A NOVEL PROTON TRANSFER COMPOUND (A NEW MOLYBDATE SALT) AND ITS X-RAY STRUCTURE

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ABSTRACT. A novel proton transfer compound $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl), derived from 2-amino-2-methyl-1-propanol and $MoO_2(acac)_2$, synthesized and characterized by ^1H NMR, X-ray diffraction analysis, UV-Vis and FT-IR spectroscopy. The single crystal X-ray diffraction analysis revealed that intra- and intermolecular proton transfer from (MoO_4H_2) to $(OHRNH_2)$ results in the formation of a new molybdate salt that its fragments are connected through H-bonding and ion-pairing as shown in the X-ray crystal structure. This salt crystallizes in the space group $P2_1/n$ P_1 of the monoclinic system, with four molecules per unit cell. The unit cell parameters are a = 13.6091(11) Å, b = 6.1049(5) Å, c = 17.0840(13) Å and β = 97.745(4)°.

KEY WORDS: Proton transfer, Molybdate salt, X-ray structure, $MoO_2(acac)_2$, 2-Amino-2-methyl-1-propanol

INTRODUCTION

The different aspects of proton transfer systems have been studied by chemists in the recent years [1-5]. An interesting report in this area was investigation of the mechanism of proton transfer from intra-molecularly hydrogen-bonded acids and differences between nitrogen-to-oxygen and nitrogen-to-nitrogen proton transfer [6, 7]. Whenever the hydrogen bonding associations result in complete proton transfer to the nitrogen atom, an ionic self-assembled compound is produced [8] and considerable stability upon structure-making process which can be used in designing of novel layered crystalline material is achieved [9, 10]. Here we report the synthesis, characterization, and X-ray crystal structures of a molybdenum compound as a new molybdate salt.

EXPERIMENTAL

Materials and instruments

All the chemicals were purchased from Merck Company, and were used as such. UU-Vis spectra were recorded on a Perkin Elmer Lambda25 in the range of 200-700 nm. FT-IR spectra obtained as potassium bromide pellets in the range of 400-4000 cm^{-1} with a Nicolet-Impact 400D spectrometer. NMR spectra were recorded on Bruker advance DPX 400 MHz instrument.

Syntheses of the proton transfer compound

This compound was synthesized by refluxing the solutions of equimolar quantities of $MoO_2(acac)_2$ with 2-amino-2-methyl-1-propanol in methanol as solvent. 1.0 mmol (0.3270 g) of $MoO_2(acac)_2$ in methanol was added to the boiling methanolic solution of 1.0 mmol (0.10 mL, 0.0891 g) of 2-amin0-2-methyl-1- propanol in a 25 mL two-necked flask and reflux for 4 h and then left to stand (Scheme 1). The suitable yellow crystals (block, colourless) for X-ray analysis were obtained after two weeks. M.p. = 234 °C (with decomposition).

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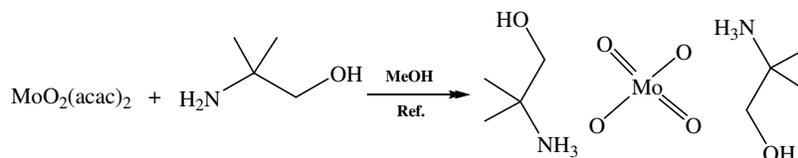
Scheme 1. The synthetic scheme for the preparation of $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) compound.

