Crystal Structures of Hydrated Lanthanide(III) Nicotinates, $La_2(C_5H_4NCO_2)_6(H_2O)_4$ and $Sm_2(C_5H_4NCO_2)_6(H_2O)_4$[1,2]

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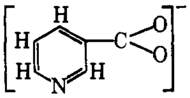
Abstract: The crystal structures of the hydrated nicotinate complexes of lanthanum(III) and samarium(III) have been determined by three-dimensional X-ray diffraction techniques using Patterson and Fourier syntheses. The compounds have the empirical formula $[Ln(C_5H_4NCO_2)_3(H_2O)_2]$ and crystallize in space group $P2_1/c$ with lattice parameters $a = 9.805\ (5)$ Å, $b = 12.167\ (5)$ Å, $c = 17.022\ (7)$ Å, $\beta = 92.80\ (1)^\circ$, $\rho_{obsd} = 1.74\ (1)$, $\rho_{calcd} = 1.77$, for the lanthanum compound, and $a = 9.642\ (3)$ Å, $b = 11.788\ (4)$ Å, $c = 17.490\ (6)$ Å, $\beta = 92.33\ (1)^\circ$, $\rho_{obsd} = 1.83\ (1)$, $\rho_{calcd} = 1.85$, for the samarium compound. The conventional discrepancy factors are 0.021 for 2388 diffractometer data (La) and 0.025 for 2398 diffractometer data (Sm). The complexes are dimeric with the two $[Ln(C_5H_4NCO_2)_3(H_2O)_2]$ units related by a crystallographic center of inversion. The two eight-coordinate metal ions are bridged by four carboxylate groups; the remaining two carboxylate groups are chelated to the metals. The eight coordination about each metal is completed by two water molecules. The nitrogen atoms in the nicotinate groups are all hydrogen bonded to water molecules of adjacent dimers, thus forming a stabilizing three-dimensional network of hydrogen bonds. The distances between metal ions in the dimers are 4.221 (2) Å (La) and 4.297 (1) Å (Sm). Comparison of magnetic moments at 23°K with room temperature values for the nicotinate complexes shows a decreased moment for the praseodymium(III) and neodymium(III) complexes but a normal moment in the gadolinium(III) complex.

Two new series of complexes of the trivalent rare earth ions with the nicotinate ion (*m*-pyridinecarboxylate)



and with its parent acid have been reported by Chupakhina and Serebrennikov.[4,5] These compounds were formulated as $[Ln(C_5H_4NCOO)_3]$ and $[Ln(C_5H_4NHCOO)_3][Cr(NCS)_6]$. The first series was subsequently postulated[6] to involve coordination of the nitrogen and two oxygens of each anion to the lanthanide(III) ion. The presumption of coordination of the nitrogen was based upon correlation of infrared stretching frequencies in the complexed and uncomplexed nicotinate ion; however, the stereochemical requirements of the nicotinate group make it unlikely that all three atoms coordinate to a single metal ion.

This paper reports the three-dimensional, single-crystal X-ray analyses of the hydrated complexes of lanthanum(III) and samarium(III) with the nicotinate ion and the magnetic properties of several of the hydrated lanthanide(III) nicotinate complexes.

Table I. Chemical Analyses and Magnetic Moments of the Lanthanide Nicotinate Dihydrates

Compd	% C		% N		% H		Magnetic moment, BM, 298°K	Magnetic moment, BM, 22°K
	Obsd	Calcd	Obsd	Calcd	Obsd	Calcd		
Lanthanum nicotinate dihydrate	40.01	39.93	7.79	7.76	3.08	2.96		
Praseodymium nicotinate dihydrate	39.56	39.79	7.66	7.74	3.09	2.95	3.53	2.42
Neodymium nicotinate dihydrate	39.30	39.54	7.36	7.69	3.25	2.93	3.56	2.68
Samarium nicotinate dihydrate	38.73	39.10	7.65	7.60	3.16	2.90		
Gadolinium nicotinate dihydrate	38.79	38.62	7.26	7.51	2.82	2.86	7.95	7.92
Holmium nicotinate dihydrate	38.19	38.10	7.47	7.41	2.90	2.82		

Experimental Section

The hydrated rare earth nicotinates were synthesized following a modification of the preparation given by Chupakhina and Serebrennikov.[4] Nicotinic acid (1 g, Eastman Kodak) and 0.5 g of hydrated rare earth nitrate (K and K Chemicals) were added to 25 ml of H_2O and the resulting mixture was refluxed at 95° until complete dissolution occurred. Concentrated ammonia was then added to the hot solution until a pH of 4.5 was reached. The solution was then allowed to reflux to remove any precipitate formed on the addition of the ammonia. Upon evaporation (95°), crystals suitable for single-crystal X-ray analysis were formed. The formation of suitable crystals was very dependent upon the pH of the reaction media.[7] The chemical analyses of the compounds studied

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(1) A preliminary report on the structure of $[La(C_5H_4NCO_2)_3(H_2O)_2]_2$ was included in a presentation at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 17, 1969.

(2) Acknowledgment is made to the National Science Foundation (GP 15070) and to the donors of The Petroleum Research Fund (No. 841-G2), administered by the American Chemical Society, for support of this research.

(3) (a) This paper is based in part on a dissertation submitted by J. W. Moore to the Graduate School of Wayne State University in partial fulfillment of the requirements for the Ph.D. degree, June 1971. (b) Wayne State University. (c) Syracuse University.

(4) R. A. Chupakhina and V. V. Serebrennikov, *Russ. J. Inorg. Chem.*, 665 (1963).

(5) R. A. Chupakhina and V. V. Serebrennikov, *ibid.*, 1406 (1962).

(6) R. A. Chupakhina, E. N. Korableva, and V. V. Serebrennikov, *ibid.*, 427 (1966).

Table II. Lattice Constants and Related Information. Lanthanide Nicotinate Dihydrates

Metal ions	a, Å	b, Å	c, Å	β, deg	Cell vol, Å^3	Obsd density, g/cc	Calcd density, g/cc	μ, cm^{-1}
La^{3+}	9.805 (5)	12.167 (5)	17.022 (7)	92.80 (1)	2029	1.74 (1)	1.77	22.04
Pr^{3+}	9.72 (2)	12.02 (3)	17.15 (5)	92.5 (2)	2002	1.78 (1)	1.80	
Nd^{3+}	9.68 (2)	12.00 (4)	17.19 (5)	92.2 (2)	1995	1.81 (1)	1.82	
Sm^{3+}	9.642 (3)	11.788 (4)	17.490 (6)	92.33 (1)	1986	1.83 (1)	1.85	30.57
Gd^{3+}	9.64 (2)	11.67 (3)	17.60 (4)	91.6 (2)	1979	1.85 (1)	1.88	
Ho^{3+}	9.53 (3)	11.54 (5)	17.82 (5)	91.5 (2)	1959	1.90 (1)	1.92	

