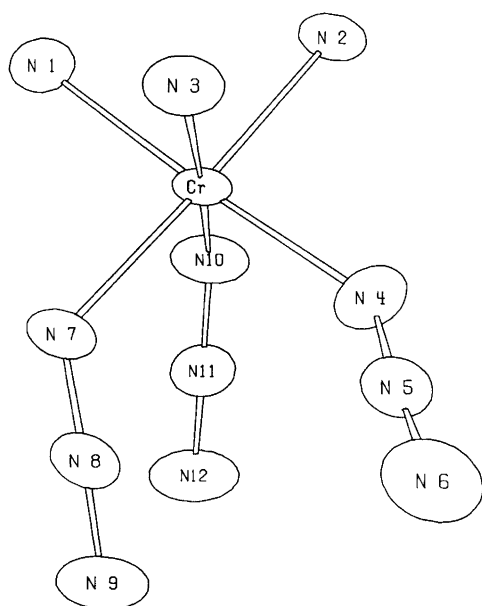


Fig. 1. ORTEP drawing of an asymmetric unit cell of *mer*-[Cr(NH₃)₃(N₃)₃].

Fig. 2. ORTEP drawing of *fac*-[Cr(NH₃)₃(N₃)₃].Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (in Å²) in *fac*-[Cr(NH₃)₃(N₃)₃].

	x	y	z	U_{eq}^a
Cr	1.013 89(4)	0.243 44(3)	0.770 30(5)	0.0258(2)
N1	1.1858(4)	0.0757(3)	0.8914(5)	0.043(1)
N2	1.2280(3)	0.3766(2)	0.9945(4)	0.037(1)
N3	1.1428(3)	0.2397(3)	0.5388(4)	0.041(1)
N4	0.8622(3)	0.4115(2)	0.6646(4)	0.047(1)
N5	0.7516(3)	0.4339(2)	0.4887(4)	0.042(1)
N6	0.6439(4)	0.4634(3)	0.3221(5)	0.078(2)
N7	0.8128(3)	0.1078(2)	0.5511(3)	0.047(1)
N8	0.6443(3)	0.1308(2)	0.4617(3)	0.038(1)
N9	0.4826(3)	0.1475(3)	0.3732(4)	0.056(1)
N10	0.9035(3)	0.2388(2)	1.0098(4)	0.045(1)
N11	0.7333(3)	0.2285(2)	0.9574(3)	0.038(1)
N12	0.5707(3)	0.2157(3)	0.9144(4)	0.061(1)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

Cr–N(azide) bond lengths are similar to those found in the complex *mer*-[Cr(py)₃(N₃)₃] (py = pyridine).⁷

It is noteworthy that an analogous cobalt(III) complex, [Co(NH₃)₃(N₃)₃], has been known for quite some time.⁸ No crystal structure has been reported, and the

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters (in Å²) in *mer*-[Cr(NH₃)₃(N₃)₃].

	x	y	z	U_{eq}^a
Cr1	0.2064	−0.1553	−0.0213	0.0230(6)
N11	0.012(1)	−0.0468(8)	−0.266(1)	0.034(3)
N12	0.119(1)	−0.3333(8)	−0.169(1)	0.038(4)
N13	0.407(1)	−0.2602(7)	0.219(1)	0.032(3)
N14	0.298(1)	0.0156(8)	0.122(1)	0.036(4)
N15	0.221(1)	0.0826(7)	0.258(1)	0.031(3)
N16	0.151(1)	0.1493(8)	0.388(1)	0.046(5)
N17	0.373(1)	−0.1744(11)	−0.254(2)	0.040(5)
N18	0.497(1)	−0.1153(8)	−0.257(1)	0.036(4)
N19	0.616(2)	−0.0629(11)	−0.271(2)	0.073(6)
N110	0.029(1)	−0.1392(9)	0.203(2)	0.031(4)
N111	−0.070(1)	−0.2123(9)	0.221(1)	0.035(4)
N112	−0.170(2)	−0.2820(13)	0.253(2)	0.070(7)
Cr2	0.6353(2)	0.3091(1)	0.0890(2)	0.0237(6)
N21	0.444(1)	0.2288(7)	−0.161(1)	0.034(4)
N22	0.712(1)	0.1241(8)	0.252(1)	0.040(4)
N23	0.834(1)	0.3948(8)	0.325(1)	0.037(4)
N24	0.544(1)	0.4878(7)	−0.053(1)	0.034(4)
N25	0.624(1)	0.5367(7)	−0.176(1)	0.032(4)
N26	0.699(1)	0.5884(10)	−0.289(2)	0.053(6)
N27	0.810(1)	0.2513(8)	−0.132(2)	0.032(4)
N28	0.942(1)	0.3053(8)	−0.126(1)	0.033(4)
N29	1.067(1)	0.3594(10)	−0.124(2)	0.051(4)
N210	0.465(1)	0.3386(10)	0.323(2)	0.033(5)
N211	0.349(1)	0.4285(7)	0.339(1)	0.032(3)
N212	0.233(1)	0.5113(9)	0.365(2)	0.052(5)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j.$$