X-ray structure analysis

Data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* (Bruker, 2009); data reduction: *APEX2* (Bruker, 2009); program(s) [11] used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) [12]. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of F2 > 2sigma (F^2) is used only for calculating R-factors (gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger. Selected crystals were mounted on a Bruker APEX-II CCD diffractometer with an APEX CCD area detector. A graphite-monochromatic Mo-Kα radiation (0.71073 Å) was used for all measurements. The nominal crystal-to-detector distance was 5.00 cm. A hemisphere of data was collected by a combination of three sets of exposures at *T* = 93 K. The structure was solved by direct methods (SHELXS97) [17]. Refinement was carried out with the full-matrix least-squares method based on F2 (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms. The numbering scheme, ORTEP, of compound is shown in Figure 1, and its packing is shown in Figure 2. A summary of crystallographic data and selected bond lengths and angles are reported in Tables 1, respectively. Hydrogen atoms were inserted in calculated positions and refined riding with the corresponding atom. Further crystallographic data of the measurements are listed in Table 1. Some selected bond lengths (Å) and angles (°) for this structure were shown in Table 2. Some selected bond angles (Å) and bond lengths (°) for this compound are shown in Table 3.
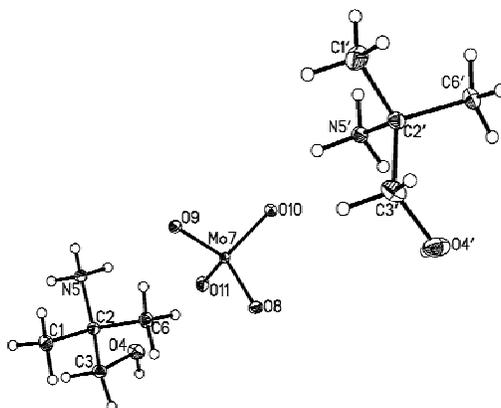
Figure 1. Molecular structure and atomic numbering for $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) as a new molybdate salt (displacement ellipsoids are drawn at the 50% probability level).
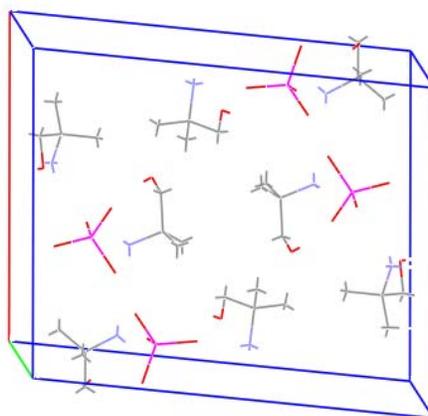

Figure 2. The crystal packing viewed along the b axis for$(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) as a new molybdate salt.

Table 1. Crystallographic data of $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) as a new molybdate salt.

$2(C_4H_{12}NO)\cdot MoO_4$	$F(000) = 704$
$M_r = 340.23$	$D_x = 1.607$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo K_α radiation, $\lambda = 0.71073$ Å
Hall symbol: -P2yn	Cell parameters from 9824 reflections
$a = 13.6091$ (11) Å	$\theta = 2.4$–$36.2°$
$b = 6.1049$ (5) Å	$\mu = 0.95$ mm^{-1}
$c = 17.0840$ (13) Å	$T = 93$ K
$\beta = 97.745$ (4)°	Block, colourless
$V = 1406.43$ (19) Å^3	$0.58 \times 0.24 \times 0.14$ mm
Z	4

Data collection	
Bruker APEX-II CCD diffractometer	6756 independent reflections
Radiation source: fine-focus sealed tube	6034 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.030$
φ and ω scans	$\theta_{max} = 36.4°$, $\theta_{min} = 2.4°$
Absorption correction: multi-scan *SADABS* (Bruker, 2009)	$h = -22 \rightarrow 22$
$T_{min} = 0.609$, $T_{max} = 0.879$	$k = -10 \rightarrow 10$
45132 measured reflections	$l = -28 \rightarrow 28$
Refinement	
Refinement on F^2	Primary atom site location: structure-invariant direct methods
$R[F^2 > 2\sigma(F^2)] = 0.021$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.054$	H-atom parameters constrained
$S = 1.06$	$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2 + 0.5911P]$ where $P = (F_o^2 + 2F_c^2)/3$
6756 reflections	$(\Delta/\sigma)_{max} = 0.002$
160 parameters	$\Delta\rangle_{max} = 0.65$ e Å^{-3}
0 restraints	$\Delta\rangle_{min} = -0.93$ e Å^{-3}

Table 2. Selected bond angles (Å) and bond angles (°) for $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) as a new molybdate salt.

Bond length (Å)			
C1—C2	1.5253 (15)	Mo7—O8	1.7695 (8)
C1—H1A	0.9800	Mo7—O10	1.7731 (8)
C1—H1B	0.9800	C1'—C2'	1.5222 (15)
C1—H1C	0.9800	C1'—H1'1	0.9800
C2—N5	1.5057 (13)	C1'—H1'2	0.9800
C2—C6	1.5245 (14)	C1'—H1'3	0.9800
C2—C3	1.5259 (14)	C2'—N5'	1.5063 (13)
C3—O4	1.4199 (13)	C2'—C6'	1.5212 (15)
C3—H3A	0.9900	C2'—C3'	1.5285 (16)
C3—H3B	0.9900	C3'—O4'	1.4129 (15)
O4—H4	0.8400	C3'—H3'1	0.9900
N5—H5A	0.9100	C3'—H3'2	0.9900
N5—H5B	0.9100	O4'—H4'	0.8400
N5—H5C	0.9100	N5'—H5'1	0.9100
C6—H6A	0.9800	N5'—H5'2	0.9100
C6—H6B	0.9800	N5'—H5'3	0.9100
C6—H6C	0.9800	C6'—H6'1	0.9800
Mo7—O11	1.7594 (8)	C6'—H6'2	0.9800
Mo7—O9	1.7645 (8)	C6'—H6'3	0.9800
Bond angle (°)			
C2—C1—H1A	109.5	O11—Mo7—O10	110.18 (4)
C2—C1—H1B	109.5	O9—Mo7—O10	108.07 (4)
H1A—C1—H1B	109.5	O8—Mo7—O10	106.85 (4)
C2—C1—H1C	109.5	C2'—C1'—H1'1	109.5
H1A—C1—H1C	109.5	C2'—C1'—H1'2	109.5
H1B—C1—H1C	109.5	H1'1—C1'—H1'2	109.5
N5—C2—C6	108.27 (8)	C2'—C1'—H1'3	109.5