Table III. Atomic Positions and Anisotropic Temperature Factors[a] ($\times 10^4$) for Lanthanum Nicotinate Dihydrate[b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
La	0.32144 (2)	0.40286 (2)	0.49519 (1)	44.9 (3)	31.6 (2)	20.33 (9)	0.0 (1)	7.2 (1)	0.59(8)
O(2)	0.2340 (2)	0.2270 (2)	0.4344 (2)	76 (3)	54 (2)	40 (1)	11 (2)	18 (1)	17 (1)
O(3)	0.1072 (3)	0.4550 (2)	0.4163 (2)	111 (4)	79 (2)	31 (1)	41 (2)	−11 (1)	−14 (1)
O(4)	0.1120 (3)	0.3963 (2)	0.5800 (2)	89 (3)	71 (2)	41 (1)	27 (2)	25 (2)	24 (1)
O(5)	0.2648 (2)	0.2713 (2)	0.6131 (1)	65 (3)	58 (2)	32 (1)	7 (2)	11 (1)	7 (1)
O(6)	0.2822 (3)	0.6013 (2)	0.5100 (2)	79 (3)	41 (2)	67 (1)	2 (2)	10 (2)	−11 (1)
O(7)	0.4664 (2)	0.7094 (2)	0.5141 (1)	58 (2)	53 (1)	40 (1)	2 (1)	11 (1)	−3 (1)
O(8)	0.5119 (3)	0.5236 (2)	0.4009 (1)	119 (3)	66 (2)	22 (1)	−1 (2)	−1 (1)	−6 (1)
O(9)	0.3717 (3)	0.3990 (2)	0.3505 (2)	103 (3)	104 (2)	26 (1)	−37 (3)	15 (1)	−3 (1)
C(10)	0.3415 (3)	0.6917 (3)	0.5207 (2)	70 (4)	41 (3)	29 (1)	6 (3)	2 (2)	5 (2)
C(11)	0.2532 (3)	0.7859 (3)	0.5435 (2)	57 (4)	37 (3)	25 (1)	1 (3)	6 (2)	−1 (1)
C(12)	0.3067 (4)	0.8852 (3)	0.5688 (2)	72 (4)	54 (3)	43 (2)	2 (3)	1 (2)	−10 (2)
C(13)	0.2197 (4)	0.9681 (3)	0.5900 (2)	93 (5)	57 (3)	56 (2)	−1 (3)	6 (3)	−22 (2)
C(14)	0.0818 (4)	0.9487 (3)	0.5857 (2)	84 (5)	61 (3)	53 (2)	17 (3)	8 (3)	−17 (2)
N(15)	0.0258 (3)	0.8533 (3)	0.5613 (2)	60 (4)	60 (3)	52 (2)	6 (3)	9 (2)	−14 (2)
C(16)	0.1121 (4)	0.7744 (3)	0.5406 (2)	71 (4)	44 (3)	36 (2)	1 (2)	5 (2)	−4 (2)
C(17)	0.1494 (4)	0.3136 (3)	0.6197 (2)	67 (4)	53 (3)	22 (1)	−6 (3)	6 (2)	−1 (2)
C(18)	0.0515 (3)	0.2648 (2)	0.6754 (2)	68 (4)	59 (3)	21 (1)	−8 (3)	5 (2)	0 (1)
C(19)	0.0971 (4)	0.1888 (3)	0.7300 (2)	84 (4)	69 (3)	28 (1)	−9 (3)	5 (2)	8 (2)
N(20)	0.0149 (3)	0.1405 (3)	0.7806 (2)	112 (5)	94 (3)	31 (1)	−26 (3)	5 (2)	18 (2)
C(21)	−0.1163 (4)	0.1687 (4)	0.7765 (2)	108 (6)	96 (4)	33 (2)	−35 (4)	16 (3)	5 (2)
C(22)	−0.1706 (4)	0.2450 (4)	0.7250 (3)	76 (5)	115 (5)	43 (2)	−13 (4)	13 (3)	12 (3)
C(23)	−0.0848 (4)	0.2943 (4)	0.6729 (2)	73 (4)	89 (4)	37 (2)	−5 (4)	9 (2)	12 (2)
C(24)	0.4652 (3)	0.4664 (3)	0.3438 (2)	65 (4)	50 (3)	23 (1)	8 (3)	3 (2)	0 (2)
C(25)	0.5253 (3)	0.4765 (3)	0.2649 (2)	62 (4)	45 (3)	21 (1)	2 (3)	4 (2)	0 (2)
C(26)	0.5002 (4)	0.3956 (3)	0.2088 (2)	83 (5)	54 (3)	27 (2)	−8 (3)	6 (2)	−5 (2)
C(27)	0.5575 (5)	0.4054 (3)	0.1365 (2)	111 (5)	64 (5)	28 (2)	0 (3)	12 (2)	−8 (2)
C(28)	0.6360 (4)	0.4968 (4)	0.1231 (2)	113 (6)	71 (4)	30 (2)	−1 (4)	17 (2)	5 (2)
N(29)	0.6581 (4)	0.5776 (3)	0.1753 (2)	120 (5)	67 (3)	31 (1)	−22 (3)	12 (2)	6 (2)
C(30)	0.6043 (4)	0.5656 (3)	0.2454 (2)	97 (5)	59 (3)	25 (1)	7 (3)	0 (2)	0 (2)

Atom	x	y	z	Atom	x	y	z
H(31)C(26)[a]	0.45	0.33	0.22	H(39)C(19)	0.19	0.17	0.74
H(32)C(27)	0.54	0.35	0.09	H(40)O(2)	0.15	0.19	0.44
H(33)C(30)	0.61	0.62	0.29	H(41)C(14)	0.01	1.01	0.60
H(34)C(16)	0.08	0.70	0.52	H(42)O(3)	0.08	0.43	0.37
H(35)C(23)	−0.12	0.35	0.63	H(43)C(13)	0.26	1.04	0.61
H(36)C(12)	0.41	0.89	0.58	H(44)C(22)	−0.28	0.27	0.72
H(37)C(21)	−0.18	0.12	0.81	H(45)O(2)	0.26	0.20	0.40
H(38)C(28)	0.69	0.50	0.07	H(46)O(3)	0.06	0.49	0.42

[a] The hydrogen isotropic thermal parameter was held constant at 4.00 throughout all refinement. The form of the anisotropic thermal parameter was $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The hydrogen atom labels reflect the atom to which the hydrogen atom is bonded. [b] In all tables, the figures in parentheses are the standard deviations of the least significant digit as obtained from the full variance-covariance matrix.

are given in Table I. The melting points of the compounds were not well defined; changes in physical appearance of the crystals began at about 170°. Magnetic moments of the hydrated nicotinates of Pr(III), Nd(III), and Gd(III), in Table I, were obtained by the Faraday method.

The crystals used for X-ray data collection were mounted with shellac in 0.5-mm diameter glass capillaries of 0.01-mm wall thickness. The dimensions of the crystals used were 0.30 × 0.29 × 0.27 mm and 0.32 × 0.30 × 0.23 mm for the lanthanum and samarium compounds, respectively. The linear absorption coefficients, μ, are 22.04 cm^{-1} for the lanthanum compound and 20.57 cm^{-1} for the samarium compound. Absorption corrections were not made.

Oscillation, Weissenberg, and precession photographs taken with Mo Kα radiation displayed monoclinic symmetry with the systematic absences of $0k0$, k = odd, and $h0l$, l = odd, for both compounds, corresponding to the space group $P2_1/c$ ($C_{2h}{}^5$). Preliminary lattice constants were obtained from these photographs; precise constants for each crystal were then obtained by the least-squares refinement of angular data for 20 reflections from a Picker four-circle, card-controlled diffractometer (λ = 0.70926).[8] The

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(7) E. Wilkes, "A Study of the Lanthanide Nicotinates," M.S. Thesis, Wayne State University, 1969.

