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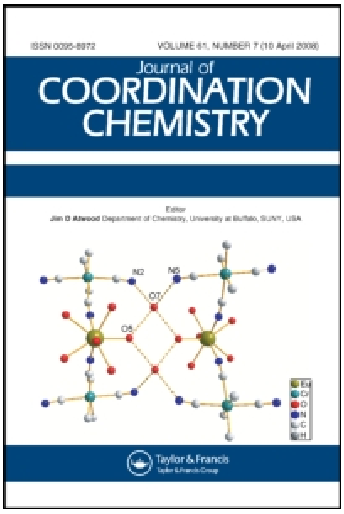

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Synthesis and characterization of solid molybdenum(VI) complexes with glycolic, mandelic and tartaric acids. Photochemistry behaviour of the glycolate molybdenum complex

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The complexes $(NH_4)_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$, $(NH_4)_2[MoO_2(C_8H_6O_3)_2]$ and $(NH_4)_2[MoO_3(C_4H_4O_6)] \cdot H_2O$ were prepared by reaction of MoO_3 with glycolic, mandelic and tartaric acids, respectively. The complexes were characterized by elemental and thermal analysis, IR spectroscopy and X-ray diffraction. Crystals of the glycolate and tartarate complexes are orthorhombic and the mandelate complex is monoclinic. Elemental and thermal analysis data showed that the glycolate and tartarate complexes are monohydrated. Hydration water is not present in the structure of the mandelate complex. IR spectra showed COO^- is involved in coordination as well as the oxygen atom of the deprotonated hydroxyl group of the α-carbon. The glycolate molybdenum complexes with general formula $M_2[MoO_2(C_2H_2O_3)_2] \cdot nH_2O$, where M is an alkali metal and $n = 1$ or ½, were also prepared and characterized. Aqueous solutions of the glycolate complex become blue and mandelate and tartarate complexes change to yellow or brown when exposed to UV-radiation.

Keywords: Molybdenum(VI); Glycolic; Mandelic; Tartaric; Photochemistry

1. Introduction

Interactions of metal species with α-hydroxycarboxylic acids and/or with the respective carboxylates have been extensively studied (refs. 1–5); several involve group VIB metals. Oxides or species containing Mo(VI) or W(VI) are among the most studied starting complexes since α-hydroxycarboxylic acids can solubilize the oxides when pH is increased. Complexes of Mo(VI) with a number of α-hydroxycarboxylic acids, like, tartaric, malic, lactic, citric, mandelic, glycolic and glyceric were described in solution, but only a few complexes have been isolated and characterized in the solid state [4, 6, 7]. Several manuscripts describe the equilibria in solution [8–10] and only a few describe structural features of the solid complexes [11–13]. Many advanced metal materials, including catalysts, have been obtained from metal complexes in which ligands can be an α-hydroxycarboxylic acid (see, for example, refs. 14 and 15). Studies on solubility of

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Nb_2O_5 in α-hydroxycarboxylic acids and photoreduction in aqueous solution under UV-radiation were carried out in our laboratories [16]. In the present article, syntheses and structural features of three solid ammonium complexes of Mo(VI), originally in the form of MoO_3, with the following α-hydroxycarboxylic acids: glycolic ($C_2H_4O_3$), mandelic ($C_8H_8O_3$) and tartaric ($C_4H_6O_6$) are described. Synthesis, characterization and photochemical behaviour of the glycolate molybdenum compounds with alkaline metals are also described. The crystal structure and biological relevance of $K_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$, potassium molybdenum glycolate, and $K_2[MoO_2(C_8H_6O_3)_2]$ potassium molybdenum mandelate were recently described [17, 18].

