Crystal Structure and Alleged Isomerism of Dithiocyanate-tetrapyridine-iron (II)

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Dithiocyanate-tetrapyridine-iron(II) has been reported to exist in two isomeric forms: A yellow compound (α) and a black one (β). The crystal structure of the yellow form has been determined from three dimensional X-ray data collected with an automatic counter diffractometer. Discrete molecules: $Fe(C_5H_5N)_4(NCS)_2$ were found. The iron atom is surrounded octahedrally by six nitrogen atoms. The thiocyanate groups occupy *trans* positions. The black compound is crystallographically equivalent with the yellow form. Evidence is presented that the black colour is caused by a strongly coloured impurity and that so far only one isomer of $Fe(C_5H_5N)_4(NCS)_2$ has been isolated in a pure state.

Stereoisomerism has been reported for numerous compounds of transition metals. Generally isolation of isomers is facilitated by the simultaneous occurrence of a low speed of isomerisation and of a considerable difference in solubilities of the isomers. Reports on preparation of isomers are therefore rare for complexes which are kinetically labile.

Until recently it has been tacitly understood that each one of the possible isomers would crystallize as a distinct crystalline compound. This assumption has been disproved by Grønbæk,[1] and by Kilbourn, Powell and Darbyshire.[2] The reported existence of isomers of tetrapyridinedithiocyanate-iron(II) attracted our attention since iron(II)-pyridine complexes are generally formed by fast reactions.

The yellow form of $Fepy_4(NCS)_2$ was prepared by Grossmann and Hünseler[3] in 1905 and the black compound was described by Spacu[4] in 1914. A number of papers have been concerned with one or both of the two compounds.

As no definite solution of the problem of the geometric structures of the alleged isomers has been presented so far we undertook an X-ray crystallographic investigation of both compounds. They were prepared according to methods reported in the literature.

EXPERIMENTAL

Chemistry. One mole of $FeCl_3,6H_2O$ was mixed with six moles of NH_4NCS in aqueous solution at 5°C. 4.15 moles of pyridine were added dropwise while the solution was kept at 0°C. A compound was formed which was recrystallized from acetone. Rosenheim *et al.*[5] give the formula: $C_5H_6N[Fe(III) (C_5H_5N)_2(NCS)_4]$. The compound is reddish-violet and strongly coloured. 50 g of this compound was refluxed with 400 ml pyridine, the solution was filtered and cooled slowly. Yellow, elongated prismatic crystals of $Fe(C_5H_5N)_4$ $(NCS)_2$ were formed. The black crystals of $Fe(C_5H_5N)_4(NCS)_2$ were formed by dissolving the yellow compound in chloroform, which was exposed to air, followed by quick evaporation of the solvent. Slow evaporation of the chloroform, when exposed to air, gave various red or orange compounds and eventually $C_5H_6N[Fe(III) (C_5H_5N)_2(NCS)_4]$ was also formed.

Analysis: The following results for $C_5H_6N[Fe(C_5H_5N)_2(NCS)_4]$ were found in the microanalysis laboratory of the Max-Planck-Institut für Kohlenforschung, Mülheim: C 43.50; H 3.20; N 18.56; S 24.12. Calc. C 43.34; H 3.06; N 18.63; S 24.36. The following results were found for α-$Fe(C_5H_5N)_4(NCS)_2$: C 54.35; H 4.42; N 17.20; S 11.55 and for the β-compound: C 53.40; H 4.34; N 16.71; S 11.08. Calc. for both compounds: C 54.05; H 4.13; N 17.21; S 13.13.

Additional analysis of the α-compound gave the following results: Fe 10.98; NCS 23.15. Calc. Fe 11.44; NCS 23.78. Iron was estimated as Fe_2O_3. NCS was determined by titration with $AgNO_3$.

Magnetic measurements were performed using the Gouy method. The field was measured with a Rawson Gaussmeter. Spectrophotometric measurements were performed on a Cary 14 spectrophotometer.

X-Ray technique. Weissenberg, precession, and retigraph photographs established lattice type and space group extinctions. CoKα and MoKα radiations were used. Guinier powder photographs were taken using FeKα radiation.

