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Coordination of (*N,N*-dibenzyl)benzene sulfenamide to pentacarbonylchromium(0) via the sulfur atom. Crystal structure of $(C_6H_5CH_2)_2NS(C_6H_5)Cr(CO)_5$

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Abstract

$C_{25}H_{19}NO_5Cr$; $M_r = 497.5$; triclinic; space group $P\bar{1}$; *a* 11.077(4), *b* 13.313(5), *c* 18.486(9) Å, α 108.69(2), β 101.58(3), γ 92.83(2)°; *V* 2510.7(2) Å^3; $Z = 4$; D_x 1.316 g.cm^{-3}; $\lambda(\text{Cu-}K_\alpha)$ 1.5418 Å; μ 48.5 cm^{-1}; $F(0,0,0) = 1024$; $R = 0.060$ at room temperature for 3963 unique observed reflections and 596 parameters. There are two independent molecules in the asymmetric unit; the both have enantiomeric configurations at the sulfur atoms, similarly distorted octahedral geometry about the chromium atoms, and sulfur and five carbonyl groups occupying the coordination sites, but they show slightly different spatial arrangements of the aromatic rings in the sulfenamide moiety. For both molecules the Cr–CO bond distance *trans* to Cr–S bond is shorter than the averaged distance for the remaining Cr–CO bonds.

Introduction

In spite of the coordination ability expected for sulfenamides, arising from the lone pairs on the sulfur and nitrogen atoms, *Δ*-(*S*)-(ethylenediamine-(*R*)-cysteine-sulfenamide)cobalt(III) perchlorate [1], is, as far as we know, the only metal complex reported to contain this type of ligand. As a part of our studies on the coordination properties of compounds having sulfur–nitrogen bonds [2], we describe here the crystal structure determination of the title compound, which is coordinated though a sulfur–metal bond other than the more usual nitrogen–metal bond.

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Table 1

Fractional coordinates for the non-hydrogen atoms

	x	y	z
Molecule 1			
Cr(1)	0.2194(1)	0.1962(1)	0.5209(1)
O(1)	0.4577(4)	0.2016(4)	0.6344(3)
O(2)	0.2870(6)	−0.0129(5)	0.4296(3)
O(3)	0.3740(5)	0.3071(5)	0.4462(3)
O(4)	0.0045(5)	0.1704(5)	0.3844(3)
O(5)	0.0622(5)	0.0790(4)	0.5930(3)
S(1)	0.1475(1)	0.3591(1)	0.5911(1)
N(1)	0.1403(4)	0.3656(4)	0.6833(3)
C(11)	0.3641(6)	0.2026(5)	0.5945(4)
C(12)	0.2597(7)	0.0685(6)	0.4653(4)
C(13)	0.3137(6)	0.2663(5)	0.4756(4)
C(14)	0.0826(6)	0.1809(6)	0.4376(4)
C(15)	0.1226(6)	0.1248(5)	0.5670(4)
C(16)	0.2412(6)	0.4795(5)	0.6036(4)
C(17)	0.1810(6)	0.5628(6)	0.5933(4)
C(18)	0.2494(9)	0.6598(7)	0.6061(6)
C(19)	0.3758(9)	0.6709(6)	0.6293(5)
C(110)	0.4371(6)	0.5884(6)	0.6400(5)
C(111)	0.3702(6)	0.4912(5)	0.6266(4)
C(112)	0.0578(7)	0.4445(5)	0.7172(4)
C(113)	−0.0739(7)	0.4150(6)	0.6684(4)
C(114)	−0.1339(9)	0.4905(7)	0.6452(6)
C(115)	−0.2569(15)	0.4653(13)	0.6021(8)
C(116)	−0.3152(9)	0.3655(17)	0.5854(6)
C(117)	−0.2568(10)	0.2909(8)	0.6091(7)
C(118)	−0.1358(8)	0.3157(7)	0.6502(6)
C(119)	0.2611(6)	0.3822(6)	0.7407(4)
C(120)	0.2473(6)	0.3535(5)	0.8109(4)
C(121)	0.2954(7)	0.4256(5)	0.8844(5)
C(122)	0.2834(8)	0.4012(6)	0.9499(4)
C(123)	0.2260(7)	0.3043(6)	0.9424(4)
C(124)	0.1816(7)	0.2306(6)	0.8705(4)
C(125)	0.1919(6)	0.2545(5)	0.8037(4)
Molecule 2			
Cr(2)	0.1722(1)	0.0054(1)	0.1460(1)
O(21)	0.2233(6)	0.0884(6)	0.0193(5)
O(22)	−0.0580(7)	0.1106(7)	0.1460(6)
O(23)	0.3049(8)	0.2130(5)	0.2643(5)
O(24)	0.0940(6)	−0.0676(6)	0.2701(4)
O(25)	0.0257(4)	−0.1904(4)	0.0116(3)
S(2)	0.3574(1)	−0.0785(1)	0.1355(1)
N(2)	0.3340(5)	−0.2122(4)	0.1197(3)
C(21)	0.2058(7)	0.0581(7)	0.0700(5)
C(22)	0.0321(8)	0.0706(7)	0.1454(6)
C(23)	0.2575(9)	0.1321(6)	0.2204(6)
C(24)	0.1282(7)	−0.0432(7)	0.2215(4)
C(25)	0.0824(6)	−0.1181(5)	0.0658(4)
C(26)	0.4859(7)	−0.0242(5)	0.2224(6)
C(27)	0.4657(10)	0.0031(7)	0.2980(8)
C(28)	0.5687(18)	0.0418(7)	0.3620(7)
C(29)	0.6814(13)	0.0492(10)	0.3422(15)
C(210)	0.7076(15)	0.0271(11)	0.2744(13)

