Crystal Structures and Magnetic Behaviour of the Two Forms of Tetra-*n*-butylammonium Tetraisothiocyanatochromate(II)†

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From single-crystal X-ray studies, the red form of $[NBu_4]_2[Cr(CNS)_4]$, which has a temperature-independent magnetic moment of 4.76 μ_B over the range 85–300 K, has been found to contain planar $[Cr(NCS)_4]^{2-}$ ions in which the Cr–N bond distances are essentially equal [2.010(3) and 2.012(2) Å]. On the other hand, the blue form, which exhibits antiferromagnetic behaviour, has been found to contain dinuclear anions $[Cr_2(NCS)_8]^{4-}$. In these there are two thiocyanate bridges, and the distorted square-pyramidal co-ordination of each Cr is completed by three isothiocyanate ligands, the nitrogen atom of a bridging thiocyanate group, and the sulfur atom of the other bridging thiocyanate at the apex. The Cr–N distances are similar to those in the red salt, but the Cr–S distance at 2.72(2) Å is long. The magnetic behaviour can be reproduced by the substitution of the values $J = 8.76$ cm^{-1}, $g = 1.92$ and $N(\alpha) = 100 \times 10^{-6}$ cm^3 mol^{-1} in the standard expression for a dinuclear species with $S = 2$. The Cr$\cdots$Cr separation is 5.837(3) Å, and the structure is unrelated to that of quadruply bonded dinuclear chromium(II) complexes.

Chromium(II) forms[1] a series of tetrathiocyanato complexes: $A_2[Cr(CNS)_4]$ where A = NMe_4, NEt_4, NPr_4, NBu_4, Hhex, Hpy, $\frac{1}{2}H_2en$ or H_2L [hex = hexamine (hexamethylenetetramine; 1,3,5,7-tetraazatricyclo[3.3.1.1^{3,7}]decane), py = pyridine, en = ethylenediamine, and L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene]. Since most are antiferromagnetic they were assigned thiocyanate-bridged structures. However, $[NBu_4]_2[Cr(CNS)_4]$ was obtained in two crystal forms, one blue and one referred to earlier as brown (the more crystalline samples are red), which exhibited antiferromagnetic and simple paramagnetic behaviour respectively. It was assumed, from their reflectance spectra, that the complexes have thiocyanate-bridged structures in which the metal is tetragonally distorted six-co-ordinate, but that in 'brown' $[NBu_4]_2[Cr(CNS)_4]$ the bridging SCN groups are too distant to transmit magnetic interaction. These deductions are partly correct: from single-crystal X-ray investigations the red form contains isolated planar $[Cr(NCS)_4]^{2-}$ anions, but the blue antiferromagnetic isomer contains dimeric $[Cr_2(NCS)_8]^{4-}$ units in which the metal ion is in distorted square-pyramidal co-ordination with thiocyanate bridges.

Experimental

Preparation of Complexes.—As recorded earlier,[1] preparation of the two forms of $[NBu_4]_2[Cr(CNS)_4]$ is difficult because they are air-sensitive and tend to interconvert, especially in contact with solvent. One sample of the red crystals slowly turned blue over several weeks, some crystals showing a clearly defined boundary between the differently coloured regions. Red needles of $[NBu_4]_2[Cr(NCS)_4]$ were obtained by fairly rapid crystallisation induced by the application of an oil pump vacuum to a blue solution in absolute ethanol. Needles of the blue modification were prepared by slow crystallisation. All operations were carried out under nitrogen or in vacuum in glass apparatus or in an inert-atmosphere box with a recirculatory gas-purification system.

Crystal Structure Determination of the Red Form.—A needle-shaped single crystal of the red form of $[NBu_4]_2[Cr(NCS)_4]$ of approximate dimensions 0.2 × 0.2 × 0.4 mm was sealed in a Lindemann capillary under dry nitrogen. Unit-cell parameters were measured on an Enraf-Nonius CAD4 diffractometer from 25 accurately centred reflections in the range $11 \leqslant \theta \leqslant 14°$. Intensity data were collected over the range θ 1–25° covering the index ranges $-12 \leqslant h \leqslant +12$, $-14 \leqslant k \leqslant +14$ and $0 \leqslant l \leqslant 14$ using the ω–2θ scan method with a standard reflection measured hourly. After the usual Lorentz-polarisation reduction of the 4362 reflections, 3061 reflections had $I \geqslant 2.58\sigma(I)$. The standard reflection showed a loss of intensity of 12% over the data collection period, which was corrected for, and an empirical absorption correction was also applied using ψ-scan data.