Cr–N(azide) are not significantly affected by the nature of the ligand (NH₃ or N₃[−]) located in the *trans* position. The azido ligands are asymmetric, the longer N–N distance being between the nitrogen coordinated to the chromium atom and the central nitrogen atom. The Cr–N(ammonia) bond lengths are similar to those of other ammine complexes of chromium(III)⁶ and the

configurational assignment of this complex is still uncertain.^{9,10}

Configurational assignment. The configuration of **I** is determined from the crystal structure. From absorption spectra it was seen that hydrolysis of complexes **II–IX** in 1 M HClO₄ (Hg²⁺-assisted in the case of **VI**) resulted

Table 4. Selected distances (in Å) and angles (in °) in *mer*-[Cr(NH₃)₃(N₃)₃].

Cr1-N11	2.086(7)	Cr2-N21	2.067(8)
Cr1-N12	2.099(8)	Cr2-N22	2.116(8)
Cr1-N13	2.080(7)	Cr2-N23	2.092(8)
Cr1-N14	2.038(8)	Cr2-N24	2.019(7)
Cr1-N17	2.014(10)	Cr2-N27	2.034(9)
Cr1-N110	2.044(9)	Cr2-N210	2.041(10)
N14-N15	1.198(10)	N24-N25	1.197(10)
N15-N16	1.145(10)	N25-N26	1.145(11)
N17-N18	1.203(14)	N27-N28	1.214(12)
N18-N19	1.135(12)	N28-N29	1.166(12)
N111-N110	1.162(12)	N211-N210	1.195(13)
N111-N112	1.146(9)	N211-N212	1.158(9)
N11-Cr1-N12	90.6(3)	N21-Cr2-N22	90.5(3)
N11-Cr1-N13	178.1(4)	N21-Cr2-N23	176.5(3)
N11-Cr1-N14	90.3(3)	N21-Cr2-N24	88.5(3)
N11-Cr1-N17	88.9(4)	N21-Cr2-N27	86.6(3)
N11-Cr1-N110	89.5(3)	N21-Cr2-N210	91.5(4)
N12-Cr1-N13	90.6(3)	N22-Cr2-N23	91.7(3)
N12-Cr1-N14	178.6(4)	N22-Cr2-N24	175.2(4)
N12-Cr1-N17	87.1(4)	N22-Cr2-N27	89.3(3)
N12-Cr1-N110	90.9(3)	N22-Cr2-N210	82.5(4)
N13-Cr1-N14	88.5(3)	N23-Cr2-N24	89.5(3)
N13-Cr1-N17	89.7(4)	N23-Cr2-N27	90.7(3)
N13-Cr1-N110	92.0(3)	N23-Cr2-N210	91.5(4)
N14-Cr1-N17	91.9(4)	N24-Cr2-N27	95.3(3)
N14-Cr1-N110	90.2(3)	N24-Cr2-N210	92.8(4)
N17-Cr1-N110	177.4(5)	N27-Cr2-N210	171.6(4)
Cr1-N14-N15	120.1(6)	Cr2-N24-N25	122.2(6)
Cr1-N17-N18	128.6(8)	Cr2-N27-N28	121.7(7)
Cr1-N110-N111	127.9(7)	Cr2-N210-N211	129.0(7)
N14-N15-N16	178.2(9)	N24-N25-N26	177.2(9)
N17-N18-N19	176.3(11)	N27-N28-N29	178.3(10)
N110-N111-N112	175.8(11)	N210-N211-N212	176.6(9)

