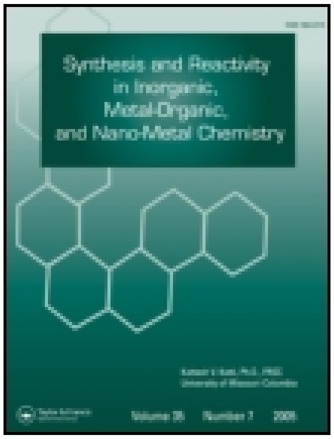
This article was downloaded by: [University of Colorado - Health Science Library]
On: 30 March 2015, At: 11:20
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

# Synthesis, Crystal Structure, and Thermal Analysis of a Dioxomolybdenum(VI) Complex Derived from N,N′-bis(5-methylsalicylidene)-1,3-diaminopropane

Ling-Wei Xue [a] , Xing-Wu Li [a] , Gan-Qing Zhao [a] & Wei-Chun Yang [a]
[a] College of Chemistry and Chemical Engineering , Pingdingshan University , Pingdingshan Henan , P. R. China

Accepted author version posted online: 23 May 2013.Published online: 25 Aug 2013.

To cite this article: Ling-Wei Xue , Xing-Wu Li , Gan-Qing Zhao & Wei-Chun Yang (2013) Synthesis, Crystal Structure, and Thermal Analysis of a Dioxomolybdenum(VI) Complex Derived from N,N′-bis(5-methylsalicylidene)-1,3-diaminopropane, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 43:10, 1514-1517, DOI: 10.1080/15533174.2012.762793

To link to this article: http://dx.doi.org/10.1080/15533174.2012.762793

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

*Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 43:1514–1517, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1553-3174 print / 1553-3182 online
DOI: 10.1080/15533174.2012.762793

# Synthesis, Crystal Structure, and Thermal Analysis of a Dioxomolybdenum(VI) Complex Derived from *N,N′*-bis(5-methylsalicylidene)-1,3-diaminopropane

**Ling-Wei Xue, Xing-Wu Li, Gan-Qing Zhao, and Wei-Chun Yang**
*College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan Henan, P. R. China*

**A new dioxomolybdenum(VI) complex, [$MoO_2L$], where L is the dianionic form of *N,N′*-bis(5-methylsalicylidene)-1,3-diaminopropane ($H_2L$), has been synthesized and characterized by elemental analysis, FT-IR spectrum, and single-crystal X-ray determination. The crystal of the complex is triclinic: space group $P\bar{1}$, $a = 9.1630(4)$, $b = 9.7986(4)$, $c = 10.9257(5)$ Å, $\alpha = 73.062(1)$, $\beta = 72.329(1)$, $\gamma = 75.002(1)°$, $V = 878.37(7)$ Å$^3$, $Z = 2$. The Mo atom in the complex is coordinated by two phenolate O and two imine N atoms of the Schiff base ligand, and by two oxo O atoms, forming an octahedral coordination. Thermal analysis of the complex was performed.**

**Keywords** crystal structure, dioxomolybdenum, Schiff base, thermal analysis

## INTRODUCTION

The coordination chemistry of dioxomolybdenum complexes with multi-dentate ligands has received considerable attention in recent years for their catalytic properties[1–4] and versatile structures.[5–7] Among the multidentate ligands, bis-Schiff bases derived from salicylaldehyde and its derivatives with propane-1,3-diamine have been widely used for the preparation of complexes with various metal ions.[8–12] To date, thousands of complexes of copper, nickel, cobalt, zinc, and cadmium with such bis-Schiff bases have been reported. However, due to the best of our knowledge, only two dioxomolybdenum complexes with such bis-Schiff bases have been reported so far.[13,14] We report herein the synthesis and characterization of a new dioxomolybdenum(VI) complex, [$MoO_2L$], derived from *N,N′*-bis(5-methylsalicylidene)-1,3-diaminopropane ($H_2L$).

