Sulfur(II)–Metal Coordination Compounds. Group VI Metal Carbonyl Complexes with N,N′-Thiobisamines Ligands

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The novel complexes $M(CO)_5S(NR_2)_2$ (M = Cr, Mo or W) have been prepared by the addition of N,N′-thiobisamine (NR_2 = dimethylamine, piperidine, morpholine or dibenzylamine) to UV-irradiated tetrahydrofuran solutions of $M(CO)_6$. The IR, ^{1}H-NMR, and UV-visible spectral data used for characterizing the products support the coordination of the thiobisamine via *the sulfur(II) atom.*

Introduction

N,N′-thiobisamines are known to be stable and unreactive species that can be crystallized from water or alcohols only undergoing hydrolysis or alcoholysis reactions in the presence of acids [1–3]. In spite of the nucleophilic characteristics expected from the lone pairs on sulfur and nitrogen atoms, only a reduced number of often unstable adducts with boron(III) compounds, BX_3 (X = H, F or C_6H_5) have been reported [1–4]. Attempts to prepare complexes with Cu(II), Cu(I) and Ag(I) ions have failed; thiobisamines are unreactive towards these metal ions under anhydrous conditions, undergoing hydrolysis followed by redox processes in the presence of water [2]. The low nucleophilicity of such compounds can be attributed to the nature of the S–N linkage that, according to spectral as well as X-ray structural determinations [5–7], has some double bond character. Nevertheless, by considering that in the sulfur atom besides the lone electron pairs there are also d orbitals that could be able to act as π-acceptor, we have undertaken the coordination of thiobisamine to metals in a rather low oxidation state. In this work we describe the synthesis of novel carbonyl complexes of thiobisamines with metal carbonyls of the group VI.

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Experimental

N,N′-thiobisamines were prepared according to literature procedures [8]. Commercially available metal carbonyls (Merck) were used without further purification. Tetrahydrofuran (THF) was dried with sodium. All reactions were performed under an oxygen-free nitrogen atmosphere. IR, ^{1}H-NMR and UV-visible spectral data were obtained by using the Perkin Elmer model 621, Varian T-60, and Cary 17 spectrometers respectively.

The general procedure for the synthesis of the thiobisamine metalcarbonyl complexes: a solution of 3.5 mmol $M(CO)_6$ in *ca.* 60 ml THF was irradiated (UV Lamp Hanovia, medium pressure 150 w) for 90 min. (for Mo(CO_6, 120 min.) at room temperature. A solution of 3 mmol of thiobisamine in *ca.* 20 ml THF was then added and the mixture stirred for 60 min. After removing the solvent under reduced pressure, the excess of hexacarbonyl was sublimed from the residue under vacuum at room temperature. The solid was then redissolved in a n-hexane-n-pentane mixture (for 1a, pure n-pentane), filtered through kieselguhr, and recovered by evaporating the solvent. Numerous attempts to crystallize such products have failed.

Molecular weights (cryoscopic measurements in bencene): 1a: 377 (calc. 396); 3a: 500 (calc. 528). Analytical data, yields and melting points for the products are shown in Table I.

Results and Discussion

The addition of the thiobisamine to a tetrahydrofuran (THF) solution of $M(CO)_5$ (THF) photochemically generated [9, 10] gives rise to the formation of thiobisamine carbonyl complexes according to following chemical equations:

$$(CO)_5M(THF) + S(NR_2)_2 \xrightarrow[25\ ^\circ C]{THF} (CO)_5MS(NR_2)_2 + THF$$

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Nr.	M	NR_2
1a	Cr	dimethylamine
1b		piperidine
1c		morpholine
1d		dibenzylamine
2a	Mo	morpholine
3a	W	morpholine

The products are yellow solids unstable to moisture. Elemental analysis and cryoscopical molecular weight determinations indicate that the products are monosubstituted and monomeric. The molybdenum complex 2a is relatively unstable and was always found to be contamined with free amine. Because of the poor yield reached in the synthesis of 1a, this compound was identified only by spectral methods. A casual presence of water gives rise, specially for the morpholine derivatives 1c and 3a, to the amine complexes $M(CO)_5HNR_2$. Under our conditions, no formation of disubstituted compounds was observed.

