Stacked Planar Molecules in Antiferromagnetic Di-isothiocyanatobis(thiourea)chromium(II), a New Structural Type for Chromium(II) †

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The structure of $[Cr(NCS)_2(tu)_2]$ where tu is thiourea, comprises *trans*-planar units stacked along the *a* axis in infinite parallel chains with a Cr ••• Cr separation of 3.97 Å. The separation between sulphur atoms in neighbouring chains is less than a van der Waals diameter, and so S ••• S interactions may contribute to the stack formation. Other bond lengths in the co-ordination sphere are Cr–NCS 2.026(3) Å and Cr–S(tu) 2.486(1) Å. The temperature dependent magnetic behaviour ($\mu_{eff.}$ = 4.53 at 291 K and 4.05 at 90 K) can be reproduced by substitution of $J = -2.7$ cm^{-1} and $g = 1.96$ in Smith and Friedberg's expression for antiferromagnetism in a chain of interacting spins with $S = 2$. The weak interaction probably arises from direct Cr ••• Cr interaction but weak interchain interaction cannot be excluded.

Several different structural types of chromium(II) complex have been demonstrated by *X*-ray single-crystal methods, or inferred from magnetic and spectroscopic properties.[1] Many have dinuclear structures analogous to that of the acetate $[Cr_2(O_2CCH_3)_4(H_2O)_2]$ in which the Cr ••• Cr separation is 2.362 Å.[2] In others, such as the tetrachlorochromates(II), $[NRH_3]_2[CrCl_4]$, R = Me[3] or Et,[4] and $CrCl_2{\cdot}4H_2O$,[5] the metal ions are in tetragonally distorted, six-co-ordination. Some planar complexes and a few five co-ordinate species are also known.[1] The title complex $[Cr(NCS)_2(tu)_2]$, where tu = thiourea, has an uncommon structure not previously encountered in chromium(II) chemistry, with stacked *trans*-$[Cr(NCS)_2(tu)_2]$ units.

Experimental

Preparation of Di-isothiocyanatobis(thiourea)chromium(II).—Bright green needles of the complex soon separated when aqueous thiourea (1.65 g, 25 cm^3) was added to an aqueous solution (50 cm^3) containing chromium(II) bromide hexahydrate (3.40 g) and ammonium thiocyanate (1.62 g) in 1:2 molar ratio. The *crystals* were filtered off, washed with ice-cold water, and dried at the pump for 12 h. The dry solid is stable for some time in air (Found: C, 15.0; H, 2.45; Cr, 16.3; N, 26.5. Calc. for $C_4H_8CrN_6S_4$: C, 15.0; H, 2.50; Cr, 16.2; N, 26.2%). I.r. spectrum: 2 068s,br [ν(CN)], 970w,br, 826m [ν(CS)], 490m, 475m, 465m, 354m,br [ν(M•NCS)], and 264s,br cm^{-1}. Diffuse reflectance spectrum: 27 000s, vbr, 15 600s ($5B_{1g} \longrightarrow {}^5B_{1g}, {}^5E_g$) and 10 800m cm^{-1} (${}^5B_{1g} \longrightarrow 5A_{1g}$). The last two bands were better resolved and shifted to 15 200 and 10 500 cm^{-1} at liquid nitrogen temperature.

X-Ray Structure Determination.—Unlike most chromium(II) complexes $[Cr(NCS)_2(tu)_2]$ is reasonably air-stable once dry, but to prevent slow decomposition a crystal (0.6 × 0.2 × 0.2 mm) was sealed in a Lindemann capillary under nitrogen. The unit-cell dimensions were determined by least-squares refinement of a set of 25 reflections [$0.32 \leqslant (\sin\theta)/\lambda \leqslant 0.36$].

Crystal data. $C_4H_8CrN_6S_4$, $M = 320.4$, triclinic, space group $P\bar{1}$, $a = 3.973(1)$, $b = 7.538(2)$, $c = 10.248(1)$ Å, $\alpha = 82.57(2)$, $\beta = 77.52(2)$, $\gamma = 76.91(2)°$, $Z = 1$, $U = 291.8(6)$ Å^3, $F(000) = 162$, $D_c = 1.829$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 16.3$ cm^{-1}.

The intensity data were collected on an Enraf-Nonius CAD4. four-circle diffractometer in a ω—2θ scan mode. 1 013 Reflections were collected [$(\sin\theta)/ \leqslant 0.59$] of which 915 were unique and 872 were considered to be observed [$I \geqslant 3.0\sigma(I)$]. The data were corrected for Lorentz and polarisation effects, and absorption (Ψ scans to determine the transmission surface). A reference reflection measured every 30 min of exposed *X*-ray time showed no significant change in intensity. The crystals were found to be triclinic, and an examination of the *E* statistics indicated the space group to be $P\bar{1}$.

