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Reactivity of Molybdenum(V)with 2,5-dimercapto-1,3,4-thiadiazole. X-Ray Structure of 5,5′-dimercapto-2-thiadiazolyl Disulphide

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From the reaction of $MoCl_5$ with 2,5-dimercapto-1,3,4-thiadiazole (H_2DMT) a disulphide oxidation product was obtained. Preparation, infrared spectra and X-ray diffraction analysis of this compound, 5,5-dimercapto-2-thiadiazolyl disulphide ($(HDMT)_2$), are reported.

Introduction

In a recent research program concerning chemical and structural investigations on molybdenum–sulphur and molybdenum–nitrogen interactions [1] and on the biological function of molybdenum, we examined the reactions of molybdenum(V) chloride with 2,5-dimercapto-1,3,4-thiadiazole (H_2DMT), whose the coordinating behaviour in transition metals complexes was previously investigated [2].

In this paper we report the results obtained from the reaction of H_2DMT and $MoCl_5$, in different conditions.

The X-ray diffraction analysis unambiguously established the nature of the crystalline compound (5,5′-dimercapto-2-thiadiazolyl disulphide, $[HDMT]_2$) which was obtained in the course of these reactions.

Experimental

The reactions between $MoCl_5$ and H_2DMT can be indicated in the following scheme:

$$MoCl_5 + H_2DMT \begin{cases} \xrightarrow[\text{R.T., pH} \sim 7]{\text{Na, EtOH(N}_2\text{)}} Mo(HDMT)_2Cl_3 \cdot H_2O \\ \xrightarrow[\text{R.T., pH} \sim 6]{\text{MeOH/MeCN(N}_2\text{)}} [HDMT]_2 + \text{Mo(III) complex} \end{cases}$$

In the first process a single compound, $Mo(HDMT)_2Cl_3 \cdot H_2O$ was obtained, where the organic ligand is present in its monodeprotonated form. From the second reaction two products were isolated. The former, which is unstable and non homogeneous, was not well identified, even if analytical and spectroscopic data suggest a probable polymeric Mo(III)-complex. The latter is a brown crystalline compound, whose identification was clarified by an X-ray diffraction analysis.

All reagents were accurately dried and deoxygenated before use. The reactions were always carried out under dry nitrogen atmosphere. Molybdenum(V) chloride and H_2DMT were commercially available from Merck and Aldrich respectively.

The reactions of $MoCl_5$ with H_2DMT were carried out as follows:

a) To an ethanol solution of sodium and H_2DMT (2:1 molar ratio) molybdenum(V) chloride, dissolved in ethanol, was added dropwise (metal-ligand 1:2 molar ratio). The brown-violet solution (pH ~ 7) was stirred at room temperature until NaCl precipitated. After filtration and evaporation of the solvent, a violet solid was isolated. The product, which is air stable, even if hygroscopic, shows C, H, N, Mo analytical data which agree with the formula $Mo(HDMT)_2Cl_3 \cdot H_2O$.

b) To a methanol solution of H_2DMT, molybdenum(V) chloride (2:1 molar ratio), dissolved in acetonitrile, was added. After some days, a small amount of brown crystals was deposited, which was collected and analysed.

By evaporation of the remaining solution a brown non homogeneous product was isolated. Infrared and electronic spectra [3] suggest the presence of molybdenum(III) in this not well defined complex.

The crystal data of the brown crystals are: $C_4H_2N_4S_6$, $a = 5.918(1)$, $b = 15.808(2)$, $c = 5.716(1)$ Å, $\alpha = 98.30(1)$, $\beta = 104.04(1)^\circ$, $\gamma = 94.36(2)^\circ$, $V = 509.9$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.94$ g cm^{-3}, $D_m = 1.95$ g cm^{-3}, $\mu(MoK\alpha) = 12.5$ cm^{-1}.

Intensity data were collected on a Siemens AED single-crystal computer controlled diffractometer, with MoKα radiation. A total of 2457 independent reflections were measured of which only 1452 $[I > 2\sigma(I)]$ were considered to be observed and were used in the subsequent analysis.

The structure was solved by direct methods using the program SHELX [4].

Full matrix least squares refinement gave a final R value of 0.072.

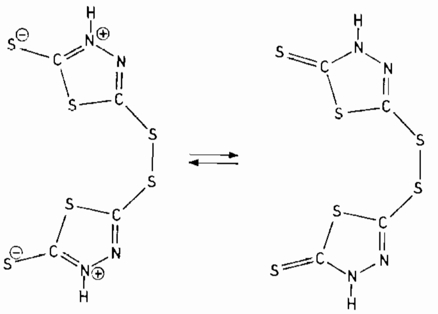
Scattering factors for non-hydrogen atoms were taken from Cromer and Mann [5] and that for the hydrogen atom from Stewart, Davidson and Simpson [6].

Results and Discussion

The X-ray diffraction analysis of brown crystals showed that the molybdenum atom had not been taking part in the compound even if it was responsible of the oxidation of H_2DMT to the corresponding disulphide derivative. The initially formed Mo-complexes are probably unstable under atmosphere conditions then affording R–S–S–R and Mo(III) species.

