

has been investigated by two-dimensional X-ray methods. The structure of the amine was known previously<sup>1</sup> and our chief interest was the structure of the anion, the symmetry of which generally seems to depend on the size of the cation.

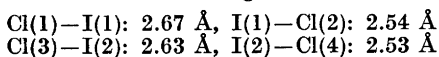
The crystals are orthorhombic with unit cell parameters  $a = 9.92 \text{ \AA}$ ,  $b = 19.86 \text{ \AA}$ , and  $c = 7.58 \text{ \AA}$  and containing four formula units. The two space groups  $Pnn2$  and  $Pnmm$  are both compatible with the systematic absent reflections, but the latter eventually turned out to be the more probable.

The structure was solved from the projections along the  $a$  and  $c$  axes using Patterson methods; least-squares refinements gave final conventional  $R$ -values of 14 % and 10 % for the  $(hk0)$  and  $(0kl)$  data, respectively.

Large standard deviations in the positional parameters of the lighter atoms do not permit a discussion of the structure of the cationic part of the salt, but there were no significant deviations from the structure of the amine, however.

There are two non-equivalent dichloroiodide ions; both are linear within the accuracy of the measurement and both are non-symmetrical.

The relevant bond lengths are



with standard deviations of  $0.03 \text{ \AA}$ . The Cl(1) and Cl(3) atoms are situated closer to nitrogen atoms than the other halogen atoms, and are thus probably carrying the negative charge. This agrees well with the results obtained in the structure determination of piperazinium bis-dichloroiodide<sup>2</sup> where a corresponding geometric arrangement was found, the two Cl-I bond lengths being  $2.69 \text{ \AA}$  and  $2.47 \text{ \AA}$ , respectively.

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## Preparation of 2-Nitrothiophene of High Isomeric Purity

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In connection with current work on nitration of -I-M substituted thiophenes<sup>1</sup> it was necessary to obtain an isomerically pure sample of 2-nitrothiophene. The direct nitration of thiophene invariably seems to result in an isomeric mixture consisting of about 85 % 2-nitrothiophene and 15 % of the 3-isomer.<sup>2</sup> Since this mixture is difficult to separate in its components, the isomers have instead been obtained through the selective dechlorosulfonation of the synthetic mixture of 5-nitro- and 4-nitro-2-thiophene-sulphonylchloride.<sup>3</sup> The yield, however, of 2-nitrothiophene is only about 4 %, contaminated with about 5 % 3-nitrothiophene, but under favorable conditions the method may yield practically pure 2-nitrothiophene.<sup>2</sup> On the other hand 3-nitrothiophene is always obtained in reasonable yields in 99 % isomeric purity<sup>1,2</sup> with the same method.

Since 4-nitro-2-thiophenesulphonylchloride is dechlorosulfonated at about  $130^\circ\text{C}$  and the 5-nitro-isomer at about  $160^\circ\text{C}$ <sup>3</sup> and since the reaction is probably reversible, it is to be expected that the chlorosulfonation of a mixture of 2- and 3-nitrothiophene, if interrupted at an early stage, would give a mixture of 4-nitro-2-thiophene-sulphonylchloride and 2-nitrothiophene. Also investigations of mono-substituted -I-M thiophenes indicate that the 5-position in 3-nitrothiophene is nitrated faster than the same position in 2-nitrothiophene.<sup>1</sup>

Thus the isomeric mixture of nitrothiophene obtained from nitration of thiophene (Experimental) was chlorosulfonated with chlorosulphonic acid at  $40^\circ\text{C}$ , and the course of reaction was followed with NMR. Since the 2-proton quartet of 3-nitrothiophene is shifted downfield with about 24 cps from the lowest field quartet (3-proton) of 2-nitrothiophene a convenient measure of change in isomeric composition is at hand. Thus, as the reaction proceeded the 2-proton quartet gradually disappeared and was replaced with an AB quartet with  $J_{AB} = 1.8$  cps, which

according to well established facts<sup>4</sup> shows that a 2,4-disubstituted thiophene is formed, in this case presumably 4-nitro-2-thiophenesulphonylchloride. After about 25 min from start the 2-proton quartet had disappeared completely and other AB quartets appeared, probably due to formation of 2-nitro-5- and 4-thiophenesulphonylchlorides. The reaction was therefore interrupted and after work up and recrystallization, GLC analysis showed that the product, obtained in 60% yield, was now isomerically pure 2-nitrothiophene.

