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Heterobinuclear chelates of some transition metal ions with chromium(III)-diethylenetriaminepentaacetato complex

Remo Bucci [a,*], Andrea D. Magrì [a], Antonio L. Magrì [a] and Aldo Napoli [b]

[a] *Dipartimento di Chimica, Università "La Sapienza", 00185 Rome (Italy)*
[b] *Dipartimento di Chimica, Università della Calabria, 87030 Arcavacata di Rende (CS) (Italy)*

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Abstract

The reactions of chromium(III)-DTPA "chelating agent" with manganese(II), iron(II), cobalt(II), nickel(II), copper(II) and zinc(II) have been investigated in aqueous solution by potentiometric methods. The heterobinuclear chelates with 1:1:1 metal(II):chromium(III):DTPA molar ratio have been precipitated and characterized by spectroscopic and thermoanalytical techniques.

All the metal ions are six-coordinated with an octahedral configuration (except the four-coordinated copper(II)) and are covalently bound to the free iminodiacetic group of the chromium(III)-DTPA complex.

The thermal stability depends on the furnace atmosphere (N_2 or O_2), whereas the nature of the metal(II) ion is less important because the anhydrous complexes begin to decompose at about the same temperature. Exceptions to this rule are the copper(II) and iron(II) complexes, which are less stable.

INTRODUCTION

In a previous paper [1] complex formation of chromium(III) with diethylenetriaminepentaacetic acid (DTPA,H_5L) has been studied in aqueous solution. DTPA behaves as a pentadentate ligand, one iminodiacetic group being free from coordination. The chromium complex is inert, so it can be considered as a large molecule of *N*-substituted iminodiacetic acid. The formation of heterobinuclear complexes of copper(II) with this "metal complex" chelating agent has been investigated in aqueous solution and a solid compound has been obtained and characterized [2].

In the present paper extensive information on the reaction of chromium(III)-DTPA complex with manganese(II), iron(II), cobalt(II),

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* Corresponding author.

nickel(II), copper(II) and zinc(II) is reported. The synthesis, spectroscopic characteristics and thermal properties of the solid compounds are described (as determined by thermogravimetry (TG), differential thermogravimetry (DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC)) and the corresponding equilibria in aqueous solution are investigated.

EXPERIMENTAL

Apparatus

Thermal measurements were carried out using a Perkin-Elmer TGS-2 thermal analyser, DTA 1700 differential thermal analyser and DSC-7 differential scanning calorimeter connected to a model 3600 data station equipped with a software package running on the data station itself. TG, DTA and DSC runs were effected in a stream of nitrogen or oxygen (flow rate 50 ml min^{-1}); the heating rate was 10°C min^{-1}, with samples of 0.5–2 mg.

The reflectance, IR and visible spectra were recorded using Beckman DGB, Pye Unicam P.U. 9800 FTIR and Perkin-Elmer 320 UV–vis spectrophotometers. The water content of the complexes was determined by TG analysis and the metal ions by ICP.

E.m.f. measurements of hydrogen ion concentration were performed with an Amel 337 potentiometer (resolution 0.1 mV), interfaced with a Macintosh computer for the automatic recording and treatment of the data. An Ingold glass electrode was calibrated in concentration units and the reference electrode was a double junction calomel electrode, filled with 1.0 mol l^{-1} $NaClO_4$.

Reagents

Distilled deionized water and analytical grade reagents were used throughout.

Diethylenetriaminepentaacetic acid (Fluka) and its chromium(III) complex (disodium salt, Aldrich), were checked as previously reported [1].

The chromium(III)–DTPA complex in the acid form was prepared and analysed as already described [2].

The metal ions were in the form of perchlorate (Alfa).

Preparation of the solid compounds

The following general procedure was applied to preparation of the solid heterobinuclear complex with 1:1:1 Me(II):Cr(III):DTPA molar ratio.

