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SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR OF SOME *N*-2,3-DIMETHYL-PHENYLGLYCINE COMPOUNDS OF Al(III), Mn(II), Fe(III), Y(III), Cd(II), La(III), Ce(III) AND Pb(II)

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ABSTRACT

Eight compounds containing *N*-2,3-dimethyl-phenylglycine (2,3-PGH) have been prepared and characterized. The compounds of the formula type M(2,3-PGH) are complexes containing bidentate ligands, whilst the compounds $M(2,3\text{-PGH})_3$ present a salt-like structure. The thermal behaviour of these compounds has been studied using TG, DTG and DSC curves. Heats of dehydration have been calculated from DSC curves.

INTRODUCTION

Following the studies of a variety of glycine derivatives with metal ions [1–5] the present work reports the thermal behaviour of the compounds obtained by reaction between the metal ions Al(III), Mn(II), Fe(III), Y(III), Cd(II), La(III), Ce(III) and Pb(II) with *N*-2,3-dimethylphenylglycine (2,3-PGH) (Scheme 1), which presents pharmaceutical applications.

EXPERIMENTAL

The *N*-2,3-dimethylphenylglycine (2,3-PGH) was synthesized by a previously described method [6]. All the chemicals used were of analytical reagent grade.

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Synthesis of the complexes

An NaOH dilute solution was added dropwise to a 20-ml suspension of 2,3-PGH (10 mmol) until all the ligand was dissolved. The resulting clear solution was added with continuous stirring to a 20-ml solution of the corresponding metal nitrate. In all cases, the complexes precipitated immediately, and were filtered off, washed with cold water, and dried over concentrated H_2SO_4.

Methods

Carbon, hydrogen and nitrogen contents were determined by elemental analysis at the Institute of Bio-organic chemistry of Barcelona. Infrared spectra of the studied compounds were recorded in KBr medium, in the region 4000–200 cm^{-1}, using a Beckman 4250 spectrophotometer. The TG studies were carried out in air on a Mettler TG-50 thermobalance, using samples varying in weight from 5.4 to 13.1 mg and a heating rate of 10°C min^{-1}. The DSC curves were recorded in a Mettler differential scanning calorimeter (Model DSC-20) at a heating rate of 5°C min^{-1}, in the temperature range 40–560°C, using samples varying in weight from 2.3 to 7.0 mg. Magnetic susceptibilities were measured by Faraday's method. The appropiate diamagnetic corrections were calculated using Pascal's constants [7].

Analytical data for the complexes are given in Table 1.

RESULTS AND DISCUSSION

The most significant IR bands for 2,3-PGH and its complexes are given in Table 2.

The compound 2,3-PGH shows a broad band in the 2900–2500 cm^{-1} region, corresponding to ν(OH) of the COOH group, which indicates that

TABLE 1

Analytical data for the isolated compounds

Compound	Colour	%C		%H		%N		μ_{eff}
		Calcd.	Found	Calcd.	Found	Calcd.	Found	
$Al(2,3\text{-}PGH)_3 \cdot 2H_2O$	Yellow	60.29	59.32	6.75	6.16	7.03	6.81	–
$Mn(2,3\text{-}PGH)_2 \cdot 2H_2O$	White	53.69	53.94	6.31	6.22	6.26	6.31	5.84
$Fe(2,3\text{-}PGH)_3$	Brown	60.96	59.70	6.09	5.97	7.11	7.14	3.37
$Y(2,3\text{-}PGH)_3 \cdot 4H_2O$	Yellow	51.80	52.55	6.38	6.07	6.04	6.07	–
$Cd(2,3\text{-}PGH)_2 \cdot 2H_2O$	White	47.58	47.57	5.59	5.48	5.55	5.52	–
$La(2,3\text{-}PGH)_3 \cdot H_2O$	Yellow	52.10	51.81	5.54	5.46	6.08	6.06	–
$Ce(2,3\text{-}PGH)_3 \cdot H_2O$	Yellow	52.01	52.03	5.53	5.29	6.07	6.11	2.33
$Pb(2,3\text{-}PGH)_2 \cdot H_2O$	White	41.30	41.86	4.51	4.30	4.82	4.77	–

TABLE 2

Infrared data (cm^{-1})

