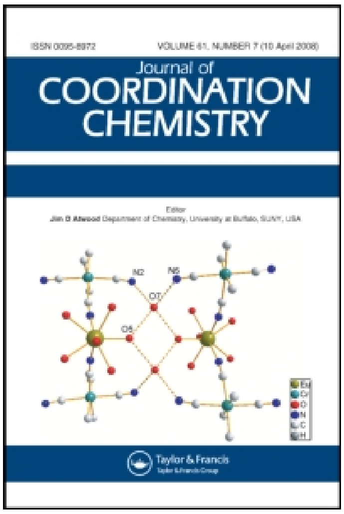

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TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS. PART 25. SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF *cis*-DIOXO [(SALICYLALDEHYDE THIOSEMICARBAZONATO(1-))] AQUOMOLYBDENUM (VI)CHLORIDE MONOHYDRATE, $[MoO_2(HL)H_2O]Cl \cdot H_2O$

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The synthesis and crystal structure analysis of the diamagnetic complex $[MoO_2(HL)H_2O]Cl \cdot H_2O$ (HL = monoanion of salicylaldehyde thiosemicarbazone) are reported. The complex crystallizes in the space group $P2_1/a$ (No. 14) with a = 11.003(1), b = 8.444(1), c = 15.364(1) Å, β = 104.96(1)°, V = 1379.1(2) Å^3. X-ray structure determination revealed that the complex possesses the usual *cis*-MoO_2^{2+} core and that the thiosemicarbazide ligand is present as a monoanionic tridentate donor coordinating through ONS. According to a search in the Cambridge Structural Database (state April 1994) this complex is the first in which the sixth coordination site at Mo(VI) is occupied by a water molecule forming a distorted octahedral coordination geometry together with the tridentate ligand.

KEYWORDS: dioxomolybdenum(VI) complex, salicylaldehyde thiosemicarbazone, Schiff base, X-ray structure

INTRODUCTION

Considerable current interest has been devoted to the chemistry and structures of thiosemicarbazones and their metal complexes$^{1-4}$ in view of their importance in bioorganic and analytical chemistry, *etc.* In particular, 3*d* metal complexes with the

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tridentate ONS salicylaldehyde thiosemicarbazone ligand (H_2L) have been studied in detail. As far as the 4*d* element Mo(VI) is concerned, to our knowledge, only one complex with the dianion ligand L has been prepared so far; its formula is [MoO_2(L)MeOH].[5] In addition, recently the synthesis and X-ray crystal structures of [MoO_2(HL')X_l] complexes (H_2L' = tridentate ONN salicyladehyde S-methylisothiosemicarbazone) with three different solvent ligands X_L = MeOH, EtOH and Py were reported.[6] The present paper describes the X-ray crystal structure of a newly synthesized Mo(VI) complex with the monoanion of salicylaldehyde thiosemicarbazone (HL) possessing the formula [MoO_2(HL)H_2O]Cl·H_2O.

EXPERIMENTAL

Preparation

A mixture of $(NH_4)_6MoO_7O_{24}\cdot 4H_2O$ (0.60 g) and salicylaldehyde thiosemicarbazone (H_2L) (0.20 g), obtained in a reaction of warm aqueous solution of thiosemicarbazide with an ethanolic solution of salicylaldehyde, was treated with water (20 cm^3). To the stirred suspension 10 cm^3 of conc. HCl was added slowly, stepwise at room temperature. After 24 h, the obtained yellow crystals were separated by filtration and washed 2–3 times with dilute HCl (1:5, v/v). Yield: 0.30 g. The substance (0.30 g) was recrystallized from acetone (25 cm^3) at room temperature: slow evaporation of the solvent yielded single crystals (0.15 g) suitable for X-ray analysis. *Anal.* Calcd. for $MoC_8H_{12}N_3O_5SCl$ (Mw = 393.64) (%): Mo, 24.37; C, 24.41; H, 3.07; N, 10.67; Found: Mo, 24.45; C, 25.02; H, 3.30; N, 10.36.