## EXPERIMENTAL

### Materials and Methods

5-Methylsalicylaldehyde and propane-1,3-diamine were purchased from Fluka. Other reagents and solvents were analytical grade and used without further purification. Elemental (C, H, and N) analyses were made on a Perkin-Elmer Model 240B automatic analyzer. IR spectra were recorded on an IR-408 Shimadzu 568 spectrophotometer.

### Synthesis of $H_2L$

5-Methylsalicylaldehyde (2.68 g, 0.02 mmol) and propane-1,3-diamine (0.07 g, 0.01 mol) were mixed in methanol (60 mL). The mixture was stirred at reflux for 30 min and three quarter of the solvent was evaporated, to give yellow solid product of $H_2L$, which was collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield is 2.6 g (84%). Anal. Calcd. for $C_{19}H_{22}N_2O_2$: C, 73.5; H, 7.1; N, 9.0%; Found: C, 73.3; H, 7.2; N, 9.0%.

### Synthesis of [$MoO_2L$]

$MoO_2(acac)_2$ (0.2 mmol, 65 mg) in methanol (10 mL) was added with stirring to $H_2L$ (0.2 mmol, 62 mg) in methanol (20 mL). The mixture was stirred at refluxed for 30 min to give a yellow solution. The solution was left still at room temperature in air to give yellow block-shaped single crystals, which were collected by filtration and dried in vacuum containing anhydrous $CaCl_2$. The yield is 53 mg (61%). Anal. Calcd. for $C_{19}H_{20}MoN_2O_4$: C, 52.3; H, 4.6; N, 6.4%; Found: C, 52.1; H, 4.7; N, 6.5%.

### X-Ray Diffraction

Data were collected from selected crystals mounted on glass fibers. The data for the complexes were processed with SAINT[15] and corrected for absorption using SADABS.[16] Multiscan absorption corrections were applied with $\psi$ scans.[17] The structure was solved by direct method using the SHELXS-97 program and refined by full-matrix least-squares techniques on $F^2$ using anisotropic displacement parameters.[18] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms

---

Received 17 December 2012; accepted 25 December 2012.

This research was supported by the National Sciences Foundation of China (No. 20676057 and 20877036) and Top-Class Foundation of Pingdingshan University (No. 2008010).

Address correspondence to Ling-Wei Xue, College of Chemistry and Chemical Engineering, Pingdingshan University, Pingdingshan Henan 467000, P. R. China. E-mail: pdsuchemistry@163.com

TABLE 1
Crystal and structure refinement data for the complex

| | |
|---|---|
| CCDC | 885820 |
| Molecular formula | $C_{19}H_{20}MoN_2O_4$ |
| Molecular weight | 436.3 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$ /Å | 9.1630(4) |
| $b$ /Å | 9.7986(4) |
| $c$ /Å | 10.9257(5) |
| $\alpha$ /° | 73.062(1) |
| $\beta$ /° | 72.329(1) |
| $\gamma$ /° | 75.002(1) |
| $V$ /Å$^3$ | 878.37(7) |
| $Z$ | 2 |
| $D_{\mathrm{calc}}$ (g cm$^{-3}$) | 1.650 |
| Crystal dimensions (mm) | 0.20 × 0.18 × 0.18 |
| $\mu$ (mm$^{-1}$) | 0.774 |
| Radiation λ | Mo K$\alpha$ (0.71073 Å) |
| $T_{\mathrm{min}}/T_{\mathrm{max}}$ | 0.8605/0.8732 |
| Reflections measured | 8106 |
| Range/indices ($h$, $k$, $l$) | –10, 11; –11, 11; –13, 13 |
| $\theta$ limit (°) | 2.4–30.8 |
| Unique reflections | 3234 [$R_{\mathrm{int}} = 0.0191$] |
| Observed reflections ($I > 2\sigma(I)$) | 3018 |
| Parameters | 237 |
| Restraints | 0 |
| Goodness of fit on $F^2$ | 1.171 |
| $R_1$, $wR_2$ [$I \geq 2\sigma(I)$]$^a$ | 0.0273, 0.0698 |
| $R_1$, $wR_2$ (all data)$^a$ | 0.0291, 0.0709 |

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR_2 = [\sum w(F_o^2\text{-}F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

