

**Table I.** Isotropic EPR Parameters for NSF<sub>2</sub>, FNSF, and Related Radicals<sup>a</sup>

Radical	<i>g</i>	Hyperfine interaction, MHz		Ref
		<i>a</i> ( <sup>14</sup> N)	<i>a</i> ( <sup>19</sup> F)	
NSF <sub>2</sub>	2.002 21 (1) <sup>b</sup>	14.69 (3)	246.95 <sup>c</sup> (3)	This work
FSO <sub>2</sub>	2.002 6		401	<i>d</i>
FPO <sub>2</sub> <sup>-</sup>	2.001 1		472	<i>e</i>
FNSF	2.004 40 (1)	66.53 (6)	354.1 (1)	This work
			267.9 (1)	
NF <sub>2</sub>	2.005 2	48	168	<i>f</i>

<sup>a</sup> Data for NSF<sub>2</sub>, FNSF obtained at 110 K in SF<sub>6</sub>. <sup>b</sup> Numbers in parentheses are standard errors in the last significant figure as determined from a least-squares fit of all lines in the spectrum.

<sup>c</sup> Hyperfine interaction for two equivalent <sup>19</sup>F nuclei. <sup>d</sup> J. R. Morton and K. F. Preston, *J. Chem. Phys.*, **58**, 2657 (1973).

<sup>e</sup> R. W. Fessenden, *J. Magn. Reson.*, **1**, 277 (1969). <sup>f</sup> C. A. McDowell, H. Nakajima, and P. Raghunathan, *Can. J. Chem.*, **48**, 805 (1970).

of the irradiation<sup>5</sup> of *N*-halogenosulfur difluoride imides or of their reaction with Na. We strongly suspect that the other center observed in irradiated SF<sub>6</sub>/NSF mixtures is the isomeric radical FNSF which arises from fluorine atom attack on the nitrogen atom in NSF.

NSF<sub>2</sub> is isoelectronic with the prototypal 25-electron AB<sub>3</sub> radical SO<sub>3</sub><sup>-</sup>, and would, therefore, be expected to have a pyramidal structure with the unpaired electron largely located in a sulfur sp<sup>3</sup> hybrid orbital.<sup>6,7</sup> Measurement of the <sup>33</sup>S (*I* = 3/2) hyperfine interaction, the most critical test of such a structure, was not possible for NSF<sub>2</sub> (or FNSF) unfortunately, since the estimated intensities of the <sup>33</sup>S satellite spectra in natural abundance (0.74%) were well below the limit of detectability. However, comparison of the isotropic <sup>19</sup>F hyperfine interaction and *g* value with those of the isoelectronic species FSO<sub>2</sub> and FPO<sub>2</sub><sup>-</sup> (Table I) shows that the assignment to a pyramidal NSF<sub>2</sub> is not unreasonable. An alternative possibility, that the carrier is a nitrogen-centered radical, i.e., N=SF<sub>2</sub>, in a valence-bond description, seems much less plausible to us since the <sup>14</sup>N hyperfine interaction is appreciably smaller than in NCH<sub>2</sub> (29 MHz)<sup>8</sup> or NSF<sub>4</sub> (24 MHz).<sup>9</sup> On the other hand, the N 2s unpaired spin density indicated by the isotropic hyperfine interaction is compatible with a sulfur-centered pyramidal structure, i.e., N≡SF<sub>2</sub>.

Somewhat surprisingly, INDO I calculations<sup>10</sup> which we have carried out suggest that the radical NSF<sub>2</sub> is planar with a ground-state electronic wave function of the representation A<sub>1</sub> in C<sub>2v</sub> symmetry. An analogous ground-state wave function has been proposed<sup>11</sup> for the radical SF<sub>3</sub>. The present experimental results, unfortunately, do not permit a distinction to be made between planar and pyramidal σ radicals.

The spectral parameters (Table I) for the species which we have labeled FNSF are suggestive of a derivative of the nitrogen-centered π radical NF<sub>2</sub>.<sup>12</sup> A large hyperfine interaction of the unpaired electron with the <sup>19</sup>F nucleus which is more remote from the nitrogen nucleus in FNSF can be accommodated by assuming a nonplanar structure for the radical, a structure which is predicted by INDO I calculations. The magnitude of the <sup>14</sup>N and <sup>19</sup>F hyperfine interactions dictates against the alternative formulation as a sulfur-centered radical F—N=Š-F.