(8) Local versions of the following major computer programs were used in the solution and refinement of these structures: J. Ibers, "A Diffractometer Setting and Cell Constant Parameter Refinement Program for the Picker 4-Circle Automatic Diffractometer," Chemistry Department, Northwestern University (based upon W. C. Hamilton's MODE 1); D. L. Smith, "A Crystallographic Data Reduction Program," Eastman Kodak; A. Zalkin, "A Crystallographic Fourier and

Table IV. Atomic Positions and Anisotropic Temperature Factors (×10⁴) for Samarium Nicotinate Dihydrate[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sm	0.31475 (2)	0.39856 (2)	0.49463 (1)	39.2 (4)	30.7 (2)	16.4 (1)	2.0 (1)	5.8 (1)	−0.7 (8)
O(2)	0.2411 (3)	0.2217 (3)	0.4363 (2)	68 (3)	52 (3)	38 (1)	−12 (2)	14 (2)	−15 (1)
O(3)	0.1032 (3)	0.4387 (2)	0.4185 (2)	71 (4)	55 (3)	27 (1)	14 (3)	−4 (2)	−10 (1)
O(4)	0,1126 (3)	0.4054 (3)	0.5783 (2)	68 (4)	74 (3)	28 (1)	17 (3)	15 (2)	16 (2)
O(5)	0.2561 (3)	0.2658 (2)	0.6050 (2)	78 (4)	54 (3)	33 (1)	18 (3)	19 (2)	6 (1)
O(6)	0.2867 (4)	0.5974 (2)	0.4936 (2)	76 (4)	37 (3)	41 (2)	−2 (2)	−2 (2)	−4 (1)
O(7)	0.4744 (3)	0.7076 (3)	0.5090 (2)	44 (4)	50 (3)	38 (1)	4 (2)	5 (2)	−3 (2)
O(8)	0.5476 (4)	0.5298 (3)	0.4014 (2)	139 (5)	95 (3)	23 (1)	23 (3)	−15 (2)	−15 (2)
O(9)	0.3810 (4)	0.4121 (3)	0.3635 (2)	99 (5)	100 (4)	27 (1)	−3 (3)	19 (2)	3 (2)
C(10)	0.3482 (4)	0.6890 (4)	0.5106 (2)	68 (5)	35 (3)	21 (2)	6 (4)	2 (2)	5 (2)
C(11)	0.2560 (4)	0.7841 (3)	0.5352 (2)	44 (4)	38 (3)	22 (1)	−4 (3)	5 (2)	0 (2)
C(12)	0.3125 (5)	0.8856 (4)	0.5623 (3)	61 (6)	44 (4)	43 (2)	−1 (3)	5 (3)	−9 (2)
C(13)	0.2238 (6)	0.9698 (4)	0.5850 (4)	103 (7)	49 (4)	52 (3)	4 (4)	4 (3)	−16 (3)
C(14)	0.0852 (5)	0.9493 (4)	0.5826 (3)	85 (6)	55 (5)	50 (3)	12 (4)	2 (3)	−15 (3)
N(15)	0.0275 (4)	0.8526 (4)	0.5556 (3)	55 (5)	63 (4)	46 (2)	10 (3)	9 (2)	−6 (2)
C(16)	0.1142 (5)	0.7729 (4)	0.5332 (3)	64 (5)	46 (4)	31 (2)	−7 (4)	3 (3)	−3 (2)
C(17)	0.1453 (4)	0.3172 (4)	0.6157 (2)	61 (5)	49 (4)	19 (2)	−7 (4)	2 (2)	−2 (2)
C(18)	0.0487 (4)	0.2732 (4)	0.6740 (2)	61 (5)	53 (4)	20 (2)	−6 (3)	7 (2)	1 (2)
C(19)	0.0958 (5)	0.1959 (5)	0.7281 (3)	83 (6)	79 (5)	25 (2)	−11 (4)	4 (3)	6 (3)
N(20)	0.0159 (5)	0.1524 (4)	0.7810 (3)	103 (6)	108 (5)	30 (2)	−22 (4)	2 (2)	23 (2)
C(21)	−0.1164 (5)	0.1856 (5)	0.7805 (3)	90 (7)	117 (6)	27 (2)	−32 (5)	9 (3)	8 (3)
C(22)	−0.1919 (5)	0.2635 (5)	0.7296 (3)	77 (6)	114 (6)	35 (2)	−14 (5)	14 (3)	14 (3)
C(23)	−0.0879 (4)	0.3080 (4)	0.6751 (3)	63 (6)	89 (5)	32 (2)	1 (4)	3 (3)	12 (3)
C(24)	0.4841 (5)	0.4728 (4)	0.3515 (3)	64 (5)	59 (4)	20 (2)	21 (4)	7 (2)	2 (2)
C(25)	0.5334 (4)	0.4746 (4)	0.2712 (2)	52 (5)	44 (3)	19 (2)	3 (3)	0 (2)	0 (2)
C(26)	0.4995 (5)	0.3885 (4)	0.2208 (3)	79 (6)	57 (4)	23 (2)	−10 (4)	7 (3)	−6 (2)
C(27)	0.5493 (6)	0.3930 (4)	0.1471 (3)	108 (7)	74 (5)	25 (2)	7 (4)	8 (3)	−11 (2)
C(28)	0.6289 (6)	0.4848 (5)	0.1289 (3)	119 (7)	90 (5)	24 (2)	3 (5)	19 (3)	9 (3)
N(29)	0.6597 (5)	0.5692 (4)	0.1758 (3)	117 (6)	77 (4)	30 (2)	−13 (4)	16 (3)	10 (2)
C(30)	0.6132 (5)	0.5635 (4)	0.2466 (3)	91 (6)	50 (4)	28 (2)	−12 (4)	0 (3)	1 (2)

Atom	x	y	z	Atom	x	y	z
H(31)C(14)[a]	0.01	1.02	0.60	H(39)C(23)	−0.13	0.36	0.63
H(32)C(16)	0.06	0.70	0.51	H(40)C(27)	0.52	0.35	0.11
H(33)C(21)	−0.17	0.14	0.82	H(41)C(26)	0.44	0.33	0.23
H(34)C(19)	0.19	0.17	0.73	H(42)C(28)	0.66	0.50	0.07
H(35)C(13)	0.28	1.05	0.61	H(43)O(3)	0.10	0.42	0.37
H(36)C(30)	0.64	0.62	0.29	H(44)O(3)	0.06	0.48	0.43
H(37)C(12)	0.42	0.90	0.56	H(45)O(2)	0.26	0.20	0.40
H(38)C(22)	−0.28	0.29	0.73	H(46)O(2)	0.16	0.20	0.44

[a] The hydrogen atoms were assigned a thermal parameter of 4.00, with this parameter being held constant in all refinement.

lattice constants for the other nicotinates studied were obtained from photographic studies and densities were determined by the flotation method. Table II contains the lattice constants, unit cell volumes, and experimental and calculated densities. The asymmetric units consist of $Ln(C_5H_4NCO_2)_3(H_2O)_2$.

The methods used to collect intensity data for the lanthanum and samarium compounds were identical. The data were collected on the previously described diffractometer, with Mo Kα radiation, using the moving crystal–moving counter (θ–2θ) scan technique with a take-off angle of 1.7°. A symmetric scan of 2.0° was used for all reflections with a scan rate of 1.0°/min and a stationary background count of 15 sec at each end of the scan. A 2.0-mil zirconium foil was employed as a β-filter and the pulse height analyzer was set to accept approximately 90%. All reflections whose peak intensities were greater than 10,000 counts per second were attenuated using a 2.0-mil brass foil. Data were collected with the counter aperture 30.1 cm from the crystals and with the a^* axes approximately parallel to the φ axis.

Within a limiting 2θ of 45°, 2842 (La) and 2784 (Sm) independent reflections in the ±*hkl* quadrant were collected. Four standards were measured at intervals of 200 reflections in order to monitor crystal and diffractometer stability; these standards were constants, within statistical significance, for both crystals throughout the data collection.

