Journal of Organometallic Chemistry, 352 (1988) 321–326
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Semicarbazones and thiosemicarbazones

IX *. Tungsten carbonyl thiosemicarbazone organometallic compounds **

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(Received January 13th, 1988)

Abstract

In the reactions between $W(CO)_6$ and thiosemicarbazide or 4-methylthiosemicarbazide using acetone as solvent, in the presence of trimethylamine *N*-oxide (TMNO) or UV light, yellow compounds were obtained (**1** and **2** respectively). It is proposed that **1** and **2** are hexacoordinated with molecular formula $[W(CO)_5L]$, where L is the corresponding acetonethiosemicarbazone acting as a monodentate ligand, coordinated through the sulphur atom. The structure of **1** was confirmed by a single crystal X-ray study.

Introduction

Interest in the coordination chemistry of thiosemicarbazones has increased since their biological activity was shown to be related to their metal complexing ability [2]. Thiosemicarbazide and thiosemicarbazones have proved to be important ligands in "classical" transition metal chemistry, but there are very few reports of organometallic compounds with these ligands [3,4]. In the organometallic compounds described until now, the thiosemicarbazones are proposed to coordinate as bidentate ligands through sulphur and hydrazine nitrogen atom [3,4]. To our knowledge, there has been no report of X-ray structures of organometallic compounds with thiosemicarbazones.

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* For part VIII see ref. 1.

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In this paper, we report the results obtained from the reaction between $W(CO)_6$ and the thiosemicarbazones derived from, thiosemicarbazide ($NH_2NHC(S)NH_2$, TSC) and 4-methylthiosemicarbazide ($NH_2NHC(S)NH(Me)$, MeTSC) and acetone, as well as the X-ray structure of acetonethiosemicarbazonepentacarbonyltungsten(0).

Results and discussion

The molecular ion observed in the mass spectra of both **1** and **2**, corresponds to $[W(CO)_5L]^+$, where L is a thiosemicarbazone obtained, in situ, from the reaction between the thiosemicarbazide and acetone (**1**, L = acetonethiosemicarbazone, ATSC; **2**, L = acetone-4-methylthiosemicarbazone, AMeTSC). The mass spectra of both compounds show, below $m/e = 184$ ($[W]^+$), fragments in agreement with the ones observed in the mass spectra of the free ligands. These were obtained as reported in the literature [5] in order to use them as a reference. Furthermore, an organic compound with spectroscopic properties in exact agreement with ATSC [6] was also isolated from the mixture resulting from the preparation of **1**. The ^1H NMR spectra of **1** and **2** also support the proposed structure for the ligands. The mass spectra of **1** and **2** show the stepwise loss of five carbonyl groups.

In most of the complexes studied [7,8], thiosemicarbazones coordinate to metals as bidentate ligands, bonding to the metal through the sulphur and hydrazine nitrogen atoms. If the sulphur is alkylated, bonding may occur through the hydrazine and amide nitrogen atoms [9], in a few cases thiosemicarbazones behave as monodentate ligands, bonding only through the sulphur atom [10].

Tomlinson et al. [10], proposed that, on complexation, the band at ca. 1500 cm^{-1}, which is believed to arise mainly from $\nu(CN) + \delta(NH)$, is shifted only slightly in the monodentate complexes (10–20 cm^{-1}) whilst in the bidentate complexes, it shifts by 50–60 cm^{-1}. In **1** and **2**, this band shifts 10 cm^{-1} from 1510 to 1520 cm^{-1} in **1**, and from 1480 to 1490 cm^{-1} in **2**, suggesting a monodentate behavior.

According to this result, the tungsten atom compounds **1** and **2** are hexacoordinated with molecular formula $[W(CO)_5L]$, where L is a thiosemicarbazone which is acting as a monodentate ligand coordinating through the sulphur atom.

To confirm our results, the structure of **1** has been determined by X-ray diffraction study. Final atomic positional parameters are listed in Table 1. Table 2 lists the bond lengths and angles. The structure of **1** is shown in Fig. 1.

The molecular structure of **1** is approximately octahedral, with an ATSC molecule and five CO molecules bonded to the W atom. The ATSC molecule is coordinated, as predicted by the spectroscopic results, through the S atom.

