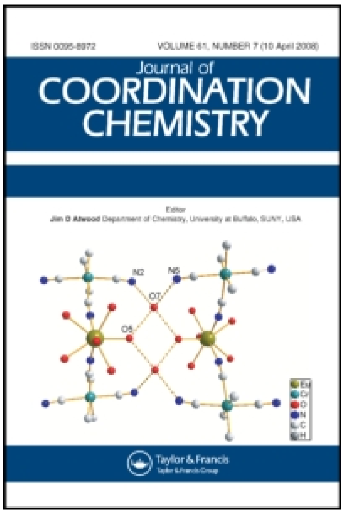

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A *CIS*-DIOXO MOLYBDENUM(VI) COMPLEX OF THE SCHIFF BASE GIRARD REAGENT T (SALT)

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NOTE

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The title complex [$MoO_2(O\text{-}C_6H_4CH{=}NN{=}COCH_2N(CH_3)_3)$ CH_3OH] I was prepared and characterized by elemental analysis, TGA and IR spectra. The crystal structure of the complex was determined. The complex crystallizes in space group $P2_1/a$ with $a = 12.782(1)$, $b = 7.052(1)$, $c = 19.732(1)$ Å, $\beta = 86.71(1)°$, $V = 1775.7$ Å^3 and $Z = 4$. X-ray structure analysis reveals that the complex possesses the usual *cis*-MoO_2^{2+} core and that the ligand SALT [SALT=$HO\text{-}C_6H_4CH = NNHCOCH_2N(CH_3)_3$] is present as a monoanionic terdentate donor coordinating through ONO. The sixth coordination site at Mo is occupied by a methanol molecule, which gives a distorted octahedral coordination geometry.

KEYWORDS: molybdenum (VI), Schiff base, X-ray structure

INTRODUCTION

The coordination chemistry of molybdenum has aroused considerable interest in recent years in view of its importance in catalytic, material and biochemical sciences. The *cis*-$(MoO_2)^{2+}$ group present in certain molybdoenzymes[2] has stimulated search for new structures in which this moiety is coordinated to ligands through nitrogen, oxygen and/or sulphur donors.[3] Now, many molybdenum (VI)-Schiff base complexes have been synthesized; the majority of these contain the *cis*-MoO_2^{2+} moiety proposed as a model for the active site of oxo-transfer molybdoenzymes.[4]

In the present paper, we report a new complex containing the *cis*-MoO_2^{2+} moiety prepared by reaction of the Schiff base SALT and $MoO_2(acac)_2$. Its spectroscopic properties have been characterized. An X-ray diffraction analysis has been performed on the title complex.

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EXPERIMENTAL

Materials and Measurements

Girard reagent T [$H_2NNHCOCH_2N(CH_3)_3Cl$] was obtained from the British Drug Houses Ltd. All chemicals were used without subsequent purification. $MoO_2(acac)_2$ was prepared according to the literature.[5] The ligand SALT was prepared by the usual method. Elemental analyses were performed on an Italy 1106 apparatus. TGA curves were recorded on a Dupont 1090 apparatus. IR spectra were recorded in KBr discs on a Nicolet 170SX spectrophotometer.

[$MoO_2(O\text{-}C_6H_4CH{=}NN{=}COCH_2N(CH_3)_3)CH_3OH$]I, **I.**

$MoO_2(acac)_2$ (163 mg, 0.5 mmol) was dissolved in methanol (30 cm^3). Addition of SALT (135.8 mg, 0.5 mmol) resulted in a yellow precipitate. Iodine (126.9 mg, 0.5 mmol) was added. When refluxed for 1.5h, the precipitate dissolved and the reaction solution turned red. Yellow, prismatic crystals of the complex were obtained after slow evaporation of solvent. Yield 80%, Found: C, 30.26; N, 8.02; H, 3.70%; Calc. for $C_{13}H_{20}MoN_3O_5I$: C, 29.96; N, 8.06; H, 3.87%.

Determination of the crystal structure

A single crystal with appoximate dimensions 0.15 × 0.15 × 0.40 mm was mounted in a glass capillary. All intensity data were collected on an Enraf-Nonius CAD4 diffractometer using graphite monochromated Cu-K_α radiation ($\lambda = 1.54184$ Å). The scan mode was ω–2θ. Some 2882 independent reflections were collected in the range $2° < 2\theta < 120.0°$, and 2205 independent reflections with $I > 3\sigma(I)$ were used for further computation.

