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MORPHOLINODITHIOCARBAMATE COMPLEXES OF MOLYBDENUM

by

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Abstract : *Six new complexes of molybdenum with morpholino-4-carbodithioate (mdtc) as a ligand were synthesized. Three of them are molybdenum (v) chloride complexes of the types*: $MoCl_4$ *(mdtc)*, $MoCl_3$ *(mdtc)*$_2$, $MoCl_2$ *(mdtc)*$_3$ *and the other three oxomolybdenum complexes of the type*: MoO_2 *(mdtc)*$_2$, Mo_2O_3 *(mdtc)*$_4$ *and* MoO_2 *(mdtc)*$_4$ *with the oxygen atom either in terminal or bridging position. The prepared compounds were characterized and studied by analyses and spectroscopic techniques.*

INTRODUCTION

As far as we know, dithiocarbamate complexes of Mo(vi) and Mo(v) were first prepared by *Malatesta*[1]. The structure of these complexes have been determined by the same author[2]. *Larson* and *Moore*[3] have reported, as well, the synthesis of complexes of the general type MoO_2L_2, where L = dialkyldithiocarbamate group. These complexes were reduced by SO_2, $Na_2S_2O_3$ or PPh_3 and gave simple Mo(v) dialkyldthiocarbamate complexes. In recent years numerous dithiocarbamate complexes of molybdenum have been reported [4-9].

In this paper we describe the preparation and study of six new morpholinodithiocarbamate complexes of Mo(v) and Mo(vi). Three of them are molybdenum (v) chloride complexes, namely: Morpholinodithiocarbamato molybdenum (v) tetrachloride, $MoCl_4$ (mdtc), bis (morpholinodithiocarbamato) molybdenum (v) trichloride, $MoCl_3(mdtc)_2$ and tris (morpholinodithiocarbamato) molybdenum (v) dichloride, $MoCl_2(mdtc)_3$. The other three are oxomolybdenum complexes, with the oxygen atoms in either terminal or bridging position namely:
dioxobis-(morpholinodithiocarbamato) molybdenum (vi), $MoO_2(mdtc)_2$, μ-oxobis{oxobis - (morpholinodithiocarbamato) molybdenum (v)}, $Mo_2O_3(mdtc)_4$ and di-μ-oxo-bis {(dimorpholinodithiocarbamato) molybdenum (iv)}, $Mo_2O_2(mdtc)_4$.

EXPERIMENTAL.

The reaction of the Mo (v) chloride with dithiocarbamate were carried out under anhydrous and inert gas conditions. Solvents were purified and dried by standard procedures. The infrared spectra were recorded with a Perkin-Elmer Model 257 spectrophotometer, in the region from 4000 to 600 cm^{-1} in Nujol mulls and KBr pellets. The visible-ultraviolet spectra were obtained with a Zeiss PMQ II spectrophotometer. The proton NMR spectra were measured on a Varian 60 Mc/sec instrument using TMS as internal standard. Conductance measurements were made using a conductivity bridge (Model RC 216 B2).

ANALYSIS.

The molybdenum was determined gravimetrically as molybdenum oxide by direct ignition of a sample for the oxygen complexes and as benzoinoxime for the chloride complexes. The chloride was determined according to the known method by volumetric titration after the removal of sulfide.

*Preparation of dioxobis (morpholinodithiocarbamato) molybdenum (*VI*),* $MoO_2(mdtc)_2$. — The procedure was similar to that of *Moore and Larson*[3]. A solution of sodium morpholinodithiocarbamate was prepared by adding 4 ml CS_2 (0.07 mole) to a stirred solution of 5.22 g (0,06 mole) morpholine and 2.40 g (0.06 mole) sodium hydroxide in 250 ml water. In this solution 10 g (0.041 mole) of sodium molybdate was dissolved and then cooled to 5°C. On slow acidification with 250 ml of 0.43 N nitric acid, at 5° C, a brown tar was separated. The tar was dissolved in benzene and the complex was precipitated with petroleum ether and was further purified by recrystallization from toluene-ligroine.

The obtained yellow crystalls decomposed at 161° C. Yield 56%.

