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4-ETHYLPHENYLAMINO-N,N-DIACETIC ACID

Synthesis, characterization, thermal behaviour and complexing capacity

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The thermal behaviours of 4-ethylphenylamino-N,N-diacetic acid (H_2EFAD) and its monosodium salt have been investigated from their TG and DSC curves. Likewise, some 4-ethylphenylamino-N,N-diacetato compounds of several di- and trivalent metal ions have been synthesized, characterized and studied by TG and DSC. Most of these compounds show a 1 : 1 stoichiometry and contain crystallization or coordination water. From the DSC curves, the dehydration enthalpies have been calculated. The nature of the pyrolysis residues have been investigated by X-ray diffraction methods.

Numerous studies have been performed on the complexing capacity of iminodiacetic acid towards different metal ions in aqueous solution or the solid phase. In general, in the resulting complexes iminodiacetic acid and its derivatives act as mono-, bi- or tridentate ligands [1–8]. Investigations on the thermal behaviour of iminodiacetic acid, its derivatives and their metal complexes are scanty [9–12]. In order to amplify the chemical information concerning these compounds, we are continuing studies on the thermal stabilities of different iminodiacetic acid derivatives and their complexes [13–15]. As party of this research, in this paper we describe the thermal behaviour of 4-ethylphenylamino-N,N-diacetic acid (H_2EFAD) and its compounds with Na(I), Al(III), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Cd(II), Ba(II) and Pb(II) ions.

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Experimental

The neutral sodium salt of H_2EFAD was prepared by reaction in basic medium (Na_2CO_3) between 4-ethylphenylamine and monochloroacetic acid. Subsequent treatment of this salt (Na_2EFAD) with 5 *N* HCl yielded the monosodium salts (pH 3). To prepare the free acid H_2EFAD, 3.7 g of NaHEFAD was dissolved in 100 ml of water. This aqueous solution was taken in a separating funnel, and a mixture (1 : 1) of diethyl ether and 5 *N* hydrochloric acid was added. A white precipitate appeared, which was slowly transferred to the organic layer. The extraction process was repeated several times and the extract was concentrated by evaporation. By the slow addition of petroleum ether, H_2EFAD was obtained. The precipitate was filtered by suction, washed with petroleum ether and dried in vacuum over H_2SO_4 (yielded 54% with respect to the monosodium salt).

4-Ethylphenylamine-N,N-diacetato compounds were synthesized in a similar way: 7.7 mmol of NaHEFAD was suspended in 30 ml of distilled water; to this solution, several drops of 2 *M* NaOH solution were added with stirring until all the salt was dissolved. At this point, a solution containing 9.2 mmol of the corresponding metal nitrate was slowly added. In all cases, the compounds precipitated rapidly. The precipitates were separated from the mother liquor, washed with cold water, and then dried in vacuum over H_2SO_4 at room temperature.

The elemental analyses of C, H, and N in these compounds were performed in the microanalytical laboratories of the Department of Bioorganic Chemistry (C.S.I.C.), Barcelona. The data obtained are shown in Table 1.

The infrared spectra were recorded in the range 4000–200 cm^{-1} on a Beckman 4250 spectrophotometer, with KBr and polyethylene as dispersant agents.

Thermogravimetry was carried out under dynamic conditions (100 $ml \cdot min^{-1}$ of pure air) with a Mettler TG–50 thermobalance at a heating rate of 10 $deg \cdot min^{-1}$, with samples varying in weight from 4.28 mg (monosodium salt) to 13.95 mg (Cd(II) compound). In all cases, the temperature range 35–600° was studied.

DSC curves were taken at a heating rate of 5 $deg \cdot min^{-1}$ in a static atmosphere of air in the temperature range 35–500°. In these cases, the sample weights employed varied between 2.03 mg (Al(III) compound) and 4.98 mg (Cd(II) compound).

X-ray measurements were made on a Philips PW 1710 diffractometer provided with a Philips PW 1050/81 goniometer.