Routine examination of the IR spectrum of the 2-nitrothiophene thus obtained revealed, when compared to the IR data given by Katritzky and Boulton<sup>5</sup> for 2-nitrothiophene, that the absorption at 834  $\text{cm}^{-1}$  reported by these authors, was absent in our spectrum. It was present, however, in the spectrum of the isomeric mixture used as starting material for the chlorosulphonation. Hence, this absorption which was assigned as ring breath<sup>6</sup> must be due to the presence of 3-nitrothiophene. The spectrum of 3-nitrothiophene confirmed this, since a strong absorption ( $\epsilon=145$ ) is found at 830  $\text{cm}^{-1}$  (0.323 mole/l in  $\text{CS}_2$ ).

It is therefore suggested that the ring breathing mode of 2-nitrothiophene corresponds to an absorption at 852.7  $\text{cm}^{-1}$  (0.318 mole/l in  $\text{CS}_2$ ), which under normal operating conditions is barely observable as a shoulder of the 858  $\text{cm}^{-1}$  absorption band ( $\gamma\text{-CH}$  vibration<sup>6</sup>). The two peaks may be resolved, however, and the molar extinction coefficient (852.7  $\text{cm}^{-1}$ ) is found to be  $\epsilon=39$ . The latter figure is compatible with the  $\epsilon$ -values given<sup>5</sup> for the ring breathing mode for a series of 2-substituted thiophenes.

Using the present data and those given by Katritzky and Boulton<sup>5</sup> the fraction 3-nitrothiophene present in their sample of 2-nitrothiophene was found to be about 16%. Since their sample was a commercial product, probably obtained through direct nitration of thiophene that proportion 3-nitrothiophene is expected. Also previous determinations<sup>2</sup> with GLC of this isomer ratio of a commercial product gave about the same figure. The absorption at 1433  $\text{cm}^{-1}$  which has been ascribed as anomalous<sup>5</sup> in the spectrum of 2-nitrothiophene, is similarly due to the presence of the 3-isomer.

*Experimental.* NMR spectra were obtained with a Varian A 60 A Analytical NMR Spectrometer at ambient temperature. The GLC analyses were performed with an Aerograph 1520 gas chromatograph equipped with a flame ionization detector and a 3 m Reoplex column held at 144°C (5% Reoplex on Aeropak 80–100 mesh, 1/8", 20 ml  $\text{N}_2$ /min). Infrared spectra were recorded with a Perkin Elmer Model 225 Grating Infrared Spectrometer (0.1 mm NaCl cells at ambient temperature).

Thiophene (0.63 mole) was nitrated according to Babasinian<sup>6</sup> with fuming nitric acid (0.76 mole) in acetic anhydride-acetic acid solution at +10°C. 49 g of the crude material (yield 85%) was recrystallized from 400 ml hexane containing 5% isopropylether. GLC analysis of the recrystallized product (37 g, m.p. 40–42°C) showed that it had the composition 85% of 2-nitrothiophene and 15% of 3-nitrothiophene. The two GLC peaks (retention times 23.6 and 25.6 min, respectively) were almost completely resolved which is an essential improvement of the earlier GLC analysis.<sup>2</sup>

