

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,  
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## Structural Studies of Bridged Lanthanide(III) Complexes. Diaquotri(nicotinic acid)holmium(III) Hexa(isothiocyanato)chromate(III) Dihydrate and Diaquotris(isonicotinato)lanthanum(III)<sup>1</sup>

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The structures of the crystalline neutral complex of the isonicotinate ion with lanthanum(III) and of the crystalline salt of the cationic complex of nicotinic acid with holmium(III) have been determined by three-dimensional X-ray diffraction techniques. The complexes crystallize in  $P2_1/c$ . The crystal parameters for  $\text{Ho}(\text{C}_5\text{H}_4\text{NCOOH})_3(\text{H}_2\text{O})_2\text{Cr}(\text{NCS})_6 \cdot 2\text{H}_2\text{O}$  are  $a = 9.578$  (5) Å,  $b = 25.954$  (13) Å,  $c = 15.784$  (7) Å,  $\beta = 108.48$  (2)°,  $d_{\text{calcd}} = 1.797$ ,  $d_{\text{measd}} = 1.78$  (2) g/cm<sup>3</sup>. The conventional discrepancy factor for this structure is 0.048 for 2989 diffractometer data. The crystal parameters for  $\text{La}(\text{C}_5\text{H}_4\text{NCOO})_3(\text{H}_2\text{O})_2$  are  $a = 9.744$  (3) Å,  $b = 19.908$  (9) Å,  $c = 11.607$  (4) Å,  $\beta = 68.20$  (2)°,  $d_{\text{calcd}} = 1.72$ ,  $d_{\text{measd}} = 1.70$  (2) g/cm<sup>3</sup>. The discrepancy factor for this structure is 0.038 for 2554 diffractometer data. The primary structural units in both compounds are polymer chains made up of lanthanide(III) ions alternately linked by four and two bridging carboxylate groups. The eight coordination about each metal is completed by two water molecules. In the acid complex, two additional waters and one hexaisothiocyanatochromate ion are also present. The acid ligand appears to be present as a zwitterion with the hydrogen attached to the nitrogen. These linear polymeric structures are compared with the dimeric structures found in the complexes of the rare earth metals with the nicotinate ion.

### Introduction

The coordination of trivalent rare earth ions with the carboxylate and carbonyl functional groups has been the subject of a number of studies.<sup>2-8</sup> Chupakhina and Serebrennikov<sup>3,4</sup> have described the preparation and properties of the trivalent lanthanide complexes with nicotinic acid (pyridine-3-carboxylic acid) and the nicotinate anion (pyridine-3-carboxylate). These compounds were formulated as  $[\text{Ln}(\text{C}_5\text{H}_4\text{NCOO})_3] \cdot [\text{Cr}(\text{NCS})_6]$  and  $[\text{Ln}(\text{C}_5\text{H}_4\text{NCOO})_3]$ . The structure of the nicotinate complexes has been shown<sup>6</sup> to consist of two lanthanide(III) ions, related by a crystallographic inversion center, bridged by four carboxylate groups, with an additional carboxylate group chelating to each metal ion; the coordination sphere is completed by two water molecules per metal (coordination number, 8). Extensive three-dimensional hydrogen bonding serves both to stabilize these complexes in the solid state and to partially dictate their structures. Although rare earth complexing is primarily ionic, more structural data is needed to establish the extent of any directional character present.

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TABLE I

PHYSICAL CONSTANTS AND EXPERIMENTAL DATA

	$\text{Ho}(\text{C}_5\text{H}_4\text{NCOOH})_3 \cdot (\text{H}_2\text{O})_2\text{Cr}(\text{NCS})_6 \cdot 2\text{H}_2\text{O}$	$\text{La}(\text{C}_5\text{H}_4\text{NCOO})_3(\text{H}_2\text{O})_2$
Formula weight	1006.82	541.25
Space group	$P2_1/c$ ( $Z = 4$ )	$P2_1/c$ ( $Z = 4$ )
$a$	9.578 (5) Å	9.744 (3) Å
$b$	25.954 (13) Å	19.908 (9) Å
$c$	15.784 (7) Å	11.607 (4) Å
$\beta$	108.48 (2)°	68.20 (2)°
Unit cell volume	3721.1 Å <sup>3</sup>	2090.8 Å <sup>3</sup>
Density, obsd	1.78 (2) g/cm <sup>3</sup>	1.70 (2) g/cm <sup>3</sup>
Density, calcd	1.80 g/cm <sup>3</sup>	1.72 g/cm <sup>3</sup>
% C(obsd)/% C(calcd)	28.51/28.63	39.91/39.93
% H(obsd)/% H(calcd)	2.34/2.30	3.00/2.96
% N(obsd)/% N(calcd)	12.41/12.52	7.63/7.76
Crystal size	0.13 × 0.11 × 0.14 mm	0.30 × 0.29 × 0.22 mm
Linear abs coeff	28.79/cm	21.38/cm
Data collected	4230	3660
Data obsd	2989	2554
$\theta$ (max)	22.5	25.0

$$\sigma(I) = [(I\sigma(A)/A)^2 + A^2(P + \sigma^2(B)) + (I \cdot PCTI)^2]^{1/2}$$

$$\sigma^2(B) = (B^2/(B1 + B2)) + (30(B1 + B2)/(SR \cdot TB))^2(2\sigma^2(2\theta))$$

$$B = |2\theta_2 - 2\theta_1|(30/(SR \cdot TB))(B1 + B2)$$

$$PCTI = 0.04$$

$$\sigma(2\theta) = 0.0025$$

By coordination of ligands which closely resemble the nicotinate ion but have different hydrogen bonding sites, the hydrogen bonding patterns and packing are altered. The dependence of the detailed stereochemistry about the metal upon the hydrogen bonding is a function of the stability of the coordination geometry and the directional character of the metal-ligand bonding. Pursuant to the above discussion, we have investigated the structures of the hydrated complexes of holmium(III) and lanthanum(III) with nicotinic acid and the isonicotinate anion (pyridine-4-carboxylate), respectively.