Crystal data. $C_{36}H_{72}CrN_6S_4$, red form, $M_r = 769.27$, triclinic, space group $P\bar{1}$, $a = 10.077(1)$, $b = 11.796(2)$, $c = 11.819(1)$ Å, $\alpha = 108.2(1)$, $\beta = 107.8(2)$, $\gamma = 104.5(1)°$, $U = 1174(3)$ Å^3, $Z = 1$, $D_c = 1.087$ g cm^{-3}, $F(000) = 418$, graphite-monochromated, Mo-Kα radiation ($\lambda = 0.710\,73$ Å), μ(Mo-Kα) = 4.35 cm^{-1}.

Structure solution and refinement. Intensity statistics revealed a centric distribution indicating probable space group $P\bar{1}$, which considering the chemical formula implied that the Cr atom was at a centre of symmetry. From a Patterson map the position of one S atom was obtained and the usual structure factor/Fourier methods revealed the remaining non-hydrogen atoms.

Isotropic refinement of these atoms, with H atoms in calculated positions, but not refined, reduced R to 0.075. Anisotropic refinement of the non-hydrogen atoms reduced R' to 0.053 with $B = 5.0$ (methylene) and 8.0 Å^2 (methyl) for the calculated H-atom positions. At this point there appeared a small peak in the difference map of 0.7 e Å^{-3} at a position 1.5 Å from C(43), indicating an alternative site for the terminal methyl carbon [C(44)]. Refinements with occupancy factors for C(44) and C(44A) indicated the sites were 0.65 and 0.35 occupied

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

respectively. This ratio was kept fixed in the final refinement cycles when convergences were recorded at $R = 0.045$, $R' = 0.070$, estimated standard deviation (e.s.d.) of unit weight = 1.017 using a weighting scheme[2] $w^{-1} = \sigma(F^2) + (0.05F)^2 + 5.0$. The largest peak in the final Fourier difference map was 0.3 e Å^{-3}. Table 1 lists the atomic coordinates and Table 2 selected bond lengths and angles. The structure of the anion, atom numbering scheme, and the packing are shown in Fig. 1. All calculations were performed using the Enraf-Nonius Structure Determination Package.[3]

Crystal Structure Determination of the Blue Form.—Because of the sensitivity to air, a blue needle crystal of approximate dimensions 0.15 × 0.1 × 0.3 mm was sealed in a Lindemann capillary under dry nitrogen. Unit-cell parameters were measured as for the red form. Intensity data were collected in the range θ 1–25° covering the index ranges $0 \leqslant h \leqslant 15$, $0 \leqslant k \leqslant 12$ and $-18 \leqslant l \leqslant 18$ using the ω–2θ scan method with a standard reflection measured hourly. No ψ reflections were available.

After the usual Lorentz and polarisation corrections, of the 5471 unique reflections 2202 had $I \geqslant 2.58\sigma(I)$. Analysis of the intensity of the standard reflection showed negligible decay. The space group was uniquely determined as $P2_1/c$.

Crystal data. $C_{36}H_{72}CrN_6S_4$, blue form, $M_r = 769.27$, monoclinic, space group $P2_1/c$, $a = 14.099(4)$, $b = 21.399(4)$, $c = 17.290(4)$ Å, $\beta = 113.5(1)°$, $U = 4873(6)$ Å^3, $Z = 4$, $D_c = 1.068$ g cm^{-3}, $F(000) = 1672$, μ(Mo-Kα) = 4.28 cm^{-1}.

