Oxotetrabromomolybdenum(V) Complex Compounds with *s*-Triazine Derivatives

HARITINA CHIVU[1], BEATRICE BRAUN[2], OLIMPIA MICU[1], CORNELIA GURAN[1]*

[1] Department of Inorganic Chemistry, Politehnica University, 1 Polizu Str., 011061, Bucharest, Romania

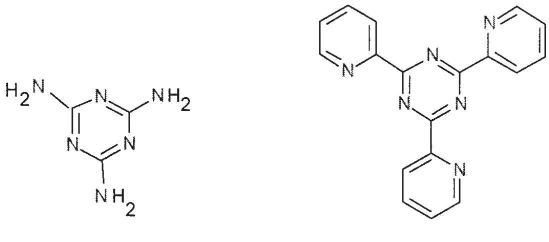
[2] Institute of Inorganic Chemistry, RWTH Aachen University, 1 Landoltweg,, 52074, Aachen, Germany

*Our current interest is focused on the preparing of novel molybdenum(V) complexes with s-triazine derivatives, 2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2-pyridyl)-[1,3,5]-triazine, L^2. On the basis of elemental chemical analysis, molar electrical conductivities, UV-Vis, IR and RPE spectra we established the formulae $(LH_2)_2[MoOBr_4(OH_2)]Br_3$ for monomers **1**, **2** and $[Mo_2O_4Br_2(OH_2)_2L_2]$ for dimmers **3** and **4**. The structure of $(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$ was established by X-ray diffraction spectroscopy.*

Keywords: molybdenum(V), oxomolybdenum complex compounds, s-triazine derivatives

Molybdenum is a relevant element for the synthesis of coordination compounds, many of these having biological or catalytic activity. The chemical properties of molybdenum make it suitable for preparation of these types of compounds but the most important features are related to the stability and readily attainable oxidation states. The presence of oxo groups lead to the stabilization of high oxidation states (V) and (VI) [1]. Oxomolybdenum complexes are the dominant type especially for the oxidation state (V) and an enormous number of mono- and dinuclear species are known [2-12]. In our recent work [13] we reported the synthesis and characterization of three novel Mo(V) complex compounds, $LH[MoOBr4(H_2O)]$, where L = pyridazone derivatives (6-p-tolyl-2H-pyridazin-3-one, 6-(4-chloro-phenyl)-2H-pyridazin-3-one and 6-(4-bromo-phenyl)-2H-pyridazin-3-one).

The aim of this work is to present some other new molybdenum(V) complexes containing *s*-triazine derivatives, 2,4,6-triamine-[1,3,5]-triazine, $\mathbf{L^1}$ and 2,4,6-tri(2-pyridyl)- [1,3,5]-triazine, $\mathbf{L^2}$ (fig. 1).



L1 L2

Fig. 1. The structures of 2,4,6-triamine-[1,3,5]-triazine, $\mathbf{L^1}$ and 2,4,6-tri(2-pyridyl)-[1,3,5]-triazine, $\mathbf{L^2}$

The new compounds **1-4** have the next general formulae for monomeric **1**,**2** and dimeric respectively **3**, **4** species:

$(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$	**1**	$[Mo_2O_4Br_2(OH_2)_2L^1_2]$	**3**
$(L^2H_2)_2[MoOBr_4(H_2O)]\ Br_3$	**2**	$[Mo_2O_4Br_2(OH_2)_2L^2_2]$	**4**

The complex compounds **1-4** were characterized by elemental analysis, molar electrical conductivities UV-Vis, IR and RPE spectra. The structure of $(L^1H_2)_2[MoOBr_4(H_2O)]$, where L^1 = 2,4,6-triamine-[1,3,5]-triazine (melamine) was established by X-ray diffraction.

Experimental part

The organic reagents (2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2-pyridyl)- [1,3,5]-triazine, L^2) were analytical grade and used as received. MoO_3 was obtained by heating of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ at 550 ^{0}C.

Preparation of $(LH_2)_2[MoOBr_4(OH_2)]Br_3$, (L = s-triazine derivatives: 2,4,6-triamine-1,3,5 -triazine, L^1 and 2,4,6-tri(2-pyridyl)-triazine, L^2).

