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# Structures of ($N,N$-dicyclohexyl)benzenesulfenamide and its pentacarbonylchromium(0) complex via the sulfur atom

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**Abstract**

The crystal structures of the title compounds are reported and discussed.

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## Introduction

Sulfenamides, which contain trivalent nitrogen bonded to divalent sulfur, have been of interest for some years because of their industrial applications, their utility as synthetic reagents, and their interesting stereochemical properties [1]. In spite of the range of coordination properties expected for such compounds as a consequence of the presence of lone pairs on the sulfur and nitrogen atoms, only a small number of metal complexes containing these ligands have been reported [2].

As a part of our studies of the coordinating properties of sulfenamides [3] we report below the crystal and molecular structure of the novel sulfenamide: ($N,N$-dicyclohexyl)benzenesulfenamide and its pentacarbonylchromium(0) complex in which it is coordinated through the sulfur atom.

## Experimental

The compounds were prepared as previously described [4].

*Pentacarbonyl(* N,N *-dicyclohexyl)benzenesulfenamidechromium(0) (I),* $C_{23}H_{27}CrNO_5S$

Yellow crystals grown from n-hexane. Reflection intensities were recorded on a four-circle computer-controlled Siemens–Stoe diffractometer, using graphite monochromated Cu-$K_\alpha$ radiation and the $\omega:\theta$ scan mode. Two standard reflections monitored every hour showed no significant decay. Cell parameters were

Table 1

Atomic coordinated and equivalent isotropic temperature factors of the non-H atoms (with esd's in parentheses) for compound I. Values for equivalent atoms in the independent molecules are given in successive lines

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Cr | 0.0581(1) | 0.3834(1) | 0.1560(1) | 446(1) |
| | −0.2556(1) | −0.2008(1) | 0.2656(1) | 511(1) |
| O1 | 0.3037(3) | 0.4926(2) | 0.2752(2) | 728(1) |
| | −0.4136(4) | −0.2313(3) | 0.0833(2) | 1035(2) |
| O2 | 0.2034(4) | 0.3154(3) | 0.0125(2) | 951(2) |
| | −0.2445(5) | 0.0056(3) | 0.2811(3) | 1200(2) |
| O3 | −0.0021(3) | 0.5558(2) | 0.0981(3) | 899(2) |
| | −0.0160(3) | −0.2138(3) | 0.1896(2) | 991(2) |
| O4 | −0.0704(3) | 0.4743(3) | 0.3015(2) | 833(1) |
| | −0.2954(4) | −0.4118(3) | 0.2243(2) | 858(2) |
| O5 | 0.1396(5) | 0.2287(3) | 0.2351(2) | 1005(2) |
| | −0.5082(3) | −0.1882(3) | 0.3244(2) | 836(2) |
| S1 | −0.1244(1) | 0.2764(1) | 0.0537(1) | 491(1) |
| | −0.1347(1) | −0.1590(1) | 0.4183(1) | 480(1) |
| N1 | −0.2160(3) | 0.2189(2) | 0.0984(2) | 558(1) |
| | −0.2027(3) | −0.2056(2) | 0.4829(2) | 565(1) |
| C11 | 0.2090(4) | 0.4507(3) | 0.2273(3) | 553(2) |
| | −0.3529(4) | −0.2205(4) | 0.1530(3) | 709(2) |
| C12 | 0.1469(4) | 0.3404(3) | 0.0652(2) | 539(2) |
| | −0.2452(5) | −0.0722(3) | 0.2774(3) | 747(2) |
| C13 | 0.0180(4) | 0.4882(3) | 0.1159(3) | 574(2) |
| | −0.1029(4) | −0.2090(3) | 0.2210(3) | 628(2) |
| C14 | −0.0264(4) | 0.4347(3) | 0.2452(2) | 539(2) |
| | −0.2765(4) | −0.3316(3) | 0.2437(3) | 595(2) |
| C15 | 0.1038(4) | 0.2850(3) | 0.2029(3) | 592(2) |
| | −0.4110(4) | −0.1931(3) | 0.3045(3) | 565(2) |
| C16 | −0.2271(4) | 0.3379(3) | −0.0078(3) | 545(2) |
| | 0.0265(3) | −0.1934(3) | 0.4304(2) | 488(2) |
| C17 | −0.2502(5) | 0.3075(4) | −0.0987(3) | 737(2) |
| | 0.1267(4) | −0.1324(3) | 0.4912(3) | 621(2) |
| C18 | −0.3243(7) | 0.3602(6) | −0.1470(3) | 950(3) |
| | 0.2519(5) | −0.1569(4) | 0.5019(4) | 815(2) |
| C19 | −0.3712(5) | 0.4393(6) | −0.1048(5) | 973(3) |
| | 0.2766(5) | −0.2415(5) | 0.4530(4) | 813(3) |
| C110 | −0.3463(5) | 0.4700(5) | −0.0142(5) | 948(3) |
| | 0.1772(5) | −0.3032(4) | 0.3931(4) | 811(2) |
| C111 | −0.2756(4) | 0.4184(4) | 0.0331(3) | 635(2) |
| | 0.0516(4) | −0.2785(3) | 0.3812(3) | 688(2) |
| C112 | −0.2813(4) | 0.2688(3) | 0.1665(2) | 522(2) |
| | −0.2222(4) | −0.3069(3) | 0.4665(2) | 466(1) |
| C113 | −0.4272(4) | 0.2634(3) | 0.1335(3) | 694(2) |
| | −0.3653(4) | −0.3420(3) | 0.4556(3) | 616(2) |
| C114 | −0.4872(5) | 0.3185(4) | 0.2071(4) | 932(3) |
| | −0.3850(5) | −0.4479(3) | 0.4342(3) | 746(2) |
| C115 | −0.4522(8) | 0.2867(4) | 0.2878(5) | 1174(3) |
| | −0.3000(5) | −0.4810(3) | 0.5031(3) | 750(2) |
| C116 | −0.3072(7) | 0.2928(4) | 0.3196(3) | 988(3) |
| | −0.1590(5) | −0.4491(4) | 0.5126(3) | 714(2) |
| C117 | −0.2448(6) | 0.2373(4) | 0.2484(3) | 781(2) |
| | −0.1337(4) | −0.3422(3) | 0.5342(3) | 657(2) |

