Journal of Organometallic Chemistry, 249 (1983) 289–292
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CRYSTAL AND MOLECULAR STRUCTURE OF $[CH_3C(S)CHC(S)CH_3][CH_3S(O)(CH_2)_2]Ni$

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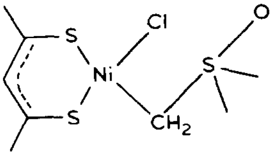
(Received February 21st, 1983)

Summary

The formation of chelating sulfur ylides has been suggested previously. This study reports the first structural evidence for their existence. The title compound contains a chelating bis(methylene)methylsulfoxonium ligand and a *cis*-NiC_2S_2 coordination geometry. The material crystallizes in the space group $P2_1/c$ with a 13.371(4), b 5.8381(15) and c 15.116(4) Å, β 100.18°, $Z = 4$. With 1206 reflections, $R = 0.067$. The material appears to be stable to the atmosphere.

Introduction

As a continuation of our work with complexes having sulfur chelates [1] and/or ylides [2] as ligands, we attempted the preparation of I via the reaction of excess dimethylsulfoxonium methylide with a (SacSac)(phosphine)Ni chloride, analogous to similar reactions carried out with dithiocarbamate complexes in this laboratory [3]. A definite formulation for the product could not be made on the basis of spectral



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* Few chemists are as avid or successful in their efforts to fool the wary trout with a fly as Harry Emeléus. The (too few) trips we made together combining chemistry with this most noble sport will always be remembered. Stories, both true and not so true, flow easily when one enters the warm pub for a pint and lunch. This paper is my feeble attempt to recognize a true gentleman, horticulturist, naturalist (mayflies) and scholar on the great occasion of 80 years residence on this globe of ours.

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data. Therefore, an X-ray structure determination was undertaken. The title complex is the first example of a chelating sulfur ylide to be characterized structurally although some chelating sulfoxonium ylide complexes have been suggested previously [8].

Experimental

Needles of the title compound were grown by the slow evaporation (in air) of an acetone solution. The crystal selected for X-ray study was cut to the dimensions given in Table 1, and standard procedures used for data collection [4]. Duplicate data ($h,k,\pm l$ and $h,-k,\pm l$) were collected, an empirical absorption correction applied with Flack's CAMEL JOCKEY program [5], and equivalent reflections averaged.

The Ni atom was located by heavy atom techniques, and all remaining non-hydrogen atoms located from successive difference-Fourier maps. Anisotropic refinement converged to $R = 0.076$, $R_w = 0.064$, and GOF = 1.89 [6]. A difference map at this stage revealed all hydrogen atoms. These were fixed at the positions located from the map with isotropic temperature factors of 6.0 Å^2. Further refinement of the non-hydrogen atoms converged to the results in Table 1. Scattering factors, including real and imaginary anomalous dispersion terms for Ni, were taken from reference 7. The largest residual peak in the final difference map was ~ 0.5 eA^{-3} and ~ 1.2 Å from the Ni atom.

Table 2 gives final positional parameters for the non-hydrogen atoms, while Table 3 gives pertinent bond length and angle data. Figure 1 depicts a single molecule, while Figure 2 shows a packing diagram.

Tables of non-hydrogen thermal parameters, hydrogen coordinates, bond lengths

TABLE 1

CRYSTAL DATA FOR $[CH_3C(S)CHC(S)CH_3][CH_3S(O)(CH_2)_2]Ni$

Formula	$NiS_3OC_8H_{14}$
Mol.wt.	281.1 g mol^{-1}
Space group	$P2_1/c$
a	13.371(4) Å
b	5.8381(15) Å
c	15.116(4) Å
β	100.18(2)°
V	1161.5(6)Å^3
Z	4
ρ_{calc}	1.61 g cm^{-3}
λ(Mo-K_α)	0.71073 Å
cryst. size	0.13×0.09×0.25 mm
μ	21.6 cm^{-1}
2θ limits	$2.0° \le 2\theta \le 50.0°$
refl. $I \ge 2.5_\sigma(I)$	1206
R	0.067
R_w	0.053
GOF	1.56
Largest peak in final diff. map	0.5 eÅ^{-3}

TABLE 2

FRACTIONAL COORDINATES FOR NON-HYDROGEN ATOMS IN $[CH_3C(S)CHC(S)CH_3]$-$[CH_3S(O)(CH_2)_2]Ni$

	x	*y*	*z*
Ni	0.25973(9)	0.1767(2)	0.18632(9)
S(1)	0.1246(2)	0.0190(4)	0.1185(2)
S(2)	0.2892(2)	−0.0104(5)	0.3094(2)
S(3)	0.3820(2)	0.4435(4)	0.1176(2)
O	0.4283(5)	0.6590(12)	0.0958(5)
C(1)	−0.0105(8)	−0.324(2)	0.1187(7)
C(2)	0.0814(7)	−0.2106(16)	0.1719(7)
C(3)	0.1233(7)	−0.2906(16)	0.2559(7)
C(4)	0.2051(7)	−0.2282(15)	0.3170(7)
C(5)	0.2290(8)	−0.358(2)	0.4039(7)
C(6)	0.2539(7)	0.3949(16)	0.0818(6)
C(7)	0.3824(7)	0.3742(16)	0.2273(7)
C(8)	0.4454(7)	0.2200(16)	0.0702(8)