A yellow crystal of dimensions $1 \times 0.4 \times 0.4$ mm³ was selected for intensity measurements and sealed in a capillary. It was oriented along the longest dimension which was the *c*-axis. Three dimensional data were measured using a linear diffractometer designed by Arndt and Phillips[6] and manufactured by Hilger and Watts. Mo-radiation was employed. Balanced filters SrO, ZrO_2 in conjunction with pulse height analysis ensured a practically monochromatic MoKα beam. No absorption correction was employed. During the data collection, which lasted about three weeks, the crystal turned dark gradually. No decline in the intensity of a standard reflexion was detected.

The intensities measured were symmetry related in pairs. The diffractometer output was processed by a GIER computer using an ALGOL program[7] which evaluated intensities, calculated averages of symmetry related reflexions, applied Lp corrections and gave the standard deviations. 1956 of the 3464 independent reflexions showed intensities greater than twice their standard deviation estimated as the square root of the total number of counts in an intensity measurement.

STRUCTURE DETERMINATION

An absolute scale was evaluated by calculating quotients

$$\langle I_{obs} \rangle / \langle F^2(hkl)_{calc} \rangle$$

(Fig. 1) in suitable $\sin\theta$ intervals and by extrapolation to $\sin\theta = 0$ and from a Wilson plot which also gave an average temperature factor. The program employed was written by Danielsen.[8]

A three dimensional Patterson function was calculated using a program written by Lauesen.[9] The space group $C2/c$ was in accordance with the Patterson function. Since the general position in this space group is eightfold and since there are four formula units of $Fepy_4(NCS)_2$ per unit cell the iron

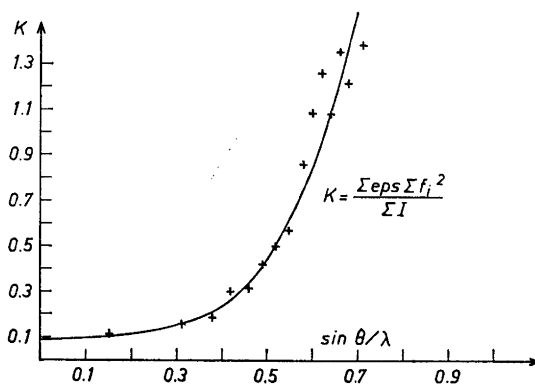*Fig. 1.* Plot of $\langle I_{obs}\rangle/\langle F^2_{calc}\rangle$ as function of $\sin\theta/\lambda$ for establishing an absolute scale.

atom must be in a special position. The Patterson function established 0, 0, 0, as the location of the iron atom. The sulphur atom was readily located and using iron and sulphur as searcher atoms, an octahedron of atoms, presumably nitrogen atoms, were located using image seeking methods. Also the carbon atom of the thiocyanate group was located in this way. A structure factor calculation based on the location of 1/2 Fe, 3N, C, and S in an asymmetric unit was performed using a program written by Danielsen.[10] It gave a conventional R-value of 39.4 %. A Fourier synthesis was calculated using 1723 reflexions. Planes with $F_o > 3F_c$ were not included. This Fourier map revealed the positions of the ten carbon atoms of the pyridine rings. After two cycles of Fourier and difference Fourier refinement R was 21.5 %. Three cycles of least squares refinement using a program, written by Danielsen,[11] lowered R to 14.1 %. The program employs isotropic temperature factors and the diagonal approximation. The calculations mentioned so far were carried out on a GIER computer at the computing center of Aarhus University.

Further refinement was carried out on an IBM 7090 at NEUCC, Lundtofte. A full matrix least squares program using anisotropic temperature factors was used. The program was written by Gantzel, Sparks, Long, and Trueblood.[12] After convergence was obtained a difference Fourier synthesis revealed the positions of the hydrogen atoms. Structure factor computations for Fourier calculations were performed on GIER using a program written by Grønbæk Hazell.[13]

The weights used in the least squares analysis were:

$$w = 1/(-F + \sqrt{\sigma F^2 + aF^2 + F^2})^2$$

where σF^2 is the standard deviation from the counting statistics and $a = 0.04$. This weighting scheme gave weighted residuals which were independent of the value of F. At convergence of refinement an R-value of 6.35 % was obtained using 1782 reflexions. The positions of the hydrogen atoms were not refined. They were found at about 1 Å from the carbon atoms

and were fixed at 1.00 Å distance from the C-atoms in the planes of the pyridine rings.