Structure solution and refinement. The position of the Cr atom was determined from the Patterson map and the usual heavy-atom method revealed the rest of the structure. Isotropic refinement of all non-hydrogen atoms, with H atoms in fixed calculated positions ($d_H = 1.0$ Å), converged at $R = 0.13$. The geometry of the dimeric $[Cr(NCS)_4]_2$ group was revealed but it became clear that the reduced number of good reflections was going to prevent an accurately refined structure. Large thermal disorder was present, particularly for the terminal methyl groups of the tetrabutylammonium ions where correlation between the coordinates and thermal vibration parameters was creating unrealistic interaction distances. Accordingly the methyl hydrogen atoms were excluded from the calculations. Anisotropy was carefully introduced, heavy atoms first, then the C and N atoms, keeping the terminal groups isotropic. The final $R = 0.075$, $R' = 0.101$, and e.s.d. of unit weight = 1.187 were obtained using[2] a weighting scheme $w^{-1} = \sigma(F^2) + (0.055F)^2 + 5.5$. The largest peak in the final difference map was 0.3 e Å^{-3}.

Final atomic coordinates are listed in Table 3, and selected bond distances and angles in Table 4. In the ORTEP[4] drawing of the dimeric anion (Fig. 2) the thermal ellipsoids have been drawn at 30% probability. The unattached terminal S atoms, S(1), S(2), S(3), are undergoing large thermal oscillations B_{eq} = 10–14 Å^2, while S(4), which forms the dimeric link, is more restricted. The overall packing of the structure is loose and only three intermolecular contacts are less than 3.7 Å.

The determination of the geometry of the tetrabutylammonium groups is far from satisfactory. That based on N(5) is better than that based on N(7), but in both ions the thermal vibration parameters increase greatly along each butyl chain attaining unrealistically high values of B = 21, 30 and 25 Å^2 for C(74), C(82) and C(86) respectively. This high thermal disorder, which is probably the cause of the restricted data set, also extends to the third carbon atom position in the chain, where high B values also occur, and, as a result, the interaction distances are well below expected values. However, the bond angles do not seem to have been affected. The lack of an absorption correction is not thought to play an important role as the absorption coefficient is relatively small.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Final atomic coordinates for non-hydrogen atoms in the red form of $[NBu_4]_2[Cr(NCS)_4]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cr	0.000	0.000	0.000
S(1)	0.237 1(1)	0.415 77(9)	0.359 52(8)
S(2)	0.333 48(9)	0.146 13(8)	−0.183 49(7)
N(1)	0.106 5(2)	0.169 2(2)	0.160 2(2)
N(2)	0.146 5(3)	0.061 3(2)	−0.071 9(2)
C(1)	0.161 1(3)	0.271 2(3)	0.244 7(2)
C(2)	0.223 3(3)	0.098 1(2)	−0.118 7(2)
N	0.674 4(2)	0.272 8(2)	0.267 1(2)
C(11)	0.545 7(3)	0.174 8(2)	0.269 8(2)
C(12)	0.523 6(3)	0.214 9(3)	0.394 8(3)
C(13)	0.403 0(4)	0.102 4(3)	0.387 7(3)
C(14)	0.373 8(5)	0.135 1(4)	0.508 9(4)
C(21)	0.647 6(3)	0.396 1(2)	0.280 1(2)
C(22)	0.506 9(3)	0.384 3(2)	0.175 4(2)
C(23)	0.502 1(3)	0.517 4(3)	0.200 3(3)
C(24)	0.363 9(4)	0.513 1(3)	0.101 4(4)
C(31)	0.679 6(3)	0.207 6(2)	0.135 8(2)
C(32)	0.789 7(3)	0.288 2(3)	0.102 7(2)
C(33)	0.778 4(3)	0.208 9(3)	−0.031 8(3)
C(34)	0.892 7(4)	0.279 0(4)	−0.069 2(3)
C(41)	0.823 9(3)	0.312 0(2)	0.380 4(2)
C(42)	0.870 9(3)	0.204 0(3)	0.393 8(3)
C(43)	1.008 5(4)	0.251 0(3)	0.522 3(3)
C(44)	0.985 2(6)	0.288 8(6)	0.639 1(5)
C(44A)	1.024(2)	0.147(1)	0.560(2)

Table 2 Selected bond lengths (Å) and angles (°) for the red form, with e.s.d.s in parentheses