Table 1 Chemical analysis data

Compound	C, %		H, %		N, %		Composition
	Calcd.	Found	Calcd.	Found	Calcd.	Found	
Al(EFAD)(HEFAD)·3H_2O	52.17	52.01	6.02	6.05	5.07	5.31	$AlC_{24}H_{33}N_2O_{11}$
Mn(EFAD)·H_2O	46.77	46.22	4.91	5.10	4.54	4.48	$MnC_{12}H_{15}NO_5$
Fe(EFAD)·H_2O	46.63	46.06	4.89	5.11	4.53	4.38	$FeC_{12}H_{15}NO_5$
Co(EFAD)·4H_2O	39.36	40.03	5.78	5.50	3.82	4.07	$CoC_{12}H_{21}NO_8$
Ni(EFAD)·2H_2O	43.68	44.19	5.19	5.16	4.24	4.20	$NiC_{12}H_{17}NO_6$
Zn(EFAD)·H_2O	45.23	45.71	4.75	4.84	4.40	4.42	$ZnC_{12}H_{15}NO_5$
Cd(EFAD)·H_2O	39.42	39.62	4.14	4.18	3.83	3.80	$CdC_{15}H_{15}NO_5$
Ba(EFAD)	38.68	39.02	3.52	3.36	3.76	3.76	$BaC_{12}H_{13}NO_4$
Pb(EFAD)	32.58	33.42	2.96	2.99	3.17	3.28	$PbC_{12}H_{13}NO_4$

Results and discussion

Using the preparative methods described above, we isolated nine 4-ethylphenylamine-N,N-diacetato complexes, whose simplified formulae, deduced from the analytical data, are collected in Table 1. With the exception of the Al(III) compound, these compounds show a stoichiometry ratio M(II)/EFAD = 1/1, and contain crystallization or coordination water molecules (only Ba(II) and Pb(II) are anhydrous).

The TG and DSC curves for the isolated 4-ethylphenylamino-N,N-diacetic acid and its monosodium salt are given in Fig. 1. From the TG and DSC in Fig. 1 it can be seen that H_2EFAD is stable in a short temperature range (35–98°); at higher temperature it undergoes a rapid and strong decomposition process, which finishes at ~450° with total elimination of the sample. The DSC curve of H_2EFAD displays an endothermic effect at ~98°, corresponding to fusion. The value of the fusion

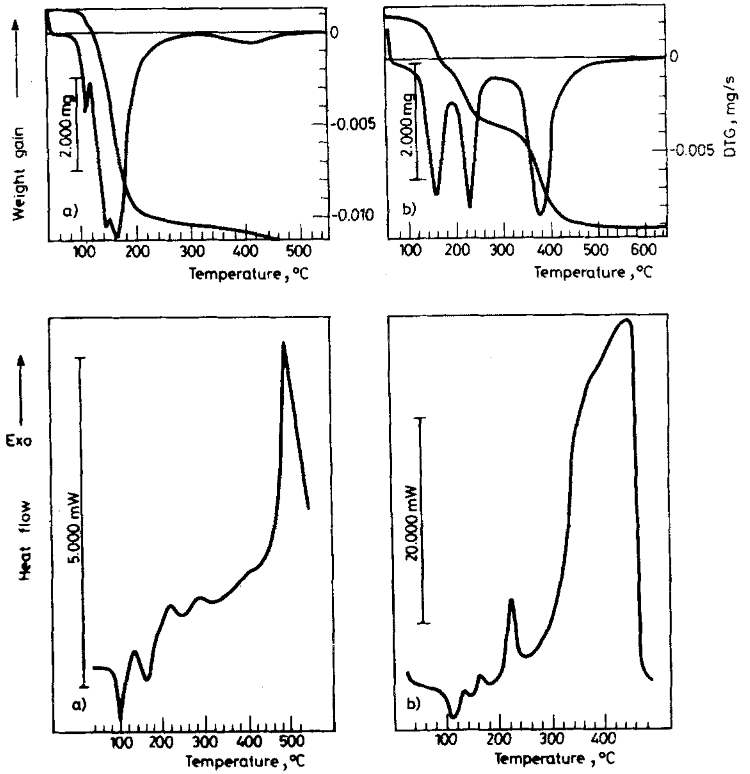

Fig. 1 TG and DSC curves for H_2EFAD (a) and NaHEFAD (b)

