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Synthesis, Spectral and Thermal Properties of Na/K-Nickel Nitrilotriacetate Hydrazinates

GANPAT K. NAIK† and JAYANT S. BUDKULEY*
Department of Chemistry,
Goa University
Taleigao Plateau, Goa, 403 203, India

Bimetal nitrilotriacetate hydrazinate salts with sodium/potassium and nickel metals have been synthesized. Spectral and thermal properties of these salts have been defined. All the three carboxylates of the nitrilotriacetic acid have been found to be dissociated and ionized in these salts.

INTRODUCTION

Nitrilotriacetic acid[1] (NTA), commercially known as Trilon-A, with the chemical formula $N(CH_2COOH)_3$, is widely used as a complexing agent in the electrodeposition[2] processes. As a constituent of the electrocleaners[3] in the pre-treatment of the electropolishers[4] in the post-treatment, the role of this acid is well established. NTA is also used as a substitute[5] to cyanide for complexation of the metal in the electroplating baths. Addition of the Ni-NTA salt in the electroplating bath is found[6] to improve the hardness of the deposits. In the electroless plating baths where hydrazine[7] is used as the reducing agent, NTA is found to be a useful complexing agent.

In some of these electrodeposition or electroless deposition processes, the plating baths are maintained alkaline ($pH > 7$) and better efficiency is obtained at the elevated temperatures[8]. Where the alkalinity is controlled by the addition of hydroxide/carbonate of sodium or potassium, there is a possibility of the formation of bimetal Na/K-Ni-NTA salts. It is therefore important to understand the thermal stability of these bimetal salts.

EXPERIMENTAL

In the synthesis of these bimetal salts, the aqueous solution of nickel nitrilotriacetate was first prepared *in situ* by treating[9] dibasic nickel carbonate with nitrilotriacetic acid (Ni : NTA equal to 1), in a warm aqueous suspension. 0.05 N M_2CO_3 (M = Na or K) solution was then added to this solution (pH *ca.* 4.8) until the pH was increased[9] to 6.9, and then followed by the addition of hydrazine hydrate, $N_2H_4 \cdot H_2O$ (stoichiometric $Ni : N_2H_4$ equal to one or excess). The compound separating out was filtered and dried over P_2O_5 in a vacuum desiccator.

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† Permanent address: S.P. Chowgule College, Margao Goa, 403 601, India.

The composition of the salts was fixed by chemical analysis. For the estimation of the metals, known amount of the salt was first decomposed[10] by heating with 1.0 c.c. conc. HNO_3 and 3 c.c. H_2O_2 to dryness. The residue was then extracted with H_2O for the estimation of the metals. The nickel content was determined by titrating with 0.01 M EDTA[11]. Sodium (or potassium) was estimated by employing ELICO CL 22D flame photometer. The hydrazine content in the salts was determined volumetrically by titrating against 0.025 M KIO_3 solution[11].

Pyknometric tube was used to determine the densities of the samples. The mass of the displaced CCl_4 in the tube by the known amount (m) of the solid sample was found out. By using the density value of this liquid at the ambient temperature, its volume (v) was calculated, which corresponds to the volume of the sample. The density was then calculated by using the equation $\rho = m/v$.

The magnetic susceptibility (χ) measurements of the samples were carried out by using Gouy's balance.[12] The χ values were then used to calculate the effective magnetic moment (μ_{eff}) of the samples. The infrared spectral data of the samples was recorded on Perkin-Elmer 577 spectrophotometer in KBr disc.

The thermogravimetric analysis of the samples was carried out by using Shimadzu Thermobalance (model TD-30). All the experiments were done in N_2 atmosphere employing the heating rate of 10°/min.