Physical Measurements

All measurements (diamagnetism, molar conductivity, IR and electronic UV-vis, spectra) were carried out as described in our previous work.[7]

X-ray Crystallography

A single crystal of dimensions 0.35×0.25×0.08 mm was mounted on an Enraf-Nonius turbo-CAD-4 diffractometer equipped with a graphite monochromator. Intensities were recorded with MoKα radiation (λ = 0.71070 Å) using ω-2θ scan technique in the range $2.4 < \theta < 40.0°$. Three standard reflections were monitored every hour; no decay correction was applied. Cell constants were determined by least squares refinement of diffractometer angles for 25 automatically centered reflections collected in the range $19 < \theta < 20°$.

The title compound (F.W. 393.66) is monoclinic, space group $P2_1/a$ (No. 14) with a = 11.003(1), b = 8.444(1), c = 15.364(1) Å, β = 104.96(1)°, V = 1379.1(2) $Å^3$, Z = 4, D_{calc} = 1.896 $g.cm^{-3}$, F(000) = 784, μ = 1.314 mm^{-1}.

A total of 9050 reflections were collected of which, after conventional data reduction, 8512[R(int) = 0.0134] were unique, non-zero and not systematically absent. The crystallographic phase problems were solved by direct methods using the program SHELXS(86).[8] Full matrix least squares refinement minimized $\Sigma w(\Delta F^2)^2$ with $w = 1/[\sigma^2(F_o^2) + (0.0471P) + 0.18P]$ where $P = [Max(F_o^2,0) + 2F_c^2]/3$ and resulted in the final R values: $R_1[I > 2\sigma(I)] = 0.0325$, wR_2 = 0.0825, R_1(total)

= 0.0667, wR_2 = 0.0959, S = 1.023. The lowest and highest peaks in the final $\Delta\rho$ map were −0.96 and 1.00 e.$Å^{-3}$ For the H atom coordinates a riding model refinement was applied. Those which are bound to the ligand HL were generated from assumed geometries and checked in difference Fourier syntheses, while the coordinates of the water hydrogens were obtained directly from difference maps. These hydrogen positions were refined with constrained geometry. Scattering factors were taken from standard tables incorporated in the program SHELXL(93).[9] Fractional atomic coordinates of non-hydrogen atoms and equivalent atomic displacement parameters are given in Table 1. Relevant bond distances and angles are listed in Table 2 and the atomic numbering scheme employed is shown in Figure 1. Listing of anisotropic displacement parameters, H atom parameters and all bond distances and angles together with structure factor tables are available from AK on request.

RESULTS AND DISCUSSION

Physico-Chemical Properties and Spectroscopy

The title compound $[MoO_2(HL)H_2O]Cl \cdot H_2O$, is a diamagnetic complex in which the monoanionic Schiff base (HL) is formed by deprotonation of the phenolic hydroxyl group. It is worth noting that, in the presence of a proton acceptor, this ligand is usually coordinated as a dianion (L), generated by an additional deprotonation of the $N = C(NH_2)\text{-}SH$ fragment.[1,2,5,10]

The yellow crystals are stable in open air. They dissolve well in DMF and MeOH, and less in EtOH, Me_2CO and Et_2O. The molar conductivity of the MeOH solution of 105 S cm^2 mol^{-1}, measured at room temperature, corresponds to a 1:1 electrolyte.[11]

Table 1 Atomic coordinates (× 10^4) and eqivalent isotropic displacement parameters ($Å^2 \times 10^3$). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	*y*	*z*	U(eq)
Mo(1)	1205(1)	3551(1)	2226(1)	30(1)
O(2)	1404(1)	1572(1)	2406(1)	43(1)
O(3)	187(2)	3713(2)	1199(1)	56(1)
S(1)	-371(1)	3664(1)	3115(1)	45(1)
O(1)	2712(1)	4311(2)	1938(1)	42(1)
N(1)	-1051(2)	6132(2)	3921(1)	46(1)
N(2)	293(1)	6695(1)	3062(1)	31(1)
N(3)	1040(1)	6217(1)	2520(1)	28(1)
C(1)	-366(1)	5630(2)	3385(1)	32(1)
C(2)	1568(1)	7341(2)	2176(1)	31(1)
C(3)	2402(1)	7083(2)	1605(1)	32(1)
C(4)	2722(2)	8398(2)	1147(1)	41(1)
C(5)	3518(2)	8230(3)	587(1)	46(1)
C(6)	4037(2)	6778(3)	498(1)	48(1)
C(7)	3770(2)	5463(2)	957(1)	41(1)
C(8)	2937(1)	5605(2)	1500(1)	33(1)
Cl(1)	-2536(1)	3714(1)	4962(1)	45(1)
O(4)	2569(1)	3854(1)	3622(1)	35(1)
O(5)	16(2)	9560(2)	3752(1)	55(1)