### Experimental Section

NSF, CINSF<sub>2</sub>, and BrNSF<sub>2</sub> were all prepared from the mercury compound Hg(NSF<sub>2</sub>)<sub>2</sub> which was obtained by the reaction of HgF<sub>2</sub> with FCONSF<sub>2</sub>.<sup>5,13</sup> NSF was also generated via the reactions of SF<sub>4</sub> with urea and with ammonia.<sup>5</sup> Cylinder SF<sub>6</sub> (Matheson) was used as received.

Degassed mixtures of substrate (~5%) in SF<sub>6</sub> were sealed off in quartz EPR tubes and γ irradiated at 77 K for 2 h in a 9000 Ci <sup>60</sup>Co source. EPR spectra we recorded and measured with a Varian E-12

spectrometer and ancillary equipment.<sup>11</sup> <sup>19</sup>F NMR analysis carried out on the samples prior to γ irradiation confirmed the identity and purity of the reactants.

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**Registry No.** NSF, 13537-38-7; CINSF<sub>2</sub>, 13816-65-4; BrNSF<sub>2</sub>, 25005-08-7; SF<sub>6</sub>, 2551-62-4; NSF<sub>2</sub>, 39466-65-4; FNSF, 66142-12-9.

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### Structure of Thiotriithiazyl Nitrate (S<sub>4</sub>N<sub>3</sub><sup>+</sup>NO<sub>3</sub><sup>-</sup>): Evidence for a Triangular Arrangement with Short Contacts between an Oxygen Atom and the Disulfide Group

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Crystals of a number of compounds containing the disulfide group show unusually short intermolecular contacts of an external atom with both sulfur atoms of the disulfide group.<sup>1-7</sup> Examples summarized by Hordvik<sup>8</sup> include several 1,2-dithiolium and thiuret salts.

The external atom X which most commonly is a chlorine, bromine, or iodine atom generally lies in or close to the plane of the π-bonded system of which the disulfide group is a part. The arrangement has been described as a weak three-center two-electron bond established through partial transfer of charge from a filled orbital on X into empty orbitals on the sulfur atoms.<sup>8</sup> This interpretation is in agreement with the conclusion by Rosenfield, Parthasarathy, and Dunitz,<sup>9</sup> based on the analysis of intermolecular contacts with sulfur, that nucleophiles tend to approach the divalent sulfur atom in the plane of the adjacent bonds.

In the halides described by Hordvik the S...X distance is between 0.25 and 0.51 Å shorter than the sum of the corresponding van der Waals radii. An even larger shortening has been described to occur, however, in the salt thiotriithiazyl nitrate S<sub>4</sub>N<sub>3</sub>NO<sub>3</sub> by Cordes, Kruh, and Gordon,<sup>10</sup> who, from a partial three-dimensional x-ray analysis, report an S—S...O distance of 2.66 and S...O distance of 2.48 Å, compared with a sum of the van der Waals radii of 3.25 Å. As strong intermolecular interactions with sulfur atoms are of considerable importance for the properties of pseudo-one-dimensional molecular metals<sup>11,12</sup> we have redetermined the crystal structure of the title compound.

### Experimental Section

The title compound was prepared by treating thiotriithiazyl chloride (S<sub>4</sub>N<sub>3</sub>Cl) with hot fuming nitric acid. The crystals of S<sub>4</sub>N<sub>3</sub>NO<sub>3</sub> are

Table I. Positional ( $\times 10^4$ ) and Thermal Parameters ( $\times 10^4$ ) for  $S_4N_3NO_3$ 