RESULTS AND DISCUSSION

Basic nickel carbonate reacts[9] with nitrilotriacetic acid in a warm aqueous suspension to give aqueous monobasic nickel nitrilotriacetate.

$$NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O + 3N(CH_2COOH)_3 \rightarrow 3HNi[N(CH_2COO)_3] \cdot aq + CO_2 + 9H_2O$$

The third proton is neutralized by the addition of Na_2CO_3[9] and $N_2H_4 \cdot H_2O$ (or N_2H_5OH), both being weak bases.

$$4HNi[N(CH_2COO)_3] + Na_2CO_3 + 4N_2H_5OH \rightarrow 2Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot aq + 2N_2H_4 + CO_2 + 5H_2O$$

The salts isolated from the solution are found to have a general formula $M(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot xN_2H_4 \cdot 3H_2O$ (where M = Na or K). The value of x depends upon the amount of $N_2H_4 \cdot H_2O$ added (Table-1). Whereas monohydrazinate appears to form with the addition of stoichiometric amount of $N_2H_4 \cdot H_2O$, a dihydrazinate results with the excess. These salts are bluish green in colour and moderately hygroscopic.

The densities of the salts are given in Table-1. When compared with the density of the monobasic nickel nitrilotriacetate salt[13] the densities of these bimetal-hydrazinium nickel nitrilotriacetates are found to be lower. This can be attributed to the increased molecular volume of these mixed salts. The effective magnetic moments, calculated from the magnetic susceptibility measurements, indicate that the complexes are of high spin variety.

TABLE-1

CHEMICAL ANALYSIS DATA, PYKNOMETRIC DENSITIES AND EFFECTIVE MAGNETIC MOMENTS OF $M(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot xN_2H_4 \cdot 3H_2O$ WHERE M = Na or K

Chemical Analysis Data						Formula assigned Y = $[N(CH_2COO)_3]$	Density g cc^{-1}	μ_{eff}
Ni content		M content		N_2H_4 content				
% obsd.	% theor.	% obsd.	% theor.	% obsd.	% theor.			
19.25	19.44	3.81	3.80	15.19	15.10	$Na(N_2H_5)Ni_2Y_2 \cdot N_2H_4 \cdot 3H_2O$	1.492	5.0204
18.08	18.46	3.55	3.61	10.75	10.6	$Na(N_2H_5)Ni_2Y_2 \cdot 2N_2H_4 \cdot 3H_2O$	1.1542	4.983
18.5	18.94	6.35	6.29	10.45	10.31	$K(N_2H_5)Ni_2Y_2 \cdot N_2H_4 \cdot 3H_2O$	1.6035	5.2031
18.3	18.01	5.55	5.98	14.98	14.73	$K(N_2H_5)Ni_2Y_2 \cdot 2N_2H_4 \cdot 3H_2O$	1.5498	5.0515

The infrared spectra of these salts do not show[14] any absorptions *ca.* 1720 cm^{-1} (Fig. 1) indicating the dissociation of all three —COOH groups from nitrilotriacetic acid. In addition, absorptions observed *ca.* 1640 cm^{-1} and

