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Polyhedron 22 (2003) 2839–2845

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$[Cr(C_6H_{18}N_4)(SbS_3)]$, a chromium complex containing an unusual bidentate SbS_3^{3-} ligand

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Received 6 May 2003; accepted 19 June 2003

Abstract

A new chromium-antimony–sulfide, $[Cr(C_6H_{18}N_4)(SbS_3)]$, has been synthesised under solvothermal conditions from $CrCl_3 \cdot 6H_2O$, Sb_2S_3 and S in the presence of triethylenetetramine at 433 K and characterised by single-crystal X-ray diffraction, thermogravimetry, elemental analysis and SQUID magnetometry. The structure of $[Cr(C_6H_{18}N_4)(SbS_3)]$ consists of neutral mononuclear chromium-centred complexes, in which the Cr^{3+} is chelated by one tetradentate triethylenetetramine molecule and a bidentate SbS_3^{3-} ligand, yielding distorted octahedral coordination. Intermolecular hydrogen bonds link individual molecules into layers within the *ac* plane. Within a layer, molecules occur in pairs with each member related by a centre of inversion. The $Cr\cdots Cr$ separation within a pair is approximately 6.5 Å. Magnetic susceptibility data reveal Curie–Weiss behaviour with $\mu_{eff} = 3.819(3)\mu_B$ and a negligible Weiss constant, indicative of non-interacting Cr^{3+} ions.

Keywords: Solvothermal synthesis; Chromium thioantimonates; Crystal structure

1. Introduction

Solvothermal synthesis, in which a template molecule such as an organic amine directs the crystallisation of an inorganic matrix, is increasingly used to prepare novel solid-state materials. The technique has been applied with great success to the synthesis of a range of oxide materials [1–3] that are inaccessible by conventional high-temperature preparative methods. Following the report [4] that template-directed synthesis could be applied to effect the crystallisation of tin and germanium sulfides, there has been considerable interest in the solvothermal synthesis of chalcogenides. The majority of materials produced to date contain the main-group elements arsenic, antimony, tin, indium and germanium. The structural features of these materials have been recently reviewed [5,6]. In the case of antimony, the primary structural unit is the SbS_3 trigonal pyramid, linkage of which may generate a range of chain-like motifs, exemplified by the $Sb_4S_7^{2-}$ chains [7] formed by three corner-sharing SbS_3 units arranged into Sb_3S_6 rings and connected through a fourth SbS_3 unit. Two types of SbS_2^- chains, in which SbS_3 pyramids are either vertex-linked [8] or edge-linked [9], are also commonly observed. Considerable structural variety is introduced by the ability of Sb(III) to extend its coordination number beyond three and the resulting secondary Sb–S interactions serve to link individual chains to form structures of higher dimensionality. In addition, S–S [10] and Sb–Sb [11] linkages have been reported.

There have been relatively few reports of the incorporation of transition-metal ions into the primary bonding antimony–sulfide network. The majority of solvothermal reactions carried out in the presence of transition metals result in the formation of anionic antimony–sulfide frameworks charge-balanced by a cationic transition-metal complex, as exemplified by $[M(en)_3][Sb_2S_4]$ (M = Co, Ni), $[M(en)_3][Sb_4S_7]$ (M = Fe, Ni) [8] and $[Fe(C_4H_{13}N_3)_2][Sb_6S_{10}] \cdot 0.5H_2O$ [12]. However, incorporation of transition-metal ions into the primary bonding network does occur in

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0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00403-0

$[Co(en)_3][CoSb_4S_8]$ [13], in which parallel SbS_2^- chains are linked by tetrahedrally coordinated Co(II) atoms into $CoSb_4S_8^{2-}$ layers that contain rectangular holes, above and below which reside the $[Co(en)_3]^{2+}$ cations. Similarly, the preparation of $[C_3H_{10}N_2][Mn_2Sb_2S_5]$, a neutral manganese–antimony–sulfide framework containing MnS_6 octahedra, has been described [14]. Copper ions appear to be more readily incorporated than the early transition-series elements into the primary bonding network. In $[M(NH_3)_6][Cu_8Sb_3S_{13}]$ (M = Fe, Mn, Ni) [15], Cu_8S_{13} cores are linked by antimony atoms to form channels which contain transition-metal hexamine cations. The mixed-valent Cu(I)/Cu(II) sulfide $[C_2H_8N_2]_{0.5}[Cu_2SbS_3]$ [16] and the isostructural selenide [17] have also been reported and the copper–antimony–sulfide, $[C_4H_{12}N_2]_{0.5}[CuSb_6S_{10}]$, in which pairs of edge-sharing CuS_4 distorted tetrahedra form pillars that link $Sb_6S_{10}^{2-}$ layers together, has recently been described [18].

