

Synthesis and Crystal Structures of Ethanol-Coordinated Molybdenum(VI) Oxo Complexes with Tridentate Hydrazone Ligands

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Abstract

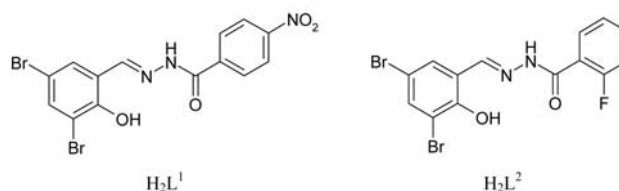
Reaction of $[\text{MoO}_2(\text{acac})_2]$ (where acac = acetylacetonate) with two similar hydrazone ligands in ethanol yielded two ethanol-coordinated mononuclear molybdenum(VI) oxo complexes with general formula $[\text{MoO}_2\text{L}(\text{EtOH})]$, where $\text{L} = \text{L}^1 = (N'-(3,5\text{-dibromo-2-hydroxybenzylidene)-4-nitrobenzohydrazide})$ (H_2L^1), and $\text{L} = \text{L}^2 = (N'-(3,5\text{-dibromo-2-hydroxybenzylidene)-2-fluorobenzohydrazide})$ (H_2L^2). Crystal and molecular structures of the complexes were determined by single crystal X-ray diffraction method. All of the investigated compounds were further characterized by elemental analysis and FT-IR spectra. Single crystal X-ray structural studies indicate that the hydrazone ligands coordinate to the MoO_2 cores through enolate oxygen, phenolate oxygen and azomethine nitrogen. The Mo atoms in both complexes are in octahedral coordination. Thermal stability of the complexes has also been studied.

Keywords: Molybdenum complex; Hydrazone ligand; Crystal structure; X-ray diffraction; Thermal property.

1. Introduction

Coordination chemistry of molybdenum(VI) has attracted considerable attention due to its biochemical significance¹ as well as for the efficient catalytic properties in several organic synthesis procedures.² Schiff bases are a kind of interesting ligands in coordination chemistry.³ In recent years, a number of molybdenum(VI) complexes with Schiff bases derived from salicylaldehyde and primary amines have been reported.⁴ Hydrazones, bearing $-\text{C}(\text{O})-\text{NH}-\text{N}=\text{CH}-$ groups, are a kind of special Schiff bases, which are of particular interest in coordination chemistry and biological applications. Molybdenum complexes with hydrazone ligands have been reported to possess interesting antibacterial activities.⁵ However, molybdenum(VI) complexes derived from hydrazone ligands have been much less studied. $N'-(3,5\text{-Dibromo-2-hydroxybenzylidene)-4-nitrobenzohydrazide}$ (H_2L^1) is a tridentate hydrazone compound. The crystal structure of the methanol solvated species of H_2L^1 has been reported.⁶ In the present work, we report the synthesis and structures of two new dioxomolybdenum(VI) complexes with general

formula $[\text{MoO}_2\text{L}(\text{EtOH})]$, where $\text{L} = \text{L}^1$, and $\text{L} = \text{L}^2 = (N'-(3,5\text{-dibromo-2-hydroxybenzylidene)-2-fluorobenzohydrazide})$ (H_2L^2).



2. Experimental

2.1. Materials and Measurements

Commercially available 3,5-dibromosalicylaldehyde, 4-nitrobenzohydrazide, and 2-fluorobenzohydrazide were purchased from Aldrich and used without further purification. Other solvents and reagents were made in China and used as received. C, H and N elemental analyses were performed with a Perkin-Elmer elemental

analyser. Infrared spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region.

2. 2. Synthesis of H_2L^1

3,5-Dibromosalicylaldehyde (1.0 mmol, 0.28 g) and 4-nitrobenzohydrazide (1.0 mmol, 0.18 g) were dissolved in methanol (30 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a yellow solution. The solvent was evaporated to give yellow crystalline product of H_2L^1 . Yield, 90%. Analysis: Found: C 37.8%, H 2.1%, N 9.6%. Calculated for $\text{C}_{14}\text{H}_9\text{Br}_2\text{N}_3\text{O}_4$: C 38.0%, H 2.0%, N 9.5%.

