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Scientific paper

Some Chemistry of Tris(pyrazolyl)methylthiolate Derivatives[1]

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Dedicated to Prof. Dr. Boris Žemva on the occasion of receiving the Zois´ award for lifetime achievements.

Abstract

An efficient synthetic method for the preparation of TAS tris(pyrazolyl)methylthiolate (**3**) is reported. Nucleophilic exchange reactions with **3** gave (pyr)C(=S)SC(pyr)$_3$ (**4**) and MeSC(pyr)$_3$ (**5**). **5** acts as scorpionate ligand in [MeSC(pyr)$_3$Cr(CO)$_3$] (**6**), from the decomposition of TDAE^{2+} [SC(pyr)$_3$Mo(CO)$_3^-$]$_2$ by SO$_2$FCl TDAE^{2+}[O=MoF$_4$-F-Mo(=O)Cl$_4$]$^{2-}$ (**8**) was isolated. The X-ray structures of **3**–**6** and **8** are discussed.

Keywords: scorpionates, tris(azolyl)methylthiolates, chromium complexes, molybdenum complexes, X-ray structures

1. Introduction

Since Trofimenko reported the first tris(pyrazolyl) borates [RB(pyr)$_3$]$^-$ 45 years ago[2], thousands of papers have shown the versatility of this type of anion as ligand in coordination chemistry, comparable with or even surpassing the coordinatively similar cyclopentadienyl ligand[3]. Because the coordination mode resembles the attack of a scorpion, the name “scorpionates” was coined for these tripodal donors. Possible variations of the properties are the introduction of more or less bulky groups at the pyrazole rings, exchange of a pyrazole by σ – or π – ligands, and exchange of the [RB-] by an isoelectronic HC- methin[4] or other tetra-; penta- or hexavalent centers. A further step was the replacement of the proton at the carbon in tris(pyrazolyl)methane by various organic and inorganic groups to give neutral RC(pyr)$_3$ systems. Kläui et al. reported with Li[(pyr)$_3$CSO$_3$] the first anionic methane derivative[5], our group contributed the preparation of tris(azolyl)methylthiolates [az$^1_3$CS]$^-$.(az=pyrazole, triazole)[6]. For these multidentate systems two synthetic methods have been developed : (a) nucleophilic exchange of the fluorines in trifluoromethylthiolate [F$_3$CS]- by silylated azoles, and (b) addition of ”naked” azolides az^1 to bis(azolyl)thiourea (az$^1_2$)$_2$C=S or (az^{2}az^3)C=S to give tris(azolyl)methylthiolates with two or even three different azolyl substituents. For these systems we expected a coordination chemistry even broader than that of the tridentate scorpionates , due to the tetradenticity of these anions and the possibility to use them as nucleophiles towards organic and inorganic substrates for the preparation of ligand systems with higher denticity than 4.

In the following paper we report some first results obtained with the most simple tris(azolyl)methylthiolate, the tris(pyrazolyl) derivative **3**. From the reaction with the organic halide MeI tripodal (pyr)$_3$CSMe (**5**) was obtained, from SC(pyr)Cl multidentate (pyr)$_3$CSC(=S) (pyr)(**4**). **5** reacts with [(OC)$_3$Cr(NCMe)$_3$] straight forward to [MeSC(pyr)$_3$Cr(CO)$_3$] (**6**), while the interaction of [(OC)$_3$Mo(NCMe)$_3$] with the anion [SC(pyr)$_3$]$^-$ gives a dark, probably polymeric, insoluble product. Attempts to crystallize the compound failed. With SO$_2$FCl reaction occurs, a few crystals of a salt with the anion [F$_4$(O=)MoFMoCl$_4$(=O)]$^{2-}$ (**8**) were isolated and characterized by X-ray crystallography.

2.Experimental Section

2. 1. Materials and Methods

The starting materials Me$_3$Si-pyr[7], TDAE^{2+}(S-C(pyr)$_3^-$)$_2$[6], [MeCN)$_3$Cr(CO)$_3$][8,9] and [(MeCN)$_3$Mo(CO)$_3$][8,9] were synthesized as described in the literature. For S=C (pyr)$_2$[10] and TAS $^+$[S-C(pyr)$_3$]$^-$ [7] we used modified methods (TDAE: Tetrakis(DimethylAmino)Ethylene $(Me_2N)_2C=C(NMe_2)_2$; TAS: Tris(dimethylAmino)Sulfonium cation $(Me_2N)_3S^+$). Because of the moisture sensitivity of most of the compounds, all operations were performed under dry nitrogen (glove box, M. Braun, Garching). Volatile ligands were transferred at a standard vacuum line, nonvolatile ligands by syringes under dry nitrogen. NMR-spectra were recorded with a Bruker DPX 200..

