Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 579-587

PREPARATION, IR CHARACTERIZATION AND THERMAL PROPERTIES OF SOME METAL COMPLEXES OF ISATIN-3-OXIME

A. Hudák and A. Košturiak

Department of Physical and Analytical Chemistry, P. J. Šafarik University, Moyzesova 11
041 54 Košice, Slovak Republic

(Received February 10, 1998)

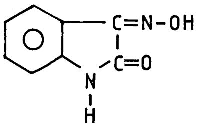
Abstract

The synthesis and characterization of Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II) and Hg(II) complexes of isatin-3-oxime (H_2OXI) are reported. Elemental analysis, infrared spectroscopy, thermal analysis and X-ray powder diffraction were used to characterize the complexes. The IR spectral data show that the ligand behaves in a monodentate or a bidentate manner in the different complexes. The compositions of the prepared complexes were Ag(HOXI), Hg(OXI) and $M(HOXI)_2$ for *M*=Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).

Keywords: complexes, isatin-3-oxime, thermal properties

Introduction

During recent years, we have seen a rapid increase in attempts to design and synthesize a new class of magnetic materials based on organometallic systems. Organic ferromagnets have been prepared in which the magnetic ordering is connected with the molecular rather than the atomic or ionic lattice [1]. The large family of such materials includes some complex compounds of 3-substituted derivatives of 2,3-dioxoindole (isatin) [2, 3]. Our interest has therefore concentrated on the synthesis and the study of the properties of complex compounds of a well-known derivative of isatin: isatin-3-oxime (H_2OXI):



The ability of isatin-3-oxime to form complexes and its applications in analytical chemistry have long been known [4, 5]. This compound has been used for the gravimetic determination of uranium(IV) [6] and for the polarographic determination of various metals [7]. Eckschlager [5] described the preparation of Ag(HOXI), Hg(OXI) and $UO_2(HOXI)_2$, and formation of the slightly soluble Fe(II), Co(II), Ni(II) and Cu(II) compounds of H_2OXI. These compounds have not been investi-

1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

gated to date. A previous paper [8] dealt with the physicochemical properties of H_2OXI. The present work is aimed at the preparation, characterization and thermal properties of H_2OXI complexes of Co(II), Ni(II), Cu(II), Zn(II), Ag(I), Cd(II) and Hg(II).

Experimental

Preparation of the complexes

The ligand H_2OXI, dissolved in hot ethanol, was added to an aqueous solution of the appropriate metal nitrate or chloride in stoichiometric proportion. The pH of the resulting solution was raised to 8.5–9.0 by addition of an aqueous solution of sodium acetate (20% w/w). The resulting complexes were obtained in granular form from the reaction mixtures. (If the syntheses were performed at laboratory temperature, bulky and amorphous precipitates were obtained.) It is also possible to obtain the Hg(II) complex with H_2OXI without the addition of sodium acetate, but the reaction is then not quantitative.

The Zn(II) and Cd(II) complexes were prepared by mixing stoichiometric amounts of the appropriate aqueous salt solutions with an aqueous ethanol solution (50% v/v) of H_2OXI. The pH of the resulting solutions was raised to 10.1–10.6 by addition of NaOH solution (1 M). In the cases of the Zn(II) and Cd(II) complexes, yellow precipitates were obtained.

The reaction of Fe(II) sulphate with H_2OXI gives a green precipitate after the addition of an aqueous solution of sodium acetate. This compound is unstable and readily decomposes in the air. Therefore, we did not succeed in the preparation of the Fe(II) complex of H_2OXI in the pure state.

The products were filtered off, washed with hot water and ethanol, and dried in an electric oven for 3 h at 110°C. All the chemicals used were of analytical reagent grade (Lachema, Brno, Czech Republic).

Instrumentation

The metal contents were determined with an AAS (Spectra A 30, Hewlett-Packard). Carbon, hydrogen and nitrogen were determined with a CHN analyser (Perkin Elmer 2400 CHN).

The infrared spectra were recorded with a Specord IR M/80 spectrophotometer, using the KBr pellet technique in the range 4000–200 cm^{-1}.