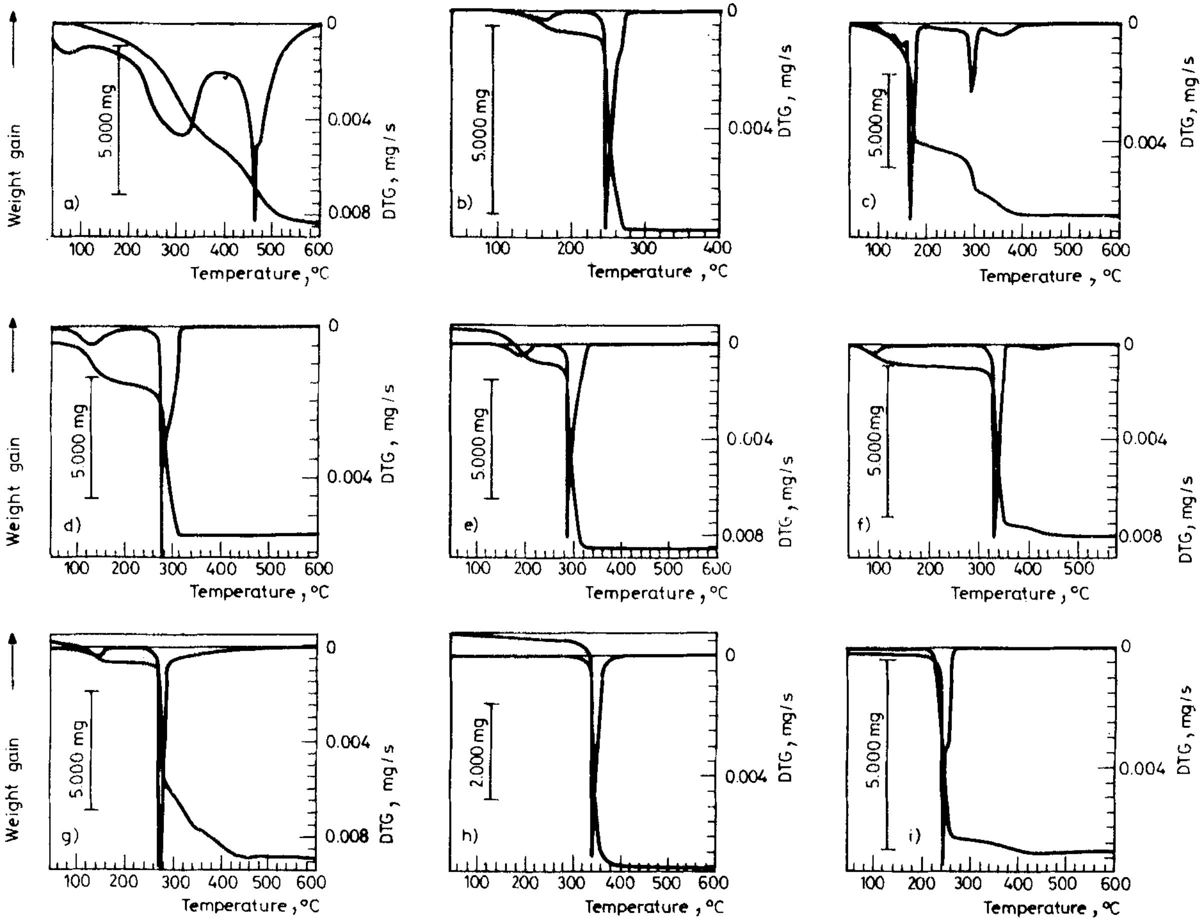

Fig. 2 TG curves for the 4-ethylphenylamine-N,N-diacetatos of: Al(III) (a); Mn(II) (b); Fe(II) (c); Co(II) (d); Ni(II) (e); Zn(II) (f); Cd(II) (g); Ba(II) (h) and Pb(II) (i)