Table 1 (continued)

	x	y	z
Molecule 2			
C(211)	0.5999(12)	−0.0143(7)	0.2098(9)
C(212)	0.3296(7)	−0.2433(5)	0.1885(4)
C(213)	0.2657(8)	−0.3554(5)	0.1655(4)
C(214)	0.3267(8)	−0.4308(7)	0.1891(5)
C(215)	0.2648(13)	−0.5326(8)	0.1716(6)
C(216)	0.1466(15)	−0.5578(8)	0.1317(7)
C(217)	0.0845(8)	−0.4831(9)	0.1081(5)
C(218)	0.1446(10)	−0.3828(7)	0.1249(5)
C(219)	0.4189(7)	−0.2709(6)	0.0742(5)
C(220)	0.3886(9)	−0.2657(6)	−0.0089(6)
C(221)	0.2727(11)	−0.2929(6)	−0.0526(6)
C(222)	0.2387(10)	−0.2897(7)	−0.1268(8)
C(223)	0.3276(19)	−0.2603(12)	−0.1578(7)
C(224)	0.4458(17)	−0.2327(14)	−0.1195(9)
C(225)	0.4790(8)	−0.2354(10)	−0.0437(7)

Experimental

The compound was prepared as previously described [2–4]. Colourless crystals were grown from n-hexane. Diffraction maxima were collected on a four circle computer-controlled Siemens AED diffractometer, using graphite monochromated Cu-K_α radiation and the ω/θ scan mode. Two standard reflections measured every hour showed no significant intensity decay. Cell parameters were established by least-square adjustment of the setting angles of 33 strong reflections in the range $21° < 2\theta < 35°$. Of a total of 4945 independent reflections measured in the range $3° < 2\theta < 122°$, 3963 with $I > 3\sigma(I)$ were considered as observed, corrected for Lorentz and polarization factors, and used for the resolution and the structure refinement; index range h: 0,12, k: −15,15 and l: 20,20. The structure was solved by Patterson and sucessive Fourier syntheses [5]. In the course of the isotropic least-squares refinement of the positional parameters on non-hydrogen atoms an empirical absorption correction [6] was made (correction range 0.803 to 1.405). The structure was refined ($\Sigma w(\Delta F)^2$ minimized) by full-matrix least-squares [7], with anisotropic thermal parameters. The hydrogen atoms were placed at calculated positions (C–H, 1.00 Å) [8] and included with a fixed isotropic contribution in the last refinement. A weighting scheme [9] was chosen to obtain flat dependence of $\langle \Delta^2 F \rangle$ versus $\langle F_o \rangle$ and $\langle \sin\theta/\lambda \rangle$. Final agreement factors $R = 0.060$ and $R_w = 0.059$. Maximum electron density in final difference synthesis map 0.20 e.Å^{-3}, maximum Δ/σ in final refinement 0.469.

Discussion

The fractional coordinates for the non-H atoms are given in Table 1, and selected bond angles and distances in Table 2. The numbering scheme together, with the relative orientations of the two molecules of the asymmetric unit, are shown in Fig. 1.