Cr–N(1)	2.012(2)	N(1)–Cr–N(2)	89.79(9)
Cr–N(2)	2.010(3)	Cr–N(1)–C(1)	173.5(3)
S(1)–C(1)	1.614(2)	Cr–N(2)–C(2)	175.4(3)
S(2)–C(2)	1.617(3)	S(1)–C(1)–N(1)	178.2(3)
N(1)–C(1)	1.154(3)	S(2)–C(2)–N(2)	178.1(3)
N(2)–C(2)	1.156(4)		

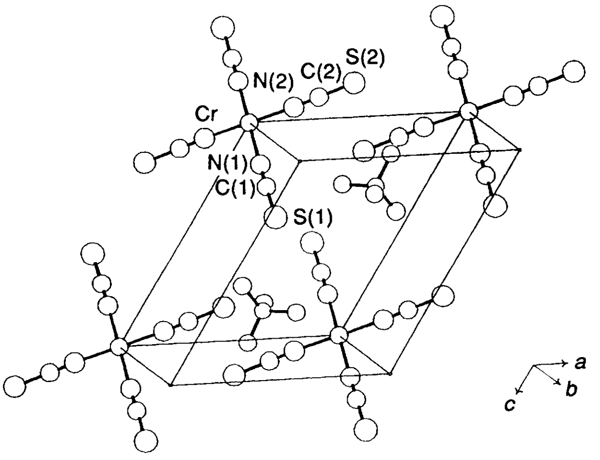

Fig. 1 Packing diagram, atom numbering scheme and structure of the square-planar anion of the red form of $[NBu_4]_2[Cr(NCS)_4]$. Only the nitrogen and neighbouring carbon atoms of the cations are shown

Discussion

Properties of the Red Form.—The effective magnetic moment μ_{eff} of red $[NBu_4]_2[Cr(CNS)_4]$ is 4.76 μ_B independent of temperature down to liquid-nitrogen temperature.[1] Since for a high-spin 3d^4 ion ($S = 2$) the spin-only magnetic moment μ_{SO} is 4.90 μ_B this is consistent with the monomeric planar structure found for the $[Cr(NCS)_4]^{2-}$ ions (Fig. 1). The simplified packing diagram shows how the discrete planar anions are well separated by the large $[NBu_4]^+$ cations so that there is no pathway for magnetic interaction. There are no short interion distances within the structure. In planar $[Cr(NCS)_4]^{2-}$ the

Table 3 Final atomic coordinates for non-hydrogen atoms in the blue form of $[NBu_4]_2[Cr(NCS)_4]$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cr	0.047 9(2)	0.899 05(8)	0.408 0(1)
S(1)	0.183 7(3)	0.690 1(2)	0.463 1(2)
S(2)	−0.285 8(3)	0.820 5(2)	0.231 6(3)
S(3)	0.350 4(4)	0.953 8(3)	0.364 0(3)
S(4)	−0.080 1(3)	1.103 7(1)	0.426 1(2)
N(1)	0.102 8(7)	0.811 0(4)	0.429 2(5)
N(2)	−0.097 1(8)	0.867 0(5)	0.347 6(6)
N(3)	0.179 2(7)	0.928 9(5)	0.400 4(6)
N(4)	−0.005 0(7)	0.987 4(4)	0.398 7(5)
C(1)	0.136 2(8)	0.760 3(6)	0.443 1(6)
C(2)	−0.172 8(9)	0.847 9(5)	0.297 1(7)
C(3)	0.251(1)	0.938 9(6)	0.386 3(7)
C(4)	−0.035 9(8)	1.035 3(5)	0.408 4(6)
N(5)	0.038 6(7)	0.702 6(4)	0.653 6(5)
N(7)	0.392 3(7)	−0.010 2(4)	0.706 1(6)
C(51)	−0.008 5(8)	0.728 8(5)	0.711 2(6)
C(52)	−0.027(1)	0.798 0(6)	0.706 5(7)
C(53)	−0.089(1)	0.816 5(6)	0.753 6(8)
C(54)	−0.106(1)	0.883 5(9)	0.750(1)
C(55)	−0.028(1)	0.714 5(5)	0.561 2(7)
C(56)	−0.138(1)	0.688 3(6)	0.528 1(8)
C(57)	−0.192(1)	0.701 5(7)	0.435 5(9)
C(58)	−0.303(1)	0.677(1)	0.402(1)
C(59)	0.141 7(9)	0.733 0(5)	0.670 1(7)
C(60)	0.222(1)	0.725 4(6)	0.757 6(8)
C(61)	0.325(2)	0.753(1)	0.762(1)
C(62)	0.386(2)	0.753(2)	0.831(2)
C(63)	0.051 3(9)	0.631 0(5)	0.670 0(7)
C(64)	0.100(1)	0.596 5(5)	0.619 9(7)
C(65)	0.107(1)	0.528 8(6)	0.640 0(8)
C(66)	0.154(1)	0.490 7(8)	0.596(1)
C(71)	0.464 7(9)	0.038 0(7)	0.764 1(9)
C(72)	0.534(1)	0.018 8(9)	0.849(1)
C(73)	0.589(2)	0.072(1)	0.908(1)
C(74)	0.538(2)	0.105(1)	0.946(2)
C(75)	0.331(1)	−0.045 9(6)	0.746 8(8)
C(76)	0.275(1)	−0.009 4(6)	0.783 2(8)
C(77)	0.223(1)	−0.050 1(7)	0.826 1(8)
C(78)	0.165(1)	−0.014(1)	0.862(1)
C(79)	0.455(1)	−0.056 0(7)	0.680(1)
C(80)	0.406(1)	−0.105 0(8)	0.623 0(9)
C(81)	0.483(2)	−0.153(1)	0.613(1)
C(82)	0.450(3)	−0.190(2)	0.562(2)
C(83)	0.315(1)	0.023 7(6)	0.628 1(8)
C(84)	0.350(1)	0.058 6(9)	0.575(1)
C(85)	0.269(1)	0.101(1)	0.509 5(9)
C(86)	0.301(2)	0.144(2)	0.481(2)

