

Preliminary Note

Solid state photochemistry and photochromism of oxalato complexes of molybdenum(VI)

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1. Introduction

In the past few years we have investigated [1, 2] the solid state photochemistry of uranyl carboxylates and, in order to find applications to new printing processes [3], we have decided to turn our attention to complex molybdenum(VI) compounds. Some of these complexes have already been patented [4] and the photochromic properties of those cited in refs. 5 - 8 have already been investigated; however, to the best of our knowledge the photochemistry of molybdenum(VI) oxalato complexes [9] has never been reported. The photochromic behaviour of $K_2[MoO_3(C_2O_4)] \cdot H_2O$, which we have recently evidenced, prompted the present work. It is worthwhile noting that the photochromism of the corresponding oxalato molybdic acid had already been claimed by Rosenheim [10] at the end of the last century; however, it has never since been confirmed by any author.

2. Synthesis of the complexes

The molybdenum trioxide used for the synthesis of the oxalato complexes was obtained by heating purified $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ at approximately 870 K in the presence of air. This MoO_3 was readily soluble in boiling aqueous 1 M solutions of oxalates $M_2C_2O_4$ ($M \equiv H, Na, K, NH_4$) or in 2 M solutions of hydroxides MOH ($M \equiv K, Na$) to which the calculated amount of oxalic acid was then added. These solutions were filtered and were concentrated by gentle heating; after cooling and slow evaporation they yielded small colourless crystals. In Table 1 we report the complexes I - VI which have been obtained together with their presently known structural data. Their stoichiometry has been confirmed by chemical analysis; their IR absorption spectra and X-ray diffraction patterns are in agreement with those published in ref. 9.

TABLE 1

Molybdenum(VI) oxalato complexes and their structural data [11]

Formula	Compound	Cell parameters	Space group	Z	Number of hkl	R
$K_2[MoO_3(C_2O_4)] \cdot H_2O$	I	$a = 8.696(1) \text{ \AA}$ $b = 12.744(2) \text{ \AA}$ $c = 7.544(1) \text{ \AA}$ $\beta = 95.11(2)^\circ$	$P2_1/c$	4	1920	0.0196
$(NH_4)Na[MoO_3(C_2O_4)] \cdot H_2O$	II ^a	$a = 9.061(1) \text{ \AA}$ $b = 13.334(1) \text{ \AA}$ $c = 7.812(2) \text{ \AA}$ $\beta = 98.05(2)^\circ$	$P2_1/c$	4	1768	0.0237
$K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$	III ^b	$a = 7.499(2) \text{ \AA}$ $b = 14.236(4) \text{ \AA}$ $c = 6.601(3) \text{ \AA}$ $\beta = 94.45(3)^\circ$	$P2_1/c$	2	1120	0.0257
$(NH_4)_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$	IV	$a = 7.584(3) \text{ \AA}$ $b = 14.361(4) \text{ \AA}$ $c = 6.741(1) \text{ \AA}$ $\beta = 94.15(2)^\circ$	$P2_1/c$	2	1252	0.0255
$(NH_4)_2[MoO_3(C_2O_4)] \cdot H_2O$	V	$a = 7.624(2) \text{ \AA}$ $b = 14.978(2) \text{ \AA}$ $c = 22.617(4) \text{ \AA}$	$Pnam$ or $Pna2_1$	12	1604	In progress
$Na_2[MoO_3(C_2O_4)] \cdot 3H_2O$	VI	?				

^a Already described [12] but with erroneous results.^b Already described [13] but redetermined.

3. Photochemical properties

All the complexes reported in Table 1 develop various colours when they are exposed to ambient light. For all these compounds we investigated the evolution of their IR absorption spectra (recorded on a Perkin-Elmer model 257 spectrophotometer) after successive UV irradiations (Philips HPK 125 mercury lamp delivering an incident polychromatic beam of approximately 2.5×10^{-6} einsteins min^{-1} on a sample 2 cm^2 in area). Our observations may be summarized as follows.

(1) For an increasing coloration of the samples the fundamental IR absorption bands are not or only very slightly affected; this might be a result of the small transformation rate occurring at the surface of the powdered samples.

(2) On irradiation a characteristic absorption band appears at 2350 cm^{-1} which corresponds to gaseous CO_2 trapped in the solid undergoing photodecomposition. The presence of this band, which only appears after an irradiation period depending on the sample, shows that the CO_2 evolved is a

photoproduct for all the complexes investigated. There does not seem to be any proportionality between the area of the band at 2350 cm^{-1} and the visual intensity of the coloration of the solid.

Furthermore, all the irradiated specimens give an electron spin resonance signal corresponding to molybdenum(V) formation (Varian E-9 spectrometer at 77 K). For instance the anisotropic g factors for complexes I and III are respectively 1.951, 1.919, 1.888 and 1.938, 1.929, 1.896 [7, 14, 15]. Accordingly, in terms of photochemistry this process is of the redox type: the molybdenum(VI) centres are reduced to molybdenum(V) species whereas the oxalato groups are oxidized to CO_2 . A similar redox process has already been established for uranyl formate where uranium(VI) is reduced to uranium(V) whereas the formate groups are oxidized to CO_2 [1, 2]. In the present work only the results for compound I will be reported.