The title complex is monoclinic, space group $P2_1/a$, F. W. 521.17, cell dimensions $a = 12.782(1)$, $b = 7.052(1)$, $c = 19.732(1)$ Å, $\beta = 86.71(1)°$, $V = 1775.7$ Å^3, $Z = 4$, $Dcalc. = 1.95$ g cm^{-3}, $F(000) = 1016$, $\mu = 202.2$ cm^{-1}.

All calculations were carried out on a PDP 11/44 computer using the SDP program. The position of the molybdenum atom was determined by direct methods. The positions of the other non-hydrogen atoms were located in difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations but their positions were not refined. The structure was refined by full-matrix least-squares methods to final $R_w = 0.085$, $R = 0.076$. Scattering factors were taken from International Tables for X-ray Crystallography (1974).

RESULTS AND DISCUSSION

Structural studies

Atomic coordinates of non-hydrogen atoms and equivalent isotropic thermal parameters are given in Table 1. Selected bond distances and angles are listed in Table 2. The unit cell containing the complex and the molecular structure are shown in Figures 1 and 2, respectively. The complex consists of an [$MoO_2(O\text{-}C_6H_4CH{=}NN{=}COCH_2N(CH_3)_3)CH_3OH$]$^{+1}$ cation and an iodine anion. X-ray

Table 1 Atomic coordinates and thermal parameters for the non-hydrogen atoms of the complex*.

Atom	*x*/*a*	*y*/b	*z*/*c*	*Beq*Å^2
Mo	0.9791(1)	0.0518(2)	0.68761(7)	2.14(3)
I	1.0506(1)	-0.2482(2)	0.91882(6)	3.02(3)
O1	1.098(1)	0.152(2)	0.6925(5)	3.6(3)
O2	0.904(1)	0.219(3)	0.6535(8)	5.3(4)
O3	0.995(1)	-0.117(2)	0.6117(5)	2.6(3)
O4	0.932(1)	0.099(2)	0.7844(6)	2.9(3)
O5	1.057(1)	-0.210(2)	0.7432(6)	2.5(3)
N1	0.849(1)	-0.150(2)	0.7121(7)	2.4(3)
N2	0.806(1)	-0.130(2)	0.7819(6)	2.2(3)
N3	0.758(1)	0.242(2)	0.8897(7)	2.1(3)
C1	0.930(2)	-0.220(3)	0.5772(9)	2.7(4)
C2	0.954(2)	-0.249(3)	0.5085(8)	2.3(4)
C3	0.889(2)	-0.355(3)	0.4717(9)	3.4(5)
C4	0.801(2)	-0.437(3)	0.4986(9)	3.1(4)
C5	0.776(2)	-0.413(3)	0.5681(9)	2.4(4)
C6	0.840(1)	-0.303(3)	0.6069(8)	1.8(4)
C7	0.807(1)	-0.273(3)	0.6779(8)	2.0(4)
C8	0.851(2)	0.002(3)	0.8090(9)	2.8(4)
C9	0.814(2)	0.049(3)	0.8841(7)	2.4(4)
C10	0.682(2)	0.265(4)	0.835(1)	4.3(5)
C11	0.835(2)	0.401(3)	0.886(1)	3.8(5)
C12	0.703(2)	0.251(3)	0.9552(9)	3.2(5)
C13	1.052(2)	-0.405(3)	0.726(1)	3.5(5)

$^*Beq = 4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ac(\cos\beta)B_{13}]$.

analysis indicates a distorted octahedral environment around molybdenum (VI) and SALT acts as a uninegative terdentate ligand in the complex.

The two oxygen atoms of the ligand occupy opposite vertices of the octahedron. The nitrogen atom of the Schiff base, two terminal oxygen atoms and one oxygen atom from a methanol moecule form the equatorial plane. These characteristics along with the bond lengths and angles of the complex are similar to those of

Table 2 Selected bond distances (Å) and angles (°) for the complex.