Compound	ν(OH)	ν(NH)	ν(C=O)	ν(C=C)	$\nu(C\overset{\cdots}{-}O)$	ν(C–N) [a]
2,3-PGH	–	3.420	1.710	1.585	1.430 1.255 [c]	1.150
$Al(2,3\text{-}PGH)_3 \cdot 2H_2O$	3.420	[b]	1.610 [d]	1.590	1.430 [e]	1.190
$Mn(2,3\text{-}PGH)_2 \cdot 2H_2O$	3.140 [c]	3.370	1.605 [d]	1.590	1.425 [e]	1.140
$Fe(2,3\text{-}PGH)_3$	–	3.420	1.590 [d]	1.590	1.410 [e]	1.150
$Y(2,3\text{-}PGH)_3 \cdot 4H_2O$	3.420 3.360	[b]	1.590 [d]	1.560	1.410 [e]	1.150
$Cd(2,3\text{-}PGH)_2 \cdot 2H_2O$	3.520 3.430	3.320	1.590	1.560	1.410	1.110
$La(2,3\text{-}PGH)_3 \cdot H_2O$	3.420 [f]	[b]	1.580 [d]	1.560	1.410 [e]	1.150
$Ce(2,3\text{-}PGH)_3 \cdot H_2O$	3.420 [f]	[b]	1.590 [d]	1.560	1.400 [e]	1.150
$Pb(2,3\text{-}PGH)_2 \cdot H_2O$	3.370	[b]	1.590 [d]	1.550	1.400 [e]	1.140

[a] ν(C–N) of the $N\text{–}CH_2$ group.

[b] Included in ν(OH).

[c] Corresponding to $\nu(C\text{–}O) + \delta(OH)$.

[d] Corresponding to $\nu_{as}(COO^-)$.

[e] Corresponding to $\nu_s(COO^-)$.

[f] Wide band.

the compound is dimeric [8], i.e., intermolecular hydrogen bonds exist between the COOH groups of two molecules of 2,3-PGH. This glycine derivative does not exist as "zwitterions" in the solid state, since it shows characteristic absorption of unionized carboxylic acid at 1710 cm^{-1}.

Compounds of the type M(II) $(2,3\text{-}PGH)_2$ (M = Mn(II), Cd(II) and Pb(II)), present a shift of the NH stretching mode towards a lower wavenumber, which is indicative of a direct N–M coordination [9]. Also, the stretching mode of the C–N–C group is shifted to lower frequencies (~ 40 cm^{-1}), with respect to the free ligand, confirming the formation of the coordinative metal–nitrogen bond [9].

In view of the IR data for these complexes and these corresponding to the formation of 2,3-PGH complexes with the metal ions Fe(II), Co(II), Ni(II) and Zn(II) [1,10,11], the N–H bond becomes weaker and the strength of

TABLE 3

Shift of NH stretching mode vs. ionic radius for the compounds studied

Compound	$\Delta\nu(cm^{-1})$	r_+ (Å)
$Mn(2,3\text{-}PGH)_2 \cdot 2H_2O$	50	0.80
$Fe(2,3\text{-}PGH)_2$	120	0.76
$Co(2,3\text{-}PGH)_2 \cdot 3H_2O$	160	0.74
$Ni(2,3\text{-}PGH)_2 \cdot 4H_2O$	160	0.74
$Zn(2,3\text{-}PGH)_2 \cdot 2H_2O$	140	0.74