2. 2. Preparation of $S=C(pyr)_2$

Onto 3.0 gs of $S=CCl_2$ in 50 ml toluene 1.00 g (6.43 mmol) of trimethyl silyl pyrazole were dropped. The reaction mixture was heated to 110 °C and stirred at this temperature for 24 hours. After removal of all volatiles at a rotary evaporator, almost analytically pure product **2** remained behind. Further purification was achieved by recrystallisation from n-pentane.

2. 3. Preparation of $TAS^+[S\text{-}C(pyr)_3]^-$ (3) and $(pyr)_3C\text{-}S\text{-}C(=S)(pyr)$ (4)

In a glove box into a λ-shaped glass vessel with a stirring bar into one leg 1.00 g (4.3 mmol) TAS^+pyr^-, into the other 0.89 g (5.00 mmol) **2** were filled. At a vacuum line 20 ml of CH_3 CN were condensed onto **2**, the solution was transferred to the other leg with TAS^+pyr^-, slowly warmed to room temperature and stirred for 15 min. At –40 °C the solution was covered with an ether layer and kept at this temperature for three days. Under vacuum all volatiles were removed, product **3** remained as colorless crystals, mp 105 °C, in quantitative yield. In some of our reactions a few crystals of $(pyr)_3C\text{-}S\text{-}C(=S)(pyr)$ **4** were isolated and characterized by X-ray crystallography (s. below). **3** was also characterized by X-ray crystallography and by ^1H-NMR(CD_3CN):

$\delta(CH_3, TAS^+)$ = 2.84 ppm (s) (Intens. 6); $\delta(C^3H)$ = 8.1 ppm (d,d(1); $^3J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 0.9 Hz); $\delta(C^4H)$ = 6.1 ppm (d,d(1); $^3J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 1.6 Hz); $\delta(C^5H)$ = 7.3 ppm (d,d(1); $^3J_{HH}$ = 1.6 Hz, $^4J_{HH}$ = 0.9 Hz).

2. 4. Preparation of $Me\text{-}S\text{-}C(pyr)_3$ (5)

In an inert atmosphere 0.5 g (1.22 mmol) of **3** were filled into a reaction vessel equipped with a Teflon valve and a stirring bar. 20 ml MeCN and 0.30 g (2.11 mmol) MeI were condensed onto the TAS-salt at a vacuum line at –196 °C. The mixture was warmed to room temperature and stirred for 30 minutes. The volatiles were removed under dynamic vacuum. The air-stable product **5** was separated from TAS^+I^- by dissolution in ether, followed by further purification through sublimation. 0.2 g (0.76 mmol, 62% yield) **5**, mp 95 °C, were isolated. ^1H-NMR(CD_3CN) : $\delta(CH_3, \text{-}S\text{-}CH_3)$ 2.2 ppm (s) (intens.1); $\delta(C^3H)$ 7.7 ppm (d,d(1); $^3J_{HA}$ = 1.6 Hz, $^4J_{HH}$ = 0.8 Hz); $\delta(C^4H)$ 6.3 ppm (d,d(1); $^3J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 1.6 Hz); $\delta(C^5H)$ 7.2 ppm (d,d(1); $^3J_{HH}$ = 2.5 Hz, $^4J_{HH}$ = 0.8 Hz).

2. 5. Preparation of $[MeSC(pyr)_3Cr(CO)_3]$ (6)

Similar to the preparation of **3** the starting materials **5** (0.20 g, 0.77 mmol) and $[(MeCN)_3Cr(CO)_3]$ (0.20 g, 0.77 mmol) were filled into a λ-shaped reaction vessel, 10 ml MeCN were added by condensation at –196 °C at a vacuum line. After warming to room temperature the reaction mixture was stirred for 30 minutes. The solvent was removed by evaporation until the product started to crystallize. The mixture was kept at –40 °C for three days to complete the precipitation.

The remaining solvent was decanted, the product was dried for ½ hour by dynamic vacuum to give 0.25 g (0.63mmol, 83% yield) yellow crystals, mp. 85 °C.