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S(1)	1829 (2)	4410 (1)	1199 (1)	434 (5)	328 (4)	426 (5)	47 (4)	84 (4)	33 (3)
S(2)	5134 (2)	3880 (1)	1983 (1)	402 (5)	344 (4)	410 (4)	-45 (4)	24 (4)	-18 (4)
S(3)	4889 (2)	1107 (1)	1307 (1)	484 (6)	306 (4)	595 (6)	32 (4)	189 (4)	7 (4)
S(4)	284 (2)	1863 (1)	183 (1)	502 (6)	473 (5)	451 (5)	-14 (5)	1 (4)	-25 (4)
N(1)	2422 (5)	961 (3)	565 (2)	592 (20)	343 (14)	421 (15)	-74 (13)	180 (16)	-46 (12)
N(2)	434 (5)	3268 (3)	577 (2)	396 (17)	437 (16)	463 (16)	-11 (14)	33 (13)	50 (13)
N(3)	5589 (5)	2427 (3)	1820 (2)	373 (17)	385 (15)	510 (16)	8 (13)	57 (14)	41 (11)
N(4)	4866 (5)	7059 (3)	1496 (2)	426 (17)	375 (14)	344 (14)	-56 (13)	82 (12)	-12 (11)
O(1)	4095 (5)	6367 (2)	2211 (2)	799 (20)	461 (14)	450 (14)	-180 (13)	326 (14)	-50 (11)
O(2)	5708 (7)	6545 (3)	749 (3)	1396 (31)	591 (17)	688 (19)	-271 (20)	728 (21)	-10 (15)
O(3)	4786 (6)	8227 (3)	1570 (3)	881 (23)	336 (14)	806 (20)	82 (15)	191 (17)	66 (13)

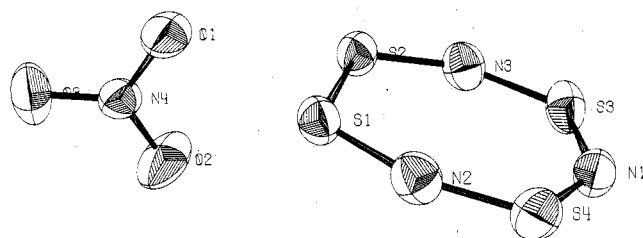


Figure 1. Numbering of atoms. The thermal ellipsoids enclose 50% probability.

formed by slow cooling of the solution. The precursor  $S_4N_3Cl$  can be prepared from ammonium chloride and disulfur dichloride according to the method described by Jolly and Maguire.<sup>13</sup> The yellow crystals of  $S_4N_3NO_3$  were mounted in Lindemann glass capillaries. Initial photographic experiments confirmed the space group and cell dimensions as determined earlier by Cordes et al. The intensity data were collected on a Picker FACS-I four-circle diffractometer in the  $\theta$ - $2\theta$  step scan mode using Nb-filtered Mo  $K\alpha$  ( $\lambda$  0.71069 Å) radiation. The refined cell parameters are  $a = 5.830$  (3) Å,  $b = 10.456$  (4) Å,  $c = 12.028$  (6) Å, and  $\beta = 99.87$  (2)° with space group  $P2_1/n$ ,  $Z = 4$ , and  $V = 722.36$  Å<sup>3</sup>. Three standard reflections recorded after every 60 reflections showed no significant fluctuations in intensity. The method of Blessing, Coppens, and Becker<sup>14</sup> was used to analyze reflection profiles. Absorption corrections were calculated by numerical integration ( $\mu = 7.41$  cm<sup>-1</sup>). Symmetry-related reflections were averaged to give 1421 independent reflections within the region scanned ( $(\sin \theta)/\lambda = 0.60$  Å<sup>-1</sup>). A weighting scheme  $w(F^2) = [\sigma^2(F^2)_{\text{counts}} + (0.02F^2)^2]^{-1}$  was employed during refinements. Positional and thermal parameters as obtained by Cordes et al.<sup>10</sup> were used as input to the least-squares refinement. Scattering factors were as listed in "International Tables for X-Ray Crystallography", 1974. For the S atom the anomalous dispersion factors of Cromer and Liberman<sup>15</sup> were applied. An isotropic extinction parameter was also refined.