The thermal decompositions were invesigated under dynamic conditions with an OD 102 derivatograph (MOM Budapest, Hungary). Ceramic crucibles and a Pt/Pt-Rh thermocouple were used. The measurements were performed under the following conditions: weighed amount 100 mg, rate of heating 9 deg min^{-1}, air atmosphere.

The X-ray powder diffraction patterns were taken with a Dron 2.0. CuK_α radiation ($\lambda=1.54178\cdot10^{-10}$ m) was used for these measurements.

Results and discussion

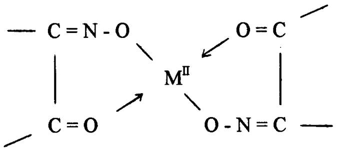
The analytical results presented in Table 1 show that the compositions of the prepared complexes were: Ag(HOXI), Hg(OXI) and $M(HOXI)_2$ for *M*=Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). These compounds are insoluble in water and common organic solvents, with the exception of $Ni(HOXI)_2$, which is slightly soluble in methanol and ethanol. The Co(II), Ni(II), Cu(II), Zn(II), Ag(I) and Cd(II) complexes are soluble in ammonium hydroxide.

Table 1 Results of analyses

Complex	Colour	*M*/%		C/%		H/%		N/%	
		calc.	found	calc.	found	calc.	found	calc.	found
$Co(HOXI)_2$	brown	15.46	15.09	50.41	51.02	2.64	2.71	14.70	14.75
$Ni(HOXI)_2$	brown	15.41	15.11	50.44	51.03	2.64	2.73	14.71	14.78
$Cu(HOXI)_2$	green	16.47	16.18	49.81	50.01	2.61	2.69	14.52	14.59
$Zn(HOXI)_2$	yellow	16.86	16.64	49.57	49.28	2.60	2.53	14.45	14.40
Ag(HOXI)	orange	40.10	39.87	35.72	35.63	1.87	1.82	10.41	10.39
$Cd(HOXI)_2$	yellow	25.86	25.79	44.21	44.11	2.32	2.29	12.89	12.82
Hg(OXI)	yellow	55.61	55.01	26.64	26.73	1.12	1.10	7.77	7.81

The IR spectra of H_2OXI and the prepared complex compounds are illustrated in Table 2. The absorption bands of H_2OXI were identified in accordance with the literature data [9]. The IR spectrum of the ligand in KBr displays ν(N–H) at 3184 cm^{-1} and a broad band at 2904 cm^{-1}, which can be assigned to ν(O–H) of the associated OH groups. The very strong bands at 1714 cm^{-1} and 1026 cm^{-1} are due to ν(C=O) and ν(N–O), respectively.

In case of the complexes ($M(HOXI)_2$, the O–H and N–O vibrations are no longer present, suggesting deprotonization of the oxime OH group due to complexation. The shift of ν(C=O) to lower stretch suggests coordination of the C=O oxygen to the metal. In the complexes $M(HOXI)_2$, the ligand H_2OXI behaves as a mononegative bidentate ligand, coordinating via the CO and the OH after its deprotonation, as shown in Scheme I:



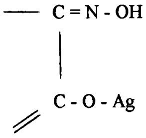
Scheme I

In case of the complex Ag(HOXI), both ν(N–H) and ν(C=O) are absent, and a new C–O band observed at 1230 cm^{-1} indicates that the C=O oxygen is coordinated

Table 2 Infrared spectral characteristics (cm^{-1})

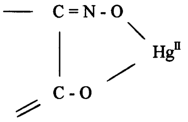
Assignment	Complex							
	H_2OXI	Co(HOXI)$_2$	Ni(HOXI)$_2$	Cu(HOXI)$_2$	Zn(HOXI)$_2$	Ag(HOXI)$_2$	Cd(HOXI)$_2$	Hg(OXI)
ν(N–H)	3184 w		3190 w	3195 w	3190 w		3195 w	
ν(C–H)	3095 w							
ν(O–H)$_{asoc.}$	2904 m					2880 m		
ν(C=O)	1714 vs	1664 s	1664 s	1670 s	1688 m		1672 s	
ν(C=N)	1664 w					1668 w		1636 m
						1624 m		
ν(C=C)	1620 s	1618 s	1618 s	1620 s	1616 m	1624 s	1618 s	1592 s
	1462 s	1458 s	1458 s	1462 s	1452 s	1444 s	1456 s	1448 s
ν(C–O)						1230 m		1248 m
ν(N–O)	1026 vs					1044 s		
δ(C–H)	748 s	750 m	750 m	760 m	752 m	752 m	750 m	760 m
ν(M–O)		502 w	502 w	508 w	504 w	504 w	502 w	504 m