		Distances		
Mo-O(1)	1.679(2)		O(3)-C(1)	1.325(3)
Mo-O(2)	1.683(3)		O(4)-C(8)	1.317(4)
Mo-O(3)	1.914(2)		O(5)-C(13)	1.415(4)
Mo-O(4)	1.996(3)		N(1)-N(2)	1.462(3)
Mo-O(5)	2.394(3)		N(1)-C(7)	1.240(4)
Mo-N(1)	2.221(2)		N(2)-C(8)	1.231(4)
		Angles (°)		
O(1)-Mo-O(2)	105.4(1)		O(3)-Mo-N(1)	79.58(9)
O(1)-Mo-O(3)	104.31(8)		O(4)-Mo-O(5)	78.48(7)
O(1)-Mo-O(4)	95.56(8)		O(4)-Mo-N(1)	73.70(9)
O(1)-Mo-O(5)	84.22(9)		O(5)-Mo-N(1)	74.36(8)
O(1)-Mo-N(1)	157.5(1)		N(2)-N(1)-C(7)	115.4(2)
O(2)-Mo-O(3)	99.3(2)		N(1)-N(2)-C(8)	108.8(2)
O(2)-Mo-O(4)	96.8(2)		N(1)-C(7)-C(6)	120.7(3)
O(2)-Mo-O(5)	169.8(1)		O(4)-C(8)-N(2)	127.7(3)
O(2)-Mo-N(1)	95.7(1)		O(4)-C(8)-C(9)	115.6(3)
O(3)-Mo-O(4)	149.93(9)		N(2)-C(8)-C(9)	116.5(3)
O(3)-Mo-O(5)	81.29(7)			

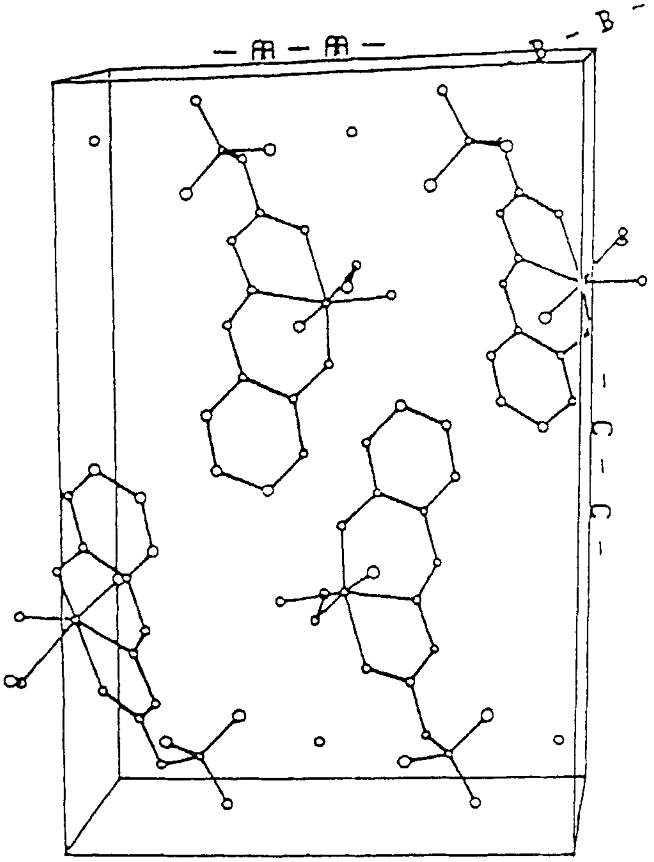

Figure 1 The unit cell of the complex.

cis-dioxomolybdenum(VI) complexes of terdentate Schiff base ligands already reported[6,7]. N(1)–C(7) [1.240(4) Å] and N(2)–C(8) [1.231(4) Å] bond distances in the complex are typical of double bonds [a normal single bond is 1.364 Å[8]]. Bonds Mo–O[1.914(2)–1.996(3) Å] and Mo–N(1)[2.221(2) Å] are in the known range for molybdenum- Schiff base complexes. The Mo–O(5) [2.394(3) Å] bond is relatively long due to the labile coordinated solvent molecule (CH_3OH). The average Mo-O bond length of 1.681(2) Å and the O–Mo–O bond angle (105.4(1)° is comparable to other such data reported for the *cis*-MoO_2^{2+} group.[6–9] Torsion angles O(4)–Mo–N(1)–N(2) [0.78(1.03)°] and Mo–N(1)–N(2)–C(8) [2.63(1.77)°] indicate that the Mo–N(1)–N(2)–C(8)–O(4) atoms form a pentatomic ring in one plane. It is shown in Table 2 that the molybdenum atom is in the equatorial plane O(1)–O(2)–N(1)–O(5) [O(1)–Mo–O(5) = 84.22(9)°; O(1)–Mo–O(2) = 105.4(1)°; O(2)–Mo–N(1)=95.7(1)°; O(5)–Mo–N(1) = 74.36(8)°]. The sum of the four angles in the plane is 359.68°.

