metal-organic compounds

Hexakis(dimethyl sulfoxide-κO)-chromium(III) trichloride

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In the title compound, $[Cr(C_2H_6OS)_6]Cl_3$, each Cr^{III} ion is located on a three-fold inversion axis and is coordinated by six dimethylsulfoxide ligands [Cr—O = 1.970 (2)–1.972 (2) Å; O—Cr—O = 88.19 (9) and 91.81 (9)°] in a slightly distorted octahedral geometry. The Cl$^-$ anions take part in the formation of weak C—H$\cdots$Cl hydrogen bonds, which contribute to the crystal packing stabilization.

Related literature

For related literature, see: Chan *et al.* (2004); Desiraju & Steiner (1999); Öhrström & Svensson (2000); Persson *et al.* (1995, and references therein); Reynolds (1970).
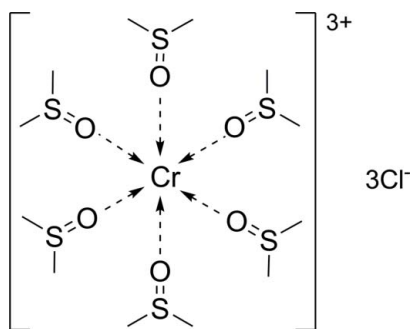
Experimental

Crystal data

$Cr(C_2H_6OS)_6]Cl_3$
M_r = 627.12

Trigonal, $R\bar{3}$
a = 10.5499 (6) Å
c = 21.1370 (13) Å
V = 2037.4 (2) Å^3
Z = 3

Mo $K\alpha$ radiation
μ = 1.20 mm^{-1}
T = 120 (2) K
0.34 × 0.29 × 0.20 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(North *et al.*, 1968)
T_{min} = 0.688, T_{max} = 0.795

10865 measured reflections
1044 independent reflections
855 reflections with $I > 2\sigma(I)$
R_{int} = 0.051

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.135
S = 1.14
1044 reflections

46 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C1—H1$B\cdots$Cl1	0.98	2.75	3.647 (3)	153
C1—H1$A\cdots$Cl2^i	0.98	2.64	3.614 (4)	176

Symmetry code: (i) $x + \frac{1}{3}, y + \frac{2}{3}, z - \frac{1}{3}$.

Data collection: *APEX2* (Bruker, 2004); cell refinement: *DENZO/SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO/SCALEPACK*; program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2410).

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supporting information

Hexakis(dimethyl sulfoxide-*κO*)chromium(III) trichloride

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S1. Comment

Dimethylsulfoxide (dmso) has often been used as solvent and a ligand in inorganic chemistry since the beginning of the 1960th. Dimethylsulfoxide is a monodentate O–,*S*-donor ligand (Reynolds, 1970). Solvates of some transition metal ions have been prepared and structurally charaterized (Persson *et al.*, 1995 and references therein).

The title compound, (I), is composed of $[Cr(C_2H_6OS)_6]^{3+}$ cations and chloride anions. The Cr(III) ion is located on a 3-fold inversion axis being coordinated by the six dimethylsulfoxide ligands in a slightly distorted octahedral geometry (Fig. 1), with Cr—O 1.970 (2)–1.972 (2) Å interatomic distances and O—Cr—O 88.19 (9), 91.81 (9)° bond angles. A search in the Cambridge Structural Database revealed 14 reports of compounds containing transition metal hexakis(dimethylsulfoxide) cations, of which two described the structure of the $[Cr(C_2H_6OS)_6]^{3+}$ cation in $[Cr(C_2H_6OS)_6](ClO_4)_3$ (Chan *et al.*, 2004) and $[Cr(C_2H_6OS)_6](NO_3)_3$ (Ohrstrom & Svensson, 2000). The S═O bond lengths in the aforementioned compounds are almost identical, 1.542 (3) Å *versus* 1.543 (2) Å for the title compound, as well as the O—Cr—O angles, 87.9/92.2° *versus* 88.19–91.81°. In the present structure the average value of Cr—O—S angles (121.9°) is somewhat smaller than that in $[Cr(C_2H_6OS)_6](NO_3)_3$ (123.6°). All other angles and bonds of the title compound are very similar to the above mentioned structures.