### Experimental Section

Crystals of the holmium(III) nicotinic acid complex were obtained using the procedure outlined by Chupakhina and Serebrennikov.<sup>3</sup> The synthesis straightforwardly yielded well

formed, stable, violet crystals. A representative single crystal in the form of a rectangular parallelepiped, with dimensions  $0.13 \times 0.11 \times 0.14$  mm was mounted on a glass fiber with Kodak-910 adhesive and used for intensity data collection. The lanthanum isonicotinate compound was synthesized using a modified form of the procedure given by Chupakhina and Serebrennikov<sup>4</sup> for the rare earth nicotinate dihydrates. The crystal used for intensity data collection, which measured  $0.30 \times 0.29 \times 0.22$  mm, was mounted in a 0.5-mm diameter glass capillary of 0.01-mm wall thickness, using shellac as an adhesive. The results of chemical analyses for both compounds are given in Table I.

For both compounds, oscillation, Weissenberg, and precession photographs, with Mo  $K\alpha$  radiation, exhibited Laue symmetry  $2/m$ , and the systematic extinctions:  $0k0$ ,  $k = 2n + 1$ ; and  $h0l$ ,  $l = 2n + 1$ ; consistent with the monoclinic space group  $C_{2h}^2-P2_1/c$ . Pseudo A centering was indicated by the low intensities of data with  $k + l = 2n + 1$ . For the isonicotinate, a zero-level Weissenberg photograph (using a crystal other than the one used for data collection) about an inclined axis showed diffraction spots characteristic of high thermal motion or disordering.

Using Mo  $K\alpha_1$  peaks, reflections were accurately centered on a Picker four-angle card controlled X-ray diffractometer. From the setting angles of these reflections, the preliminary lattice constants were refined by the method of least squares.<sup>9</sup> The resultant lattice constants as well as data collection parameters and physical constants for both compounds are summarized in Table I.

The moving crystal-moving counter ( $\theta-2\theta$ ) scan technique<sup>10</sup> was used to collect intensity data. A combination of Zr foil and pulse-height analysis was used for energy discrimination. All reflections whose peak intensities were greater than 10,000 cps were attenuated with brass foils. A sorting routine was used in the data generation program in order to reject overlapping reflections. The scan widths were calculated to compensate for the Mo  $K\alpha_1$   $K\alpha_2$  separation. The standard reflections used to monitor crystal and instrument stability were constant within statistical error.

The data were corrected for Lorentz and polarization effects. Standard deviations of  $F^2$  were calculated according to the formula for  $\sigma(I)$  given in Table I where  $I$  is the net intensity,  $P$  is the integrated intensity,  $B1$  and  $B2$  are the background counts,  $SR$  is the scan rate,  $TB$  is the background counting time (at each end of the scan),  $A$  is the attenuator factor, and  $PCTI$  is a factor that primarily affects those higher intensity reflections where the contribution to  $\sigma(F^2)$  from counter statistics is small.<sup>11</sup> All data with net intensities less than 2.5 times their standard deviations were rejected.

### Solution and Refinement of Structure

**Diaquotri(nicotinic acid)holmium(III) Hexa(isothiocyanato)chromate(III) Dihydrate.**—Three dimensional Patterson analysis yielded the positional parameters for the holmium ion as  $x = 0.25$ ,  $y = 0.00$ ,  $z = 0.50$  corresponding to A centering for the metal ions. These parameters were used to calculate structure factors, and a conventional discrepancy factor [ $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$ ] of 0.66 resulted. An electron-density map phased on these parameters allowed positioning of the chromium ion and subsequent electron-density maps resulted in the positioning

(9) Local versions of the following major computer programs were used in the solution and refinement of all structures in this work: 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 Data Reduction Program," Chemistry Department, Lawrence Radiation Laboratory, University of California, Berkeley; W. R. Busing, K. O. Martin, and H. A. Levy, "OR FLS-A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratories, Oak Ridge, Tenn., 1962; W. R. Busing, K. O. Martin, and H. A. Levy, "OR FFE—A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratories, Oak Ridge, Tenn., 1964; C. K. Johnson, "ORTEP—A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations," ORNL-3794, Oak Ridge National Laboratories, Oak Ridge, Tenn., 1965; T. A. Hamor, "A Least Squares Planes Program."

(10) T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Company, 1966, p 129.

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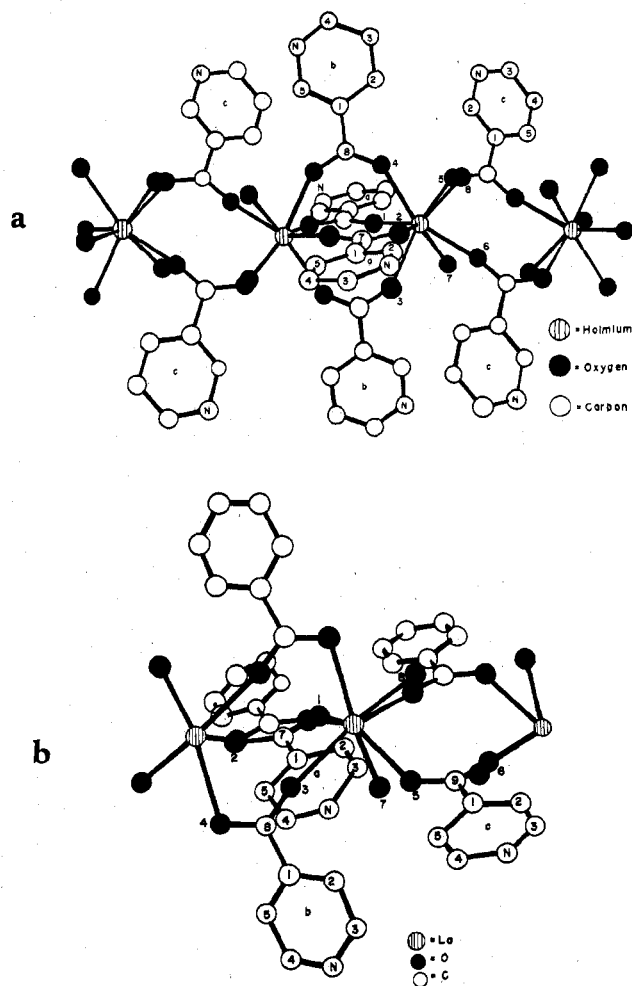


Figure 1.—(a) Diaquotri(nicotinic acid)holmium(III) hexa(isothiocyanato)chromate(III) dihydrate; the diaquotri(nicotinic acid)holmium(III) polymeric chain. (b) Diaquotris(isonicotinato)lanthanum(III).

of all of the nonhydrogen atoms in the asymmetric unit. The nitrogens in the nicotinic acid rings were distinguished from the meta carbons by noting hydrogen bonding patterns, as well as differences in distances and thermal parameters.