### Results and Discussion

Bond lengths and angles given in Table II (see Figure 1 for numbering of atoms) indicate double-bond character in the S-N bonds (of length 1.538–1.568 Å) as found in other salts of  $S_4N_3^+$  and  $S_5N_5^{+}$ ,<sup>15,16</sup> while the S-S bond of 2.070 Å is slightly longer than in orthorhombic sulfur.<sup>16</sup> The 2.48 Å S-O distance (3.005 Å) of Cordes et al. is not confirmed by the analysis, this contact being only slightly shorter than the sum of the van der Waals radii. On the other hand, the distances of one of the nitro group oxygen atoms with the disulfide sulfur atoms are unusually short (2.620 and 2.695 Å); the shortest, S(1)···O(1), is 0.63 Å below the sum of the van der Waals radii, though still considerably above the covalent S-O bond length which, for example, is 1.444 Å in sulfamic acid  $NH_2SO_3$ .<sup>17</sup> Expressed as a fraction of the sum of the van der Waals radii the S-O distances are 0.81 and 0.83, respectively, compared with 0.70 for the S-S distance in tetrasulfur tetranitride<sup>18</sup> which corresponds to a covalent interaction and 0.90 for the "across the ring" S-S distance in orthorhombic sulfur, which is normally considered to be a short nonbonded contact.<sup>16</sup>

The effect of the three-center interaction is also apparent in the nitro group, where the N-O(1) bond is 0.043 Å longer than the average of the other two N-O distances. The O(1)

Table II

(a) Bond Lengths (Å) and Angles (Deg)			
S(1)-S(2)	2.070 (1)	S(4)-N(2)	1.541 (3)
S(1)-N(2)	1.562 (3)	N(4)-O(1)	1.265 (3)
S(2)-N(3)	1.560 (3)	N(4)-O(2)	1.218 (3)
S(3)-N(3)	1.538 (3)	N(4)-O(3)	1.226 (4)
S(3)-N(1)	1.565 (3)	S(1)···O(1)	2.620 (3)
S(4)-N(1)	1.568 (3)	S(2)···O(1)	2.695 (3)
S(1)-S(2)-N(3)	111.6 (1)	O(1)···S(1)-S(2)	69.01 (7)
S(2)-N(3)-S(3)	152.2 (2)	O(1)···S(2)-S(1)	65.17 (7)
N(3)-S(3)-N(1)	118.2 (2)	O(1)-N(4)-O(2)	119.1 (3)
N(1)-S(4)-N(2)	118.9 (2)	O(2)-N(4)-O(3)	121.0 (3)
S(3)-N(1)-S(4)	135.6 (2)	O(3)-N(4)-O(1)	119.9 (3)
S(4)-N(2)-S(1)	150.9 (2)	N(4)-O(1)···S(1)	109.9 (2)
N(2)-S(1)-S(2)	112.4 (1)	N(4)-O(1)···S(2)	111.8 (2)
S(1)-O(1)-S(2)	45.82 (5)		

### (b) Least-Squares Planes<sup>a</sup>

Atom	Dev, Å	Atom	Dev, Å	Atom	Dev, Å
(1) Plane through S(1), S(2), S(3), S(4), N(1), N(2), N(3)					
Equation of the Plane is $3.0136x + 2.4689y - 10.8160z = 0.33844$					
S(1)	0.005	N(1)	0.017	O(1)*	0.076
S(2)	0.022	N(2)	-0.025		
S(3)	-0.006	N(3)	-0.023		
S(4)	0.009				
(2) Plane through S(1), S(2), S(3), S(4)					
Equation of the Plane is $3.0134x + 2.4261y - 10.8300z = 0.3324$					
S(1)	0.010	N(1)*	0.018	O(1)*	0.051
S(2)	0.009	N(2)*	-0.034		
S(3)	-0.006	N(3)*	-0.030		
S(4)	0.007				

<sup>a</sup> \* denotes atoms not included in the calculation of the plane.

atom is only 0.076 Å out of the plane of the  $S_4N_3^+$  ion (Table IIb) which is close to planar, with the  $S_4N_3^+$  and  $NO_3^-$  planes almost perpendicular to each other (angle between normals 93.3°). The N(4)-O(1)···S angles are such (109.0 and 111.8°) that the oxygen lone pairs may be expected to point closely toward the disulfide group in agreement with the presumed nucleophilic behavior of the oxygen atom.

