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BINUCLEAR CHELATES OF DIETHYLENETRIAMINE-PENTAACETIC ACID WITH CHROMIUM(III) AND OXOVANADIUM(IV) IONS

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Abstract

The reactions of diethylenetriaminepentaacetic acid (DTPA = H_5L) or chromium(III)-DTPA, a 'chelating agent', with oxovanadium(IV) were investigated in aqueous solution by potentiometric methods. Homo- and hetero-binuclear species were evidenced as well as mixed complexes with hydrogen or hydroxide ions. The stability constants for these equilibria were calculated in 1.0 mol l^{-1} $NaClO_4$ solution at 20°C. The mononuclear $(VO)H_3L{\cdot}H_2O$ and the heterobinuclear $(VO)CrL{\cdot}5H_2O$ complexes were also obtained as solid compounds and were characterized by IR spectroscopy and thermoanalytical techniques (TG and DSC).

Keywords: chromium(III), complexes, DTPA, oxovanadium(IV), stability constants

Introduction

Diethylenetriaminepentaacetic acid (DTPA = H_5L) reacts with chromium(III) forming a 1:1 chelate. This complex is inert and one iminodiacetate group is free from coordination. For this reason, it can be considered as a large molecule of N-substituted iminodiacetic acid [1]. The formation of heterobinuclear complexes of some divalent metal ions with this 'metal complex' chelating agent has been investigated in aqueous solution and the obtained solid compounds have been characterized [2–4].

In the present paper reactions of oxovanadium(IV) with DTPA and with chromium–DTPA complex are reported.

The stability constants of the homo- and hetero-binuclear complexes were calculated and some data on the synthesis, spectroscopic characteristics and thermal properties of solid compounds were described.

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Experimental

Apparatus

Hydrogen ion concentrations were measured with an Amel 337 potentiometer (precision 0.1 mV), interfaced with a Macintosh computer for the automatic recording and treatment of data. A Crison 2030 microburette was used with a 5.00 ml syringe, with a precision of 1/2500 of the total volume. An Ingold glass electrode was calibrated in concentration units, so that, in this paper, the symbol *pH* corresponds to $-\log[H^+]$. The reference electrode was a double junction calomel electrode, the bridge electrolyte being 1.0 mol l^{-1} $NaClO_4$.

The thermoanalytical measurements were carried out with a Perkin-Elmer TSG-2 thermal analyser, connected to a model 3600 Data Station, and a DSC-7 differential scanning calorimeter. TG and DSC runs were made in a stream of nitrogen or oxygen (flow rate about 50 ml min^{-1}). The heating rate was 10°C min^{-1}, with 2–3 mg samples.

IR spectra were recorded on a Perkin-Elmer 125 grating spectrophotometer.

Reagents

Diethylenetriaminepentaacetic acid (Fluka) and chromium(III)-DTPA complex (disodium salt, Aldrich) were used. The purity of these compounds was confirmed by potentiometric titrations with sodium hydroxide and thermal analysis, respectively.

A stock solution of oxovanadium(IV) perchlorate was prepared from oxovanadium(IV) sulphate (Merck) and analyzed as already described [5]. The excess of perchloric acid in the solution was controlled by Gran titration [6].

Other chemicals were of analytical grade.

Distilled-deionized water was used throughout.

Preparation of the solid compounds

The heterobinuclear complex with 1:1:1 VO:Cr:DTPA molar ratio was prepared by adding 150 ml of ethanol to 50 ml of equimolar solution of oxovanadium(IV) sulphate and chromium(III)-DTPA (50 mmol l^{-1}) at $pH=3$.

The violet precipitate was filtered off, washed with water-ethanol mixture until free of sulphate, then with ethanol, and finally dried in vacuum. Analysis of the compounds confirmed the formula $(VO)CrL\cdot 5H_2O$.

The oxovanadium(IV)-DTPA complex was prepared by adding 0.9 g of H_5L to 40 ml of 0.013 mol l^{-1} oxovanadium(IV) sulphate. The solution was brought to the boil and then cooled to room temperature.

