Synthesis and Characterization of Lanthanide Tris-cyanoacetates

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Abstract

Hydrated lanthanide tris-cyanoacetates, $Ln(NCCH_2COO)_3 \cdot 2H_2O$ (where Ln = La, Ce, Pr, Nd, Eu, Gd, Tb, Dy, Yb, Lu or Y) have been synthesized. The compounds were characterized by elemental analysis, infrared spectroscopy (4000–200 cm^{-1}), thermogravimetric analysis, X-ray diffraction powder patterns, molar conductance, magnetic susceptibility measurements, and ^1H and ^{13}C NMR spectroscopic studies.

Possible sites of bonding and structural aspects of the compounds are discussed in the light of the shifts in the $\nu(C{\equiv}N)$, $\nu_{asym}(COO)$, $\nu_{sym}(COO)$, $\delta(-C-C{\equiv}N)$ and $\nu(Ln-O)$ bonds. The metal–ligand bonds seem to get stronger with increasing polarizability of the Ln^{3+} ion.

Introduction

Rare earth acetates have been extensively investigated [1–5], but much less work has been carried out with acetic acid having more than one functional group. The interest in cyanoacetic acid originated from the fact that the substituent cyano group itself is a potential donor group which could coordinate to the metal atom either through σ-electrons or through π-electrons. It was also thought of interest to investigate how the presence of a cyano group would modify the coordination behaviour of the carboxylate group and whether the dual functionality of the cyanoacetate ligand would result in the formation of the coordination polymers.

Experimental

Rare earth oxides (99.9% purity) were obtained from Nuclear Corporation of America and Michigan Chemical Corporation (U.S.A.). The oxides were converted to metal chlorides by reacting them with boiling HCl (H_2SO_4 in the case of cerium oxide). $Ln_2(CO_3)_3$ were precipitated from the acid solution by adding $(NH_4)_2CO_3$ solution and washed with distilled water to be free from Cl^- or $SO_4{}^{2-}$ ions. The metal carbonate precipitate was dissolved in a slight excess of cyanoacetic acid and the solution was subjected to evaporation *in vacuo*. The cyanoacetate $Ln(NCCH_2COO)_3 \cdot nH_2O$ obtained was washed with methanol before drying *in vacuo* for several hours. In each case two water molecules were found to remain associated with the cyanoacetates even after drying them in an oven at 105–110 °C for several days.

The metal content in the products was determined gravimetrically as stable oxide by direct ignition. Microanalysis for C, H and N contents was carried out by the Analytical Chemistry Division of this centre. The analytical results are reported in Table I.

The infrared spectra (4000–200 cm^{-1}) of the compounds were recorded on a Perkin-Elmer spectrophotometer, Model 577, using CsI optics. Mulls of the compounds were prepared in Nujol and in Fluorolube. Infrared results of interest are reported in Table II.

Thermogravimetric measurements of some representative compounds were carried out (~200 mg) both in air and in argon (2.5 l/h) at a heating rate of 4 K/min using a Stanton thermobalance. The decomposed volatile and residue fractions were studied by IR spectroscopy.

X-ray powder patterns were obtained by a diffractometer technique using Cu Kα radiation. A thin layer of the sample was spread evenly on a glass slide using colloidion in amyl acetate and the diffraction pattern was recorded on a chart. Interplanar *d*-spacings and the diffraction line intensities were determined from the chart recordings.

Magnetic susceptibility measurements were carried out using the Gouy method at room temperature. The tube constant was determined by using $CuSO_4 \cdot 5H_2O$ as the standard material. The compound in the form of a fine powder was packed densely in the Gouy tube and weights were recorded at various field strengths. Susceptibilities were corrected for the presence of diamagnetic components.

The ^1H (80 MHz), ^{13}C (20 MHz) NMR spectra were recorded on a Varion FT-80A spectrometer in dimethyl sulfoxide-d_6 and water, respectively.