In Fig. 1 the structure of the $[HDMT]_2$ molecule is shown. From the bond lengths and angles it appears that the oxidation has not modified the geometry of the thiadiazole rings [7]. Mainly two resonance structures are present, in the crystalline state with partly double bonds in S(1)–C(1) (1.67(1) Å), C(1)–N(2) (1.34(1) Å), S(6)–C(4) (1.64(1) Å), C(4)–N(3) (1.35(2) Å) and completely double bonds in C(2)–N(1) (1.25(1) Å) and C(3)–N(4) (1.29(2) Å). One thiadiazole ring is perfectly planar, the other is not planar; in fact the S(5) atom is significantly out of the mean plane (0.06 Å), probably for packing requirements (S(5). . .$S(2)^{i*}$ = 3.57 Å).

According to Shefter the S–S bond length, in symmetric aromatic uncomplexed disulphides, is related to the values of X–C–S–S torsion angles (X = C or N); with both X–C–S–S torsion angles near 0° or 180° the disulphide conformation is equatorial and S–S bond length is short (1.999–2.047 Å), in the axial conformation, the torsion angles are near 90° and S–S bond length is larger (2.059–2.108 Å) [8, 9]. In the present work the two torsion angles values are different: N(1)–C(2)–S(3)–S(4) = 10.8(9)° and N(4)–C(3)–S(4)–S(3) = 67.5(9)°. Consequently one thiadiazole ring has the equatorial conformation, the other the axial conformation (Fig. 2) and the S–S bond length show intermediate value (2.050(4) Å). The torsion angle C(2)–S(3)–S(4)–C(3) is 78.7(5)°. The molecule is characterized as having a left-handed helical sense as observed in several L-cystine compounds [10].



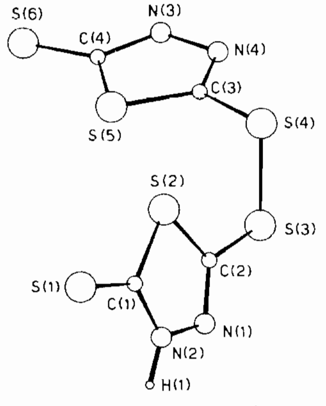


Fig. 1. Projection of 5,5'-dimercapto-2-thiazolyl disulphide in the (001) plane.

A difference-Fourier map revealed only the H(1) atom, while it was not possible to fix the position of the hydrogen atoms of the other thiadiazolic ring, the situation being complicated by a region of positive electron density surrounding all the sulphur atoms. Although the position of the second hydrogen atom was not clear, it is obvious from a consideration of the molecular dimensions that this compound, as the 5-amino-2-thiol-1,3,4-thiadiazole [11] and the monomer 2,5-dimercaptothiadiazole [7], crystallizes as a thione.

The packing is influenced by S(1). . .H–N(2) (3.23 Å) hydrogen bonds and by van der Waals

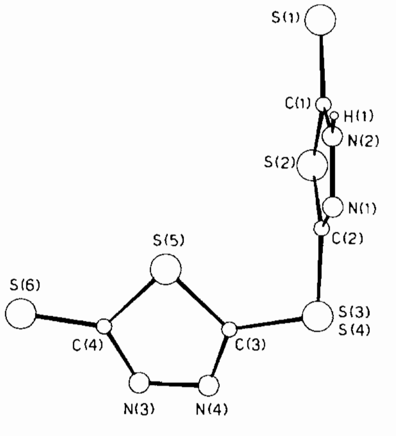


Fig. 2. Projection of 5,5'-dimercapto-2-thiazolyl disulphide view down S–S bond.

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*i = x, y, z − 1.

contacts S. . .S(3.17, 3.39, 3.51 Å) and S. . .N(3.40, 3.52 Å) and S. . .C(3.52, 3.58 Å). The small contact S. . .S(3.17 Å) support that the element does not display a unique van der Waals radius [12, 13].

Small differences between the IR absorptions of H_2DMT and of $[HDMT]_2$ are observed, which can be indicated as follows (Table I):

i) ν(NH) shifts to higher frequency values as a consequence of a decrease of the intra- and intermolecular hydrogen bonds

ii) no significant changes are observed for thioamide I, II, III bands, while thioamide IV band shifts to lower values, owing to a decrease of the bond order of the C=S group

iii) ν(SH) completely disappears, while a new band is present at 530 cm^{-1}, which can be attributed to ν(S–S) vibrational mode [14].

The infrared spectra were registered on a spectrophotometer Perkin-Elmer Mod. 457 using the KBr technique.

TABLE I. Main Vibrational Bands (cm^{-1}) and Relative Assignments of H_2DMT, $[HDMT]_2$.

H_2DMT	$[HDMT]_2$	Assignment
3060m	3200ms	ν(NH)
	3050m	
2980w	2960m	
2900sh	2900w	
2860m	2840mw	
2480m		ν(SH)
1500vs	1500ms	δ(NH) + thioamide I
1470m	1470ms	
1450ms	1445ms	
1230ms	1230s	thioamide II
1050s	1020sh	thioamide III
940m		thioamide IV
920m		
920m		
750m, br	710s	δ(NH)
710vs		
	695sh	thioamide IV
	530mw	ν(S–S)

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