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SYNTHESIS, CHARACTERIZATION, SPECTRAL AND THERMAL PROPERTIES OF METAL-HYDRAZINIUM NITRILOTRIACETATES

J. S. Budkuley and G. K. Naik[*]

Department of Chemistry, Goa University, Taleigao Plateau, Goa 403 203, India

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Abstract

Hydrazine derivatives of the monobasic nitrilotriacetate salts of zinc and alkaline earth metals have been prepared. IR absorption frequencies and thermal properties of these metal-hydrazinium nitrilotriacetates, $(N_2H_5)M[N(CH_2COO)_3]\cdot xH_2O$ have been defined. All the three –COOH appear to be dissociated in these salts. In thermal decomposition, these salts initially undergo dehydration followed by dehydrazination and via acetate intermediate step to metal oxycarbonates.

Keywords: metal-hydrazinium nitrilotriacetates

Introduction

Nitrilotriacetic acid (NTA), $N(CH_2COOH)_3$ is a triprotic acid [1] having three different dissociation constants with pK values [2] 1.89, 2.49 and 9.73. This acid is known [3–6] to react with metal ions to form monobasic metal nitrilotriacetate salts. With potent N and O (from $-COO^-$), NTA finds application as a complexing agent in various fields such as electroplating [7], detergents [8], etc.

These monobasic salts $HM[N(CH_2COO)_3]$ have a replaceable proton. Two metals salt of the type M_1M_2 $[N(CH_2COO)_3]$ with uni and bivalent metal ions have been synthesized earlier [4, 5]. Recently [9], we have reported the synthesis and properties of dihydrazinium nitrilotriacetate salt. During the studies on metal ion – NTA and hydrazine hydrate system, we have isolated new salts of NTA. The synthesis and some of the physical properties of hydrazinium metal nitrilotriacetate salts of alkaline earth and zinc are presented in this paper.

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[*] Permanent address: Department of Chemsitry, S. P, Chowgule College, Margao Goa 403 602 India

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Experimental

Metal nitrilotriacetate $HM[N(CH_2COO)_3]$ solution was prepared in situ [10] by warming an aqueous suspension of stoichiometric mixture of NTA and MCO_3 (M=Mg, Ca, Sr and Zn). The solution (pH~4.85) was then treated with hydrazine hydrate, $N_2H_4 \cdot H_2O$, such that, the proportion M:NTA:N_2H_4 was 1:1:1. The solution (Method-I) was concentrated on a steam bath to reduce the volume and allowed to stand for a few days in a vacuum desiccator. The solid compound was then filtered and recrystallized in water. In another method (II) of preparation, the compound was precipitated out by the addition of alcohol.

Metal content in these compounds was found out [11] by decomposing the samples with 1 cm^3 conc. HNO_3 and 3 cm^3 H_2O_2 to dryness. The residue was then extracted with H_2O and used as such for the estimation of metal ion.

Estimation of Mg, Ca and Zn was carried out by titrating against [12] standard 0.01 M EDTA solution, using Eriochrome Black T indicator. Sr was estimated [13] by flame photometry using ELICO CL 22D flame photometer. The hydrazine content in these compounds was found out volumetrically using 0.025M KIO_3 under Andrews [12] conditions. Densities of the solid samples were determined by pycnometric method.

Infrared spectra of the solid samples were recorded by dispersing them in Nujol and also in KBr disc. TOSHNIWAL IR-408 Spectrophotometer was used for this purpose. Simultaneous TG – DTA was recorded using NETZSCH STA – 409 Thermal Analyser by heating the samples in N_2 atmosphere at a heating rate of $10^oC\ min^{-1}$. For comparison, TG was also carried out at a heating rate of $20^oC\ min^{-1}$, in air, using SHIMADZU THERMO BALANCE model TD – 30 Thermal Analyser.

Results and discussion

Nitrilotriacetic acid dissolved in warm water and reacted with metal carbonate to form soluble monobasic M-NTA salt.

$$MCO_3+N(CH_2COOH)_3 \rightarrow HM[N(CH_2COO)_3]+H_2O+CO_2$$

when the clear solution ($pH \approx 4.85$) of the salt was treated with hydrazine hydrate, increase in the pH was observed due to the neutralization of the third proton from the carboxylic acid.

$$HM[N(CH_2COO)_3]+N_2H_4 \cdot H_2O(N_2H_5OH) \rightarrow (N_2H_5)M[N(CH_2COO)_3]+H_2O$$

where M=Mg, Ca, Sr and Zn.