About 150 ml of ethanol was added to 50 ml of aqueous solution (pH = 3) of each metal(II) ion (50 mmol dm^{-3}) and of Cr–DTPA chelating agent (45 mmol dm^{-3}). The precipitate was filtered off, washed with ethanol and purified by dissolving it in about 20 ml of water and precipitating again with ethanol. Finally it was washed with ethanol and dried in vacuum. The analysis of the compounds obtained agrees with the general formula [Me(Cr–DTPA)$(H_2O)_x$].

RESULTS AND DISCUSSION

The above-mentioned preparation of the solid compounds is based on the results obtained by a potentiometric study of the reaction in aqueous solution of chromium–DTPA chelating agent and metal(II) ion. In fact, both in equimolar solution and with metal(II) ions in excess, the acidimetric titration curves are lower than that of the ligand alone and a sharp inflection is seen when two moles of sodium hydroxide are added per mole of ligand, meaning that complexes in a 1:1 molar ratio (metal(II):ligand) are formed in solution. The corresponding reaction is (coordinated water molecules omitted)

$$Me^{2+} + H_2CrL + 2OH^- \rightleftharpoons MeCrL + 2H_2O$$

Analysis of the formation functions (in the pH range 2–5) allows the stability constants to be calculated by applying the curve fitting method [3]. The values, (reported in Table 1) are referred to 20°C and 1.0 mol l^{-1} $NaClO_4$.

Complexes in a 1:2 molar ratio (metal(II):ligand) are shown in the solution with excess ligand, and hydrolytic species are also formed, but the study of these complexes is the object of a future paper.

The solid compounds were characterized by spectroscopic and thermal analysis. For the best reproducibility of results, before thermal analysis any water of absorption was eliminated by flowing each compound at 30°C with

TABLE 1

Equilibrium constants of metal(II)–chromium(III)–DTPA complexes (coordinated water molecules are omitted; $\theta = 20°C$; 1.0 mol l^{-1} $NaClO_4$)

Equilibrium	log K [a]
$Mn^{2+} + CrL^{2-} \rightleftharpoons MnCrL$	4.60
$Fe^{2+} + CrL^{2-} \rightleftharpoons FeCrL$	4.95
$Co^{2+} + CrL^{2-} \rightleftharpoons CoCrL$	5.90
$Ni^{2+} + CrL^{2-} \rightleftharpoons NiCrL$	7.02
$Cu^{2+} + CrL^{2-} \rightleftharpoons CuCrL$	8.85
$Zn^{2+} + CrL^{2-} \rightleftharpoons ZnCrL$	6.17

[a] The uncertainties on the reported values are about ±0.05.

TABLE 2

Electronic and IR spectral data for the analysed compounds

Compound	Diffuse reflectance absorption maxima (cm^{-1})	Most important IR peaks (cm^{-1}) in the carbonyl region
H_5DTPA	–	1740(s), 1705(s), 1642 (s), 1450(m), 1360(ms)
$[Cr(H_2DTPA)(H_2O)]$	18200–25550	1740(m), 1650(s), 1360(ms), 1320(sh)
$Na_2[Cr(DTPA)(H_2O)]2H_2O$	18200–25550	1650(s), 1600(sh), 1400(m), 1360(ms), 1320(sh)
$[Mn\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	18200–25550	1650(s), 1450(m), 1360(ms), 1320(sh)
$[Fe\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	10400–18200–29200	1650(s), 1450(m), 1360(ms), 1320(sh)
$[Co\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	8080–18200–25550	1650(s), 1450(m), 1360(ms), 1320(sh)
$[Ni\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	8950–18200–25550	1650(s), 1450(m), 1360(ms), 1320(sh)
$[Cu\{Cr(DTPA)(H_2O)\}(H_2O)]$	13300–18200–25550	1650(s), 1450(m), 1360(ms), 1320(sh)
$[Zn\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	18200–25550	1650(s), 1450(m), 1360(ms), 1320(sh)

Key: s, strong; m, medium; ms, medium strong; sh, shoulder.