The thin blue precipitate formed was filtered off and washed with water until free of sulphate. The precipitate was dried in vacuum. Analysis of the compound confirmed the formula $(VO)H_3L\cdot H_2O$.

We were not able to prepare a 2:1 (VO:DTPA) solid compound.

Results and discussion

The complex formation of chromium(III) with DTPA has already been studied in aqueous solution and a 1:1 protonated species (CrH_2L) has been found to be formed at $pH=1$. The corresponding acid-base equilibria have been investigated by potentiometric and spectrophotometric methods [1].

Starting from the chromium-DTPA species, potentiometric titrations were performed with sodium hydroxide of the ligand (chromium complex) in the acid form, in the absence and presence of oxovanadium(IV) ions in molar ratios of 1:1 and 1:2. Comparison of the curves indicates that in the first part of the titration, at $pH<4$, only 1:1 complexes are formed even with an excess of ligand. Furthermore, in the second part of the curves, at $pH>4$, the formation of mixed complexes with OH^- is evident, according to the reactions:

$$(VO)CrL + OH^- \rightleftarrows (VO)CrL(OH)^-$$

$$(VO)CrL(OH)^- + OH^- \rightleftarrows (VO)CrL(OH)_2^{2-}$$

Therefore, in the first *pH* range, potentiometric titrations were performed according to Leden [7]. During each titration, metal ion concentration, C_M, and hydrogen ion concentration, C_H, were kept constant, while the ligand concentration was progressively increased (up to 12.5 mmol l^{-1}). By working at different values of C_M and C_H (from 2.05 to 5.15 mmol l^{-1} the existence of polynuclear and mixed complexes can be checked. Indeed, if the formation function is independent of C_M, formation of polynuclear complexes is considered negligible, if the formation function is independent of C_H, mixed complexes with hydrogen ions are not present in solution.

From the protonation constants of the ligand, determined in the same experimental conditions [1], the formation function, $\bar{n} = f(\log[CrL^{-2}])$, can be obtained. The amounts of hydrolysis products of the metal ion [8] were proved to be negligible in our conditions. Analysis of the formation function shows that the form prevailing in solution is the (VO)CrL species, the stability constant of which has been calculated.

In the second part of the titration curves, in which hydroxo-complexes are formed, the stability constants were calculated by applying the curve fitting method proposed by Sillèn [9] to the formation function $\bar{n}_H = f(pH)$.

Homonuclear complexes of oxovanadium(IV) with DTPA have been studied earlier in 0.5 mol l^{-1} $NaClO_4$ concentration and at 25°C, and 1:1 and 2:1 complexes have been found to exist [10].

In order to compare the values of the stability constants of the homo- and hetero-binuclear complexes, this system was reconsidered under the new experimental conditions (in 1.0 mol^{-1} $NaClO_4$ and at 20°C) and in a wide *pH* range (from 1.9 to 4), performing titrations at 1:1 and 2:1 metal-DTPA molar ratios with sodium hydroxide and with perchloric acid. From the analysis of the

Table 1 Logarithms of the equilibrium constants of the DTPA complexes with chromium(III) and oxovanadium(IV) ions. T=20°C, ionic medium 1.0 mol l^{-1} $NaClO_4$

