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Synthesis and Structural Characterization of a Novel Metalladithiatriazine Containing Sulfur and Molybdenum in High Oxidation States

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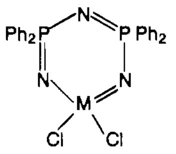
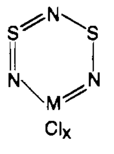
Introduction

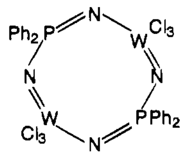
Heterocyclic ring systems containing early transition metals in their highest oxidation states are of considerable interest. E.g., metallacyclophosphazenes can be polymerized by ring opening polymerization yielding polymers containing metals in the backbone,[1] on the other hand they might serve as catalysts due to the unsaturated coordination sphere of the metal atoms. In 1986 we reported on the first six-membered cyclophosphazene in which one phosphorus atom is replaced by a transition metal fragment.[2] Different routes to these systems (A) have been developed by our group since.[3] Earlier, we[4] and Dehnicke et al.[5] have described the syntheses of metalladithiatriazines (B) with the sulfur atoms in the formal oxidation state +II and +IV. Similar ring systems with sulfur +II, +IV have been synthesized by Oakley et al.[6] Metalladithiatriazines with sulfur +VI and the coordination number 4 comparable to phosphorus +V in phosphazenes are hitherto unknown; the attempted synthesis of a P +V and S +VI containing metallaheterocycle resulted in the formation of a dimetallatetrazadiphosphocine (C) instead.[7]



A



B



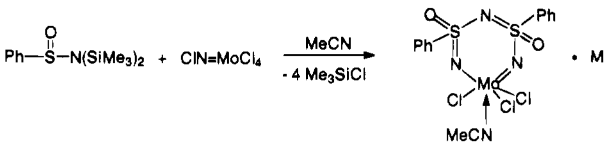
C

Table 1. Crystallographic Data for $C_{18}H_{19}N_6O_2S_2Cl_3Mo$ (Including 3 CH_3CN)

cryst syst: monoclinic
space group: $P2_1/c$
unit cell dimens
$a = 7.931(1)$ Å
$b = 14.431(2)$ Å
$c = 22.575(5)$ Å
$\beta = 90.31(1)°$
volume = 2583.7(7) Å^3
$Z = 4$
formula weight fw = 617.8
density(calc.) = 1.59 Mg/m^3
abs coeff = 0.99 mm^{-1}
$F(000) = 1240$
color; habit: orange needles
cryst size = 0.3 × 0.1 × 1
temp = 293 K
radiation: Mo Kα ($\lambda = 0.71073$ Å)

Structure Solution and Refinement
program used: SHELXTL PLUS (PC Version)
index ranges: $-8 < h < 8$, $-15 < k < 15$; $-24 < l < 24$
no. of reflcns collcd: 5652
no. of indep reflcns: 3371 ($R_{int} = 1.40\%$)
no. of observed reflcns: 2972 ($F > 3.0\,\sigma(F)$)
abs cor: semiempirical by azimuthal scans
structure solution: heavy atom
refinement method: full-matrix least-squares
quantity minimized: $\sum w(F_o - F_c)^2$
absolute configuration: N/A
extinction cor: N/A
hydrogen atoms: riding model, fixed isotropic U
weighting scheme: $w^{-1} = \sigma^2(F) + 0.0004F^2$
final R indices (obsd data): $R = 3.25\%$, $R_w = 3.99\%$
R indices (all data): $R = 3.81\%$, $R_w = 4.13\%$
goodness-of-fit: 1.40
largest and mean: Δ/σ 0.006, 0.001
data-to-param ratio: 10.3 : 1
largest difference peak: 0.69 e Å^{-3}
largest difference hole: −0.52 e Å^{-3}

In this paper we report on the synthesis and X-ray structure of a metalladithiatriazine with molybdenum and sulfur both in the oxidation state +VI. Compound **1** is available in moderate yields by the reaction of *N*,*N*-bis(trimethylsilyl)benzenesulfinamide with the *N*-chloronitrene complex of molybdenum, as shown in reaction 1.



(1)

Experimental Section

All manipulations were carried out in an atmosphere of dry nitrogen, using standard Schlenk tube techniques. The solvents were freshly distilled under dry nitrogen from the appropriate drying agents. *N*,*N*-bis(trimethylsilyl)benzenesulfinamide has been prepared as described in the literature;[8] the N-chloronitrene complex of molybdenum has been prepared according to a procedure reported by Görge and Dehnicke.[9]

Synthesis of 1. In a typical experiment 1.43 g (5.0 mmol) *N*,*N*-bis(trimethylsilyl)benzenesulfinamide in CCl_4 (20 mL) were added to a suspension of 0.72 g (2.5 mmol) $ClNMoCl_4$ in CCl_4 (40 mL) through a dropping funnel. The resulting mixture was refluxed for 8 h and a light brown solid was filtered off. This solid was extracted with 40 mL of boiling MeCN. The solvent was removed in vacuo to give 0.37 g (24%) of **1** with mp 124 °C dec. Recrystallization from MeCN gave