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TABLE I. Analytical Results

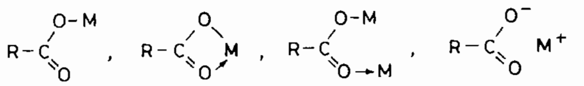
Compound	Colour	Analysis, found (calc.) (%)			
		C	H	N	Metal
$Y(NCCH_2COO)_3\cdot 2H_2O$	white	29.56 (28.66)	2.12 (2.65)	11.37 (11.14)	24.26 (23.59)
$La(NCCH_2COO)_3\cdot 2H_2O$	white	25.40 (25.30)	1.79 (2.34)	10.37 (9.84)	33.12 (32.54)
$Ce(NCCH_2COO)_3\cdot 2H_2O$	white	23.17 (25.23)	1.96 (2.34)	9.10 (9.81)	33.10 (32.73)
$Pr(NCCH_2COO)_3\cdot 2H_2O$	green	25.50 (25.18)	2.65 (2.33)	10.50 (9.79)	31.52 (32.85)
$Nd(NCCH_2COO)_3\cdot 2H_2O$	violet pink	25.6 (25.0)	2.56 (2.32)	11.8 (9.72)	32.8 (33.37)
$Eu(NCCH_2COO)_3\cdot 2H_2O$	white	24.98 (24.54)	1.88 (2.27)	10.46 (9.55)	35.89 (34.55)
$Gd(NCCH_2COO)_3\cdot 2H_2O$	white	24.66 (24.25)	1.70 (2.25)	9.61 (9.43)	34.71 (35.32)
$Tb(NCCH_2COO)_3\cdot 2H_2O$	white	25.61 (24.7)	1.83 (2.24)	10.39 (9.4)	36.55 (35.56)
$Dy(NCCH_2COO)_3\cdot 2H_2O$	white	25.1 (24.0)	1.67 (2.22)	9.8 (9.3)	35.32 (36.07)
$Yb(NCCH_2COO)_3\cdot 2H_2O$	white	24.65 (23.43)	1.70 (2.17)	9.65 (9.11)	37.74 (37.53)
$Lu(NCCH_2COO)_3\cdot 2H_2O$	white	24.55 (23.33)	1.64 (2.16)	9.49 (9.07)	– (37.8)

The chemical shifts are reported in ppm downfield from TMS for ^1H. The $^{13}C\{^1H\}$ NMR shifts are relative to neat dioxane (δ 66.5 ppm) containing a capillary of D_2O.

Results and Discussion

Analytical results of the rare earth cyanoacetates prepared are presented in Table I. They are in the hydrated form and can be represented by the general formula $Ln(NCCH_2COO)_3\cdot 2H_2O$. The water molecules could neither be removed by heating the samples in an oven at 110 °C nor by pumping *in vacuo* for several hours at 60–70 °C. The water molecules can, however, be replaced by chelating ligands such as 2,2′-bipyridyl and 1,10-phenanthroline forming 1:1 adducts*. An attempt to replace the water molecules with a monodentate ligand such as $(CH_3)_2SO$ and C_5H_5N was unsuccessful. This suggests that the water molecules in the cyanoacetates are coordinated. The infrared results further support this assumption, as discussed under IR in the text. The cyanoacetates do not melt but decompose, are non-hydrolysable and can be handled in air. They readily dissolve in water but are insoluble in organic solvents such as acetone, acetonitrile, benzene, methanol, tetrahydrofuran and other common non-polar solvents. This clearly implies that in the solid state the cyanoacetates are polymeric in nature; the cyanoacetate ion bridges two or more metal ions depending on the possible modes of bonding of the carboxylate and cyano groups.

In metal carboxylates, the carboxylate group can structurally be present as monodentate, bidentate chelate, bidentate bridge or ionic [2].



In addition to a carboxylate group, the cyanoacetate anion has a –C≡N group which can act as a potential donor site to the metal atom either through σ-electrons or through π-electrons [5]. The linear nature of the –C–C≡N part of the molecule will not allow all three donor atoms to bond to the same metal atom, but they can certainly coordinate by bridging two or three metal atoms, as shown in Scheme 1.