Table 1 (continued)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| C118 | −0.2521(4) | 0.1173(3) | 0.0567(3) | 568(2) |
| | −0.2268(4) | −0.1430(3) | 0.5645(2) | 551(2) |
| C119 | −0.1374(5) | 0.0631(3) | 0.0746(3) | 732(2) |
| | −0.3367(4) | −0.0844(3) | 0.5446(3) | 679(2) |
| C120 | −0.1771(6) | −0.0421(4) | 0.0381(4) | 921(3) |
| | −0.3693(5) | −0.0255(4) | 0.6287(4) | 899(2) |
| C121 | −0.2428(6) | −0.0698(3) | −0.0588(4) | 913(3) |
| | −0.2505(6) | 0.0362(4) | 0.6905(3) | 811(2) |
| C122 | −0.3555(5) | −0.0143(3) | −0.0773(4) | 870(2) |
| | −0.1400(6) | −0.0222(4) | 0.7102(3) | 784(2) |
| C123 | −0.3150(5) | 0.0916(3) | −0.0398(3) | 733(2) |
| | −0.1066(4) | −0.0813(3) | 0.6258(3) | 638(2) |

established by least squares adjustment of the setting angles of 19 strong reflections in the range $18 < 2\theta < 40°$. Of 5422 measured independent reflections ($3 < 2\theta < 120°$), 4724 (index range $h$: 0 to 12; $k$ : −10 to 16; $l = -18$ to 17) with $I > 3\sigma(I)$ were considered as observed, and used after correction for Lorentz and polarization effects for the structure solution and refinement. The structure was solved by Patterson and successive Fourier syntheses [5]. Refinement on $F$ was by full-matrix least-squares. An empirical absorption correction was carried out at the isotropic level of refinement (correction range 0.745 to 1.507) [6]. The hydrogen atom were placed in calculated positions. A weighting scheme based on a flat dependence of $\Delta^2F$ vs. $F_o$ and $\sin\theta/\lambda$ was performed [7]. Final weighted full-ma-