Full-matrix least-squares refinement, including real and imaginary anomalous dispersion corrections and anisotropic temperature factors for Ho, Cr, and S, proceeded routinely to  $R = 0.048$  and a weighted discrepancy factor  $wR = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$  of 0.060.<sup>12,13</sup> The error of fit,  $[\sum w(F_o - F_c)^2 / (NO - NV)]^{1/2}$ , is 1.85, and the data/parameter ratio is 12.2. The electron-density difference map contained peaks corresponding to some, but not all, hydrogen atoms. The largest nonmetal peak was observed to be  $0.73 \text{ e}/\text{\AA}^3$ .

**Diaquotris(isonicotinato)lanthanum(III).**—Three-dimensional Patterson techniques yielded the position of the lanthanum ion as  $x = 0.225$ ,  $y = 0.50$ , and  $z = 0.50$ , corresponding to A centering for the metal ions. The lanthanum coordinates resulted in an  $R$  value of 0.351. A subsequent three-dimensional electron-density map contained a pseudomirror plane parallel to the  $ac$

(12) Scattering factors for La(III) and Ho(III) were taken from D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); and those for hydrogen, carbon, nitrogen, oxygen, and sulfur, 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. Macgillivray, G. D. Rieck, and K. Lonsdale, Ed., 1962, p 201.

(13) Calculated and observed structure factors 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 code number INORG-72-2818. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