A vibrational study of the compounds was only achieved by analysing the IR spectra; decomposition of the samples by the laser irradiation (CR-4 Argon-ion laser, line 4880 Å) prevented the recording of the Raman spectra. In Table II are reported the frequency values assigned to the vibrations ν(CO), ν(MC), and δ(MCO). The frequency and the relative intensities of the bands corresponding to stretching vibrations of the CO group indicate, as expected for $M(CO)_5L$ structures, a symmetry fundamentally C_{4v} [11]. Nevertheless, some deviations from this symmetry are suggested by the splitting of the E band as well as by the activity of the B_1 band in the infrared [11]. The IR spectra of the thiobisamines coordinated to the metal carbonyls show patterns that are similar to those of the free thiobisamines [6], pointing to a nearly symmetrical metal–thiobisamine interaction. Nevertheless, the frequencies assigned to $\nu(SN)_{as}$ in the free ligand [6] are shifted to lower values in the complex, as can be observed in data shown in Table III.

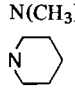
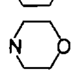
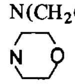
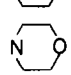
^{1}H NMR and UV-visible spectra of the compounds are also compatible with a symmetrical interaction, indicating that the coordination occurs though the sulfur atom of the thiobisamine. Thus, the ^{1}H NMR

TABLE I. Analytical Data, Yield and Melting Point of $M(CO)_5S(NR_2)_2$ Complexes.

Compound	Analysis (%): Found (Calculated)				Yield (%)	M.p. (°C)
	C	H	N	S		
1a[a]	–	–	–	–	8	70–71
1b	46.13(45.91)	5.68(5.1)	7.67(7.14)	8.64(8.16)	30	61–62
1c	40.58(39.36)	4.81(4.04)	7.50(7.07)	7.45(8.07)	40	79–80
1d	64.23(64.28)	5.27(4.54)	4.88(4.54)	5.20(5.19)	30	90 (dec)
2a	36.72(35.43)	4.60(3.63)	7.49(6.35)	8.20(7.26)	35	80 (dec)
3a	29.43(29.53)	3.47(3.03)	5.26(5.30)	6.65(6.06	42	93–95

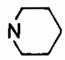
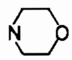
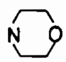
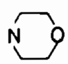
[a]Poor yield, only spectral analysis.

TABLE II. IR Spectra of $M(CO)_5S(NR_2)_2$ Complexes (cm^{-1})[a].

No.	M	NR_2	νCO[b]				νMC[c]		δMCO[c]	
			$A_1^{(2)}$	B_1	E	$A_1^{(1)}$	A_1	E	E	A_1
1a	Cr	$N(CH_3)_2$	2063w	1988w	1954,1943vs	1932m	550w	443m	658s	630m
1b			2065w	1989w	1951,1940vs	1929m	560m	443m	660s,sh	646s,sh
1c			2069w	1989w	1952,1946vs	1935m	552w	488m	668s	645vs
1d		$N(CH_2C_6H_5)_2$	2069w	1990w	1952,1948vs	1936m	554w	445s	662s	643vs
2a	Mo		2079w	1989w	1958,1950vs	1940m	390w	350s	540m	600s
3a	W		2078w	1985w	1950,1945vs	1932m	440w	365s	600s	580w

[a]The assignments were made according to references [11], [14] and [22]. [b]n-hexane solution. [c]KBr, solid.
Abbreviations: s: strong, m: medium, w: weak, v: very, sh: shoulder.

TABLE III. Selected Spectral Data for $M(CO)_5S(NR_2)_2$ Complexes.

No.	M	NR_2	$\nu(S–N)_{as}$ [a]		λ_{max} (Log) [b]	δ ^1H NMR [c]
			Free	Complex		
1a	Cr	$N(CH_3)_2$	945s	928s	392	2.98 [d]
1b			937s,915s	923s,sh;906s	392(3.22)	$3.23((CH_2)_2)$ [e], $1.53((CH_2)_3)$ [e]
1c			950s,922s	930s,sh;920s	393(3.19)	$3.53(OCH_2)$ [e], $3.30(NCH_2)$ [e]
1d		$N(CH_2C_6H_5)_2$	940m	922m	395(3.4)	$7.13(C_6H_5)$ [d], $4.13(CH_2)$ [d]
2a	Mo		950s,922s	938s,sh;921s	398	$3.50(OCH_2)$ [e], $3.18(NCH_2)$ [e]
3a	W		950s,922s	933s,918s	370(3.23)	$3.56(OCH_2)$ [e], $3.30(NCH_2)$ [e]