TABLE 3

Thermogravimetric data for the analysed compounds

Compound	Gas	θ (°C) range [a]	Weight loss (%)		Residue	
			Calc [b]	Found	Calc [c]	Found
H_5DTPA	N_2	210–280 (250)	–	43.0		
		280–520	–	41.0		
		520–780	–	16.0	–	0.0
	O_2	210–280 (245)	–	46.6		
		280–580	–	53.4	0.00	0.0
$[Cr(H_2DTPA)(H_2O)]$	N_2	50–170	3.91 (H_2O)	3.9		
		210–360 (280)	19.11 ($2CO_2$)	19.0		
		360–550 (390)	–	59.8	–	17.3
	O_2	210–310 (250)	19.11 ($2CO_2$)	18.9		
		310–325 (320)	–	60.2	16.50	17.0
$Na_2[Cr(DTPA)(H_2O)]2H_2O$	N_2	50–280	9.99 ($3H_2O$)	9.9		
		300–400 (375)	–	30.0		
		400–600	–	27.6	–	32.5
	O_2	300–470 (350)	–	57.4	33.68	32.7
$[Mn\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	N_2	50–225	12.69 ($4H_2O$)	12.3		
		335–470 (395)	–	45.0		
		470–820	–	18.1	–	24.6
	O_2	300–440 (350)	–	61.2	25.89	25.7
$[Fe\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	N_2	50–225	12.67 ($4H_2O$)	12.5		
		260–440 (392)	–	39.0		
		440–700	–	20.8	–	27.7
	O_2	220–520 (290)	–	59.5	27.37	28.0
$[Co\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	N_2	50–225	12.60 ($4H_2O$)	12.5		
		320–470 (395)	–	44.0		
		470–820	–	18.4	–	25.1
	O_2	280–440 (345)	–	61.3	26.42	26.2
$[Ni\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	N_2	50–225	12.61 ($4H_2O$)	12.4		
		320–430 (390)	–	43.8		
		430–800	–	21.6	–	22.2
	O_2	280–440 (335)	–	61.2	26.38	26.2
$[Cu\{Cr(DTPA)(H_2O)\}(H_2O)]$	N_2	50–130	6.67 ($2H_2O$)	6.7		
		130–430 (280) (390)	–	46.7		
		430–820	–	18.8	–	27.8
	O_2	130–270 (250) (265)	–	64.8	28.81	28.5
$[Zn\{Cr(DTPA)(H_2O)\}(H_2O)_3]$	N_2	50–230	12.46 ($4H_2O$)	12.2		
		340–480 (405)	–	42.0		
		480–840	–	22.4	–	23.4
	O_2	290–500 (365)	–	60.3	27.24	27.5

[a] In oxygen atmosphere only the decomposition temperature ranges of anhydrous compounds are reported. Temperature of the maximum decomposition rate is reported in parentheses.

[b] Volatile products are reported in parentheses.

[c] Assuming the following metal oxides or carbonates: Cr_2O_3, MnO, Fe_2O_3, CoO, NiO, CuO, ZnO, Na_2CO_3.