2. Experimental

2.1. *Preparation of the complexes*

The three complexes were easily obtained by the same procedure. A mass corresponding to 20.0 mmol of the α-hydroxycarboxylic acid was dissolved in 30.0 mL of distilled water and pH was adjusted to 5.0 with ammonia. For the molybdenum-glycolate complex with alkali metals pH was adjusted to 5.0 with hydroxide (Li^+, Na^+ or K^+) or carbonate (Rb^+ or Cs^+). The solution was heated at 60°C under stirring and 1.44g (10.0 mmol) of solid MoO_3 was added slowly (M : L molar ratio of 1 : 2) with stirring. After 3 h, at 60°C with stirring, complete dissolution of the oxide occurred. The volume of the solution was reduced until it became viscous and, then, it was cooled at room temperature. Ethanol or acetone (20.0 mL) was added for precipitation (ethanol for the tartaric and mandelic complexes and acetone for the glycolic complexes). White solid complexes were precipitated in good yields (about 90%). The three ammonium complexes are formulated as: $(NH_4)_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$, $(NH_4)_2[MoO_2(C_8H_6O_3)_2]$ and $(NH_4)_2[MoO_3(C_4H_4O_6)] \cdot H_2O$. The glycolate molybdenum complexes have the coordination formula $M_2[MoO_2(C_2H_2O_3)_2] \cdot nH_2O$, where $M = Li^+$, Na^+, K^+, Rb^+ or Cs^+ and $n = 1$ or ½.

2.2. *Reagents and equipments*

All reagents were analytical grade (Merck or Aldrich). The following equipment was used for elemental analysis and physical measurements: Elemental Analyser EA1110 CHNS-O CE Instruments (for C, H, N and O), Thermo Jarrell Ash Iris/AP Duo (for molybdenum), IR-Perkin Elmer – FTIR Spectrophotometer Spectrum 2000 (KBr disks), Thermoanalyser TF/DTA-SDT 2960 Simultaneous DTA-TGA, X-Ray Diffractometer Siemens D 5000, Perkin Elmer Lambda 14P for UV-Vis spectra and Bruker ESP300E for EPR spectra.

3. Results and discussion

3.1. *Elemental analysis*

Molybdenum was determined by atomic emission spectroscopy. Elemental analysis for oxygen gave values corresponding to the organic part of the complexes of tartaric and glycolic acids. The values *in parenthesis* correspond to the organic elemental oxygen of the complexes. The total percentages for elemental oxygen are in brackets. For mandelic acid elemental oxygen analysis is in an excellent agreement with the calculated value, probably due to a higher C content (41.4%) of this complex in comparison to the other two (both around 14%). $(NH_4)_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$: Anal. Calcd for $C_4H_{14}N_2O_9Mo$: C, 14.5; H, 4.24; N, 8.48; O, [43.6] and (29.1); Mo, 29.1. Found: C, 14.5; H, 4.32; N, 8.53; O, 29.1; Mo, 28.9%. $(NH_4)_2[MoO_2(C_8H_6O_3)_2]$: Anal. Calcd for $C_{16}H_{20}N_2O_8Mo$: C, 41.4; H, 4.31; N, 6.03; O, 27.6; Mo, 20.7. Found: C, 41.5; H, 4.32; N, 6.12; O, 28.5; Mo, 20.8%. $(NH_4)_2[MoO_3(C_4H_4O_6)] \cdot H_2O$: Anal. Calcd for $C_4H_{14}N_2O_{10}Mo$: C, 13.9; H, 4.05; N, 8.09; O, [46.2] and (27.7); Mo, 27.7. Found: C, 13.8; H, 4.02; N, 8.14; O, 26.3; Mo, 27.4%.

Glycolate molybdenum complexes with alkaline metals were analyzed by C and H elemental analysis. $Li_2[MoO_2(C_2H_2O_3)_2] \cdot \frac{1}{2}H_2O$, Anal. Calcd for $C_4H_5O_{8.5}Li_2Mo$: C, 16.1, and H, 1.68. Found: C, 16.5, and H, 1.62. $Na_2[MoO_2(C_2H_2O_3)_2] \cdot \frac{1}{2}H_2O$, Anal. Calcd for $C_4H_5O_{8.5}Na_2Mo$: C, 14.5 and H, 1.52. Found: C, 14.5 and H, 1.58. $K_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$, Anal. Calcd for $C_4H_6O_9K_2Mo$: C, 12.9 and H, 1.63. Found: C, 12.9 and H, 1.50. $Rb_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$, Anal. Calcd for $C_4H_6O_9Rb_2Mo$: C, 10.3 and H, 1.30. Found: C, 10.1 and H, 1.21. $Cs_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$, Anal. Calcd for $C_4H_6O_9Cs_2Mo$: C, 8.58 and H, 1.08. Found: C, 9.08 and H, 1.08.