At the end of the structure refinement the system of programs edited by Stewart:[14] "X-ray-63" became available to us. It was used partly as a check on previous calculations and partly for additional calculations, *e.g.* on bond lengths, best planes, and vibrational corrections.

No intensity measurements were carried out with the black crystals of the so-called β-isomer. Powder photographs of α and β isomers were identical with respect to lattice constants and intensity distribution estimated visually. Rotation photographs and *hk*0 Weissenberg photographs of the two forms also showed complete identity according to visual inspection. As good crystals of the black form were difficult to obtain we performed no quantitative intensity measurements on this compound as it was improbable that any difference between the α and the β forms could be detected by X-ray crystallographic measurements.

CRYSTAL DATA

The pertinent crystal data are presented below:

Crystal system: Monoclinic
Unit cell from Guinier powder diagrams with $\mathrm{Fe}K\alpha$-radiation:

$a = 12.25$ Å, $b = 13.18$ Å, $c = 16.46$ Å (± 0.01 Å), $\beta = 117.9° \pm 0.1°$

Space group: $C2/c$ No. 15, $(C_{2h}{}^6)$
Chemical formula: $\mathrm{Fe(C_5H_5N)_4(NCS)_2}$
Four formula units per unit cell

The coordinates found, their estimated standard deviations and the temperature factors are given in Table 1. Interatomic distances bond angles etc. are given in Tables 2—5. Structure factors are given in Table 6. A drawing of a molecule is shown in Fig. 2.
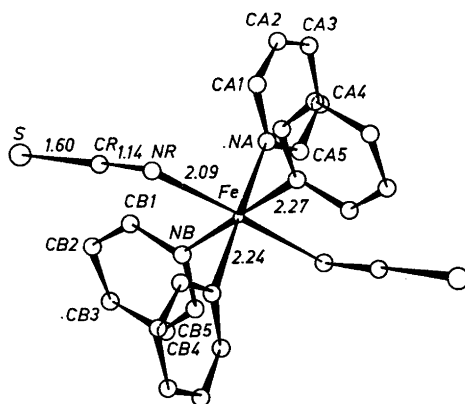

Fig. 2. Projection of a $\mathrm{Fepy_4(NCS)_2}$ molecule. Distances and angles are given in Tables 2—4.

Table 1a. Geometric parameters and their standard deviations as fractions of cell edges.

Atom	x/a	σx	y/b	σy	z/c	σz
Fe	0.50000		0.50000		0.50000	
S	0.09337	(12)	0.60538	(11)	0.41766	(11)
NR	0.34233	(34)	0.57914	(31)	0.48142	(27)
NA	0.55383	(32)	0.63072	(29)	0.43909	(25)
NB	0.39339	(32)	0.43756	(29)	0.35523	(25)
CR	0.23924	(40)	0.59042	(33)	0.45556	(29)
CA1	0.53468	(47)	0.72823	(41)	0.45293	(37)
CA2	0.57171	(53)	0.81063	(42)	0.42011	(42)
CA3	0.63111	(53)	0.79215	(52)	0.36987	(44)
CA4	0.64991	(58)	0.69305	(54)	0.35480	(44)
CA5	0.61084	(50)	0.61420	(42)	0.38932	(39)
CB1	0.29480	(44)	0.48568	(41)	0.28967	(34)
CB2	0.22653	(51)	0.44790	(56)	0.20250	(37)
CB3	0.25898	(53)	0.35630	(56)	0.17927	(36)
CB4	0.35916	(50)	0.30555	(46)	0.24542	(40)
CB5	0.42316	(45)	0.34862	(41)	0.33131	(36)
HA1	0.4893		0.7420		0.4892	
HA2	0.5559		0.8817		0.4337	
HA3	0.6608		0.8484		0.3449	
HA4	0.6910		0.6786		0.3163	
HA5	0.6261		0.5424		0.3763	
HB1	0.2701		0.5535		0.3039	
HB2	0.1524		0.4859		0.1574	
HB3	0.2119		0.3288		0.1163	
HB4	0.3844		0.2378		0.2319	
HB5	0.4965		0.3126		0.3773	

Table 1b. Thermal parameters and their standard deviations as u_{ij}. Mean square amplitudes, Å^2.