The composition of the crystallized product was fixed on the basis of the chemical analysis (Table 1). All the salts were hydrated and the number of H_2O molecules depended on the metal ion in the salt. It also depended on the method

Table 1 Chemical analysis data and pycnometric densities of metal-hydrazinium nitrilotriacetates

Metal	Metal content		Hydrazine content		Formula assigned	Densities*
	%obsd.	%theo.	%obsd.	%theo.	Y=N(CH$_2$COO)$_3$	g (cm^3)$^{-1}$
Mg(I)	09.19	09.22	12.29	12.14	$(N_2H_5)Mg[Y]\cdot H_2O$	1.73 (1.6900)
Mg(II)	08.55	08.63	12.58	11.36	$(N_2H_5)Mg[Y]\cdot 2H_2O$	2.24 (1.6900)
Ca	12.77	13.48	10.72	10.76	$(N_2H_5)Ca[Y]\cdot 2H_2O$	1.95 (1.6541)
Sr	27.07	26.81	10.18	09.76	$(N_2H_5)Sr[Y]\cdot H_2O$	1.63 (1.9727)
Zn	21.48	21.49	10.76	10.50	$(N_2H_5)Zn[Y]\cdot H_2O$	1.8274 (1.566)

* Densities of monobasic salts are given in brackets

Table 2 Infrared spectral data (cm^{-1}) of $(N_2H_5)M[N(CH_2COO)_3]\cdot xH_2O$

Assignment	M=Mg	M=Mg	M=Ca	M=Sr	M=Zn
	x=1	x=2	x=2	x=1	x=1
–OH	3425 s	3400 m	3475 m	3400 m	3400 m
	2900 s	2900 s	2900 s	2900 s	2900 s
Unionised					
–COOH	–	–	–	–	–
Co-ordinated	1670 w	1660 r			1662 m
–COOM	1630 m	1630 m	1605 m	1625 m	1625 m
Stretching					
$\nu_{asym}COO^-$	1585 m	1570 m	1585 m	1585 m	1590 m
Stretching		1430 m	1470 m	1440	1450 m
$\nu_{sym}COO^-$	1425 m		1440 s. r	1412 m	
–COO$^-$		1370 s	1370 s		
	1310 s	1305	1310 m	1325	1305
C–N	1155				
	1125 m	1115 r	1120 w	1125 w	1122 w
–COO$^-$	1020 r	1020	1012 w	1018 s, r	1015 w
C–C	0970 s	0985 s	0990 m, r	0992 r	0980
	0910 s	0905 s	0930 s, r	0922 s, r	0905
Stretch					
ν_{N-N}	0940 m	0950 m	0960 m	0950 m	0945 m
–COO$^-$	0720 m	0730 m	0720 s. r	0712 m	0725 r

s – strong; m – medium; r – sharp; w – weak of preparation as is obvious from the observation made in the case of Mg. Monohydrate salt of Mg was obtained from the alcoholic precipitation, whereas a dihydrate was formed when crystallisation method was used. Ba did not yield any compound. These salts are colourless and highly hygroscopic.

Pycnometric densities of the salts are given in Table 1. On hydrazination of M-NTA salts the densities are found to increase in case of Mg, Ca and Zn salts, whereas opposite was found for Sr salt. This is probably due to the complexation of the metal ion with both NTA and N2H4, in the case of Mg, Ca and Zn salts, thus reducing the molecular volume. This phenomenon does not occur in the case of Sr.

Further characterization of the salts was done by the infrared spectral studies. Strong absorption at ~1720 cm^{-1} characterizes [6, 10, 14, 15] the undissociated carboxylic group(s). While non-existance of this band and a strong absorption at ~1620 cm^{-1} indicate the presence of dissociated, ionic carboxylic group(s). IR