Equilibrium	log*K*	Ref.
$CrL^{2-}+H^+ \rightleftarrows CrHL^-$	6.15	1
$CrHL^-+H^+ \rightleftarrows CrH_2L$	2.85	1
$CrH_2L+H^+ \rightleftarrows CrH_3L^+$	1.45	1
$VO^{2+}+CrL^{2-} \rightleftarrows (VO)CrL$	7.25 ± 0.05	this work
$(VO)CrL+H_2O \rightleftarrows (VO)CrL(OH)^- + H^+$	−4.68 ± 0.05	"
$(VO)CrL(OH)^-+H_2O \rightleftarrows (VO)CrL(OH)_2^{2-} +H^+$	−6.64 ± 0.05	"
$VO^{2+}+L^{5-} \rightleftarrows (VO)L^{3-}$	16.45 ± 0.05	"
$(VO)L^{3-}+H^+ \rightleftarrows (VO)HL^{2-}$	7.15 ± 0.05	"
$(VO)HL^{2-}+H^+ \rightleftarrows (VO)H_2L^-$	2.50 ± 0.05	"
$(VO)H_2L^-+H^+ \rightleftarrows (VO)H_3L$	1.68 ± 0.1	"
$VO^{2+}+(VO)L^{3-} \rightleftarrows (VO)_2L$	6.90 ± 0.05	"

The error represents the mean deviation.

data, using protonation constants of DTPA in our conditions [11, 12], the stability constants of the complexes were recalculated and two further protonated forms were evidenced. The overall results are summarized in Table 1.

The values of the protonation constants for the equimolar complexes of oxovanadium(IV) with DTPA are very similar to those of chromium(III) with this ligand. However, in the former system, no hydrolytic complexes are formed, because oxovanadium(IV) is usually penta-coordinated (while chromium(III) is hexa-coordinated and one water molecule is bound to the metal ion in the complex).

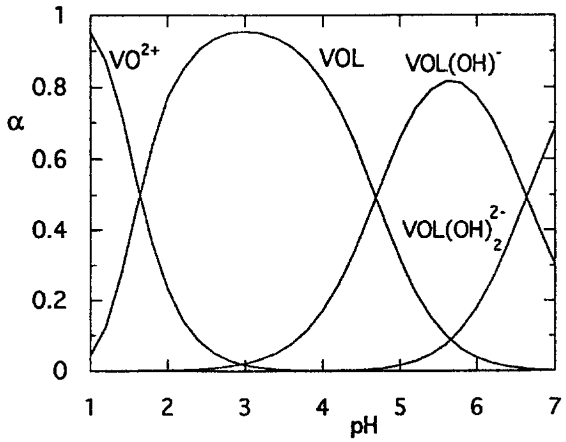

Fig. 1 Distribution diagram for the system (VO)–CrL complexes under equimolar conditions

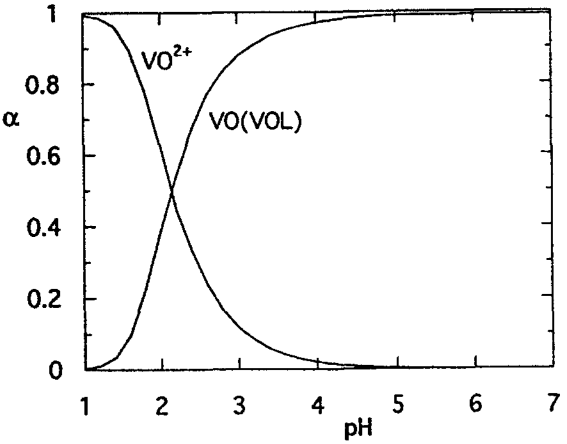

Fig. 2 Distribution diagram for the system (VO)–(VO)L complexes under equimolar conditions

The structures of the homo- and hetero-binuclear complexes are similar, as can be seen by comparing the stability constants with the ligand basicity (the ligand is the *ML* complex, *M*=Cr or VO). The log*K*/logβ_{031} ratio is of the same order in both cases (0.69 for VO-Cr-DTPA, 0.61 for VO-VO-DTPA) as well as for the oxovanadium(IV)-iminodiacetate complex (0.69) [13].

The distribution diagrams for both binuclear complexes of DTPA are shown in Figs 1 and 2, and are referred to equimolar conditions.

Study of the solid compounds

(VO)CrL·5H$_2$O

The IR spectrum of this compound is similar to those of other hetero-binuclear complexes previously described [3]. The absence of the band at 1740 cm^{-1} ($\nu_{c=o}$) and the intense bands at 1646 cm^{-1} and 1362 cm^{-1}, assigned to the asymmetric and symmetric stretching frequencies of carboxylate anion [14], prove that all carboxylate groups are involved in the chelation with a high degree of covalency in the metal–oxygen bonds.