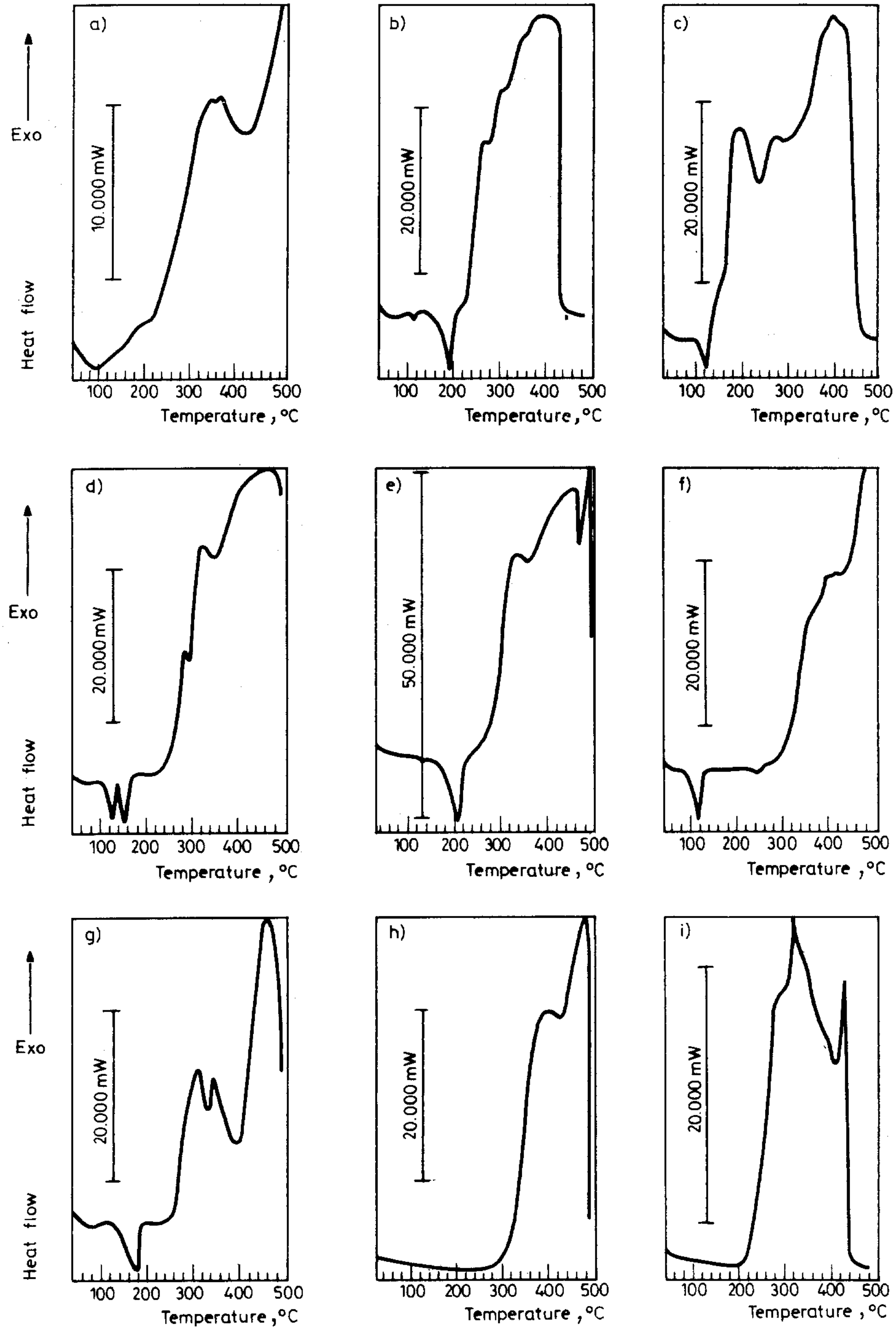

Fig. 3 DSC curves for 4-ethylphenylamine-N,N-diacetato of: Al(III) (a); Mn(II) (b); Fe(II) (c); Co(II) (d); Ni(II) (e); Zn(II) (f); Cd(II) (g); Ba(II) (h) and Pb(II) (i)

enthalpy calculated from the area of this effect was 22 kJ · mol^{-1}. This value is very similar to the fusion enthalpy found for 2,6-xylyliminodiacetic acid [13].

Liquid H_2EFAD decomposed immediately, showing a new endothermic effect at 166°, which we have assigned to the elimination of one water molecule per molecule of acid. This dehydration process, in which 7.7% of the initial sample is eliminated, can be observed in the TG curve. The measured value is in good agreement with the theoretical value (7.59%). This fact accords with the results obtained by Khramov et al. [9] and González-Vilchez et al. [11] in their studies on the thermal behaviour of iminodiacetic acid and its disodium salt, and a similar decomposition mechanism for H_2EFAD could therefore be proposed.