Table 4 Selected bond lengths (Å) and angles (°) for the blue salt, with e.s.d.s in parentheses

Cr ⋯ Cr	5.837(3)	S(4)–C(4)	1.667(11)
Cr–N(1)	2.016(9)	N(1)–C(1)	1.168(15)
Cr–N(2)	2.009(10)	N(2)–C(2)	1.150(13)
Cr–N(3)	2.010(11)	N(3)–C(3)	1.15(2)
Cr–N(4)	2.016(9)	N(4)–C(4)	1.153(14)
S(1)–C(1)	1.627(12)	Cr–S(4′)	2.72(2)
S(2)–C(2)	1.651(11)		
S(3)–C(3)	1.63(2)		
N(1)–Cr–N(2)	90.7(4)	S(1)–C(1)–N(1)	179.5(6)
N(1)–Cr–N(3)	90.7(4)	S(2)–C(2)–N(2)	175(1)
N(1)–Cr–N(4)	174.4(4)	S(3)–C(3)–N(3)	179(1)
N(2)–Cr–N(3)	147.8(4)	S(4)–C(4)–N(4)	178(1)
N(2)–Cr–N(4)	90.6(4)	S(4′)–Cr–N(1)	84.2(4)
N(3)–Cr–N(4)	91.1(4)	S(4′)–Cr–N(2)	104.4(4)
Cr–N(1)–C(1)	178.5(7)	S(4′)–Cr–N(3)	107.7(4)
Cr–N(2)–C(2)	164(1)	S(4′)–Cr–N(4)	90.3(4)
Cr–N(3)–C(3)	169(1)	Cr′–S(4)–C(4)	105.0(4)
Cr–N(4)–C(4)	166.6(9)		

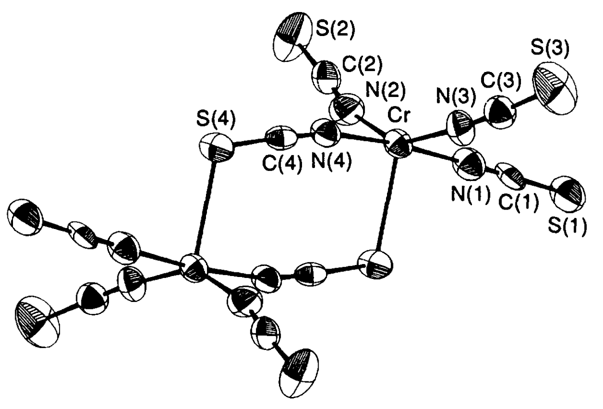

Fig. 2 Atom numbering scheme and structure of the centrosymmetric dimeric anion $[Cr_2(NCS)_8]^{4-}$ in the blue form of $[NBu_4]_2[Cr(NCS)_4]$