TABLE II  
 ATOMIC COORDINATES AND THERMAL PARAMETERS<sup>a</sup>

Atom	x	y	z	$\beta_{11}$ or (B)	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Diaquotri(nicotinic acid)holmium(III) Hexa(isothiocyanato)chromate(III) Dihydrate									
Ho	0.26520 (5)	0.00563 (2)	0.49493 (3)	31.3 (7)	9.2 (1)	23.5 (3)	-0.6 (3)	14.1 (3)	-0.8 (2)
Cr	0.3891 (3)	0.6507 (1)	0.3370 (2)	96 (3)	17.0 (6)	36 (1)	-7 (1)	15 (2)	1.8 (6)
S(1)	-0.0097 (4)	0.6918 (2)	0.0814 (3)	84 (5)	24 (1)	62 (3)	2 (2)	10 (3)	11 (1)
S(2)	0.7909 (5)	0.6406 (2)	0.6056 (3)	116 (6)	24 (1)	51 (2)	1 (2)	-4 (3)	2 (1)
S(3)	0.1344 (5)	0.4949 (2)	0.3164 (3)	146 (6)	21 (1)	82 (3)	-13 (2)	47 (4)	2 (2)
S(4)	0.8272 (6)	0.6246 (3)	0.2782 (3)	169 (8)	53 (2)	57 (3)	19 (3)	40 (4)	-14 (2)
S(5)	0.4851 (5)	0.8280 (2)	0.2999 (4)	155 (7)	19 (1)	92 (4)	-4 (2)	42 (4)	6 (2)
S(6)	0.1110 (5)	0.6794 (2)	0.5322 (4)	156 (7)	23 (1)	99 (4)	-7 (2)	82 (4)	-7 (2)
C(1)	0.127 (2)	0.6748 (6)	0.165 (1)	3.3 (3)					
C(2)	0.649 (2)	0.6402 (6)	0.516 (1)	3.5 (3)					
C(3)	0.241 (2)	0.5452 (7)	0.327 (1)	3.8 (3)					
C(4)	0.657 (2)	0.6276 (7)	0.276 (1)	5.5 (4)					
C(5)	0.458 (2)	0.7680 (7)	0.321 (1)	3.8 (3)					
C(6)	0.192 (2)	0.6720 (6)	0.458 (1)	4.0 (3)					
C(7)	0.401 (1)	-0.0131 (5)	0.3302 (8)	2.2 (2)					
C(8)	0.511 (1)	0.1984 (6)	0.4815 (8)	2.4 (3)					
C(9)	0.050 (1)	0.0698 (5)	0.5915 (7)	1.9 (2)					
C <sub>a</sub> (1)	0.384 (1)	-0.0265 (5)	0.2364 (8)	2.0 (2)					
C <sub>a</sub> (2)	0.244 (1)	-0.0260 (6)	0.1748 (9)	3.0 (3)					
C <sub>a</sub> (3)	0.343 (2)	-0.0542 (7)	0.061 (1)	5.2 (4)					
C <sub>a</sub> (4)	0.481 (2)	-0.0539 (7)	0.122 (1)	4.3 (3)					
C <sub>a</sub> (5)	0.502 (1)	0.0392 (6)	0.2106 (9)	3.3 (3)					
C <sub>b</sub> (1)	0.515 (1)	0.1534 (5)	0.4591 (8)	2.2 (2)					
C <sub>b</sub> (2)	0.388 (2)	0.1850 (7)	0.437 (1)	3.9 (3)					
C <sub>b</sub> (3)	0.394 (2)	0.2366 (7)	0.411 (1)	4.9 (4)					
C <sub>b</sub> (4)	0.527 (2)	0.2566 (7)	0.409 (1)	4.9 (4)					
C <sub>b</sub> (5)	0.647 (1)	0.1754 (6)	0.4571 (9)	2.9 (3)					
C <sub>c</sub> (1)	0.030 (1)	0.1196 (5)	0.6350 (8)	2.3 (2)					
C <sub>c</sub> (2)	0.120 (1)	0.1584 (6)	0.6354 (9)	3.0 (3)					
C <sub>c</sub> (3)	-0.013 (2)	0.2135 (7)	0.703 (1)	5.1 (4)					
C <sub>c</sub> (4)	-0.100 (2)	0.1718 (7)	0.709 (1)	4.0 (3)					
C <sub>c</sub> (5)	-0.083 (1)	0.1247 (6)	0.6740 (9)	3.2 (3)					
N <sub>a</sub>	0.226 (1)	-0.0409 (5)	0.0885 (8)	4.4 (3)					
N <sub>b</sub>	0.647 (1)	0.2256 (6)	0.4816 (8)	4.5 (3)					
N <sub>c</sub>	0.096 (1)	0.2070 (5)	0.6676 (8)	4.3 (3)					
N(1)	0.227 (1)	0.6622 (5)	0.2229 (9)	4.8 (3)					
N(2)	0.548 (1)	0.6417 (5)	0.4521 (8)	4.1 (3)					
N(3)	0.324 (1)	0.5770 (6)	0.3345 (8)	4.7 (3)					
N(4)	0.536 (2)	0.6331 (6)	0.2743 (9)	5.6 (3)					
N(5)	0.441 (1)	0.7250 (6)	0.3339 (9)	4.9 (3)					
N(6)	0.253 (1)	0.6684 (5)	0.4086 (9)	4.5 (3)					
O(1)	0.4693 (9)	0.0074 (4)	0.6167 (5)	2.8 (2)					
O(2)	0.2854 (8)	-0.0067 (4)	0.3521 (5)	2.7 (2)					
O(3)	0.3697 (9)	-0.0746 (4)	0.4952 (6)	3.0 (2)					
O(4)	0.3858 (9)	0.0794 (4)	0.4754 (6)	3.0 (2)					
O(5)	0.1703 (9)	0.0643 (4)	0.5735 (6)	2.8 (2)					
O(6)	0.0522 (8)	-0.0373 (4)	0.4276 (5)	2.5 (2)					
O(7)	0.0856 (9)	0.0623 (4)	0.3832 (5)	2.7 (2)					
O(8)	0.2099 (9)	-0.0457 (4)	0.6118 (6)	3.2 (2)					
O(9)	0.219 (1)	0.2718 (6)	0.5819 (9)	7.5 (3)					
O(10)	-0.061 (1)	-0.0598 (5)	-0.0199 (8)	5.9 (3)					
Diaquotris(isonicotinato)lanthanum(III)									
La	0.21817 (4)	0.49937 (2)	0.51011 (3)	46.1 (6)	10.4 (1)	35.7 (4)	1.6 (3)	-12.7 (3)	-2.2 (2)
O(7)	0.2867 (6)	0.5760 (3)	0.3354 (5)	103 (8)	20 (2)	54 (5)	0 (3)	-8 (5)	10 (2)
O(8)	0.3222 (6)	0.4162 (3)	0.6306 (5)	81 (8)	22 (2)	72 (6)	-1 (3)	-31 (6)	11 (3)
O(6)	0.6247 (7)	0.4356 (3)	0.4061 (6)	99 (8)	23 (2)	91 (6)	-1 (3)	-49 (6)	-11 (3)
O(5)	0.4241 (6)	0.4342 (3)	0.3598 (5)	83 (7)	20 (2)	61 (5)	12 (3)	-29 (5)	-4 (2)
O(3)	0.1056 (7)	0.4903 (3)	0.3511 (5)	104 (8)	17 (2)	43 (5)	-1 (3)	-24 (5)	2 (2)
O(4)	-0.0564 (7)	0.4997 (3)	0.2610 (5)	69 (7)	42 (2)	47 (5)	14 (4)	-14 (5)	-6 (3)
O(1)	0.0859 (7)	0.3898 (3)	0.5333 (5)	113 (9)	15 (2)	81 (7)	-4 (3)	-51 (6)	2 (3)
O(2)	-0.1053 (6)	0.3851 (3)	0.4721 (6)	61 (7)	14 (2)	111 (8)	5 (3)	-32 (6)	-6 (3)
C(9)	0.5416 (8)	0.4080 (4)	0.3604 (7)	59 (10)	12 (2)	38 (7)	0 (4)	-4 (7)	3 (3)
C <sub>c</sub> (1)	0.5824 (9)	0.3394 (4)	0.3062 (8)	74 (11)	15 (2)	76 (9)	4 (4)	-28 (8)	-10 (4)
C <sub>c</sub> (2)	0.685 (2)	0.3053 (7)	0.313 (3)	334 (37)	36 (5)	807 (64)	73 (11)	-437 (45)	-134 (15)
C <sub>c</sub> (3)	0.713 (2)	0.2391 (9)	0.266 (3)	368 (45)	45 (7)	851 (83)	81 (14)	-439 (55)	-133 (21)
N <sub>c</sub>	0.650 (1)	0.2106 (5)	0.210 (1)	182 (18)	26 (3)	202 (16)	10 (6)	-34 (14)	-39 (6)
C <sub>c</sub> (4)	0.542 (4)	0.2451 (9)	0.196 (2)	879 (91)	34 (7)	429 (43)	83 (20)	-433 (55)	-87 (13)
C <sub>c</sub> (5)	0.507 (3)	0.3115 (8)	0.239 (2)	620 (60)	39 (6)	432 (41)	88 (16)	-398 (45)	-82 (13)
C(8)	0.0704 (9)	0.4917 (4)	0.2570 (7)	61 (10)	27 (3)	30 (6)	1 (4)	-4 (6)	-2 (4)
C <sub>b</sub> (1)	0.1924 (9)	0.4797 (5)	0.1300 (7)	65 (10)	28 (3)	32 (7)	-6 (4)	-7 (7)	-3 (3)
C <sub>b</sub> (2)	0.3172 (9)	0.4426 (5)	0.1187 (8)	65 (11)	29 (3)	57 (8)	13 (5)	-11 (8)	-9 (4)
C <sub>b</sub> (3)	0.416 (1)	0.4300 (5)	0.0009 (9)	72 (12)	38 (4)	64 (9)	0 (6)	-6 (8)	-8 (5)
N <sub>b</sub>	0.4025 (9)	0.4548 (4)	-0.1046 (7)	92 (11)	34 (3)	59 (8)	-9 (5)	-8 (7)	-5 (4)

TABLE II (Continued)