2. 3. Synthesis of H_2L^2

3,5-Dibromosalicylaldehyde (1.0 mmol, 0.28 g) and 2-fluorobenzohydrazide (1.0 mmol, 0.15 g) were dissolved in methanol (30 mL) with stirring. The mixture was stirred for about 30 min at room temperature to give a colorless solution. The solvent was evaporated to give colorless crystalline product of H_2L^2 . Yield, 87%. Analysis: Found: C 40.5%, H 2.1%, N 6.8%. Calculated for $\text{C}_{14}\text{H}_9\text{Br}_2\text{FN}_2\text{O}_2$: C 40.4%, H 2.2%, N 6.7%.

2. 4. Synthesis of $[\text{MoO}_2\text{L}^1(\text{EtOH})]$ (1)

An ethanolic solution (10 mL) of $[\text{MoO}_2(\text{acac})_2]$ (0.1 mmol, 32.6 mg) was added to an ethanolic solution (10 mL) of H_2L^1 (0.1 mmol, 44.3 mg) with stirring. The mixture was stirred for 20 min to give an orange solution. The resulting solution was allowed to stand in air for a few days. Orange block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold ethanol, and dried in a vacuum over anhydrous CaCl_2 . Yield, 53%. Analysis: Found: C 31.0%, H 2.2%, N 7.0%. Calculated for $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{MoN}_3\text{O}_7$: C 31.2%, H 2.1%, N 6.8%.

2. 5. Synthesis of $[\text{MoO}_2\text{L}^2(\text{EtOH})]$ (2)

An ethanolic solution (10 mL) of $[\text{MoO}_2(\text{acac})_2]$ (0.1 mmol, 32.6 mg) was added to an ethanolic solution (10 mL) of H_2L^2 (0.1 mmol, 41.6 mg) with stirring. The mixture was stirred for 20 min to give an orange solution. The resulting solution was allowed to stand in air for a few days. Orange block-shaped crystals suitable for X-ray single crystal analysis were formed at the bottom of the vessel. The isolated product was washed three times with cold ethanol, and dried in a vacuum over anhydrous CaCl_2 . Yield, 62%. Analysis: Found: C 32.6%, H 2.3%, N 4.7%. Calculated for $\text{C}_{16}\text{H}_{13}\text{Br}_2\text{FMoN}_2\text{O}_5$: C 32.7%, H 2.2%, N 4.8%.

Table 1. Crystallographic data and refinement parameters for the complexes

	1	2
Chemical formula	$\text{C}_{16}\text{H}_{13}\text{Br}_2\text{MoN}_3\text{O}_7$	$\text{C}_{16}\text{H}_{13}\text{Br}_2\text{FMoN}_2\text{O}_5$
<i>Mr</i>	615.0	588.0
Crystal color, habit	Orange, block	Orange, block
Crystal size (mm^3)	$0.22 \times 0.20 \times 0.17$	$0.20 \times 0.18 \times 0.15$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell parameters		
<i>a</i> (Å)	13.8054(9)	14.6399(7)
<i>b</i> (Å)	8.0699(6)	17.8471(8)
<i>c</i> (Å)	17.776(1)	7.4344(3)
β (°)	91.397(2)	101.572(1)
<i>V</i> (Å ³)	1979.8(2)	1903.0(2)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm^{-3})	2.063	2.053
Temperature (K)	298(2)	298(2)
μ (mm^{-1})	4.743	4.928
<i>F</i> (000)	1192	1136
Number of unique data	3684	3626
Number of observed data [$I > 2\sigma(I)$]	2626	2929
Number of parameters	263	255
Number of restraints	0	2
<i>R</i> ₁ , <i>wR</i> ₂ [$I > 2\sigma(I)$]	0.0376, 0.0671	0.0345, 0.0852
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0702, 0.0783	0.0506, 0.0941
Goodness of fit on <i>F</i> ²	1.012	0.927
Max and min electron density (e Å^{-3})	0.600, −0.590	0.853, −0.698