In (I), the Cl anions take part in formation of weak C—H⋯Cl hydrogen bonds (Table 1), which contribute to the crystal packing stabilization.

S2. Experimental

Complex (I) was synthesized during the attempt to prepare chromium (III) complex with 1*H*-pyrazole-3,5-dicarbohydrazide (Fig. 2) by adding $CrCl_3.6H_2O$ (0.3 mmol, 3 ml of 0.1*M* aqueous solution) to the 1*H*-pyrazole-3,5-dicarbohydrazide (0.0552 g, 0.3 mmol) in dimethylsulfoxide solution (6 ml). The mixture was stirred for 30 min at ambient temperature. The resulting green solution was filtered and the filtrate was left to stand at room temperature. Slow evaporation of the solvent during 2 weeks yielded green crystals of (I).

S3. Refinement

The H atoms were positioned geometrically (C—H 0.98 Å) and allowed to ride on their parent atoms, with $U_{iso}(H) = 1.5U_{eq}(C)$.
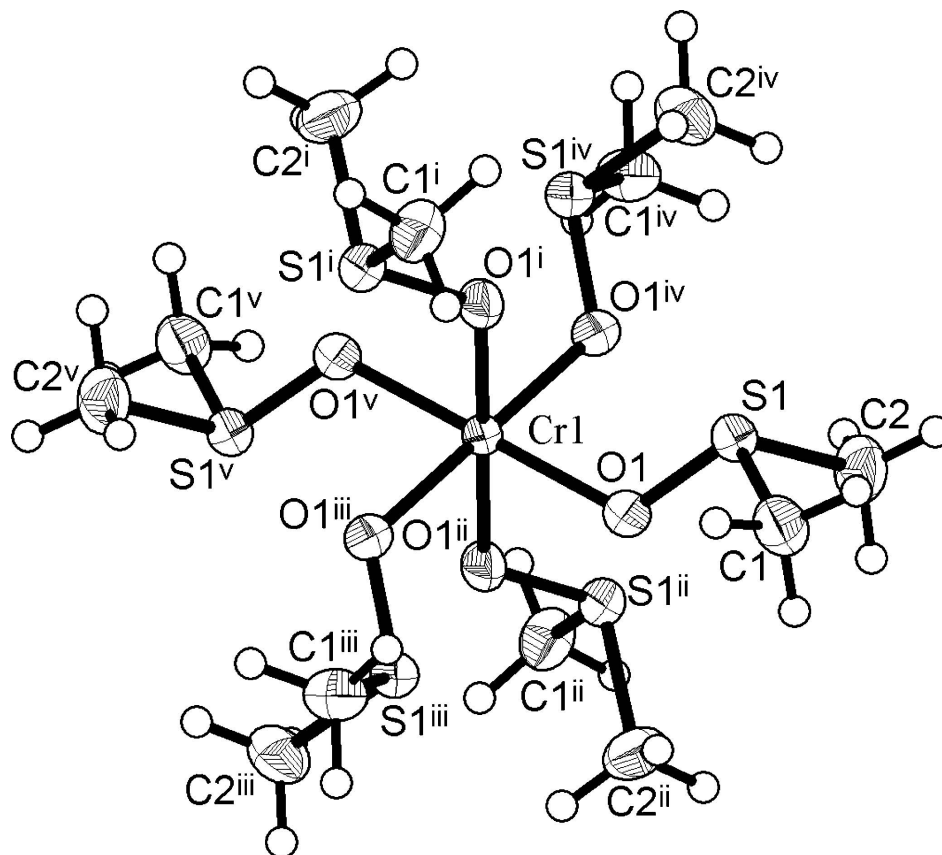
Figure 1