Atom	$x$	$y$	$z$	$\beta_{11}$ or (B)	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
C <sub>b</sub> (4)	0.173 (1)	0.5062 (5)	0.0254 (8)	95 (12)	32 (3)	48 (7)	-12 (5)	-23 (7)	-2 (4)
C <sub>b</sub> (5)	0.2839 (12)	0.4914 (5)	-0.0900 (8)	117 (14)	40 (4)	40 (7)	-23 (7)	-21 (8)	2 (4)
C(7)	0.0093 (9)	0.3622 (4)	0.4829 (7)	68 (10)	17 (2)	50 (9)	1 (5)	-12 (8)	2 (3)
C <sub>a</sub> (1)	0.0548 (9)	0.2916 (4)	0.4331 (8)	79 (11)	19 (3)	71 (9)	15 (4)	-26 (9)	-10 (4)
C <sub>a</sub> (2)	0.153 (3)	0.2571 (9)	0.459 (2)	680 (62)	57 (7)	396 (37)	151 (18)	-432 (44)	-101 (13)
C <sub>a</sub> (3)	0.190 (3)	0.1911 (9)	0.415 (2)	712 (72)	51 (7)	386 (40)	152 (19)	-369 (48)	-87 (14)
N <sub>a</sub>	0.151 (1)	0.1648 (5)	0.330 (1)	238 (20)	27 (3)	183 (15)	43 (7)	-104 (15)	-41 (6)
C <sub>a</sub> (4)	0.066 (3)	0.1977 (9)	0.304 (2)	542 (54)	51 (7)	477 (45)	119 (16)	-411 (45)	-115 (14)
C <sub>a</sub> (5)	0.002 (2)	0.2604 (9)	0.362 (2)	530 (52)	65 (8)	553 (48)	141 (16)	-465 (45)	-154 (16)

<sup>a</sup> Standard deviations from the full variance-covariance matrix are given in parentheses for the least significant digit(s). The form of the anisotropic temperature factor is  $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$ . The  $\beta$ 's are multiplied by  $10^4$ .

