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Research Article

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Synthesis and spectroscopic studies of two novel proton transfer compounds containing $(MoO_4)^{2-}$ ion

Mahdeyeh Ghazizadeh[1,2], Iran Sheikhshoai[1,2*] and A. Badiei[3]

[1]Chemistry Department, Shahid Bahonar University of Kerman, Iran
[2]International Center for Science, High Technology & Environmental Sciences, Kerman, Iran
[3]School of Chemistry, University College of Science, University of Tehran, Iran

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ABSTRACT

By using MoO_2 $(acac)_2$ and OHR_1NH_2 or OHR_2NH_2 (where R_1=2-amino-1-butanol and R_2= 3-amino-1-propanol), two novel proton transfer compounds $(OHR_1NH_3)_2{}^{2+}(MoO_4)^{2-}$ and $(OHR_2NH_3)_2{}^{2+}(MoO_4)^{2-}$ were synthesized. In order to studying more about the proton transfer compounds, the electronic spectra, infrared spectra and NMR spectra of the components were recorded. The evidence gives this theory that intra- and intermolecular proton transfer from (MoO_4H_2) to (OHR_1NH_2) or (OHR_2NH_2) results in the formation of a cocrystal that its fragments are connected through H-bonding and ion-pairing.

Keywords: Proton transfer, Molybdenum, Hydrogen bond, $(MoO_4)^{2-}$ ion.

INTRODUCTION

Hydrogen bonds play a key role in a large number of chemical and biological processes [1, 2]. Hydrogen bonding is one of the several types of non-covalent interactions in many organic and inorganic species, which results in aggregation and controls self-assembly, in some cases [3-6]. The interactions among hydrogen bonds contribute significantly to the structural feature and the stability of molecules [7, 8]. A proton transfer compound involves reversible intramolecular proton transfer from an oxygen atom to the neighboring nitrogen atom [9-11]. The proton transfer have attracted increased interest over the last years, because it has led to a wide range of application[12], such as laser dyes [13], polymer stabilizer, Raman filters [14], environmental probes in bio-molecules, etc. The proton transfer interactions have been also utilized for the estimation of different pharmaceuticals [15]. They can be used in the field of drug acceptor binding mechanism [16]. The proton transfer complexes were reported due to their antimicrobial activities [17, 18]. The interaction studies between drug and DNA is one of the most important aspects in biological investigations aimed at discovering and developing new type of antiproliferative agents [19, 20].

EXPERIMENTAL SECTION

2.1. Materials and physical measurements

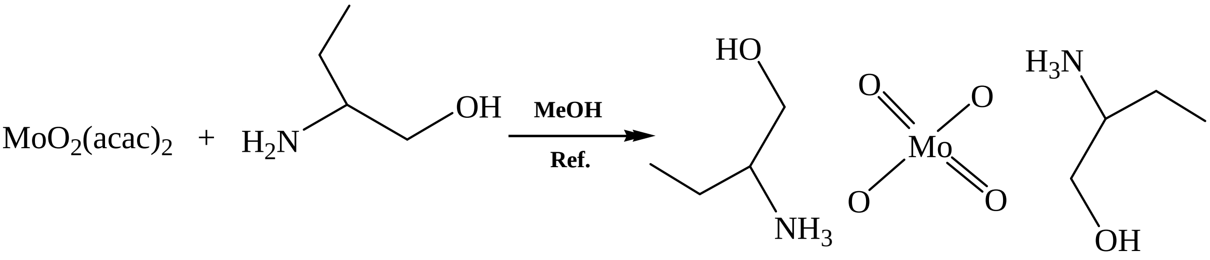
All the materials were prepared from Merck Co. and were used as such. Infrared spectra obtained as potassium bromide pellets in the range 400-4000 cm^{-1} with a Nicolet-Impact 400D spectrometer. Electronic spectra were recorded on a PerkinElmer Lambda25 in the range of 200-700 nm. NMR spectra were recorded on Bruker advance DPX 400 MHz instrument.

2.2. Syntheses of the proton transfer compounds

$(OHR_1NH_3)_2^{2+}(MoO_4)^{2-}$ and $(OHR_2NH_3)_2^{2+}(MoO_4)^{2-}$ compounds were synthesized by refluxing the solutions of equimolar quantities of $MoO_2(acac)_2$ with OHR_1NH_2 or OHR_2NH_2 in methanol as solvent. The mixture was refluxed for 4h and then left to stand. After that the product was collected, washed in small portion of methanol and dried under air condition.