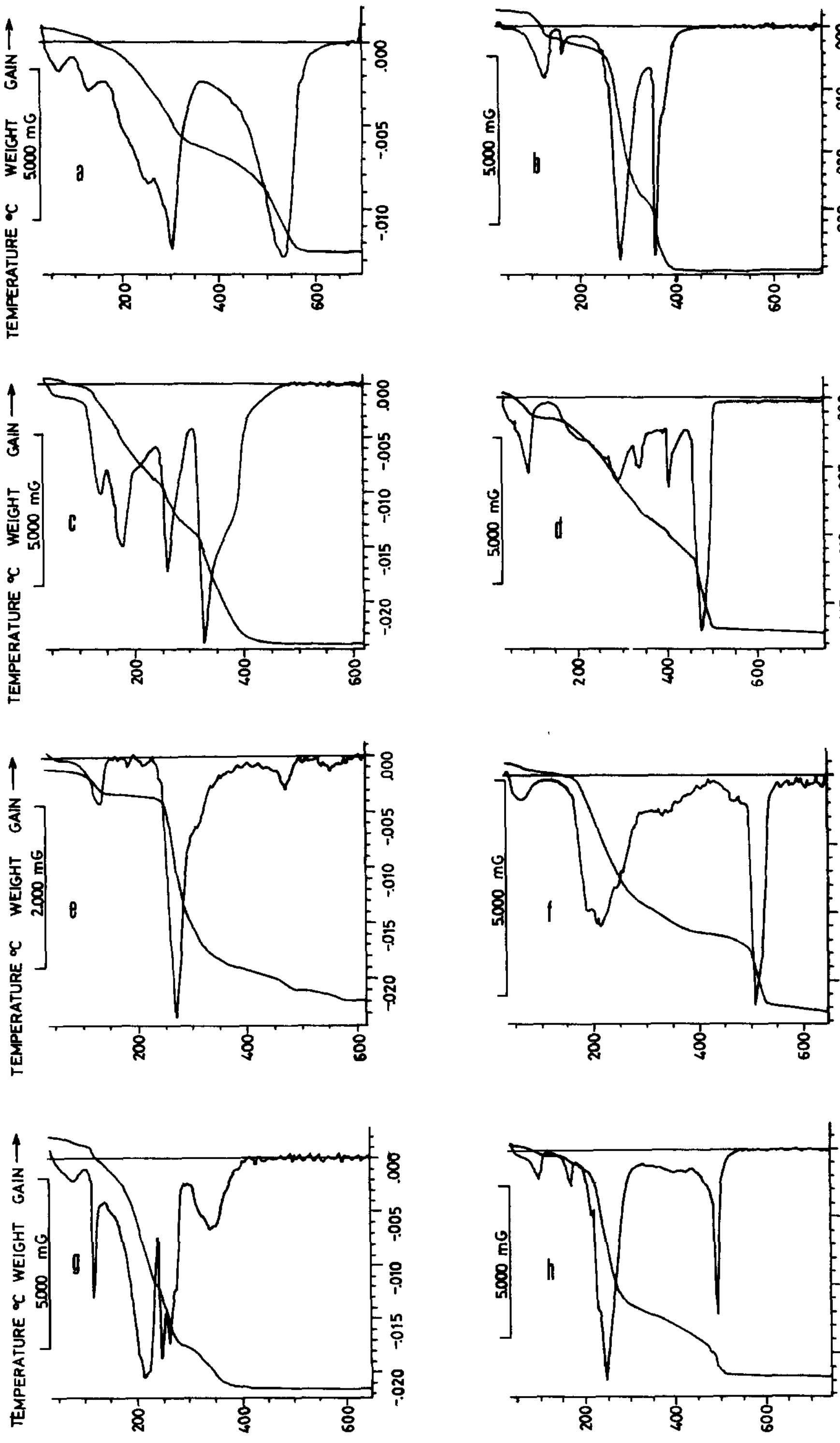


Fig. 1. TG curves for: $Al(2,3\text{-}PGH)_3 \cdot 2H_2O$ (a); $Mn(2,3\text{-}PGH)_2 \cdot 2H_2O$ (b); $Fe(2,3\text{-}PGH)_3$ (c); $Y(2,3\text{-}PGH)_3 \cdot 4H_2O$ (d); $Cd(2,3\text{-}PGH)_2 \cdot 2H_2O$ (e); $La(2,3\text{-}PGH)_3 \cdot H_2O$ (f); $Ce(2,3\text{-}PGH)_3 \cdot H_2O$ (g) and $Pb(2,3\text{-}PGH)_2 \cdot H_2O$ (h).