The compounds $(LH_2)_2[MoOBr_4(OH_2)]Br_3$ (**1-2**), where L=2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2-pyridyl)-triazine, L^2, were obtained from hydrobromic solutions of MoO_3 (2.7 mmol dissolved in 1.6 mL of 9M HBr) and L^1 or L^2 dissolved in HBr 9M under slow heating. By evaporation of these solutions (molar ratio Mo: L=1:1), monomeric compounds have been obtained as yellow-green (**1**) or green-brown (**2**) powders:

$(L^1H_2)_2[MoOBr_4(OH_2)]Br_3$ **1**
$(L^2H_2)_2[MoOBr_4(OH_2)]Br_3$ **2**

Preparation of, $[Mo_2O_4Br_2(OH_2)_2L_2]$ (L = s-triazine derivatives: 2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2- pyridyl)-triazine, L^2).

The compounds $[Mo_2O_4Br_2(OH_2)_2L_2]$ (**3-4**), where L = 2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2-pyridyl)-triazine, L^2 were obtained from hydrobromic solutions (9M) of $(LH_2)_2[MoOBr_4(OH_2)]Br_3$ monomers and ammonia-water solution (2 M) at *p*H = 8. By evaporation of these mixed solutions, the dimeric compounds **3-4** have been obtained as brown powders:

$[Mo_2O_4Br_2(OH_2)_2L^1_2]$ **3**
$[Mo_2O_4Br_2(OH_2)_2L^2_2]$ **4**

The electronic spectra were recorded at the room temperature on a Jasco V560 using the diffuse reflectance technique.

The EPR spectra were registered on the polycrystalline powders of compounds, by using a JEOL JES- FA spectrophotometer of ICF Bucharest.

The vibration spectra were recorded with a Bruker Equinox55 spectrophotometer in the wavenumbers range of 400 - 4000 cm^{-1}.

---

* email: cornelia_guran@yahoo.com

Table 1
EXPERIMENTAL X-RAY
DIFFRACTION PARAMETERS AND CRYSTAL DATA
FOR $(L^1H_2)_2[MoOBr_4(OH_2)]Br_3$

	$(L^1H_2)_2[MoOBr_4(OH_2)]Br_3$
Empirical formula	$C_6H_{18}Br_7MoN_{12}O_2$
Formula mass	945.24
Crystal habit, color	rod, yellow
Crystal dim. (mm)	0.05x0.05x0.69
Crystal system	Monoclinic
Space Group	$P2_1/c$
a [Å]	9.6929(15)
b [Å]	18.157(3)
c [Å]	14.238(2)
$\beta[^0]$	90.540(4)
V [Å^3]	2505.6(6)
Z	2
D [g.cm^{-1}]	2.507
F000	1764
μ(Mo-K) [cm^{-1}]	11.715
T [K]	110 (2)
θ range	2.24- 25.00
Refl. collected	14926
Unique refl.	4417
R_{int}	0.0990
Reflections used	4417
Parameters refined	262
R_1	0.0488
wR_2	0.1007
Flack's parameter	-
GooF	0.969
Diff. peak/ hole [e/Å^3]	1.64/ -1.16

The molar electrical conductivities were determined (in dimethylformamide 10^{-3} M solutions of compounds **1-4**) at 25°C with OK 102/1 Radelkis Conductometer.

X-ray structure determination

Data collections were performed at 110 K with a Bruker Smart APEX CCD (Mo-K_α radiation, λ= 0.71073 Å, graphite monochromator) area detector. The unit cell parameters were obtained by the least-squares refinement of up to 8096 reflections. The structures were solved by direct methods (SHELXS-97) [14] and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL-97) [15]. The SADABS [16] program was used for absorption correction of the structures. Non-hydrogen atoms were refined anisotropically, and H atoms were introduced in their idealized positions (dC–H = 0.98 Å, dN–H = 0.95 Å) and were refined using a riding model. Some H atoms were located in a difference Fourier map and refined freely along with an isotropic displacement parameter.

Crystallographic data (excluding structure factors) for the structures reported in this paper (table 1) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- 275223 $(LH_2)_2[MoOBr_4(OH_2)]Br_3$). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: int. code + (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk; web, www: http://www.ccdc.cam.ac.uk).