This assumption is supported by the infrared spectrum of H_2EFAD, which appears with that of its monosodium salt in Fig. 4. The infrared spectrum of H_2EFAD clearly indicates that in the solid phase H_2EFAD has a dimeric structure, with bands at 2600 cm^{-1} and 2520 cm^{-1} (weak) (ν(—O—H)), 1710 cm^{-1} (ν(C=O)) and 880 cm^{-1} (δ(O—H)) characteristic of dimeric carboxylic acids [15–16].

The dehydrated H_2EFAd is thermally unstable and decomposes pyrolytically to give exothermic effects at 220, 300 and 490° in its DSC curve.

The TG and DSC curves for NaHEFAD show a marked difference from those for H_2EFAD. Thus, the thermogravimetric curve exhibits a first weight loss effect in the temperature range 100–170°, where 21.9% of the initial sample weight is eliminated. The observed weight loss for this process is in good agreement with the theoretical value calculated for the elimination of one molecule of water and one molecule of carbon dioxide (22.38%). Both processes appear in the DSC curve of NaHEFAD, as endothermic effects at 113 and 140° On the other hand, the hydrated nature of this monosodium salt was corroborated by chemical analysis [5] and is reflected in the infrared spectrum of this salt (Fig. 4, band at 3450 cm^{-1}). The dehydrated and partially decarboxylated compound decomposes in the temperature range 170–500°, with exothermic effects at 220 and 440° in its DSC curve. At 500°, the residual weight (14.9%) is in good agreement with the required value of Na_2O_2 (14.08%), which, under the experimental conditions used to obtain the TG curve of NaHEFAD, is the most stable sodium compound [17].

The TG and DSC curves for the 4-ethylphenylamino-N,N-diacetato compounds of the divalent and trivalent metal ions are given in Figs 2 and 3, respectively. For all the isolated complexes, two processes can occur: (i) dehydration (except for the Ba(II) and Pb(II) compounds) and (ii) pyrolytic decomposition. Thermoanalytical data on each of the dehydration processes are tabulated in Table 2. The high dehydration enthalpies for most of these compounds suggest a strong interaction of the water molecules with the metal ions. Once dehydrated, the 4-ethylphenylamino-N,N-diacetato compounds decompose pyrolytically, giving the residues indicated

Table 2 Thermoanalytic data for dehydration processes of 4-ethylphenylamino-N,N-diacetato compounds

Process	Weight loss, %		Effect	Temperature	ΔH, kJ·mol^{-1} H_2O
	Found	Calcd.			
Al(EFAD)(HEFAD)·$3H_2O$ → Al(EFAD)(HEFAD)	10.1	9.78	Endo	97	45.5
Mn(EFAD)·H_2O → Mn(EFAD)	6.8	5.85	Endo	115	75.7
Fe(EFAD)·H_2O → Fe(EFAD)	5.7	5.83	Endo	126	45.3
Co(EFAD)·$4H_2O$ → Co(EFAD)·$2H_2O$	17.7	19.68	Endo	125	21.1
Co(EFAD)·$2H_2O$ → Co(EFAD)				154	27.1
Ni(EFAD)·H_2O → Ni(EFAD)	10.9	10.92	Endo	191	75.5
Zn(EFAD)·H_2O → Zn(EFAD)	6.1	5.65	Endo	116	75.1
Cd(EFAD)·H_2O → Cd(EFAD)	5.0	4.93	Endo	175	74.9

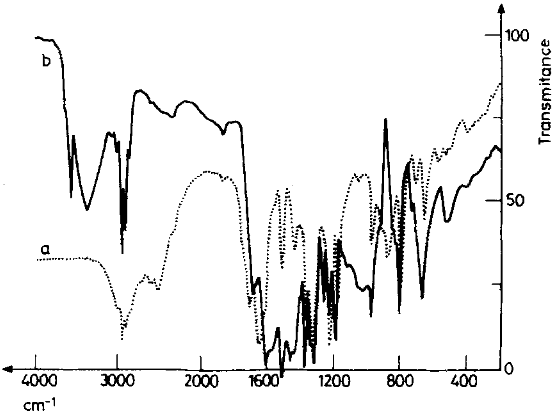

Fig. 4 Infrared spectra of H_2EFAD (a) and NaHEFAD (b)

in Table 3. The nature of the residues of pyrolytic decompositions were establish from their corresponding X-ray diffraction patterns (see Table 4).

All the isolated compounds show the characteristic unsymmetrical ai symmetrical, tension, vibrations and bands of carboxylate groups in the rang 1620–1550 cm^{-1} and 1420–1400 cm^{-1}.