2. 6. Preparation of $TDAE^{2+}[O=MoF_4\text{-}F\text{-}Mo(=O)Cl_4]^{2-}$ (8)

Similar to the preparation of **6** the reaction of $TDAE^{2+}[S\text{-}C(pyr)_3)^-]_2$ with two equivalents of $[(MeCN)_3Mo(CO)_3]$ in MeCN gave a dark precipitate , not soluble in common organic solvents. With SO_2FCl reaction took place, a few crystals of **8**, suitable for X-ray crystallography ,were isolated.

2. 7. X-ray Crystallographic Studies

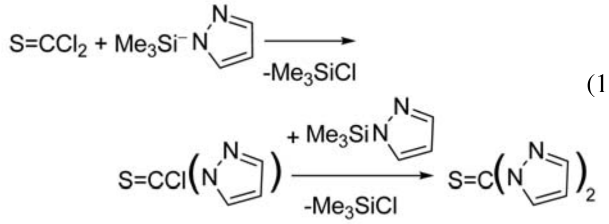
The single-crystal X-ray structure determinations (Table 1, Table 2) were carried out on a Siemens P4 diffractometer, using Mo-K_a(0.71073Å) radiation with a graphite monochromator. Refinement based on F^2; $R1 = ||F_o| - |F_c||/|F_o|$; $wR2 = \{[w(F_o^2 - F_c^2)^2/[w(F_o^2)^2]\}^{1/2}$.Programs used: SHELX-97[11] and DIAMOND[12]. The single crystals were mounted on a thin glass fiber using KEL-F oil. The structures were solved by direct methods (SHELXS[11]). Subsequent least-squares refinements (SHELXL-97-2[11]) located the positions of the remaining atoms in the electron density maps. All non-H atoms were refined anisotropically.

CCDC 905372 (for **4**), 905374 (for **5**), 905375 (for **6**), 905373 (for **8**) the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.can.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk

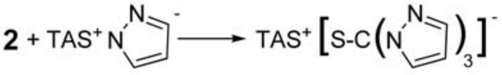
3. Results and Discussion

3. 1. Synthetic Aspects

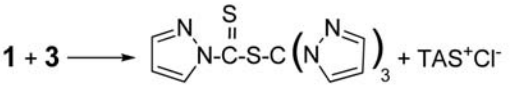
In a short communication we have reported the formation of tris(azolyl)methyl thiolates from trifluoromethyl thiolates and silylated azoles[6]. As intermediates in this surprising reaction we suggested the formation of FC(=S)(az) and S=C(az)$_2$ and the az$^-$ ion (az = pyrazole, imidazole, triazole). Because we expected for this class of compounds a broad application as ligands in coordination chemistry, we started to develop a more straightforward and easily accessible synthetic method. S=C(az)$_2$ **2** is readily available from S=CCl$_2$ and Me$_3$Si(az), with TAS$^+$(az)$^-$ the final product **3** is formed in quantitative yield:



1 **2** (1)



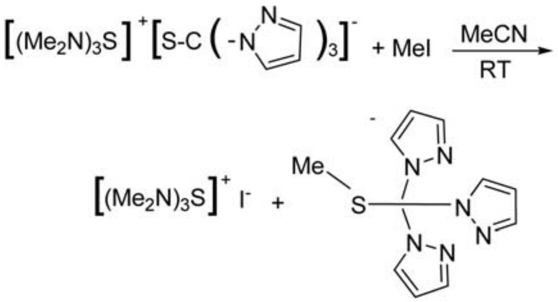
3 (2)



4 (3)

If ClC(=S)(az) is present as impurity, this will be attacked by **3** to give the new multidentate ligand **4** (eq.3), which was characterized by X-ray crystallography. The structure of compound **4** is shown in Fig.1. The formation of **5** also demonstrates, that tris(azolyl)methyl thiolates are highly reactive nucleophiles.

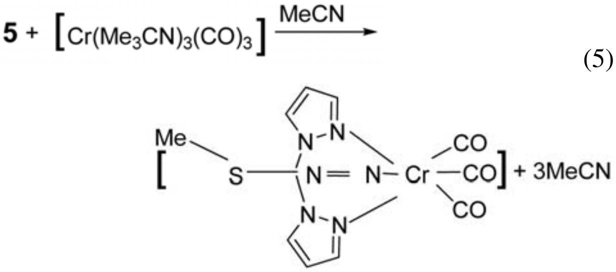
Compared to normal tripodal scorpionate ligands[2], which contain three nitrogen donor sites in **4** with the negatively charged sulfur we have an additional coordination site, which causes some problems (s. below). These can be avoided by introducing a shielding group, by transforming the thiolate into a thioether function, e.g. by methylating the sulfur.



