

Chromous hydrazine sulfate

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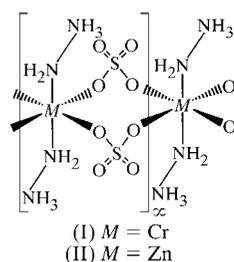
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The title compound, *catena*-poly[dihydrazi­niochromium(II)-di- μ -sul­fate-*O*:*O'*], $[\text{Cr}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2]$, was studied at 100 K and contains chains of chromium(II) ions linked by pairs of sulfate anions and coordinated to hydrazinium ions. The unique Cr atom lies on an inversion centre. All five H atoms were experimentally located and are involved in hydrogen bonding to O atoms of the sulfate groups.

Comment

Chromous hydrazine sulfate, (I), was originally reported by Traube & Passarge (1913) and is unusual in that it is an air-stable complex of chromium(II). Although often encountered as a preparative experiment in undergraduate practical courses (Adams & Raynor, 1965; Palmer, 1954), the structure of chromous hydrazine sulfate has never been determined, as it is usually obtained as a microcrystalline solid unsuitable for single-crystal X-ray diffraction. The structure of zinc hydrazine sulfate, (II), has been reported and shows chains of zinc(II) cations with bridging sulfate anions and coordinated hydrazinium cations. Both compounds are best formulated as $[\text{M}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2]$ (Prout & Powell, 1961). The cell dimensions of a number of metal hydrazine sulfates, including the Cr^{II} complex, were reported and it was suggested that the compounds were all of the same structural type (Hand & Prout, 1966).



On one occasion, we were fortunate enough to obtain good quality crystals of (I) from a preparation carried out in a practical class. The sample was prepared by reacting chromous acetate with hydrazine sulfate in dilute sulfuric acid (Adams & Raynor, 1965). The original formulation of Traube & Passarge

(1913) without water of crystallization is confirmed by our crystallographic study. Both Adams & Raynor (1965) and Palmer (1954) formulated the compound as a hydrate. The present crystal is triclinic with dimensions close to those reported previously (Hand & Prout, 1966).

The structure of (I) is very similar to that of the analogous zinc compound and consists of chains of chromium(II) cations linked by pairs of sulfate anions (Fig. 1). The chains are parallel to the *b* axis and the Cr–Cr distance is the same as the *b*-cell dimension, *i.e.* 5.4568 (5) Å. Selected geometric parameters are given in Table 1. The structure is centrosymmetric, with the chromium(II) ion on a centre of symmetry, and the asymmetric unit is one half a formula unit, *i.e.* $\frac{1}{2} \times [\text{Cr}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2]$. As with the zinc analogue, there is pronounced asymmetry in the Cr–O distances to the sulfate ion, 2.0535 (17) and 2.3791 (19) Å. Asymmetry of this type is not unusual (Hathaway, 1987). Each chromium(II) ion is also coordinated to two hydrazinium (N_2H_5^+) cations. We have used the same choice of axes as Prout & Powell (1961), and labelled the atoms in a corresponding manner, except that O1 and O2 have been interchanged, so that Cr–O1 remains the ‘short’ metal–oxygen bond in both structures, and have given symmetry equivalent coordinates for N1 and N2 to achieve connectivity within the asymmetric unit.

All five H atoms are involved in hydrogen bonding to O atoms of sulfate groups. Fig. 1 shows the hydrogen bonding within the chromium/sulfate chains and Fig. 2 the hydrogen bonding between the chains. While atoms H1 to H4 are only involved in interaction with one O atom, H5 has interactions with O1 within the chain and with O1 and O2 from an adjacent chain. Atom H5 is therefore involved in hydrogen bonding to three O atoms in what has been described as four-centre bonding (Jeffrey, 1997). The hydrogen bonding in (I) is similar to that suggested for (II), although there is no H atom linking N1 and O4 of the same chain. The N–H...O distances are close to those observed previously for N–H hydrogen bonds to the O atoms of sulfate groups (Chertanova & Pascard, 1996).

Since the structure of (II) was initially reported, several structures of the general formula $[\text{Zn}(\text{N}_2\text{H}_4)_2\text{X}_2]$, in which X is

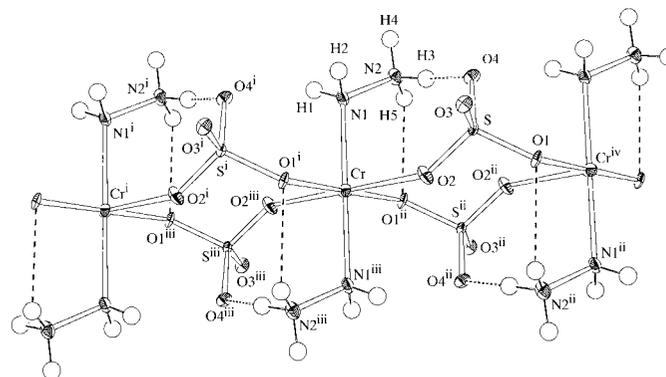


Figure 1

View of a fragment of a chromium/sulfate chain of (I) showing the hydrogen bonding within the chain which runs along the *b* axis, and the atom-numbering scheme. Displacement ellipsoids of non-H atoms are shown at the 70% probability level. The symmetry codes are as given in Tables 1 and 2, with the addition of (iii) $-x, -y, -z$.

a monovalent anion, have been investigated. In contrast to the sulfate, the complexes with mononegative anions have unprotonated bridging hydrazine molecules, with the anions completing a pseudo-octahedral geometry at the metal (Ferrari *et al.*, 1965, and references therein).