Table 2. Selected bond lengths (Å) and angles (°)

Molecule 1		Molecule 2	
Distances		*Distances*	
Cr(1)–C(11)	1.861(7)	Cr(2)–C(21)	1.851(11)
Cr(1)–C(12)	1.812(7)	Cr(2)–C(22)	1.816(10)
Cr(1)–C(13)	1.851(8)	Cr(2)–C(23)	1.861(7)
Cr(1)–C(14)	1.882(7)	Cr(2)–C(24)	1.850(10)
Cr(1)–C(15)	1.888(8)	Cr(2)–C(25)	1.891(6)
Cr(1)–S(1)	2.409(2)	Cr(2)–S(2)	2.396(2)
C(11)–O(1)	1.149(8)	C(21)–O(21)	1.177(15)
C(12)–O(2)	1.165(9)	C(22)–O(22)	1.154(13)
C(13)–O(3)	1.154(11)	C(23)–O(23)	1.144(10)
C(14)–O(4)	1.137(9)	C(24)–O(24)	1.170(12)
C(15)–O(5)	1.151(10)	C(25)–O(25)	1.139(7)
C(16)–S(1)	1.790(7)	C(26)–S(2)	1.834(9)
C(112)–C(113)	1.513(10)	C(212)–C(213)	1.509(10)
C(112)–N(1)	1.494(9)	C(212)–N(2)	1.467(10)
C(119)–C(120)	1.500(17)	C(219)–C(220)	1.530(15)
C(119)–N(1)	1.489(8)	C(219)–N(2)	1.473(10)
S(1)–N(1)	1.697(6)	S(2)–N(2)	1.707(5)
mean C–C in Ph 1.373(11)		mean C–C in Ph 1.368(20)	
Angles		*Angles*	
C(15)–Cr(1)–S(1)	87.6(3)	C(25)–Cr(2)–S(2)	88.3(3)
C(14)–Cr(1)–S(1)	87.1(3)	C(24)–Cr(2)–S(2)	98.4(3)
C(14)–Cr(1)–C(15)	90.1(4)	C(24)–Cr(2)–C(25)	90.5(4)
C(13)–Cr(1)–S(1)	92.3(3)	C(23)–Cr(2)–S(2)	93.4(3)
C(13)–Cr(1)–C(15)	179.7(4)	C(23)–Cr(2)–C(25)	176.1(4)
C(13)–Cr(1)–C(14)	88.8(3)	C(23)–Cr(2)–C(24)	92.7(4)
C(12)–Cr(1)–S(1)	175.1(3)	C(22)–Cr(2)–S(2)	174.7(4)
C(12)–Cr(1)–C(15)	89.2(4)	C(22)–Cr(2)–C(25)	90.1(4)
C(12)–Cr(1)–C(14)	89.2(4)	C(22)–Cr(2)–C(24)	86.7(4)
C(12)–Cr(1)–C(13)	90.1(4)	C(22)–Cr(2)–C(23)	87.9(5)
C(11)–Cr(1)–S(1)	98.7(3)	C(21)–Cr(2)–S(2)	85.7(3)
C(11)–Cr(1)–C(15)	92.5(3)	C(21)–Cr(2)–C(25)	89.2(4)
C(11)–Cr(1)–C(14)	173.3(4)	C(21)–Cr(2)–C(24)	175.9(4)
C(11)–Cr(1)–C(13)	87.7(4)	C(21)–Cr(2)–C(23)	87.4(4)
C(11)–Cr(1)–C(12)	85.2(4)	C(21)–Cr(2)–C(22)	89.23(5)
Cr(1)–C(11)–O(1)	174.0(7)	Cr(2)–C(21)–O(21)	177.2(9)
Cr(1)–C(12)–O(2)	179.1(8)	Cr(2)–C(22)–O(22)	178.3(10)
Cr(1)–C(13)–O(3)	177.6(7)	Cr(2)–C(23)–O(23)	176.1(9)
Cr(1)–C(14)–O(4)	176.0(7)	Cr(2)–C(24)–O(24)	174.6(8)
Cr(1)–C(15)–O(5)	178.0(6)	Cr(2)–C(25)–O(25)	177.7(7)
C(111)–C(16)–S(1)	122.1(6)	C(211)–C(26)–S(2)	117.0(9)
C(17)–C(16)–S(1)	117.3(6)	C(27)–C(26)–S(2)	121.4(8)
C(113)–C(112)–N(1)	111.1(6)	C(213)–C(212)–N(2)	111.8(6)
C(112)–C(113)–C(118)	121.1(8)	C(212)–C(213)–C(218)	121.3(8)
C(112)–C(113)–C(114)	119.4(8)	C(212)–C(213)–C(214)	120.2(8)
C(120)–C(119)–N(1)	112.1(6)	C(220)–C(219)–N(2)	110.0(7)
C(119)–C(120)–C(125)	121.8(7)	C(219)–C(220)–C(225)	122.8(9)
C(119)–C(120)–C(121)	119.2(7)	C(219)–C(220)–C(221)	120.5(9)
Cr(1)–S(1)–C(16)	115.3(3)	Cr(2)–S(2)–C(26)	114.5(4)
C(1)–S(1)–N(1)	104.9(3)	C(26)–S(2)–N(2)	105.6(4)
Cr(2)–S(1)–N(1)	112.2(2)	Cr(2)–S(2)–N(2)	112.6(3)
C(119)–N(1)–S(1)	116.5(5)	C(219)–N(2)–S(2)	111.6(5)
C(112)–N(1)–S(1)	112.6(5)	C(212)–N(2)–S(2)	116.5(5)
C(112)–N(1)–C(119)	110.0(5)	C(212)–N(2)–C(219)	112.2(6)
mean C–C–C in Ph 120.1(9)		mean C–C–C in Ph 120.0(12)	