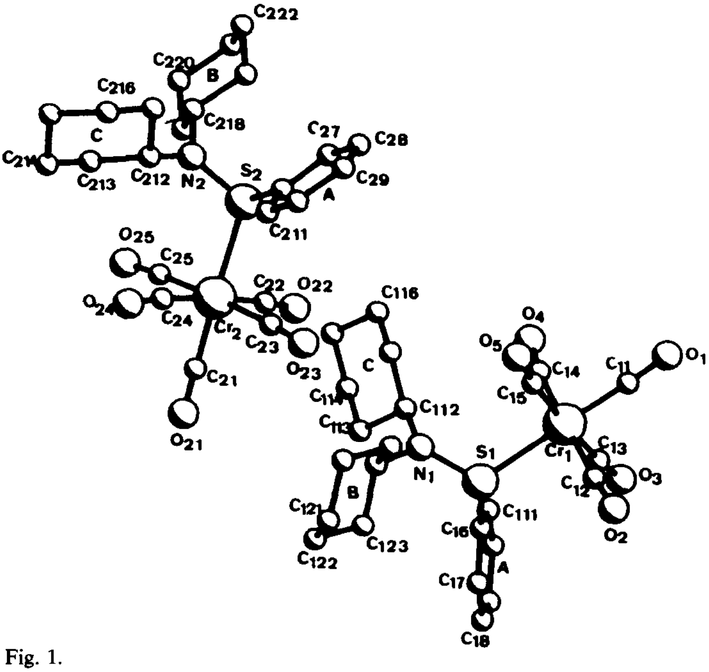

Fig. 1.

Table 2

Selected bond lengths (Å) and angles (°) in compound I

| Molecule 1 | | Molecule 2 | |
|---|---|---|---|
| *Distances* | | | |
| Cr1–C11 | 1.830(4) | Cr2–C21 | 1.844(4) |
| Cr1–C12 | 1.900(4) | Cr2–C22 | 1.878(5) |
| Cr1–C13 | 1.892(5) | Cr2–C23 | 1.905(5) |
| Cr1–C14 | 1.872(4) | Cr2–C24 | 1.884(5) |
| Cr1–C15 | 1.877(5) | Cr2–C25 | 1.884(5) |
| Cr1–S1 | 2.445(1) | Cr2–S2 | 2.441(2) |
| C11–O1 | 1.164(4) | C21–O21 | 1.147(5) |
| C12–O2 | 1.140(6) | C22–O22 | 1.149(7) |
| C13–O3 | 1.145(6) | C23–O23 | 1.140(6) |
| C14–O4 | 1.149(5) | C24–O24 | 1.151(6) |
| C15–O5 | 1.149(7) | C25–O25 | 1.144(6) |
| C16–S1 | 1.783(4) | C26–S2 | 1.796(4) |
| C112–N1 | 1.479(4) | C212–N2 | 1.463(5) |
| C118–N1 | 1.480(5) | C218–N2 | 1.481(5) |
| S1–N1 | 1.666(5) | S2–N2 | 1.670(4) |
| mean distances for C–C in phenyl group 1.387(9) | | mean distances for C–C in phenyl group 1.380(7) | |
| mean distances for C–C in cyclohexyl group 1.519(9) | | mean distances for C–C in cyclohexyl 1.525(7) | |
| *Angles* | | | |
| C15–Cr1–S1 | 87.7(2) | C25–Cr2–S2 | 89.0(2) |
| C14–Cr1–S1 | 98.2(2) | C24–Cr2–S2 | 98.3(2) |
| C14–Cr1–C15 | 91.8(2) | C24–Cr2–C25 | 89.7(2) |
| C13–Cr1–S1 | 95.8(2) | C23–Cr2–S2 | 93.6(2) |
| C13–Cr1–C15 | 176.2(2) | C23–Cr2–C25 | 177.3(2) |
| C13–Cr1–C14 | 86.2(2) | C23–Cr2–C24 | 90.4(2) |
| C12–Cr1–Si | 84.2(1) | C22–Cr2–S2 | 86.9(2) |
| C12–Cr1–C15 | 91.8(2) | C22–Cr2–C25 | 89.6(2) |
| C12–Cr1–C14 | 176.0(2) | C22–Cr2–C24 | 174.7(2) |
| C12–Cr1–C13 | 90.1(2) | C22–Cr2–C23 | 90.0(2) |
| C11–Cr1–S1 | 172.0(2) | C21–Cr2–S2 | 174.1(2) |
| C11–Cr1–C15 | 87.5(2) | C21–Cr2–C25 | 88.4(2) |
| C11–Cr1–C14 | 88.4(2) | C21–Cr2–C24 | 87.0(2) |
| C11–Cr1–C13 | 89.3(2) | C21–Cr2–C23 | 89.0(2) |
| C11–Cr1–C12 | 89.6(2) | C21–Cr2–C22 | 87.8(2) |
| Cr1–C11–O1 | 177.5(4) | Cr2–C21–O21 | 179.0(5) |
| Cr1–C12–O2 | 178.0(4) | Cr2–C22–O22 | 176.5(5) |
| Cr1–C13–O3 | 174.7(4) | Cr2–C23–O23 | 176.0(4) |
| Cr1–C14–O4 | 173.2(4) | Cr2–C24–O24 | 174.9(4) |
| Cr1–C15–O5 | 175.1(4) | Cr2–C25–O25 | 176.9(4) |
| C111–C16–S1 | 121.5(3) | C211–C26–S2 | 121.6(3) |
| C17–C16–S1 | 118.5(4) | C27–C26–S2 | 118.5(3) |
| C117–C112–N1 | 111.0(4) | C217–C212–N2 | 113.8(3) |
| C113–C112–N1 | 113.1(4) | C213–C212–N2 | 111.8(4) |
| C123–C118–Ni | 113.9(4) | C223–C218–N2 | 114.2(4) |
| C119–C118–N1 | 111.2(4) | C219–C218–N2 | 111.4(4) |
| Cr1–S1–C6 | 110.1(2) | Cr2–S2–C26 | 113.0(2) |
| C16–S1–N1 | 108.2(2) | C26–S2–N2 | 105.2(2) |
| Cr1–S1–N1 | 115.8(1) | Cr2–S2–N2 | 114.9(2) |
| C118–N1–S1 | 118.2(3) | C218–N2–S2 | 118.9(3) |
| C112–N1–S1 | 121.6(3) | C212–N2–S2 | 121.1(3) |
| C112–N1–C118 | 119.2(4) | C212–N2–C218 | 119.6(3) |