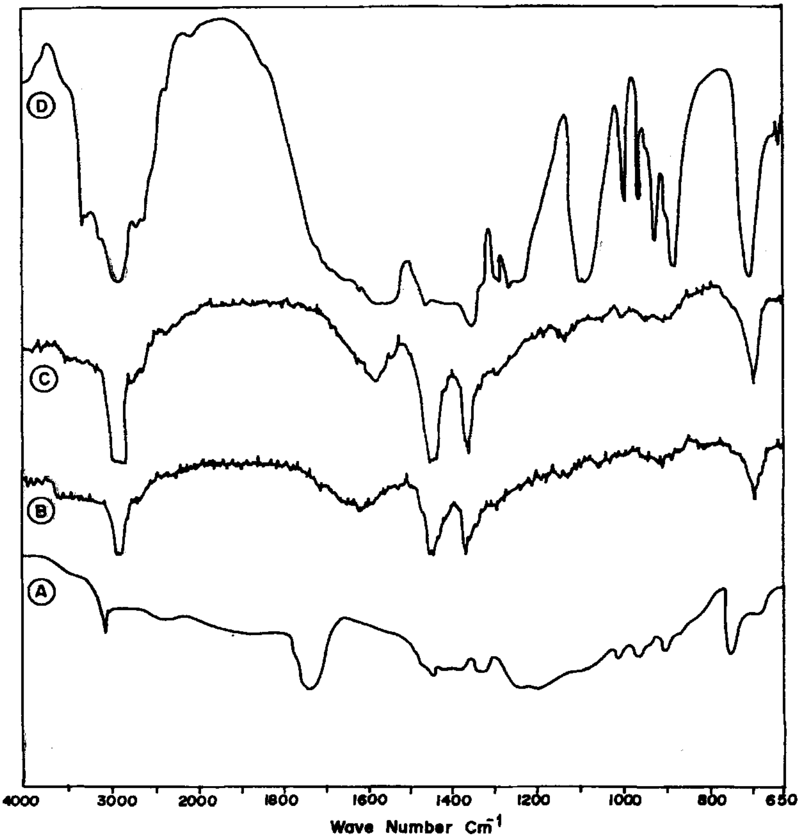

Fig. 1 IR of A – $H_3N(CH_2COO)_3$; B – $HMgN(CH_2COO)_3 \cdot 3H_2O$; C – $(N_2H_5)MgN(CH_2COO)_3 \cdot H_2O$; D – $(N_2H_5)MgN(CH_2COO)_3 \cdot 2H_2O$

Table 3 Thermoanalytical data of the metal-hydrazinium nitrilotriacetate salts, $(N_2H_5)M[Y]\cdot xH_2O$ where $Y=N(CH_2COO)_3$

	Step No.	T_{range}/ °C	Reaction		Mass loss/% obsd.	calc.	$T_{DTA\ peak}$/ °C
M=Mg	1	210–300	(i)	H_2O (L)	20.0	18.97	293(–)
x=1	2	400–460	(ii)(iii)(iv)	$MgO\cdot 1.5CO_2$ (R)	59.8	59.65	400(+) 430(–)
	3	460–640	(v)	$2MgO\cdot CO_2$ (R)	79.24	76.5	to 480(+) continous
M=Mg	1	160–280	(i)	H_2O (L)	6.25	6.42	260(–)
x=2	2	400–460	(i)(ii)	$H_2O+N_2H_4$ (L)	25.0	24.26	309(+)
	3	403–580	(iii)(iv)(v)	MgO (R)	85.70	85.67	424.7(+)
M=Ca	1	42.6–118	(i)	H_2O (L)	6.31	6.06	100(–)
x=2	2	280–351	(ii)(ii)	$H_2O+N_2H_4$ (L)	23.75	22.89	332.2(+)
	3	400–423	(iii)(iv)		continous		415.6(+)
	4	423.5–491	(v)	$CaO\cdot CO_2$ (R)	66.20	66.33	462.6(+)
M=Sr	1	72.5–142.5	(i)	H_2O (L)	5.10	5.50	115(–)
x=1	2	142.5–195	(ii)	N_2H_4 (L)	13.80	15.33	180(+)
	3	372.5–480	(ii)(iv)(v)	$SrO\cdot CO_2$ (R)	51.03	54.82	442.5(+)
M=Zn	1	220–310	(i)	H_2O (L)	5.40	5.91	238(–)broad
x=1	2	310–350	(ii0	N_2H_4 (L)	16.10	16.42	341(–)
	3	350–650	(iii)(iv)(v)	$ZnO\cdot CO_2$ (R)	60.69	58.82	389(–) 468(+)

L= Loss, R=Residue

spectra of hydrazine derivatives of the metal nitrilotriacetates do not show (Fig. 1) any absorption at ~1720 cm^{-1} which indicate the absence of undissociated –COOH. Obviously, of the three –COOH, two are coordinated to the metal ion and the third is neutralized by $N_2H_4\cdot H_2O$ (or N_2H_5OH). This is further confirmed by the appearance of an additional band ~945 cm^{-1}, which is characteristic [16, 17] of N–N stretching of $N_2H_5^+$, hydrazinium ion. Different absorption bands observed in the infrared spectra of the samples are assigned for the carboxylate groups and the $N_2H_5^+$ ion in Table 2. Most of the characteristic absorptions [14–17] of these species either overlap or appear as closed bands such as ~1640 (–COOM and –NH_2 bending); ~1560 (ν_{asym} COO^- stretching and

