Journal of Thermal Analysis, Vol. 29 (1984) 515–521

SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOME METAL INDIGODISULPHONATES

*J. M. Salas-Peregrin** and *J. Suarez-Varela* ***

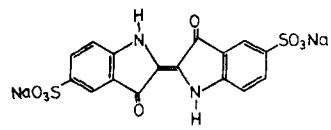
DEPARTMENT OF INORGANIC CHEMISTRY, FACULTY OF SCIENCES, UNIVERSITY OF GRANADA, GRANADA, SPAIN, ** DEPARTMENT OF GENERAL CHEMISTRY, FACULTY OF SCIENCES, UNIVERSITY OF GRANADA, GRANADA, SPAIN

(Received December 22, 1983)

Some indigodisulphonates of Cr(III), Cu(II), Ag(I), An(II) and Cd(II) have been prepared in aqueous medium and characterized on the basis of elemental analyses, diffuse reflectance infrared spectra and magnetic measurements.

The thermal behaviours of these salts were studied by TG, DTG and DSC techniques. Cr(III), Cu(II), Zn(II) amd Cd(II) indigodisulphonates contain 12, 2, 2 and 2 molecules of crystallization water, respectively. The end-products of thermal decomposition have been verified by infrared spectroscopy and X-ray diffraction. Values of dehydration enthalpies have been calculated from the DSC curves.

The synthetic food dye indigocarmine, is the disodium salt of 1-indigotin-5,5′-disulphonic acid (Structure 1). This dye has been used as an indicator in the titration



of antimony(V) with titanium(III) [1] and of iron(III) with chromium(II) [2, 3] in an atmosphere of carbon dioxide.

Studies carried out in solution on the colour-fading of this dye have indicated that the fading is due to oxidation–reduction processes as well as to a dependency on the light intensity [4].

Although the photodecomposition of indigocarmine appears to be the main cause of colour instability, the thermal decomposition of this dye in solution has been reported [4–7]. From the Arrhenius plot of the dye at pH 7.0, a half-life of 234 days at 25° was reported [6].

No studies have been performed in the solid phase on the thermal stability of indigodisulphonates.

The aim of the present paper was to investigate the thermal behaviours of several indigodisulphonates in the solid phase, using thermogravimetric and differential scanning calorimetry methods.

* To whom all correspondence should be addressed.

Experimental

Materials

Indigocarmine was purchased from Eastman Kodak. All the inorganic salts used were of analytical reagent grade.

Methods

Elemental analyses of C, H and N were carried out in a Carlo Erba 1106 Microanalyzer; metal ions were analyzed by atomic absorption on a Perkin–Elmer 290 spectrometer. Infrared spectra of the studied compounds were recorded in KBr medium, in the region 4000–200 cm^{-1}, using a Beckman 4250 spectrophotometer. In order to obtain the diffuse reflectance spectra, the indigosulphonate samples were dispersed in $BaSO_4$ and a Beckman Acta(III) spectrophotometer was used. Magnetic measurements were made on a Bruker BM-4 apparatus.

TG studies were carried out in a dynamic atmosphere (100 ml min^{-1} of pure air) on a Mettler TG 50 thermobalance, using samples varying in weight from 2.921 to 7.360 mg at a heating rate of 10 deg min^{-1}. The DSC curves were recorded with a Mettler DSC 20 differential scanning calorimeter at a heating rate of 5 deg min^{-1} in the temperature range 40–560°.

Preparation of the indigodisulphonates

Indigodisulphonates $M(Ind) \cdot 2\,H_2O$ (where M = Cu(II), Zn(II) and Cd(II) and Ind = indigodisulphonate anion), $Ag_2(Ind)$ and $Cr_2(Ind)_3 \cdot 12\,H_2O$ were obtained by mixing aqueous metal nitrate. After a few hours, precipitates appeared; these were filtered, washed consecutively with water, ethanol and ether, and dried in air. The indigodisulphonates prepared, along with their elemental analyses are presented in Table 1. All the indigodisulphonates were blue.