Atom	$\overline{U_{11}^2}$	$\overline{\sigma U_{11}^2}$	$\overline{U_{22}^2}$	$\overline{\sigma U_{22}^2}$	$\overline{U_{33}^2}$	$\overline{\sigma U_{33}^2}$
Fe	0.0334	(04)	0.0401	(05)	0.0390	(04)
S	0.0399	(06)	0.0657	(09)	0.0748	(09)
NR	0.0428	(21)	0.0566	(25)	0.0550	(22)
NA	0.0414	(20)	0.0458	(24)	0.0492	(21)
NB	0.0455	(21)	0.0486	(24)	0.0422	(18)
CR	0.0458	(24)	0.0373	(24)	0.0375	(21)
CA1	0.0654	(33)	0.0532	(33)	0.0618	(30)
CA2	0.0733	(39)	0.0482	(33)	0.0718	(35)
CA3	0.0676	(37)	0.0790	(45)	0.0752	(36)
CA4	0.0899	(44)	0.0845	(48)	0.0782	(38)
CA5	0.0659	(34)	0.0632	(35)	0.0671	(31)
CB1	0.0528	(26)	0.0683	(38)	0.0465	(24)
CB2	0.0585	(34)	0.1104	(54)	0.0414	(28)
CB3	0.0629	(36)	0.1186	(56)	0.0389	(26)
CB4	0.0620	(33)	0.0816	(42)	0.0570	(29)
CB5	0.0519	(28)	0.0586	(33)	0.0521	(27)

Atom	$\overline{U_{12}^2}$	$\overline{\sigma U_{12}^2}$	$\overline{U_{13}^2}$	$\overline{\sigma U_{13}^2}$	$\overline{U_{23}^2}$	$\overline{\sigma U_{23}^2}$
Fe	0.0026	(04)	0.0189	(04)	0.0018	(04)
S	0.0080	(06)	0.0239	(06)	0.0018	(08)
NR	0.0039	(19)	0.0268	(19)	−0.0010	(20)
NA	0.0021	(18)	0.0235	(18)	0.0056	(18)
NB	0.0023	(18)	0.0248	(17)	0.0015	(18)
CR	0.0026	(21)	0.0197	(20)	0.0032	(20)
CA1	0.0053	(27)	0.0349	(27)	0.0077	(27)
CA2	−0.0018	(29)	0.0259	(32)	0.0152	(29)
CA3	−0.0123	(33)	0.0367	(32)	0.0290	(35)
CA4	−0.0046	(38)	0.0594	(36)	0.0155	(36)
CA5	−0.0030	(28)	0.0432	(29)	0.0035	(29)
CB1	0.0103	(27)	0.0242	(22)	0.0120	(27)
CB2	0.0028	(35)	0.0161	(26)	0.0095	(32)
CB3	−0.0227	(37)	0.0243	(26)	−0.0147	(32)
CB4	−0.0148	(31)	0.0326	(28)	−0.0215	(31)
CB5	0.0002	(25)	0.0253	(24)	−0.0023	(25)

All hydrogens were given $\overline{U^2} = 0.0633$

Table 2. Interatomic distances and standard deviations in Å, uncorrected for thermal vibration.

Bond	l	σl
Fe−NR	2.088	(4)
Fe−NA	2.241	(4)
Fe−NB	2.268	(4)
NR−CR	1.140	(5)
CR−S	1.604	(4)
NA−CA1	1.348	(6)
CA1−CA2	1.378	(7)
CA2−CA3	1.343	(8)
CA3−CA4	1.363	(9)
CA4−CA5	1.374	(8)
CA5−NA	1.322	(6)
NB−CB1	1.341	(6)
CB1−CB2	1.370	(8)
CB2−CB3	1.373	(9)
CB3−CB4	1.372	(8)
CB4−CB5	1.371	(7)
CB5−NB	1.341	(6)

Table 3. The bond angles and their standard deviations (°).

	v	σv
NR−Fe−NA	89.80	0.14
NR−Fe−NB	89.46	0.14
NA−Fe−NB	87.35	0.13
Fe−NR−CR	155.28	0.40
NR−CR−S	179.04	0.43

Table 3. Continued.