vs = very strong, s = strong, m = medium, w = weak to the Ag following deprotonation in the enolic tautomer. ν(N–O) is shifted toward higher wavenumber: 1044 cm^{-1}. The bands at 1668 and 1685 cm^{-1} are assigned to ν(C=N). In the complex Ag(HOXI), the lignad H_2OXI behaves as a mononegative monodentate ligand, coordinating through the enolic oxygen of isatin, as shown in Scheme II:



Scheme II

The IR spectrum of the complex Hg(OXI) reveals that H_2OXI behaves as a binegative bidentate ligand, coordinating through the enolic oxygen and the oxygen of the OH group after its deprotonation, as shown in Scheme III:



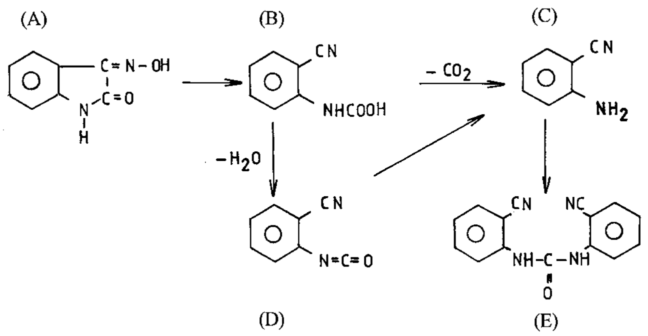
Scheme III

This mode of complexation is confirmed by the following evidence: (i) the disappearance of ν(O–H), ν(N–H), ν(C=O) and ν(N–O); and (ii) the appearance of new bands at 1636 and 1248 cm^{-1}, due to ν(C=N) and ν(C–O).

Thermal behaviour

The thermal decomposition curves (TG and DTA) of the complexes Ag(HOXI), $M(HOXI)_2$ and Hg(OXI) are presented in Figs 1–3. The temperature intervals, the observed and calculated mass loss values and the products of thermal decomposition are listed in Table 3. There are small differences between the individual mass losses which follow immediately after one another. For this reason, the process of isolation and identification of the intermediates of thermal decomposition could not be carried out. However, the IR spectra of the products of thermal decomposition of the complexes, obtained at various temperatures, were measured and compared with data on the thermal characteristics of free isatin-3-oxime. It has been shown [9] that during heating above 200°C isatin-3-oxime (A) changes into a carbamide derivative (B), which not only partly splits off CO_2 to produce anthranilic acid nitrile (C), but also undergoes dehydration, producing the isocyanatane (D). At increased temperature N,N-di-(*o*-cyanophenyl) urea (E) is formed (Scheme IV).

The thermal decomposition of Ag(HOXI) (Fig. 1) is characterized by a sudden mass loss at 180°C. A further slower mass loss can be observed up to 400°C. The IR spectra of Ag(HOXI) and the products of its thermal decomposition at several temperatures are presented in Fig. 4. Some changes in the IR spectra are visible at 190°C. The absorption band at 1044 cm^{-1} which characterizes the oxime group in



Scheme IV Thermal decomposition of isatin-3-oxime

Ag(HOXI) is missing. The weak absorption band of ν(C≡N) is observed at 2200 cm^{-1}. These changes confirm the starting process of the decomposition and the presence of the product (B) just before the sudden decomposition of Ag(HOXI), similarly as in the case of the free ligand. There are no absorption bands in the IR spectrum confirming the presence of the organic compounds at 250°C. It is obvious that the total decomposition of the molecule of the ligand has proceeded. Silver was identified on the basis of X-ray powder diffraction [10] as the final product of the thermal decomposition of the complex Ag(HOXI).