The deviation of **1** from octahedral symmetry, is indicated by the bond angles, C(3)–W–C(5) and C(4)–W–S which deviate from the ideal octahedral 180° (176.3(3) and 171.9(2)°, respectively), the twelve angles subtended at the metal atoms by adjacent donor atoms range from 84.4(2)° in C(2)–W–S to 96.8(2)° in C(3)–W–S. No interaction between atoms of the ligands which might explain this deviation could be observed.

The W–C length in the CO *trans* to the S atom (1.976(8) Å), is shorter than the W–C distance with the remaining CO molecules, which have an average bond length of 2.035 Å, this may be explained by the better π-acceptor character of the

Table 1

Atom coordinates ($\times 10^4$) and temperature factors ($\text{A}^2 \times 10^3$)

Atom	x	y	z	U_{eq} [a]
W	2365(1)	6883(1)	5997(1)	47(1)
C(1)	4651(10)	7413(7)	6365(5)	62(3)
O(1)	5948(7)	7716(5)	6583(5)	86(2)
C(2)	48(10)	6334(6)	5622(6)	63(3)
O(2)	− 1243(8)	6000(5)	5429(5)	95(3)
C(3)	3276(10)	6232(6)	4826(5)	59(3)
O(3)	3782(8)	5820(5)	4194(5)	96(3)
C(4)	2822(10)	5525(6)	6617(5)	64(3)
O(4)	3014(8)	4727(4)	6968(4)	86(3)
C(5)	1517(11)	7454(7)	7215(6)	68(3)
O(5)	1077(11)	7741(7)	7900(5)	112(3)
S	1343(2)	8619(1)	5270(1)	56(1)
C(6)	2693(8)	9215(5)	4538(5)	45(2)
N(1)	2278(8)	10107(5)	4145(5)	65(3)
N(2)	4150(7)	8785(4)	4356(4)	48(2)
N(3)	5173(7)	9307(5)	3742(4)	54(2)
C(7)	6533(8)	8848(6)	3536(5)	51(2)
C(8)	7135(11)	7820(7)	3928(6)	76(3)
C(9)	7607(10)	9399(7)	2876(6)	75(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor

Table 2

Bond lengths and angles for [W(CO)$_5$(ATSC)]

Bond lengths (Å)

W–C(1)	2.012(8)	W–C(2)	2.045(8)
W–C(3)	2.045(8)	W–C(4)	1.976(8)
W–C(5)	2.046(9)	W–S	2.568(2)
C(1)–O(1)	1.146(10)	C(2)–O(2)	1.147(10)
C(3)–O(3)	1.141(10)	C(4)–O(4)	1.143(10)
C(5)–O(5)	1.126(12)	S–C(6)	1.711(7)
C(6)–N(1)	1.308(10)	C(6)–N(2)	1.321(8)
N(2)–N(3)	1.396(8)	N(3)–C(7)	1.278(9)
C(7)–C(8)	1.499(11)	C(7)–C(9)	1.479(11)

Bond angles (deg.)

C(1)–W–C(2)	179.6(3)	C(1)–W–C(3)	91.0(3)
C(2)–W–C(3)	88.8(3)	C(1)–W–C(4)	90.7(3)
C(2)–W–C(4)	89.0(3)	C(3)–W–C(4)	87.9(3)
C(1)–W–C(5)	88.2(3)	C(2)–W–C(5)	92.0(3)
C(3)–W–C(5)	176.3(3)	C(4)–W–C(5)	88.5(3)
C(1)–W–S	95.9(2)	C(2)–W–S	84.4(2)
C(3)–W–S	96.8(2)	C(4)–W–S	171.9(2)
C(5)–W–S	86.9(2)	W–C(1)–O(1)	179.4(7)
W–C(2)–O(2)	177.9(7)	W–C(3)–O(3)	176.5(7)
W–C(4)–O(4)	177.0(7)	W–C(5)–O(5)	177.6(8)
W–S–C(6)	115.8(2)	S–C(6)–N(1)	119.8(5)
S–C(6)–N(2)	121.1(5)	N(1)–C(6)–N(2)	119.1(6)
C(6)–N(2)–N(3)	117.8(5)	N(2)–N(3)–C(7)	116.8(6)
N(3)–C(7)–C(8)	125.2(7)	N(3)–C(7)–C(9)	116.6(7)
C(8)–C(7)–C(9)	118.2(7)		