The intensity data were corrected for Lorentz and polarization effects. Standard deviations were assigned to the I's according to the formula

$$\sigma(I) = [P + 4(B_1 + B_2) + (0.0316^2 I)]^{1/2}$$

where P is the integrated intensity, B_1 and B_2 are the background counts, and I is the net intensity. The totals of 2388 (La) and 2398 (Sm) independent reflections satisfied the condition, $F^2 \geq 2.5\sigma(F^2)$ and were considered above background.

Solution and Refinement. Straightforward application of three-dimensional Patterson techniques to the data from the lanthanum compound yielded the position of the lanthanum ion. The discrepancy factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) based upon partial structure amplitudes that included only the lanthanum contribution was 0.339. The positions of the remaining nonhydrogen atoms were determined from a subsequent three-dimensional Fourier calculation. Six cycles of full-matrix isotropic refinement resulted in $R = 0.056$ and a weighted discrepancy factor, wR, of 0.087, where $wR = [\Sigma w(|F_o| - |F_c|)^2]^{1/2}/[\Sigma wF_o^2]^{1/2}$. All least-squares refinement[9] minimized the function $\Sigma w(|F_o| - |F_c|)^2$. Hydrogen atoms were then located on a difference Fourier map. The nitrogen atoms of the pyridine rings were unambiguously identified by

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Data Reduction Program," Chemistry Department, Lawrence Radiation Laboratory, University of California, Berkeley; W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS-A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratories, 1962; W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE—A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratories, 1964; C. K. Johnson, "ORTEP—A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratories, 1965.

(9) Scattering factors for La(III) and Sm(III) were taken from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965), and those for oxygen, carbon, nitrogen, and hydrogen, as well as the anomalous contributions to the rare earth scattering, are taken from the "International Tables for X-ray Crystallography," Vol. III, C. H. Macgillavry, G. D. Rieck, and K. Lonsdale, Ed., The Kynoch Press, Birmingham, 1962, p 201.

Table V. Bonding Distances for Lanthanum Nicotinate Dihydrate

Atoms[a]	Distance, Å	Atoms	Distance, Å
La–O(6)	2.460 (3)	C(14)–N(15)	1.340 (5)
La–O(7)′	2.500 (2)	C(14)–H(41)	1.1
La–O(2)	2.509 (3)	N(15)–C(16)	1.338 (5)
La–O(8)′	2.512 (3)	C(16)–H(34)	1.0
La–O(3)	2.517 (3)	C(17)–C(18)	1.503 (5)
La–O(9)	2.534 (3)	C(18)–C(19)	1.371 (5)
La–O(4)	2.568 (3)	C(18)–C(23)	1.383 (5)
La–O(5)	2.646 (3)	C(19)–N(20)	1.342 (5)
La–O(8)	2.918 (3)	C(19)–H(39)	1.0
O(2)–H(40)	0.9	N(20)–C(21)	1.330 (6)
O(2)–H(45)	0.7	C(21)–C(22)	1.366 (6)
O(3)–H(42)	0.9	C(21)–H(37)	1.1
O(3)–H(46)	0.7	C(22)–C(23)	1.387 (6)
O(4)–C(17)	1.256 (4)	C(22)–H(44)	1.1
O(5)–C(17)	1.253 (4)	C(23)–H(35)	1.0
O(6)–C(10)	1.253 (4)	C(24)–C(25)	1.498 (5)
O(7)–C(10)	1.253 (4)	C(25)–C(26)	1.384 (5)
O(8)–C(24)	1.262 (4)	C(25)–C(30)	1.382 (5)
O(9)–C(24)	1.240 (4)	C(26)–H(31)	1.0
C(10)–C(11)	1.498 (5)	C(26)–C(27)	1.381 (6)
C(11)–C(12)	1.377 (5)	C(27)–C(28)	1.378 (6)
C(11)–C(16)	1.389 (5)	C(27)–H(32)	1.0
C(12)–C(13)	1.380 (6)	C(28)–N(29)	1.335 (5)
C(12)–H(36)	1.1	C(28)–H(38)	1.1
C(13)–C(14)	1.371 (6)	N(29)–C(30)	1.336 (5)
C(13)–H(43)	1.0	C(30)–H(33)	1.0
N(15)–O(2)^{ii}	2.734 (4)		
N(15)–H(40)^{ii}	1.9		
N(20)–O(3)^{iii}	2.703 (5)		
N(20)–H(42)^{iii}	1.8		
N(29)–O(2)^{iv}	2.846 (4)		
N(29)–H(45)^{iv}	2.2		

[a] In this and the following tables, these notations will be used: ii refers to the symmetry equivalent position $-x, 1 - y, 1 - z$; iii refers to the symmetry equivalent position $x, 0.5 - y, 0.4 + z$; iv refers to the symmetry equivalent position $1 - x, 0.5 + y, 0.5 - z$. [c] The prime notation (′) refers to the atom at the equivalent position $1 - x, 1 - y, 1 - z$.

consideration of the higher electron densities at these positions, the absence of hydrogen peaks adjacent to these positions, and the unique opportunities for hydrogen bonding offered by those positions in the rings corresponding to the nitrogen atoms.

Two cycles of isotropic refinement, varying all parameters with the exception of the thermal parameters of the hydrogens which were held constant at 4.00, yielded an R value of 0.051 and a wR of 0.83. Three cycles of full-matrix anisotropic refinement, varying all parameters except the thermal parameters of the hydrogen atoms, produced a final R of 0.021, a wR of 0.027, and an error of fit of 1.4023. The greatest residual electron density on the final difference Fourier map, in the vicinity of the metal position, was 0.39 e/Å^3. The final R and wR values including all reflections were 0.032 and 0.056, respectively, with an error of fit of 1.52.

A similar procedure was used to solve and refine the structure of the samarium nicotinate and yielded a final anisotropic R of 0.025 and a wR of 0.034. The error of fit was 1.87, and the residual electron density on the final difference synthesis, near the metal position, was 0.43 e/Å^3. The final R and wR values including all reflections were 0.031 and 0.53, respectively, with an error of fit of 2.603.[10] Comparison of the observed and calculated structure amplitudes for the strongest reflections in both structures shows some secondary extinction, but with the low discrepancy factors obtained, this was not considered significant.

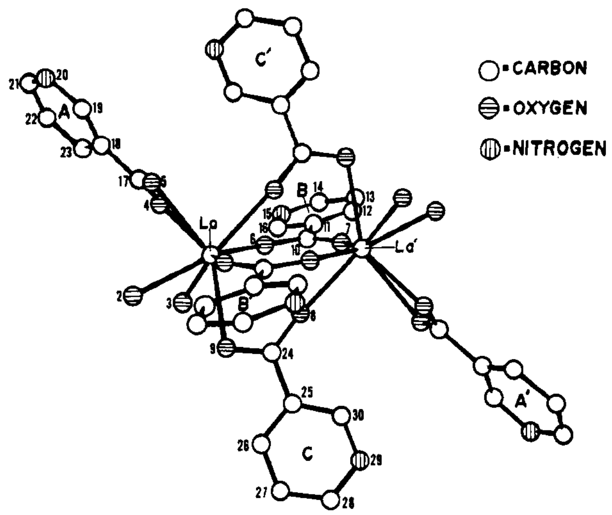

Figure 1a. View of the lanthanum(III) nicotinate dihydrate dimer with labeling of atoms.

The final atomic positions and anisotropic thermal parameters, for both compounds, are listed in Tables III (La) and IV (Sm). Table V contains bonding distances with their estimated standard deviations, and Table VI contains all pertinent angles for the La(III) structure. Tables VII and VIII, respectively, contain the analogous information for the Sm(III) compounds. Figure 1a gives the generalized numbering scheme corresponding to the tables.

