

Available online at www.sciencedirect.com



Spectrochimica Acta Part A 64 (2006) 913-917

SPECTROCHIMICA ACTA PART A

www.elsevier.com/locate/saa

Spectroscopic and thermal studies of chromium(III), molybdenum(VI) and ruthenium(0) complexes of maleic hydrazide

Hassan A. Mohamed^a, Saadia A. Ali^b, Ramadan M. Ramadan^{c,*}

^a Department of Chemistry, Faculty of Science, Cairo University, El-Faiyum Branch, El-Faiyum, Egypt
^b Chemistry Department, University College for Girls, Ain Shams University, Cairo, Egypt
^c Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

Received 20 May 2005; received in revised form 30 August 2005; accepted 30 August 2005

Abstract

Interaction of maleic hydrazide (LH₂) with [Cr(CO)₆] in air at atmospheric pressure resulted in the formation of the complex [(LH)Cr(μ -O)₂Cr(LH)] (1). Reaction of LH₂ with [Mo(CO)₆] in air also gave the complex [(LH₂)O₂Mo(μ -O)₂MoO₂(LH₂)] (2). Under the same conditions, the reaction of LH₂ with [Ru₃(CO)₁₂] resulted in the formation of the tricarbonyl complex [Ru(CO)₃(LH₂)] (3). The complexes were characterized by elemental analysis, IR, and ¹H NMR spectroscopy. The thermal properties of the complexes were investigated by thermogravimetry technique. © 2005 Elsevier B.V. All rights reserved.

Keywords: ¹H NMR spectra; Ruthenium carbonyl complexes; Maleic hydrazide/3,6-dihydroxypyridazine complexes; IR spectra; Thermogravimetry

1. Introduction

3,6-Dihydroxypyridazine (maleic hydrazide, LH_2), Scheme 1 [1], is found to be important biologically active compound. It can act either as purine or pyrimidine analogs, forming base pairs with uracil and thymine (by nucleoside formation through O), or with adenine (by nucleoside formation through N), respectively. It was determined in agricultural products (as inhibitor) by gas chromatography, solid-phase extraction and anion-exchange high-performance liquid chromatography and spectrophotometry [2-5]. Voltammetric behavior of maleic hydrazide pesticide dissolved in a Britton-Robertson buffer was investigated by cyclic voltammetry and differential cyclic voltammetry [6]. Also, studies have been done on the significant reduction of the genotoxic effects caused by herbicide maleic hydrazide in Vicia faba seedings [7]. The reaction of chlorination of maleic hydrazide with POCl₃ was found to be specific to the substrate polymorph [8] (Fig. 1).

Our interest in the reactions of $M(CO)_6$, M=Cr and Mo, and $Ru_3(CO)_{12}$ with various ligands containing nitrogen and/or oxygen donor ligands [9–15] has prompted us to investigate the reactions of this important biologically active compound (maleic

1386-1425/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.saa.2005.08.021

hydrazide, LH_2) with the metal carbonyls. Three complexes with interesting structural features were isolated.

2. Experimental

2.1. Reagents

 $[Ru_3(CO)_{12}]$ and $[M(CO)_6]$, M=Cr and Mo, were supplied by Aldrich. Maleic hydrazide (LH_2) was purchased from BDH. All solvents were of analytical grade and were purified by distillation before use.

2.2. Instrumentation

Infrared measurements were carried out on a Unicam-Mattson 1000 FT-IR spectrometer using KBr pellets. Nuclear magnetic resonance measurements were performed on a Spectrospin-Bruker AC 200 MHz spectrometer. Samples were dissolved in DMSO, d_6 using TMS as internal reference. UV–vis measurements were carried out on a Unicam UV2-300 spectrophotometer with 10 mm quartz cell. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra of the solid complexes (70 eV, EI) were carried out on a Finnigan MAT SSQ 7000 spectrometer. Thermogravimetric analysis (TG) was carried out under nitrogen atmosphere with a heating rate of 10 °C/min using a Schimadzu DT-50 thermal

^{*} Corresponding author. Tel.: +20 22717431; fax: +20 24831836. *E-mail address:* r_m_ramadan@yahoo.com (R.M. Ramadan).



Scheme 1. The keto and enol forms of maleic hydrazide.

analyzer. Table 1 gives the elemental analysis and mass spectrometry data for the complexes.