Table 2 (continued)

| Molecule 1 | Molecule 2 |
|---|---|
| *Angles* | |
| mean angle C–C–C in phenyl group: 120.0(6) | mean angle C–C–C in phenyl group: 120.0(5) |
| mean angle C–C–C in cyclohexyl group: 111.4(5) | mean angle C–C–C in cyclohexyl group: 111.1(5) |

trix refinement with anisotropic thermal parameters for all non-H atoms and fixed isotropic contribution for the hydrogen atoms, converged to final agreement factors of $R = 0.045$ and $R_w = 0.053$. Maximum shift/$\sigma$ 0.7910, maximum electron density in final difference synthesis map 0.14 e $A^{-3}$.

*(N,N-dicyclohexyl)benzenesulfenamide(II),* $C_{18}H_{27}NS$

Colourless crystals grown from n-hexane. Diffraction maxima collected as above. Cell parameters were established by least-squares adjustment of the setting angles of 26 strong reflections in the range $19 < 2\theta < 40°$. Of a total of 2707 independent measured reflections ($3 < 2\theta < 122°$) 2523 with $I > 3\sigma(I)$ and index range $h$: 0 to 10; $k$: 0 to 19; $l$: $-11$ to 11 were considered as observed and used after correction for Lorentz and polarization factors for the structure resolution and refinement. The structure was solved by direct methods [8] and refined on $F$ by full-matrix least squares [5]. During the isotropic refinement for non-H atoms an empirical absorption correction was carried out (correction range 0.765 to 1.420) [6]. The

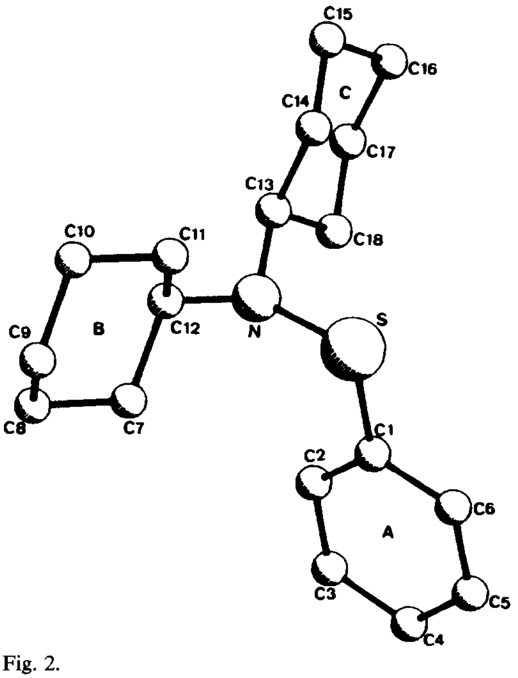

Fig. 2.