Results and discussions

According to the literature data, in acidic medium (HBr 9M), MoO_3 is reduced to monomeric Mo(V) species, $[MoOBr_4]^-$, $[MoOBr_5]^{2-}$ and $[MoOBr_4(OH_2)]^-$. The equilibrium is modified in the presence of small amounts of water and at pH > 7, the dominant species resulted being the dimers $[Mo_2O_2(OH)_4Br_4]^{2-}$, $[Mo_2O_3Br_8]^{4-}$, $[Mo_2O_4Br_4\ (H_2O)_2]^{2-}$ or $[Mo_2O_4Br_2(H_2O)_4]$.

The monomeric species **1-2**, $(LH_2)_2[MoOBr_4(OH_2)]Br_3$ have been obtained as yellow-green (**1**) or green-brown (**2**) powders from acidic solutions of $[MoOBr_4(OH_2)]^-$ (pH < 1) by adding *s*- triazine derivatives (2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2-pyridyl)-triazine, L^2). The ligands act as diprotonated bases, as results from X-ray diffraction spectrum of $(L^1H_2)_2[MoOBr_4(OH_2)]Br_3$ where L^1 was 2,4,6-triamine-[1,3,5]-triazine.

The $[Mo_2O_4Br_2(OH_2)_2L_2]$ dimmers (**3, 4**), where L = 2,4,6-triamine-[1,3,5]-triazine, **L¹** and 2,4,6-tri(2-pyridyl)-triazine, **L²** were obtained from the mixture of hydrobromic solutions (9M) of monomers $(LH_2)_2[MoOBr_4(OH_2)]Br_3$ and ammonia – water solution (2M) at pH = 8. By evaporation of these mixed solutions, brown powders of the dimeric compounds **3-4** have been obtained:

$[Mo_2O_4Br_2(OH_2)_2L^1_2]$ **3**
$[Mo_2O_4Br_4(OH_2)_2\ L^2_2]$ **4**

The general proposed formulae of $(LH_2)_2[Mo\ OBr_4(OH_2)]Br_3$, monomers **1, 2** and $[MoOBr_2(OH_2)_2L_2]$, dimmers **3, 4** were obtained by elemental chemical analysis, molar electrical conductivities, electronic, infrared and RPE spectra. For $(L^1H_2)_2[MoOBr_4(OH_2)]Br_3$, **1** the structure was established based on the X-ray spectrum.

Molar electrical conductivity

The compounds **1** and **2** are electrolytes and the organic groups are located out of coordination sphere as diprotonated species and the protons are bonded at two cyclic nitrogen atoms, perhaps the atoms with the highest electron density as result from X-ray spectrum of $(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$, **1**. The compounds **3** and **4** are nonelectrolytes, and the organic ligands L^1 and L^2 act as monodentate ligands bonded to molybdenum atoms by nitrogen atoms (table 2).

Table 2
ELEMENTAL CHEMICAL
ANALYSES AND MOLAR
ELECTRICAL
CONDUCTIVITIES

Compound/		%Mo		%N		%Br		*Molar conductivity*
		calcd	*found*	*calcd*	*found*	*calcd*	*found*	*µS cm⁻¹mol⁻¹*
1	$(L^1H_2)_2[MoOBr_4(OH_2)]Br_3$	10.74	11.50	17.76	16.98	59.17	58.92	> 260
2	$(L^2H_2)_2[MoOBr_4(OH_2)]Br_3$	7.25	7.88	12.68	11.92	42.26	41.86	> 260
3	$[Mo_2O_4Br_2(OH_2)_2L^1_2]$	27.26	27.52	23.87	24.57	22.70	23.14	32
4	$[Mo_2O_4Br_2(OH_2)_2L^2_2]$ /	17.73	16.98	15.52	14.95	14.77	15.11	35