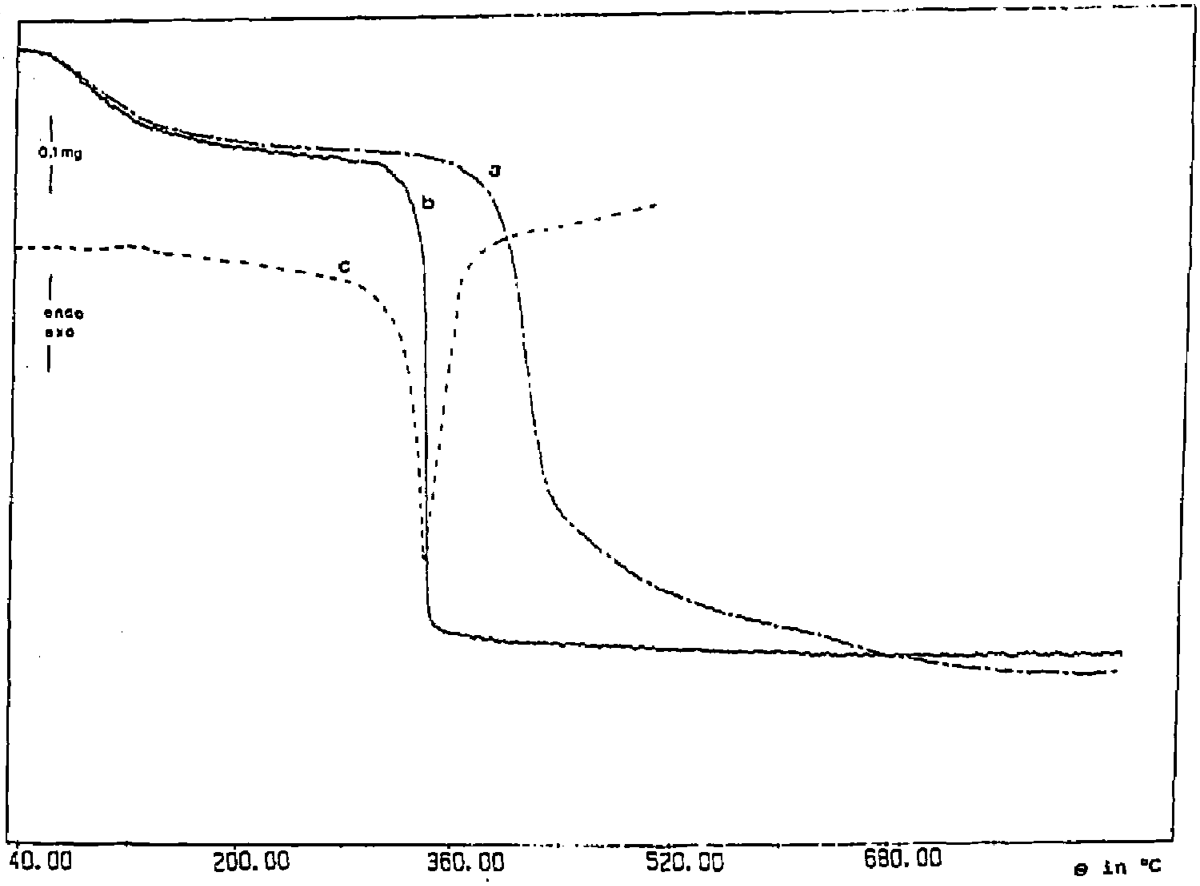

Fig. 1. TG curves of nickel(II)–chromium(III)–DTPA complex (a) in nitrogen, (b) in oxygen; (c) DSC curve in oxygen.

a gas stream up to constant weight. The results are summarized in Tables 2 and 3, and the thermal behaviour is reported in Figs. 1–3.

Because the characteristics of such complexes are similar, for the sake of brevity we give below in detail the discussion of only one compound (nickel(II) complex), whereas the others are discussed briefly underlining its peculiar features.

[Triaqua{(aqua)(diethylenetriaminepentaacetato)chromium(III)}nickel-(II)] [Ni{Cr(DTPA)(H_2O)}(H_2O)$_3$] was prepared and analysed according to the procedure described above. The complex is red–violet like the Cr–DTPA chelating agent, and in aqueous solution it absorbs in the UV–vis with maxima at 386 nm and 545 nm. The presence of the nickel ion does not change either the maxima positions or the molar absorptivities of the chelating agent. The pH of the solution being about 5, taking into account the pH values of the solutions of H_2CrDTPA (pH = 2.8) and of Na_2CrDTPA (pH = 6.9), we assume that the nickel ion is covalently bonded to the ligand and the dinuclear complex is not quite dissociated in water. This assumption is confirmed by the diffuse reflectance spectrum that exhibits absorption bands at about 8950, 18 200 and