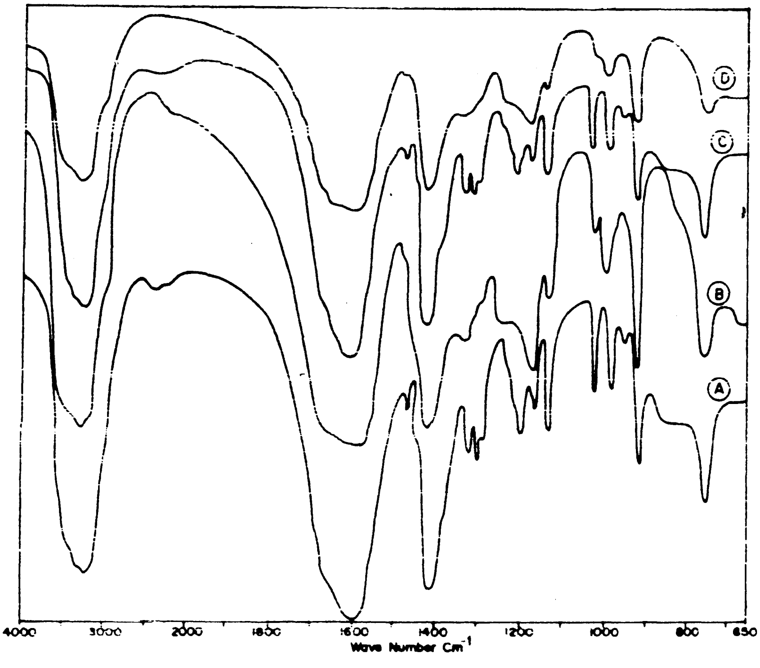

Fig. 1 IR of (A) $Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot N_2H_4 \cdot 3H_2O$,
(B) $Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot 2N_2H_4 \cdot 3H_2O$,
(C) $K(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot N_2H_4 \cdot 3H_2O$,,
(D) $K(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot 2N_2H_4 \cdot 3H_2O$

1560 cm^{-1} further confirm[15] ionic carboxylates in these salts. N—N stretching frequencies are observed *ca.* 960 and 920 cm^{-1}. The former can be assigned[16] to $N_2H_5^+$ ion and the latter to N_2H_4 in the salts. Similarly, other characteristic absorptions are seen (Fig. 1) for —CN (*ca.* 1160 cm^{-1}), —COO^- (*ca.* 1560 cm^{-1}). Assignments for the various absorptions are given in Table-2.

TABLE-2

INFRARED SPECTRAL DATA (cm^{-1}) OF $M(N_2H_5)\cdot Ni_2[N(CH_2COO)_3]_2\cdot xN_2H_4\cdot 3H_2O$

S. No.	Assignment	M = Na x = 1	M = Na x = 2	M = K x = 1	M = K x = 2
1.	—OH	3500 m 3250 s	3500 m 3300 s	3500 m 3250 s	3500 m 3300 s
2.	Unionised —COOH	—	—	—	—
3.	—COO^-	1670 s	1670 s	1675 m	1665 m
4.	Co-ordinated —COOM	1620 s	1610 s	1620 s	1625 s
5.	Stretching $\nu_{asym}(COO^-)$	1580 s	1585 s	1590 s	1580 s
6.	Stretching $\nu_{sym}(COO^-)$	1410 s	1425 s	1420 s, r	1425 s
7.	—COO^-	1320 m 1300 m	1325 m	1330 m 1308 m	1330 m
8.	C—N	1130 m	1130 m	1170 m 1135 m	1170 s 1130 m
9.	—COO^-	1020 m	1020 m	1023 m	1020 m
10.	C—C	980 s, r	990 s, r	985 s	990 m
11.	Stretch ν(N—N) of $N_2H_5^+$	950 m	948 m	950 m	950 w
12.	C—C and ν(N—N) of N_2H_4	915 s, r	920	918 s, r	920 s, r
13.	—COO^-	750 s	750 s	750 s	750 m

Key: m = medium; w = weak; s = strong; r = sharp.

These salts are stable below 100°C. When heated beyond this temperature in the thermogravimetric analysis, the monohydrazinate salt undergoes total dehydration in a single step (Table-3).

$$Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2\cdot N_2H_4\cdot 3H_2O$$
$$\rightarrow Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2\cdot N_2H_4 + 3H_2O$$

On further heating, two N_2H_4 molecules are lost as is evident from the observed weight loss in the second step.

$$Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2\cdot N_2H_4$$
$$\rightarrow NaHNi_2[N(CH_2COO)_3]_2 + 2N_2H_4(N_2 + NH_3)$$

However, in the case of the dihydrazinate salts, all H_2O molecules and two N_2H_4 are together lost in a single step as seen in Fig. 2 for Na based salts.

The TG curves of these salts are similar to the one reported[13] for the nickel nitrilotriacetate salt and almost superimposable especially after the loss of N_2H_4. In this third step, these salts appear to decompose disproportionately to metal oxide/metal oxycarbonate and metal.