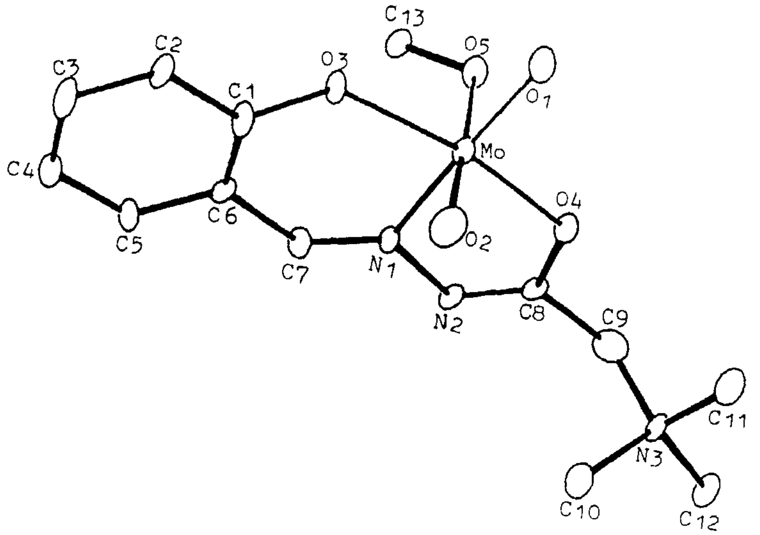

Figure 2 A view of the $[MoO_2(SALT)(CH_3OH]^{+1}$ cation with atom numbering shown.

IR Spectra

IR data for the SALT ligand and the complex an provided in Table 3. The characteristic ligand band $\nu(C{=}O)$ at 1701 cm^{-1} disappears in the complex, thus suggesting reaction of the enol form with elimination of a proton.[6] The $\nu(C{=}N)$ band at 1630 cm^{-1} displays a shift to lower frequency (1611 cm^{-1}) in the complex, indicating coordination of the azomethine nitrogen atom to molybdenum.[10] A new band in the complex at 1238 cm^{-1} may be due to enolic $\nu(C\text{–}O)$. The phenolic $\nu(C\text{–}O)$ band (1272 cm^{-1}) of the ligand shifts to lower frequency (1266 cm^{-1}) in the complex, revealing coordination of the phenolic C–O group.[11]Bands at 578 and 540 cm^{-1} are assigned to $\nu(Mo\text{–}N)$ and $\nu(Mo\text{–}O)$ respectively.[10] The presence of a new band at 1011 cm^{-1} is due to the $\nu(C\text{–}O)$ stretch which suggests methanol coordination to the molybdenum.[12] Dioxomolybdenum (VI) complexes containing *cis*-MoO_2 moiety exhibit two strong bands at 905–948 and 875–914 cm^{-1} assignable to symmetrical $\nu(O{=}Mo{=}O)$ and asymmetrical $\nu(O{=}Mo{=}O)$, respectively.[8,10] A *trans*-MoO_2 group shows only one IR-active band. Bands at 943 and 909 cm^{-1} indicate the presence of a *cis*-MoO_2 moiety. IR results thus agree well with the X-ray analysis.

Table 3 IR data for the ligand and the complex.

Compound	$\nu(C{=}N)$	$\nu(C\text{–}O)$ phenolic	$\nu(C\text{–}O)$ enolic	$\nu(C{=}O)$	$\nu(O{=}Mo{=}O)$	$\nu(Mo\text{–}N)$	$\nu(Mo\text{–}O)$	$\nu(C\text{–}O)$ CH_3OH
SALT	1630	1272		1701				
$[MoO_2(SALT)(CH_3OH)]I$	1611	1266	1238		943,909	578	540	1011

TGA Studies

TGA studies indicate that the complex decomposes in two stages to a final residue of MoO_3. The first weight loss at 150°C indicates elimination of CH_3OH from the complex, afact which suggests that methanol is coordinated.[6,7] The second loss (240–510°C) is occasioned by decomposition of the Schiff base.

SUPPLEMENTARY MATERIAL

Atomic coordinates for the hydrogen atoms, thermal parameters, full lists of bondlengths, bond angles, torsion angles and observed and calculated structure factors are available from the authors on request.

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