Cr–N bonds are of equal length within experimental error, as are the corresponding bonds within the N-bonded ligands (Table 2). The C–N (1.155 Å) and C–S (1.616 Å) distances are within the ranges found in other isothiocyanato complexes.[5] The bond lengths and angles of the tetrabutylammonium cations show no unusual features except that the disorder of one terminal methyl group leads to an apparent shortening of the C(43)–C(44) [1.423(7)] and C(43)–C(44A) [1.45(2) Å] bonds below that expected for carbon–carbon single bonds.

Properties of the Blue Form.—The temperature-dependent magnetic moment of blue $[NBu_4]_2[Cr(CNS)_4]$ (μ_{eff} = 4.30 and 3.36 μ_B at 295 and 90 K respectively) was earlier assumed to be due to antiferromagnetic interaction in a thiocyanate-bridged infinite linear chain, but the magnetic data could be fitted[1] only approximately to Smith and Friedberg's expression. However, although the crystal structure (Fig. 2) is very different from that of the brown form, only dimeric anions are present. These are well separated by the cations and the magnetic data can be fitted much more satisfactorily by the standard expression[6] (1) for a dinuclear species with $S = 2$, where $x = e^{J}/kT$, $K = Ng^2\beta^2/3k = 0.1251g^2$ and J = 8.76 cm^{-1}, g = 1.92 and $N(\alpha)$ = 100 × 10^{-6} cm^3 mol^{-1}.

$$\chi_{Cr} = \frac{3K}{T}\left(\frac{30 + 14x^8 + 5x^{14} + x^{18}}{9 + 7x^8 + 5x^{14} + 3x^{18} + x^{20}}\right) + N(\alpha) \quad (1)$$

This anion is the first of its type for chromium(II). Dinuclear chromium(II) carboxylates in which there is strong metal–metal interaction are well known.[7] The metal–metal separation is 2.2–2.6 Å and the compounds are almost diamagnetic.[8] The Cr ⋯ Cr separation is much greater in $[Cr_2(NCS)_8]^{4-}$ [5.837(3) Å] so that direct metal–metal interaction is excluded. Fig. 2 shows that the square-planar nature of the four NCS groups around the metal atoms in the centrosymmetrical anions $[Cr_2(NCS)_8]^{4-}$ is approximately retained but that distorted square-pyramidal co-ordination is achieved through weak binding to the terminal sulfur atom S(4) of an adjacent unit. Although atoms N(1), N(2), N(3) and N(4) lie approximately in the same plane, the angles these atoms subtend at the metal atom differ considerably from 90 or 180°, notably N(2)–Cr–N(3) which is 147.8°, and the apical Cr–S bond makes angles ranging from 84 to 108° with the Cr–N bonds. The square-pyramidal arrangement is grossly distorted towards a trigonal-bipyramidal structure in which the N(4),Cr,N(1) atoms would be along the principal axis. The Cr–N bonds are similar in length (Table 4) to those of the red form, as are the C–S and C–N bonds of the isothiocyanate ligands. The Cr–S distance (2.72 Å) is longer than that in the planar anion of $[NEt_4]_2[Cr(S_2C_2H_4)_2]$ (average 2.39 Å),[9] indicating the distortion in this structure and the weakness of the Cr–S bond. However, there is considerable variation in the dimensions of the ligands of the blue form: C–S, 1.627 to 1.667 Å; C–N, 1.150 to 1.168 Å; and angle at carbon, 175 to 179.5°. This explains the greater complexity of the thiocyanate infrared spectrum[1] of the blue form compared with that of the red form. The formation of the red from the blue form must involve breaking of the weak Cr–S bonds accompanied by insertion of the $[Cr(NCS)_4]^{2-}$ residues between the cations. The reverse processes seem equally facile, but the energetics have not been investigated.

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