Our investigations have focused on introducing transition-series elements into antimony sulfide networks through reactions in which long-chain polyamines are present as structure-directing agents. Here we report the synthesis and characterisation of a new monomeric chromium-antimony sulfide, $[Cr(C_6H_{18}N_4)(SbS_3)]$, prepared in the presence of a triethylenetetramine template. This material contains the very unusual feature of a bidentate SbS_3^{3-} ligand and represents, after $[Cr(en)_2(SbS_3)]$ [19], only the second reported example of its occurrence.

2. Experimental

2.1. Synthesis and characterisation

Sb_2S_3 (0.25 g; 0.75 mmol), $CrCl_3 \cdot 6H_2O$ (0.39 g; 1.5 mmol) and S (0.096 g; 3 mmol) were loaded into a Teflon-lined stainless steel autoclave (23 ml). An aqueous solution (4 ml) of 75 vol.% triethylenetetramine (trien, Aldrich, 60%) was then added to form a mixture with an approximate molar composition Sb_2S_3:$CrCl_3 \cdot 6H_2O$:S:trien:H_2O of 1:2:4:27:74. After stirring the mixture, the container was closed, heated at 433 K for 7 days, and then cooled to room temperature using a cooling rate of 20 K h^{-1}. The solid product was filtered, washed with ethanol and deionised water and dried in air at room temperature. The product consists of a mixture of black blocks of the title compound and a small amount of polycrystalline powder. Powder X-ray diffraction data on a ground portion of the bulk sample were collected with nickel-filtered Cu Kα radiation ($\lambda = 1.5418$ Å), using a Philips PA2000 powder diffractometer. All peaks in the diffraction pattern can be indexed on the basis of the orthorhombic unit cell determined from the single-crystal diffraction study, with refined lattice parameters, $a = 13.666(7)$, $b = 13.961(5)$, $c = 14.632(6)$ Å suggesting that the sample is monophasic.

The black blocks were separated from the bulk sample by handpicking. Combustion analysis gave C, 17.15; H, 4.56 and N, 13.06% which compares favourably with the values calculated from the crystallographically determined formula $[Cr(C_6H_{18}N_4)(SbS_3)]$ (C, 17.3; H, 4.3 and N, 13.5%). Thermogravimetric analysis was performed using a DuPont Instruments 951 thermal analyser. Approximately 9 mg of finely ground crystals were heated under a flow of dry nitrogen over the temperature range 298–683 K at a heating rate of 4 K min^{-1}. The sample decomposes in a single narrow step, the onset of which is at 603 K. The total weight loss, 36.5%, is slightly larger than that expected for the total removal of the amine (calculated 35%), which may indicate the concomitant loss of a fraction (approximately 6%) of the sulfur. Powder X-ray diffraction of the decomposition product indicates that thermal decomposition produces a poorly crystalline material, in which only antimony can be identified. Analytical electron microscopy was performed with a Philips XL30 scanning microscope, equipped with an EDAX 'Phoenix' detection system. The observed Cr:S and Cr:Sb ratios are 0.32(5) and 0.94(6), respectively, in good agreement with the values of 0.33 and 1 for the crystallographically determined composition.

Magnetic measurements were performed using a Quantum Design MPMS2 SQUID susceptometer. 33 mg of crystals were loaded into gelatin capsules at room temperature and data were collected over the range $20 \leq T/K \leq 300$ after cooling in the measuring field of 1000 G.