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

1			
Mo(1)–O(1)	1.923(3)	Mo(1)–O(2)	1.997(3)
Mo(1)–N(1)	2.258(3)	Mo(1)–O(5)	1.679(4)
Mo(1)–O(6)	2.312(3)	Mo(1)–O(7)	1.696(3)
O(5)–Mo(1)–O(7)	105.7(2)	O(5)–Mo(1)–O(1)	98.7(2)
O(7)–Mo(1)–O(1)	103.6(2)	O(5)–Mo(1)–O(2)	97.2(2)
O(7)–Mo(1)–O(2)	98.5(1)	O(1)–Mo(1)–O(2)	148.0(1)
O(5)–Mo(1)–N(1)	91.5(1)	O(7)–Mo(1)–N(1)	161.2(1)
O(1)–Mo(1)–N(1)	80.6(1)	O(2)–Mo(1)–N(1)	71.4(1)
O(5)–Mo(1)–O(6)	169.4(1)	O(7)–Mo(1)–O(6)	84.7(1)
O(1)–Mo(1)–O(6)	80.1(1)	O(2)–Mo(1)–O(6)	79.2(1)
N(1)–Mo(1)–O(6)	77.9(1)		
2			
Mo(1)–O(1)	1.928(3)	Mo(1)–O(2)	1.996(3)
Mo(1)–O(3)	1.687(3)	Mo(1)–O(5)	1.694(3)
Mo(1)–N(1)	2.249(3)	Mo(1)–O(4)	2.344(3)
O(3)–Mo(1)–O(5)	105.8(1)	O(3)–Mo(1)–O(1)	99.5(1)
O(5)–Mo(1)–O(1)	103.3(1)	O(3)–Mo(1)–O(2)	96.2(1)
O(5)–Mo(1)–O(2)	97.8(1)	O(1)–Mo(1)–O(2)	149.1(1)
O(3)–Mo(1)–N(1)	92.4(1)	O(5)–Mo(1)–N(1)	159.8(1)
O(1)–Mo(1)–N(1)	81.7(1)	O(2)–Mo(1)–N(1)	71.1(1)
O(3)–Mo(1)–O(4)	170.1(1)	O(5)–Mo(1)–O(4)	83.8(1)
O(1)–Mo(1)–O(4)	80.1(1)	O(2)–Mo(1)–O(4)	80.0(1)
N(1)–Mo(1)–O(4)	77.7(1)		

2. 6. X-ray Crystallography

Diffraction intensities for the complexes were collected at 298(2) K using a Bruker D8 VENTURE PHOTON diffractometer with MoK α radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program,⁷ and multi-scan absorption corrections were performed using the SADABS program.⁸ The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using the SHELXTL.⁹ All of the non-hydrogen atoms were refined anisotropically. H atoms were placed in idealized positions and constrained to ride on their parent atoms. The F1, C10, and C14 atoms in **2** are disordered over two sites with occupancies of 0.72(2) and 0.28(2). The crystallographic data for the complexes are summarized in Table 1. Selected bond lengths and angles are given in Table 2.

3. Results and Discussion

3. 1. General

Replacement of two acetylacetonate ligands in [MoO₂(acac)₂] by hydrazone ligands in absolute ethanol resulted in the formation of ethanol-coordinated mononuclear molybdenum(VI) oxo complexes. In both complexes, the dinegative ligands are coordinated to the *cis*-MoO₂ cores *via* the phenolate-oxygen, imino-nitrogen, and enolate-oxygen. The sixth coordination site is occupied by the oxygen atom from ethanol solvent. The complexes are soluble in methanol, ethanol, and acetonitrile. Molar conductance of complexes **1** and **2** at the concentrations of 10⁻⁴ M are 13 and 16 Ω^{-1} cm² mol⁻¹, respectively, indicating they are non-electrolytes.