hydrogen atoms were placed in calculated positions. Final refinement with anisotropic thermal parameters for the non-H atoms and the hydrogen atoms added as fixed isotropic contribution converged to a standard crystallographic residual of $R = 0.050$ (unit weight), maximum shift/$\sigma = 0.023$, maximum electron density in final difference synthesis map 0.32 e $A^{-3}$.

Scattering factors for both structures were taken from the *International Tables for X-Ray Crystallography*.

## Discussion

### *Compound I*

Fractional atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms are listed in Table 1. Selected interatomic distances and bond angles are given in Table 2. Figure 1 shows the molecular structure of the complex together with the atom labelling scheme.

The crystal is made up of discrete molecules with two symmetry-independent molecules in the asymmetric unit.

The Cr atom is octahedrally coordinated to five carbonyl group and to the sulfur atom of the sulfenamide moiety. Four carbonyl ligands lie in the equatorial plane of the octahedron, and the remaining carbonyl ligand and the sulfur atom are in the apical positions. The C–Cr–C, Cr–C–O and C–Cr–S angles in the coordination sphere (Table 2) indicate a slightly distorted $C_{4v}$ symmetry, the large deviations being associated with angles involving the sulfur atom.

For the CO ligand *trans* to the sulfur atom in both molecules the Cr–C bond distances [Cr1–C11 = 1.830(4) and Cr2–C21 = 1.844(4) Å] are shorter than the average values (1.885 Å in molecule 1 and 1.887 Å in molecule 2) for the remaining equatorial carbonyl ligands. Those $d_\pi$–$p_\pi$ metal–CO back-bonding effects are similar to those observed for other pentacarbonyl chromium complexes with sulfur ligands [2] (Tab. 3). The Cr–S bond distances of 2.445(1) Å for molecule 1 and 2.441(2) Å for molecule 2 also suggest a metal–ligand $\pi$-interaction [9]. The Cr–S bond length in pentacarbonyl(trimethylphospinethio)chromium(0), in which there is assumed to be interaction, is 2.510(12) Å [10].

In both molecules the angles around the nitrogen atom are close to 120° (see Table 2), suggesting a trigonal geometry. Both sulfur nitrogen bond distances [1.666(5) and 1.670(4) Å] are shorter than those corresponding to a sulfur–nitrogen single bond (1.74 Å), indicating some $\pi$-bond character. The sulfur atoms have a

Table 3

Some bond lengths (Å) in pentacarbonylchromium complexes containing sulfur ligands

| Ligands | Cr–C(*cis*) | Cr–C(*trans*) | Cr–S | References |
|---|---|---|---|---|
| $(C_6H_5CH_2)S(C_2H_5)$ | 1.879(21) | 1.859(7) | 2.459(2) | [2a] |
| $(C_2H_5)_3PCS_2$ | 1.86(1) | 1.78(2) | 2.389(4) | [2c] |
| $SO_2$ | 1.899(19) | 1.887(19) | 2.188(6) | [2d] |
| $(CH_3)_2NNS$ | 1.903(5) | 1.846(2) | 2.386(1) | [2b] |
| $(C_6H_5)_2NNS$ | 1.900(9) | 1.848(7) | 2.357(2) | [2e] |
| $(C_6H_5)_2NS(C_6H_5)$ | 1.871(17) | 1.814(3) | 2.409(10) | [3] |