Table 3
ELECTRONIC SPECTRA OF THE COMPOUNDS **1-4**

Compound		$^2B_2 \rightarrow {}^2E_1$ λ(nm) ν(cm)	$^2B_2 \rightarrow {}^2B_1$ λ(nm) ν(cm)
1	$(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$	430 23250	704 14205
2	$(L^2H_2)_2[MoOBr_4(H_2O)]Br_3$	420 23810	696 14368
3	$[Mo_2O_4Br_2(OH_2)_2L^1_2]$	430 23250	680 14706
4	$[Mo_2O_4Br_2(OH_2)_2L^2_2]$	400 25000	620 16129
5	$BipyH_2[MoOBr_5]$	470 21000	720 14400

Table 4
CHARACTERISTIC IR BANDS FOR L^1, L^2 AND **1-4** COMPLEX COMPOUNDS

	γNH_2 cm^{-1}	MoO_2Mo cm^{-1}	$\nu_{Mo=O}$ cm^{-1}	ρNH_2 cm^{-1}	δ_{NH2}, $\delta_{H\text{-}OH}$ cm^{-1}	ν_{NH}, $\nu_{NH2s,as}$ $\delta_{H\text{-}OH}$ cm^{-1}	$\delta_{C=N,cicle}$ cm^{-1}	ν_{MoN} cm^{-1}
L^1	630	-		1200	1600	3230	1030 1400	-
$(L^1H_2)_2[MoOBr_4(OH_2)]Br_3$ **1**	640	-	990	1180	1550	3200	1025 1380	-
$[Mo_2O_4Br_2(OH_2)_2L^1_2]$ **3**	635	625 760	985	1185		3185	1030 1400	450
L^2	-	-		-	1610	33240	1050 1400	-
$(L^2H_2)_2[MoOBr_4(OH_2)]Br_3$ **2**	-	-	980	-	1580	3220	1050 1425	-
$[Mo_2O_4Br_2(OH_2)_2L^2_2]$ **4**	-	620 760	9980	-	1580	3200	1050 1420	440

The nature of organic groups L^1 and L^2 is strongly influenced by the *p*H of synthesis medium: *p*H < 1 for the compounds **1**, **2** and *p*H > 8 in the case of compounds **3** and **4**.

The electronic spectra of all **1-4** compounds exhibit d-d transitions specific for $Mo^{5+}(d^1)$;

$$^2B_2 \rightarrow {}^2B_1\ (d_{x^2-y^2}\ d_{xy}) \approx 23000\ cm^{-1}$$
$$^2B_2 \rightarrow {}^2E_1\ (d_{x^2-y^2}\ d_{xz,}\ d_{yz,}) \approx 15000\ cm^{-1}$$

The position and shape of the absorption bands (Table 3) are specific for Mo(V) coordination species (the absorption bands of $BipyH_2[MoOBr_5]$ were included) and confirm the distorted octahedral geometry for all the **1 – 4** complex compounds [17].

The vibrational infrared spectra of the **1-4** complex compounds were used in order to supply additional data on their stereochemistry, particularly on the coordination manner of the s-triazine derivatives, L^1 and L^2 (table 4).

A comparative examination of the presented data suggests several conclusions.

The L^1 and L^2 s-triazine derivatives act as protonated ligands in the compounds **1** and **2**.

This results from the shifting of the N-H or C=N specific bands (ν_{NH}, ρ_{NH2}, δ_{NH2}, $\delta_{C=N\ cycle}$) toward smaller frequencies and the presence of new bands in the 2350 cm^{-1} range assigned to stretching frequencies $\nu_{NH}{}^+$. For the **3** and **4** dimmers the shifting of the N-H or C=N specific bands (ν_{NH}, ρ_{NH2}, δ_{NH2}, $\delta_{C=N\ cycle}$) is associated with the formation of coordinative bonds Mo-N, supported also by the presence of new band, ν_{MoN} in the 450 cm^{-1} range.

The presence of the strong absorption bands in 990-1010 cm^{-1} range was assigned to stretching frequencies $\nu_{Mo=O}$ specific for molybdenum-oxygen terminal group which exist in all the compounds **1-4.**

For the compounds **3** and **4** the bands from 760 cm^{-1} and 620 - 640 cm^{-1} were assigned to double bridge MoO_2Mo and confirm the dimeric nature of these complex compounds.