3.2. *Thermal analysis*

The three ammonium complexes were analyzed by thermogrametric (TG) and differential thermal analysis (DTA) from 40 to 900°C, using an air flow rate of $10^\circ C\,min^{-1}$ and a synthetic air atmosphere (α-Al_2O_3 crucible). Figure 1 shows the TG and DTA curves for the glycolate complex, $(NH_4)_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$. At the beginning of heating a mass loss due to hydration water occurs in two steps, one at 95°C and the other at 180°C. This endothermic process is confirmed by the DTA curve. From 180 to 470°C total decomposition of the organic ligand occurs as observed in the DTA curve, with an intense exothermic peak at 466.2°C. After ligand decomposition only MoO_3 remains as the final residue, identified by X-ray analysis.

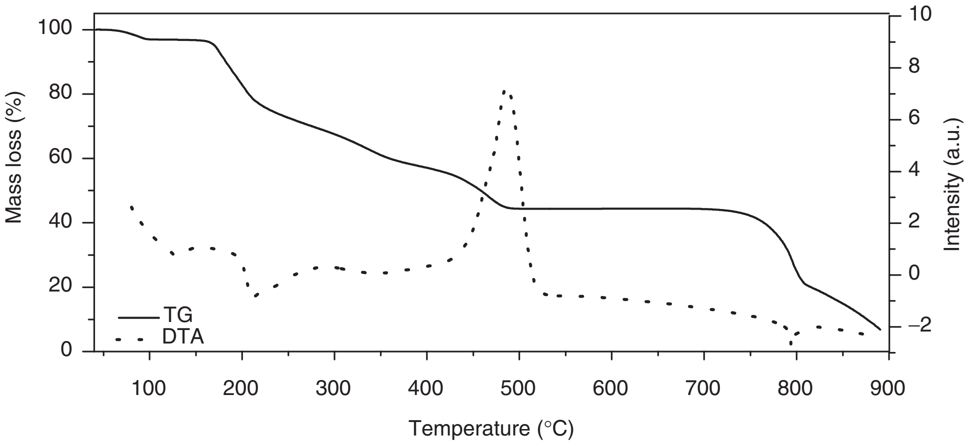

Figure 1. TG and DTA curves for the glycolate complex.

For $(NH_4)_2[MoO_2(C_8H_6O_3)_2]$ no mass loss was observed below 200°C. At 484.6°C complete decomposition of the organic ligand occurs. Above this temperature only MoO_3 exists. Water loss occurs at the beginning of heating for $(NH_4)_2[MoO_3(C_4H_4O_6)] \cdot H_2O$. The endothermic peaks occur, in this case, at 232.9 and 422.7°C.

Powder diffractograms of the residues of the thermogravimetric analysis show the final product of the thermal treatment is MoO_3 in the three cases. Crystal lattice parameters for the residues are in absolute agreement with the literature values for MoO_3 [19].

3.3. *X-ray diffractometry*

The X-ray diffraction powder diagrams were obtained from 4 to 70° with a graphite monochromator crystal and Cu-Kα radiation. Parameters of crystal lattice were determined using a set of programs, called AFPAR, which are based on least-squares approach. Glycolate and tartarate complexes belong to the orthorhombic crystalline system and the parameters are: $a = 16.00$ Å, $b = 5.93$ Å, $c = 21.05$ Å and $a = 15.02$ Å, $b = 5.93$ Å, $c = 13.48$ Å, respectively. The mandelate complex is monoclinic with the parameters: $a = 16.095$, $b = 11.47$, $c = 22.00$ Å and $\beta = 99.5°$.

The glycolate molybdenum complexes belong to the orthorhombic crystalline system. Parameters and volume of the cells and the corresponding ionic radii of the alkali metal are shown in table 1. The values of the cell volume increase with the ionic radii of the alkali metal (from 717.6 Å^3 for Li$^+$ to 2237 Å^3 for Cs$^+$)

3.4. *IR vibrational spectra*

IR spectra of the complexes were compared with the respective ammonium salt and the free α-hydroxycarboxylic acid. Figure 2 shows the IR spectra in the region 1800–700 cm^{-1} for mandelic acid (a), ammonium mandelate (b) and the mandelate complex (c). The other two sets of spectra (for glycolate and tartarate) are similar to the mandelate and are not shown here.

The main frequencies of the IR spectra show a strong and broad band in the spectra of the glycolic and tartaric complexes in the region 3450 to 3300 cm^{-1} assigned to the OH stretching vibration due to H_2O of the hydrated complexes. The main bands of each acid and the respective anion are observed in the spectra of the complex and the ligand is coordinated as the anion form (glycolate, mandelate or tartarate) since the strong band

Table 1. Ionic radii, parameter and volume of cells.