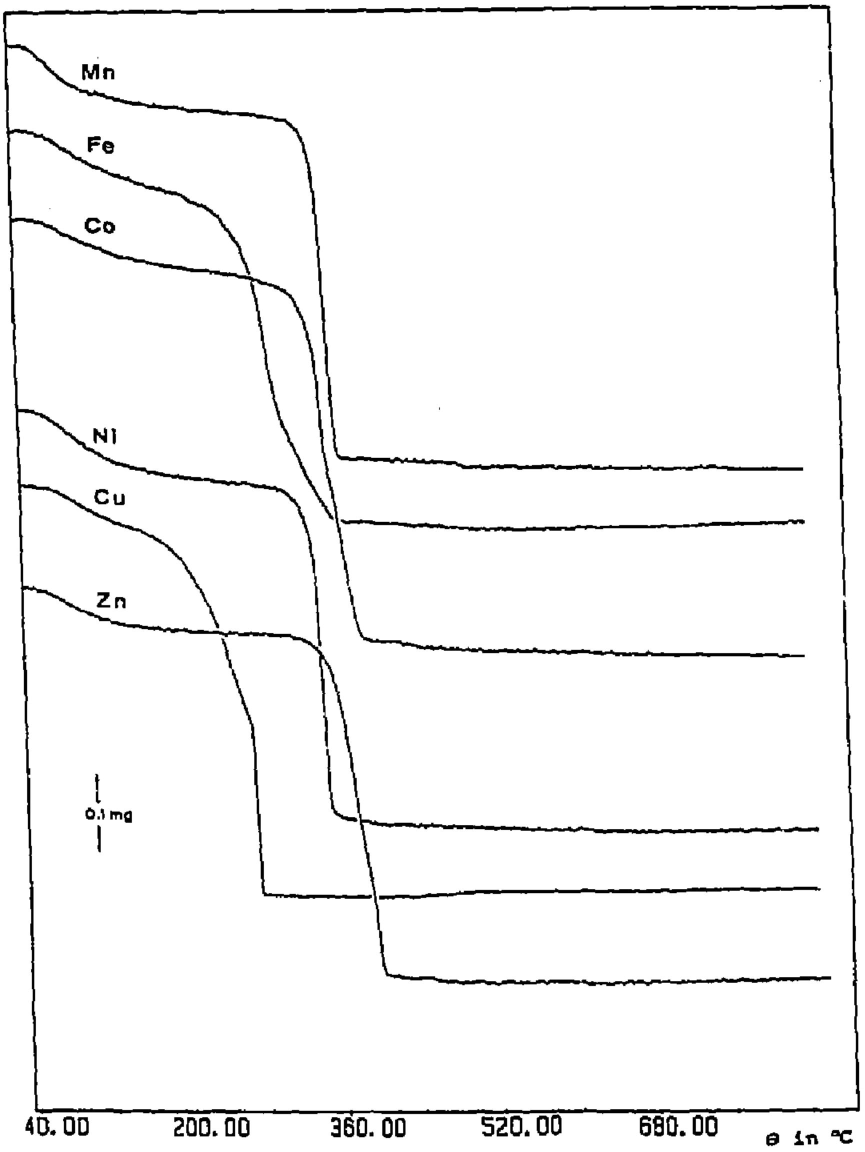

Fig. 2. TG curves of heterobinuclear chelates in oxygen.