TABLE III  
SIGNIFICANT INTERNUCLEAR SEPARATIONS<sup>a</sup>

Atoms	Distance, Å	Atoms	Distance, Å	Atoms	Distance, Å	Atoms	Distance, Å
Diaquotri(nicotinic acid)holmium(III)				Diaquotris(isonicotinato)lanthanum(III)			
Hexa(isothiocyanato)chromate(III) Dihydrate				(1) Bonding Distances			
Ho-O(1)	2.266 (8)	C(7)-O(1) <sup>I</sup>	1.264 (13)	La-O(6)	2.465 (6)	C <sub>c</sub> (2)-C <sub>c</sub> (3)	1.42
Ho-O(2)	2.345 (8)	C(7)-O(2)	1.275 (13)	La-O(3)	2.479 (5)	C <sub>c</sub> (3)-N <sub>c</sub>	1.19
Ho-O(3)	2.309 (9)	C(8)-O(3) <sup>I</sup>	1.248 (14)	La-O(5)	2.481 (5)	N <sub>c</sub> -C <sub>c</sub> (4)	1.31
Ho-O(4)	2.307 (9)	C(8)-O(4)	1.270 (14)	C <sub>c</sub> (4)-O(1)	2.496 (6)	C <sub>b</sub> (1)-C <sub>b</sub> (5)	1.40
Ho-O(5)	2.323 (9)	C(9)-O(5)	1.280 (13)	La-O(2) <sup>IV</sup>	2.524 (6)	C(8)-C <sub>b</sub> (1)	1.53 (1)
Ho-O(6)	2.272 (8)	C(9)-O(6) <sup>II</sup>	1.254 (14)	La-O(4) <sup>IV</sup>	2.536 (6)	C <sub>b</sub> (1)-C <sub>b</sub> (2)	1.39 (1)
Ho-O(7)	2.512 (8)	C(7)-C <sub>a</sub> (1)	1.478 (16)	La-O(7)	2.582 (6)	C <sub>b</sub> (1)-C <sub>b</sub> (5)	1.40 (1)
Ho-O(8)	2.465 (9)	C(8)-C <sub>b</sub> (1)	1.475 (18)	La-O(8)	2.603 (8)	C <sub>b</sub> (2)-C <sub>b</sub> (3)	1.37 (1)
Cr-N(1)	1.991 (14)	C(9)-C <sub>a</sub> (1)	1.503 (18)	La-O(3) <sup>IV</sup>	2.969 (6)	C <sub>b</sub> (3)-N <sub>b</sub>	1.37 (1)
Cr-N(2)	1.982 (13)	N <sub>a</sub> -C <sub>a</sub> (2)	1.373 (17)	O(7)-N <sub>b</sub> <sup>V</sup>	2.772 (9)	N <sub>b</sub> -C <sub>b</sub> (4)	1.32 (1)
Cr-N(3)	2.006 (15)	N <sub>a</sub> -C <sub>a</sub> (3)	1.373 (19)	O(8)-N <sub>a</sub> <sup>VI</sup>	2.80 (1)	C <sub>b</sub> (4)-C <sub>b</sub> (5)	1.40 (1)
Cr-N(4)	2.011 (15)	N <sub>b</sub> -C <sub>b</sub> (4)	1.355 (19)	O(6)-C(9)	1.247 (9)	C(7)-C <sub>a</sub> (1)	1.52 (1)
Cr-N(5)	1.994 (16)	N <sub>b</sub> -C <sub>b</sub> (5)	1.364 (18)	O(5)-C(9)	1.261 (9)	C <sub>a</sub> (1)-C <sub>a</sub> (2)	1.30
Cr-N(6)	2.027 (13)	N <sub>c</sub> -C <sub>c</sub> (2)	1.406 (18)	O(3)-C(8)	1.260 (9)	C <sub>a</sub> (1)-C <sub>a</sub> (5)	1.29
N(1)-C(1)	1.146 (16)	N <sub>c</sub> -C <sub>c</sub> (3)	1.345 (19)	O(4)-C(8)	1.23 (1)	C <sub>a</sub> (2)-C <sub>a</sub> (3)	1.41
N(2)-C(2)	1.155 (16)	C <sub>a</sub> (1)-C <sub>a</sub> (2)	1.384 (16)	O(1)-C(7)	1.236 (9)	C <sub>a</sub> (3)-N <sub>a</sub>	1.29
N(3)-C(3)	1.132 (18)	C <sub>a</sub> (3)-C <sub>a</sub> (4)	1.365 (20)	O(2)-C(7)	1.25 (1)	N <sub>a</sub> -C <sub>a</sub> (4)	1.18
N(4)-C(4)	1.159 (19)	C <sub>a</sub> (4)-C <sub>a</sub> (5)	1.406 (20)	C(9)-C <sub>c</sub> (1)	1.49 (1)	C <sub>a</sub> (4)-C <sub>a</sub> (5)	1.45
N(5)-C(5)	1.157 (19)	C <sub>a</sub> (5)-C <sub>a</sub> (1)	1.360 (17)	C <sub>c</sub> (1)-C <sub>c</sub> (2)	1.24	O(7)-N <sub>c</sub> <sup>VII</sup>	2.78 (1)
N(6)-C(6)	1.115 (17)	C <sub>b</sub> (1)-C <sub>b</sub> (2)	1.415 (19)	C <sub>c</sub> (1)-C <sub>c</sub> (5)	1.37		
C(1)-S(1)	1.596 (15)	C <sub>b</sub> (2)-C <sub>b</sub> (3)	1.405 (22)			(2) Nonbonded Distances	
C(2)-S(2)	1.619 (15)	C <sub>b</sub> (3)-C <sub>b</sub> (4)	1.385 (21)	La-C(8) <sup>V</sup>	3.099 (7)	O(5)-O(3)	3.336 (8)
C(3)-S(3)	1.631 (17)	C <sub>b</sub> (5)-C <sub>b</sub> (1)	1.393 (17)	O(7)-O(5)	2.874 (9)	O(3)-O(1)	2.865 (8)
C(4)-S(4)	1.623 (18)	C <sub>c</sub> (1)-C <sub>c</sub> (2)	1.325 (18)	O(7)-O(2) <sup>IV</sup>	2.926 (8)	O(3)-O(2)	2.905 (8)
C(5)-S(5)	1.631 (18)	C <sub>c</sub> (3)-C <sub>c</sub> (4)	1.385 (23)	O(7)-O(6) <sup>VIII</sup>	2.971 (8)	O(3)-C(7)	2.94 (1)
C(6)-S(6)	1.614 (16)	C <sub>c</sub> (4)-C <sub>c</sub> (5)	1.374 (21)	O(7)-O(8)	3.009 (8)	O(3)-O(1) <sup>IV</sup>	3.018 (8)
		C <sub>c</sub> (5)-C <sub>c</sub> (1)	1.409 (18)	O(7)-O(3)	3.174 (9)	O(3)-O(2) <sup>IV</sup>	3.217 (8)
				O(7)-C <sub>a</sub> (4)	3.43	O(3)-O(3) <sup>IV</sup>	3.32 (1)
		(2) Nonbonded Distances		O(8)-O(5)	2.945 (8)	O(4)-O(1) <sup>IV</sup>	3.178 (8)
Ho-Ho <sup>I</sup>	4.459 (2)	O(5)-O(6) <sup>II</sup>	2.237 (12)	O(8)-O(4) <sup>IV</sup>	2.946 (8)	O(4)-O(2)	3.251 (8)
Ho-Ho <sup>II</sup>	5.141 (2)	O(5)-O(7)	2.853 (12)	O(8)-O(1)	2.964 (8)	O(1)-C(8) <sup>IV</sup>	3.32 (1)
O(1)-O(2) <sup>I</sup>	2.243 (11)	O(5)-O(8)	2.917 (14)	O(8)-O(6) <sup>VIII</sup>	2.998 (9)	O(2)-C(8)	3.24 (1)
O(1)-O(3)	2.821 (12)	O(6)-O(7)	2.725 (13)	O(8)-C(9)	3.074 (9)	C <sub>c</sub> (2)-C <sub>a</sub> (5) <sup>IX</sup>	3.44
O(1)-O(4)	2.824 (12)	O(6)-O(8)	2.827 (12)	O(8)-O(6)	3.149 (9)	C <sub>c</sub> (3)-C <sub>a</sub> (5) <sup>IX</sup>	3.40
O(1)-O(8)	2.821 (12)	N <sub>a</sub> -O(10)	2.781 (17)	O(8)-C <sub>a</sub> (4)	3.41	C <sub>b</sub> (2)-N <sub>b</sub> <sup>V</sup>	3.36 (1)
O(2)-O(3)	2.775 (12)	N <sub>c</sub> -O(9)	2.654 (19)	O(6)-O(2) <sup>IX</sup>	3.166 (8)	C <sub>b</sub> (3)-C <sub>b</sub> (3) <sup>V</sup>	3.23 (2)
O(2)-O(4)	2.920 (12)	S(4)-O(7) <sup>III</sup>	3.339 (10)	O(6)-O(4) <sup>IX</sup>	3.200 (9)	C <sub>b</sub> (3)-N <sub>b</sub> <sup>V</sup>	3.38 (1)
O(2)-O(7)	2.777 (12)	O(9)-S(6) <sup>IV</sup>	3.349 (15)	O(5)-O(1)	3.282 (8)	C <sub>a</sub> (5)-C <sub>c</sub> (3) <sup>X</sup>	3.40
O(3)-O(4) <sup>I</sup>	2.242 (11)	O(1)-O(5)	3.099 (12)	O(5)-C <sub>b</sub> (2)	3.33 (1)		
O(3)-O(8)	2.842 (12)	O(2)-O(6)	2.955 (11)				
O(4)-O(7)	2.816 (12)						

<sup>a</sup> The Roman numerals in Tables III, IV, and V refer to the following symmetry transformations of an element at fractional coordinates  $x, y, z$ : (I)  $1-x, -y, 1-z$ ; (II)  $-x, -y, 1-z$ ; (III)  $1-x, 1/2+y, 1/2-z$ ; (IV)  $-x, 1-y, 1-z$ ; (V)  $1-x, 1-y, -z$ ; (VI)  $x, 1/2-y, 1/2+z$ ; (VII)  $1-x, 1/2+y, 1/2-z$ ; (VIII)  $1-x, 1-y, 1-z$ ; (IX)  $1+x, y, z$ ; (X)  $x-1, y, z$ ; (XI)  $x, 1-y, 1-z$ . <sup>b</sup> Atoms C<sub>a</sub>(2) → C<sub>a</sub>(5) and C<sub>c</sub>(2) → C<sub>c</sub>(5) in diaquotris(isonicotinato)lanthanum are subject to disorder as explained in the text. The root-mean-square thermal displacements for these atoms range as high as 0.7 Å. Thus the estimated standard deviations for distances and angles involving these atoms have no physical significance and are not given in Tables III and IV.

plane and intersecting the  $b$  axis at  $y = 0.50$ . Three of the largest peaks, which did not lie on the pseudomirror plane and whose coordinates fitted the geometry of a bridging carboxylate group, were used along with the lanthanum coordinates in an electron-density calculation. The results of this calculation did not contain the pseudomirror plane to any great degree and the remaining atoms were positioned. Six cycles of full-matrix

isotropic refinement yielded an  $R$  value of 0.069. However, the isotropic thermal parameters of eight carbon atoms ranged from 11 to 17. These were the carbon atoms meta and ortho to the nitrogen atom in isonicotinates a and c.