Table 1
Crystallographic data for $[Cr(C_6H_{18}N_4)(SbS_3)]$

Formula	$[Cr(C_6H_{18}N_4)(SbS_3)]$
M_r	416.15
Crystal system	orthorhombic
Space group	*Pcab*
Temperature (K)	293
a (Å)	13.6528(2)
b (Å)	13.9971(3)
c (Å)	14.6556(3)
V (Å^3)	2800.7
Z	8
μ (cm^{-1})	3.129
Measured data	29082
Unique data	3212
Observed data ($I > 3\sigma(I)$)	2091
R_{merg}	0.052
R	0.026
R_w	0.024

2.2. Crystal structure determination

A crystal of [Cr($C_6H_{18}N_4$)(SbS_3)] (dimensions 0.07 × 0.12 × 0.2 mm) was mounted on a glass fibre and X-ray intensity data collected at room temperature using a Nonius Kappa CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data were processed using the DENZO [20] and SCALEPACK [21] suite of programs. Full crystallographic details are given in Table 1.

The structure was solved by direct methods using the program SIR-92 [22] which located Cr, Sb and all S atoms. Subsequent Fourier calculations and least-squares refinements on F were carried out in the CRYSTALS program suite [23]. The C, N and H atoms of the amine were located in difference Fourier maps. During the refinement procedure, the positional parameters of the H atoms were allowed to vary with the isotropic temperature factors fixed at 0.05 Å^2 and the N–H and C–H distances restrained to be 1.000(2) Å. In the final cycles, positional and anisotropic thermal parameters for all non-hydrogen atoms, and positional parameters for the hydrogen atoms were refined. A three-term Chebyshev polynomial was applied as a weighting scheme [24] giving a final residual R of 0.0260 and R_w of 0.0239. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

3. Results and discussion

The local coordination and atom labelling scheme is depicted in Fig. 1 and selected bond lengths and angles are given in Table 2. The crystal structure of [Cr($C_6H_{18}N_4$)(SbS_3)] consists of neutral chromium complexes held together by a network of hydrogen bonds. The Cr^{3+} ion is coordinated by two S atoms of the SbS_3^{3-} anion, with Cr–S distances of 2.372(1) and 2.370(1) Å, and by four N atoms of the trien ligand, yielding distorted octahedral coordination. There are three possible geometric isomers for octahedral complexes containing a tetradentate trien ligand: *trans*, *cis*-α, and *cis*-β [25]. The configuration observed for the complex [Cr($C_6H_{18}N_4$)(SbS_3)] corresponds to the *cis*-α geometric isomer. The Cr–S distances lie within the range reported for chromium-antimony sulfides [19,26]. The Cr–N(4) distance of 2.079(1) Å is within the expected range for a Cr^{3+} cation octahedrally coordinated by nitrogen atoms [27,28]. However, the three