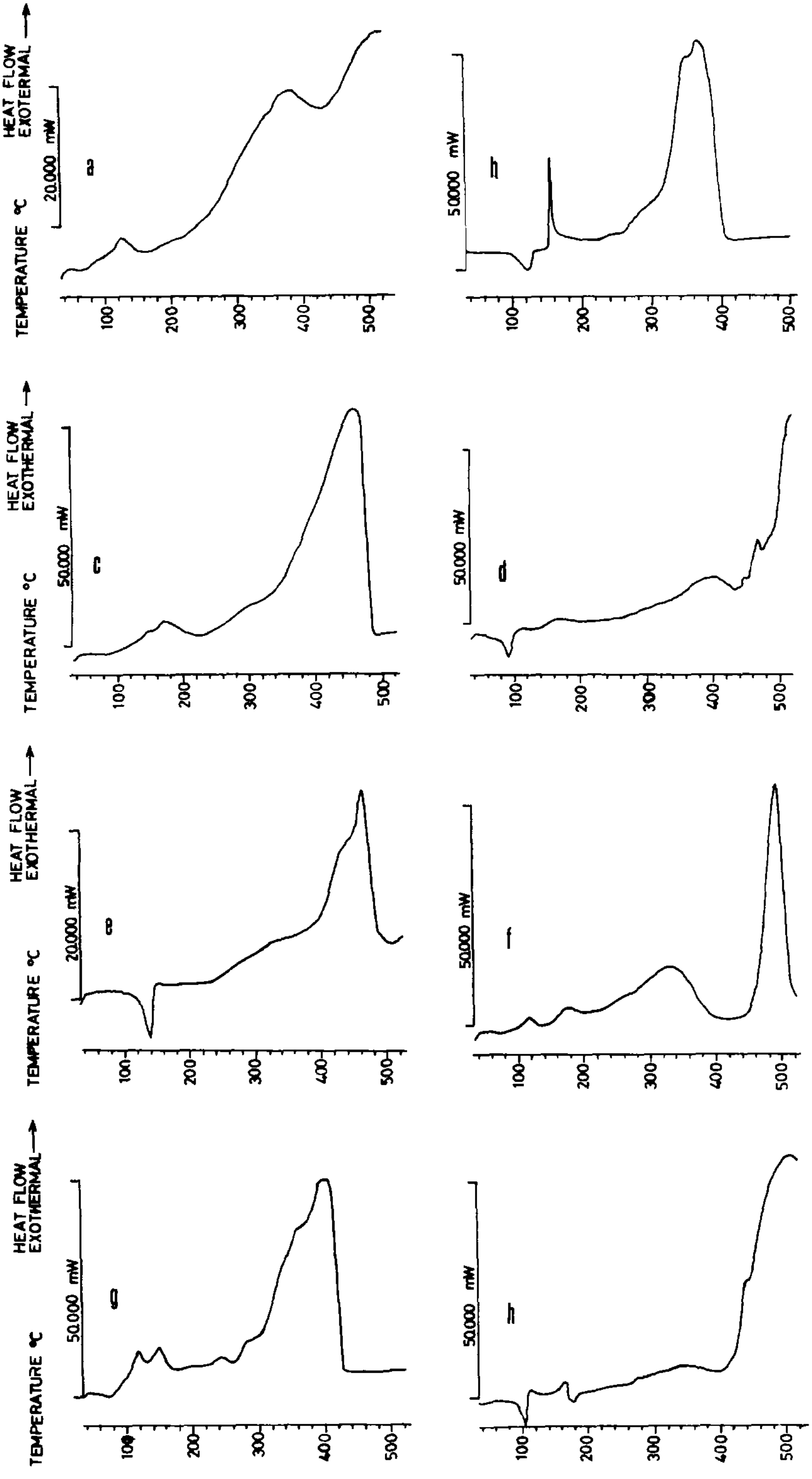
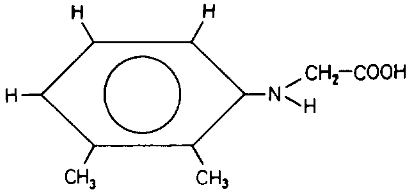


Fig. 2. DSC curves for: Al(2,3-PGH)$_3$·2H$_2$O (a); Mn(2,3-PGH)$_2$·2H$_2$O (b); Fe(2,3-PGH)$_3$ (c); Y(2,3-PGH)$_3$·4H$_2$O (d); Cd(2,3-PGH)$_2$·2H$_2$O (e); La(2,3-PGH)$_3$·H$_2$O (f); Ce(2,3-PGH)$_3$·H$_2$O (g) and Pb(2,3-PGH)$_2$·H$_2$O (h).



Scheme 1

N–M increases in the order: Co(II) = Ni(II) > Zn(II) > Fe(II) > Cd(II) > Mn(II) ≈ Pb(II) > Tl(I), which is inversely proportional to the ionic radii. For the metal ions of the first row (Table 3), the plot of $\Delta\nu$ (shift of the NH stretching mode), vs. ionic radius, leads to a straight line which obeys the following equation: $\Delta\nu$ $(\mathrm{cm}^{-1}) = 1720\ r_+$ (Å) + 1427. This fact indicates a direct relationship between the polarization effect and the strength of the NM bond.

Finally, although the ν(M–O) band has not been clearly observed in the IR spectra, we believe that in these complexes 2,3-PGH acts in bidentate form (N,O) coordinated to the metal ion. This coordination mode has also been found in other metal complexes of analogous glycine derivatives [12].

In the case of compounds of the type $M(2,3\text{-PGH})_3$ (M = Al(III), Y(III), La(III) and Ce(III)), the IR spectra show that the band corresponding to ν(N–H) does not undergo an important shift, which seems to indicate that there is no direct N–M coordination. In view of this, we propose as more probable for these compounds a salt-like structure in which the charge of the metal ion is neutralized by the corresponding PG anions.

TG and DSC curves for these complexes are given in Figs. 1 and 2, respectively.