5 (4)

When MeI is added to a solution of TAS$^+$[SC(pyr)$_3$]$^-$ in MeCN, TAS$^+$I$^-$ precipitates while the product stays in solution. By adding diethylether quantitative separation is achieved. Pure **6** is obtained after filtration, removal of the solvent under vacuum, followed by sublimation.

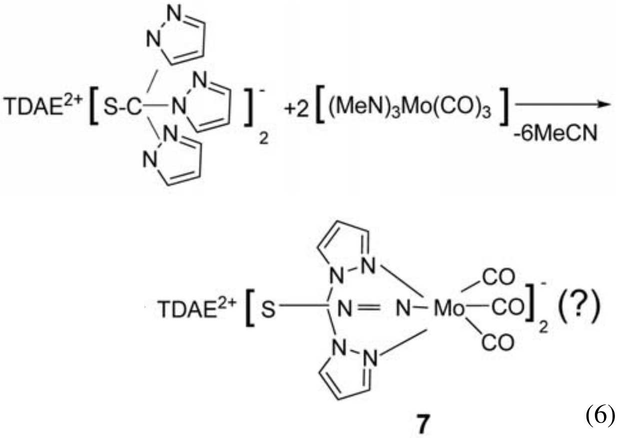
In analogy to reactions described in the literature[13] the chromium tricarbonyl complex **6** is formed by exchange of the three monodentate MeCN ligands by the tridentate thioether **5**. **5** and **6** were characterized by NMR spectroscopy and X-ray crystallography (Fig. 2 and Fig. 3).



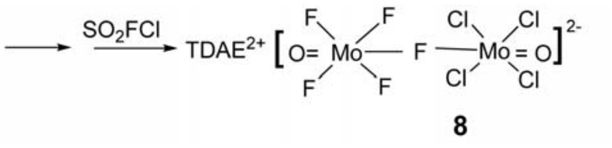
6 (5)

Much more reactive than the methylthioether are the thiolates. With [Mn(CO)$_5$Br], [CpFe(CO)$_2$I] or [(CH$_3$CN)$_3$Cr(CO)$_3$] reaction starts already at –20 °C, indicated by the formation of a precipitate.

The primary product of the reaction with [(MeCN)$_3$Mo(CO)$_3$] might be polymeric **7**, but all attempts to crystallize the compound failed. With SO$_2$FCl an interesting oxidative decomposition occurs with the formation of an – according to our knowledge – unprecedented chlorofluoro complex with molybdum in two different oxidation states.



7 (6)



8

3. 2. Structural Studies

Crystal and structure refinement data for compounds **4–6** and **8** are given in Table 1 and Table 2. Figures 1–4 show the molecular structures of these compounds with labeling of the atoms. A common feature of **4**, **5**, and **6** is the -S-C(pyr)$_3$ unit, the influence of variations at the sulfur and at the pyrazole rings on this unit will be discussed first Details of the structural properties of the anion of **8** follow in a separate chapter below.

3. 2. 1. Tris(pyrazolyl)methyl Sulfur Derivatives

In Table 3 selected bond distances and bond angles for compounds **3–6** are listed. The most significant differences between the anion and its covalent derivatives are the C-S and the C-N bond distances around the tetrahedral carbon. In **3** the shortest C-S bond (178.2pm) is followed by the longest C-N bond (148pm). With increasing electron withdrawing properties of the substituents the C-S bonds of **5** (184.2pm) and the C-N bonds of **5** (145.4 pm)

Table 1. Crystal data and structure refinement for 4 and 5

	4	**5**
Empirical formula	$C_{14}H_{12}N_8S_2$	$C_{11}H_{12}N_6S$
Formula weight	356.44	260.33
Temperature/K	173(2)	173(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$
a/Å	8.5510(10)	6.9530(10)
b/Å	8.9760(10)	7.229(2)
c/Å	10.7200(10)	24.608(5)
α/°	90.00	90.00
β/°	100.400(10)	90.00
γ/°	90.00	90.00
Volume/Å^3	809.28(15)	1236.9(5)
Z	2	4
ρ_{calc}mg/mm^3	1.463	1.398
m/mm^{-1}	0.343	0.253
F(000)	368.0	544.0
Crystal size/mm^3	0.6 × 0.4 × 0.3	0.5 × 0.5 × 0.5
2Θ range for data coll.	5.62 to 54.98°	5.88 to 55.02°
Index ranges	$-11 \le h \le 5, -11 \le k \le 11, -13 \le l \le 13$	$-9 \le h \le 6, -9 \le k \le 9, -31 \le l \le 31$
Reflections collected	2677	7066
Independent reflections	2253[R(int) = 0.0343]	2826[R(int) = 0.0567]
Data/restraints/parameters	2253/1/219	2826/0/166
Goodness-of-fit on F^2	1.026	1.035
Final R indexes [I>=2σ (I)]	$R_1 = 0.0390, wR_2 = 0.0923$	$R_1 = 0.0436, wR_2 = 0.1052$
Final R indexes [all data]	$R_1 = 0.0485, wR_2 = 0.0974$	$R_1 = 0.0506, wR_2 = 0.1108$
Largest diff. peak/hole / e Å^{-3}	0.32/–0.35	0.35/–0.34
Flack parameter	–0.01(9)	–0.02(10)