The molecular structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 60% probability level [symmetry codes: (i) $-x + y$, $1 - x$, z; (ii) $2/3 + x-y$, $1/3 + x$, $1/3 - z$; (iii) $1 - y$, $1 + x-y$, z; (iv) $-1/3 + y$, $1/3 - x + y$, $1/3 - z$; (v) $2/3 - x$, $4/3 - y$, $1/3 - z$.]
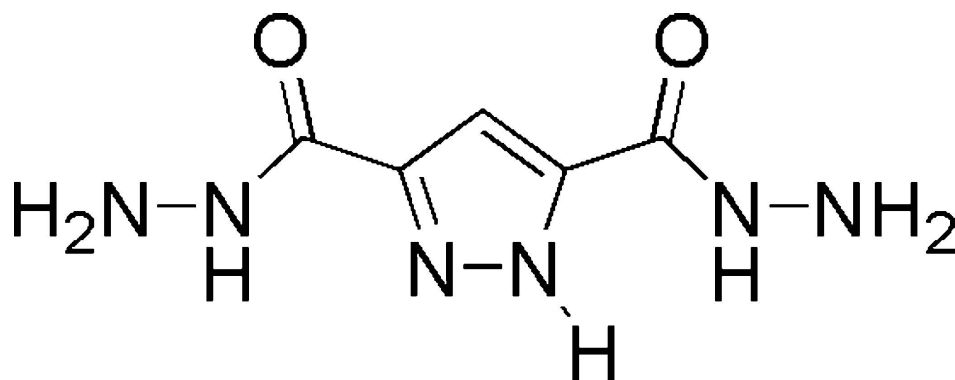
Figure 2

1*H*-pyrazole-3,5-dicarbohydrazide

Hexakis(dimethyl sulfoxide-*κ*O)chromium(III) trichloride

Crystal data

[Cr(C₂H₆OS)₆]Cl₃	$D_x = 1.533$ Mg m⁻³
$M_r = 627.12$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Trigonal, $R\overline{3}$	Cell parameters from 6073 reflections
Hall symbol: -R 3	$\theta = 1.0$–27.5°
$a = 10.5499$ (6) Å	$\mu = 1.20$ mm⁻¹
$c = 21.1370$ (13) Å	$T = 120$ K
$V = 2037.4$ (2) Å³	Block, green
$Z = 3$	$0.34 \times 0.29 \times 0.20$ mm
$F(000) = 981$	

Data collection

Nonius KappaCCD diffractometer	$T_{min} = 0.688$, $T_{max} = 0.795$
Radiation source: fine-focus sealed tube	10865 measured reflections
Horizontally mounted graphite crystal monochromator	1044 independent reflections
	855 reflections with $I > 2\sigma(I)$
Detector resolution: 9 pixels mm⁻¹	$R_{int} = 0.051$
φ scans and ω scans with κ offset	$\theta_{max} = 27.6°$, $\theta_{min} = 2.4°$
Absorption correction: multi-scan	$h = -13\rightarrow13$
(North *et al.*, 1968)	$k = -13\rightarrow13$
	$l = -26\rightarrow27$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.042$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.135$	
$S = 1.14$	H-atom parameters constrained
1044 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0789P)^2 + 3.3338P]$
46 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.82$ e Å⁻³
	$\Delta\rho_{min} = -0.48$ e Å⁻³

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Cr1	0.3333	0.6667	0.1667	0.0214 (3)
Cl1	0.0000	0.0000	0.0000	0.0324 (5)
Cl2	0.0000	0.0000	0.25064 (7)	0.0416 (4)
S1	0.24193 (8)	0.38772 (8)	0.08860 (4)	0.0261 (3)
O1	0.3687 (2)	0.5325 (2)	0.11455 (10)	0.0270 (5)