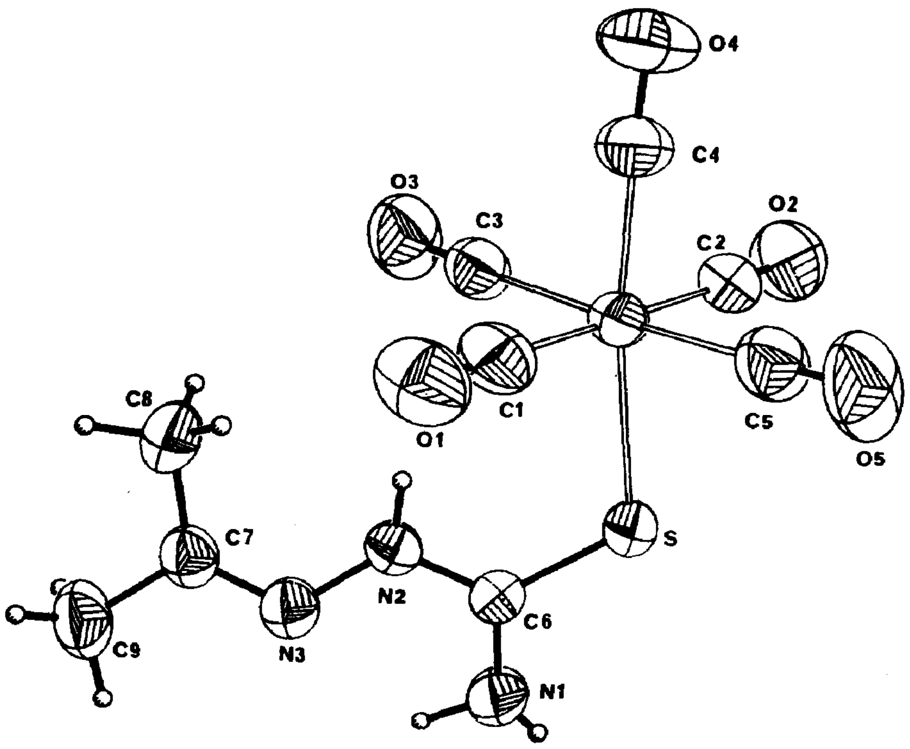

Fig. 1. ORTEP drawing of [W(CO)$_5$(ATSC)] molecule giving the number scheme for the atoms.

CO with respect to the S atom. The W-S bond length (2.568(2) Å) is similar to those reported in other [W(CO)$_5$S] systems [11-14].

The W-C-O angles deviate slightly from linearity with an average value of 177.7°.

Structurally there are few significant differences between free and coordinated ATSC. The C=S length increases from 1.690(5) in free ATSC [15] to 1.711(7) Å in **1**. The angles N(2)-C(6)-S and N1-C(6)-S change from 119.3(4) and 122.8(4)° respectively, in ATSC to 121.1(5) and 119.8(5)°, respectively, in **1**. This last modification may be accounted for, by the presence of hydrogen bonds in free ATSC [15]. The ATSC molecule in **1** is practically planar.

The angle between the least squares planes formed by O(1),O(2),O(4),S and N(2),C(6),S,N(1),N(3) in coordinated ATSC is 47.7°.

According to these results the presence of five ν(CO) vibrations in the IR spectra of **1** and **2** may be accounted for, by the lack of symmetry in the molecules, and the band at 365 cm^{-1} observed in the IR spectra of **1** and **2** which is not observed in the spectra of the free ligands, might be assigned to an W-S vibration.

Experimental

All reactions were carried out under inert atmosphere. Photochemical reactions were carried out on a Rayonet Srinivasan-Griffin apparatus with Hg lamps (2537 Å). For column chromatography 70-230 mesh Merck silica gel was used.

NMR spectra were recorded on a Varian FT-80A spectrometer at 80 MHz, tetramethylsilane was used as reference for all spectra. IR spectra were recorded on a Nicolet FT-SX spectrophotometer. Mass spectra were obtained with a Hewlett-Packard 5985 B. Melting points were determined with a Fischer-Jones apparatus and are uncorrected.