RESULTS AND DISCUSSION

FT- IR studies

The IR spectra of this compound in KBr matrix confirm the presence OH group as a broad band at 2600-3400 cm^{-1} which is assigned to the intramolecular H-binding vibration (O−H⋯N) [13, 14]. The bands related to N-H stretching vibrations at 3197 cm^{-1}, the aliphatic C-H vibrations are observed at 2584-2875 cm^{-1}. The Mo=O bands are exhibited at 1084 and 1053 cm^{-1} in this compound [15-18] (Figure 3).
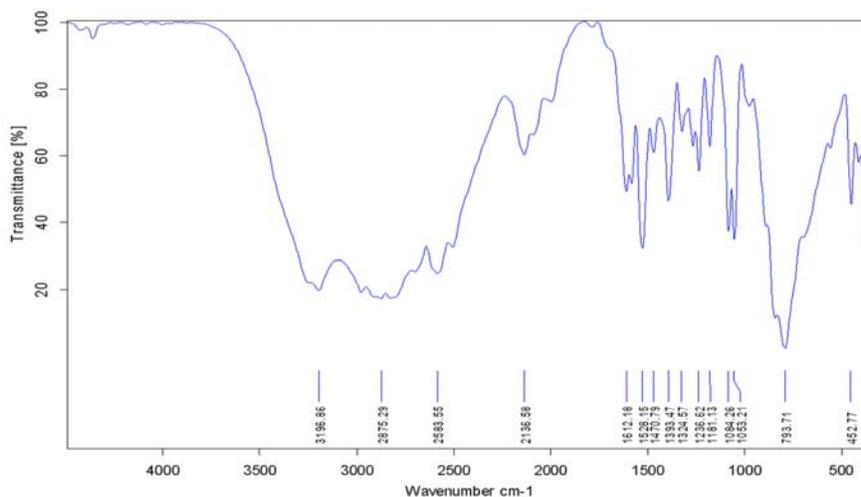

Figure 3. FT-IR spectra of $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) as a new molybdate salt.

UV- Vis studies

In order to studying more about the proton transfer compound, the electronic spectra of the components was recorded in methanol as solvent. Mo(VI) and 2- amino-2-methyl-1-propanol show maximum absorbance at 212 and 224 nm, respectively, while the resulting proton transfer compound shows three maxima at 214, 280 and 400 nm. The appearance of a new peak and at larger wavelength is due to the proton transfer from the diacid to the amine and the consequent interaction of the resulting oppositely charged species [19, 20].

^{1}H NMR studies

The ^{1}H NMR spectrum of the proton transfer compound shows the presence of a sharp singlet at 3.16 ppm (s, 1H) which is rationalized to the O−H proton. Two signals that are recorded at 1.17 ppm (s, 3H) and 3.60 ppm (s, 2H) in PTC refer to and CH_3 and CH_2 protons, respectively. The signals related to N−H protons appear at 3.30 ppm (s, 2H) and 3.78 ppm (s, 1H) (Figure 4).
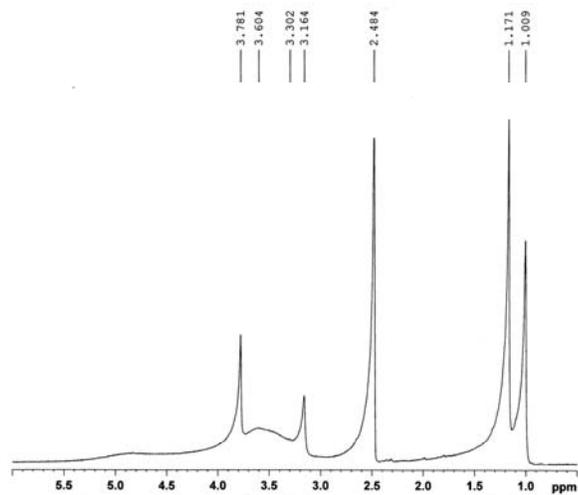
Figure 4. ^{1}H NMR spectra of $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) as a new molybdate salt.