The three-dimensional Patterson synthesis revealed the positions in the unit cell of the chromium atom and one of the sulphur atoms. Conventional Fourier techniques then revealed the positions of all non-hydrogen atoms in the structure.

Five cycles of least-squares refinement, with all thermal parameters anisotropic, reduced *R* to 0.033. All hydrogen atoms were then found from a Fourier difference synthesis. Introducing these into the structure factor calculations, but not into the least-squares procedure, further reduced *R* to 0.030. At this stage the Cruickshank weighting scheme $w = 1/(a + bF_o + cF_o^2 + dF_o^3)$ was applied with $a = 28.22$, $b = 1.0$, $c = 0.0024$, and $d = 0.000\,01$. Four cycles of further refinement produced final values of $R = 0.026$ and $R' = 0.038$.

Final atomic parameters are given in Table 1 and bond lengths and angles in Table 2. The computations were carried out using the SDP-Plus suite of programs[6] on a DEC PDP 11/73 computer.

Additional material available from the Cambridge Crystallographic data centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths.

Results and Discussion

The structure (Figure 1) consists of *trans*-$[Cr(NCS)_2(tu)_2]$ units (Figure 2) stacked along the *a* axis of the unit cell so that the Cr ions lie in infinite parallel linear chains. Other examples of this type of structure, where direct interaction between metal ions is possible, are limited to d^8 metal complexes, *e.g.* $[Ni(dmg)_2]$[7] (Hdmg = dimethylglyoximate), which are diamagnetic; $[Cr(NCS)_2(tu)_2]$ is the first example of chains of directly interacting paramagnetic metal ions. However, the Cr ••• Cr separation is large (3.97 Å) and the complex is consequently only weakly antiferromagnetic. The effective

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: χ_A(c.g.s.) = 4π × 10^{-6} cm^3 mol^{-1}.

Table 1. Final atomic co-ordinates for $[Cr(NCS)_2(tu)_2]$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Cr	0.000	0.000	0.000
S(1)	0.418 3(2)	0.289 9(1)	−0.452 19(8)
S(2)	0.293 3(2)	0.244 2(1)	0.033 88(7)
N(1)	0.120 3(7)	0.100 8(4)	−0.193 5(3)
N(2)	0.354 3(8)	0.447 9(4)	0.211 6(3)
N(3)	0.119 9(8)	0.200 1(4)	0.301 1(3)
C(1)	0.243 9(8)	0.179 0(4)	−0.291 0(3)
C(2)	0.250 2(8)	0.300 1(4)	0.195 6(3)

Table 2. Bond lengths (Å) and angles (°) in $[Cr(NCS)_2(tu)_2]$ with e.s.d.s in parentheses

Cr–S(2)	2.486(1)	S(2)–Cr–N(1)	81.26(8)
Cr–N(1)	2.026(3)	Cr–S(2)–C(2)	117.9(3)
N(1)–C(1)	1.163(5)	Cr–N(1)–C(1)	162.6(3)
C(1)–S(1)	1.822(3)	N(1)–C(1)–S(1)	174.7(3)
S(2)–C(2)	1.726(3)	S(2)–C(2)–N(2)	117.8(3)
C(2)–N(2)	1.313(5)	S(2)–C(2)–N(3)	122.4(3)
C(2)–N(3)	1.315(5)	N(2)–C(2)–C(3)	119.9(4)
Cr • • • Cr[a]	3.973(0)		
S(1) • • • S(1)[b]	3.357(2)		

[a] $1 + x, 1 + y, 1 + z$. [b] $1 - x, 1 - y, -1 - z$.

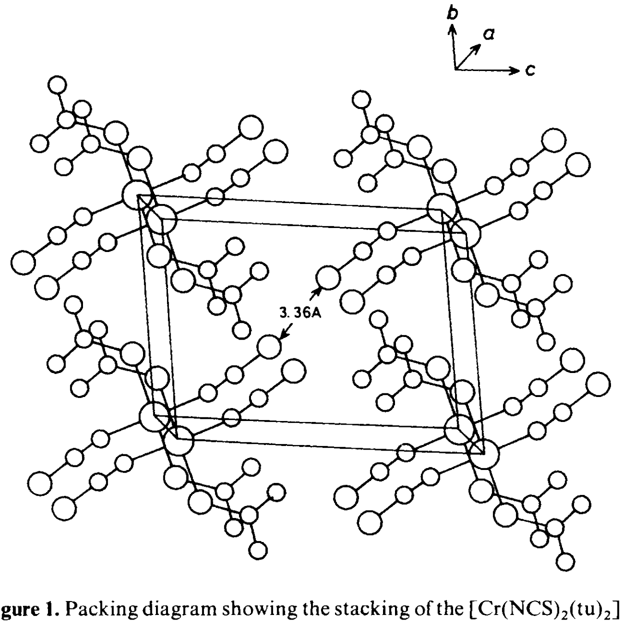

Figure 1. Packing diagram showing the stacking of the $[Cr(NCS)_2(tu)_2]$ molecules along the *a* axis