25 550 cm^{-1}. The last two bands are also present in the Cr–DTPA spectrum and are assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions, as expected for the octahedral chromium(III) derivatives (4O and 2N). These bands cover up those of the six-coordinated nickel(II) compounds at 13 800–18 500 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$) and 25 300–30 000 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) so only the band at 8950 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{2g}$) is evident [4, 5]. In the IR spectrum the absence of the band at 1740 cm^{-1} (–COOH) and the intense bands around 1650 and 1360 cm^{-1} (assigned to the asymmetric and symmetric stretching frequencies of coordinated carboxylate anion [6]) prove that all the carboxylic groups are involved in the complex with a high degree of covalency in the metal–oxygen bonds.

The thermal decomposition trend of the complex is consistent with the

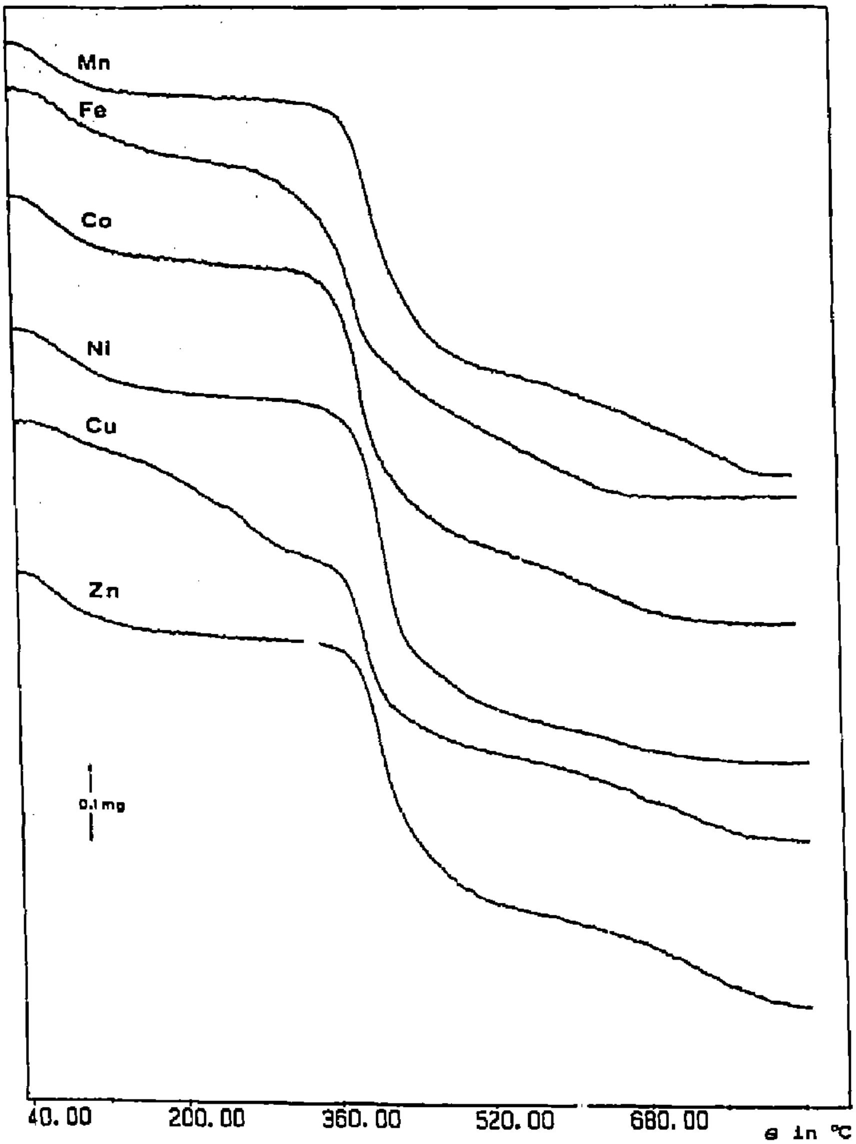

Fig. 3. TG curves of heterobinuclear chelates in nitrogen.