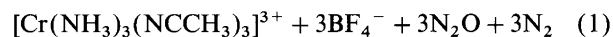
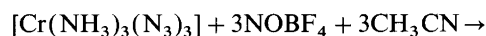
 Table 5. Selected distances (in Å) and angles (in °) in *fac*-[Cr(NH₃)₃(N₃)₃].

Cr-N1	2.089(2)	N4-N5	1.177(3)
Cr-N2	2.080(2)	N5-N6	1.147(3)
Cr-N3	2.089(2)	N7-N8	1.202(3)
Cr-N4	2.003(2)	N8-N9	1.145(3)
Cr-N7	2.034(2)	N10-N11	1.195(3)
Cr-N10	2.045(2)	N11-N12	1.152(3)
N1-Cr-N2	89.6(1)	N3-Cr-N10	175.9(1)
N1-Cr-N3	86.9(1)	N4-Cr-N7	94.8(1)
N1-Cr-N4	176.7(1)	N4-Cr-N10	91.2(1)
N1-Cr-N7	88.4(1)	N7-Cr-N10	93.3(1)
N1-Cr-N10	89.2(1)	Cr-N4-N5	131.7(2)
N2-Cr-N3	91.0(1)	Cr-N7-N8	125.4(2)
N2-Cr-N4	87.1(1)	Cr-N10-N11	119.5(2)
N2-Cr-N7	177.7(1)	N4-N5-N6	176.1(3)
N2-Cr-N10	87.7(9)	N7-N8-N9	177.3(3)
N3-Cr-N4	92.6(1)	N10-N11-N12	177.2(3)
N3-Cr-N7	87.9(1)		

in quantitative formation of the complex ion [Cr(NH₃)₃(OH₂)₃]³⁺, the meridional isomer in the cases of II–VI and facial isomer in the cases of VII–IX. It is noted that the nitrosation of the triamminetriaazido chromium(III) complexes occur stereoretentively.

Syntheses. Nitrosation of azide complexes was first described by Taube,¹¹ who showed that the complex

[Co(NH₃)₅(N₃)²⁺ reacted with NO₂⁻ in acidic aqueous solution yielding [Co(NH₃)₅(OH₂)³⁺. Further studies showed that nitrosation also occurred in various nitriles by use of salts of the nitrosonium ion, such as NOCF₃SO₃.^{12–14} The present work shows that nitrosation of [Cr(NH₃)₃(N₃)₃] with NOBF₄ in acetonitrile solution occur analogously as shown in eqn. (1).



Other nitriles such as propionitrile or acrylonitrile could be used as well. Traces of water in the nitrile solvent were conveniently removed by stirring the mixture of NOBF₄ and solvent for ca. 5 min before the addition of the triammine triazidochromium(III) complex.

The complex *fac*-[Cr(NH₃)₃(OSO₂CF₃)₃] has been used as a synthetic precursor for other *fac*-[Cr(NH₃)₃(X)₃] complexes, such as *fac*-[Cr(NH₃)₃(NCCH₃)₃](CF₃SO₃)₃.¹ The complex *mer*-[Cr(NH₃)₃(OSO₂CF₃)₃] is not readily available because of the isomerisation from meridional to facial ammine configuration in the treatment of *mer*-[Cr(NH₃)₃F₃] with CF₃SO₃H.² Complex II may instead serve as a useful starting material in the preparation of novel *mer*-[Cr(NH₃)₃(X)₃] complexes. The substitution of coordinated nitriles by other ligands (charged or uncharged) is

an important class of reactions, and nitrile complexes are widely used as precursors for other coordination- or organometallic compounds. The syntheses of V and VI are examples of such types of displacements. Complex V has previously been described as one of the products in the reaction of the highly explosive complex $[\text{Cr}(\text{NH}_3)_3(\text{O}_2)_2]$ with HCl.¹⁵ The preparation of the facial isomer of VI was published recently¹ but the meridional isomer has so far been unknown. Other examples of chromium(III) nitrile complexes were reported by Kern,¹⁶ who prepared the compounds $[\text{CrCl}_3(\text{NCR})_3]$ ($\text{R} = \text{CH}_3\text{CH}_2$ or CH_2CH). The configuration of these complexes were not determined.