2.3. Synthesis of $[(LH)Cr(\mu-O)_2Cr(LH)]$ (1).

A mixture of $[Cr(CO)_6]$ (0.10 g, 0.45 mmol) and maleic hydrazide (0.05 g, 0.45 mmol) in 30 ml ethanol was heated to reflux for 16 h at which a green preciptate was formed. The residue was isolated by filtration and then washed several times with hot ethanol followed by petroleum ether. The complex was then recrystallized from DMSO to give green crystals. The complex was left to dry under vacuum for several hours (yield 75%).

2.4. Synthesis of $[(LH_2)O_2Mo(\mu-O)_2MoO_2(LH_2)]$ (2)

Similar procedure was employed as used for the synthesis of $[(LH)Cr(\mu-O)_2Cr(LH)]$ complex with a reaction period of 6 h. Brown crystals with a yield of 70% were obtained.

2.5. Synthesis of $[Ru(CO)_3(LH_2)](3)$

A mixture of $[Ru_3(CO)_{12}]$ (0.10 g, 0.16 mmol) and maleic hydrazide (0.054 g, 0.48 mmol) in benzene was heated to reflux for 30 h. The reaction mixture was cooled and the solvent was removed on a vacuum line. The brown residue was washed several times by hot petroleum ether and then recrystallized from hot ethanol to give brown crystals. The complex was dried in vacuo for few hours (yield 73%).

3. Results and discussion

3.1. IR and NMR studies

Reaction of $[Cr(CO)_6]$ with maleic hydrazide (LH_2) in THF in air resulted in the formation of the chromium complex $[(LH)Cr(\mu-O)_2Cr(LH)]$ (1). The IR spectrum of LH₂ ligand (Fig. 1) showed characteristic bands due to the ν (NH), ν (C=O), ν (OC-NH) and ν (C=C) bands, Table 2 [16]. The IR spectrum of the chromium complex (Fig. 1) displayed the ligand bands

Table 2

Important IR data for maleic hydrazide and its chromium, molybdenum and ruthenium complexes

Compound	IR data (cm ⁻¹) ^a							
	v(OH)	v(NH)	v(C=O)	v(OCNH)	v(C=C)			
LH ₂	_	3168(m)	1661(m)	1578(s)	1411(s)			
		3128(m)		1550(s)				
1 ^b	3385(s)	3260(s)	1658(m)	1576(s)	1456(s)			
				1510(m)				
2 ^c	3338(m)	3177(m)	1650(m)	1549(s)	1440(s)			
	3376(m)	3140(m)		1519(m)				
3 ^d	3389(m)	3200(m)	1646(m)	1512(m)	1430(s)			
				1505(m)				

^a s, strong; m, medium; w, weak.

^b ν (M-O-M) = 688(w), 658(w) cm⁻¹.

^c ν (M=O) = 957(m), 850(s) cm⁻¹; ν (M-O-M) = 741(s), 690(m) cm⁻¹.

^d ν (M-C=O) = 2054(s), 1978(s), 1920(m) cm⁻¹.



Scheme 2. The proposed structure of complex 1.

with appropriate shift due to complex formation (Table 2). In addition, the IR spectrum of the complex displayed two strong bands at 1576 and $1510 \,\mathrm{cm}^{-1}$ due to stretching frequencies of ν (OC–NH). Interestingly, the chromium complex exhibited a band at 3385 cm⁻¹ due to a ν (OH) stretching frequency. This band, which did not observed in the spectrum of ligand, indicated that the ligand in its enolic form (Scheme 1) coordinated oxidatively to the metal with the loss of a proton. The presence of the ν (OC–NH) and ν (OH) bands may indicate that the complex existed in two isomers A and B (Scheme 2). Furthermore, two bands at 688 and 658 cm⁻¹ were assigned to two Cr–O–Cr stretching vibrations [17]. From elemental analysis and spectroscopic data, it can be concluded that the complex may have the structure in Scheme 2 with the formation of 4-membered (LH) chelating ring. However, we cannot rule out that the LH ligand can act as a bridging ligand with the formation of a coordination polymer by means of weak intermolecular Cr · · · O bonds [18]. The reaction of $W_2(O_2CBu^t)_4$ with maleic hydrazide (LH₂) in toluene gave the complex $[(Bu^tCO_2)_3W_2]_2(\mu$ -LH) with the existence of maleic hydrazide as a bridging ligand [19].