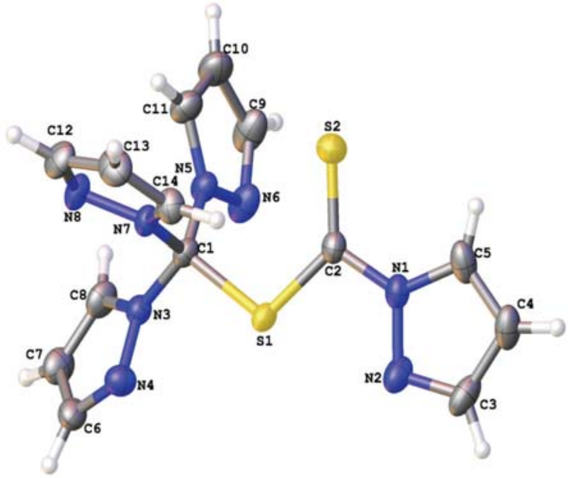


Figure 1. Molecular structure of (pyr)C(=S)SC(pyr)$_3$ (**3**)

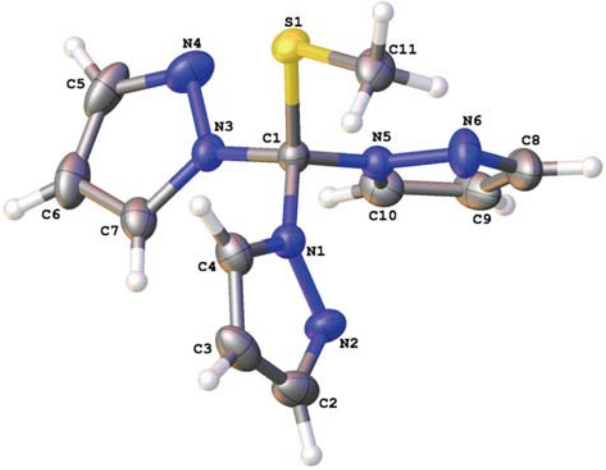
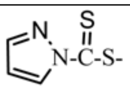


Figure 2. Molecular structure of MeSC(pyr)$_3$ (**5**)

Table 2. Crystal data and structure refinement for 6 and 8

Identification code	**6**	**8**
Empirical formula	$C_{14}H_{12}N_6O_3SCr$	$C_{10}H_{24}N_4O_4SMo_2Cl_4F_5$
Formula weight	396.36	725.07
Temperature/K	173(2)	173(2)
Crystal system	orthorhombic	monoclinic
Space group	Pbca	$P2_1/n$
a/Å	14.337(6)	12.3020(10)
b/Å	13.619(6)	12.5220(10)
c/Å	17.031(6)	16.4490(10)
α/°	90.00	90.00
β/°	90.00	105.16(5)
γ/°	90.00	90.00
Volume/Å^3	3325(2)	2445.7(3)
Z	8	4
ρ_{calc}mg/mm^3	1.583	1.969
m/mm^{-1}	0.841	1.609
F(000)	1616.0	1428.0
Crystal size/mm^3	0.6 × 0.4 × 0.4	0.6 × 0.5 × 0.5
2Θ range for data coll.	4.78 to 50.02°	5.14 to 55°
Index ranges	$-17 \le h \le 5, -16 \le k \le 16, -20 \le l \le 9$	$-8 \le h \le 15, -16 \le k \le 16, -21 \le l \le 20$
Reflections collected	3699	6989
Independent reflections	2896[R(int) = 0.0245]	5553[R(int) = 0.0198]
Data/restraints/parameters	2896/0/228	5553/0/281
Goodness-of-fit on F^2	1.026	1.044
Final R indexes [I>=2σ (I)]	$R_1 = 0.0569$, $wR_2 = 0.1123$	$R_1 = 0.0295$, $wR_2 = 0.0706$
Final R indexes [all data]	$R_1 = 0.1094$, $wR_2 = 0.1320$	$R_1 = 0.0369$, $wR_2 = 0.0743$
Largest diff. peak/hole / e Å^{-3}	0.394/–0.511	0.50/–0.66

Table 3. Selected Bond Distances (pm) and Bond Angles (°) for 3–6.