magnetic moment decreases as the temperature is lowered (Table 3) and the magnetic data fit well by Smith and Friedberg's expression[8] for an infinite chain of $S = 2$ ions with $J = -2.7$ cm^{-1} and $g = 1.96$. It is presumably direct Cr • • • Cr interaction *via* σ overlap of the half-filled d_{z^2} orbitals which leads to the antiferromagnetism. The Cr • • • Cr separation of 3.97 Å is much greater than in the acetate (which is almost diamagnetic and formally considered to contain one σ, two π, and one δ bond[2]), and is too great to provide a conductance pathway. Consequently a single crystal of the complex was found to be an insulator.

The distance between the sulphur atoms S(1) and S(1) of molecules in neighbouring chains is 3.36 Å. This is less than the sum (3.70 Å)[9] of the van der Waals radii of two sulphur atoms so there appears to be a weak interaction between the stacked chains *via* the unsaturated isothiocyanato-ligands: Cr–N≡C–S • • • S–C≡N–Cr. This may provide a super-exchange pathway although effects transmitted through six atoms would be expected to be very weak. The contribution of this interaction to the lattice energy may however be important, and favour the observed stacked structure over alternative thiocyanato-bridged structures. Stacking is also favoured by the Cr • • • Cr interaction, and the growth axis (from oscillation photographs) coincides with the stacking direction. The isolation of the stacked complex was surprising since many thiocyanato-bridged complexes are known.[10]

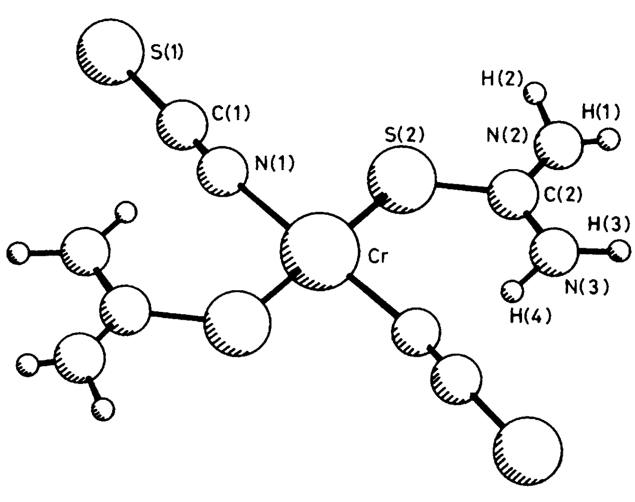

Figure 2. Atom numbering scheme for $[Cr(NCS)_2(tu)_2]$

Table 3. Variation of effective magnetic moment, $\mu_{eff.}$, and molar susceptibility, χ_A, of $[Cr(NCS)_2(tu)_2]$ with temperature

$10^6\ \chi_A$/c.g.s. units[a,b]	$\mu_{eff.}$[c]	*T*/K
8 818	4.53	290.5
9 708	4.53	262.3
10 950	4.49	230.0
12 610	4.47	198.5
14 390	4.38	166.5
16 850	4.27	135.5
20 610	4.13	108.5
22 880	4.05	89.5

[a] Corrected for diamagnetism, $10^6\chi_L = 146$. [b] Curie–Weiss law followed, Weiss constant $\theta = 36°$. [c] $\mu_{eff.} = 2.828\ (\chi_A T)^{\frac{1}{2}}$.

The Cr–N bond distance (2.025 Å) is similar to that in planar $[Cr(NCS)_4]^{2-}$,[11] but the Cr–S bond distance (2.486 Å) is somewhat greater than in the planar anion $[Cr(S_2C_2H_4)_2]^{2-}$ (2.390 Å).[12] The dimensions of the NCS^- ligands are similar to those found in other isothiocyanato complexes.[10,11] In the thiourea ligand the C(2)–S(2) bond length of 1.73 Å is longer than expected for a double bond, and the C(2)–N(3) bonds of *ca.* 1.31 Å are shorter than expected for single bonds; the bond order is approximately 1.33 in each case.

The i.r. spectrum of $[Cr(NCS)_2(tu)_2]$ is consistent with N-bonded thiocyanate ligands since the CN stretching vibration (Experimental section) is typical of chromium(II) in a highly distorted environment.

Some examples of chromium(II) halides with thiourea and substituted thioureas have been reported.[13] Only the chlorides, *e.g.* $[CrCl_2(tu)_2]$, exhibited antiferromagnetic behaviour which was presumed due to chloride-bridged polymeric structures.

However, no crystallographic data were obtained, and the possibility of stacked structures can no longer be excluded.

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