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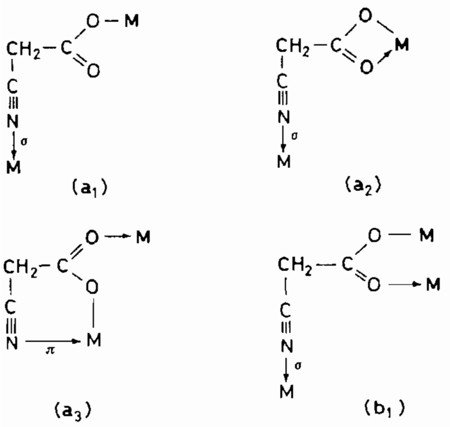
*Work on adducts is being presented in a separate publication.

TABLE II. Selected Infrared Bands of Rare Earth Cyanoacetates (cm^{-1})[a]

Na	Y	La	Ce	Pr	Nd	Eu	Gd	Tb	Dy	Yb	Lu	Assignments
	3500 to 3300	3600 to 3500	3600 to 3300	3600 to 3200	3600 to 3200	3600 to 3400	3600 to 3200	3600 to 3200	3600 to 3300	3600 to 3400	3600 to 3400	ν(OH) broad
2254m	2320m 2310m	2315m 2305sh	2310m	2310m 2300sh	2315m 2300m	2320s 2300m	2325m 2310m	2320m 2300m	2320m 2300m	2310m	2325w 2310m	ν(C≡N)
	1620s	1615s	1635sh	1625s	1625sh	1620s	1620sh	1615s	1600s	1620s	1630s	δ(HOH)
1596vs	1695s 1675s	1695vs 1670vs	1680s 1620s	1685s 1610sh	1660sm 1640s	1665ms 1640sh	1670s	1675s 1665s	1675s 1655s	1695s 1665ms	1700s 1665ms	ν_{asym}(COO)
1422s 1405ms	1440s	1440s 1430s	1440s 1420sh	1440s 1410s	1440sh 1420s	1430s	1430s	1430s	1430s 1410sh	1440s 1425s	1440s 1430s	ν_{sym}(COO)
174 191	255 235	255 240	240 200	245 200	220 220	240 210	240	255 235	240 245	255 230	260 230	$\Delta[\nu_{asym}(COO) - \nu_{sym}(COO)]$
394m	445w	425br	435w 425w	430w	430w 420w	430w 425sh	435w 425sh	440w 435sh	435w	445sh 420w	455w	δ(–C–C≡N)
	565m	540sh 550mw	545mw	550m	555m	555m	570sh	565	565m	565m	565m	ν(Ln–O), (COO)
	475w	445mw 440sh	445w	445w	445w	460wm	465wm	462wm	464wm	465wm	470wm	ν(Ln–O), (H_2O)
	285m	270m	270m	270m	270m	280m	285m	285m	280m	285m	295m	ν(Ln–N)

[a] vs = very strong, s = strong, m = medium, w = weak, br = broad, sh = shoulder.



Scheme 1.

As can be seen from configuration **a**$_3$, chelate formation involving a –C≡N group is only possible if π-electrons of the triple bond participate in bonding.

Infrared Results

Infrared spectroscopy has been extensively used as a means of differentiating between the different modes of bonding of carboxylate [1, 2] and cyano [5] groups. The position and the magnitude of separation of the antisymmetric and symmetric carboxylate stretching frequencies, ν_{asym}(COO) and ν_{sym}(COO), have been widely used to distinguish between unidentate and bidentate or bridging coordination of the carboxylate groups in the compounds [1, 2]. The IR results of the rare earth cyanoacetates are reported in Table II and the assignments are based on those reported previously [6, 7]. For compounds where the carboxylate group acts as unidentate the ν_{asym}(COO) is expected to increase and the ν_{sym}(COO) should decrease, as the M–O bond becomes stronger. Such a trend is not expected for the compounds having a chelated or bridged –COO group. In the case of a symmetrically bridged carboxylate, both the stretching bands are shifted in the same direction [8]. The σ-bonded cyano group is known to show a positive shift (hypsochromic effect) in the ν(C≡N) as a result of coordination and the π-bonded cyano group on the other hand displays a negative shift (bathochromic effect) [9].