NA—CA1—CA2	124.56	0.53
CA1—CA2—CA3	118.02	0.60
CA2—CA3—CA4	118.13	0.58
CA3—CA4—CA5	121.70	0.58
CA4—CA5—NA	121.14	0.56
CA5—NA—CA1	116.43	0.45
NB—CB1—CB2	123.03	0.54
CB1—CB2—CB3	120.03	0.56
CB2—CB3—CB4	117.94	0.55
CB3—CB4—CB5	118.77	0.58
CB4—CB5—NB	124.25	0.52
CB5—NB—CB1	115.98	0.44
Fe—NA—CA1	123.31	0.32
Fe—NA—CA5	120.21	0.35
Fe—NB—CB1	122.21	0.34
Fe—NB—CB5	121.78	0.32

Table 4. Interatomic distances in Å corrected for thermal motion assuming that second atom rides on first.

Bond	l	σl
Fe—NR	2.097	(4)
Fe—NA	2.247	(4)
Fe—NB	2.272	(4)
NR—CR	1.223	(6)
CR—S	1.629	(4)

Table 5. The shortest van der Waals distances in Å.

Bond	l
HB5—HB5	2.564
HB5—HB4	2.999
HB1—HA4	2.819
HB2—HA4	2.962
HB2—HA5	2.983
CB2—HA5	2.964
HB3—CR	3.042
HB3—S	3.045

DISCUSSION

The most obvious difference between the so-called α- and β-isomers is the colours. Their magnetic moments at room temperature are almost equal as first shown by Asmussen [15] and we have confirmed his results. We have also

Table 6. Observed and calculated structure factors.

Table 6. Continued.

Table 7. Determination of magnetic moments.

	T °K	$\chi_g \times 10^6$	μ_{eff} BM	Ref.
α-Fepy$_4$(NCS)$_2$		25.5	5.47	15
»			5.40	16
»	294.5	24.6	5.38	This paper
»	77	95.8	5.39	»
β-Fepy$_4$(NCS)$_2$		24.8	5.40	15
»			5.48	16
»	296	25.8	5.52	This paper
»	77	95.4	5.38	»
pyHFepy$_2$(NCS)$_4$	295.5	27.7	5.93	»
»	77	110.4	6.04	»

measured the magnetism at liquid nitrogen temperature and again found no detectable difference between the two forms. The magnetic measurements are given in Table 7.

The yellow α-isomer keeps its absorption spectrum unchanged for days and weeks when dissolved in pyridine. The black compound, however, quickly becomes yellow when dissolved in pyridine at room temperature and then exhibits an absorption spectrum which is identical with that of the α-compound. When the α-compound is dissolved in chloroform at 0°C it is almost colourless and remains so for hours. When the cold solution is heated to room
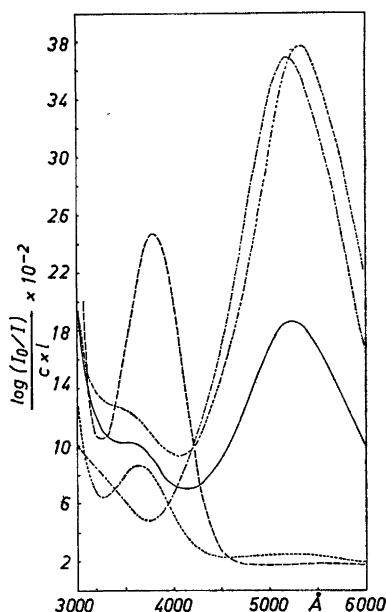

Fig. 3. Absorption spectra of iron-pyridine thiocyanates.
Full line: β-Fepy$_4$(NCS)$_2$ in chloroform,
- - - - - - : α-Fepy$_4$(NCS)$_2$ in ice-cold chloroform,
— — — : α-Fepy$_4$(NCS)$_2$ in pyridine,
· · · · · · : α-Fepy$_4$(NCS)$_2$ in chloroform after 20 min, at room temperature,
· · · · · : (C$_5$H$_6$N)Fepy$_2$(NCS)$_4$ in chloroform.

temperature in the presence of air it quickly turns red-violet. The β-form when dissolved in ice-cold pyridine remains red-violet for several minutes. The solution becomes yellow *via* a brownish colour when heated. Chloroform solutions of the yellow form which have turned red-violet recover their yellow colour when mixed with pyridine. Absorption spectra are shown in Fig. 3. Burbridge, Cleare, Goodgame [16] and Erickson and Sutin [17] report various physical measurements on the $Fe(C_5H_5N)_4(NCS)_2$. The latter authors report that solutions of the yellow compound in oxygen-free chloroform do not turn violet over prolonged periods. Both papers, Refs. 16 and 17, suggest that the α-compound is *trans* and that the β-compound is merely impure α.