Discussion and Description of Structure

The three-dimensional X-ray analyses of the crystals of the lanthanum(III) and samarium(III) nicotinates lead to the dimeric formulation $[Ln(C_5H_4NCO_2)_3(H_2O)_2]_2$ for the solid state. The structures of these compounds are depicted in Figures 1b (La) and 2 (Sm). Figure 3 shows the packing of the lanthanum compound.

For each compound, equivalent structural units corresponding to one-half of the dimer are related by a crystallographic center of inversion. In both compounds, the two symmetry-related metal ions are joined by four bridging carboxylate groups and are 4.221 (2) and 4.297 (1) Å apart for La(III) and Sm(III), respectively. Examination of the two structures (Figures 1 and 2), as well as diffraction patterns of other rare earth nicotinates (Table II), reveals that all the nicotinates studied have similar structures.

The nicotinate groups are coordinated to the metal ions solely through the carboxylate oxygens with four bridging and two chelating carboxylates per dimer. The carboxylate groups of nicotinate A are chelated to the metal with La–O distances of 2.586 (3) [La–O(4)] and 2.646 (3) Å [La–O(5)] and Sm–O distances of 2.486 (3) [Sm–O(4)] and 2.565 (3) Å (Sm–O(5)]. The carboxylate groups of nicotinate B are bridged in such a manner that each oxygen is bound to only one metal ion. The La–O and Sm–O distances are 2.460 (3) [La–O(6)], 2.500 (2) [La–O(7)′], 2.360 (3) [Sm–O(6)], and 2.391 (3) Å [Sm–O(7)′], respectively. The differences between structurally equivalent bonds in the two compounds are in agreement with the 0.10-Å difference in ionic radii[11] between La(III) and Sm(III).

The most prominent difference between the two structures is the orientation of the bridging nicotinate

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(10) Calculated and observed structure factors, tables of nonbonded distances, results of least-squares planes calculations, and graphical results of hydrogen bond calculations corresponding to Figure 4 for nicotinates B and C will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche.

(11) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., B*, 25, 925 (1969).

Table VI. Pertinent Angles in the Lanthanum Nicotinate Dihydrate Structure

Atoms defining angle	Angle, deg	Atoms defining angle	Angle, deg
H(45)–O(2)–H(40)	104	C(10)–C(11)–C(14)	176.8 (5)
H(46)–O(3)–H(42)	101	C(12)–C(11)–C(16)	117.5 (3)
O(3)–O(2)–O(5)	87.70 (9)	C(11)–C(12)–C(13)	119.4 (3)
O(4)–O(3)–O(2)	71.87 (9)	C(11)–C(12)–H(36)	119
O(3)–O(4)–O(5)	113.6 (1)	C(13)–C(12)–H(36)	122
La–O(4)–C(17)	96.1 (2)	C(12)–C(13)–C(14)	118.7 (4)
O(2)–O(5)–O(4)	80.5 (1)	C(12)–C(13)–H(43)	119
La–O(5)–C(17)	92.4 (2)	C(14)–C(13)–H(43)	122
O(9)–O(6)–O(8)′	81.61 (9)	C(13)–C(14)–N(15)	123.5 (3)
La–O(6)–C(10)	143.3 (2)	C(13)–C(14)–H(41)	122
O(9)–O(7)′–O(8)′	94.1 (1)	N(15)–C(14)–H(41)	114
La′–O(7)–C(10)	136.9 (2)	C(14)–N(15)–C(16)	116.6 (3)
C(24)–O(8)–La	85.8 (2)	N(15)–C(16)–C(11)	124.0 (3)
C(24)–O(8)–La′	159.4 (2)	N(15)–C(16)–H(34)	119
O(7)–O(8)–O(6)′	100.3 (1)	C(11)–C(16)–H(34)	117
C(24)–O(9)–La	104.9 (2)	O(4)–C(17)–O(5)	121.4 (3)
O(7)′–O(9)–O(6)	82.5 (1)	O(4)–C(17)–C(18)	118.4 (3)
O(6)–C(10)–C(11)	116.0 (3)	O(5)–C(17)–C(18)	120.0 (3)
O(7)–C(10)–C(11)	118.1 (3)	C(17)–C(18)–C(19)	119.8 (3)
O(6)–C(10)–O(7)	125.8 (3)	C(17)–C(18)–C(23)	121.6 (3)
C(10)–C(11)–C(12)	122.3 (3)	C(17)–C(18)–C(21)	177.2 (6)
C(10)–C(11)–C(16)	120.0 (3)	C(19)–C(18)–C(23)	118.5 (3)
C(18)–C(19)–N(20)	122.9 (4)	C(24)–C(25)–C(28)	179.3 (4)
C(18)–C(19)–H(39)	122	C(30)–C(25)–C(26)	118.4 (3)
N(20)–C(19)–H(39)	114	C(25)–C(26)–C(27)	119.0 (3)
C(19)–N(20)–C(21)	117.6 (4)	C(25)–C(26)–H(31)	121
N(20)–C(21)–C(22)	123.5 (4)	C(27)–C(26)–H(31)	120
N(20)–C(21)–H(37)	115	C(26)–C(27)–C(28)	118.2 (4)
C(22)–C(21)–H(37)	122	C(26)–C(27)–H(32)	122
C(21)–C(22)–C(23)	118.3 (4)	C(28)–C(27)–H(32)	119
C(21)–C(22)–H(44)	123	C(27)–C(28)–N(29)	123.8 (4)
C(23)–C(22)–H(44)	119	C(27)–C(28)–H(38)	122
C(22)–C(23)–C(18)	118.9 (4)	N(29)–C(28)–H(38)	114
C(22)–C(23)–H(35)	122	C(28)–N(29)–C(30)	117.1 (3)
C(18)–C(23)–H(35)	120	N(29)–C(30)–C(25)	123.3 (4)
O(8)–C(24)–O(9)	122.4 (3)	C(25)–C(30)–H(33)	115
O(8)–C(24)–C(25)	120.0 (3)	N(29)–C(30)–H(33)	121
O(9)–C(24)–C(25)	117.5 (3)	O(2)–H(40)–N(15)^{ii}	171
C(24)–C(25)–C(26)	119.7 (3)	O(3)–H(42)–N(20)^{iii}	172
C(24)–C(25)–C(30)	121.9 (3)	O(2)–H(45)–N(29)^{iv}	157

Table VII. Bonding Distances for Samarium Dihydrate

Atoms	Distance, Å	Atoms	Distance, Å
Sm–O(6)	2.360 (3)	C(12)–H(37)	1.0
Sm–O(8)′	2.362 (3)	C(13)–C(14)	1.359 (7)
Sm–O(7)′	2.391 (3)	C(13)–H(37)	1.2
Sm–O(9)	2.409 (4)	C(14)–N(15)	1.346 (7)
Sm–O(2)	2.415 (3)	C(14)–H(31)	1.1
Sm–O(3)	2.435 (3)	N(15)–C(16)	1.327 (6)
Sm–O(4)	2.486 (3)	C(16)–H(32)	1.0
Sm–O(5)	2.565 (3)	C(17)–C(18)	1.500 (6)
O(2)–H(45)	0.7	C(18)–C(19)	1.377 (7)
O(2)–H(46)	0.8	C(18)–C(23)	1.382 (6)
O(3)–H(44)	0.7	C(19)–N(20)	1.331 (6)
O(3)–H(43)	0.9	C(19)–H(34)	1.0
O(4)–C(17)	1.263 (5)	N(20)–C(21)	1.335 (7)
O(5)–C(17)	1.249 (5)	C(21)–C(22)	1.373 (8)
O(6)–C(10)	1.262 (5)	C(21)–H(33)	1.1
O(7)–C(10)	1.238 (5)	C(22)–C(23)	1.378 (7)
O(8)–C(24)	1.244 (6)	C(22)–H(38)	1.1
O(9)–C(24)	1.249 (6)	C(23)–H(39)	1.0
C(10)–C(11)	1.504 (6)	C(24)–C(25)	1.499 (6)
C(11)–C(16)	1.372 (6)	C(25)–C(26)	1.377 (6)
C(11)–C(12)	1.389 (6)	C(25)–C(30)	1.377 (7)
C(12)–C(13)	1.379 (7)	C(26)–C(27)	1.395 (8)
N(15)–H(46)^{ii}	1.9	C(26)–H(41)	1.0
N(15)–O(2)^{ii}	2.745 (5)	C(27)–C(28)	1.369 (8)
N(20)–H(43)^{iii}	1.9	C(27)–H(40)	0.9
N(20)–O(3)^{iii}	2.736 (5)	C(28)–N(29)	1.318 (7)
N(29)–H(45)^{iv}	2.2	C(28)–H(42)	1.1
N(29)–O(2)^{iv}	2.853 (5)	N(29)–C(30)	1.335 (7)
		C(30)–H(36)	1.0