Discussion on infrared results will mainly be restricted to the ν(C≡N), δ(C–C≡N), ν_{asym}(COO), ν_{sym}(COO), δ(COO), ν(Ln–O) and ν(Ln–N) modes, as they are expected to be more sensitive to coordination. The cyanoacetates prepared and studied in the present work invariably display ν(C≡N) bands shifted to the higher wave number region by about 50 cm^{-1} as compared to the band position in sodium cyanoacetate at 2254 cm^{-1} [6]. An increase in the ν(C≡N) on complex formation strongly suggests the involvement of the cyano group in coordination where σ-electrons are bonded to the metal atom [5]. Further support of cyano-nitrogen bonding to metal is reflected in the shift of the δ(C–C≡N) bands from 394 cm^{-1} to 430–45 cm^{-1}. The splitting of the ν(C≡N) and δ(C–C≡N) bands can be attributed to the solid effect.

Since the ν_{asym}(COO) and ν_{sym}(COO) bands move in the same direction in the rare earth cyanoacetates (as compared to those for sodium salt), the carboxylate groups in these compounds are either chelating or bridging, as there is no spectral criterion for distinguishing between them [10]. The magnitude of separation Δ(COO) = ν_{asym}(COO) – ν_{sym}(COO) lies in the range 210–260 cm^{-1} as compared to 170–190 cm^{-1} for the ionic Na salt. The Δ values in the present work are of the same order as reported for Ln trifluoro acetates and 2-picoline *N*-oxide complexes [3], where the CF_3COO^- group behaves as a symmetrically bridging and symmetrically chelating bidentate group.

The presence of coordinated water is confirmed from the IR absorption at ~3500 cm^{-1} and ~1625 cm^{-1} due to ν(OH) and δ(HOH) respectively.

Far Infrared Results

Low frequency IR spectroscopy has been used to examine metal–ligand bonds. In the far IR region new bands are observed in the regions 550, 450 and 270 cm^{-1} which can be assigned to metal–ligand bands. As the metal–nitrogen bond is expected to be weaker than the metal–oxygen, the 270 cm^{-1} bands are assigned to ν(Ln–N) and the bands at ~450 cm^{-1} and ~550 cm^{-1} to ν(Ln–O) associated with coordinated water and carboxylate, respectively. It is interesting to note that there is an abrupt change in the position of the Ln–ligand bands near Eu–Gd as we move from La to Lu. If the positions of the ν(Ln–O) bands are plotted *vs.* the polarizing power (e/r^2) of the cation, it is observed that a break occurs in the plots at gadolinium (Fig. 1). The overall trend is an increase in frequency, indicating stronger metal–ligand bonding as the polarizing power increases. The abrupt change at gadolinium in the rare earths can be attributed to the stabilization caused by a half-filled 4f shell. The corresponding bands for the yttrium compound are observed towards the higher frequency side as expected since Y is a d-block element.

If we consider that all the three donor atoms of the cyanoacetate anion and two molecules of water are coordinated in the rare earth cyanoacetates $Ln(NCCH_2COO)_3 \cdot 2H_2O$, then the metal atom should have a coordination number of 11 with bridging C≡N and COO groups in a polymeric solid state. Trivalent rare earth ions when bonded to multidentate ligands are known to form complexes with high coordination numbers [11, 12]. The resulting