Table 2. Relevant bond lengths (Å) and angles (deg).

Mo(1)-S(1)	2.4697(5)
Mo(1)-O(1)	1.9336(12)
Mo(1)-O(2)	1.6988(12)
Mo(1)-O(3)	1.689(2)
Mo(1)-O(4)	2.2925(13)
Mo(1)-N(3)	2.3119(12)
S(1)-C(1)	1.711(2)
O(1)-C(8)	1.339(2)
N(2)-N(3)	1.373(2)
N(1)-C(1)	1.320(2)
N(2)-C(1)	1.329(2)
N(3)-C(2)	1.294(2)
C(2)-C(3)	1.441(2)
O(3)-Mo(1)-S(1)	97.07(7)
O(2)-Mo(1)-S(1)	91.62(5)
O(1)-Mo(1)-S(1)	151.65(4)
O(4)-Mo(1)-S(1)	82.08(3)
N(3)-Mo(1)-S(1)	75.73(3)
O(3)-Mo(1)-O(2)	104.95(7)
O(3)-Mo(1)-O(1)	99.18(8)
O(2)-Mo(1)-O(1)	106.31(6)
O(3)-Mo(1)-O(4)	168.95(6)
O(2)-Mo(1)-O(4)	86.10(6)
O(1)-Mo(1)-O(4)	77.54(5)
O(3)-Mo(1)-N(3)	92.13(6)
O(2)-Mo(1)-N(3)	159.99(6)
O(1)-Mo(1)-N(3)	80.59(5)
O(4)-Mo(1)-N(3)	76.96(4)
N(1)-C(1)-S(1)	119.76(12)
N(2)-C(1)-S(1)	122.24(11)
N(1)-C(1)-N(2)	117.99(14)
C(1)-N(2)-N(3)	119.86(12)
C(2)-N(3)-N(2)	115.72(12)
N(3)-C(2)-C(3)	124.11(13)

In the range of the valence vibrations, there are two characteristic IR bands of the *cis*-MoO_2 group of which the one at higher energy (932 cm^{-1}) can undoubtedly be ascribed to ν_s, and the one observed at lower energy (900 cm^{-1}) to the ν_{as} of this group.[12] The ν(C-O) band of the deprotonated phenolic hydroxyl moiety located at 1542 cm^{-1}, is shifted by *ca* 15 cm^{-1} to higher energies compared to that of the uncoordinated ligand. The electronic spectrum of the complex displays a broad low-energy absorption band at ν_{max} = 390 nm (ε = 20.000 dm^3 mol^{-1} cm^{-1}), assignable to a S(pπ) → Mo(dπ) transition.[13] The other bands in the UV region, at 330, 303 and 292 nm, respectively, indicate that they belong to intraligand transitions.

Crystal Structure

The complex consists of an $[MoO_2(O\text{-}C_6H_4CH = N\text{-}NH\text{-}CS\text{-}NH_2)\cdot H_2O]^+$ cation and chloride anion accompanied by a second water molecule bound to the nitrogen atoms of the thiosemicarbazide moiety *via* hydrogen bonds. The geometry of the Schiff base is similar to those of the free ligand (H_2L)[14] and the closely related