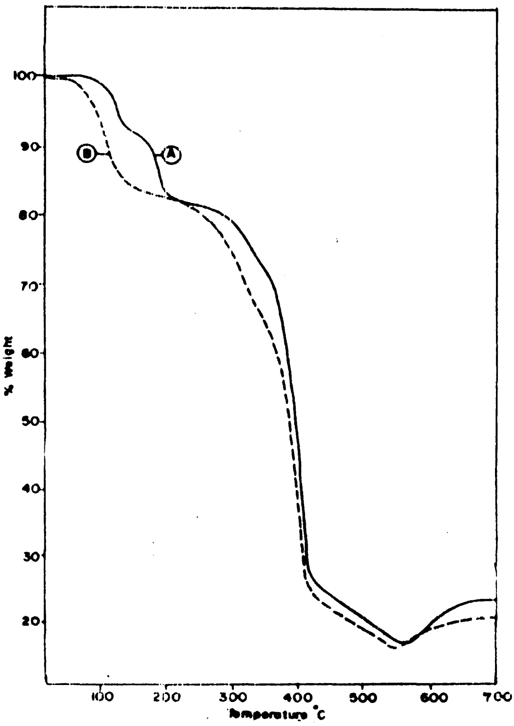

Fig. 2 TG of A. $Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot N_2H_4 \cdot 3H_2O$
B. $Na(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot 2N_2H_4 \cdot 3H_2O$

TABLE-3
THERMOGRAVIMETRIC DATA OF $M(N_2H_5)Ni_2[N(CH_2COO)_3]_2 \cdot xN_2H_4 \cdot 3H_2O$

	Step No.	Temp. range 0°C	Loss (L)/Residue (R) Disproportionation (D)	Weight Loss %	
				Obsd.	Calcd.
M = Na x = 1	1.	98–155.2	$3H_2O$ (L)	8.0	8.94
	2.	155.2–210	$2N_2H_4$ (L)	18.4	19.55
	3.	243-408.4	$Ni + NiO \cdot xCO_2 + Na_2O$ (D)	73.0	—
	4.	409–574	Partial CO_2 (L)	83.0	—
	5.	574–670	$NiO \cdot yCO_2 + Na_2O$ (R)	75.2	—
M = Na x = 2	1.	80–175	$3H_2O + 2N_2H_4$ (L)	17.4	18.56
	2.	176–408.2	$Ni + NiO \cdot xCO_2 + Na_2O$ (D)	76.2	—
	3.	410–550.6	Partial CO_2 (L)	84.3	—
	4.	550.6–680	$NiO \cdot yCO_2 + Na_2O$ (R)	76.0	—
M = K x = 1	1.	100–168	$3H_2O$ (L)	7.56	8.71
	2.	176–242	$2N_2H_4$ (L)	17.8	19.04
	3.	300–418.6	$Ni + NiO \cdot xCO_2 + K_2O$ (D)	69	—
	4.	419–552.8	Partial CO_2 (L)	77	—
	5.	552.8–668	$NiO \cdot yCO_2 + K_2O$ (R)	71	—
M = K X = 2	1.	50–196	$3H_2O + N_2H_4$ (L)	15.4	13.2
	2.	199–408	$Ni + NiO \cdot xCO_2 + K_2O$ (D)	68	—
	3.	410–541	Partial CO_2 (L)	76.6	—
	4.	542–620	$NiO \cdot yCO_2 + K_2O$ (R)	73.0	—

The further weight loss, in the next step, is due to the partial loss of CO_2 from oxycarbonates, as reported earlier[13, 17] in the case of the single metal salt (Table-3).

When heated up to 600°C, the last step in the TG shows gain in weight which is due to the oxidation of metal and subsequent formation of oxycarbonates by reaction with CO_2. This CO_2 gas is excessively generated during the decomposition of the salt.

Table-3 summarizes the different steps in the TG for these salts on the basis of the observed weight loss. Identical decomposition pattern is seen in the case of the potassium based salts.These salts therefore appear to be stable below 100°C and decompose to oxycarbonate at *ca.* 350°C.

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