The TG curve recorded in O$_2$ (Fig. 3, curve a) shows that the water content is lost below 120°C (calcd. 14.92%, found 15.3%); neither CO nor CO$_2$ was found in the evolved gas. The anhydrous compound slowly loses mass up to about 270°C, then the process speeds up suddenly and the residue, formed at 340°C, consists mainly of (VO)CO$_3$ and Cr$_2$O$_3$ (calcd. 33.64%, found 32.9%). This decomposition process is a strongly exothermic reaction, as showed by the DSC curve (Fig. 4, curve a). At about 530°C (VO)CO$_3$ decomposes and the residue obtained at 600°C consists of V$_2$O$_5$ and Cr$_2$O$_3$ (calcd. 27.68%, found 28.1%). In dynamic N$_2$ atmosphere (Fig. 3, curve b) dehydratation occurs in

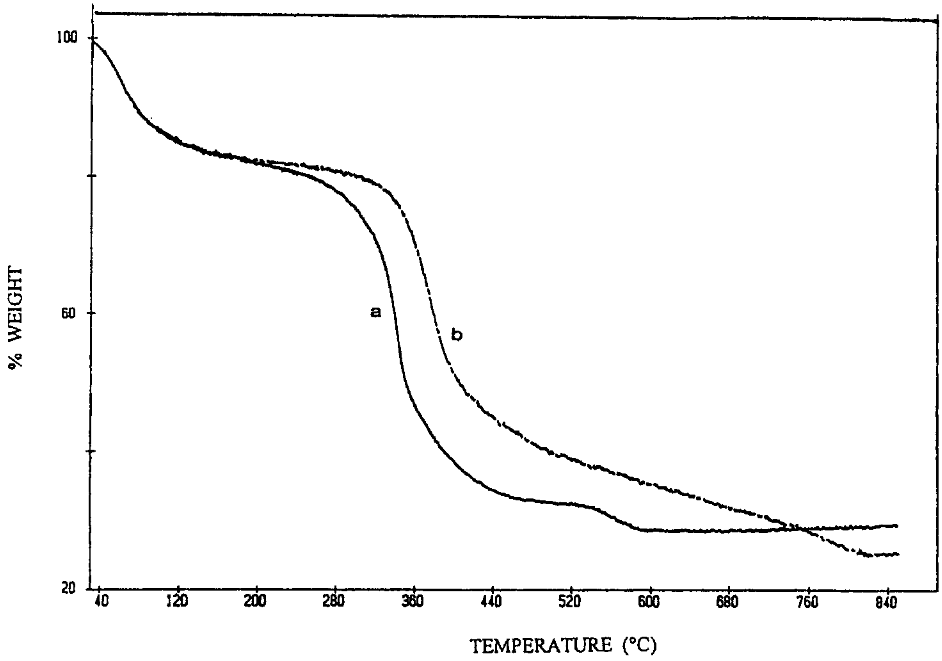

Fig. 3 TG curves of the (VO)CrL·5H_2O complex in oxygen (a) and in nitrogen (b) atmosphere; heating rate 10°C min^{-1}

the same temperature range, but the decomposition process of the anhydrous compound is delayed (maximum rate at 380°C) and complete decomposition occurs over a large temperature range, connected with weakly endothermic processes (Fig. 4, curve b).

Comparison of the TG and DSC curves of this complex with those of the hetero-binuclear chelates of other transition metal ions with chromium(III)-DTPA proves that, also in this case, the temperature and the decomposition trend of the complex is conditioned by the thermal stability of the 'metal complex' chelating agent.

(VO)H_3L·H_2O

The bands of the carboxyl group (1744 cm^{-1} and 1230 cm^{-1}) as well as the bands of the covalent bond (1645 cm^{-1} and 1360 cm^{-1}) are present in the IR spectrum, proving that one iminodiacetate group of the DTPA is free from coordination.