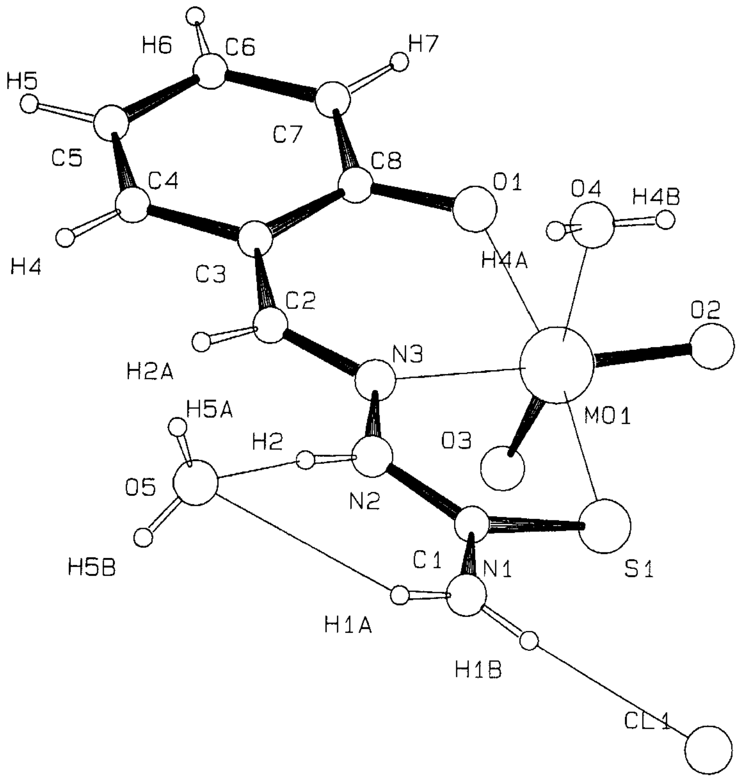

Figure 1 A view of the complex with atomic numbering. The principal hydrogen bonds within one unit of the complex are also shown

1-phenylthiosemicarbazide.[15] The deprotonated phenolic hydroxyl group exhibits only a slightly shorter C-O distance than that of H_2L (1.356(3) Å).

Mo(VI) with one of its covalently bonded oxygen O(2) and the half-moon like uninegative tridentate (ONS) Schiff base defines a grand mean plane of the complex. These sheets are stacked approximately parallel with the *b* axis and perpendicular to the short diagonal of the *ac* plane (Figure 2). The second terminal O(3) atoms and the coordinated water molecules protruding from these planes form the vertices of a distorted $[MoX_6]$ octahedron with the largest diagonal angle of 169.95(6)°. This water ligand (X_L) occupies the sixth coordination site around molybdenum(VI) and together with the terminal oxygens of the *cis*-MoO_2^{2+} cation and the nitrogen atom of the Schiff base form the best equatorial plane of the octahedron. Within this quadrilateral plane Mo(VI) with two almost equal Mo-O bond lengths, assumes similar distances from the water oxygen and the nitrogen atom giving thus a trapezoid shape of the fourfold coordination. The sum of the four angles around Mo(VI) amounts to 360.14°.

According to a search in the Cambridge Structural Database (CSD)[16] (issue of April, 1994) this is the first case when the *sixth* site of the octahedral Mo(VI) coordination dominated by a tridentate (ONO, ONS) Schiff base is occupied by