3. 2. Crystal Structure Description of the Complexes

The molecular structures and atom numbering schemes of complexes **1** and **2** are shown in Figures 1 and 2, respectively. The coordination geometry around each Mo atom is highly distorted octahedral. In each complex, the hydrazone ligand behaves in a tridentate manner in which the phenolate O, imino N, and enolate O atoms occupy a meridional plane. The coordination geometry around molybdenum can be described as distorted octahedral in the complexes. The dianionic hydrazone ligands act in planar tridentate manner, forming one five- and one six-membered chelate rings with the Mo atom. The hydrazone ligand in each of the complexes is bonded to the MoO₂ core in a planar fashion, coordinating through the phenolate O, imino N, and enolate O, and an oxo group lying *trans* to the nitrogen donor. In each of the complexes, an ethanol molecule completes the distorted octahedral coordination sphere which lies *trans* to the other oxo group. The

Mo–O(ethanol) bonds are significantly longer than the other Mo–O bonds, indicating that the ethanol molecules are weakly bonded to the MoO₂ core and this position holds the possibility of functioning as a substrate binding site.

The atoms O(1), O(5), O(2), and N(1) in both complexes that define a plane show high degree of planarity, the Mo atoms are displaced by 0.304(1) Å for **1** and 0.308(1) Å for **2** toward the axial oxo groups. The Mo=O bonds in the complexes are almost equal within the standard deviations, and are within previously reported ranges.¹⁰ The angular distortion in the octahedral environment around Mo comes from the five- and six-membered chelate rings taken by the hydrazone ligands. For the same reason, the *trans* angles significantly deviate from the ideal values of 180°. The hydrazone ligands in the complexes are approximately planar, with the corresponding two benzene rings make dihedral angles of 2.3(2)° for **1** and 6.3(3)° for **2**.

In the crystal structure of **1** (Figure 3), adjacent two molecules are linked by ethanol molecules through

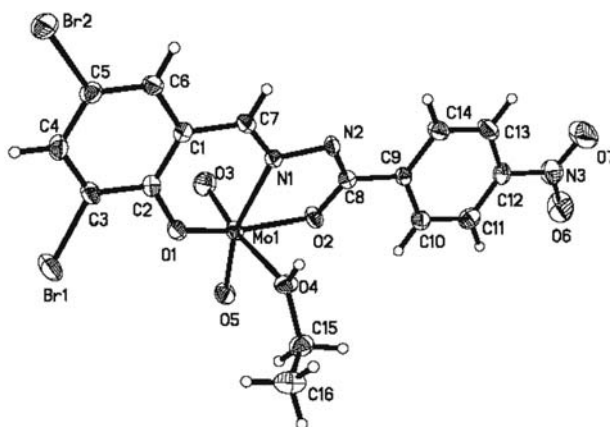


Figure 1. ORTEP plot of the crystal structure of **1**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level.

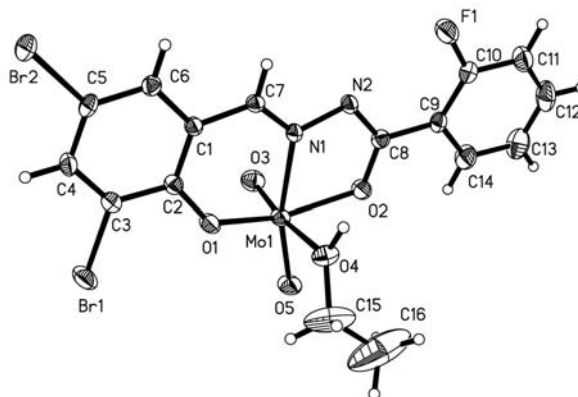


Figure 2. ORTEP plot of the crystal structure of **2**. Displacement ellipsoids of non-hydrogen atoms are drawn at the 30% probability level. Only the major component of the disordered F atom is shown.