Anal. Found: C=26.83; H=3.48; N=6.04; S=28.41; Mo=21.09 %
Calcd: C=26.50; H=3.56; N=6.19; S=28.35; Mo=21.20 %

Preparation of μ*-oxo-bis [oxobis - (morpholinodithiocarbamato) molybdenum (*V*)],* $Mo_2O_3(mdtc)_4$.— To a solution of 11.1 g (0.06 mole) sodium morpholinodithiocarbamate and 10 g (0.041 mole) sodium molybdate in 200 ml of water, 0.25 N nitric acid was added dropwise under continuous stirring. The solution was stirred for an hour and it was allowed to stand for six hours at room temperature. The molybdenum complex was filtered and washed with water. After recrystallization from chloroform and petroleum ether the product was filtered and dried under vacuum to give 12.4 g of purple solid. Yield 47%.

Anal. Found: C=26.83; H=3.56; N=6.28; S=28.81; Mo=22.09 %
Calcd: C=27.02; H=3.43; N=6.30; S=28.86; Mo=21.59 %

*Preparation of di-μ-oxo-bis [dimorpholinodithiocarbamato) molybdenum (*IV*)]*, $\mathrm{Mo_2O_2(mdtc)_4}$. — During the preparation of the above complexes a green product of the type $\mathrm{Mo_2O_2(mdtc)_4}$ was also isolated. The yield of the reaction increases considerably when the proportion of dithiocarbamate to molybdenum is 1:1. It was recrystallized from chloroform and petroleum ether. Yield 34%.

Anal. Found: C=27.15; H=3.65; N=6.40; S=30.07; Mo=21.06 %
Calcd: C=27.52; H=3.69; N=6.42; S=29.39; Mo=21.98 %

*Preparation of morpholinodithiocarbamato molybdenum (*V*) tetrachloride*, $\mathrm{MoCl_4(mdtc)}$.— Molybdenum pentachloride 1.366 g (0.005 mole) was added to a suspension of 0.815 g (0.0032 mole) morpholinium morpholine-4-carbodithioate or 0.925 g (0.005 mole) sodium morpholinodithiocarbamate in 50 ml acetone. The reaction mixture was stirred at room temperature for one hour and then was filtered to give a green precipitate. The precipitate was washed many times with chloroform and petroleum ether and finely dried under vacuum over $\mathrm{CaCl_2}$ for twenty four hours. Attempts to recrystallize this product resulted in its decomposition and therefore it was used without further purification. M.p. 165° C decomposed. Yield 55%.

Anal. Found: C=14.78; H=2.06; N=3.15; S=15.85; Cl=35.19;
Mo=23.40% Calcd: C=15.01; H=2.02; N=3.50;
S=16.03; Cl=35.45; Mo=23.99%.

*Preparation of bis (morpholinodithiocarbamato) molybdenum (*V*) trichloride* $\mathrm{MoCl_3(mdtc)_2}$.— Molybdenum pentachloride 2.52 g (0.009 mole) was added to a suspension of 3.26 g (0.013 mole) morpholinium morpholine-4-carbodithioate or 3.7 g (0.02 mole) sodium morpholinodithiocarbamate in 50 ml acetone, and after two hours stirring at room temperature, gave a yellow precipitate. Crystallization from chloroform and petroleum ether gave the product, m.p. 155° C, decomposed. Yield 63%.

Anal. Found: C=23.00; H=3.00; N=5.20; S=22.04; Cl=20.50;
Mo=17.95%. Calcd: C=22.80; H=3.06; N=5.32;
S=24.35; Cl=20.19; Mo=18.21%.

Preparation of tris (morpholinodithiocarbamato) molybdenum (v) *dichloride* $MoCl_2(mdtc)_3$.— This compound was prepared in a similar manner to the above using 1.07 g (0.005 mole), molybdenum pentachloride and 3.26 g (0.013 mole) morpholinium morpholine-4-carbodithioate or 3.7 g (0.02 mole) sodium morpholinodithiocarbamate in 50 ml acetone. A violet product was obtained after crystallization from chloroform-petroleum ether solvent, m.p. 125° C, decomposed. Yield 68%.