Table 4

Dihedral angles between mean least squeres planes of the rings A, B, and C in compounds I and II

| Ring | Plane | Dihedral angle (°)[a] | |
|---|---|---|---|
| A′ | (C16–C17–C18–C19–C110–C111) | A′–B′ | 149.5(2) |
| B′ | (C118–C119–C120–C121–C122–C123) | A′–C′ | 138.3(2) |
| C′ | (C112–C113–C114–C115–C116–C117) | B′–C′ | 118.0(2) |
| A* | (C26–C27–C28–C29–C210–C211) | A*–B* | 163.5(2) |
| B* | (C218–C219–C220–C221–C222–C223) | A*–C* | 104.9(2) |
| C* | (C212–C213–C214–C215–C216–C217) | B*–C* | 117.8(1) |
| A | (C1–C2–C3–C4–C5–C6) | A–B | 75.2(1) |
| B | (C7–C8–C9–C10–C11–C12) | A–C | 97.2(1) |
| C | (C13–C14–C15–C16–C17–C18) | B–C | 157.6(1) |

[a] ′ = compound I, molecule 1; * = compound I, molecule 2.

pyramidal geometry with bond angles ranging from 105.2° [C26–S2–N2 in molecule 2] to 115.8(1)° [Cr1–S1–N1 in molecule 1].

The phenyl rings are planar [maximum deviation −0.02(6) Å in molecule 1]. Rings B and C are in a chair conformation in both molecules (absolute values for ring torsion angles vary from 54.4 to 56.3° for B rings and 54.6 to 57.1° for C rings). The values for the dihedral angles between the phenyl ring and the best least-squares planes for cycohexyl rings (Table 4) are comparable for the two molecules.

Comparison of the structure of present complex with that of the related pentacarbonyl(*N*,*N*-dibenzyl)benzenesulfenamidechromium(0) [3] shows expected

Table 5

Atomic coordinates and equivalent isotropic temperature factors of the non-H atoms for compound II with esd's in parentheses)

| Atom | *x* | *y* | *z* | $U_{eq}$ |
|---|---|---|---|---|
| S | 0.0254(1) | 0.1509(1) | 0.1102(1) | 569(1) |
| N | −0.0130(3) | 0.2045(1) | 0.2302(2) | 477(1) |
| C1 | 0.1357(3) | 0.0759(2) | 0.1904(3) | 509(1) |
| C2 | 0.1842(4) | 0.0702(2) | 0.3242(3) | 626(1) |
| C3 | 0.2759(4) | 0.0113(2) | 0.3804(4) | 754(1) |
| C4 | 0.3189(4) | −0.0432(2) | 0.3025(5) | 874(2) |
| C5 | 0.2686(4) | −0.0389(2) | 0.1687(5) | 862(2) |
| C6 | 0.1779(4) | 0.0202(2) | 0.1122(3) | 671(1) |
| C7 | 0.2250(3) | 0.2689(2) | 0.3096(3) | 655(1) |
| C8 | 0.3038(4) | 0.3453(2) | 0.3422(4) | 774(1) |
| C9 | 0.2737(4) | 0.3991(2) | 0.2265(4) | 852(2) |
| C10 | 0.1118(4) | 0.4097(2) | 0.1728(4) | 784(2) |
| C11 | 0.0344(4) | 0.3333(2) | 0.1378(3) | 644(1) |
| C12 | 0.0622(3) | 0.2794(2) | 0.2550(3) | 519(1) |
| C13 | −0.1650(3) | 0.2016(2) | 0.2471(3) | 517(1) |
| C14 | −0.2814(4) | 0.2291(2) | 0.1304(3) | 709(1) |
| C15 | −0.4345(4) | 0.2255(2) | 0.1571(4) | 875(2) |
| C16 | −0.4704(4) | 0.1456(2) | 0.1960(4) | 804(2) |
| C17 | −0.3569(4) | 0.1197(2) | 0.3131(4) | 744(1) |
| C18 | −0.2025(3) | 0.1224(2) | 0.2868(3) | 618(1) |