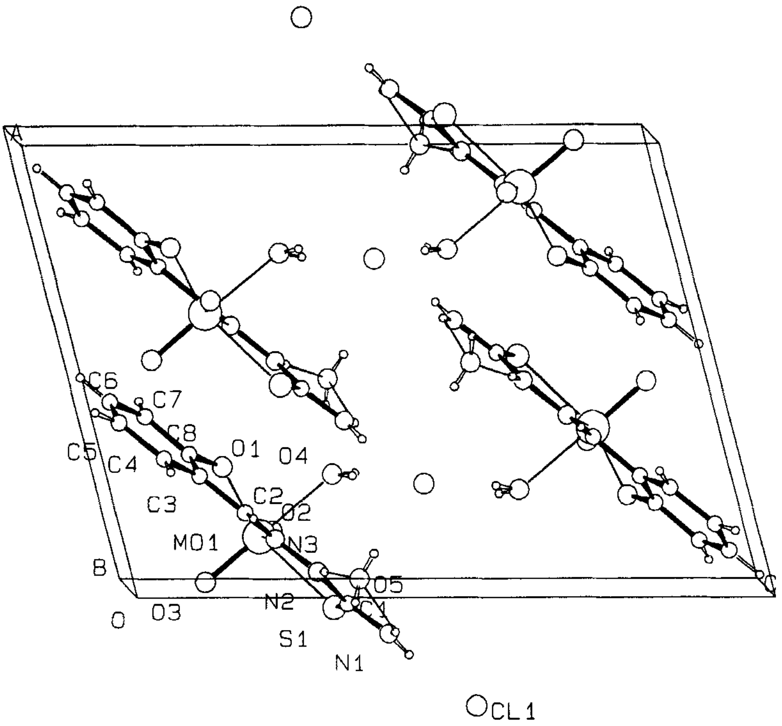

Figure 2 The unit cell of the complex.

water molecule. In 59 hits (published with atomic coordinates) there are water molecules but none of them is coordinated directly to a MoO_2^{2+} core. There is only one structure (its CSD refcode[16]: *LAPPOH*) in which a MoO_2Cl_2 molecule is supplemented by two water ligands to form the usual octahedral coordination. A review of these (59) complexes has shown that the coordination polyhedra generated by tridentate donors around MoO_2^{2+} prefer larger ligands like *e.g.*, MeOH (*SAVMIL, KUJCEH* and a novel complex of $[MoO_2(SALT)MeOH]I$[17]), EtOH,[6] DMSO (*JEWMIH*) Py (*KUJKAT*), *etc.* at the exchangeable sixth site. In the title complex the Mo···O(W) distance (2.293(1) Å) is considerably shorter than the Mo···O(H)Me values in the above mentioned structures (av. 2.373 ± 0.018 Å) but quite close to the Mo···O = S(Me)$_2$ distance (2.305(5)Å) in *JEWMIH*. Furthermore, a search on tridentate ligands of ONS type gave only two hits (*JEWMIH* and *SAVMOR*). Three structures have tridentate ligands of the NNS type coordinated to binuclear Mo_2O_5 moieties (*CEDTUA DARBAL* and *GADTUA*) and there is one structure with a tridentate ligand of the SNS type (*CAHHEY*). Their Mo···S distances vary in the range 2.40–2.47 Å and are comparable to that of the title compound (1.4697(5)Å).

The second water molecule acts as an acceptor in one strong and one weak NH···O interaction of which only the stronger can be regarded as a hydrogen bond (Table 3). One of the hydrogen atoms of this water molecule is donated to a Cl^- anion sitting in the adjacent layer of the complex. The second water proton forms a weak OH···O contact with the coordinated (X_L) water molecule. The chloride anion is

Table 3 Hydrogen bonds

	D...A(Å)	H...A(Å)	DH..A(°)
N(1)-H(1A)...Cl(xyz)	3.278(2)	2.42(1)	171.9(1)
O(4)-H(4A)...C1(−x, 1 − y, 1 − z)	2.999(1)	2.21(3)	170(3)
O(4)-H(4B)...C1($\frac{1}{2}$ + x, $\frac{1}{2}$ − y, z)	3.013(1)	2.21(3)	168(3)
O(5)-H(5A)...C1($\frac{1}{2}$ + x, + $\frac{1}{2}$ + 1 − y, z)	3.202(2)	2.44(2)	170(3)
N(2)-H(2).....O(5)(xyz)	2.690(2)	1.86(2)	163.2(1)
N(1)-H(1A)...O(5)(xyz)	3.159(3)	2.48(2)	137.0(1)
O(5)-H(5A)...O(4)(−$\frac{1}{2}$ + x, $\frac{1}{2}$ + 1 − y, z)	2.967(2)	2.24(2)	149(3)

connected to the cation by a strong hydrogen bond of the NH···Cl type (Figure 1). In addition, the Cl^- anion takes part in three other hydrogen bonds maintained with hydrogen atoms of the coordinated water ligands donated by the neighbouring layers of the stacked complex molecules.

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Supplementary information of anisotropic displacement parameters and hydrogen coordinates are available from A.K.

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