Barring steric factors, a freely rotating or thermally disordered pyridine ring might be expected in the nicotinate ligand since the pyridine group is free to rotate about the bond between the

TABLE IV: STRUCTURAL ANGLES

Atoms	Angle, deg	Atom	Angle, deg
Diaquotri(nicotinic acid)holmium(III) Hexa(isothiocyanato)chromate(III) Dihydrate			
O(1)-Ho-O(2)	120.4 (3)	O(7)-Ho-O(8)	125.4 (3)
O(1)-Ho-O(3)	76.1 (3)	N(1)-Cr-N(2)	177.9 (9)
O(1)-Ho-O(4)	76.3 (3)	N(1)-Cr-N(3)	88.8 (5)
O(1)-Ho-O(5)	84.9 (3)	N(1)-Cr-N(4)	93.1 (6)
O(1)-Ho-O(6)	144.3 (3)	N(1)-Cr-N(5)	87.7 (6)
O(1)-Ho-O(7)	142.9 (3)	N(1)-Cr-N(6)	91.0 (5)
O(1)-Ho-O(8)	73.1 (3)	N(2)-Cr-N(3)	92.8 (5)
O(2)-Ho-O(3)	73.2 (3)	N(2)-Cr-N(4)	88.2 (5)
O(2)-Ho-O(4)	77.7 (3)	N(2)-Cr-N(5)	90.7 (5)
O(2)-Ho-O(5)	140.2 (3)	N(2)-Cr-N(6)	87.6 (5)
O(2)-Ho-O(6)	79.6 (3)	N(3)-Cr-N(4)	92.0 (6)
O(2)-Ho-O(7)	69.3 (3)	N(3)-Cr-N(5)	176.3 (5)
O(2)-Ho-O(8)	138.5 (3)	N(3)-Cr-N(6)	88.7 (6)
O(3)-Ho-O(4)	120.9 (3)	N(4)-Cr-N(5)	89.5 (6)
O(3)-Ho-O(5)	146.3 (3)	N(4)-Cr-N(6)	175.9 (6)
O(3)-Ho-O(6)	83.3 (3)	N(5)-Cr-N(6)	90.1 (5)
O(3)-Ho-O(7)	136.8 (3)	Cr-N(1)-C(1)	168.9 (13)
O(3)-Ho-O(8)	73.0 (3)	Cr-N(2)-C(2)	172.9 (12)
O(4)-Ho-O(5)	79.9 (3)	Cr-N(3)-C(3)	154.5 (14)
O(4)-Ho-O(6)	139.3 (3)	Cr-N(4)-C(4)	150.0 (15)
O(4)-Ho-O(7)	71.4 (3)	Cr-N(5)-C(5)	171.0 (13)
O(4)-Ho-O(8)	141.6 (3)	Cr-N(6)-C(6)	168.4 (14)
O(5)-Ho-O(6)	97.2 (3)	N(1)-C(1)-S(1)	177.8 (16)
O(5)-Ho-O(7)	72.2 (3)	N(2)-C(2)-S(2)	177.8 (19)
O(5)-Ho-O(8)	75.0 (3)	N(3)-C(3)-S(3)	173.7 (16)
O(6)-Ho-O(7)	69.2 (3)	N(4)-C(4)-S(4)	175.5 (19)
O(6)-Ho-O(8)	73.2 (3)	N(5)-C(5)-S(5)	178.4 (17)
N(6)-C(6)-S(6)	176.5 (16)	C(7)-C <sub>a</sub> (1)-C <sub>a</sub> (5)	120.9 (11)
Ho-O(1)-C(7) <sup>I</sup>	164.7 (8)	C <sub>a</sub> (2)-C <sub>a</sub> (1)-C <sub>a</sub> (5)	120.4 (12)
Ho-O(2)-C(7)	128.5 (7)	C <sub>a</sub> (1)-C <sub>a</sub> (2)-N <sub>a</sub>	118.8 (12)
Ho-O(3)-C(8) <sup>I</sup>	143.4 (9)	N <sub>a</sub> -C <sub>a</sub> (3)-C <sub>a</sub> (4)	119.0 (15)
Ho-O(4)-C(8)	144.2 (8)	C <sub>a</sub> (3)-C <sub>a</sub> (4)-C <sub>a</sub> (5)	120.0 (14)
Ho-O(5)-C(9)	136.4 (8)	C <sub>a</sub> (4)-C <sub>a</sub> (5)-C <sub>a</sub> (1)	119.8 (12)
Ho-O(6)-C(9) <sup>II</sup>	163.6 (8)	C(8)-C <sub>b</sub> (1)-C <sub>b</sub> (2)	122.3 (12)
O(1) <sup>I</sup> -C(7)-O(2)	124.1 (10)	C(8)-C <sub>b</sub> (1)-C <sub>b</sub> (5)	119.7 (11)
O(1) <sup>I</sup> -C(7)-C <sub>a</sub> (1)	118.0 (10)	C <sub>b</sub> (2)-C <sub>b</sub> (1)-C <sub>b</sub> (5)	118.0 (13)
O(2)-C(7)-C <sub>a</sub> (1)	117.9 (10)	C <sub>b</sub> (1)-C <sub>b</sub> (2)-C <sub>b</sub> (3)	120.9 (14)
O(3) <sup>I</sup> -C(8)-O(4)	125.8 (13)	C <sub>b</sub> (2)-C <sub>b</sub> (3)-C <sub>b</sub> (4)	119.2 (16)
O(3)-C(8)-C <sub>b</sub> (1)	117.2 (11)	C <sub>b</sub> (3)-C <sub>b</sub> (4)-N <sub>b</sub>	118.4 (16)
O(4)-C(8)-C <sub>b</sub> (1)	117.0 (11)	N <sub>b</sub> -C <sub>b</sub> (5)-C <sub>b</sub> (1)	119.8 (12)
O(5)-C(9)-O(6) <sup>II</sup>	124.0 (12)	C(9)-C <sub>c</sub> (1)-C <sub>c</sub> (2)	118.6 (11)