Table 4 Diffraction data for the pyrolytic residues at 600 °C

Residue Mn(EFAD)·H_2O	—Mn_2O_3		Residue Fe(EFAD)·H_2O	−Fe_2O_3 Hematite	
d_{obs}	*hkl*	$d_{calc.}$	d_{obs}	*hlk*	$d_{calc.}$
4.910	101	4.92	3.664	012	3.66
3.072	112	3.08	2.693	104	2.69
2.861	020	2.88	2.512	110	2.51
2.750	103	2.76	2.204	113	2.201
2.479	211	2.49	1.838	024	1.838
2.349	004	2.36	1.696	116	1.690
1.574	321	1.57	1.600	018	1.596
1.539	224	1.54	1.482	214	1.484
1.444	314 040	1.44	1.453	300	1.452

Table 4 (continuation)

Residue $Co(EFAD)\cdot 4H_2O$	Co_3O_4 Cobalt Spinel		Residue $Ni(EFAD)\cdot 2H_2O$	NiO Bunsenite	
d_{obs}	*hkl*	$d_{calc.}$	d_{obs}	*hkl*	$d_{calc.}$
4.640	111	4.669	2.408	111	2.410
2.846	220	2.860	2.088	200	2.088
2.431	311	2.438	1.477	220	1.476
2.018	400	2.021	1.260	311	1.259
1.554	511	1.556	1.206	222	1.206
1.429	440	1.429			

Residue $Zn(EFAD)\cdot H_2O$	ZnO Zincite		Residue $Cd(EFAD)\cdot H_2O$	CdO	
d_{obs}	*hkl*	$d_{calc.}$	d_{obs}	*hkl*	$d_{calc.}$
2.799	100	2.816	2.695	111	2.712
2.592	002	2.602	2.337	200	2.349
2.467	101	2.476	1.657	220	1.661
1.906	102	1.911	1.414	311	1.416
1.622	110	1.626	1.355	222	1.355
1.474	103	1.477	1.173	400	1.174
1.405	200	1.407			
1.377	112	1.379			
1.356	201	1.359			

Residue Ba(EFAD)	$BaCO_3$ Whiterite		Residue Pb(EFAD)	PbO Massicot	
d_{obs}	*hkl*	$d_{calc.}$	d_{obs}	*hkl*	$d_{calc.}$
4.511	110	4.56	5.840	001	5.893
3.680	021	3.68	3.100	111	3.067
3.195	012	3.025	3.057		
2.611	112	2.628	2.933	002	2.946
2.576	130	2.590	2.737	200	2.744
2.268	220	2.281	2.370	020	2.377
2.140	221	2.150	2.002	202	2.008
2.097	041	2.104	1.847	212	1.850
				022	
2.040	202	2.048	1.795	220	1.797
2.010	132	2.019	1.726	113	1.724
1.929	113	1.940	1.639	311	1.640
1.678	311	1.677	1.533	222	1.534
1.625	151	1.633	1.473	131 004	1.474
1.373	332 204	1.375			

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Zusammenfassung — Das thermische Verhalten von 4-Äthylphenylamino-N,N-diessigsäure (H_2EFAD) und dem Mononatriumsalz dieser Säure wurde aus TG- und DSC-Diagrammen ermittelt. Ebenso wurden einige Salze dieser Säure mit zwei- und dreiwertigen Metallionen synthetisiert, charakterisiert und mittels TG und DSC untersucht. Die meisten dieser Verbindungen weisen eine 1 : 1-Stöchiometrie auf und enthalten Kristall- oder Koordinationswasser. Aus DSC-Diagrammen wurden die Dehydratisierungsenthalpien berechnet. Die Natur der Pyrolyserückstände wurde röntgendiffraktometrisch untersucht.

Резюме — Методами ТГ и ДСК изучено термическое поведение 4-этилфениламино-N,N-диуксусной кислоты и ее мононатриевой соли. Синтезировано также несколько солей с двух- и трехвалентными металлами, термическое поведение которых также изучено методами ТГ и ДСК. Большинство их этих солей имеют стехиометрический состав 1 : 1 и включают кристаллизационную и координационную воду. Исходя из данных ДСК были вычислены энтальпии дегидратации. Характер конечных продуктов пиролиза исследован рентгено-диффракционными методами.