C1	0.3083 (4)	0.3721 (4)	0.01371 (16)	0.0336 (7)
H1A	0.3141	0.4485	−0.0145	0.050*
H1B	0.2416	0.2757	−0.0044	0.050*
H1C	0.4058	0.3834	0.0186	0.050*
C2	0.2577 (4)	0.2497 (4)	0.12936 (18)	0.0384 (8)
H2A	0.3576	0.2670	0.1248	0.058*
H2B	0.1883	0.1538	0.1116	0.058*
H2C	0.2360	0.2518	0.1743	0.058*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cr1	0.0165 (4)	0.0165 (4)	0.0311 (6)	0.00824 (19)	0.000	0.000
Cl1	0.0245 (6)	0.0245 (6)	0.0480 (11)	0.0123 (3)	0.000	0.000
Cl2	0.0421 (6)	0.0421 (6)	0.0405 (9)	0.0211 (3)	0.000	0.000
S1	0.0221 (4)	0.0207 (4)	0.0346 (5)	0.0099 (3)	−0.0004 (3)	−0.0004 (3)
O1	0.0202 (10)	0.0222 (10)	0.0374 (12)	0.0096 (9)	−0.0015 (8)	−0.0045 (8)
C1	0.0339 (17)	0.0279 (16)	0.0331 (17)	0.0111 (13)	0.0028 (13)	−0.0017 (13)
C2	0.045 (2)	0.0278 (16)	0.044 (2)	0.0196 (15)	−0.0007 (16)	0.0063 (14)

Geometric parameters (Å, º)

Cr1—O1^i	1.972 (2)	S1—C1	1.772 (3)
Cr1—O1^{ii}	1.971 (2)	C1—H1A	0.9800
Cr1—O1^{iii}	1.971 (2)	C1—H1B	0.9800
Cr1—O1	1.970 (2)	C1—H1C	0.9800
Cr1—O1^{iv}	1.971 (2)	C2—H2A	0.9800
Cr1—O1^v	1.971 (2)	C2—H2B	0.9800
S1—O1	1.542 (2)	C2—H2C	0.9800
S1—C2	1.770 (3)		
O1^i—Cr1—O1^{ii}	180.0	O1—S1—C1	102.86 (14)
O1^i—Cr1—O1^{iii}	91.81 (9)	C2—S1—C1	98.87 (17)
O1^{ii}—Cr1—O1^{iii}	88.19 (9)	S1—O1—Cr1	121.86 (12)
O1^i—Cr1—O1	91.81 (9)	S1—C1—H1A	109.5
O1^{ii}—Cr1—O1	88.19 (9)	S1—C1—H1B	109.5
O1^{iii}—Cr1—O1	91.81 (9)	H1A—C1—H1B	109.5
O1^i—Cr1—O1^{iv}	88.19 (9)	S1—C1—H1C	109.5
O1^{ii}—Cr1—O1^{iv}	91.81 (9)	H1A—C1—H1C	109.5
O1^{iii}—Cr1—O1^{iv}	180.0	H1B—C1—H1C	109.5
O1—Cr1—O1^{iv}	88.19 (9)	S1—C2—H2A	109.5
O1^i—Cr1—O1^v	88.19 (9)	S1—C2—H2B	109.5
O1^{ii}—Cr1—O1^v	91.81 (9)	H2A—C2—H2B	109.5
O1^{iii}—Cr1—O1^v	88.19 (9)	S1—C2—H2C	109.5
O1—Cr1—O1^v	179.999 (1)	H2A—C2—H2C	109.5
O1^{iv}—Cr1—O1^v	91.81 (9)	H2B—C2—H2C	109.5
O1—S1—C2	104.46 (15)		

C2—S1—O1—Cr1	−112.64 (17)	O1ⁱⁱ—Cr1—O1—S1	140.87 (18)
C1—S1—O1—Cr1	144.52 (16)	O1ⁱⁱⁱ—Cr1—O1—S1	−131.00 (10)
O1ⁱ—Cr1—O1—S1	−39.13 (18)	O1ⁱᵛ—Cr1—O1—S1	49.00 (10)

Symmetry codes: (i) −*x*+*y*, −*x*+1, *z*; (ii) *x*−*y*+2/3, *x*+1/3, −*z*+1/3; (iii) −*y*+1, *x*−*y*+1, *z*; (iv) *y*−1/3, −*x*+*y*+1/3, −*z*+1/3; (v) −*x*+2/3, −*y*+4/3, −*z*+1/3.

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
C1—H1*B*⋯Cl1	0.98	2.75	3.647 (3)	153
C1—H1*A*⋯Cl2ᵛⁱ	0.98	2.64	3.614 (4)	176

Symmetry code: (vi) *x*+1/3, *y*+2/3, *z*−1/3.