Table 1 Analytical data on the isolated indigodisulphonates (%) *

Compound	C	H	N	M
$Cr_2(C_{16}H_8N_2O_8S_2)_3 \cdot 12\,H_2O$	36.3 (36.5)	3.1 (3.1)	5.1 (5.3)	6.7 (6.6)
$CuC_{16}H_8N_2O_8S_2 \cdot 2\,H_2O$	36.9 (37.0)	2.2 (2.3)	5.3 (5.4)	12.3 (12.2)
$Ag_2C_{16}H_8N_2O_8S_2$	29.7 (30.2)	1.3 (1.3)	4.2 (4.4)	33.4 (33.9)
$ZnC_{16}H_8N_2O_8S_2 \cdot 2\,H_2O$	36.7 (36.8)	2.1 (2.3)	5.2 (5.4)	11.5 (12.5)
$CdC_{16}H_8N_2O_8S_2 \cdot 2\,H_2O$	34.2 (33.8)	2.2 (2.1)	4.7 (4.9)	19.4 (19.8)

* Calculated values in parentheses.

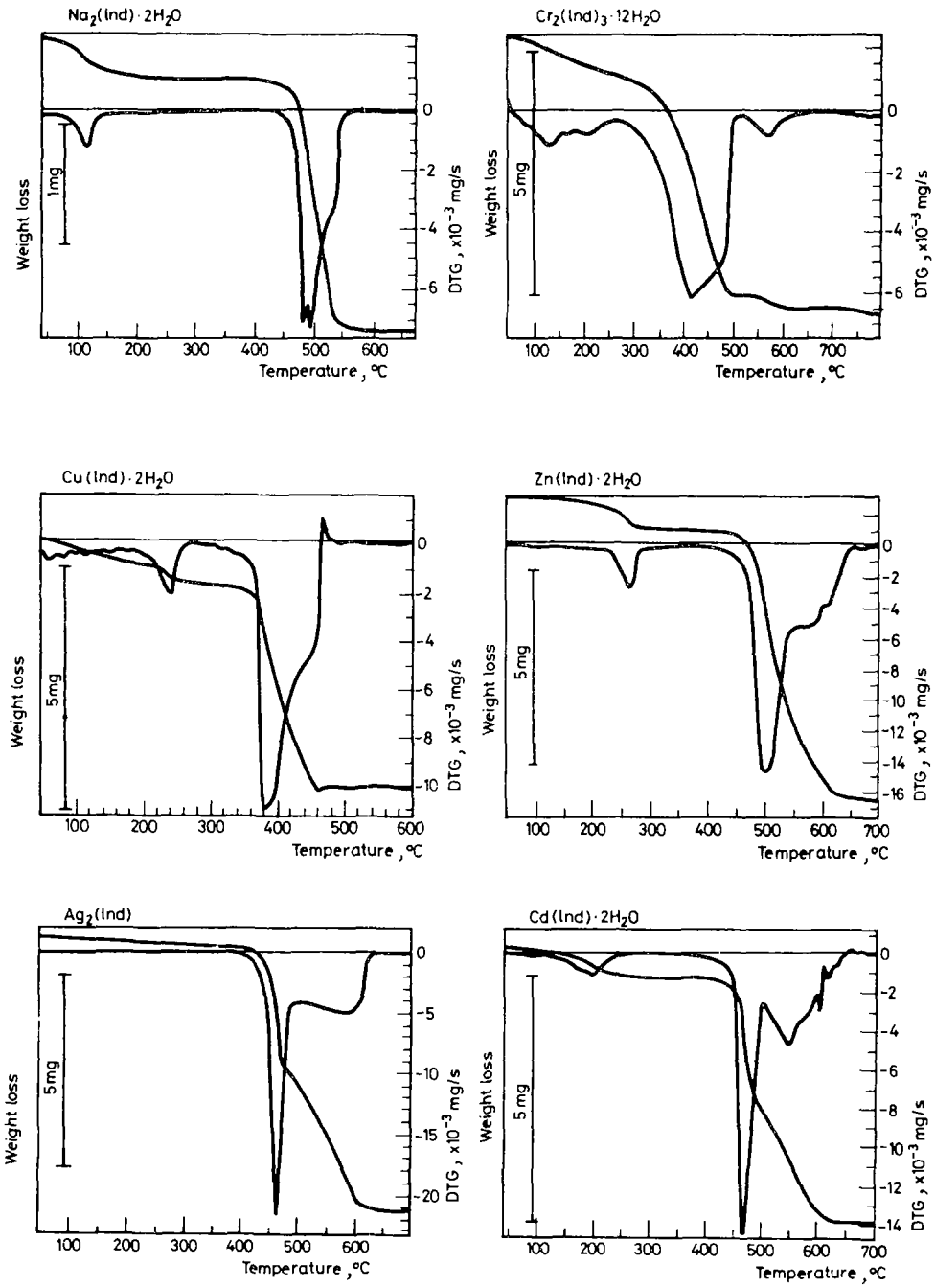


Fig. 1 TG and DTG curves of some indigodisulphonates

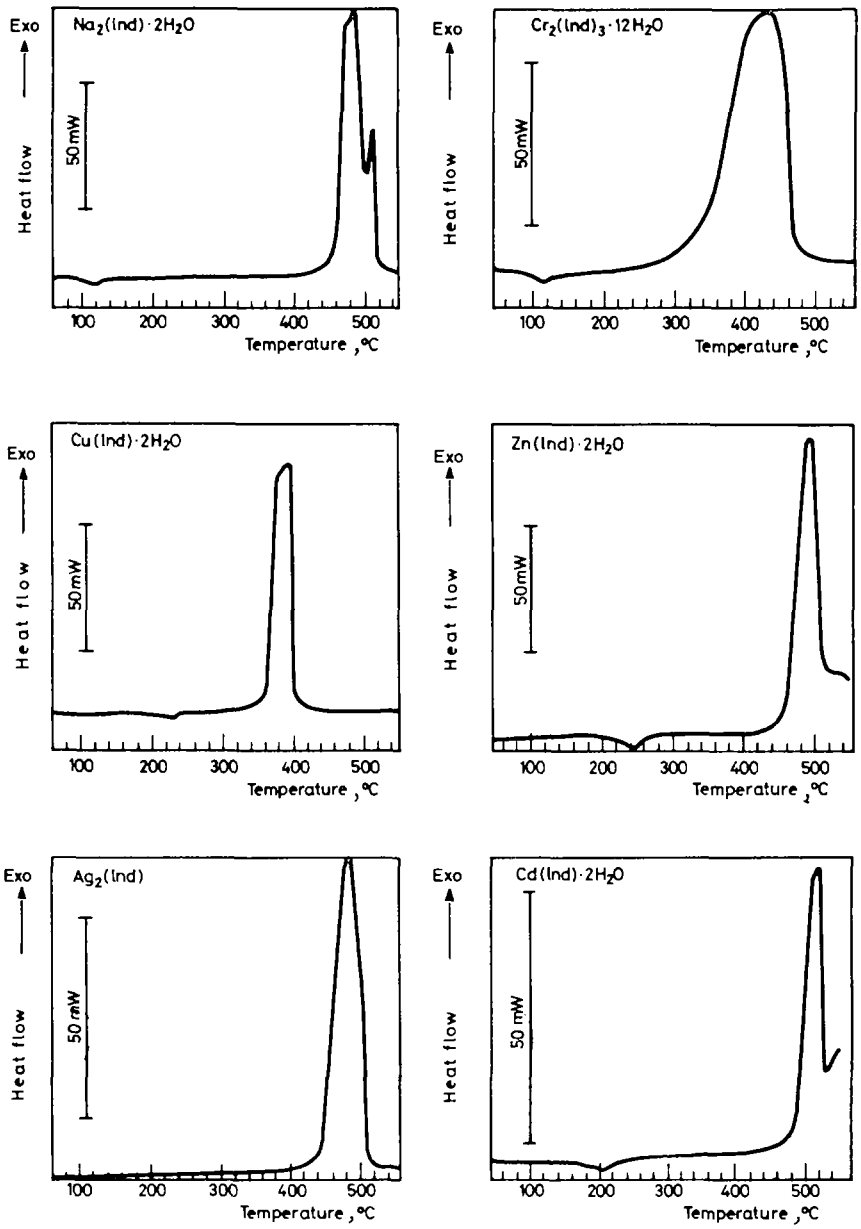


Fig. 2 DSC curves of some indigodisulphonates

Results and discussion

The IR data on the indigodisulphonates isolated are tabulated in Table 2, together with those corresponding to indigocarmine [8]. The positions of the principal infrared and reflectance bands in the new indigodisulphonates are in accordance with the salt nature of these compounds.

At 291 K the values found for the magnetic moments of Cr(III) and Cu(II) in the corresponding indigodisulphonates (3.70 and 1.83 B. M., respectively) are in good agreement with those found in the literature for the spin-only moments. In the