Compound	Ionic radii (Å)	Parameter cells (Å) *a*	*b*	*c*	Cell volumes (Å)^3
$Li_2[MoO_2(C_2H_2O_3)_2] \cdot ½H_2O$	0.60 (Li$^+$)	9.472	5.739	13.20	717.6
$Na_2[MoO_2(C_2H_2O_3)_2] \cdot ½H_2O$	0.95 (Na$^+$)	16.13	6.055	19.85	1939
$K_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$	1.33 (K$^+$)	16.13	6.095	20.32	1997
$Rb_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$	1.48 (Rb$^+$)	16.13	6.145	20.76	2058
$Cs_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$	1.69 (Cs$^+$)	15.24	7.244	20.26	2237

at ~1700 cm^{-1} assigned to the carbonyl of the COOH group was not observed in the spectra of the salts and complexes. The COO$^-$ group is involved in coordination to the metal, since the frequencies ν_{asym}(COO$^-$) and ν_{sym}(COO$^-$) changed after complexation. The differences ($\Delta\nu$) between ν_{asym}(COO$^-$) and ν_{sym}(COO$^-$) for the three complexes are around 230 cm^{-1}. This value is higher than those of the salts (from 180 to 195 cm^{-1}), which suggests COO$^-$ is monodentate [20, 21]. The band related to ν(H_2O) bending

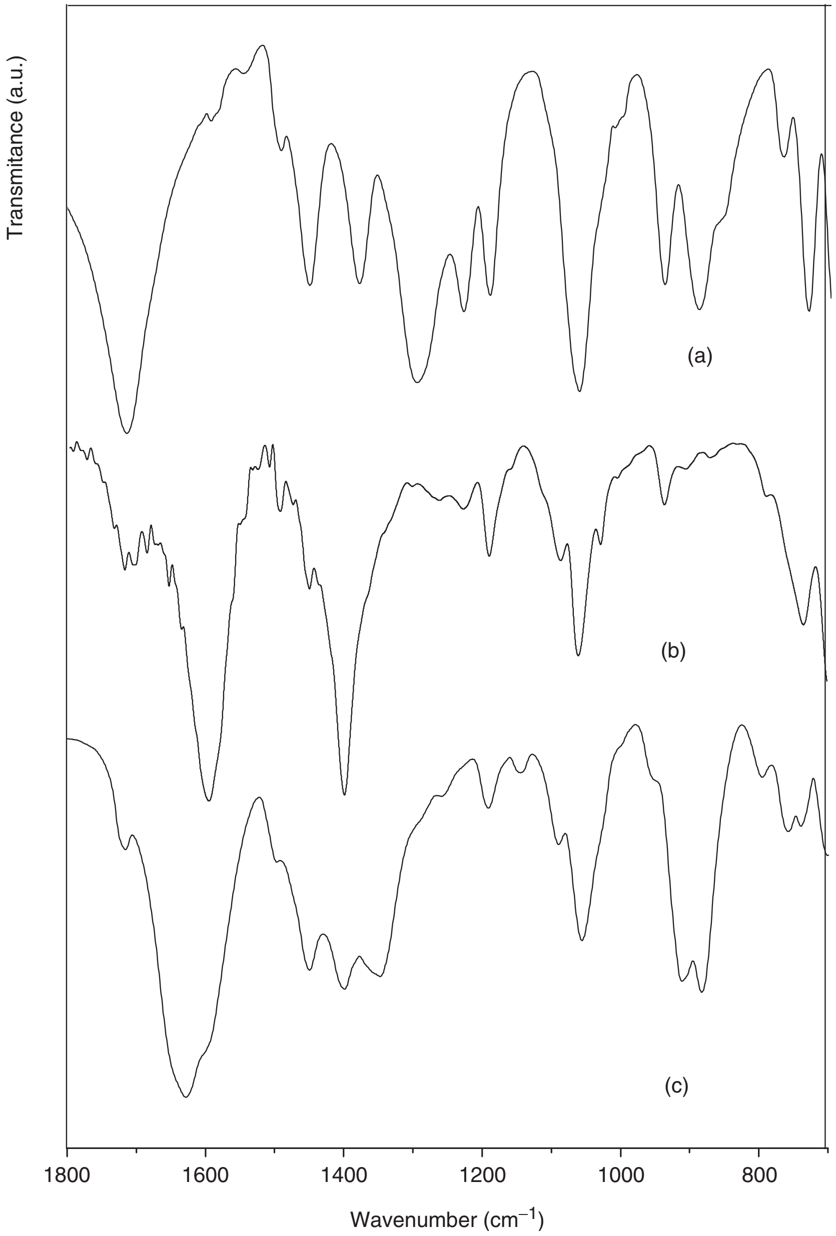

Figure 2. IR spectra for mandelic acid (a), ammonium mandelate (b) and the mandelate complex (c).