The presence of coordination H_2O is supported by some additional bands in 1600 cm^{-1} and 3000-3500 cm^{-1} ranges (δ_{H2O} and ν_{OH}) but these are superposed with δNH_2 and ν_{NH} specific vibrational bands for **1** and **3** [18].

The EPR spectra of complex compounds **1** and **2** have relatively identical shapes and RPE parameters (table 5) prove the distorted octahedral geometry, with $g_{||} > g_{\perp}$. The absence of RPE signals for the compounds **3** and **4** suggests their dinuclear structure.

The complex compound $(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$, **1** crystalizes in the centrosymmetric space group $P2_1/c$. The crystal structure consists in two diprotonated ligands, three

Table 5
EPR DATA FOR THE COMPOUNDS $(LH_2)_2[MoOBr_4(H_2O)]Br_3$

Complex compound	$g_{\|}$	$g_{\perp}$
$(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$	1.94	1.92
$(L^2H_2)_2[MoOBr_4(H_2O)]Br_3$	2.09	1.95

Table 6
SELECTED BOND LENGTHS (Å) AND ANGLES (°)
AROUND Mo1 IN $(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$
L^1 = 2,4,6-TRIAMINE-[1,3,5]-TRIAZINE (MELAMINE)

Mo(1)-O(2)	1.6564(7)
Mo(1)-O(1)	2.2978(7)
Mo(1)-Br(2)	2.5276(3)
Mo(1)-Br(3)	2.5381(4)
Mo(1)-Br(1)	2.5417(3)
Mo(1)-Br(4)	2.5591(3)
O(2)-Mo(1)-O(1)	179.46(3)
O(2)-Mo(1)-Br(2)	98.33(3)
O(1)-Mo(1)-Br(2)	82.11(2)
O(2)-Mo(1)-Br(3)	99.20(2)
O(1)-Mo(1)-Br(3)	81.111(17)
Br(2)-Mo(1)-Br(3)	88.655(6)
Br(2)-Mo(1)-Br(4)	165.621(5)
O(2)-Mo(1)-Br(1)	98.84(2)
O(1)-Mo(1)-Br(1)	80.832(18)
Br(2)-Mo(1)-Br(1)	90.185(9)
Br(3)-Mo(1)-Br(1)	161.894(5)
O(2)-Mo(1)-Br(4)	95.96(3)
O(1)-Mo(1)-Br(4)	83.61(2)
Br(3)-Mo(1)-Br(4)	87.470(6)
Br(1)-Mo(1)-Br(4)	89.214(8)

Br^- anions and a $[MoBr_4O(H_2O)]^-$ unit (fig. 2). Weak H bonds form an infinite three-dimensional framework around the neighbouring molecules. Selected bonds and angles around Mo atom are presented in table 6.

Conclusions

Four new complex compounds of Mo(V) with *s*-triazine derivatives (2,4,6-triamine-[1,3,5]-triazine, L^1 and 2,4,6-tri(2-pyridyl)-triazine L^2) as organic ligands have been obtained. The general proposed formula, $(LH_2)_2[MoOBr_4(OH_2)]Br_3$ for **1** and **2** monomers and $[Mo_2O_4Br_2(OH_2)_2L_2]$ for **3** and **4** dimmers were supported by elemental chemical analysis, molar electrical conductivities, UV-Vis, IR and EPR spectra. The structure of $(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$ was established by X-ray diffraction spectroscopy. In monomers **1** and **2** the organic groups are located out of coordination sphere as diprotonated species and the protons are bonded at two cyclic nitrogen atoms, as result from X-ray spectrum of $(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$, **1**. The compounds **3** and **4** have dimeric nature and the organic groups L^1 and L^2 act as neutral monodentate ligands, bonded to molybdenum atoms by nitrogen atoms. The EPR spectra of complex compounds **1** - **4** confirm their monomeric (for **1**, **2**) and dimeric (for **3** and **4**) nature. The spectral data (UV-Vis, IR and EPR) prove the distorted octahedral geometry for all compounds. The *s*-triazine derivatives, L^1 and L^2 act as protonated species in the compounds **1** and **2** and as neutral ligand for **3** and **4** and the nature of the organic groups L^1 and L^2 is strongly influenced by the *p*H of synthesis medium: *p*H < 1 for **1**, **2** and *p*H > 8 in the case of **3** and **4**.