Table 2 Infrared and reflectance diffuse data on some indigodisulphonates (in cm^{-1})

Compound	ν(O–H)	ν(N–H)	ν(C=O)	ν_{as}(S–O)	ν_s(S–O)	Reflectance bands	
$Na_2(Ind) \cdot 2\,H_2O$	3450	3360	1630	1200	1155	39680	34365
						29851	16447
$Cr_2(Ind)_3 \cdot 12\,H_2O$		3360	1640	1200	1155	41667	34602
						28985	16949
$Cu(Ind) \cdot 2\,H_2O$	3440	3380	1630	1210	1145	39370	33557
						29412	16420
$Ag_2(Ind)$		3310	1630	1200	1140	40000	34364
						29673	16666
$Zn(Ind) \cdot 2\,H_2O$		3390	1630	1215	1150	39215	34483
						28985	16774
$Cd(Ind) \cdot 2\,H_2O$	3440	3340	1650	1195	1140	40816	35714
						31250	16584

temperature range 291–78.5 K, the susceptibility values for Cr(III) and Cu(II) indigodisulphonates satisfied the Curie–Weiss law with Weiss constants equal to 23.7 and 30.1, respectively.

Figures 1 and 2 show TG and DSC plots of indigocarmine and indigodisulphonates. The thermal behaviours of these salts consist of two major processes: (i) dehydration of the hydrated salt, and (ii) decomposition of the anhydrous salt to the metal oxide, except for Cu(II), Ag(I) and Na(I) indigosulphonates, which decompose to give metallic copper, silver and sodium sulphate, respectively.

Under the experimental conditions used in the present work, the dehydration process occurs in one step for the hydrated indigodisulphonates. These dehydrations are observed in the TG curves in the temperature ranges 50–250° ($Cr_2(Ind)_3 \cdot 12\,H_2O$); 200–270° ($Zn(Ind) \cdot 2\,H_2O$) and 140–250° ($Cd(Ind) \cdot 2\,H_2O$.

The expected endothermic behaviour for the dehydration processes associated with these compounds is observed in almost the same temperature ranges in the DSC curves. The dehydration temperatures, observed weight losses, calculated weight losses and dehydration enthalpies calculated from the DSC curves in Fig. 2 are indicated in Table 3.

In anhydrous indigosulphonates are stable over an extensive temperature range (except for $Cr_2(Ind)_3 \cdot 12\ H_2O$) and undergo fast pyrolytic decomposition. The peak temperatures of these decomposition processes, the weight percentages of the residues and the end-products of the pyrolytic reactions are indicated in Table 4. In all cases, the nature of the residue was corroborated by infrared spectroscopy and X-ray diffraction. These techniques clearly demonstrate the presence of a small amount of $Cr_2(SO_4)_3$ in the Cr_2O_3 residue.