Optical absorption spectra. The holohedrized symmetry of a *fac*- $[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$ type complex is O_h , and the first two spin-allowed transitions are therefore assigned as ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$. The holohedrized symmetry of the complex *mer*- $[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$ is D_{2h} , and the lower symmetry results in a splitting of each of the ${}^4T_{2g}$ and ${}^4T_{1g}$ states into B_{1g} , B_{2g} and B_{3g} . However, the splitting is so small that only a broadening of each of the two absorption bands and not a splitting into three distinct bands is observed on going from the facial to meridional isomer of a $[\text{Cr}(\text{NH}_3)_3(\text{X})_3]$ complex. From the energy of the first spin allowed transition in VIII and IX (20.66×10^3 and $20.83 \times 10^3 \text{ cm}^{-1}$) we can calculate¹ the magnitude of Δ_0 in the hypothetical complexes $[\text{Cr}(\text{NCCH}_2\text{CH}_3)_6]^{3+}$ and $[\text{Cr}(\text{NCCHCH}_2)_6]^{3+}$ to be 19.7×10^3 and $20.0 \times 10^3 \text{ cm}^{-1}$. These values are close to the value of Δ_0 in the complex $[\text{Cr}(\text{NCCH}_3)_6]^{3+}$ which was calculated¹ to be $19.9 \times 10^3 \text{ cm}^{-1}$, and we can con-

clude that the nature of the R group in RCN complexes of chromium(III), not unexpectedly, has little influence on the spectral properties of these complexes.

References

1. Døssing, A. *Acta Chem. Scand.* 48 (1994) 269.
2. Andersen, P., Døssing, A., Glerup, J. and Rude, M. *Acta Chem. Scand.* 44 (1990) 346.
3. Altomare, A., Cascarano, G., Guagliardi, A., Burla, M. C., Polidori, G. and Camalli, M. *J. Appl. Crystallogr.* 27 (1994) 435.
4. Busing, W. T., Martin, K. O. and Levy, H. A. *ORLFS, Report ORNL-TM-305*, Oak Ridge National Laboratory, Tennessee 1962.
5. Johnson, C. K. *ORTEP II, Report ORNL-5138*, Oak Ridge National Laboratory, Tennessee 1976.
6. House, D. A. *Comprehensive Coordination Chemistry*, Vol. 2. Pergamon Press, New York 1987, p. 26.
7. Goher, M. A. S., Aby-Youssef, M. A. M. and Mautner, F. *A. Z. Naturforsch., Teil B* 47 (1992) 139.
8. Linhard, M. and Weigel, M. *Z. Anorg. Allg. Chem.* 263 (1950) 250.
9. Au-Yeung, S. C. F. and Eaton, D. R. *Can. J. Chem.* 61 (1983) 2431.
10. Siebert, H. *Z. Anorg. Allg. Chem.* 389 (1972) 22.
11. Haim, A. and Taube, H. *Inorg. Chem.* 2 (1963) 1199.
12. Jordan, R. B., Sargeson, A. M. and Taube, H. *Inorg. Chem.* 5 (1966) 1091.
13. Butler, D. G., Creaser, I. I., Dyke, S. F. and Sargeson, A. M. *Acta Chem. Scand., Ser. A* 32 (1978) 789.
14. Creaser, I. I., Harrowfield, J. MacB., Keene, F. R. and Sargeson, A. M. *J. Am. Chem. Soc.* 103 (1981) 3559.
15. Schlessinger, G. G. *Inorganic Laboratory Preparations*, Chemical Publishing Company, New York, 1962.
16. Kern, R. J. *J. Inorg. Nucl. Chem.* 25 (1963) 5.

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