A high-resolution low-temperature analysis is being carried out in an attempt to assess the degree of covalency of this unusual interaction from the experimental charge density distribution.

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**Registry No.**  $S_4N_3NO_3$ , 12033-50-0.

**Supplementary Material Available:** A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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### Synthesis of *cis*- and *trans*-[Cr(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> and [Cr(en)(NH<sub>3</sub>)<sub>4</sub>]<sup>3+</sup>

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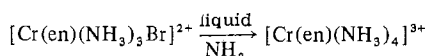
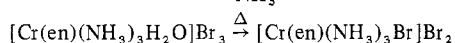
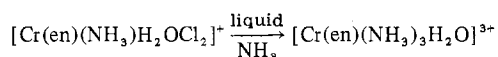
Only a few complexes of chromium(III) with mixed amine ligands have been reported,<sup>1,4</sup> few of these contain only neutral ligands,<sup>1</sup> and no general synthetic methods for their preparation exist. We wish to report the synthesis of *cis*- and *trans*-[Cr(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> and [Cr(en)(NH<sub>3</sub>)<sub>4</sub>]<sup>3+</sup> and their spectral properties.

The most obvious route to compounds of this type is ammonolysis of acido-ethylenediamine starting materials in liquid ammonia. Prior studies of the reactions of acidochromium(III) complexes in liquid ammonia have shown, however, that thermal substitution with *trans* → *cis* stereochemical rearrangement is of common occurrence,<sup>5</sup> suggesting that although preparation of *cis*-[Cr(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>2+</sup> would probably be straightforward, the *trans* isomer would be more difficult.

In agreement with our expectations we found that *cis*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> reacted smoothly in liquid ammonia at low temperature to yield [Cr(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>, with a few percent *trans* (ca. 3%?). Both *trans*-[Cr(en)<sub>2</sub>Br<sub>2</sub>]<sup>+</sup> and *trans*-[Cr(en)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, however, reacted with almost complete isomerization to yield about 95% *cis*-[Cr(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>.

A reasonable yield of the *trans* compound was finally achieved by ammonolysis of the more inaccessible compound *trans*-[Cr(en)<sub>2</sub>NH<sub>3</sub>Cl]<sup>2+</sup>, the synthesis of which has been previously reported.<sup>5</sup> This reaction gave approximately one-third *trans* product.

Since [Cr(en)<sub>2</sub>X<sub>2</sub>]<sup>+</sup> compounds, where X is an easily substituted acido ligand, are not available to prepare [Cr(en)(NH<sub>3</sub>)<sub>4</sub>]<sup>3+</sup>, a three-stage synthesis was required starting with [Cr(en)(NH<sub>3</sub>)<sub>2</sub>H<sub>2</sub>OCl<sub>2</sub>]<sup>+</sup> and involving the steps



The compounds were characterized by elemental analysis

**Table I.** UV-Visible Spectral Data for [Cr(en)<sub>n</sub>(NH<sub>3</sub>)<sub>6-2n</sub>]<sup>3+</sup> Complexes

Complex <sup>a</sup>	λ <sub>max</sub> <sup>b</sup>	λ <sub>min</sub>	λ <sub>max</sub> <sup>b</sup>	Ref
[Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	351 (32.7)	395 (7.3)	463 (39.4)	9
	354 (33.7)		466 (40.7)	10
	350 (32)	395 (8.7)	462 (39)	11
[Cr(en)(NH <sub>3</sub> ) <sub>4</sub> ] <sup>3+</sup>	351 (42.4)	396 (9.8)	462 (51.0)	This work
<i>trans</i> -[Cr(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>3+</sup>	347 (36.7)	391 (9.5)	454 (47.0)	This work
<i>cis</i> -[Cr(en) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ] <sup>3+</sup>	351 (53.7)	395 (13.0)	460 (65.8)	This work
[Cr(en) <sub>3</sub> ] <sup>3+</sup>	350 (61.3)	394 (13.9)	456 (75.7)	9
	351 (60.7)		457 (76.5)	12

<sup>a</sup> All solutions were in 0.1 N HCl. <sup>b</sup> Absorption wavelengths in nm. Values in parentheses are the molar absorptivities.