RS=	**$^-$S- (3)**	 **(4)**	**H_3CS- (5)**	**H_3C-S(Cr) (6)**
CS	178.2	186.0	184.2	180.9
C-N1	148.0	144.9	145.4	146.4
N1-N2	135.6	136.6	135.7	136.5
N2-C3	132.9	132.4	132.5	132.7
C3-C4	137.4	140.0	138.8	139.5
C2-C5	137.8	136.3	136.0	136.4
C5-N1	134.4	136.0	136.0	136.2
N-C-N	105.7, 106.8, 107.9	108.7, 108.7, 109.9	108.5, 108.6, 109.3	108.8, 107.6, 109.4

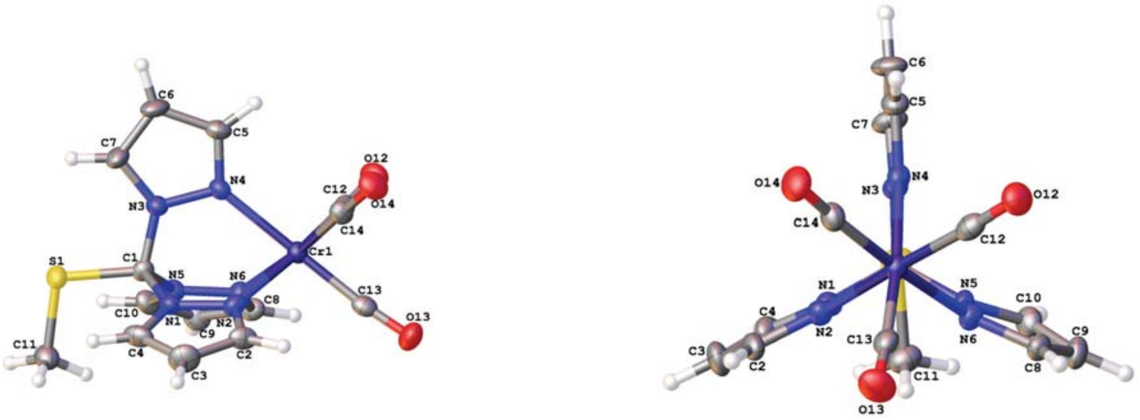


Figure 3. Molecular structure of [MeSC(pyr)$_3$Cr(CO)$_3$] (**8**), side view and view along Cr-C1-S. Selected distance (pm) and angles(°): Cr-N2 211.7(4), Cr-N4 212.1(4), Cr-N6 212.6(4); Cr-C12 182.4(6), Cr-C13 180.3(6), Cr-C14 181.3(6) ; N4-Cr-N2 82.08(16), N4-Cr-N6 82.07(16), N2-Cr-N6 78.60(16); C12-Cr-N2172.9(2), C14-Cr-N6174.6(2), C13-Cr-N4 175.4(2)

and **4** (144.9 pm) seem to follow this trend (although the last two bond lengths are identical within the limits of error).

The structure of **8** is the first of a tris(pyrazolyl)methane chromium tricarbonyl derivative to be reported, only the closely related structures of [MeSi(pyr)$_3$Cr(CO)$_3$][13] and the 17-electron complex [(pyr)B(pyr)$_3$Cr(CO)$_3$][14] are known. The chromium center is incorporated into a six-membered ring in a boat conformation. The boat is formed by a carbon, four nitrogen from two pyrazoles and the chromium center. The third pyrazole ring bridges the ring withN3N4. The Cr-N distances in 8 (average 211pm) are a little shorter than in the silyl derivative (average 217.4 pm), but longer than in the borate complex (average 208 pm).