Table VIII. Pertinent Angles in the Samarium Nicotinate Dihydrate Structure

Atoms defining angle	Angle, deg	Atoms defining angle	Angle, deg
H(45)–O(2)–H(46)	95	C(11)–C(12)–C(13)	118.5 (4)
H(43)–O(3)–H(44)	109	C(11)–C(12)–H(37)	120
O(3)–O(2)–O(5)	87.5 (1)	C(13)–C(12)–H(37)	121
O(4)–O(3)–O(2)	77.0 (1)	C(12)–C(13)–C(14)	119.1 (5)
O(3)–O(4)–O(5)	108.0 (2)	C(12)–C(13)–H(35)	113
Sm–O(4)–C(17)	95.3 (3)	C(14)–C(13)–H(35)	127
O(2)–O(5)–O(4)	85.2 (2)	C(13)–C(14)–N(15)	123.6 (5)
Sm–O(5)–C(17)	91.9 (3)	C(13)–C(14)–H(31)	120
O(9)–O(6)–O(8)′	86.1 (3)	N(15)–C(14)–H(31)	116
Sm–O(6)–C(10)	142.7 (3)	C(14)–N(15)–C(16)	116.5 (4)
O(9)–O(7)′–O(8)′	91.3 (1)	N(15)–C(16)–C(11)	124.4 (4)
Sm′–O(7)–C(10)	138.2 (3)	N(15)–C(16)–H(32)	110
C(24)–O(8)–Sm′	168.1 (4)	C(11)–C(16)–H(32)	126
O(7)–O(8)–O(6′)	96.2 (1)	O(4)–C(17)–O(5)	121.3 (4)
C(24)–O(9)–Sm	116.3 (3)	O(4)–C(17)–C(18)	119.3 (4)
O(7)–O(9)–O(6)	93.6 (3)	O(5)–C(17)–C(18)	119.5 (4)
O(6)–C(10)–C(11)	115.3 (4)	C(17)–C(18)–C(19)	119.9 (4)
O(7)–C(10)–C(11)	117.8 (4)	C(17)–C(18)–C(23)	121.6 (4)
O(6)–C(10)–O(7)	126.9 (4)	C(17)–C(18)–C(21)	177.3 (5)
C(10)–C(11)–C(12)	120.7 (4)	C(19)–C(18)–C(23)	118.5 (4)
C(10)–C(11)–C(16)	121.4 (4)	C(18)–C(19)–N(20)	123.2 (5)
C(10)–C(11)–C(14)	177.9 (4)	C(18)–C(19)–H(34)	123
C(12)–C(11)–C(16)	117.9 (4)	N(20)–C(19)–H(34)	114
C(19)–N(20)–C(21)	117.6 (5)	C(25)–C(26)–C(27)	118.8 (4)
N(20)–C(21)–C(22)	123.2 (5)	C(25)–C(26)–H(41)	125
N(20)–C(21)–H(33)	111	C(27)–C(26)–H(41)	116
C(22)–C(21)–H(33)	125	C(26)–C(27)–C(28)	117.5 (5)
C(21)–C(22)–C(23)	118.6 (5)	C(26)–C(27)–H(40)	126
C(21)–C(22)–H(38)	122	C(28)–C(27)–H(40)	116
C(23)–C(22)–H(38)	119	C(27)–C(28)–N(29)	124.5 (5)
C(22)–C(23)–C(18)	118.9 (5)	C(27)–C(28)–H(42)	125
C(22)–C(23)–H(39)	121	N(29)–C(28)–H(42)	110
C(18)–C(23)–H(39)	120	C(28)–N(29)–C(30)	117.5 (4)
O(8)–C(24)–O(9)	124.3 (4)	N(29)–C(30)–C(25)	122.8 (5)
O(8)–C(24)–C(25)	118.9 (4)	C(25)–C(30)–H(36)	113
O(9)–C(24)–C(25)	116.9 (4)	N(29)–C(30)–H(36)	124
C(24)–C(25)–C(26)	120.7 (4)	O(2)–H(46)–N(15)^{ii}	175
C(24)–C(25)–C(30)	120.5 (4)	O(3)–H(43)–N(20)^{iii}	153
C(24)–C(25)–C(28)	177.8 (7)	O(2)–H(45)–N(29)^{iv}	148
C(30)–C(25)–C(26)	118.8 (4)		

C. In the lanthanum compound, one oxygen in each carboxylate group is bound to one lanthanum, whereas the second oxygen may be considered to interact with two lanthanums. The latter carboxylate oxygen, O(8), is 2.512 (3) Å from La′ and 2.918 (3) Å from La; the other La–O distance, La–O(9), is 2.534 (3) Å. The 2.918 (3) Å distance represents, at most, a very weak interaction; Hoard and coworkers[12] considered a La–N distance of 2.86 Å, in the La(III) chelate of ethylenediamine-tetraacetic acid, to represent a weak lanthanum–nitrogen interaction. The nicotinate group C in the samarium compound is more symmetrically disposed with respect to the two Sm(III) ions. Each of these oxygens is within bonding distance of only one samarium at distances of 2.409 (4) [Sm–O(9)] and 2.362 (3) Å [Sm–O(8)′]; the Sm–O(8) distance is 3.223 (4) Å. The La–O and Sm–O distances predicted by adding ionic radii are 2.46 and 2.36 Å, respectively.[10]

The coordination group of each metal is completed by two water molecules. The metal–water oxygen distances, Ln–O(2) and Ln–O(3), are 2.509 (3) and 2.517 (3) Å, and 2.415 (3) and 2.435 (3) Å for the lanthanum and samarium compounds, respectively. The water molecules are situated so as to permit hydrogen bonding to all nitrogen atoms (Figure 3). This hy-

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(12) M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, **87**, 1611 (1965).

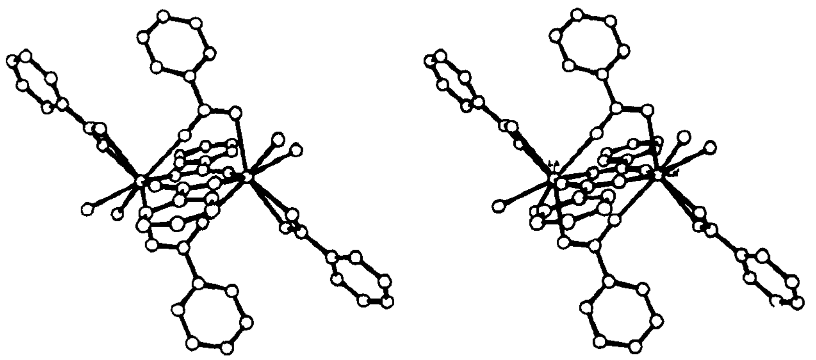

Figure 1b. A stereoscopic view of the lanthanum(III) nicotinate dihydrate dimer.