Anal. Found: C=27.06; H=3.50; N=6.10; S=28.95; Cl=10.70;
Mo=14.50%. Calcd: C=27.57; H=3.70; N=6.40;
S=29.43; Cl=10.85; Mo=14.68%.

RESULTS AND DISCUSSION.

The new chloride complexes were generally prepared by reacting of the proper amounts of sodium morpholinodithiocarbamate (mdtcNa) and $MoCl_5$. The following sequence of substitution reactions seems reasonable in view of the obtained chloride complexes,

$$\begin{aligned} &MoCl_5 &&+ mdtcNa \rightleftharpoons MoCl_4(mdtc) &&+ NaCl \\ &MoCl_4(mdtc) &&+ mdtcNa \rightleftharpoons MoCl_3(mdtc)_2 &&+ NaCl \\ &MoCl_3(mdtc)_2 &&+ mdtcNa \rightleftharpoons MoCl_2(mdtc)_3 &&+ NaCl \end{aligned}$$

The reversibility of these reactions is demonstrated by the fact that using certain amount of $MoCl_5$ we obtain tri- and tetra-chloroderivatives from the di-, or tri- ones, respectively,

$$\begin{aligned} &MoCl_5 + 2MoCl_2(mdtc)_3 \rightleftharpoons 3MoCl_3(mdtc)_2 \\ &MoCl_5 + MoCl_3(mdtc)_2 \rightleftharpoons 2MoCl_4(mdtc) \end{aligned}$$

The proposed formulations of the prepared complexes are confirmed by elemental analysis. The obtained mono-, di-, and tri-, substituted complexes were green, yellow and violet solids respectively. They are unstable in solution turning blue upon exposure to the air. Their solubility in common organic solvents is increasing from mono- to tri- substituted products.

The oxo-molybdenum dithiocarbamate complexes have been prepared according to the known method[3]. The obtained oxo-molybdenum complexes are insoluble in water soluble in common organic solvents and stable in air. The oxidation state of molybdenum was very difficult to be determined directly, because of interference by the oxidisable sulfur of the ligands.

An interesting question in the elucidation of dithiocarbamate complexes is the coordination sites of the ligands. In most cases the dithiocarbamate group coordinates to the metal atom through both sulfur atom (bidentate ligand) but it is also known to coordinate, through the one sulfur atom (monodentate ligand). If the dithiocarbamate ligand is bidentate there is a simple band in the region 1000 cm^{-1} indicating two equivalent C-S bonds[10]. In the case of monodentate dithiocarbamates a doublet occurs in this region which is due to two non equivalent C-S bonds. Also in the case of bidentate linking the streching vibration of the C-N bond is shifted to higher frequencies, 1520-1530 cm^{-1} showing more double bond character. The relationship between the relative strengths of C-N and C-S bonds has been reported previously[11].

A comparison of the $\mathrm{C}\overset{\cdots}{-}\acute{\mathrm{N}}$ streching mode of the studied compounds to those of the dialkyldithio-analog leads to the conclusion that there is less double bond character in the C-N bond of compounds showing that the morpholino ring is less electron withdrawing. Molybdenum-oxygen streching vibration, $\nu(\mathrm{Mo} = \mathrm{o})$, occurs at 1000-1010 cm^{-1} as it was expected[12]. The band at 920-945 cm^{-1} may arise from the antisymmetric vibration of the bridge Mo-O-Mo[3,13]. The relatively high order of the $\mathrm{Mo}{=}\mathrm{O}$ bond, is due to electron donation to molybdenum from both the σ- and π- orbitals of oxygen. Generally, the ir spectra of the studied compounds are fairly complex but they show the normal characteristics for bidentate dithiocarbamate linking.

The electronic spectra of the studied compounds exhibit the usual pattern of the dithiocarbamate complexes of the transition metals, which consists of two groups of bands. A group of bands in the ultraviolet region and another band in the visible region of the spectra.

In the ultraviolet region the highest energy band occurs at *ca.* 260 nm and contains a shoulder at *ca.* 310 nm, both assigned to intraligand

$\pi \rightarrow \pi$ transitions located mainly in -C(S)S- group.The second less intense band at *ca.* 390 nm, is usually atributed either to an $n \rightarrow \pi^*$, intraligand transition[3] or to a $L \rightarrow M$ charge transfer[3,14]. The bands in the visible region attributed to d — d transitons. The spectra of Mo (v) complexes charged considerably on standing because the molybdenum (v) compounds were oxidized by oxygen.