$[(Me_2N)_2CC(NMe_2)_2]^{2+}[F_4Mo(=O)-F-Mo(=O)Cl_4]^{2-}\cdot SO_2$ **(8)**

Although **8** is an accidental product and it might not be reproduced by our approach, we think that this – according to our knowledge – unprecedented type of complex is worthwhile to be published. Fig. 4 shows the molecular structure of the salt. It crystallizes with one molecule of SO_2, a byproduct of the oxidation- decomposition reaction of the primarily formed organometallic complex. In Table 4 selected bond distances and bond angles are given. The anion of **8** seems to be the first structurally characterized chloro-fluoro complex of molybdenum and also the first mixed valence Mo(VI)/Mo(V) halogen complex. In the dianion the two square pyramidal fragments $OMoF_4$ and $OMoCl_4^-$ are bridged by a fluoride ion. The shorter Mo2 – F1 distance (206.6 pm) compared to Mo1 – F1 (217.7 pm) suggests that the complex can be described as the interaction of an $[OMoF_5]^-$ anion with $[OMoCl_4]^-$. This description also suggests a (possible) straightforward synthetic method for the anion of **8**. Although $[OMoF_5]^-$ salts are not described in the literature, they might be accessible from $OMoF_4$ and strong fluoride donors. Interaction of $[OMoF_5]^-$ with the coordinately unsaturated $[MoOCl_4]^-$ anion might give the dianion of **8.**

Table 4 Selected bond distances (Å) and bond angles (°) of the $[F_4Mo(=O)-F-Mo(=O)Cl_4]^{2-}$ anion

Distances (Å)		
Mo1 – F1	217.71 (16)	Mo2 – F1 206.56 (16)
Mo1 – O1	165.62 (2)	Mo2 – O2 165.7 (2)
Mo1 – Cl1	240.3 (7)	Mo2 – F2 184.1 (2)
Mo1 – Cl2	238.75 (7)	Mo2 – F3 183.8 (2)
Mo1 – Cl3	237.66 (7)	Mo2 – F4 185.4 (2)
Mo1 – Cl4	237.60 (8)	Mo2 – F5 (184.3 (2)
Angles (°)		
F1 – Mo1 – O1	178.51 (10)	F1 – Mo2 – O2 176.59 (11)
Cl1 – Mo1 – Cl2	167.03 (3)	F2 – Mo2 – F4 166.64 (16)
Cl3 – Mo1 – Cl4	166.06 (3)	F3 – Mo2 – F5 166.41 (10)
Mo1 – F1 – Mo2	166.48 (10)	
O1 – Mo1 – Cl1	96.36 (8)	O2 – Mo2 – F2 97.07 (12)
O1 – Mo1 – Cl2	96.53 (8)	O2 – Mo2 – F3 97.38 (12)
O1 – Mo1 – Cl3	97.10 (8)	O2 – Mo2 – F4 96.15 (12)
O1 – Mo1 – Cl4	96.80 (8)	O2 – Mo2 – F5 95.74 (12)

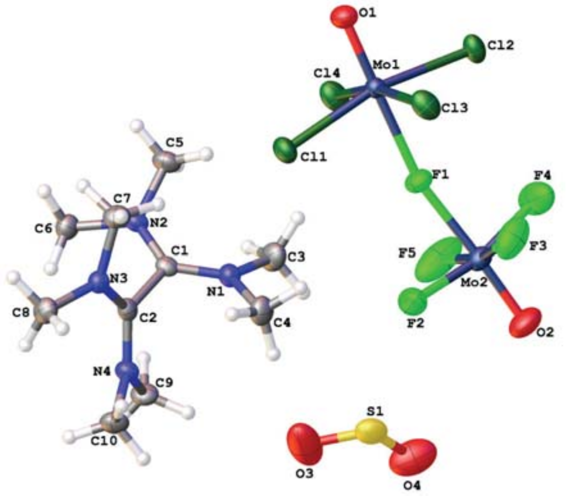


Figure 4. Molecular structure of TDAE^{2+}[O=MoF$_4$-F-Mo(=O)F$_4$]$^{2-}$SO$_2$.(**8**)

Only a limited number of structure investigations on oxofluoro molybdenum complexes is found in the literature. Besides $[OMoF_4]$[15] and $[OMoF_4\cdot SbF_5]$[16] the neutral dioxodifluoro compounds $[O_2MoF_2\cdot 2THF]$[17], $[O_2MoF_2\cdot 2DMF]$[18] and the dianion in $Na_2[MoO_2F_4]$[18] were investigated by X-ray crystallography[18]. Closely related to the $[OMoF_4\cdot F]$ fragment of **8** is the $[Mo_2O_2F_9]^-$ ion, mentioned as $H_3O^+[Mo_2O_2F_9]^-$ salt[18] from the solvolysis of MoO_2F_2 in anhydrous HF. The salt was characterized by an imperfect single crystal structure determination, details are not available.