Structural analysis

The molecular structure of the molybdenum salt crystal (Figure 1) consists of discrete $(MoO_4)^{-2}$ anion and 2 $(HORNH3)^{+1}$ cations. Anion is mononuclear. Table lists selected bond distances and angles. In the anion, the metal cation Mo^{VI} is coordinated to four oxygen anions. The Mo cation has a distorted geometry. The bond angles O_{11}-Mo_7-O_{10} (110.18^o), O_9-Mo_7-O_{10} (108.07^o), O_8-Mo_7-O_{10} (106.85^o), and the bond distances Mo_7-O_8 (1.7695 Å), Mo_7-O_{10} (1.7731 Å), Mo_7-O_{11} (1.7594 Å) and Mo_7-O_9 (1.7645 Å). Cations are linked by hydrogen bonding to the anions (see Figures 5, 6 and Table 3).
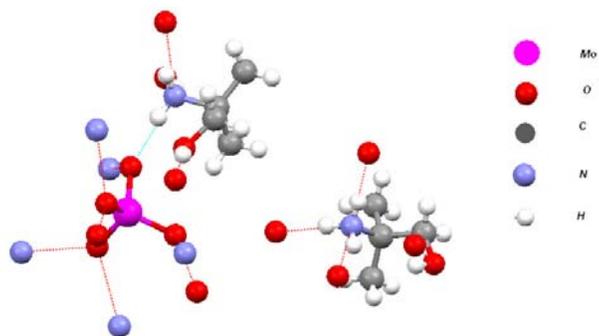

Figure 5. The hydrogen bonding in the structure of $OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) as a new molybdate salt and the cohesion between the different groups is maintained by a three dimensional network of hydrogen bonds.
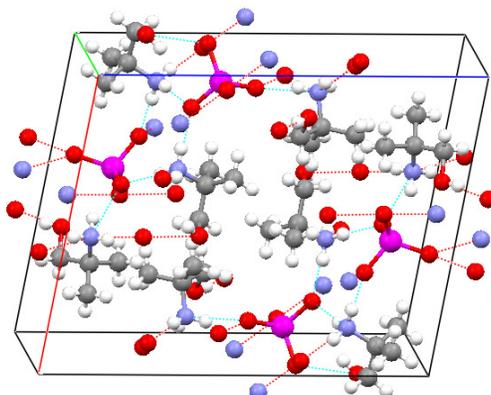
Figure 6. The crystal packing and the hydrogen bonding in the structure of $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) crystalline molybdate salt.

Table 3. The hydrogen-bond geometry (Å, °) of $(OHRNH_3)_2^{2+}(MoO_4)^{2-}$ (R = 2-methyl-1-propyl) crystalline as a new molybdate salt.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O4−H4···O11[i]	0.84	1.90	2.7286 (11)	168
N5−H5A···O8[ii]	0.91	1.89	2.7917 (12)	168
N5−H5B···O11[iii]	0.91	1.99	2.8623 (12)	160
N5−H5C···O9	0.91	2.06	2.8780 (12)	149
O4′−H4′···O8[iv]	0.84	2.07	2.6978 (12)	131
N5′−H5′1···O10[v]	0.91	1.85	2.7553 (12)	172
N5′−H5′2···O9[vi]	0.91	1.91	2.8181 (12)	172
N5′−H5′3···O10[iv]	0.91	1.92	2.7867 (12)	158

Symmetry codes: (i) -x+1, -y+2, -z; (ii) x, y-1, z; (iii) -x+1, -y+1, -z; (iv) x+1/2, -y+3/2, z+1/2; (v) -x+1, -y+1, -z+1; (vi) x+1/2, -y+1/2, z+1/2.

CONCLUSION

In summary, this article presents the synthesis and X-ray structure of a new molybdate salt as a single crystal. We have demonstrated that the proton transfer compound can be used as an appropriate starting material to synthesize a variety of interesting molybdenum compound or a molybdate salt, showing different complexation behavior of this proton transfer system as discussed previously.

Supplementary data

Crystallography data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 893992. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk

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