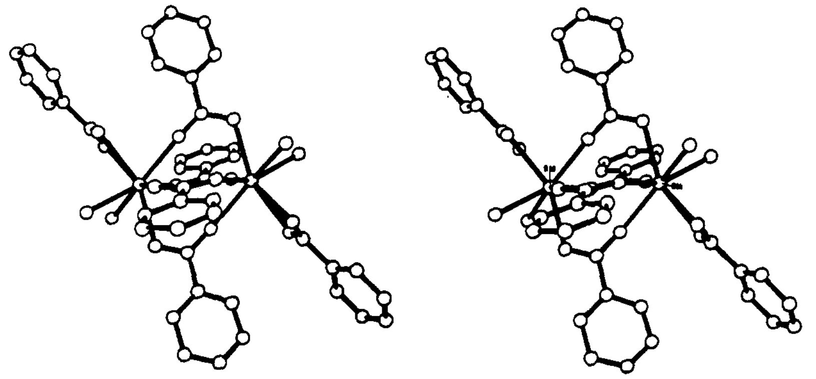

Figure 2. A stereoscopic view of the samarium(III) nicotinate dihydrate dimer.

drogen bonding occurs between different dimeric units, so that the entire crystal network is bound together by these hydrogen bonding forces. The distances from O(2) to N(15) and N(29) in adjacent dimers, respectively, are 2.734 (4) and 2.846 (4) Å in the La(III) structure and 2.745 (5) and 2.853 (5) Å in the Sm(III) structure. The distances from O(3) to N(20) in adjacent dimers are 2.703 (5) and 2.736 (5) Å in the La(III) and Sm(III) compounds, respectively. This hydrogen bonding apparently accounts for the shifts in the infrared frequencies of the C–C and C–N stretching vibrations noted by Chupakhina and Serebrennikov.[6]

The eight-coordination polyhedron, for both structures, may be thought of as a highly distorted square antiprism with O(2), O(3), O(4), and O(5) comprising the one "square" and O(6), O(7)′, O(8)′, and O(9) comprising the other "square." The dihedral angles between these two planes are 17.1° in the La(III) structure and 10.2° in the Sm(III) analog. The largest deviations of an atom from its defining plane are 0.268 Å (La) and 0.154 Å (Sm) for the O(2), O(3), O(4), and O(5) plane and 0.137 Å (La) and 0.057 Å (Sm) for the O(6), O(7)′, O(8)′, and O(9) plane. The O(2), O(3), O(4), O(5) plane contains two atoms of the same carboxylate group and consequently one would expect the greater deviation in this plane.

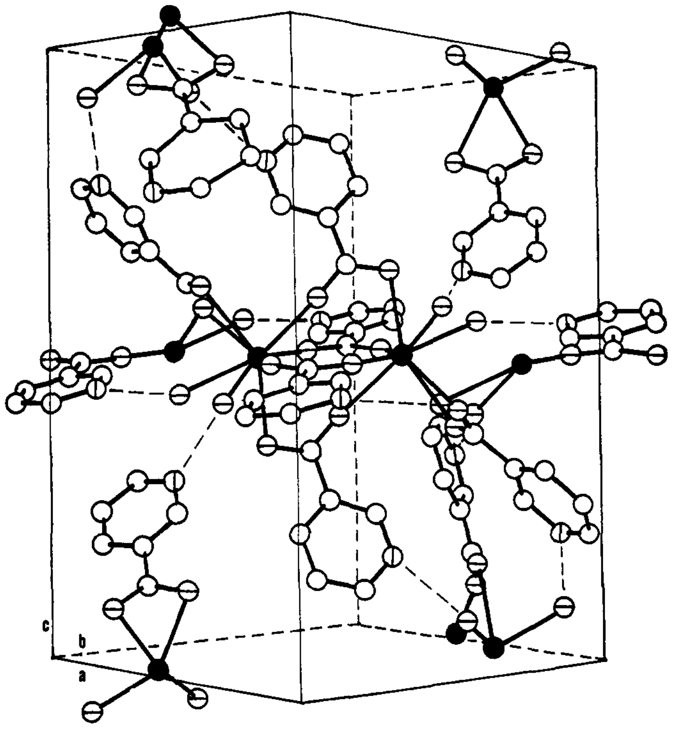

Figure 3. Packing diagram of the lanthanum(III) nicotinate dihydrate dimer. Horizontal lines indicate oxygens, vertical lines indicate nitrogens, and solid circles indicate lanthanums. The dashed lines show the hydrogen bonding.

The Sm–Sm′ distance is 0.076 (2) Å longer than the La–La′ distance. Generally, for a series of analogous compounds of lanthanide ions, as the size of the lanthanide ion decreases, the repulsions between ligands in the coordination sphere increase until the crystal structure becomes unstable. At this point, the coordination number of the Ln^{3+} ion decreases and the structure changes. In the nicotinates, as the ionic radius of the Ln^{3+} ion decreases, the Ln–Ln′ distance increases, thus alleviating the increased nonbonded interaction.

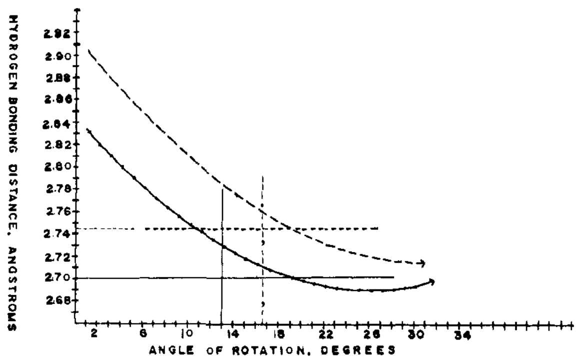

Figure 4. Graphical representation of hydrogen bond distances *vs.* rotation of pyridine rings for nicotinate A. The solid curves correspond to the lanthanum compound and the dashed lines to the samarium compound. The vertical lines represent the actual angles of rotation and the horizontal lines the actual hydrogen bond distances.

Several distortions in these structures may result from the packing of the oxygens about the metal ions to give the strongest possible binding forces and the packing of the pyridine rings in order to give the strongest possible hydrogen bonds. The pyridine rings of nicotinates A, B, and C are all rotated out of the planes of their respective carboxylate groups. Moreover, the angle formed by the carboxylate carbon, the vicinal carbon, and the transannular carbon deviates from the ideal value of 180° in all the ligands. The actual angles range from 176.8 (5) to 179.3 (4)° for the La(III) structure and from 177.3 (4) to 177.9 (4)° in the Sm(III) structure. All pyridine rings are planar within 0.014 Å. In the lanthanum compound, the dihedral angles between the carboxylate group and the attached pyridine ring are 13.0, 9.6, and 16.9° for nicotinates A, B, and C, respectively. The nonplanarity of the nicotinate groups arises primarily from the rotation of the pyridine ring about the axis defined by the carboxylate carbon, the vicinal carbon, and the transannular carbon. That this assumption is not quantitatively correct can be seen by the fact that these two ring carbons do not lie in the plane of the respective carboxylate group. Carbon C(28), the transannular carbon in nicotinate C, deviates most from the plane of its carboxylate group, lying 0.091 Å from the carboxylate plane. Therefore, although the dihedral angles arise primarily from rotation about the previously mentioned axis, a bending about the carboxylate carbon-ring carbon bond also adds to this dihedral angle.