Table 3 Data concerning the thermal decompositions of the prepared complexes

Complex	Range of TG/°C	Mass loss/%		Composition of product
		obs.	calc.	
$Co(HOXI)_2$	190–550 (exo)	80	84.54	CoO
$Ni(HOXI)_2$	190–600 (exo)	80	84.59	NiO
$Cu(HOXI)_2$	180–500 (exo)	79	83.53	CuO
$Zn(HOXI)_2$	160–550 (exo)	80	83.14	ZnO
Ag(HOXI)	180–500 (exo)	58	59.90	Ag
$Cd(HOXI)_2$	180–550 (exo)	70	74.14	CdO
Hg(OXI)	200–800 (exo)	99	61.64	

The thermal decompositions of $M(HOXI)_2$ and Hg(OXI) (Figs 1–3) have different courses from that for Ag(HOXI). Comparison with Ag(HOXI) reveals that these decompositions are rather gradual, but the individual intermediates are not sufficiently separated from each other. The IR spectra of $Cd(HOXI)_2$ and the products of its thermal decomposition at various temperatures are illustrated in Fig. 5. Marked changes in the IR spectra can be observed up to 300°C. ν(C=O) is shifted toward lower wavenumber (1630 cm^{-1}) and two intensive absorption bands relating to the vibrations of the aromatic ring appear at 1580 and 1548 cm^{-1}. At increased temperature, only decreases in intensity of the absorption bands occur. At 350°C, the absorp-

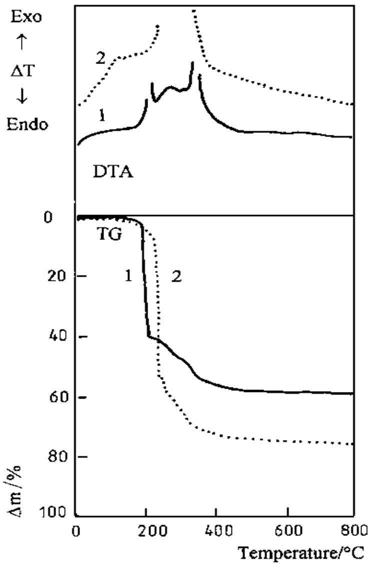


Fig. 1 Thermal decompositions of 1 – Ag(HOXI) and 2 – Cu(HOXI)$_2$

tion band of ν(M–O) originally at 508 cm^{-1} does not appear. This means that the metal-ligand bond has disappeared. At 500°C, none of the absorption bands of the organic substances are present in the IR spectrum. The further mass loss observed in the TG curve is caused by consecutive oxidation of the residues of thermal decom-

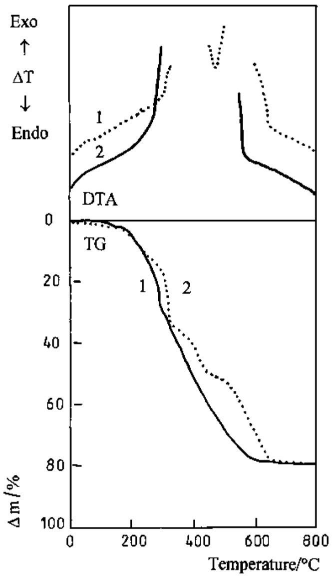


Fig. 2 Thermal decompositions of 1 – Co(HOXI)$_2$ and 2 – Ni(HOXI)$_2$

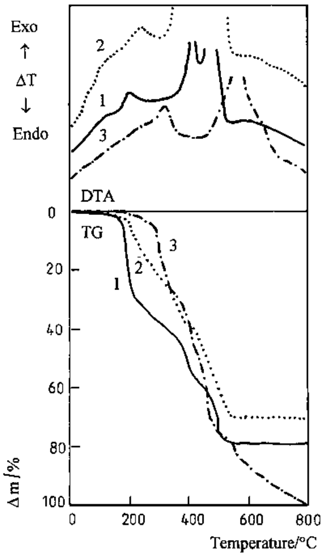


Fig. 3 Thermal decompositions of 1 – $Zn(HOXI)_2$, 2 – $Cd(HOXI)_2$ and 3 – Hg(OXI)

position of the ligand. The thermal decompositions of all the complexes $M(HOXI)_2$ are very similar. In the IR spectra of the intermediates of the thermal decompositions of $M(HOXI)_2$, the absorption bands characterizing the presence of the carbonyl group and the aromatic ring appear. We can assume that the thermal decomposition proceeds by formation of products similar to those in the case of the decomposition of the free ligand. The overall thermal decompositions of $M(HOXI)_2$ are accompanied by exothermic effects. The metal oxides were identified as the final products of thermal decomposition of these complexes [10].