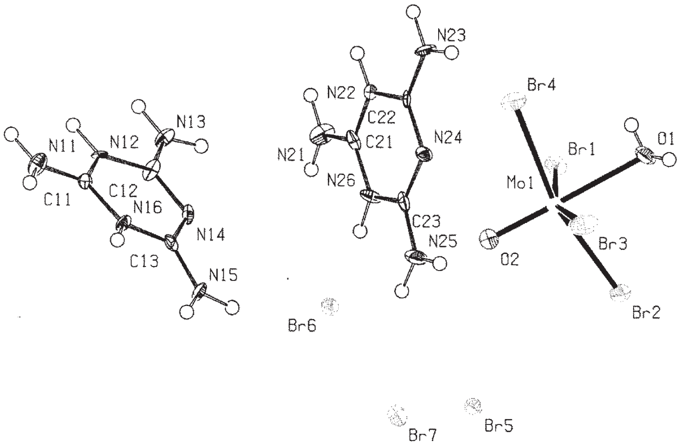


Fig.2. Displacement ellipsoids plot [19] (50%) of compound $(L^1H_2)_2[MoOBr_4(H_2O)]Br_3$, **1**.
The H atoms are shown with arbitrary radius.

Acknowledgements: The authors gratefully acknowledge Prof. Dr. Ulli Englert from RWTH Aachen University, Institute of Inorganic Chemistry, Group of Crystallography and Structural Chemistry, for the X-ray diffraction study.

References

1.MENDEL R., BITTNER B., Biochimica et Biophysica Acta **1763**, 2006, p. 621
2.LISNARD L., MIALANE P., DULBECK A., MARROT J., SECHERESSE F., Inorganic Chemistry Communications **6,** 2003, p. 503
3.GUPTA S., PAL S., BARIK A. K., ROY S., HAZRA A., MANDAL T. N., BUTCHER R., KAR K., Polyhedron **28**, 2009, p. 711
4.MATOGA D., SZLARZEWICKZ J., LEWINSKI K., Polyhedron **28**, 2010, p. 94
5.TOPALOGLU-SOZUER I., GUNYAR A., DULGER-IRDEM S., BAYA M., POLI R., Inorganica Chimica Acta **358,** 2005, p. 3303
6.TUNNEY J. M., MASTER J. M., GARNER C. D., Comprehensive Coord. Chem. Elsevier, Amsterdam, **8**, 2003, p.459
7.MORRIS M. J., Coordination Chemistry Reviews, **172**, 1998, p. 181
8. MORRIS M. J., Coordination Chemistry Reviews, **138**, 1995, p. 121
9.GHEORGHIU C., GURAN C., Rev. Chim. (Bucharesti), 35, nr. 12, 1984, p. 1085
10.GHEORGHIU C., GURAN C., MEGHEA A., Rev. Chim. (Bucharest), **33**, no. 8, 1982, p. 741
11.GHEORGHIU C., GURAN C., MEGHEA A., Revue Roum. Chim., 29(9-10), 1984, p. 747
12.MICU M., DINCULESCU M., Sci. Bull. UPB, Series B, **60** (1-2), 1998, p. 53
13. CHIVU H., CALMUSCHI-CULA B., STANICA N., MICU O., GURAN C., Rev. Chim. (Bucharest), **57**, no.7, 2006, p. 735
14.G. M. Sheldrick, SHELXS-97, Program for solution of crystal structures, University of Goettingen, Germany, 1997
15.G. M. Sheldrick, SHELXL-97. Program for refinement of crystal structures, University of Goettingen, Germany, 1997.
16.G. M. Sheldrick, **1996**, SADABS. University of Goettingen, Germany.
17.LEVER A. B. P., Inorganic Electronic Spectroscopy, Elsevier Publ. Comp. Amsterdam, London, New York, 1984
18.NAKAMOTO K., infrared Spectra of Inorganic and Coordination Compounds, Wiley Interscience, 1970
19.A. L. Spek, Acta Cryst., **1990**, A46, C-34

Manuscript received: 13.07.2010