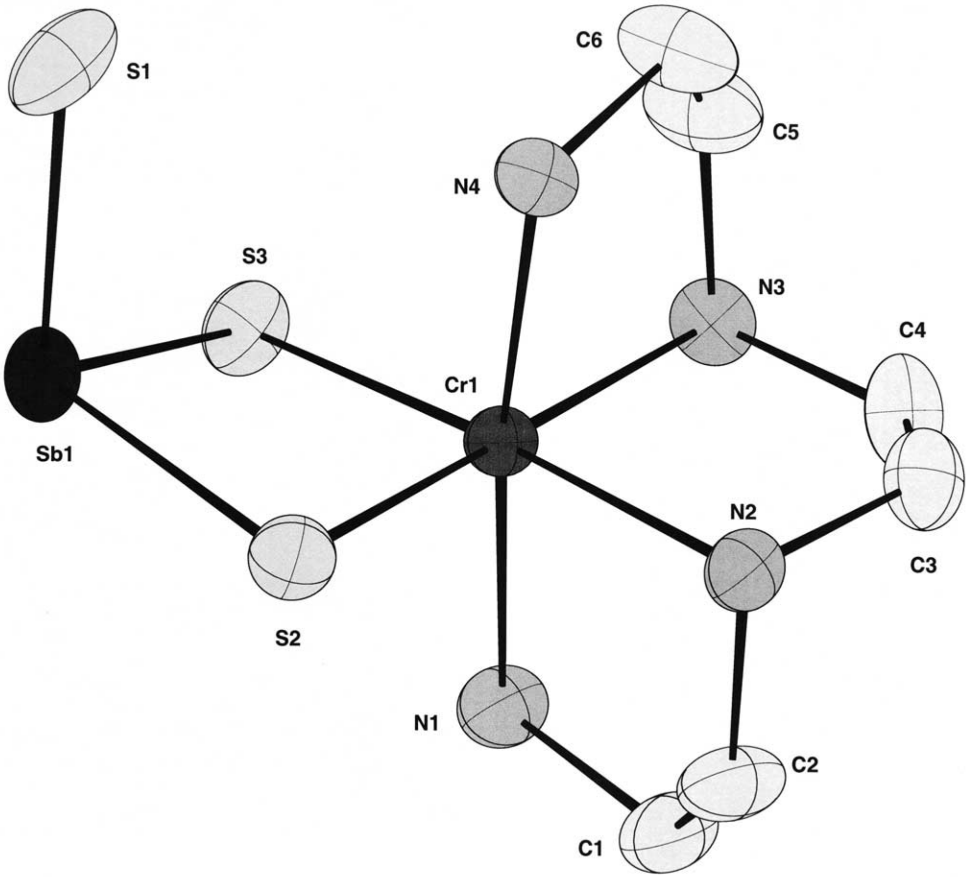

Fig. 1. Local coordination of the atoms in [Cr($C_6H_{18}N_4$)(SbS_3)] showing the atom labelling scheme and ellipsoids at 50% probability.

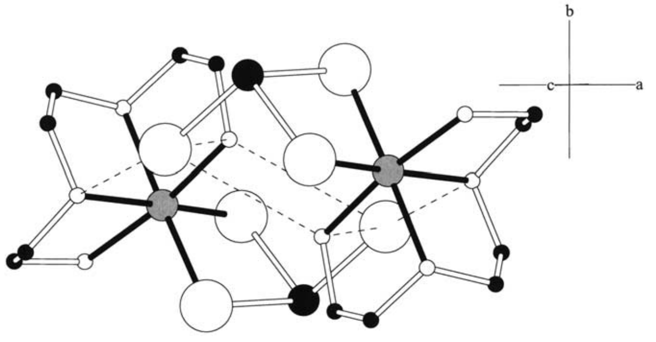

Fig. 2. View of a $[Cr(C_6H_{18}N_4)(SbS_3)]_2$ dimer. Dashed lines show the short sulfur–nitrogen distances. Hydrogen atoms have been omitted for clarity. Key: antimony, large solid circles; chromium, large shaded circles; sulfur, large open circles; carbon, small solid circles; nitrogen, small open circles.

Table 2
Selected bond lengths (Å) and bond angles (°) for $[Cr(C_6H_{18}N_4)(SbS_3)]$

Bond lengths	
Sb–S(1)	2.377(1)
Sb–S(2)	2.422(1)
Sb–S(3)	2.419(1)
Cr–S(2)	2.372(1)
Cr–S(3)	2.370(1)
Cr–N(1)	2.104(1)
Cr–N(2)	2.129(1)
Cr–N(3)	2.110(1)
Cr–N(4)	2.079(1)
Bond angles	
S(1)–Sb–S(2)	103.22(4)
S(1)–Sb–S(3)	100.81(4)
S(2)–Sb–S(3)	90.76(3)
S(2)–Cr–S(3)	93.22(4)
S(2)–Cr–N(1)	93.3(1)
S(2)–Cr–N(2)	92.18(9)
S(2)–Cr–N(4)	92.18(9)
S(3)–Cr–N(1)	90.18(9)
S(3)–Cr–N(3)	93.34(9)
S(3)–Cr–N(4)	94.19(9)
N(1)–Cr–N(2)	81.5(1)
N(1)–Cr–N(3)	92.5(1)
N(2)–Cr–N(3)	82.2(1)
N(2)–Cr–N(4)	93.6(1)
N(3)–Cr–N(4)	81.5(1)