Model substance for the $[F\cdot M(O)Cl_4]^{2-}$ part of **8** is the $[OMoCl_5]^{2-}$ anion. For $Cs_2[Mo(O)Cl_5]$[19] only unit cell parameters are reported, in $[Ph_4P^+]_2$ $[Mo(O)Cl_5]^{2-}$ O/Cl [20] disordering prevents the determination of a correct Mo-O bond distance . Besides $[CF_3C(NH_2)_2{}^+]_2[O_2Mo_2Cl_8]^{2-}$,[21] where 2 $OMoCl_4^-$ units dimerize via bent Cl- bridges, several salts of the $[Mo(O)Cl_4]^-$ anion with different counterions are described, all of them in common is the tendency of the Mo(V) center to expand the square pyramidal environment to hexacoordination under formation of oligomers or polymers[22,23] or by the addition of neutral donors, as e.g. MeCN[24,25]. Hexacoordination dominates the structural chemistry of oxofluoro-Mo (VI) - and oxochloro –Mo (V) species. This seems to be also the driving force for the formation of the anion of **8**. In $[O=MoF_4-F-Mo(O)Cl_4]^{2-}$ the two square pyramidal coordinated Mo centers are connected by a linear Mo$^{V\,I}$-F- Mo^{V} bridge. As expected, the interaction of the fluoride with the Mo^{VI} center (206.6 pm) is stronger than with the Mo^{V} center (217.7 pm). This interaction “distorts” the square pyramidal coordination of the Mo centers towards octahedral symmetry, stronger interactions lead to smaller OMoX angles (X=Cl, F). The $OMoF_5^-$ – unit seems to be a stronger donor than MeCN, the OMoCl – angles in $Tl[MeCN·Mo(O)Cl_4]$ (98.9°)[25] and in $[Ph_4As]_2[[MoOCl_4]_2 MeCN]$ (99.4°)[24] are larger than in **8** (96.8°). For the free $[MoOCl_4]^-$ anion this angle is 104.7°.[24] The Mo(VI)=O (165.7 pm), Mo(VI) = F (184–185 pm), Mo(V)=O (165.2 pm), and Mo(V)-Cl (237–240 pm) distances in **8** agree quite well with the data from the literature.[26] For $MoOF_4$ Mo-F=180–184 pm and Mo-O=164 pm,[15] for $C_6F_5OMoF_5$ Mo-F= 182–185 pm[27]; for $[OMoCl_4·MeCN]^-$ Mo-Cl= 235–237 pm and Mo-O=165–166 pm are reported.

4. Conclusions

The addition of azolides to bis(azolyl)thiourea is an efficient preparative route to tris(azolyl)methyl sulfides. Depending on the substituents at the urea tris(azolyl) methyl sulfides with one, two or three different azolyl groups can be synthesized. These tris(azolyl)methyl sulfides will undergo nucleophilic exchange reactions with organic and inorganic halides. Depending on the substrate mono, bi or even multitopic scorpionate ligands, e.g. $(az)_3CS(CH_2)_nSC(az)_3$, $(az)_3CSSSC(az)_3$ etc. will be obtained. Attempts to introduce tris(azolyl)methylsulfides directly into coordination chemistry gave polymeric species. With Me_3Si as a shielding group, followed by cleavage of the SiS bond after coordination, this problem might be circumvented.

Although $[Mo(=O)Cl_4]^-$ is an anion, the coordinative unsaturated Mo centre still adds weak donors, e.g. MeCN and also halides, e.g. Cl^-. In our accidentally isolated dianion $[O=MoF_4\text{-}F\text{-}Mo(=O)Cl_4]^{2-}$ the weak donor is the $[Mo(=O)F_5]^-$ anion. This suggests that further coordinative saturated fluoroanions might act in the same way.

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6. References

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Povzetek

Poročamo o učinkoviti sintezni metodi priprave TAS tris(pirazolil)metiltiolata (**3**). Nukleofilna substitucija na spojini **3** je dala (pir)C(=S)SC(pir)$_3$ (**4**) in H_3CSC(pir)$_3$ (**5**). **5** igra vlogo škorpionatnega liganda v [H_3CSC(pir)$_3$Cr(CO)$_3$] (**6**). Razpad TDAE^{2+} [SC(pir)$_3$Mo(CO)$_3^-$]$_2$ z SO_2FCl TDAE^{2+} je vodil do nastanka [O=MoF$_4$–F–Mo(=O)Cl$_4$]$^{2-}$ (**8**). V članku razpravljamo tudi o strukturah spojin **3**–**6** in **8**.