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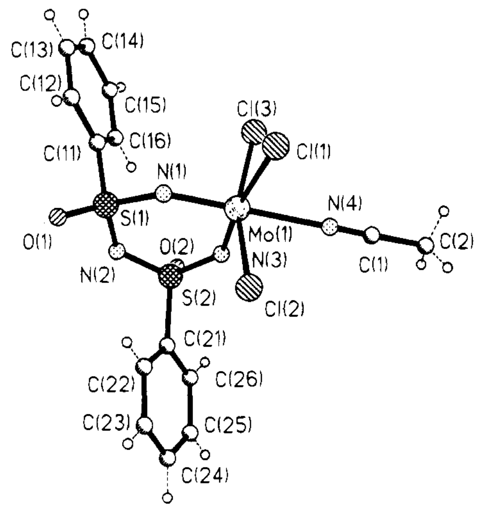


Figure 1. Crystal structure of **1**.

orange crystals suitable for crystallographic analysis. IR(CsI): ν(MeCN) 2314, ν(S=N) 1098, ν(Mo−N) 1026, 1016, 994, ν(Mo−Cl) 599.8, 555.9 cm^{-1} (assignments were made in comparison to the educt compounds[8, 9] and to the triazadiphosphamolybdenine $(Ph_2P)_2N_3MoCl_3\cdot MeCN$[3c]). ^{1}H NMR($CD_3CN$): δ 2.01−2.11 (Me-H, m), 7.4−7.7 (m, phenyl-H) ppm. Anal. Calcd for $C_{12}H_{10}N_3O_2S_2Cl_3Mo$: C, 29.1; H, 2.0; N, 8.4; S, 12.9. Found: C, 29.0; H, 2.4; N, 6.4; S, 12.5. (elemental analysis has been done from the crude product without extracting with MeCN, because the amount of coordinated MeCN varies).

Crystallography. Data were collected at room temperature on a SIEMENS-STOE four circle diffractometer AED2 with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å), using the $2\theta-\omega$ scan technique in the 2Θ range from 7 to 45°. Details of crystal data, measurements of intensities and data processing are summarized in Table 1. The structure was solved by the Patterson method supplied in SHELXTL[10] and refined by full-matrix least-squares procedures against F^2. The refinement converged to agreement factors $R = 3.25\%$ and $R_w = 3.99\%$.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

	Bond Lengths		
Mo(1)−Cl(2)	2.363(1)	Mo(1)−N(1)	1.776(3)
S(1)−N(1)	1.628(3)	S(1)−N(2)	1.557(3)
S(1)−O(1)	1.420(3)	S(1)−C(11)	1.741(3)
S(2)−O(2)	1.422(3)	S(2)−N(3)	1.600(3)
S(2)−C(21)	1.743(4)	Mo(1)−N(4)	2.323(4)
	Bond Angles		
Cl(1)−Mo(1)−Cl(2)	84.6(1)	Cl(1)−Mo(1)−N(1)	96.8(1)
N(1)−Mo(1)−N(3)	91.7(1)	N(3)−Mo(1)−N(4)	85.4(1)
O(1)−S(1)−N(2)	112.9(2)	N(1)−S(1)−N(2)	108.6(2)
N(1)−S(1)−C(11)	102.7(2)	O(1)−S(1)−C(11)	111.7(2)
Mo(1)−N(3)−S(2)	138.9(2)	Mo(1)−N(4)−C(1)	174.8(3)

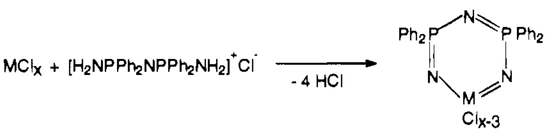
Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3)