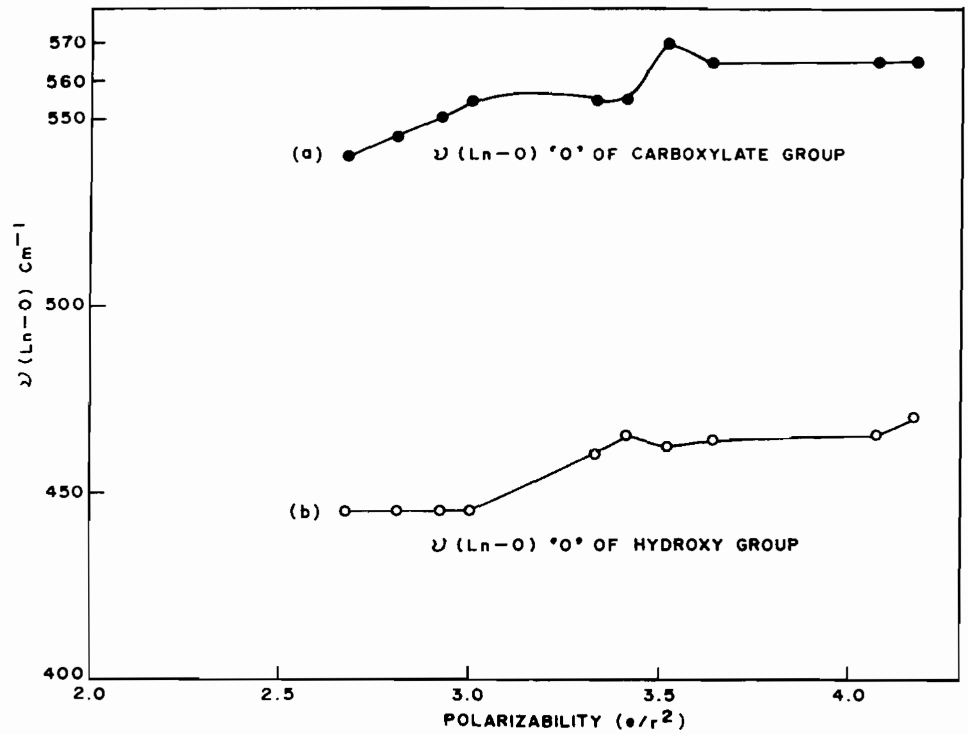


Fig. 1. Plot of positions of ν(Ln–O) bands *versus* the polarizing power of the cation.

TABLE III. X-ray Diffraction Powder Patterns of the Rare Earth Compounds

$Y(cyac)_3 \cdot 2H_2O^a$		$La(cyac)_3 \cdot 2H_2O^a$		$Pr(cyac)_3 \cdot 2H_2O^a$		$Nd(cyac)_3 \cdot 2H_2O^a$		$Eu(cyac)_3 \cdot 2H_2O^a$	
d (Å)	I/I_0 (X100)	*d* (Å)	I/I_0 (X100)	*d* (Å)	I/I_0 (X100)	*d* (Å)	I/I_0 (X100)	*d* (Å)	I/I_0 (X100)
9.0991	100	10.071	100	10.281	100	10.222	100	9.8472	85.5
8.7923	32.3	8.1166	32.86	8.9793	57	8.8893	65.2	7.7145	100
8.4732	38	6.8202	24.64	7.8648	44	7.8648	40.75	5.1702	26.94
6.9974	8.5	5.8288	7.5	6.0259	17	5.9854	32.6	4.9252	14.5
5.1404	15.4	4.9995	7.5	5.1404	17.5	5.1257	18.15	3.8667	35.6
3.9619	7.44	4.5753	11.07	3.9953	12.0	3.9689	12.2	3.5617	20.94
3.4269	7.7	4.0675	15.36	3.7385	8.6	3.4269	8.89	3.3936	17.8
		3.6746	11.07	3.4334	8.2	2.4106	12.96	2.6757	13.35