In the thermal decomposition of Hg(OXI), no final decomposition product was identified. Metallic mercury (boiling point=356.6°C), which is reduced during the decomposition of the complex, disappears together with the gaseous products of the decomposition of the organic ligand.

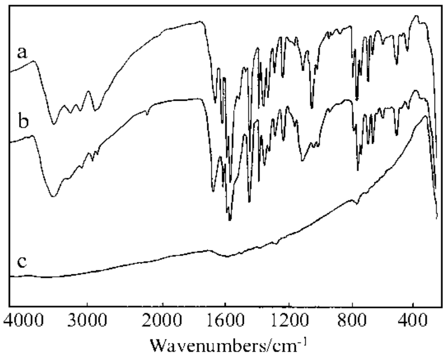


Fig. 4 IR spectra of Ag(HOXI) (a), the product obtained by heating Ag(HOXI) at 200°C (b) and that obtained at 250°C (c)

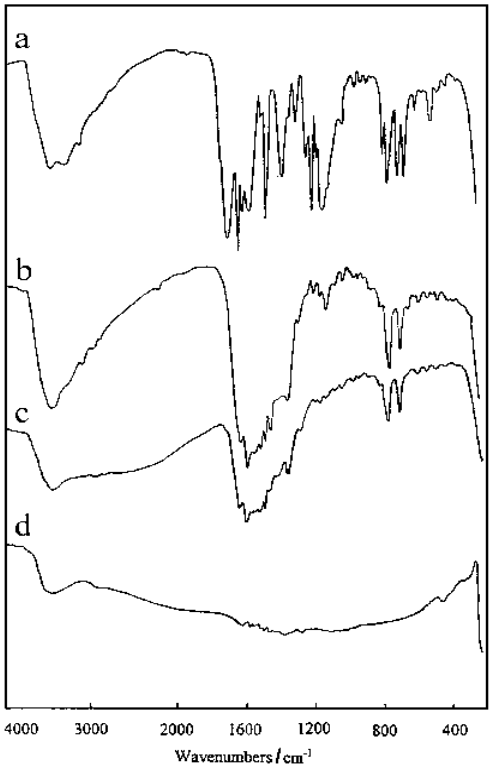


Fig. 5 IR spectra of Cd(HOXI)$_2$ (a), the product obtained by heating Cd(HOXI)$_2$ at 350°C (b), that obtained at 400°C (c), and that obtained at 500°C (d)

As concerns the initial temperatures of decomposition for the complexes Ag(HOXI), M(HOXI)$_2$ and Hg(OXI), only small differences were observed. The lowest and the highest initial temperature of decomposition were those of Zn(HOXI)$_2$ and Hg(OXI), respectively.

References

1 D. Gateschi and R. Sessoli, J. Magn. Magn. Mater., 104 (1992) 2092.
2 M. Zentková, J. Kováč, A. Zentko and A. Košturiak, M. Magn. Magn. Mater., 102 (1991) 1.
3 M. Zentková, J. Kováč, A. Zentko, A. Košturiak and A. Hudák, J. Magn. Magn. Mater., 140–144 (1995) 1453.
4 V. Hovorka and J. Morávek, Chem. Listy, 45 (1951) 235.
5 K. Eckschlager, Chem. Listy, 56 (1962) 489.
6 H. Hovorka, V. Sykora and L. Voříšek, Chim. Anal., 29 (1946) 268.
7 J. Doležal and J. Zyka, Polarometrické titrace, SNTL, Praha 1961.
8 A. Hudák, A Košturiak, A. Hanudel' and P. Mel'uch, Collect. Czech. Chem. Commun., 58 (1993) 1803.
9 G. I. Žungietu and M. A. Rechter, Izatin i jego proizvodnyje, Štiinca, Kišinev 1977.
10 L. I. Mirkin, Spravočnik po rentgenostrukturnomu analizu polikristalov, FM, Moskva 1961.