proposed hypothesis. TG in dynamic O_2 atmosphere shows a weight loss which begins at 50°C and is complete near 225°C. In this temperature range the complex loses about 12.4% of its mass, corresponding to four water molecules (calc. 12.61%). Neither CO nor CO_2 are found in the evolved gas. Then, a slow decomposition begins and continues up to about 310°C, where it speeds up suddenly, and at 360°C the loss of weight is 72.5%. The DTG curve shows a strong peak at 335°C, corresponding to the temperature of the maximum decomposition rate. The last traces of carbon are lost near 440°C, the residue consisting mainly of NiO and Cr_2O_3 (calc. 26.38%, found 26.2%). DTA and DSC curves show two peaks connected with the weight losses in TG. An endothermic process accompanies the water evolution between 50 and 225°C ($\Delta H = 2 \times 10^2$ kJ mol^{-1}). In contrast, a strong exothermic reaction occurs in the oxidative thermal decomposition of the complex ($\Delta H = -2 \times 10^3$ kJ mol^{-1}). In dynamic N_2 atmosphere, the dehydration reaction occurs in the same temperature range, but the anhydrous compound begins to lose weight at a higher temperature (around 320°C) and decomposes over a large temperature range in at least two steps (max. decomposition rate at 390°C), leading to a mixture of metals and metal oxides at 800°C (found 22.2%). This decomposition occurs with a weak endothermic process. As found in the chromium–DTPA complex [2], the IR spectrum of the residue (obtained by stopping heating the sample at 430°C, where the TG curve shows a change in direction) exhibits a new band at about 2250 cm^{-1}, suggesting the formation of double or triple carbonium–nitrogen bonds in the decomposition process. This intermediate (very reactive) may justify the explosive reaction observed in oxygen atmosphere.

Other complexes are

[triaqua{(aqua)(diethylenetriaminepentaacetato)chromium(III)}-manganese(II)] [Mn{Cr(DTPA)(H_2O)}(H_2O)$_3$];

[triaqua{(aqua)(diethylenetriaminepentaacetato)chromium(III)}-iron(II)] [Fe{Cr(DTPA)(H_2O)}(H_2O)$_3$];

[triaqua{(aqua)(diethylenetriaminepentaacetato)chromium(III)}-cobalt(II)] [Co{Cr(DTPA)(H_2O)}(H_2O)$_3$];

[aqua{(aqua)(diethlyenetriaminepentaacetato)chromiumIII)}-copper(II)] [Cu{Cr(DTPA)(H_2O)}(H_2O)];

[triaqua{(aqua)(diethylenetriaminepentaacetato)chromium(III)}-zinc(II)] [Zn{Cr(DTPA)(H_2O)}(H_2O)$_3$]

These compounds show spectroscopic and thermal behaviour similar to that of the nickel–chromium binuclear complex. The aqueous solutions are moderately acid, red–violet with a blue component only in the case of the copper compound, which shows a new large absorption band between 700 and 800 nm besides those at 386 and 545 nm. Spectroscopic data from IR and diffuse reflectance spectra (Table 2) confirm that all the carboxylic groups of DTPA are involved in the coordination bonds and the metal ions are six-coordinated with the exception of copper(II), which is four-coordinated. The decomposition trends, in oxygen or nitrogen atmospheres, do not show significant differences compared to the nickel complex: the decomposition occurs very rapidly in oxygen in only one step with a strong exothermic process, whereas in nitrogen two separate steps are evident.

The behaviour of the complexes with copper(II) and iron(II) are different. The former [2] is thermally destabilized by the copper chelation and starts to decompose at about 130°C. This decomposition temperature is not much dependent on the furnace atmosphere (maximum reaction rates at 250°C and 280°C in O_2 or N_2 respectively) but in oxygen a strong exothermic reaction is superimposed and the decomposition is almost complete at about 270°C (maximum at 265°C). In contrast, the decomposition process is slower in nitrogen (maximum at 390°C) and similar to that of the other complexes.