Potentiometric titration of the aqueous solution of the compound confirms the presence of three hydrogen ions per mole of complex, the dissociation constants being in agreement with those found in the equilibrium study in aqueous solution.

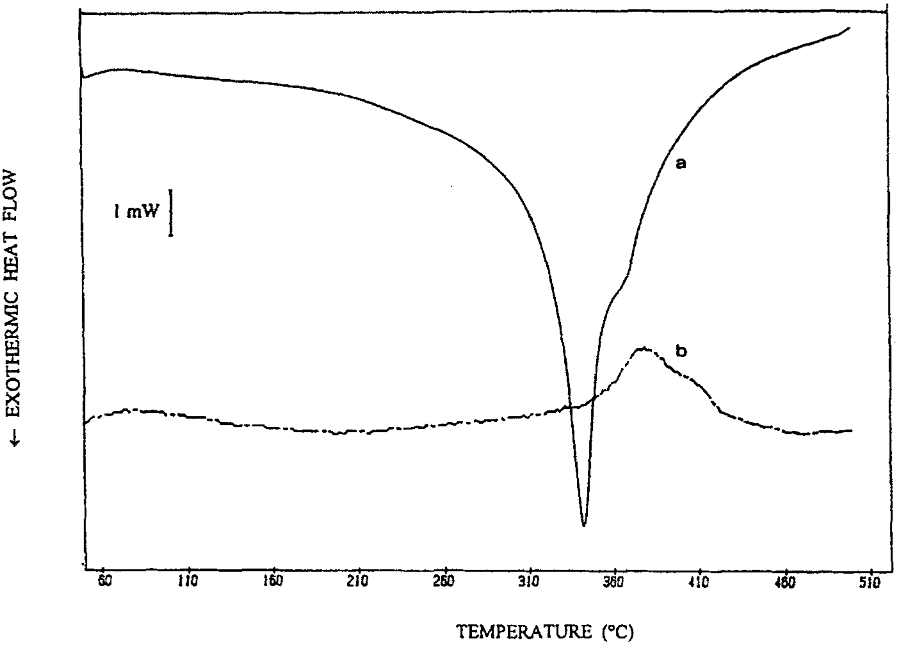

Fig. 4 DSC curve of the $(VO)CrL{\cdot}5H_2O$ complex in oxygen (a) and in nitrogen (b) atmosphere; heating rate 10°C min^{-1}