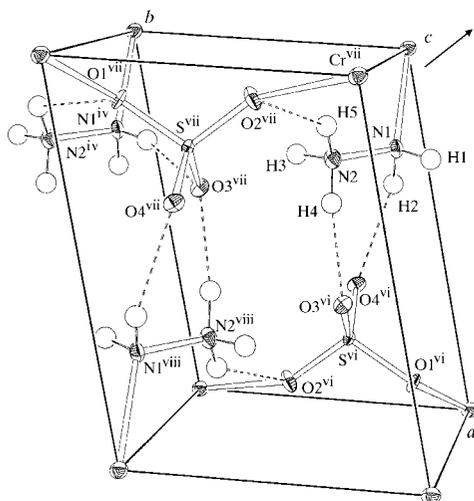


Figure 2
View of (I) showing the hydrogen bonding between adjacent chains and the outline of the unit cell. Displacement ellipsoids of non-H atoms are shown at the 70% probability level. The symmetry codes are as given in Tables 1 and 2, with the addition of (viii) $1 - x, 1 - y, -1 - z$.

Experimental

Chromous hydrazine sulfate was prepared by reacting chromous acetate with hydrazine sulfate in dilute sulfuric acid (Adams & Raynor, 1965) and was crystallized from the reaction medium.

Crystal data

$[\text{Cr}(\text{N}_2\text{H}_5)_2(\text{SO}_4)_2]$	$Z = 1$
$M_r = 310.24$	$D_x = 2.366 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.2662(3) \text{ \AA}$	Cell parameters from 1336 reflections
$b = 5.4568(5) \text{ \AA}$	$\theta = 3.6\text{--}26.0^\circ$
$c = 5.7092(6) \text{ \AA}$	$\mu = 1.83 \text{ mm}^{-1}$
$\alpha = 97.596(2)^\circ$	$T = 100(2) \text{ K}$
$\beta = 91.830(2)^\circ$	Rectangular prism, blue
$\gamma = 103.493(2)^\circ$	$0.35 \times 0.10 \times 0.10 \text{ mm}$
$V = 217.73(3) \text{ \AA}^3$	

Data collection

Nonius KappaCCD area-detector diffractometer	786 independent reflections
$2^\circ \varphi$ frames	751 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SCALEPACK; Otwinowski & Minor, 1997)	$R_{\text{int}} = 0.021$
$T_{\text{min}} = 0.567, T_{\text{max}} = 0.838$	$\theta_{\text{max}} = 26.0^\circ$
1336 measured reflections	$h = -8 \rightarrow 8$
	$k = -6 \rightarrow 6$
	$l = -6 \rightarrow 7$
	Intensity decay: none

Refinement

Refinement on F^2	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.025$	$w = 1/[\sigma^2(F_o^2) + 0.4661P]$
$wR(F^2) = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.18$	$(\Delta/\sigma)_{\text{max}} < 0.001$
786 reflections	$\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
91 parameters	$\Delta\rho_{\text{min}} = -0.58 \text{ e \AA}^{-3}$

The H atoms were located in the difference map and were refined with unconstrained isotropic displacement parameters, but with a fixed N—H distance of 0.88 \AA . When the determination was carried out, the diffractometer was incapable of collecting cusp data, and so

Table 1

Selected geometric parameters ($\text{\AA}, ^\circ$).

Cr—O1 ⁱ	2.0535 (17)	S—O2	1.468 (2)
Cr—O2	2.3791 (19)	S—O3	1.4820 (18)
Cr—N1	2.138 (2)	S—O4	1.4775 (18)
S—O1	1.5006 (18)	N1—N2	1.453 (3)
O1 ⁱ —Cr—N1	92.91 (8)	O2—S—O1	109.79 (11)
O1 ⁱ —Cr—O2	86.73 (7)	O4—S—O1	108.87 (10)
N1—Cr—O2	91.50 (8)	O3—S—O1	107.10 (10)
O2—S—O4	111.29 (11)	S—O1—Cr ^{iv}	128.35 (11)
O2—S—O3	110.22 (11)	S—O2—Cr	141.90 (11)
O4—S—O3	109.46 (11)	N2—N1—Cr	115.17 (16)

Symmetry codes: (i) $x, y - 1, z$; (iv) $x, 1 + y, z$.

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
N1—H1 \cdots O3 ^v	0.88 (3)	2.01 (3)	2.872 (3)	164 (3)
N1—H2 \cdots O4 ^{vi}	0.88 (3)	2.18 (2)	2.970 (3)	150 (3)
N2—H3 \cdots O4	0.88 (3)	1.91 (2)	2.746 (3)	158 (3)
N2—H4 \cdots O3 ^{vi}	0.88 (3)	1.92 (2)	2.792 (3)	168 (3)
N2—H5 \cdots O2 ^{vii}	0.88 (3)	2.32 (2)	3.061 (3)	142 (3)
N2—H5 \cdots O1 ⁱⁱ	0.88 (3)	2.38 (3)	2.858 (3)	114 (2)
N2—H5 \cdots O1 ^v	0.88 (3)	2.51 (3)	3.004 (3)	117 (3)

Symmetry codes: (ii) $-x, 1 - y, -z$; (v) $x, y - 1, z - 1$; (vi) $1 - x, 1 - y, -z$; (vii) $x, y, z - 1$.

we report a comparatively low completeness of possible data. The somewhat low reflection/parameter ratio is caused by the refinement of parameters for the H atoms.

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: XSeed (Barbour, 1999) and ORTEP-3 (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1427). Services for accessing these data are described at the back of the journal.

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