Table 6

Bond lengths (Å) and bond angles ( ° ) in compound II (with esd's in parentheses)

| | | | |
|---|---|---|---|
| S–N | 1.684(3) | C7–C12 | 1.512(4) |
| S–C1 | 1.765(3) | C8–C9 | 1.520(5) |
| N–C12 | 1.484(4) | C9–C10 | 1.503(5) |
| N–C13 | 1.477(4) | C10–C11 | 1.528(5) |
| C1–C2 | 1.387(4) | C11–C12 | 1.533(4) |
| C1–C6 | 1.395(5) | C13–C14 | 1.525(4) |
| C2–C3 | 1.387(5) | C13–C18 | 1.516(4) |
| C3–C4 | 1.381(6) | C14–C15 | 1.527(5) |
| C4–C5 | 1.387(7) | C15–C16 | 1.520(5) |
| C5–C6 | 1.384(5) | C16–C17 | 1.504(5) |
| C7–C8 | 1.529(5) | C17–C18 | 1.536(5) |
| N–S–C1 | 104.9(1) | C8–C9–C10 | 111.4(3) |
| S–N–C13 | 116.9(2) | C9–C10–C11 | 111.4(3) |
| S–N–C12 | 116.8(2) | C10–C11–C12 | 111.2(3) |
| C12–N–C13 | 116.2(2) | C7–C12–C11 | 110.6(3) |
| S–C1–C6 | 116.8(2) | N–C12–C11 | 114.7(2) |
| S–C1–C2 | 124.2(2) | N–C12–C7 | 110.9(2) |
| C2–C1–C6 | 119.0(3) | N–C13–C18 | 111.0(3) |
| C1–C2–C3 | 121.0(3) | N–C13–C14 | 114.8(3) |
| C2–C3–C4 | 119.8(4) | C14–C13–C18 | 110.3(3) |
| C3–C4–C5 | 119.6(4) | C13–C14–C15 | 111.3(3) |
| C4–C5–C6 | 120.8(4) | C14–C15–C16 | 111.4(3) |
| C1–C6–C5 | 119.8(3) | C15–C16–C17 | 110.0(3) |
| C8–C7–C12 | 111.8(3) | C16–C17–C18 | 111.0(3) |
| C7–C8–C9 | 111.8(3) | C13–C18–C17 | 111.5(3) |

similarities in bond lengths and angles. However the change of the groups bonded to nitrogen from benzyl in the latter to cyclohexyl in the former results in a shortening in the S–N bond, while the Cr–S distances are increased by the same amount; this suggests a weaker metal–ligand $\pi$-interaction in the present compound.

I: $C_{23}H_{27}CrNO_5S$, $M_r = 481.5$, triclinic, space group $P1$, $a$ 10.604(4), $b$ 14.971 (4), $c$ 16.301(6) Å, $\alpha$ 105.94(2), $\beta$ 102.10(3), $\gamma$ 92.74(2)°, $V = 2417.8(2)$ Å$^3$, $Z = 4$, $D_x = 1.248$ g cm$^{-3}$, $\lambda$(Cu-$K_\alpha$) 1.5418 Å, $\mu$ 50.1 cm$^{-1}$, $F(000) = 1008$, $T$ 293 K, final $R = 0.045$, $R_w = 0.053$ for 4724 observed reflections.

*Compound II*

The final positional parameters are listed in Table 5. Selected interatomic distances and bond angles are given in Table 6. Figure 2 shows the molecular structure and the atom labelling scheme.

Comparison of the structure of this compound with that of its chromium pentacarbonyl complex described above shows the expected similarities. However, the angles around the nitrogen reflect a more pyramidal geometry complex in II than in complex I (see Table 6). The S–N bond distance of 1.684(3) Å is longer than those in the complex but still shorter than that expected for a single S–N bond, suggesting some double bond character, as has suggestive for related compounds on the basis of photoelectron spectroscopy data [11]. The bonding of the sulfenamide to the $Cr(CO)_5$ fragment via the sulfur atom results in a shortening in of the S–N bond by about 0.016 Å. The major difference between the two compounds involves the relative spatial orientation of the three rings, as can be seen by comparing the values of the dihedral angles between the best least-squares planes for the two compounds (Table 4).

II: $C_{18}H_{27}NS$, $M_r = 289.5$, monoclinic, space group $P2_1/c$, $a$ 9.371(2), $b$ 17.532(4), $c$ 10.580(7) Å, $\beta$ 103.4(6)°, $V$ 1691.1(7) $Å^3$, $Z = 4$, $D_x = 1.137$ g $cm^{-3}$, $\lambda$(Cu-$K_\alpha$) 1.5418 Å, $\mu$ 15.7 $cm^{-1}$, $F(000) = 632$, $T$ 293 K, final $R = 0.050$ for 2523 observed reflections.

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