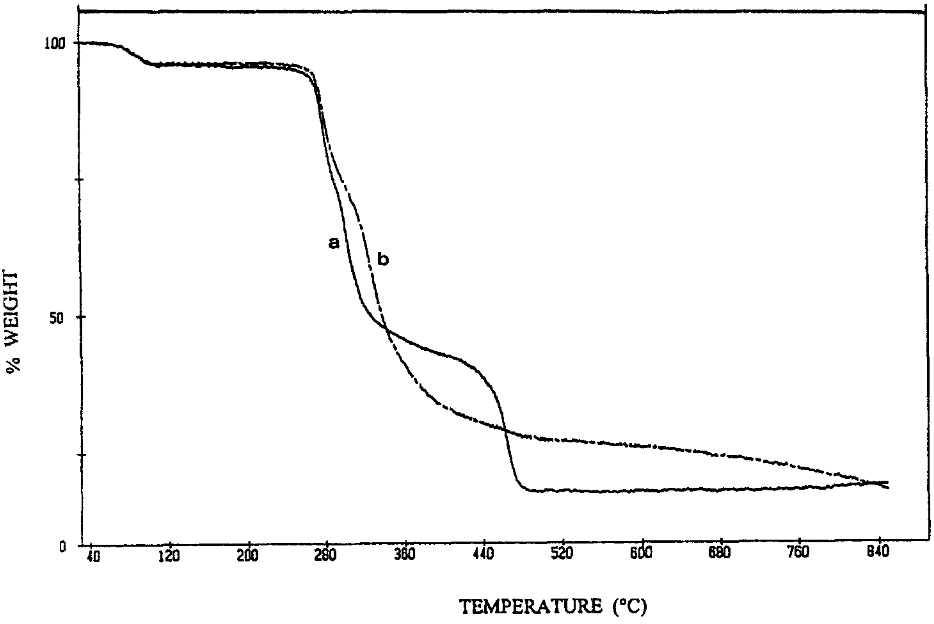

Fig. 5 TG curves of the $(VO)H_3L{\cdot}H_2O$ complex in oxygen (a) and in nitrogen (b) atmosphere; heating rate 10°C min^{-1}

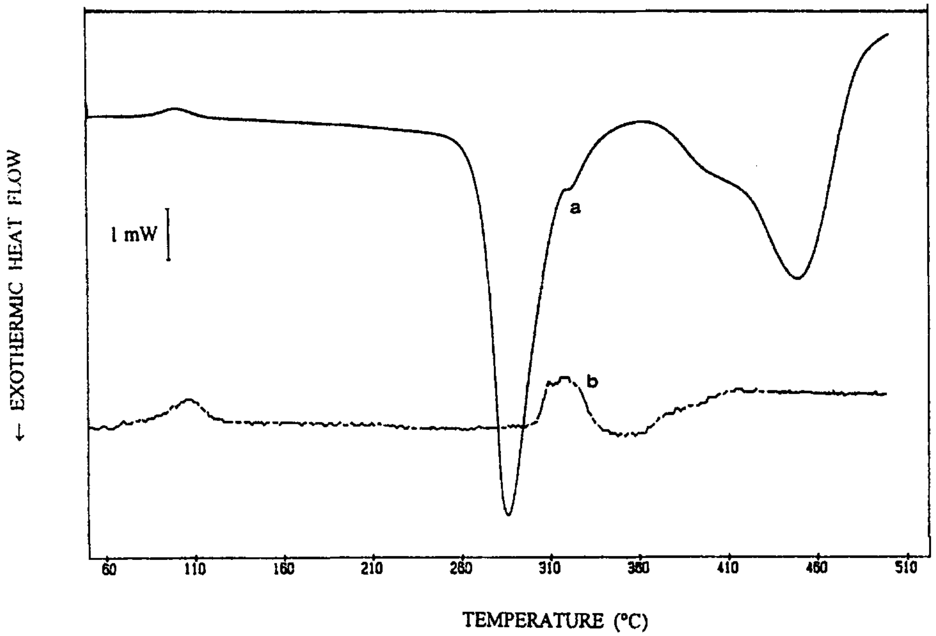

Fig. 6 DSC curves of the (VO)$H_3L \cdot H_2O$ complex in oxygen (a) and in nitrogen (b) atmosphere; heating rate 10°C min^{-1}

The TG curve recorded in dynamic O_2 atmosphere (Fig. 5, curve a) exhibits the first mass loss in the temperature range 70–110°C, due to the evolution of one water molecule (calcd. 3.78%, found 4.1%). The anhydrous compound is stable up to 255°C, then it decomposes in a three-step process yielding a residue at 480°C, consisting mainly of V_2O_5 (calcd. 19.09%, found 19.0%). An endothermic process accompanies water evolution and some sharp exothermic reactions occur during the oxidative thermal decomposition of the complex (Fig. 6, curve a).

In dynamic N_2 atmosphere (Fig. 5, curve b) the thermal behaviour is similar to that in an O_2 atmosphere up to 280°C, then the decomposition rate becomes different and no constant mass is attained up to 840°C. This decomposition is connected, as expected, with weakly endothermic processes (Fig. 6, curve b).

The TG and DSC curves prove that the thermal stability of (VO)H_3L is higher than that of the CrH_2L 'metal-complex' chelating agent, which starts to decompose at 210°C [2]. It is probable that replacement of chromium(III) by oxovanadium(IV) stabilizes the free iminodiacetate group.

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