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

| | | | |
|---|---|---|---|
| Bond distances | | | |
| Mo1-O1 | 2.092(2) | Mo1-O2 | 1.924(2) |
| Mo1-O3 | 1.707(2) | Mo1-O4 | 1.710(2) |
| Mo1-N1 | 2.154(2) | Mo1-N2 | 2.332(2) |
| Bond angles | | | |
| O1-Mo1-N1 | 78.7(1) | O2-Mo1-O1 | 83.7(1) |
| O2-Mo1-N1 | 154.8(1) | O3-Mo1-O1 | 91.5(1) |
| O3-Mo1-O2 | 105.7(1) | O3-Mo1-O4 | 104.0(1) |
| O3-Mo1-N1 | 92.7(1) | O3-Mo1-N2 | 168.0(1) |
| O4-Mo1-O1 | 160.6(1) | O4-Mo1-O2 | 102.8(1) |
| O4-Mo1-N1 | 88.8(1) | O4-Mo1-N2 | 84.3(1) |
| O2-Mo1-N2 | 80.3(1) | O1-Mo1-N2 | 78.7(1) |
| N1-Mo1-N2 | 78.7(1) | | |

were placed at the calculated positions. The crystallographic data for the complexes are listed in Table 1. Selected bond lengths and angles are given in Table 2.

## RESULTS AND DISCUSSION

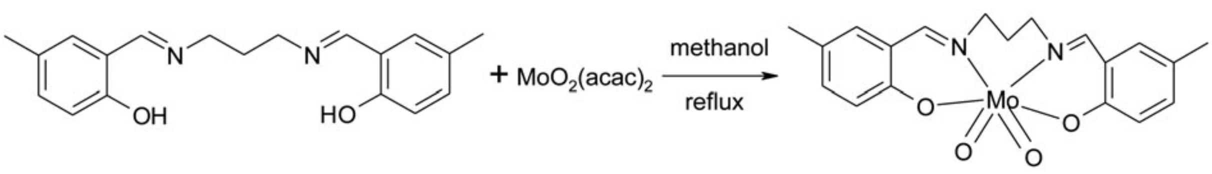
The synthesis of the complex is shown as Scheme 1.

### Crystal Structure Description of the Complex

The molecular structure of the complex is shown in Figure 1. The Mo atom in the complex is in an octahedral coordination, with the phenolate O2 and two imine N atoms of the Schiff base ligand, and the oxo O3 atom defining the equatorial plane, and with the phenolate O1 of the Schiff base ligand and the oxo O4 atom occupying the two axial positions. The Mo atom deviates from the least-squares plane defined by the four equatorial donor atoms by 0.214(1) Å in the direction of O4 atom. The Mo–O, Mo=O, and Mo–N coordinate bond lengths in the complex are comparable to the corresponding values observed in other similar dioxomolybdenum(VI) complexes with Schiff bases.[13,14] The six-membered chelate ring Mo1-N1-C8-C9-C10-N2 adopts a chair conformation. The dihedral angle between the two benzene rings C1-C6 and C12-C17 is 82.8(3)°. In the crystal, adjacent two molecules are linked through intermolecular C–H···O hydrogen bonds [C–H = 0.93 Å, H···O$^i$ = 2.53(2) Å, C···O$^i$ = 3.350(3) Å, C–H···O$^i$ = 148(2)°; symmetry code for i: 1 – $x$, 1 – $y$, – $z$], to form a dimer (Figure 2).

### Infrared Spectra

In the infrared spectrum of the free Schiff base, the weak $\nu$(O–H) band was centered at 3427 cm$^{-1}$. The band was absent after chelation, suggesting the coordination through the deprotonated form of the Schiff base. The $\nu$(C=N) band for the free Schiff base was observed at 1645 cm$^{-1}$, which was located at lower wave number for the complex, *viz*. 1623 cm$^{-1}$, indicating that the Schiff base was coordinated to the Mo atom through the azomethine N atoms.[19] The middle $\nu$(C–O) bands in the spectrum of the complex were located at 1278 cm$^{-1}$.[19] The characteristic $\nu$(Mo=O) and $\nu$(Mo–O/N) bands can be monitored at 886 and 410–580 cm$^{-1}$, respectively.[20,21]



SCH. 1. The preparation of the complex.