$Gd(cyac)_3 \cdot 2H_2O$		$Tb(cyac)_3 \cdot 2H_2O$		$Dy(cyac)_3 \cdot 2H_2O$		$Yb(cyac)_3 \cdot 2H_2O$		$Lu(cyac)_3 \cdot 2H_2O$	
d (Å)	I/I_0 (X100)	*d* (Å)	I/I_0 (X100)	*d* (Å)	I/I_0 (X100)	*d* (Å)	I/I_0 (X100)	*d* (Å)	I/I_0 (X100)
10.281	100	9.7604	73.5	10.106	28.1	9.3289	100	9.3191	100
9.8254	31.6	9.0434	13.04	9.9355	89.3	8.7060	64.3	8.8098	82.6
9.0250	67.7	7.7078	100	7.8302	81.5	7.1841	29.5	6.9864	35.14
8.5714	64.8	5.1374	25.2	7.7549	100	6.9591	26.9	5.9060	34.1
8.3613	19.8	3.8338	27.4	5.1972	24.2	6.0177	21.1	5.0848	26.8
7.8095	40.9	3.5201	17.4	4.9442	11.6	5.8904	25.7	3.8534	37.7
3.8667	17.7	3.3597	20.4	3.8750	26.5	3.8534	25.2	3.6836	24.6
3.8387	18.2	2.7715	14.35	3.5617	17.1	3.5174	21.1	3.5277	31.2

[a] (cyac) = $(NCCH_2COO)$.

polyhedra usually possess low symmetry but enable the metal ion to acquire a high coordination number. This can be expected since the bonding of the Ln(III) ion is essentially non-directional. The 11-coordinate polyhedron can be viewed as arising either from a monocapped pentagonal antiprism or a symmetrical pentacapped trigonal prism. Since we have not been able to grow single crystals and confirm the structural aspect of the compounds, it was considered worthwhile to examine the X-ray diffraction powder patterns of the compounds. We merely report here the first eight lines of each compound (Table III). From the X-ray powder patterns of the cyanoacetates where many lines appear, it seems that they have a low symmetry structure.

NMR Results

The ^{1}H NMR spectra of these complexes were recorded in DMSO-d_6 at room temperature (Table IV). The hydroxy proton resonance observed in the free ligand at $\delta = 12.11$ ppm did not appear in the spectra of the lanthanide complexes. All the spectra showed resonance in addition to methylene protons due to water molecules. The spectra of the diamagnetic complexes (Y, La and Lu) displayed reasonably sharp lines (singlet) due to CH_2 and water protons at $\delta \sim 3.4$ and ~ 3.7 ppm, respectively. However, the paramagnetic complexes showed considerable line broadening of various orders. The positions of these signals also varied from complex to complex. The variation in chemical shift for the paramagnetic lanthanide ions has been explained on the basis of a pseudo-contact term [13, 14]. No satisfactory spectra could be obtained for the Dy and Gd complexes.

The ^{13}C NMR spectra for the free ligand, its sodium salt and some of the lanthanide complexes were recorded in water and the resulting data are summarized in Table V. The ^{13}C NMR chemical shifts for the complexes are compared with the sodium salt of cyanoacetic acid. As is evident from the Table, the chemical shifts for diamagnetic Y, La and Lu complexes are comparable to that of the sodium salt. This indicates that the cyanoacetato group in the lanthanide complexes is acting as a monodentate species in aqueous solution, CN and one of the carboxylate oxygen bonds being ruptured. The vacant coordination sites are occupied by water molecules as is generally observed with the complexes of these ions. Resonances due to methylene, cyano and carbonyl carbons for paramagnetic complexes Pr, Nd and Eu showed considerable isotropic shifts which is true for these ions [13–15]. The cyano-carbon resonance for all the three complexes is shielded by ~6.5 ppm with respect to the sodium salt, whereas the methylene and carbonyl carbon resonances are either shielded or deshielded depending on the lanthanide ion.

Magnetic Susceptibility

Magnetic susceptibility of $Ln(NCCH_2COO)_3 \cdot 2H_2O$ (where Ln = Eu, Gd and Tb) was determined at room temperature. The values 3.42, 7.68 and

TABLE IV. ^{1}H NMR Spectral Data for Cyanoacetic Acid, Sodium Cyanoacetate and the Lanthanide Complexes in DMSO-d_6 at Room Temperature[a]