Table 3 TG and DSC data on the dehydration of some indigosulphonates

Compound	Dehydration temp., °C	Wt. loss, %		ΔH
		calcd.	found.	kJ · (mol H_2O)$^{-1}$
$Na_2(Ind) \cdot 2\ H_2O$	117	7.2	7.1	34
$Cr_2(Ind)_3 \cdot 12\ H_2O$	115	13.7	13.7	21
$Cu(Ind) \cdot 2\ H_2O$	225	6.9	7.7	43
$Zn(Ind) \cdot 2\ H_2O$	240	6.9	6.9	53
$Cd(Ind) \cdot 2\ H_2O$	195	6.3	6.9	26

Table 4 TG data on the thermal decomposition of some indigosulphonates

Process	Decomposition temp., %	Percentage of residue, %	
		found.	calcd.
$Na_2(Ind) \rightarrow Na_2SO_4$	480	28.7	28.39
$Cr_2(Ind)_3 \rightarrow Cr_2O_3$	434	10.7	9.61
$Cu(Ind) \rightarrow Cu$	394	11.5	12.22
$Ag_2(Ind) \rightarrow 2\ Ag$	480	33.9	33.92
$Zn(Ind) \rightarrow ZnO$	495	16.0	15.59
$Cd(Ind) \rightarrow CdO$	500	23.3	22.59

References

1 H. Holmes and G. Cornish, Analyst, 67 (1942) 221.
2 J. P. Tandon and R. C. Mehrotra, Z. Anal. Chem., 20 (1957) 158.
3 J. P. Tandon and R. C. Mehrotra, Z. Anal. Chem., 187 (1962) 410.
4 R. Kuramoto, L. Lachman and J. Cooper, Am. Pharm. Assoc (Sci. Ed.), 47 (1958) 175.
5 A. H. Saleh and S. El-Gamal, Manufacturing Chemist. and News., 49 (5) (1978) 52–59.
6 P. Turi, R. A. Tauseufreund, A. F. Michalis and C. Steren, J. Pharm. Sci., 63 (1974) 1304.
7 I. Moriguchi, S. Wada and H. Sano, Chem. Pharm. Bull., 16 (1968) 952.
8 W. H. Evans, J. A. Maenab and D. F. Wardleworth, J. Sci. Fd. Agric., 21 (1970) 207.

Zusammenfassung — Einige Indigodisulphonate von Cr(III), Zn(II), Ag(I), Zn(II) und Cd(II) wurden in wäßrigem Medium dargestellt und durch Elementaranalyse, diffuse Reflektions-IR-Spektren und magnetische Messungen charakterisiert. Das thermische Verhalten dieser Salze wurde mittels TG, DTG und DSC untersucht. Die Indigodisulphonate von Cu(II), Zn(II) und Cd(II) kristallisieren mit 2 Molekülen Kristallwasser, die von Cr(III) mit 12 Molekülen. Die Endprodukte der thermischen Zersetzung wurden infrarotspektroskopisch und röntgendiffraktometrisch identifiziert. Die Werte der Dehydratisierungsenthalpien wurden aus den DSC-Kurven berechnet.

Резюме — В водной среде подучены некоторые индигодисульфонаты серебра, трехвалентного хрома и двухвалентных меди, цинка и кадмия. Соли охарактеризованы элементарным анализом, ИК спектрами диффузного отражения и измерением магнитной восприимчивости. Термическое поведение синтезированных солей было исследовано методами ТГ, ДТГ и ДСК. Индигодисульфонаты хрома, меди, цинка и кадмия содержали, соответственно, 12, 2, 2 и 2 молекулы кристаллизационной воды. Конечные продукты термического разложения были идентифицированы ИК спектроскопией и рентгено-диффракционным методом. Из ДСК-кривых были вычислены значения энтальпий реакций дегидратации.