The coloration of compound I was analysed by diffuse reflectance spectroscopy on a Perkin-Elmer model 552 spectrophotometer equipped with an integrating sphere (Fig. 1). The reflectance spectrum of the initial sample shows that only the radiations below 380 nm (3.3 eV) are absorbed, the actinic radiation being thus lowered to about 10^{-6} einsteins min^{-1} . In the first 30 min of irradiation a pink colour appears, characterized by an absorption band at 520 nm. For longer times the colour of the specimen turns to brown; the absorption band gradually shifts towards shorter wavelengths

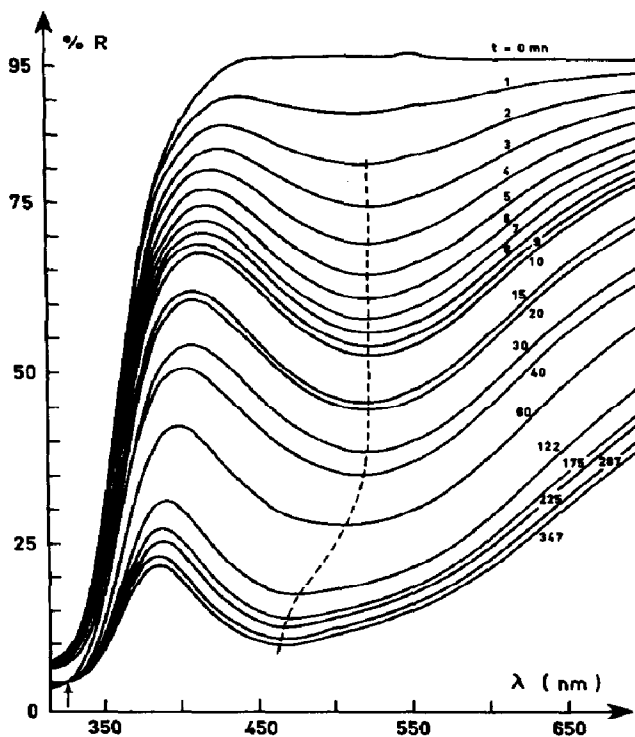


Fig. 1. Evolution of the diffuse reflectance spectrum of $\text{K}_2[\text{MoO}_3(\text{C}_2\text{O}_4)] \cdot \text{H}_2\text{O}$ with irradiation time (in minutes).

and stabilizes at 460 nm after 6 h of irradiation. Hence, the photoreduction of compound I is a two-step process. The existence of an isosbestic point at 325 nm shows that the second step is probably the transformation of the primary molybdenum(V) photoproduct into another photoproduct which has not yet been identified.

4. Photochromism of $K_2[MoO_3(C_2O_4)] \cdot H_2O$

A sample of compound I which had been irradiated for 4 min (optical density, 0.208) was heated in the dark at 353 K in an oxygen atmosphere. From Fig. 2 it can be seen that the optical density decreased with time, indicating the "singly photochromic" properties of compound I [16]. This thermally bleached sample could then be irradiated again and recoloured. For other molybdenum(VI) complexes [7, 15] it appears that oxygen is required for the bleaching. It must be emphasized that the photochromism no longer holds for irradiation times corresponding to the formation of CO_2 . Accordingly, the thermal bleaching corresponds to an oxidative process transforming a molybdenum(V) species into a molybdenum(VI) species.

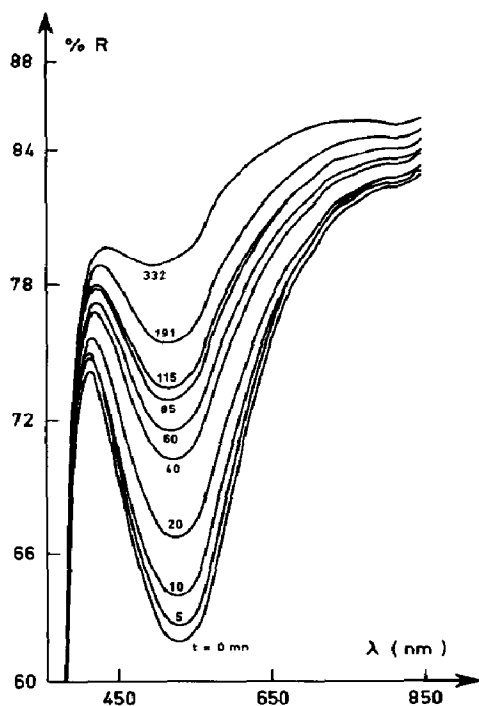


Fig. 2. Evolution of the diffuse reflectance spectrum of $K_2[MoO_3(C_2O_4)] \cdot H_2O$ as a function of time (in minutes) in the dark at 353 K in the presence of oxygen.

5. Conclusions

These preliminary investigations on dipotassium trioxooxalatomolybdenum(VI) hydrate establish its photochromic properties; other results on the photochemistry of complexes I - VI, especially those concerning the quantum yields of the molybdenum(V) formation, will soon be reported.

Furthermore, the crystal structures of these complexes (Table 1) should give a clue to the relationship between the linking of the MoO₆ octahedral units in the solid and the photochemical and photochromic properties.

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