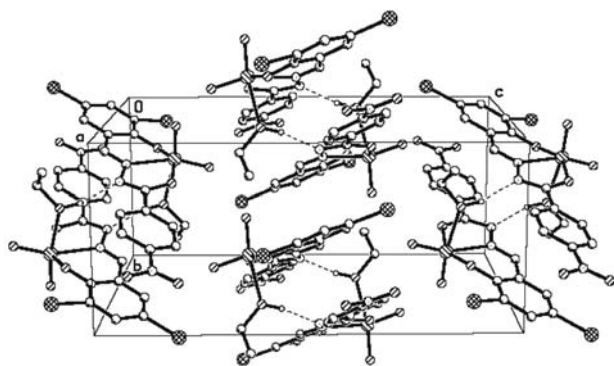


Figure 3. Packing of molecules for compound **1**. Hydrogen bonds are shown as dashed lines.

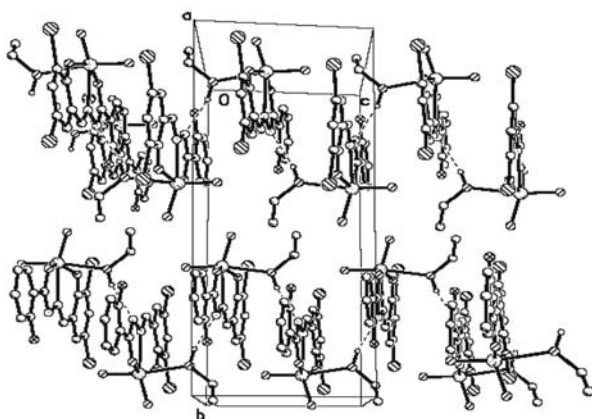


Figure 4. Packing of molecules for compound **2**. Hydrogen bonds are shown as dashed lines.

two intermolecular O–H...N hydrogen bonds [O4–H4A = 0.93 Å, H4A...N2 = 1.97 Å, O4...N2 = 2.868(5) Å, O4–H4A...N2 = 161.5(3)°], to form dimers. In the crystal structure of **2** (Figure 4), adjacent molecules are linked by ethanol molecules through intermolecular O–H...N hydrogen bonds [O4–H4A = 0.93 Å, H4A...N2 = 2.05 Å, O4...N2 = 2.928(5) Å, O4–H4A...N2 = 156.9(3)°], to form chains along the *c* axis. There are no other obvious weak interactions among the molecules of the complexes.

3. 3. IR Spectra

The hydrazone ligands showed stretching bands attributed to C=O, C=N, C–OH and NH at 1660, 1642, 1156 and 1235, and 3239 cm⁻¹ for H₂L¹, and at 1664, 1643, 1155 and 1235, and 3231 cm⁻¹ for H₂L², respectively. In addition, strong bands observed at 1609 cm⁻¹ for H₂L¹ and H₂L² are attributed to –C=N–N=C– groups. Both complexes exhibit two bands at *ca.* 915 and 938 cm⁻¹, assigned to symmetric and asymmetric vibrations

respectively, of the *cis*-MoO₂ cores. The bands due to ν_{C=O} and ν_{NH} were absent in the complexes, but new C–O stretches appeared at 1266 cm⁻¹ for **1** and 1262 cm⁻¹ for **2**. This suggests occurrence of *keto*-imine tautomerization of the ligands during complexation. The ν_{C=N} absorption observed at about 1643 cm⁻¹ in the free hydrazone ligands shifted to 1635 cm⁻¹ for **1** and **2** upon coordination to Mo atoms. The weak peaks in the low wave numbers in the region 500–850 cm⁻¹ may be attributed to Mo–O and Mo–N bonds in the complexes.

3. 4. Thermal Property

Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complexes (Figure 5 for **1** and Figure 6 for **2**). For **1**, the first step started at 165 °C and completed at 186 °C, corresponding to the loss of the ethanol ligand. The observed weight loss of 8.0% is close to the calculated value (7.5%). The second step, from 325 °C to 341 °C, corresponds to the loss of the two Br atoms. The observed weight loss of 26.3% agrees well with the calculated value (26.0%). The third step, from 341 °C to 470 °C, corresponds to the loss of remaining contents of the hydrazone ligand, and the formation of MoO₃. The MoO₃ was stable up to about 630 °C, then it was slowly evaporated, and completed at about 760 °C. For **2**, the first step started at 151 °C and completed at 206 °C, corresponding to the loss of the ethanol ligand. The observed weight loss of 8.2% is close to the calculated value (7.8%). The second step, from 260 °C to 300 °C, corresponds to the loss of the two Br atoms. The observed weight loss of 26.9% agrees well with the calculated value (27.2%). The third step, from 300 °C to 480 °C, corresponds to the loss of remaining contents of the hydrazone ligand, and the formation of MoO₃. The MoO₃ was stable up to about 630 °C, then it was slowly evaporated, and completed at about 750 °C.