The recrystallized product (0.22 mole) was then dissolved in 55 ml ethanol free chloroform and transferred to a four necked flask carrying stirrer, reflux condenser, dropping funnel, and a thermometer. While keeping the flask at 40°C, 20 ml (0.30 mole) chlorosulfonic acid was added over a period of 5 min. A sample of the reaction mixture was then withdrawn and used in order to follow the reaction with NMR (see above). Thus when according to NMR the 3-nitrothiophene was consumed, the main reaction mixture was poured into ice water. The chloroform layer was separated and the water phase was extracted with 3  $\times$  50 ml of chloroform. The combined chloroform solutions were washed with 2  $\times$  50 ml of water and then shaken with some aluminium oxide. The solution was finally dried with sodium sulfate over night. The solvent was removed with a rotary evaporator and the residue (ca. 20 g) was recrystallized from 125 ml hexane-isopropylether (5%). Thus 14.5 g was obtained (m.p. 40.5–41.5°C) which upon GLC analysis showed that 2-nitrothiophene had been obtained in more than 99% isomeric purity. The overall yield of pure 2-nitrothiophene from thiophene is then about 50%. The NMR spectrum showed the typical AMX coupling pattern of 2-nitrothiophene with the coupling constants  $J_{35}=1.6$  cps,  $J_{45}=5.6$  cps, and  $J_{34}=4.4$  cps. The IR spectrum ( $\sim 0.3$  mole/l in

$\text{CrCl}_4$ ) agreed with the spectrum of the isomeric mixture obtained in the nitration of thiophene with the exceptions noted above. (Found: C 36.83; H 2.06; N 10.87; S 24.50. Calc. for  $\text{C}_4\text{H}_3\text{NO}_2\text{S}$ : C 37.20; H 2.35; N 10.85; S 24.83).

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## On the Crystal Structure of Nitritopentamminechromium (III) Chloride

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In connection with studies of nitro and nitrito compounds of transition metals, the crystal structure of  $[\text{Cr}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$  has been investigated and a preliminary report is given in this note.

Starting with  $\text{KCr}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$   $[\text{Cr}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$  was prepared through a series of syntheses.<sup>1-3</sup> The analyses of  $[\text{Cr}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$  gave 32.6 % N, 27.4 % Cl, and 21.0 % Cr. The theoretical values are 33.1 % N, 27.9 % Cl, and 20.5 % Cr.

Integrated Weissenberg photographs corresponding to the reflections  $hk0-hk4$  have been recorded, using  $\text{CuK}\alpha$  radiation. The crystals are of orthorhombic symmetry and from the systematically absent reflec-

tions the space group was determined to be either No. 62 -  $Pnma$  or No. 33 -  $Pn2_1a$ .<sup>4</sup> The cell dimensions, as calculated from the Weissenberg data, are  $a=13.3$  Å,  $b=10.6$  Å, and  $c=7.0$  Å. The volume of the unit cell is thus approximately 990 Å<sup>3</sup>. Assuming a cell content of four formula units, a calculated density of 1.71 g/cm<sup>3</sup> is obtained. From three-dimensional Patterson calculations, based on the  $hk0-hk4$  intensities, the chromium atoms were found to occupy the four-fold position 4(c) in  $Pnma$  (No. 62) with  $x=0.12$ ,  $y=1/4$ ,  $z=0.19$ , and the chloride ions were found to occupy the eight-fold position 8(d) with  $x=0.37$ ,  $y=0.00$ , and  $z=0.19$ . The positions of the nitrogen atoms and one oxygen atom were then deduced from successive electron density calculations. The position of one oxygen atom has not yet been completely determined. A preliminary three-dimensional least squares refinement of the structure was performed giving a  $R$ -value of 0.12 and the resulting parameters are listed in Table 1. The chromium

Table 1.

Atom	Position	$x$	$y$	$z$
Cr	4(c)	0.107	1/4	0.175
Cl	8(d)	0.358	0.999	0.172
N1	8(d)	0.108	0.047	0.220
N2	4(c)	0.195	1/4	0.947
N3	4(c)	0.226	1/4	0.362
N4	4(c)	0.021	1/4	0.379
N5	4(c)	0.399	1/4	0.663
O1	4(c)	0.482	1/4	0.526
O2	4(c)	(0.32)	1/4	0.66)

atom is octahedrally coordinated by five  $\text{NH}_3$ -groups and one  $\text{NO}_2$ -group. A complete three-dimensional refinement is in progress, and a detailed presentation of the structure of  $[\text{Cr}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2$  will soon be published in *Acta Chem. Scand.*

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