The appropriate thiosemicarbazide (TSC (0.091 g, 1 mmol), MeTSC (0.105 g, 1 mmol)) was added to a stirred solution of $W(CO)_6$ (0.352 g, 1 mmol) and trimethylamine-*N*-oxide (TMNO) (0.075 g, 1 mmol) in acetone (50 ml) and heated to reflux for 12 h. The resulting solution, was concentrated and purified by chromatography using a hexane/ethylacetate mixture (10/1). Yellow compounds (**1** (42%) and **2** (48%), respectively) were obtained as the main product in both reactions. The same products were obtained when the reactions were carried out using photolytic activation.

Crystals of **1** suitable for X-ray diffraction were obtained by slow evaporation of a hexane solution.

Selected spectroscopic data for 1. IR (cm^{-1}, KBr): ν(NH): 3420m, 3300m, ν(CN) + δ(NH): 1520m, ν(W–S) 365; (cm^{-1}; (cyclohexane) ν(CO): 2072w, 1985w, 1937s, 1921s, 1900s. ^{1}H NMR (δ, $CDCl_3$): 8.8 (s, 1H, D_2O exchange, N–H), 7.35 (s, 1H, D_2O exchange, N–H), 6.40 (s, 1H, D_2O exchange, N–H), 2.11 (s, 3H, Me), 1.99 (s, 3H, Me); mass spectra (*m/e*, 70 eV) m.p. 98–100 °C): 455 [$W(CO)_5$ (ATSC)]$^+$, 315 [W(ATSC)]$^+$, 216 [W–S]$^+$, 184 [W]$^+$, 131 [ATSC]$^+$. **2** IR cm^{-1}, (KBr): ν(NH): 3440w, 3295w, ν(CN) + δ(NH): 1490m, ν(W–S) 365; (cm^{-1}, cyclohexane); ν(CO): 2071w, 1985w, 1937s, 1921s, 1910s. ^{1}H NMR, (δ, $CDCl_3$): 8.8 (s, 1H, D_2O exchange, N–H), 7.53 (s, 1H, D_2O exchange, N–H), 3.22 (d, 3H, N–Me), 2.08 (s, 3H, Me), 2.06 (s, 3H, Me); mass spectra (*m/e*, 70 eV) m.p. 100–102 °C): 469 [$W(CO)_5$ (MeACTSC)$^+$, 329 [W(MeACTSC)]$^+$, 216 [W–S]$^+$, 184 [W]$^+$, 145 [MeACTSC]$^+$.

Collection and reduction of X-ray data *

Crystal data for 1. $WC_9H_9N_3SO_5$, $M = 454.8$, monoclinic, space group $P2_1/c$, a 8.012(2), b 12.684(5), c 14.567(5) Å, β 91.30(2)°, U 1480.00 Å^3, D_c 2.04 g cm^{-3}, $F(000) = 856$, μ(Mo-$K\alpha$) 81.23 cm^{-1}, T 293 K, $Z = 4$. Using a crystal of ca. 0.12 × 0.2 × 0.4 mm, lattice parameters were obtained from 25 machine-centered reflections with $6 < 2\theta < 23°$. Reflections in one quarter of reciprocal space were measured with an index range of h; $0 \rightarrow 9$, k; $0 \rightarrow 5$, l: ± 17; using the $2\theta/\theta$-scan mode with graphite-monochromatized MoK_α radiation (λ 0.7107 Å) on a Nicolet R3m four-circle diffractometer, variable scan speed, scan width $\theta 2.0°$. The intensities were corrected for Lorentz and polarization effects. Empirical absorption correction based on 360 azimuthal scan data; the maximum and minimum transmissions being 0.249 and 0.138, respectively. Of the 2619 reflections within the 2θ range of 3–50° collected. 2160 independent reflections were considered observed with $I > 2.5\ \sigma(I)$, R(merge) = 0.015, and $R(\sigma) = 0.026$. The data were adjusted to an approximately absolute scale and an overall U value of 0.045 Å^2.

Structure determination. The structure of **1** was solved by the heavy-atom method and refined by a cascade matrix least-squares techniques with anisotropic

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* Supplementary material is available. Details on how to acquire this material can be obtained from the authors.

temperature factors for the non-hydrogen atoms. H atoms attached to N, found on a difference Fourier map, and those bonded to C on idealized positions refined with fixed isotropic temperature factor U 0.06 Å^2. The final conventional R factor was 0.0355 and $R_w = 0.0347$; scattering factors from International Tables for X-ray Crystallography [16], and the isotropic extinction parameter $X = 0.00021$. All computationals were performed on a Nova 4S computer with the SHELXTL [17] system of programs.

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