2.2.1. Synthesis of (MoO_4) $(H_3NC_4H_8OH)_2$

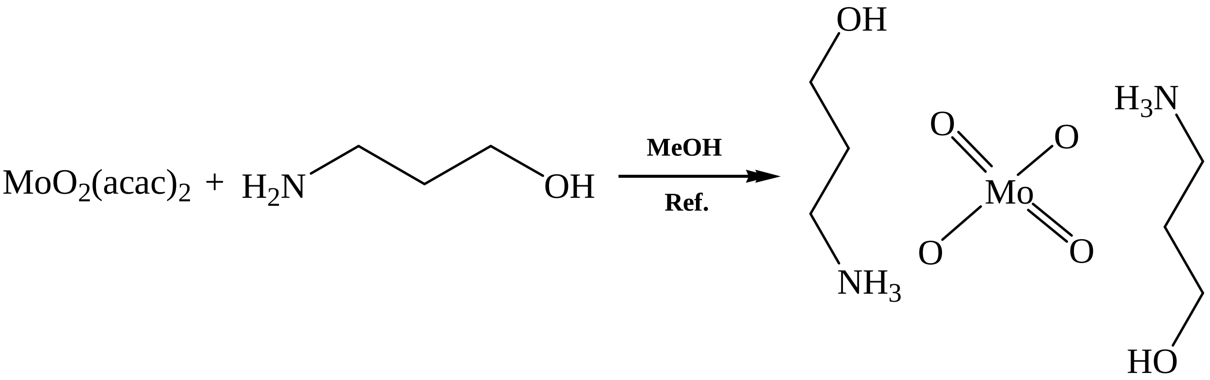
1.0 mmol (0.3270 g) of $MoO_2(acac)_2$ in methanol was added to the boiling methanolic solution of 1.0 mmol (0.10 mL, 0.0891 g) of 2- amino-1-butanol in a 25 mL two-necked flask and reflux for 4h and then left to stand[Scheme 1]. The dark white precipitate filtered and washed in small portion of methanol and dried under air condition. The product was decomposed at 150°C.



Scheme 1. Preparation of (MoO_4) $(H_3NC_4H_8OH)_2$

2.2.2. Synthesis of (MoO_4) $(H_3NC_3H_6OH)_2$

1.0 mmol (0.3270 g) of $MoO_2(acac)_2$ in methanol was added to the boiling methanolic solution of 1.0 mmol (0.08 mL, 0.0751 g) of 3- amino-1-propanol in a 25 mL two-necked flask and reflux for 4h and then left to stand[Scheme 2]. The dark white precipitate filtered, washed in small portion of methanol and dried under air condition. The product was decomposed at 196°C.