mode at ~1600 cm^{-1} was not clearly observed for the glycolate and tartarate hydrated complexes due to the occurrence of the strong $\nu_{asym}(COO^-)$ band in the same spectral region [22].

Frequencies related to Mo–O(Ligand) or M=O appear only in the spectra of the complexes. Considering the existence of the group (MoO_2^{2+}), originally from MoO_3, it was possible to identify the typical frequencies of this group [4, 23]. For $\nu_{sym}(MoO_2^{2+})$ (cm^{-1}): 917 (glycolate), 909 (mandelate) and 909 (tartarate) and for $\nu_{asym}(MoO_2^{2+})$ (cm^{-1}): 892 (glycolate), 883 (mandelate) and 867 (tartarate). A band assigned to ν(Mo–O), where the oxygen atom belongs to the organic ligand, is located at 724 cm^{-1} for glycolate, 737 cm^{-1} for mandelate and 720 cm^{-1} for tartarate [6]. Another band assigned to $^{\alpha}$C–OH was identified at 1084 cm^{-1} for glycolic acid, 1095 cm^{-1} for ammonium glycolate, 1062 cm^{-1} for mandelic acid, 1060 cm^{-1} for ammonium mandelate, 1082 cm^{-1} for tartaric acid and 1071 cm^{-1} for hydrogen-ammonium tartarate. The band assigned to $^{\alpha}C\text{–}O^-$ was identified at 1075 cm^{-1} for the glycolate complex, 1054 cm^{-1} for the mandelate complex and 1065 cm^{-1} for the tartarate complex. Band shifting in the spectra of the complexes indicates the $^{\alpha}C\text{–}O^-$ group (OH deprotonated) is coordinated to Mo(VI) through oxygen atom, as for other α-hydroxycarboxylate complexes [7–10, 23]. In the case of the mandelate complex, bands due to ν(OH) disappeared. Such bands are present in the spectra of the acids (as COOH) and of the other two complexes (hydration H_2O). The lack of ν(OH) frequencies in the spectra of the mandelate complex is further evidence that $^{\alpha}C\text{–}O^-$ is involved in coordination through oxygen. We did not find bands related to Mo–O–Mo vibrations, as found for other Mo(VI) complexes with α-hydroxycarboxylic acids [9]. Molybdenum glycolate complexes with alkaline metals showed very similar IR spectra.

4. Photochemistry

The glycolate, mandelate and tartarate Mo(VI) complexes in solution or in the solid state are photosensitive under sunlight or UV radiation. The three colorless complexes show different colors when exposed for 1 h to a UV radiation (short $\lambda = 266$ nm and long $\lambda = 315$ nm). The glycolate Mo(VI) complex in solution or in the solid state becomes blue after UV excitation. The mandelate Mo(VI) solution becomes yellow and the solid acquires a brown color, while the tartarate complex, in solution or in the solid state, becomes yellow. Changes in the color of the solutions of the three complexes are also observed when they are heated to 40–45°C. The colors are much more intense when the complexes are heated during exposure to UV light. When the solutions are cooled at room temperature in a dark room and the flasks are stirred to increase air contact the color disappears after one night and the solutions become colorless. This behaviour clearly shows a change in the oxidation state of the Mo atoms from VI to V [24].

The electronic absorption spectrum of an aqueous solution of the glycolate complex (conc. 0.10 mol L^{-1}) after exposure to UV light ($\lambda = 266$ or 315 nm) for 1 h shows an absorption band which begins at ~450 nm with maximum at ~880 nm and shows at least two shoulders at ~505 nm and ~675 nm, due to d–d transitions of the Mo(V) species formed see figure 3. For the glycolate complexes, absorption bands were not observed in the UV-Vis region of the spectra (400 to 1000 nm) before UV irradiation. The relative ε (molar absorption coefficient) values and the λ_{max} values for the glycolate complexes after 1 h of UV irradiation are shown in table 2. The ε values were calculated considering the complex $K_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$ as the maximum absorption value (100%) when exposed to 4 h of UV light. After this time, there are no changes in the intensity of the band in the spectrum of the potassium molybdenum glycolate complex.