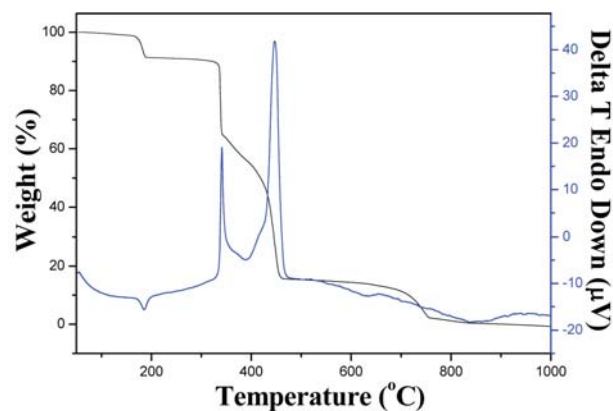


Figure 5. DT-TGA curve of **1**.

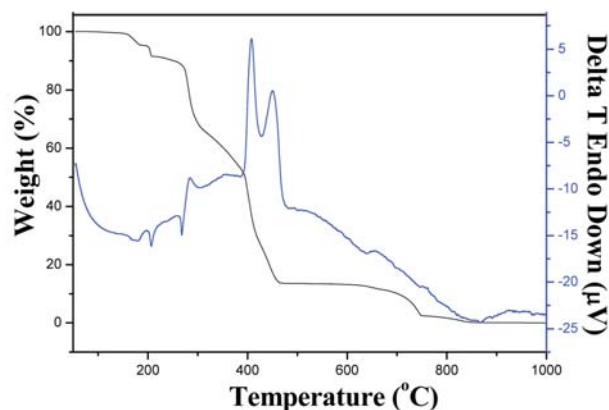


Figure 6. DT-TGA curve of 2.

4. Conclusion

In summary, two ethanol-coordinated mononuclear molybdenum(VI) oxo complexes with similar hydrazone ligands have been prepared and structurally characterized by single crystal X-ray diffraction method, as well as elemental analysis and FT-IR spectra. The hydrazone ligands coordinate to the MoO_2 cores through the enolate oxygen, the phenolate oxygen and the azomethine nitrogen. Thermal stability of the complexes has also been studied.

5. Supplementary Information

CCDC-942637 (1) and 942638 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

Povzetek

Reakcija $[\text{MoO}_2(\text{acac})_2]$ (acac = acetilacetat) z dvema sorodnima hidrazonskima ligandoma v etanolu vodi do nastanka z etanolom koordiniranih enojedrnih molibdenovih(VI) okso kompleksov s splošno formulo $[\text{MoO}_2\text{L}(\text{EtOH})]$, kjer je $\text{L} = \text{L}^1 = (N'-(3,5\text{-dibromo-2-hidroksibenziliden})-4\text{-nitrobenzohidrazid} (\text{H}_2\text{L}^1))$, in $\text{L} = \text{L}^2 = (N'-(3,5\text{-dibromo-2-hidroksibenziliden})-2\text{-fluorobenzohidrazid} (\text{H}_2\text{L}^2))$. Kristalna in molekulska struktura kompleksov je bila določena z monokristalno rentgensko difrakcijo. Vse proučevane spojine so bile nadalje okarakterizirane z elementno analizo in FT-IR spektroskopijo. Rentgenska monokristalna analiza razkriva, da se hidrazonski ligand koordinira na MoO_2 fragment preko enolatnega in fenolatnega kisika ter azometinskega dušika. Mo atomi v obeh spojinah so oktaedrično koordinirani. Termična stabilnost kompleksov je bila tudi proučena.

6. References

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