The iron(II) compound in N_2 exhibits a decomposition trend as expected, with two separate steps, although it slowly begins a weight loss at about 260°C (maximum at 392°C). In contrast in O_2 the decomposition temperature (about 220°C; maximum at 290°C) is clearly lower than expected. This behaviour could be justified by iron(II) oxidation to iron(III), as found by the analysis of the residue obtained at the beginning of the decomposition process.

CONCLUSIONS

Chromium(III)–DTPA complex can act as a chelating agent, forming heteropolinuclear complexes with metal(II) ions. In equimolar aqueous solutions, complexes in a 1:1 molar ratio metal(II):chromium(III)–DTPA prevail, the stability of which follows the Irwing–Williams order [7] Zn(II) > Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II).

The order is the same as for metal–iminodiacetic acid complexes [8], but the corresponding stability constants are lower, according to the lower basicity of the ligand.

These complexes have been precipitated as neutral species by ethanol addition and characterized by spectroscopy and thermal analysis.

The IR data proves that both free carboxylate groups of the chromium–DTPA chelating agent are involved in the chelation with a high degree of covalency in the metal(II)–oxygen bonds. The diffuse reflectance spectra, by analogy with the spectrochemical series of frequencies [4], suggest that chromium(III) and metal(II) ions are six-coordinated with an octahedral configuration, except the copper(II) ion, which is four-coordinated. A comparison of the thermal behaviour of DTPA (H_5L), H_2CrL, Na_2CrL and MeCrL complexes enables evaluation of the influence of the metal(II) and/or chromium(III) chelation on the stability of the ligand.

As partly reported in a previous paper [2], the first decomposition step of DTPA involves the decomposition of free iminodiacetic groups with CO_2 evolution. This process occurs with a strong endothermic reaction in both N_2 and O_2 atmospheres, as proved by the DSC curves.

In an oxidizing atmosphere an exothermic reaction is superimposed on the first process and the organic molecule burns without leaving a residue at 580°C. The anhydrous H_2CrL complex begins to decompose at the same temperature with CO_2 evolution and a less endothermic reaction than that of DTPA, proving that the decomposition of the free iminodiacetic group is unaffected by the presence of chromium in the molecule. The gaseous atmosphere in the furnace influences the next decomposition process: in O_2 the reaction is strongly exothermic, whereas in N_2 the decomposition occurs slowly over a large temperature range and the residue consists mainly of Cr_2O_3.

When the sodium ions take the place of the hydrogen ions in Na_2CrL, the iminodiacetic group is thermally stabilized and this compound starts to decompose at a higher temperature without any endothermic reaction in O_2 atmosphere. In fact, the DSC curve shows two exothermic peaks: the first corresponds to the decomposition of the organic molecule, the second occurs over the temperature range for which the TG curve shows only a little weight loss, probably due to the interaction of Cr_2O_3 and Na_2CO_3 with partial formation of chromate, as found by the chemical and spectroscopic analysis of the residue. This reaction also occurs in N_2 atmosphere, as proved by the same exothermic process in the DSC curve.

Thermogravimetric and calorimetric analyses of the dinuclear complexes are similar to those of the disodium salt. In a dynamic oxygen atmosphere the decomposition reaction occurs (after dehydration) in only one step with a strongly exothermic process, whereas in nitrogen the initial decomposition temperature is delayed and the complexes decompose over a large temperature range in at least two separate steps, with weakly endothermic reactions. In contrast, the nature of the coordinated metal(II) ion is less important, the thermal stability of the complexes depending mainly on the chromium ion present in all the analysed compounds. Therefore, it is very difficult to give a thermal stability order. An exception to this rule is the thermal behaviour of the copper(II) complex, the destabilizing effect of which is well-known [9]. The iron(II) complex also shows different behaviour, decomposing in oxygen near 220°C by oxidation to iron(III).

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