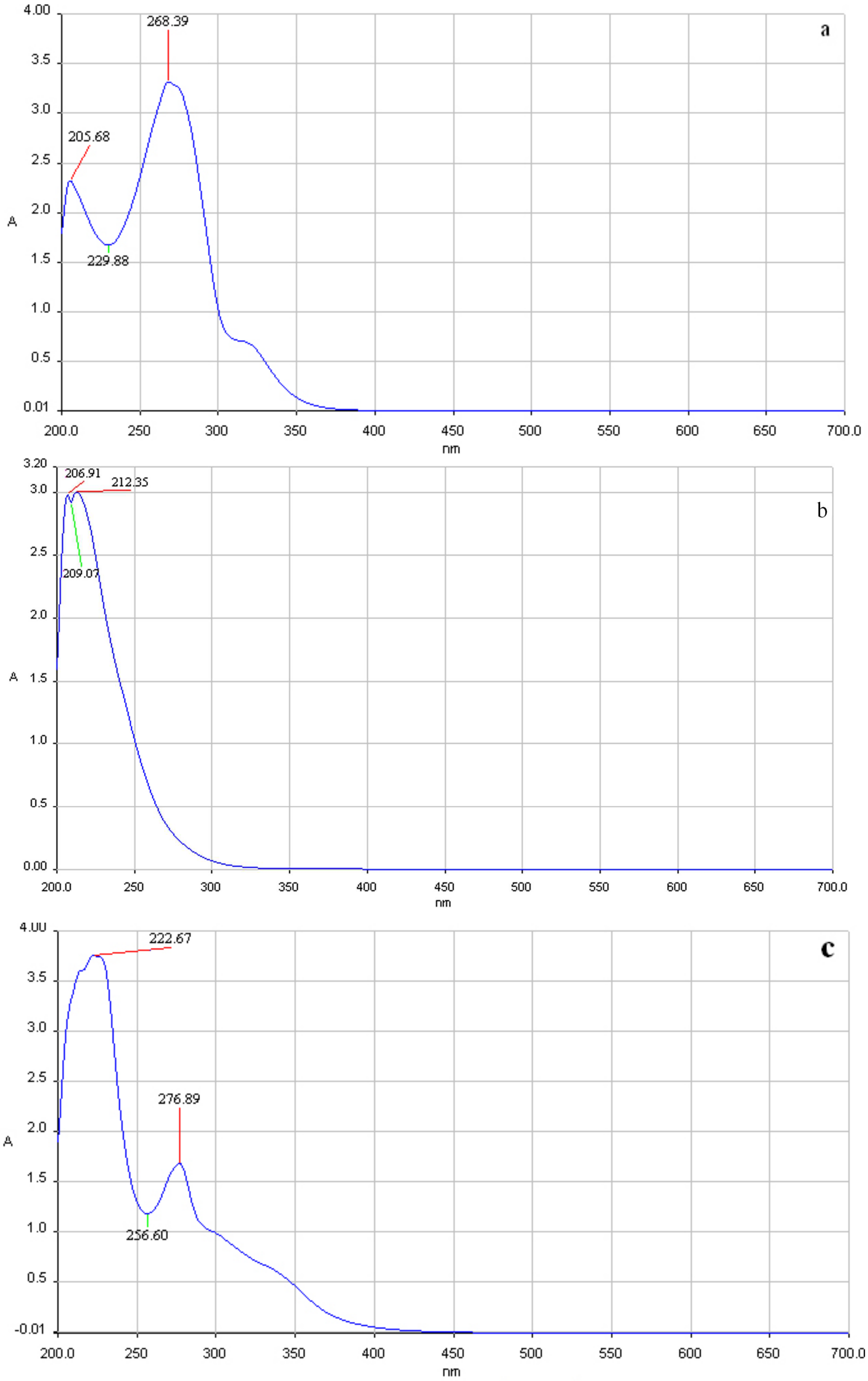


Scheme 2. Preparation of (MoO_4) $(H_3NC_3H_6OH)_2$

RESULTS AND DISCUSSION

3.1. Electronic spectra

The UV- Vis spectra (>200 nm) of the components were recorded in methanol as solvent. Mo(VI), 2-amino-1-butanol and 3-amino-1-propanol show maximum absorbances at 212, 223 and 230 nm, respectively, while the resulting proton transfer compound $\{(MoO_4)(H_3NC_4H_8OH)_2\}$ shows two maxima at 206 and 309 nm and the other one $\{(MoO_4)(H_3NC_3H_6OH)_2\}$ shows a maximum at 213 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 [21][Fig. 1].


a
4.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.01
A
268.39
205.68
229.88
200.0
250
300
350
400
450
500
550
600
650
700.0
nm
b
3.20
3.0
2.5
2.0
1.5
1.0
0.5
0.00
A
206.91
212.35
209.07
200.0
250
300
350
400
450
500
550
600
650
700.0
nm
c
4.00
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.01
A
222.67
276.89
256.60
200.0
250
300
350
400
450
500
550
600
650
700.0
nm