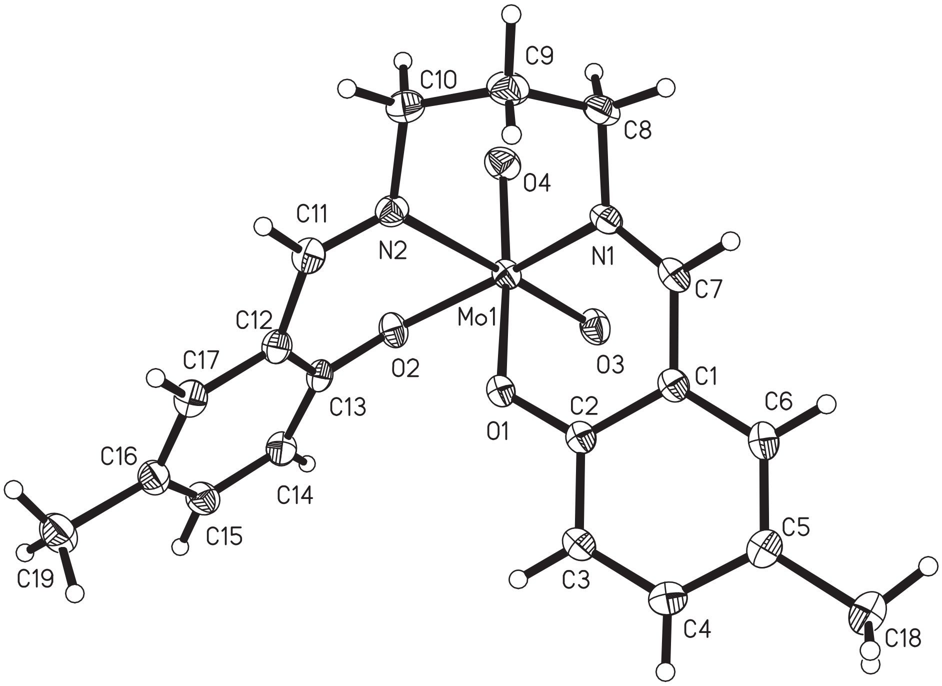


FIG. 1. Perspective view of the complex with 30% probability thermal ellipsoids.

## Thermal Stability

Differential thermal (DT) and thermal gravimetric analyses (TGA) were conducted to examine the stability of the complex (Figure 3). This complex was stable up to 250°C where the decomposition started and end at 596°C. The total observed weight loss of 68.1% was close to the calculated value (67.0%), and the formation of the final product ($MoO_3$). The $MoO_3$ was stable until 690°C. For the sublimation of $MoO_3$, it was slowly evaporated until 916°C.