and by measurement of their UV-visible and infrared spectra. The UV-visible spectral data, Table I, are consistent with expectations based on ligand field theory and an analogy to the parent complexes, [Cr(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> and [Cr(en)<sub>3</sub>]<sup>3+</sup>. The two [Cr(en)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup> isomers were carefully separated by fractional crystallization and were distinguishable by (1) their different crystal habits, (2) their UV-visible spectra, for which the molar absorptivity of the *cis* isomer was about 40% higher than for the *trans*, consistent with the trend found for a number of [Cr(en)<sub>2</sub>(NH<sub>3</sub>)X]<sup>n+</sup> isomer pairs,<sup>5</sup> and (3) the infrared band patterns<sup>6</sup> in the region between 600 and 300 cm<sup>-1</sup> where the *cis* isomer shows bands at 548 (s), 527 (ms), 473 (m), 450 (m), and 410 (w) and the *trans* isomer bands at 560 (m), 543 (sh), 479 (m), and 430 (m). Although we have experienced no difficulties in our laboratory with these compounds, it is appropriate to draw attention to the fact that the perchlorate salts are potentially very explosive and could show great sensitivity to heat or shock under some circumstances.

[Cr(en)(NH<sub>3</sub>)<sub>3</sub>H<sub>2</sub>O]Br<sub>3</sub>. [Cr(en)(NH<sub>3</sub>)(H<sub>2</sub>O)Cl<sub>2</sub>]<sup>+</sup>Cl<sup>-</sup> was reacted with dried distilled liquid ammonia (ca. 1 mL/g of complex) in a sealed Carius tube at 20 °C for ca. 0.5 h. The dried purple product (6.0 g) was dissolved in a minimum of 0.1 M HBr and one volume of 48% HBr was added. The color of the solution changed from purple to a deep orange-red, and upon addition of acetone to the solution and cooling to 0 °C, a pale orange precipitate formed. This fraction (1.5 g) was removed by filtration, washed with acetone, and dried in a desiccator. A second fraction (1.5 g), slightly more orange than the first was obtained with further addition of acetone to the filtrate. The two fractions exhibited different solubilities and different solid-state anation behaviors (see later) and are likely to correspond to the different isomers of [Cr(en)(NH<sub>3</sub>)<sub>3</sub>H<sub>2</sub>O]Br<sub>3</sub>. The UV-visible absorption maxima of fraction 1 were 359 and 469 nm, consistent with expectations based on ligand field theory and analogy to [Cr(NH<sub>3</sub>)<sub>5</sub>H<sub>2</sub>O]<sup>3+</sup> and *cis*- and *trans*-[Cr(en)<sub>2</sub>(NH<sub>3</sub>)H<sub>2</sub>O]<sup>3+</sup>. Since [Cr(en)(NH<sub>3</sub>)<sub>3</sub>H<sub>2</sub>O]Br<sub>3</sub> was to be used only as an intermediate, no further attempts were made to establish the chemical purity or isomer nature of the fractions obtained.

[Cr(en)(NH<sub>3</sub>)<sub>3</sub>Br]Br<sub>2</sub>. This was prepared by the solid-state anation of [Cr(en)(NH<sub>3</sub>)<sub>3</sub>H<sub>2</sub>O]Br<sub>3</sub>. Fractions 1 and 2 obtained above were heated and the positions of the UV-visible absorption maxima followed. After 24 h at 70 °C, these were 372 and 486 nm for fraction 1 and 377 and 510 nm for fraction 2. After further heating at 90 °C for 2 h, the absorption maxima for fraction 1 changed to 374 and 497 nm, while no change was observed for fraction 2. Fraction 1 was heated at 90 °C for a further 2 h and the two fractions were combined. No attempt was made to establish the purity or isomer nature of the sample as the compound was to be used only as an intermediate.

[Cr(en)(NH<sub>3</sub>)<sub>4</sub>](ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O. [Cr(en)(NH<sub>3</sub>)<sub>3</sub>Br]Br<sub>2</sub> was reacted with liquid ammonia (ca. 1 mL/g) in a sealed Carius