Table 1

Elemental analysis and mass spectrometry data for the chromium, molybdenum and ruthenium complexes

Complex	%C		%H		%N		Mass spectrometry	
	Calculated	Found	Calculated	Found	Calculated	Found	Molecular weight	m/z
1	26.8	26.5	1.4	1.2	13.3	12.9	358.15	359 (p ⁺)
2	18.8	18.5	1.9	1.7	10.9	10.7	511.36	512 (p ⁺)
3	28.3	28.5	1.3	1.1	9.4	9.6	297.16	298 (p ⁺)



Fig. 1. The IR spectra of: (A) maleic hydrazide (LH₂); (B) [(LH)Cr(μ -O)₂Cr(LH)] complex; (C) [(LH₂)O₂Mo(μ -O)₂MoO₂(LH₂)] complex; and (D) [Ru(CO)₃(LH₂)] complex.



Scheme 3. The proposed structure of complex 2.

Investigation of complex 1 by ¹H NMR spectroscopy gave no signal due to its paramagnetic characteristics. Magnetic measurements of the Cr(III), d^3 , complex at 298 K gave a magnetic susceptibility value of 2.26×10^{-6} emu g⁻¹ with an effective magnetic moment (μ_{eff}) 1.39 BM. This value is less than the spin only value of one unpaired electron (1.73 BM). However, this lowering in μ_{eff} could be due to strong antiferromagnetic coupling between the two Cr(III) centers mediated through the two (μ -O) groups.

The reaction of LH_2 with $[Mo(CO)_6]$ in air resulted in the formation of the oxo-molybdenum complex $[(LH_2)O_2Mo(\mu O_2MoO_2(LH_2)$] (2). The IR spectrum of the complex (Fig. 1) displayed a ν (NH) band at 3177 cm⁻¹ and a ν (C=O) band at $1650 \,\mathrm{cm}^{-1}$ with a corresponding shift from the ligand bands due to complex formation (Table 2). In addition, the IR spectrum of the complex displayed two strong bands at 1549 and $1519 \,\mathrm{cm}^{-1}$ due to stretching frequencies of v(OC–NH). Again, the presence of these bands indicated that the complex existed in two isomers (Scheme 3). Furthermore, two bands at 957 and $850 \,\mathrm{cm}^{-1}$ which were assigned owing to symmetric and asymmetric stretching frequencies of Mo=O bond, respectively, for a cis MoO₂ fragment of a dimeric structure having the core Mo₂O₆ [20,21]. In addition, the IR spectrum of the complex exhibited two bands at 741 and 690 cm⁻¹ due to two ν (Mo–O–Mo) stretching vibrations [17]. Also, the complex 2 showed a ν (OH) band at $3376 \,\mathrm{cm}^{-1}$ indicating that the ligand coordinated to the metal in its enolic form (Table 2).

The molybdenum complex with Mo(VI), d^0 , oxidation state is a diamagnetic. Unfortunately, we were not able to obtain a ¹H NMR spectrum for the complex due to its poor solubility. Scheme 2 gives the proposed structure for the complex.

[Ru₃(CO)₁₂] reacted with maleic hydrazide to give the tricarbonyl derivative [Ru(CO)₃(LH₂)] (**3**). The IR spectrum of **3** displayed the ligand bands with the appropriate shifts (Fig. 1, Table 2). Furthermore, the IR spectrum of **3** exhibited a band at 3389 cm⁻¹ due to an OH group. The presence of this OH group was not observed in the ¹H NMR spectrum (vide infra) In addition, the IR spectrum of **3** showed three bands in the terminal metal carbonyl region at 2054, 1978 and 1920 cm⁻¹ stretching vibrations due to three CO groups attached to the metal. From the number and pattern of the CO groups, it can be concluded that the ruthenium complex has a trigonal bipyramid structure and the LH₂ ligand coordinated to the metal from two equato-



Scheme 4. The proposed structure of complex 3.

rial sites. Investigation of complex **3** by ¹H NMR in DMSO, d_6 , gave two broad signals at 10.01 and 9.66 ppm. These two signals might be corresponding to two NH groups. The ¹H NMR spectrum of LH₂ itself showed a broad signal at 11.30 ppm due two OH protons, i.e., the ligand existed in solution in an enolic form (Scheme 1). Therefore, isomer F in Scheme 4 was predominant in solution, while isomer E is the predominant isomer in the solid state.

3.2. Thermogravimetric analysis

The thermal studies of the chromium, molybdenum and ruthenium complexes were carried out using thermogravimetry (TG) and differential thermogravimetry (DTG) techniques. The TG plot of the complex [(LH)Cr(μ -O)₂Cr(LH)] displayed two resolved and well-defined decomposition steps. The first decomposition step occurred in the temperature range 318–428 K with a net weight loss of 17.77% could be due to elimination of two moles of oxygen. The second decomposition step occurred in the temperature range 425–675 K with a net weight loss of 53.33% corresponded to the elimination of a C₈H₆N₄O₂ species to give finally the metallic residue of Cr with a net weight loss of 28.9%.