TABLE 3

NON-HYDROGEN BOND LENGTHS (Å) AND ANGLES (deg) FOR $[CH_3C(S)CHC(S)CH_3]$-$[CH_3S(O)(CH_2)_2]Ni$

Ni–S(1)	2.123(3)	S(2)–C(6)	1.727(10)
Ni–S(2)	2.133(3)	S(3)–C(7)	1.706(10)
Ni–C(6)	2.021(10)	S(3)–C(8)	1.775(11)
Ni–C(7)	2.011(9)	C(1)–C(2)	1.498(13)
S(1)–C(2)	1.717(10)	C(2)–C(3)	1.375(14)
S(2)–C(4)	1.715(10)	C(3)–C(4)	1.351(13)
S(3)–O	1.465(7)	C(4)–C(5)	1.502(14)
S(1)–Ni–S(2)	102.1(2)	S(2)–C(4)–C(3)	128.0(7)
S(1)–Ni–C(6)	89.1(3)	S(2)–C(4)–C(5)	113.1(7)
S(1)–Ni–C(7)	167.3(4)	C(1)–C(2)–C(3)	120.5(7)
S(2)–Ni–C(6)	168.7(4)	C(2)–C(3)–C(4)	133.4(7)
S(2)–Ni–C(7)	90.6(3)	C(3)–C(4)–C(5)	118.9(7)
C(6)–Ni–C(7)	78.3(5)	C(6)–S(3)–C(7)	95.6(5)
Ni–S(1)–C(2)	116.1(4)	C(6)–S(3)–C(8)	105.7(5)
Ni–S(2)–C(4)	114.6(4)	C(6)–S(3)–O	120.3(4)
Ni–C(6)–S(3)	87.6(5)	C(7)–S(3)–C(8)	107.4(5)
Ni–C(7)–S(3)	88.5(5)	C(7)–S(3)–O	119.6(4)
S(1)–C(2)–C(1)	113.8(7)	C(8)–S(3)–O	106.9(4)
S(1)–C(2)–C(3)	125.7(7)		

and angles involving hydrogen atoms, and observed structure factors are available from the authors.

Discussion

As is so often true in science, the result obtained was not that expected. We dedicate this account of the first structural characterization of a chelating sulfur ylide complex to Professor Harry Emeléus, who also made many similar "surprise" discoveries in his long career.

The Ni–S distances in the title complex are 0.03 Å shorter than those in Ni(SacSac)$_2$ [9], but 0.02 longer than the Ni–S *trans* to Cl in Ni(SacSac)(PEt$_3$)Cl [10]. The decreased Ni–S bond lengths relative to those in Ni(SacSac)$_2$ indicate a stronger Ni–S interaction than in the latter. Consistent with a stronger Ni–S interaction is a weakened C–S interaction, as indicated by the slightly increased S(1)–C(2) (or S(2)–C(4)) lengths relative to the above complexes.

The Ni–C distances observed here are somewhat longer than the 1.944 Å observed in $(CH_3C(O)CHC(O)CH_3)(P(C_6H_{11})_3)(CH_3)Ni$ [11] but in good agreement with the 1.988(6) to 2.031(3) Å range found in chelating phosphorus ylide-nickel complexes [12], with a four membered $P(CH_2)_2Ni$ ring giving the 2.031(3) Å [12c]. The C(6)–C(7) bite distance is 2.54 Å, while that in the $P(CH_2)_2Ni$ ring is 2.60 Å, consistent with the slightly larger covalent radius of P relative to S [13].

The coordination about the Ni is essentially C_{2v} with the coordination sphere planar to 0.02 Å. Although S(3) is 0.62 Å out of the Ni, S(1), S(2), C(6), C(7) plane, O is only 0.38 Å out of this plane. The origin of this stereochemistry is unknown and may reflect steric interactions, packing effects, or possibly an electronic delocalization involving the ring and the oxygen atom.

Acknowledgements

The National Science Foundation CHE-8013141 supported this work along with the donors of the Petroleum Research Foundation, administered by the American Chemical Society.

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GOF ("goodness of fit") $= \left|\frac{\Sigma w_i||F_0|-|F_c||^2}{(N_0-N_v)}\right|^{1/2}$; $w_i = 1/\sigma(F_0)^2$

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