In order to test the hypothesis that the rotations of the pyridine rings are a result of minimization of hydrogen bonding distances, the following procedure was followed. Positions were calculated for the pyridine atoms such that they would all lie in the plane of their respective carboxylate groups and would form a regular hexagon with sides of 1.38 Å. For the lanthanum compound, the hydrogen bonding distances using the ideal nitrogen positions are greater than the observed hydrogen bonding distances, increasing from 2.703 (5) to 2.842 Å, 2.734 (4) to 2.824 Å, and 2.846 (4) to 2.983 Å for nicotinates A, B, and C, respectively. These idealized pyridine rings were then rotated about the axes defined by the carboxylate carbon and the attached pyridine carbons. Figure 4 contains a graphical representation of these, data for nicotinate A.[10] For nicotinates A and C, the rotation of the pyridine ring does minimize the hydrogen bonding distance. The fact that the observed dihedral angle does not correspond to the angle of rotation calculated to give the minimum distance results from the assumptions in the calculation of a regular hexagon and of no bending about the carboxylate carbon–pyridine bond. However, the calculated minimum hydrogen bonding distance for nicotinate A of 2.690 Å agrees with the observed distance of 2.703 (5) Å. For nicotinate C the two distances are 2.824 and 2.846 (4) Å, respectively. For nicotinate B, the minimum distance on rotation is calculated to be 2.813 Å, whereas the observed hydrogen bonding distance is 2.734 (4) Å; minimization in the hydrogen bonding distance for this ring (B) is achieved primarily by a bending about the carboxylate carbon–ring carbon single bond. The mixing between the π systems of the carboxylate group and of the pyridine ring is small, as shown by the carboxylate carbon–ring carbon bond distance of 1.50 Å for all such bonds found in the two structures. The corresponding bond lengths for benzoic acid[13] and nicotinic acid[14] are 1.48 (2) Å. The bond order for this bond in the benzoate ion is reported to be[15] essentially 1.0 and consequently there is little, if any, barrier to rotation about the bond. Bending about this single bond is somewhat more unfavorable. However, a bending of 3.1° as in the nicotinate B is not prohibitive since the decreased hydrogen bonding distance stabilizes the lattice structure.

The above conclusions for the lanthanum structure can be equally well applied to the samarium structure. Again, the rotation of the pyridine rings of nicotinates A and C gives a minimum for the hydrogen bonding distance that is very close to the actual distance. The bending about the carboxylate carbon–ring carbon single bond minimizes the hydrogen bonding distance in nicotinate B. Similar approaches show that minimization of hydrogen bond distances is responsible for the asymmetric disposition of nicotinates and for the nonequivalence of chelating metal–oxygen distances (Δ = 0.08 Å). The differences between the Ln–chelating oxygen distances and the Ln–bridging oxygen distances are most likely related to the inherent instability of the four-membered chelating ring relative to the five-membered bridging ring.

The geometry of the pyridine rings is normal with the average aromatic C–C ring bond distances of 1.379 (6) (La) and 1.377 (7) Å (Sm). The average aromatic N–C bonds are 1.337 (5) and 1.332 (7) Å for the La(III) and Sm(III) structures, respectively. The average carboxylate carbon–ring carbon single bond distances are 1.500 (5) (La) and 1.501 (6) Å (Sm), with the average carboxylate carbon–oxygen distances of 1.253 (4) (La) and 1.251 (5) Å (Sm). All the individual bond lengths are within 3 standard deviations of their respective averages. The average O–C–O angles are 123.2 (3) (La) and 124.2 (4)° (Sm).

Quantitative magnetic behavior of dimeric lanthanide complexes is not known. Rare earth complexes in general show simple paramagnetism. Figgis[16] con-

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siders the crystal field and coupling effect to be weak as a result of the shielding of the 4f electrons by the 5s and 5p electrons. The results of magnetic studies (Faraday method) over the temperature range 300–23°K on the nicotinates of Pr(III), Nd(III), and Gd(III) are given in Table I. The moments of the Pr(III) and Nd(III) compounds are temperature dependent; the greatly reduced magnetic moments at 23°K for the Pr(III) and Nd(III) complexes as compared with their normal paramagnetic room temperature moments might be attributed to antiferromagnetic coupling between the two metal ions in the dimeric species. The absence of such a decrease in moment in the Gd(III) complex (with the $^8S_{7/2}$ ground state for the metal ion), however, suggests that the decrease results from crystal field effects. Further detailed susceptibility studies of these and other lanthanide complexes are in progress.

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Carboranes Containing Gallium and Indium Cage Heteroatoms. Synthesis, Molecular Structure, and Reactions

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Abstract: The reaction of trimethylgallium or trimethylindium with 2,3-dicarba-*nido*-hexaborane(8) yields the closed polyhedral species 1-$CH_3GaC_2B_4H_6$ and 1-$CH_3InC_2B_4H_6$, respectively, in which the metal atom in each case forms one apex of a pentagonal-bipyramidal cage. These carboranes have been structurally characterized by boron-11 and proton nmr, mass spectra, and infrared spectra, and by a single-crystal X-ray diffraction study of the gallium compound. The X-ray results have disclosed two distinctive features: (1) the gallium atom is closer to the boron atoms than to the carbon atoms in the five-membered equatorial ring, in contrast to other related carborane structures, and (2) the Ga–CH_3 axis is tilted by 20° with respect to the perpendicular to the equatorial plane. These findings are interpreted in terms of a qualitative molecular orbital model which assumes back-donation of electrons from the d_{yz} orbital of the metal atom to the e_2 antibonding orbital of the carborane ligand. The gallium and indium compounds are thermally stable to at least 100°, but pyrolysis at high temperatures generates 2,3-$C_2B_4H_8$. Both materials react readily with HCl, the gallium compound generating 2,3-$C_2B_4H_8$. Bromine attacks both metallocarboranes at room temperature, destroying the cage structure and forming the dimer of $(CH_3)_2GaBr$ and presumably the indium analog, respectively.

The remarkable variety of stable carborane cage compounds is illustrated by the many known families of isoelectronic and isostructural species. For example, the well-known icosahedral carborane isomers *o*-, *m*-, and *p*- carborane (1,2- 1,7-, and 1,12-$C_2B_{10}H_{12}$) are isoelectronic analogs of a number of other icosahedral cage systems containing transition metal or main group heteroatoms in addition to boron and carbon. Among the main group heterocarboranes are such recent discoveries as $BeC_2B_9H_{12}^-$,[1] $RAlC_2B_9H_{11}$[2] (R = CH_3 or C_2H_5), $M^{IV}C_2B_9H_{11}$[3] (M^{IV} = Ge, Sn, or Pb), $CH_3GeCB_{10}H_{11}$,[4] and $M^{V}CB_{10}H_{11}$[5] (M^{V} = P, As, or Sb), in all of which the heteroatom formally replaces an isoelectronic BH or CH group in $C_2B_{10}H_{12}$. In addition, a large number of transition metal π complexes and other species have been derived from several of the compounds listed.[6]

Few examples are known of heteroatom insertion into small carboranes, a fact which reflects the heretofore limited research effort in this area rather than inherent problems of synthesis or stability in these systems. Several recent communications from this laboratory have reported the synthesis of small carborane–transition metal π complexes[7] and of 1-$CH_3GaC_2B_4H_6$,[8] an analog of the polyhedral 2,4-$C_2B_5H_7$ system. In this paper we describe in detail the preparation, structural characterization, and some chemistry of 1-$CH_3GaC_2B_4H_6$ and 1-$CH_3InC_2B_4H_6$, as well as the results

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