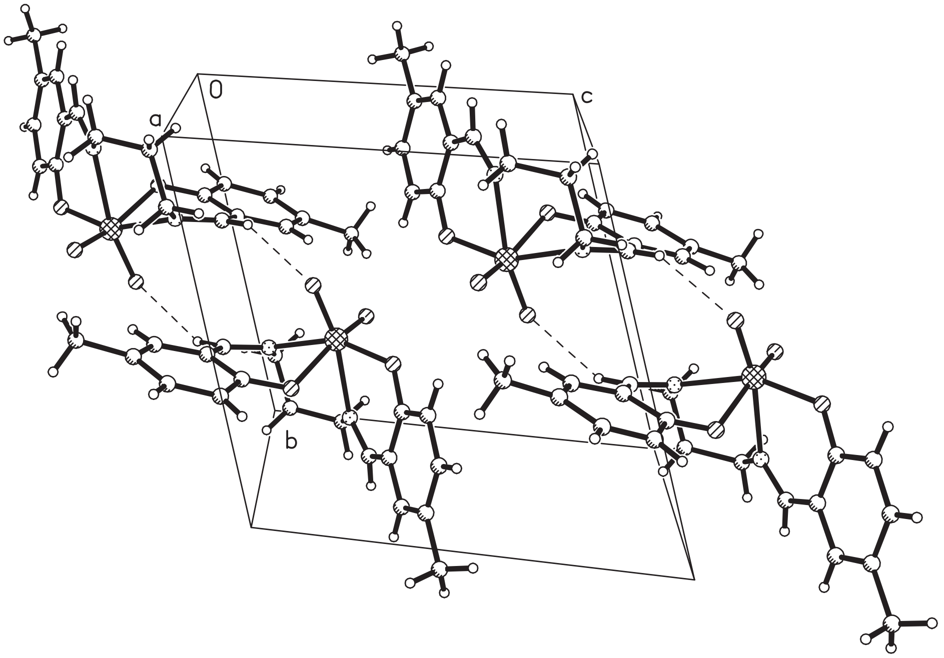


FIG. 2. The C–H···O hydrogen bonds linked dimeric structure of the complex.

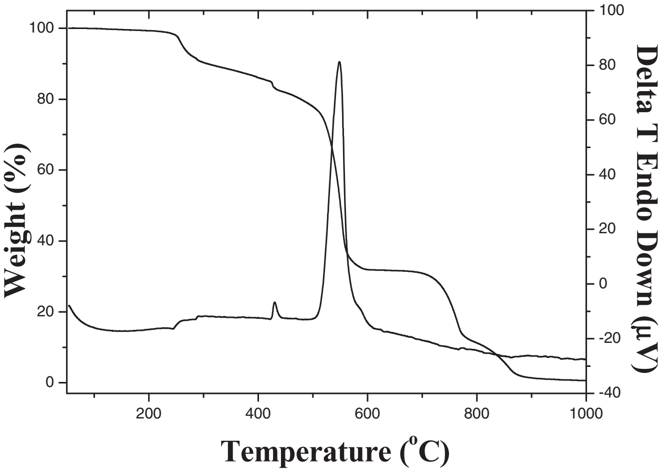


FIG. 3. DT-TGA curve of the complex in air at a heating rate of 10°C min$^{-1}$.

## SUPPLEMENTARY MATERIALS

CCDC-885820 contains the supplementary crystallographic data for this study. The 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.