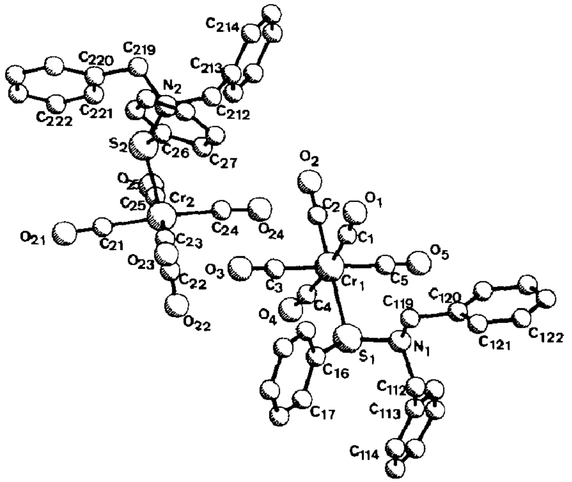

Fig. 1. PLUTO drawing of the two independent molecules of the compound $(C_6H_5CH_2)_2$-$NS(C_6H_5)Cr(CO)_5$.

In both molecules the chromium atom has a distorted octahedral geometry, with four carbonyl groups lying in the equatorial plane, and the remaining carbonyl group and the sulfur atom of the sulfenamide moiety in the apical positions. The C–Cr–C and C–Cr–S bond angles for the first molecule are in the ranges 85.2(4)–98.7(3)° and 173.3(4)–179.7(4)° for pairs of atom *cis* and *trans*, respectively, to the chromium atom. Similar values are observed for the second molecule: 85.7(3)–98.4(3)° and 174.6(4)–176.1(4)°. These values are comparable to others in the literature [10].

For the CO group in the *trans* position to the sulfur atom, the Cr–C bond distance is shorter than the mean value for the remaining carbonyl ligands, 1.812(7) Å for Cr(1)–C(2) vs. the averaged 1.870 Å in the first molecule and 1.816(9) Å for Cr(2)–C(22) vs. 1.860 Å in the second one. The Cr–S bond distance is 2.409(2) Å in the former and 2.395(2) Å in the latter molecule. These parameters are comparable to those reported for the Cr^0 complex $(CH_3)_2$ $N_2SCr(CO)_5$ [11], and can be accounted for by assuming that the carbon monoxide ligand *trans* to the sulfur more effectively competes witih sulfur for the metal d_π electrons, through $d_{\pi-\pi^*(CO)}$ back-donation, to form a partial multiple Cr–C bond which is of higher bond order than that for the carbon monoxide ligands *cis* to sulfur and *trans* to each other.

Table 3

Dihedral angles between mean least squares planes of aromatic rings

Ring	Plane	Torsion angle (°)	
A	C(16)–C(17)–C(18)–C(19)–C(110)–C(111)	A–B	14.9(3)
B	C(113)–C(114)–C(115)–C(116)–C(117)–C(118)	A–C	103.1(3)
C	C(120)–C(121)–C(122)–C(123)–C(124)–C(125)	B–C	117.5(3)
A′	C(26)–C(27)–C(28)–C(29)–C(210)–C(211)	A′–B′	96.4(4)
B′	C(213)–C(214)–C(215)–C(216)–C(217)–C(218)	A′–C′	22.5(4)
C′	C(220)–C(221)–C(222)–C(223)–C(224)–C225)	B′–C′	118.8(3)

The sulfur and nitrogen atoms of both molecules have a tetrahedral geometry. There is an enantiomeric relationship for the sulfurs, with configurations S(1)(*R*) and S(2)(*S*). The sulfur–nitrogen bond distances are 1.697(6) Å for S(1)–N(1) and 1.707(5) Å for S(2)–N(2), less than those corresponding to a S–N (1.74 Å) single bond, suggesting some π-bond character.

The main difference between the two molecules involves the relative spatial orientations of the three aromatic rings, as can be seen by comparing the values of the dihedral angles between their mean least squares planes for each molecule (Table 3).

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