remaining Cr–N distances are slightly longer. Such an elongation may be a manifestation of the *trans* effect associated with the Cr–S bonds. Steric constraints can also play a role in the elongation of the Cr–N bonds. The antimony is approximately trigonal pyramidally coordinated by sulfur, with Sb–S distances ranging from 2.377(1) to 2.422(1) Å, and S–Sb–S angles between 90.76(3) and 103.22(4). These values are typical for materials containing pyramidal SbS_3^{3-} units [5]. Although materials such as $[Ni(C_6H_{18}N_4)][Sb_2S_4]$, in which transition-metal cations are coordinated by sulfide ions belonging to an extended antimony–sulfide network, have been described [29], there have been few reports of individual SbS_3^{3-} units acting as ligands. The complex $[Cr(C_6H_{18}N_4)(SbS_3)]$ described here, represents only the second occurrence of an individual SbS_3^{3-} ligand. Furthermore, in both the complex reported here and in $[Cr(en)_2(SbS_3)]$ [19], the SbS_3^{3-} is bidentate. Further examples of ligands comprising isolated antimony–sulfide units appear to be confined to $Sb_2S_6^{2-}$ in the cationic cluster $[Fe_2(Sb_2S_6)(CO)_6]^{2+}$ [30], and the

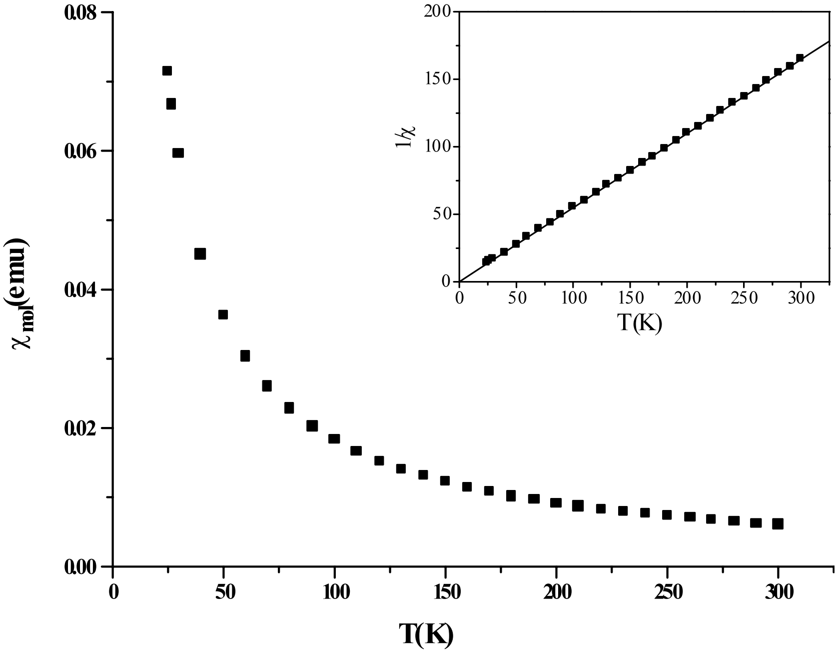

Fig. 3. Molar magnetic susceptibility data for $[Cr(C_6H_{18}N_4)(SbS_3)]$ collected after cooling in the measuring field of 1000 G. The inset shows the fit (solid line) to a Curie–Weiss expression.

Sb_2S ligand in the complex $[CpCr(CO)_3]_4(Sb_2S)$ [31], in which each Sb is bonded to two Cr atoms. This behaviour contrasts with that of the lighter congener, arsenic. Whilst there appears to be only a single example of a pyramidal AsS_3 ligand, which in the complex $[Cp'{}^{3}Ti_2(AsS_3)O]$ is tridentate [32], a wide range of anionic complex polythioarsenate(III) ligands, including $As_3S_7^{5-}$ and $As_4S_9^{6-}$, has been identified [33].