Compound	δ (CH_2) (ppm)	δ (H_2O) (ppm)
$NCCH_2COOH$[b]	3.73	
$Na(NCCH_2COO)$	3.26	
$Y(NCCH_2COO)_3 \cdot 2H_2O$	3.43	3.74
$La(NCCH_2COO)_3 \cdot 2H_2O$	3.39	3.77
$Pr(NCCH_2COO)_3 \cdot 2H_2O$	3.60(70)	5.87(5)
$Nd(NCCH_2COO)_3 \cdot 2H_2O$	3.80[c]	4.17(9)
$Eu(NCCH_2COO)_3 \cdot 2H_2O$	2.70(5)	4.44(5)
$Tb(NCCH_2COO)_3 \cdot 2H_2O$	5.44(61)	25.6(16)
$Yb(NCCH_2COO)_3 \cdot 2H_2O$	−2.31(16)	3.54(14)
$Lu(NCCH_2COO)_3 \cdot 2H_2O$	3.42	3.70

[a] Values in parentheses are the half-line width of the resonance signal and are expressed in Hz. [b] δ(OH) 12.11. [c] Broad unresolved.

TABLE V. $^{13}C\{^1H\}$ NMR Spectral Data for Cyanoacetic Acid, Sodium Cyanoacetate and some of the Rare Earth Complexes[a, b]

Compound	CH_2		CN		C=O	
	δ (ppm)	$\Delta\delta$ (ppm)	δ (ppm)	$\Delta\delta$ (ppm)	δ (ppm)	$\Delta\delta$ (ppm)
$NCCH_2COOH$	24.8	−2.5	115.4	−3.8	167.0	−2.9
$Na(NCCH_2COO)$	27.3	0	119.2	0	169.9	0
$Y(NCCH_2COO)_3 \cdot 2H_2O$	27.1	−0.2	118.2	−1.0	171.0	1.1
$La(NCCH_2COO)_3 \cdot 2H_2O$	27.2	−0.1	118.4	−0.8	171.3	1.4
$Pr(NCCH_2COO)_3 \cdot 2H_2O$	32.9	5.6	112.9	−6.3	164.4	−5.5
$Nd(NCCH_2COO)_3 \cdot 2H_2O$	35.7	8.4	113.0	−6.2	157.0	−12.9
$Eu(NCCH_2COO)_3 \cdot 2H_2O$	−3.4	−30.7	112.5	−6.7	179.7	9.8
$Lu(NCCH_2COO)_3 \cdot 2H_2O$	27.1	−0.2	118.2	−1.0	171.5	1.6

[a] Spectra were recorded in H_2O using 10-mm NMR tubes which contained a capillary (3 mm) of D_2O. In D_2O solutions D-exchange of methylene protons take place and a triplet resonance is observed for the methylene carbon. The ^{13}C shifts are referenced to neat dioxane containing a capillary of D_2O. [b] $\Delta\delta$ is the coordination or isotropic shift from the sodium salt in water.

TABLE VI. Thermal Analysis Data of Rare Earth Cyanoacetate Hydrates; $Ln(NCCH_2COO)_3 \cdot 2H_2O$

Name of 'Ln' in complex	Step	Temperature range (°C)	Weight loss (%)		Solid product
			Found	Calculated	
In argon					
Y	1	RT–240	42.17	42.03	$Y_2(CO_3)_3(CH_2CN)_2$
	2	240–340	7.40	7.59	$Y_2(CO_3)_2(OCN)_2$
	3	340–450	4.20	4.27	$Y_2O(CO_3)(OCN)_2$
Gd	1	RT–240	35.5	35.66	$Gd_2(CO_3)_3(CH_2CN)_2$
	2	240–340	6.2	6.1	$Gd_2(CO_3)_2(OCN)_2$
	3	340–450	4.1	4.33	$Gd_2O(CO_3)(OCN)_2$
Tb	1	RT–240	35.35	35.1	$Tb_2(CO_3)_3(CH_2CN)_2$
	2	240–340	6.25	6.06	$Tb_2(CO_3)_2(OCN)_2$
	3	340–450	5.2	5.7	$Tb_2O(CO_3)(OCN)_2$
Lu	1	RT–240	34.02	34.12	$Lu_2(CO_3)_3(CH_2CN)_2$
	2	240–340	6.03	6.20	$Lu_2(CO_3)_2(OCN)_2$
	3	340–450	4.52	4.49	$Lu_2O(CO_3)(OCN)_2$
In air					
Y	1	RT–340	53.02	53.38	$Y_2(CO_3)_2(CN)_2$
	2	340–450	3.65	3.71	$Y_2O(CO_3)(CN)(OCN)$
Gd	1	RT–340	56.21	56.53	$Gd_2(CO_3)_2(CN)_2$
	2	340–450	2.83	2.59	$Gd_2O(CO_3)(CN)(OCN)$
Tb	1	RT–340	44.81	45.19	$Tb_2(CO_3)_2(CN)_2$
	2	340–450	3.45	3.13	$Tb_2O(CO_3)(CN)(OCN)$
Lu	1	RT–340	44.0	43.62	$Lu_2(CO_3)_2(CN)_2$
	2	340–450	2.95	3.02	$Lu_2O(CO_3)(CN)(OCN)$