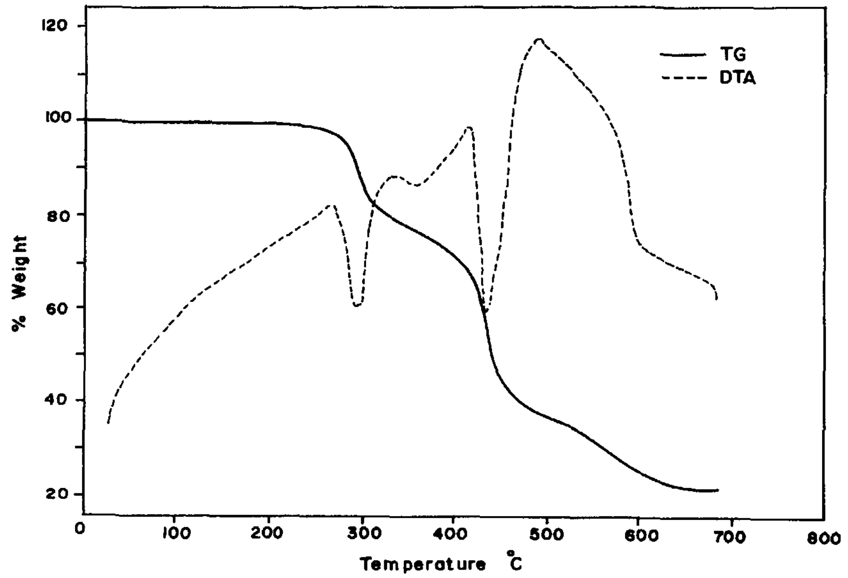

Fig. 2 TG, DTA of $(N_2H_5)Mg[N(CH_2COO)_3]\cdot H_2O$

bending of $-NH_3^+$); ~1150 (–CN and $-NH_2$ twisting) and ~980 cm^{-1} (ν_{C-C} and ν_{N-N} stretching).

Composition of the hydrazinium metal nitrilotriacetate hydrate salts was further confirmed on the basis of the thermogravimetric results. On heating, in the initial step, the monohydrate salt of Mg loses H_2O and N_2H_4 together. Whereas in other salts, initially, only dehydration as is seen in the TG (Table 3). Both dehydration and dehydrazination (from $N_2H_5^+$) endothermically leading to the metal nitrilotriacetate (monobasic). Endothermic dehydrazination (Fig. 2) suggests loosely bonded N_2H_4 to the proton of the carboxylate group in the formation of $N_2H_5^+$ (Fig. 2).

Metal nitrilotriacetates on further continuous heating appear to decompose through metal acetates to metal oxycarbonates or oxides as reported earlier [18] and as can be seen (Table 3) from the mass loss in the TG. Acetone was detected [19] as one of the gaseous products, thus confirming the formation of the metal acetate intermediate. The decomposition reactions, on the basis of the weight loss in the TG steps, can be written as follows:

$$(N_2H_5)M[N(CH_2COO)_3]\cdot xH_2O \rightarrow (N_2H_5)M[N(CH_2COO)_3]+xH_2O \quad \text{(i)}$$

(in one or more steps)

$$(N_2H_5)M[N(CH_2COO)_3] \rightarrow HM[N(CH_2COO)_3]+N_2H_4(N_2+NH_3) \quad \text{(ii)}$$

$$HM[N(CH_2COO)_3] \rightarrow M(CH_3COO)_2(+N_2+CO_2+H_2O_{vap}) \quad \text{(iii)}$$

$$M(CH_3COO)_2 \rightarrow aMO{\cdot}bCO_2{+}M({+}CH_3COCH_3{+}H_2O) \qquad (iv)$$

$$aMO{\cdot}bCO_2{+}M \rightarrow MO{\cdot}CO_2\ (MCO_3)\ \text{or}\ MO\ ({+}CO_2) \qquad (v)$$

However, it was observed that the formation of the metal oxycarbonate occurs at much lower temperatures in the thermal decomposition of hydrazine derivatives in comparison to simple metal nitrilotriacetates [18].

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