Whilst the local coordination geometry at the transition-metal centre in $[Cr(C_6H_{18}N_4)(SbS_3)]$ is similar to that in $[Cr(en)_2(SbS_3)]$ [19], the bulkier polyamine, trien, leads to marked differences in the manner in which the complexes pack in the crystal. This may be related to the different hydrogen-bond networks in the two structures. As shown in Fig. 2, each terminal sulfur atom, S(1), in $[Cr(C_6H_{18}N_4)(SbS_3)]$ has two nitrogen atoms in a neighbouring complex (N(2) and N(4)) at distances of approximately 3.40 Å, together with a third intramolecular interaction at an N···S distance of 3.45 Å. These distances suggest that both intra- and intermolecular hydrogen bonding between the trien and the SbS_3^{3-} ligands stabilises a unit, comprising a pair of $[Cr(C_6H_{18}N_4)(SbS_3)]$ complexes, related by a centre of inversion, in which the Cr···Cr separation is approximately 6.5 Å. Magnetic susceptibility data (Fig. 3) reveal that the material exhibits paramagnetic behaviour down to the lowest temperature studied. Data are well described by a Curie–Weiss law, $\chi = C/(T-\theta)$. The value of the Curie constant, $C = 1.823(2)$ emu K mol^{-1}, corresponds to an effective magnetic moment of $\mu_{\mathrm{eff}} = 3.819(3)\mu_{\mathrm{B}}$ per chromium ion, which is in good agreement with the spin-only value for Cr^{3+} ions. This, together with the negligible value of the Weiss constant, $\theta = 0.07(15)$, is consistent with a structure that contains

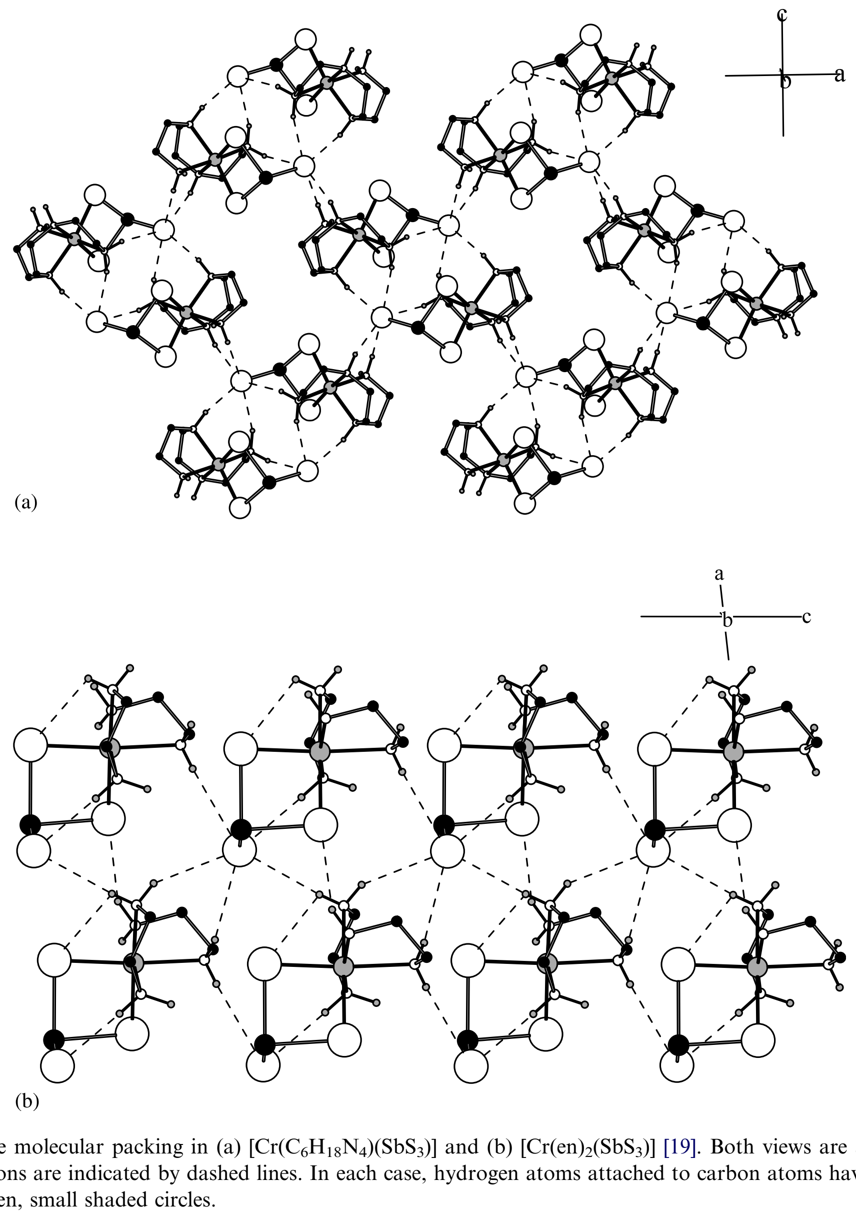

Fig. 4. Comparison of the molecular packing in (a) $[Cr(C_6H_{18}N_4)(SbS_3)]$ and (b) $[Cr(en)_2(SbS_3)]$ [19]. Both views are along [0 1 0] and the short sulfur–hydrogen interactions are indicated by dashed lines. In each case, hydrogen atoms attached to carbon atoms have been omitted for clarity. Key as for Fig. 2; hydrogen, small shaded circles.