During exposure of the glycolate complex to UV light a charge transfer from the ligand to Mo(VI) occurs, forming "$MoO_5(OH)$" with replacement of the double bond $Mo^{VI}{=}O$ by Mo^{V}–OH in the central core "MoO_6" of the complex [24].

Aqueous solutions of the colorless glycolate, tartarate and mandelate Mo(VI) complexes did not show, as expected, signals in the EPR spectrum, since Mo(VI) is a d^0 system. In the case of the glycolate complex a typical signal of a Mo(V) d^1 system appears in the EPR spectrum after exposure of the complex to the UV-radiation for 1 h, clearly showing that Mo(VI) was reduced to Mo(V). Niobium(V) is also reduced to Nb(IV) or to Nb(III) when complexes with α-hydroxycarboxylates are exposed to UV-radiation [16].

Cindric *et al.* [25] described the structure of the oxalate molybdenum complexes with alkali metals formulated as $M_2[MoO_3(C_2O_4)]$, where M = alkali metal. The most

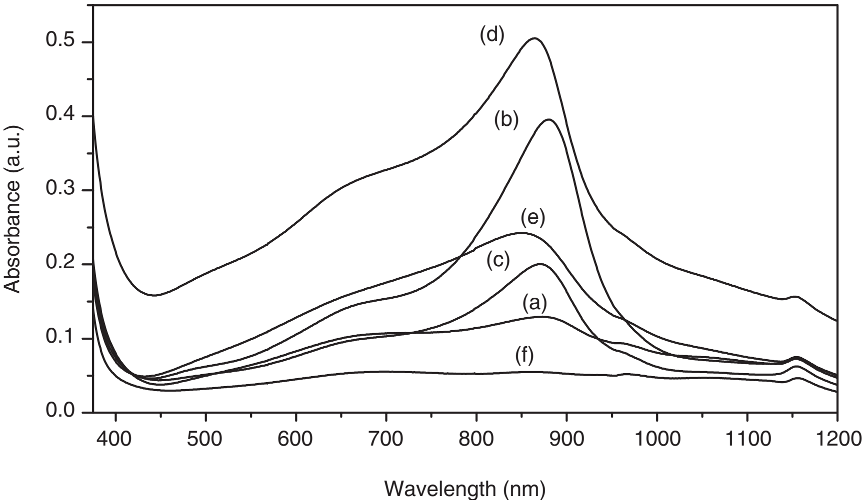

Figure 3. Electronic spectra for $(NH_4)_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$ (a), $Li_2[MoO_2(C_2H_2O_3)_2] \cdot ½H_2O$ (b), $Na_2[MoO_2(C_2H_2O_3)_2] \cdot ½H_2O$ (c), $K_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$ (d), $Rb_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$ (e), $Cs_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$ (f) solution.

Table 2. Relative ε (decreasing order) and λ_{max} values for the glycolate complexes after 1h of UV irradiation.

Complex	λ_{max} (nm)	Relative ε (%)
$K_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$	863	86
$Li_2[MoO_2(C_2H_2O_3)_2] \cdot ½H_2O$	876	67
$Rb_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$	854	41
$Na_2[MoO_2(C_2H_2O_3)_2] \cdot ½H_2O$	872	34
$(NH_4)_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$	878	22
$Cs_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$	852	10

photosensitive compound is $Li_2[MoO_3(C_2O_4)]$. In the present work the complex $K_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$ is the most photosensitive to UV-radiation (see figure 3).

5. Final remarks

The complexes $(NH_4)_2[MoO_2(C_2H_2O_3)_2] \cdot H_2O$, $(NH_4)_2[MoO_2(C_8H_6O_3)_2]$ and $(NH_4)_2[MoO_3(C_4H_4O_6)] \cdot H_2O$ were obtained and characterized. All compounds are photosensitive, although only the glycolate molybdenum complexes change from colorless to blue after exposure to sunlight or to a UV lamp. A more intense blue color was observed in case of the potassium glycolate molybdenum complex and it is much more intense when this complex is heated at 40–45°C.

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