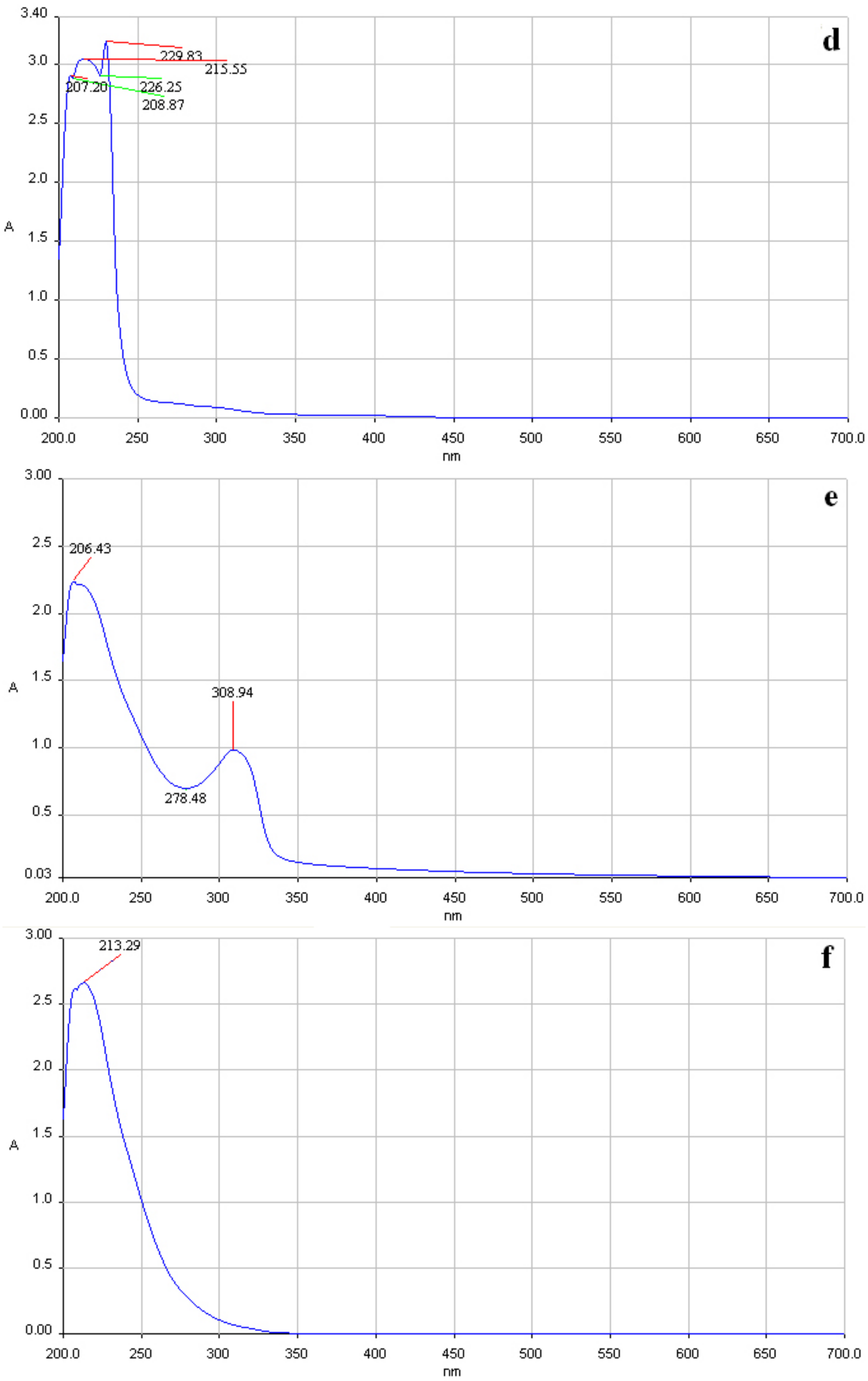
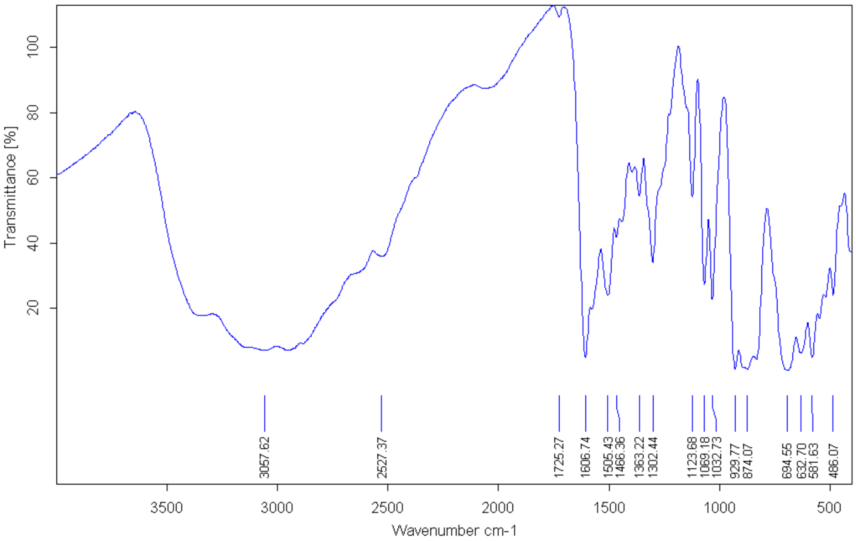