	x	*y*	*z*	*U*(eq)[a]
Mo(1)	1407(1)	1986(1)	985(1)	42(1)
Cl(1)	4020(1)	1141(1)	1168(1)	70(1)
Cl(2)	1486(2)	2283(1)	2014(1)	65(1)
Cl(3)	1348(2)	1233(1)	60(1)	67(1)
S(1)	1776(1)	3990(1)	411(1)	46(1)
S(2)	−1557(1)	3416(1)	700(1)	45(1)
O(1)	2732(4)	4750(2)	632(1)	62(1)
O(2)	−2829(3)	3267(2)	264(1)	64(1)
N(1)	2350(4)	3024(2)	725(1)	46(1)
N(2)	−156(4)	4118(2)	498(2)	55(1)
N(3)	−686(4)	2465(2)	899(1)	44(1)
N(4)	37(5)	637(2)	1273(1)	58(1)
C(1)	−710(6)	0(3)	1380(2)	68(2)
C(2)	−1644(9)	−832(4)	1523(2)	115(3)
C(11)	2185(5)	3783(2)	−334(2)	44(1)
C(12)	3845(5)	3899(3)	−519(2)	57(1)
C(13)	4235(6)	3699(3)	−1097(2)	71(2)
C(14)	2993(7)	3396(3)	−1478(2)	73(2)
C(15)	1357(6)	3296(3)	−1296(2)	66(2)
C(16)	934(5)	3490(3)	−720(2)	55(1)
C(21)	−2398(5)	3882(2)	1346(2)	45(1)
C(22)	−1397(5)	4338(3)	1748(2)	55(1)
C(23)	−2127(7)	4654(3)	2263(2)	69(2)
C(24)	−3827(7)	4521(3)	2368(2)	73(2)
C(25)	−4784(6)	4052(3)	1969(2)	73(2)
C(26)	−4093(5)	3724(3)	1448(2)	59(2)
N(1′)	2397(10)	8162(5)	1238(3)	154(4)
C(1′)	2939(9)	8468(4)	820(3)	99(3)
C(2′)	3569(8)	8868(4)	291(3)	106(3)
N(1″)	1952(6)	5434(3)	2217(2)	97(2)
C(1″)	2455(6)	6113(4)	2376(2)	66(2)
C(2″)	3087(7)	6975(3)	2590(2)	90(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Results and Discussion

While the syntheses of metallacyclophosphazenes (reactions 2 and 3) proceed straight forward from metal halides and appropriate open chain phosphazene precursors,[3,11] the same strategy is not applicable for the corresponding sulfur +VI systems due to the lack of appropriate sulfur +VI precursors.[12] A possible access seemed to us the in situ oxidation of sulfinamides with "hyperoxidized" metal fragments, in this case chloronitreno metal halides (reaction 4). Instead of the expected dithiatetrazadimolybdocine the six-membered title compound is formed in moderate yields. A stoichiometry for this unexpected reaction cannot be given, the best yields have been found with a chloronitrene/sulfinamide ratio of 1 : 2 according to the idealized reaction 5, a 2 : 2 ratio decreased the yield and



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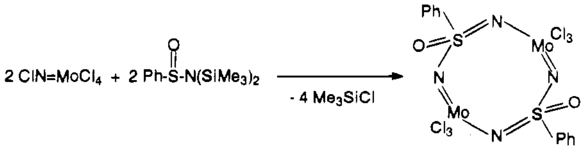

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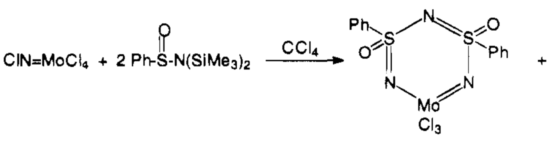

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(12) During the course of our investigations, Roy published a suitable sulfur +VI precursor, PhS(O)(NSiMe$_3$)Cl, which is currently under investigation: (a) Roy, A. K. *J. Am. Chem. Soc.* **1992**, *114*, 1530. (b) Roy, A. K. *J. Am. Chem. Soc.* **1993**, *115*, 2598.

could not be verified, the only detectable by-product was Me_3SiCl. A light brown solid was filtered off and after drying extracted with hot acetonitrile. Evaporation of the solvent resulted in an orange powder of **1** with varying amounts of acetonitrile as seen from the ^1H NMR and IR spectra of different runs. Crystals suitable for X-ray structural analysis were obtained by recrystallization from acetonitrile. Compound **1** crystallizes in the space group $P2_1/c$ with one molecule of MeCN coordinated to molybdenum (Figure 1) and two further independent molecules of MeCN. Selected bond lengths of **1**·MeCN are shown in Table 2, and atomic coordinates and equivalent isotropic displacement coefficients are given in Table 3.

The X-ray structure exhibits an almost planar six-membered ring containing three nitrogen atoms, two sulfur atoms, and one molybdenum atom. The oxygen atoms attached to the sulfur atoms are trans to each other, a feature that has also been found in related diphenyl substituted dithiatriazaphosphorine dioxides investigated by Meetsma et al.[13a-c] While the exocyclic S=O bonds of **1** lie in the range of the aforementioned, the endocyclic bonds and angles differ due to electronic and steric requirements of an octahedral Mo +VI center compared to a tetrahedral P +V moiety, the S−N bonds in **1** opposite to the heteroatom are slightly shorter and the adjacent bonds slightly longer than in the dithiatriazaphosphorine dioxides. The environment around the molybdenum atom is almost identical with that in the triazadiphosphamolybdenine $(Ph_2P)_2N_3MoCl_3$·MeCN.[3c]

Compound **1** represents the first example of a metalladithiatriazine with both the metal and the sulfur atoms in their highest oxidation states. Further investigations in this field of chemistry are in progress.

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Supporting Information Available: Tables of crystal data, atomic parameters, bond distances and angles, anisotropic displacement coefficients, and H-atom coordinates (7 pages). For ordering information consult any current masthead page.

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