[a] KBr, solid in cm^{-1}. [b] n-hexane. [c] ppm from TMS in CCl_4. [d] Singlet. [e] Multiplet.
Abbreviations: s: strong, m: medium, sh: shoulder.

spectra of the complexes (Table III column 3) are similar to those of the free ligands but shifted downfield. For N-coordination two sets of signals, as those reported for the adducts with BH_3 [4], should be expected. On the other hand the absorption maxima in UV-visible spectra (Table III column 2), observed at about 390 mμ for chromium and molybdenum, and at 370 mμ for tungsten compounds, can be ascribed to the transition $^1A_1 \rightarrow {}^1E$ that has been considered as characteristic for sulfur coordination in pentacarbonyl chromium and tungsten [12] compounds.

In Table IV are reported the force constants k_1 and k_2 for the C–O bonds calculated, according to the method of Cotton and Kreihanzel [11], from the stretching frequencies of the CO group reported in Table I. The k values obtained for the CO bonds in the thiobisamine complexes agree well with those reported for the same bonds in some $Cr(CO)_5L$ complexes in which L was a sulfur ligand [13–15]. This fact is particularly significant in the case of k_1 which is very sensitive to the nature of the donor atom, specially to its capacity as a π-acceptor [13]. The corresponding Graham δ and π parameters [16] are also reported in Table IV.

According to the effects of the thiobisamine coordination on the CO bonds appearing from these data, the N,N'-thiobisamine are weak π-acceptor ligands. However, this is the kind of interaction that permits the formation of the complex in spite of the low nucleophilicity of the sulfur atom in the ligands. Among the complexes $M(CO)_5L$ (M = Cr, Mo or W) with sulfur ligands reported at the time—with L = thioethers [17], thioamides and thioureas [18, 19], $S(MR_3)_2$ (M = Ge, Sn or Pb) [20], and SPR_3 [21]—the thiobisamine complexes described here are the first metal–sulfur complexes with sulfur in a formal oxidation state +2.

The main effects of the coordination to metal carbonyls on the properties of thiobisamine are a higher sensibility to electromagnetical radiation (Raman laser) and a greater susceptibility to hydrolysis. This latter effect is similar to that caused by the presence of acids or by the electrochemical oxidation of the thiobisamine to $(R_2N)_2S^{\dot{+}}$ radicals [3], that also activate the heterolysis of the S–N bond.

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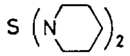
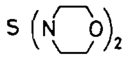
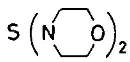
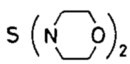
TABLE IV. Force Constants[a] and Graham Parameters[b] for C–O Bonds in $M(CO)_5S(NR_2)_2$ and other $M(CO)_5L$ Complexes.

		k_1 (md/A)	k_2 (md/A)	δ	π
$Cr(CO)_5$	$S(N(CH_3)_2)_2$	15.32	15.95	−0.12	0.05
		15.29	15.97	0.19	0.01
		15.31	15.97	0.10	0.09
	$S(N(CH_2C_6H_5)_2)_2$	15.36	15.99	0.13	0.08
	$(SCH_2)_3$	15.44[c]	15.90[c]	−0.17	0.29
	$(SCHCH_3)_3$	15.30[c]	15.91[c]	−0.01	0.14
	$(SCH_2)_4$	15.43[c]	15.92[c]	−0.12	0.26
$Mo(CO)_5$		15.40	15.97	0.10	0.19
	$S(C_2H_5)_2$	15.35[e]	15.94[e]	−0.05[e]	0.15[e]
	$(SCH_2)_3$	15.41[c]	15.99[c]	−0.1	0.22
	$(SCHCH_3)_3$	15.29[c]	15.99[c]	0.02	0.10
	$(SCH_2)_4$	15.38[c]	15.88[c]	−0.29	0.30
$W(CO)_5$		15.32	15.91	0.16	0.02
	SC_4H_8	15.29[d]	15.86[d]	0.01	0.12
	$SH(C_6H_5)$	15.37[d]	15.96[d]	0.13	0.10
	$(SCH_2)_3$	15.40[c]	15.89[c]	−0.04	0.20
	$(SCHCH_3)_3$	15.28[c]	15.90[c]	0.10	0.07
	$(SCH_2)_4$	15.39[c]	15.88[c]	−0.05	0.20

[a]Calculated according to the method of Cotton and Kreihanzel, reference [11]. [b]Calculated according to reference [16]. [c]Reference [13]. [d]Reference [14]. [e]Reference [16].

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