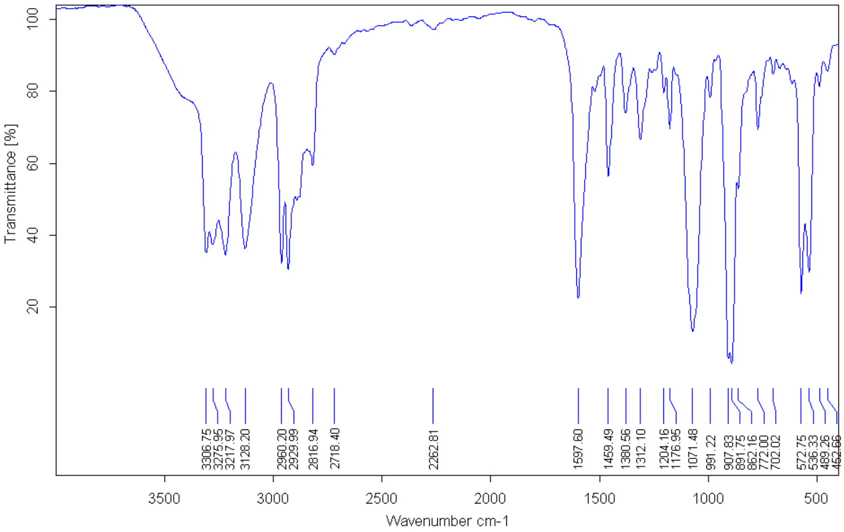
Fig. 1. UV-Vis spectra of a) MoO_2 (acac)$_2$, b) H_2MoO_4, c) $C_4H_{12}NO$, d) $C_3H_{10}NO$ e) (MoO_4) $(H_3NC_4H_8OH)_2$ and f) $(MoO_4)(H_3NC_3H_6OH)_2$

3.2. Infrared spectra

The IR spectra of the proton transfer compounds {$(MoO_4)(H_3NC_4H_8OH)_2$ and $(MoO_4)(H_3NC_3H_6OH)_2$}exhibit a broad band characteristic of the OH group at 2300-3400 cm^{-1} and 2800-3500 cm^{-1}, respectively, which are assigned to the intramolecular H-binding vibration (O—H$^{\cdots}$N) [22,23]. The bands related to C-H aliphatic vibrations are observed at 2527-3000 cm^{-1} in (MoO_4) $(H_3NC_4H_8OH)_2$ and 2718-2960 cm^{-1} in $(MoO_4)(H_3NC_3H_6OH)_2$. The Mo=O bands are exhibited at 1033 and 1069 cm^{-1} in (MoO_4) $(H_3NC_4H_8OH)_2$ and at 1177 and 1204 cm^{-1} in $(MoO_4)(H_3NC_3H_6OH)_2$ [24-27], see Scheme 3 and Scheme 4.



Scheme 3. FT-IR spectrum of (MoO_4) $(H_3NC_4H_8OH)_2$



Scheme 4. FT-IR spectrum of $(MoO_4)(H_3NC_3H_6OH)_2$

3.3. NMR spectra

The ^1H NMR spectrum of the proton transfer compound, (MoO_4) $(H_3NC_4H_8OH)_2$, shows a sharp singlet band at 3.00 ppm (s, 1) which be rationalized to the O—H proton. The signal related to N—H protons appear at 3.47 ppm (s, 3). The signal that was recorded at 2.19 ppm (t, 3H) and 2.52 ppm (m, 2H) in PTC refer to and CH_3 and CH_2 protons, respectively.

The ^1H NMR spectrum of the proton transfer compound, $(MoO_4)(H_3NC_3H_6OH)_2$, shows a sharp singlet band at 3.35 ppm (s, 1) which be rationalized to the O—H proton. The signal related to N—H protons appear at 4.31 ppm (s, 3). The signal that was recorded at 3.71 and 2.93 ppm (t, 2) and 3.18 ppm (m, 2) in PTC refer to and tree CH_2 protons, respectively.

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