magnetically isolated Cr^{3+} ions, suggesting that the Cr···Cr separation within a pair of complexes is too great to permit any magnetic interaction. Although the *cis*-α isomer is chiral, since each pair of complexes contains one (+)- and one (−)-enantiomer, the resulting crystal is a racemate. The dimeric units are in turn connected to four other pairs of complexes through a complex network of hydrogen bonds (N···S distance approximately 3.3 and 3.5 Å), resulting in the formation of layers of complexes parallel to the (0 1 0) crystallographic plane (Fig. 4(a)). Within this plane, pairs of molecules form rows along [1 0 0] with each pair inclined at an angle to the *c*-axis: the direction of the inclination alternating between successive rows. Successive layers are stacked along the [0 1 0] direction with an ABAB stacking sequence, such that the dimers in neighbouring layers are not aligned. Interlayer N···S distances are considerably larger (> 4.9 Å) than those in the (0 1 0) plane, indicating that there is only a very weak interaction between individual sheets of molecules. This packing arrangement differs considerably from that in $[Cr(en)_2(SbS_3)]$ reported previously [19]. Each terminal sulfur atom in $[Cr(en)_2(SbS_3)]$ has four neighbouring nitrogen atoms in adjacent molecules within the (0 1 0) plane, at distances in the range 3.5–3.7 Å (Fig. 4(b)). These distances, together with N–H···S angles of 145–170°, suggest the presence of in-plane intermolecular hydrogen-bonding interactions. Individual $[Cr(en)_2(SbS_3)]$ molecules are aligned to form rows along [0 0 1] and [1 0 0] with (+)- and (−)-enantiomers alternating in the former direction.

The differences in the hydrogen bonding in the two complexes may be ascribed to the presence of the additional (CH_2–CH_2) spacer between two of the coordinated nitrogen atoms in $[Cr(C_6H_{18}N_4)(SbS_3)]$. In $[Cr(en)_2(SbS_3)]$, the molecular layers arise primarily from hydrogen bonding between the nitrogen atoms that are *trans* to each of the two sulfur atoms and terminal sulfur atoms in the adjacent molecules. The added (CH_2–CH_2) group in $[Cr(C_6H_{18}N_4)(SbS_3)]$ links these two nitrogen atoms (N(2) and N(3)). This reduces the number of hydrogen atoms on each of these nitrogen atoms to one. Furthermore, the remaining hydrogen atoms are not pointing towards the position where the adjacent terminal sulfur lies in the crystal structure of $[Cr(en)_2(SbS_3)]$, but away from it, owing to the presence of the extra (CH_2–CH_2) group. Therefore, the additional (CH_2–CH_2) group introduces significant steric constraints for the formation of hydrogen bonds, and results in an entirely different molecular packing. Although hydrogen-bonding interactions are generally weak, the differences in crystal packing to which they lead, manifest themselves here in marked changes in the bulk properties. In particular, replacement of the en ligands with trien increases the thermal stability of the complex. The decomposition temperature of 603 K, determined thermogravimetrically is significantly higher than that of 543 K determined for $[Cr(en)_2(SbS_3)]$. While thermogravimetric data are influenced by a number of experimental factors, the difference in thermal stability was confirmed by thermal analysis, under identical conditions of gas flow and heating rate to those used for $[Cr(C_6H_{18}N_4)(SbS_3)]$, of a sample of $[Cr(en)_2(SbS_3)]$ prepared in our laboratory according the method reported by Schur et al. [19].

Crystallographic data for the structure reported in this paper are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 204639.

Acknowledgements

AVP and AMC thank The Royal Society of Edinburgh and The University of Reading RETF fund respectively for research fellowships.

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