The dehydration of the complexes occurs on the TG curve in the temperature range 50–150°C. The expected endothermic behaviour of the dehydra-

TABLE 4

TG and DSC data for dehydration processes

Compound	Weight loss (%)		Dehydration temp. (°C)	ΔH (kJ mol^{-1} H_2O)
	Calcd.	Found		
$Al(2,3\text{-PGH})_3\cdot 2H_2O$	6.02	5.65	70	NC
$Mn(2,3\text{-PGH})_2\cdot 2H_2O$	8.05	8.58	123.9	49.1
$Y(2,3\text{-PGH})_3\cdot 4H_2O$	10.36	10.15	91.4	41.7
$Cd(2,3\text{-PGH})_2\cdot 2H_2O$	7.14	7.44	139.9	58.1
$La(2,3\text{-PGH})_3\cdot H_2O$	2.61	2.79	80	NC
$Ce(2,3\text{-PGH})_3\cdot H_2O$	2.60	2.56	80	NC
$Pb(2,3\text{-PGH})_2\cdot H_2O$	3.10	3.43	105	35.6

NC, not calculated.

TABLE 5

TG and DSC data for decomposition process

Compound	Exothermic temp. (°C)	Residue		
		Type	% Calcd.	% Found
$Al(2,3\text{-}PGH)_3 \cdot 2H_2O$	370 > 500	Al_2O_3	8.53	10.69
$Mn(2,3\text{-}PGH)_2 \cdot 2H_2O$	160 370	Mn_2O_3	17.64	16.89
$Fe(2,3\text{-}PGH)_3$	170 450	Fe_2O_3	13.12	13.84
$Y(2,3\text{-}PGH)_3 \cdot 4H_2O$	> 500	Y_2O_3	16.23	14.26
$Cd(2,3\text{-}PGH)_2 \cdot 2H_2O$	460	CdO	25.43	24.27
$La(2,3\text{-}PGH)_3 \cdot H_2O$	120 180 340 > 500	La_2O_3	25.56	26.68
$Ce(2,3\text{-}PGH)_3 \cdot H_2O$	120 150 400	Ce_2O_3	23.69	24.80
$Pb(2,3\text{-}PGH)_2 \cdot H_2O$	160 > 500	PbO	38.37	37.27

tion process associated with these compounds has been observed from DSC curves in almost the same temperature ranges. The dehydration temperatures, observed weight losses, calculated weight losses and dehydration enthalpies calculated from the DSC curves are given in Table 4.

The anhydrous compounds are stable over a small temperature range and in all cases start to decompose in several steps around 140°C, and finish at ~ 500°C. The decarboxylation and pyrolysis processes seem to overlap under the heating conditions applied. The temperature peaks corresponding to the exothermic effects, theoretical and experimental values for the residue obtained to the end of the pyrolysis are given in Table 5 (in all cases the residue was verified by X-ray diffraction and IR spectroscopy).

REFERENCES

1 J.M. Salas Peregrin, M. Román Ceba, J.C. Avila Rosón and J. Suárez Varela, Thermochim. Acta, 76 (1984) 381.

2 M. Román Ceba, J.C. Avila Rosón, J. Suárez Varela and J.M. Salas Peregrin, Thermochim. Acta, 80 (1984) 115.

3 J.C. Avila Rosón, M. Román Ceba, J. Suárez Varela and J.M. Salas Peregrin, Thermochim. Acta, 87 (1985) 109.

4 J.M. Salas Peregrin, J.C. Avila Rosón, M. Román Ceba and J. Suárez Varela, Thermochim. Acta, 89 (1985) 151.

5 J.M. Salas Peregrin, E. Colacio Rodríguez, J. Suárez Varela and J.C. Avila Rosón, Thermochim. Acta, 91 (1985) 79.

6 F. Salinas, A. Guiraum and J.C. Avila Rosón, An. Quim., 78B (1982) 232.

7 P.W. Selwood, Magnetochemistry, Interscience, New York, 1956.

8 R.T. Conley, Infrared Spectroscopy, 2nd edn., Allyn and Bacon, Boston, MA, 1972.

9 A. Battiston, G. Sbrignadello, G. Bandoli, D.A. Clemente and G. Tomat, J. Chem. Soc., Dalton Trans., 12 (1979) 1965.

10 M. Roman Ceba, J.C. Avila Rosón, J. Suárez Varela and J.M. Salas Peregrin, An. Quim., 80B (1984) 157.

11 M. Roman Ceba, J.C. Avila Rosón, J. Suárez Varela and J.M. Salas Peregrin, Afinidad, in press.

12 E. Colacio Rodríguez, J.M. Salas Peregrin, J. Suárez Varela and J.C. Avila Rosón, Synth. React. Inorg. Met.-Org. Chem., 5 (1985) 681.