We suggest the following simple explanation of the chemistry involved. The redox potentials: Fe^{3+}/Fe^{2+} and $NCS^-/\frac{1}{2}(NCS)_2$ are almost equal (0.78 V) and addition of ligands which form stronger complexes with Fe^{2+} than with Fe^{3+} will stabilize the ferrous state in the equilibrium reaction:

$$Fe^{3+} + NCS^- \rightleftharpoons Fe^{2+} + \tfrac{1}{2}(NCS)_2 \qquad (I)$$
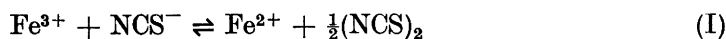
In the preparation of $C_5H_6N[Fe(III)(C_5H_5N)_2(NCS)_4]$ the pyridine concentration is too low to shift the equilibrium (I) to the right. In the next step where the compound is dissolved in pyridine the thiocyanate groups reduce the ferric state since pyridine probably forms stronger complexes with Fe^{2+} than with Fe^{3+}.

When $Fepy_4(NCS)_2$ is dissolved in oxygen free chloroform only dissociation processes are likely. When oxygen is allowed to enter the system various things may happen. The slowness of the reaction in cold chloroform suggests some form of autooxidation. It is likely that a ferric compound complexed with thiocyanate is formed as indicated by the absorption spectrum (Fig. 3) and by the fact that the yellow colour is reestablished by adding pyridine to the violet solutions. Since the alleged ferric component crystallizes in the

Table 8. Distances (in Å) and angles (°) in pyridine.

	X-Ray averaged over both molecules assuming symmetry 2	Micro-wave	Electr. diffr.
N−C1	1.338	1.340	1.377
C1−C2	1.373	1.394	1.377
C2−C3	1.363	1.394	1.377
C1−N−C5	116.20	116.83	
N−C1−C2	123.25	123.88	
C1−C2−C3	119.63	118.53	
C2−C3−C4	118.04	118.33	

lattice of $Fe(II)py_4(NCS)_2$ it is probably rather similar to this compound with respect to molecular structure.

The combined evidence from Refs. 16 and 17 and from this paper proves that so far only one isomer of $Fe(C_5H_5N)_4(NCS)_2$ has been prepared in a pure state and that the so-called "black" isomer is an impure phase.

Poraii-Koshits [18] has described the structures of $Ni(C_5H_5N)_4(NCS)_2$ and the analogus Co-compound in 1958. Although he did not determine all the atomic positions of these compounds there is enough evidence to suggest that they are isostructural with $Fe(C_5H_5N)_4(NCS)_2$. In the ferrous compound there are two crystallographically non-equivalent pyridine molecules. It is seen from Table 2 that the molecules are identical within experimental error. It is seen from Table 8 that their molecular dimensions are close to those found for free gaseous molecules by electron diffraction [19] and by microwave spectroscopy.[20] However, the pyridine molecules in this structure are apparently not strictly planar as seen from Table 9.

Table 9. Least squares planes through pyridine molecules.

The equation of the planes can be expressed as
$Px + Qy + Rz = S$ in direct space.

	Ring A		Ring B
$P =$	5.6388	$P = -$	9.6908
$Q =$	-7.9867	$Q = -$	2.0701
$R =$	5.8886	$R =$	14.695
$S =$	-0.90558×10^{-8}	$S = -$	0.95223×10^{-9}

Distances of the atoms from the least squares planes in Å:

	Ring A		Ring B
NA	-0.673	NB	-0.501
CA1	0.133	CB1	-0.391
CA2	0.772	CB2	0.146
CA3	0.584	CB3	0.612
CA4	-0.218	CB4	0.501
CA5	-0.832	CB5	-0.044

The standard deviations of the distances are for ring A 0.62 Å and for ring B 0.44 Å.

The two Fe—N distances appear to be significantly different. The iron atom and the six ligand atoms taken together have $\bar{1}$ symmetry. The dimensions of the NCS group are close to those of thiocyanate groups in a number of similar crystals. Unfortunately no structure analysis seems to be carried out using present days precision of measurements and of computations on simple ionic thiocyanates. Detailed discussion of bond order etc. is therefore not worthwhile.

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