Proton nmr spectra also provide a usefull tool studing the effect of the molybdenum coordination on the electronic enviroment of the dithiocarbamate groups and the geometry of the complex. The nmr spectra show that the compounds are diamagnetic in solution.

The signals of the dithiocarbamate groups appeared to be shifted to higher values of δ, towards those or free dithiocarbamate and this is probably due to the strong electron withdrawing ability of the chloride atoms. These shifts are decreased from mono to tris derivatives.

The singlet peak on the proton nmr spectra of the $MoCl_3(mdtc)_2$ complex shows that the protons close to the central atom are magnetically equivalents. In constrast to the protons of the $MoCl_2(mdtc)_3$ complex which should be magnetically distinct.

The nmr spectrum of the $MoO_2(mdtc)_2$ complex consists of two resonance frequencies due to the methylene protons. In the spectra of the $Mo_2O_3(mdtc)_4$ complexes the deshielding of methylene protons is less pronounced. Analogous deshieldings were observed in the spectra of the corresponding dimethyl and diethyl complexes[15]. Generally the coordination of the morpholinodithiocarbamate group causes a deshielding of methylene protons.

The molar conductivities of the solutions (concentration 10^{-3}M) of the complexes $MoCl_3(mdtc)_2$ and $MoCl_2(mdtc)_3$ were found to be 220 and 133 mhos respectively. On this evidence it is considered that the complexes are 1:1 and 1:2 electrolytes, may be the formulae $[MoCl_2(mdtc)_2]Cl$ and $[Mo(mdtc)_3]Cl_2$ respectively.

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ΠΕΡΙΛΗΨΙΣ

ΜΟΡΦΟΛΙΝΟΔΙΘΕΙΟΚΑΡΒΑΜΙΔΙΚΑ ΣΥΜΠΛΟΚΑ ΤΟΥ ΜΟΛΥΒΔΑΙΝΙΟΥ

Ὑπὸ
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Εἰς τὴν παροῦσαν ἐργασίαν παρασκευάζονται καὶ μελετῶνται ἓξ νέα μορφολινοδιθειοκαρβαμιδικὰ (mdtc) σύμπλοκα τοῦ μολυβδαινίου ἀνταποκρινόμενα εἰς τοὺς τύπους $MoCl_4(mdtc)$, $MoCl_3(mdtc)_2$, $MoCl_2(mdtc)_2$, $MoO_2(mdtc)_2$, $Mo_2O_3(mdtc)_4$ καὶ $Mo_2O_2(mdtc)_4$. Τὰ χλωριοῦχα σύμπλοκα παρεσκευάσθησαν, ὑπὸ ἀδρανῆ ἀτμόσφαιρα, δι' ἐπιδράσεως $MoCl_5$ ἐπὶ καταλλήλου ἀναλογίας μορφολινοδιθειοκαρβαμιδικοῦ νατρίου εἰς διάλυμα ἀνύδρου χλωροφορμίου ἢ ἀκετόνης. Τὰ σύμπλοκα αὐτὰ εἶναι ἀσταθῆ διασπώμενα ταχέως ὑπὸ τῆς ὑγρασίας καὶ ὀξειδουμένα ὑπὸ τοῦ ἀέρος, ἰδίως ὅταν εὑρίσκονται ἐν διαλύσει.

Τὸ σύμπλοκον $MoO_2(mdtc)_2$ παρεσκευάσθη κατὰ τὴν μέθοδον Larson καὶ Moore, διὰ τροποποιήσεως δὲ τῶν συνθηκῶν αὐτῆς παρεσκευάσθησαν τὰ ἄλλα ὀξυγονοῦχα σύμπλοκα.

Αἱ δυναταὶ δομαὶ τῶν συμπλόκων συζητῶνται βάσει τῶν ἀποτελεσμάτων τῶν φασμάτων ὑπερύθρου, ὁρατοῦ ὑπεριώδους καὶ πυρηνικοῦ μαγνητικοῦ συντονισμοῦ.