9.53 B.M. obtained for Eu, Gd and Tb compounds, respectively, are comparable to the reported values (3.61, 7.95 and 9.60 B.M.) for these ions [16]. This shows that unlike the transition metal ions the magnetic moments of the Ln^{3+} ions are not effected by the ligand field. The 4f-electrons are so well screened that they are least effected by external influences.

Thermogravimetric Studies

The results of TG–DTA studies of $Ln(NCCH_2COO)_3 \cdot 2H_2O$ (where Ln = Y, Gd, Tb and Lu) in air showed that stable intermediate phases exist in the temperature ranges of 220–240, 330–345 and 430–450 °C. Separate experiments were therefore carried out by heating the compounds in a silica boat in a horizontal furnace under the flow of air or argon. An attempt was made to keep the heating and flow rate uniform. Weight losses and IR spectra of the decomposed products were studied to identify them and propose a possible mode of decomposition. The compositions of the intermediates are those which best fit the observed weight losses in TGA. Dehydration does not take place as an independent step, but there is a simultaneous decomposition accompanied by the conversion of the C≡N group into an amido group, as indicated by the ammoniacal nature of the decomposed volatile products collected in the cold trap which converted red litmus to blue. The intermediates of each step were studied by IR spectroscopy. The absence of bands due to the carboxylate groups and the appearance of new bands in the regions 1080, 880, 1500 and 710 cm^{-1} which can be assigned to ν_1, ν_2, ν_3 and ν_4 vibrational frequencies of the CO_3 groups [17] suggest the formation of an intermediate carbonato compound. It is interesting to note that the band at 2300 cm^{-1} in the parent compound disappears and a new band appears in the 2200 cm^{-1} region for the decomposed products. The metal cyanides and cyanates usually display $\nu(C{\equiv}N)$ bands lower than these organic counterparts (Table VI shows the various decomposition products as identified on the weight losses and IR results.) Further, it was of interest to note that the residue when treated with dilute HCl gave effervescence, indicating the possible formation of carbonate intermediates. In each case the final product was stable Ln_2O_3 when the temperature was raised to red hot (750–800 °C).

Molecular Weight Determination

An attempt was made to determine the degree of polymerization through molecular weight estimation by a cryoscopic method. These estimations in water have not actually been fruitful as there appears to be strong dissociation of the clusters and the compounds. In water the molecular weights estimated were even less than the monomeric values. This suggested that the bridged cyano and carboxylate groups were being broken down in strong coordinating water. These solutions, however, were found to be non-conducting, suggesting that the compounds did not dissociate into ionic species.

Conclusions

The lanthanide cyanoacetates are polymeric in the solid state where the ligand acts as a tridentate moiety, but in aqueous solution the ligand behaves as a unidentate species. With increasing polarizability of the lanthanide ion, a strengthening of the metal–ligand bond is observed. A break is noticed at gadolinium due to the stabilizing power of half-filled f-shells. Thermal decomposition of these compounds proceeds through the formation of $Ln_2(CO_3)_2$-$(OCN)_2$ and $Ln_2(O(CO_3)(OCN)_2$ due to coordinated cyano and carboxylate groups.

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