The TG plot of the of $[(LH_2)O_2Mo(\mu-O)_2MoO_2(LH_2)]$ displayed three decomposition steps in the temperature range 313–1125 K. The first decomposition step occurred in the temperature range 313–472 K with a net weight loss of 6.82% corresponded to the elimination of two H₂O molecules. On the other hand, the second decomposition step occurred in the temperature range 477–1000 K with a weight loss of 36.93 % and corresponded to the material decomposition of C₄H₂N₄O species. The third decomposition step occurred in the temperature range 1003–1125 K with a weight loss of 56.25% and corresponded to the material decomposition of Mo₂O₆.

The $[Ru(CO)_3(LH_2)]$ complex was found to be thermally decomposed in a well-defined step in the temperature range 385–598 K with a net weight loss of 47.29% and corresponded to the elimination of L and CO species to leave a metallic residue of 52.71%.

4. Conclusion

Maleic hydrazide is an important biologically active substances. It existed in solution in three different tautomers (keto and enol forms). Few metal complexes of maleic hydrazide, which are prepared from the interaction of metal ions, are reported. The dinuclear oxo complexes [(LH)Cr(μ -O)₂Cr(LH)] and [(LH₂)O₂Mo(μ -O)₂MoO₂(LH₂)] were isolated from the interaction of the maleic hydrazide with the corresponding metal carbonyl. The cluster compound $[Ru_3(CO)_{12}]$, on the other hand, gave the tricarbonyl derivative $[Ru(CO)_3(LH_2)]$.

References

- [1] A. Katrusiak, Acta Crystallogr. Sect. B 57 (2001) 697.
- [2] N.K. Vadukul, Analyst 116 (1991) 1369.
- [3] A. Terashi, S. Yamagouchi, S. Yamamoto, S. Eto, Shokuhin. Eiseigaku. Zasshe. 37 (1996) 401 (analytical abstract no. 5908h00172).
- [4] W.H. Newsome, J. Agric. Food Chem. 28 (1980) 270.
- [5] K. Potrzebnicka, E. Cwiertniewska, Rocz. Panstw. Zakl. Hig. 31 (1980) 465 (analytical abstract no. 4103f3033).
- [6] Y. Ni, P. Qiu, S. Kokot, Talanta 63 (2004) 561.
- [7] A. De Marco, C. De Simone, C. D'Ambrosio, M. Owczarek, Environ. Mutagen. 438 (1999) 89.
- [8] A. Katrusiak, A. Katrusiak, J. Mol. Struct. 647 (2003) 203.
- [9] M.M.H. Khalil, S.A. Ali, R.M. Ramadan, Spectrochim. Acta 57A (2001) 1017.
- [10] M.M.H. Khalil, H.A. Mohamed, S.M. El-Medani, R.M. Ramadan, Spectrochim. Acta 59A (2003) 1341.

- [11] D.Y. Sabry, T.A. Youssef, S.M. EL-Medani, R.M. Ramadan, J. Coord. Chem. 56 (2003) 1375.
- [12] S.M. El-Medani, M.M. Aboaly, H.H. Aballa, R.M. Ramadan, Spectrosc. Lett. 37 (2004) 1.
- [13] M.M.H. Khalil, M.M. Aboali, R.M. Ramadan, Spectrochim. Acta 61A (2005) 157.
- [14] S.M. El-Medani, O.A.M. Ali, R.M. Ramadan, J. Mol. Struct. 738 (2005) 173.
- [15] H.A. Mohamed, J. Coord. Chem. (2005) in press.
- [16] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, fourth ed., Wiley, New York, 1981.
- [17] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., Wiley, New York, 1986.
- [18] B.E. Bursten, M.H. Chisholm, R.J.H. Clark, S. Firth, C.M. Hadad, A.M. MacIntosh, P.J. Wilson, P.M. Woodward, J.M. Zaleski, J. Am. Chem. Soc. 124 (2002) 3050.
- [19] M.H. Chisholm, R.J.H. Clark, J. Gallucci, C.M. Hadad, N.J. Patmore, J. Am. Chem. Soc. 126 (2004) 8303.
- [20] S.M.O. Quintal, H.N. Noguiera, H. Carapuca, M.V. Felix, M.G.B. Drew, J. Chem. Soc. Dalton (2001) 3196.
- [21] H. Liang, Z.F. Chen, R.X. Hu, Q. Yu, Z.Y. Zhou, X.G. Zhou, Trans. Met. Chem. 27 (2002) 102.