## REFERENCES

1. Ngan, N.K.; Lo, K.M.; Wong, C.S.R. Dinuclear and polynuclear dioxomolybdenum(VI) Schiff base complexes: Synthesis, structural elucidation, spectroscopic characterization, electrochemistry and catalytic property. *Polyhedron* **2012**, *33*, 235–251.
2. Neves, P.; Gago, S.; Pereira, C.C.L.; Figueiredo, S.; Lemos, A.; Lopes, A.D.; Goncalves, I.S.; Pillinger, M.; Silva, C.M.; Valente, A.A. Catalytic epoxidation and sulfoxidation activity of a dioxomolybdenum(VI) complex bearing a chiral tetradentate oxazoline ligand. *Catal. Lett.* **2009**, *132*, 94–103.
3. Bagherzadeh, M.; Latifi, R.; Tahsini, L.; Amani, V.; Ellern, A.; Woo, L.K. Synthesis, characterization and crystal structure of a dioxomolybdenum(VI) complex with a N,O type bidentate Schiff base ligand as a catalyst for homogeneous oxidation of olefins. *Polyhedron* **2009**, *28*, 2517–2521.
4. Castro, A.; Alonso, J.C.; Valente, A.A.; Neves, P.; Brandao, P.; Felix, V.; Ferreira, P. Nanostructured dioxomolybdenum(VI) catalyst for the liquid-phase epoxidation of olefins. *Eur. J. Inorg. Chem.* **2010**, *9*, 1405–1412.
5. Karabulut, S.; Imamoglu, Y. Recent advances in the applications of electrochemically generated molybdenum and tungsten-based catalysts for the olefins metathesis. *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.* **2008**, *38*, 734–741.
6. Rao, D.P.; Yadav, H.S.; Yadava, A.K.; Singh, S.; Yadav, U.S. In-situ preparation of macrocyclic complexes of dioxomolybdenum(VI) involving a heterocyclic precursor. *J. Coord. Chem.* **2011**, *64*, 293–299.
7. Vrdoljak, V.; Pisk, J.; Prugovecki, B.; Matkovic-Calogovic, D. Novel dioxomolybdenum(VI) and oxomolybdenum(V) complexes with pyridoxal thiosemicarbazone ligands: synthesis and structural characterization. *Inorg. Chim. Acta* **2009**, *362*, 4059–4064.
8. Gamba, I.; Gamez, P.; Monzani, E.; Casella, L.; Mutikainen, I.; Reedijk, J. Selective copper-mediated halogenation of aromatic rings under mild conditions. *Eur. J. Inorg. Chem.* **2011**, *28*, 4360–4368.
9. Rajendiran, T.M.; Kirk, M.L.; Setyawati, I.A.; Caudle, M.T.; Kampf, J.W.; Pecoraro, V.L. Isolation of the first ferromagnetically coupled Mn(III/IV) complex. *Chem. Commun.* **2003**, *7*, 824–825.
10. Reglinski, J.; Morris, S.; Stevenson, D.E. Supporting conformational change at metal centres. Part 1: octahedral systems. *Polyhedron* **2002**, *21*, 2167–2174.
11. Raimondi, A.C.; Hitchcock, P.B.; Leigh, G.J.; Nunes, F.S. Synthesis and crystal structure of a novel tetraiminediphenolate iron(II) macrocyclic complex: a six-coordinate iron-protein model. *J. Chem. Crystallogr.* **2002**, *32*, 363–367.
12. Kurtaran, R.; Emregul, K.C.; Arici, C.; Ercan, F.; Catalano, V.J.; Atakol, O. Synthesis and crystal structure of linear chain homotetranuclear complexes with $N_3^-$. *Synth. React. Inorg. Met.-Org. Chem.* **2003**, *33*, 281–296.
13. Villa, A.C.; Coghi, L.; Manfredotti, A.G.; Guastini, C. Structural researches on organometallic $\pi$-complexes - crystal and molecular-structures of ($\pi$-cyanocyclopentadienyl)tetraphenylcyclobutadienecobalt, ($\pi$-iodocyclopentadienyl)tetraphenylcyclobutadienecobalt and ($\pi$-1,2-diiodocyclopentadienyl)tetraphenylcyclobutadienecobalt. *Acta Crystallogr.* **1974**, *B30*, 2101–2112.
14. Cai, L.-Z.; Song, L.-J.; Zeng, H.-Y.; Dong, Z.-C.; Guo, G.-C.; Huang, J.-S. Synthesis and structure of a new dinuclear oxomolybdate complex containing a linear O-Mo-O-Mo-O unit. *Inorg. Chim. Acta* **2003**, *344*, 61–64.
15. Bruker. *SMART and SAINT, Area Detector Control and Integration Software*; Bruker Analytical X-Ray Instruments Inc., Madison, WI, **1997**.
16. Sheldrick, G.M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen, Germany, **1997**.
17. North, A.C.T.; Phillips, D.C.; Mathews, F.S. A semi-empirical method of absorption correction. *Acta Crystallogr.* **1968**, *A24*, 351–359.
18. Sheldrick, G.M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen, Germany, **1997**.
19. Zhou, Y.-M.; Ye, X.-R.; Xin, F.-B.; Xin, X.-Q. Solid state self-assembly synthesis of cobalt(II), nickel(II), copper(II) and zinc(II) complexes with a bis-Schiff base. *Trans. Met. Chem.* **1999**, *24*, 118–120.
20. Ngan, N.K.; Lo, K.M.; Wong, C.S.R. Synthesis, structure studies and electrochemistry of molybdenum(VI) Schiff base complexes in the presence of different donor solvent molecules. *Polyhedron* **2011**, *30*, 2922–2932.
21. Glowiak, T.; Jerzykiewicz, L.; Sobczak, J.M.; Ziolkowski, J.J. New insights into the chemistry of oxomolybdenum(VI) complexes with *N*-salicylidene-2-aminoethanol. *Inorg. Chim. Acta* **2003**, *356*, 387–392.