O(5)-C(9)-C <sub>c</sub> (1)	116.8 (11)	C(9)-C <sub>c</sub> (1)-C <sub>c</sub> (5)	120.4 (11)
O(6)-C(9)-C <sub>c</sub> (1)	119.1 (10)	C <sub>c</sub> (2)-C <sub>c</sub> (1)-C <sub>c</sub> (5)	121.0 (13)
C <sub>a</sub> (2)-N <sub>a</sub> -C <sub>a</sub> (3)	121.8 (13)	C <sub>c</sub> (1)-C <sub>c</sub> (2)-N <sub>c</sub>	120.1 (12)
C <sub>b</sub> (4)-N <sub>b</sub> -C <sub>b</sub> (5)	124.6 (13)	N <sub>c</sub> -C <sub>c</sub> (3)-C <sub>c</sub> (4)	119.7 (17)
C <sub>c</sub> (2)-N <sub>c</sub> -C <sub>c</sub> (3)	120.0 (14)	C <sub>c</sub> (3)-C <sub>c</sub> (4)-C <sub>c</sub> (5)	121.0 (15)
C(7)-C <sub>a</sub> (1)-C <sub>a</sub> (2)	118.7 (11)	C <sub>c</sub> (4)-C <sub>c</sub> (5)-C <sub>c</sub> (1)	117.8 (14)
O(4)-O(1)-O(3)	90.7 (3)	O(5)-O(7)-O(6)	76.3 (3)
O(4)-O(2)-O(3)	89.7 (3)	O(5)-O(8)-O(6)	73.8 (3)
O(1)-O(3)-O(2)	91.3 (4)	Ho <sup>I</sup> -Ho-Ho <sup>II</sup>	172.09 (8)
O(1)-O(4)-O(2)	88.3 (4)	O(10)-N <sub>a</sub> -C <sub>a</sub> (2)	116.6 (9)
O(7)-O(5)-O(8)	100.1 (4)	O(10)-N <sub>a</sub> -C <sub>a</sub> (3)	120.7 (11)
O(7)-O(6)-O(8)	105.6 (4)	O(9)-N <sub>c</sub> -C <sub>c</sub> (2)	103.5 (9)
		O(9)-N <sub>c</sub> -C <sub>c</sub> (3)	131.4 (12)
Diaquotris(isonicotinato)lanthanum(III)			
O(5)-O(7)-O(6) <sup>VIII</sup>	77.4 (2)	C <sub>c</sub> (3)-N <sub>c</sub> -C <sub>c</sub> (4)	114
O(5)-O(8)-O(6) <sup>VIII</sup>	75.9 (2)	N <sub>c</sub> -C <sub>c</sub> (4)-C <sub>c</sub> (5)	123
O(7) <sup>VIII</sup> -O(6)-O(8) <sup>VIII</sup>	99.2 (2)	C <sub>c</sub> (4)-C <sub>c</sub> (5)-C <sub>c</sub> (1)	118 (2)
La <sup>VIII</sup> -O(6)-C(9)	174.5 (6)	O(4)-C(8)-O(3)	124.2 (7)
La-O(5)-C(9)	135.4 (5)	O(4)-C(8)-C <sub>b</sub> (1)	117.8 (7)
O(7)-O(5)-O(8)	102.7 (2)	O(3)-C(8)-C <sub>b</sub> (1)	117.9 (7)
La-O(3)-C(8)	168.9 (6)	C(8)-C <sub>b</sub> (1)-C <sub>b</sub> (2)	121.0 (8)
O(1)-O(3)-O(2) <sup>IV</sup>	94.8 (2)	C(8)-C <sub>b</sub> (1)-C <sub>b</sub> (5)	118.2 (8)
La <sup>VIII</sup> -O(4)-C(8)	105 (4)	C <sub>b</sub> (1)-C <sub>b</sub> (2)-C <sub>b</sub> (3)	117.3 (8)
O(1) <sup>IV</sup> -O(4)-O(2)	88.4 (2)	C <sub>b</sub> (2)-C <sub>b</sub> (3)-N <sub>b</sub>	124.0 (9)
La-O(1)-C(7)	135.7 (5)	C <sub>b</sub> (3)-N <sub>b</sub> -C <sub>b</sub> (4)	117.0 (8)
O(3)-O(1)-O(4)	91.9 (2)	N <sub>b</sub> -C <sub>b</sub> (4)-C <sub>b</sub> (5)	124.2 (9)
O(3) <sup>IV</sup> -O(2)-O(4)	84.6 (2)	C <sub>b</sub> (4)-C <sub>b</sub> (5)-C <sub>b</sub> (1)	117 (1)
La <sup>IV</sup> -O(2)-C(7)	134.4 (5)	O(1)-C(7)-O(2)	127.0 (8)
O(6)-C(9)-O(5)	123.6 (6)	O(1)-C(7)-C <sub>a</sub> (1)	116.7 (8)
O(6)-C(9)-C <sub>c</sub> (1)	118.0 (7)	O(2)-C(7)-C <sub>a</sub> (1)	116.3 (8)
O(5)-C(9)-C <sub>c</sub> (1)	118.4 (7)	C(7)-C <sub>a</sub> (1)-C <sub>a</sub> (2)	122
C <sub>c</sub> (2)-C <sub>c</sub> (1)-C <sub>c</sub> (5)	116 (1)	C(7)-C <sub>a</sub> (1)-C <sub>a</sub> (5)	124
C <sub>c</sub> (2)-C <sub>c</sub> (1)-C(9)	125 (1)	C <sub>a</sub> (1)-C <sub>a</sub> (2)-C <sub>a</sub> (3)	121
C <sub>c</sub> (5)-C <sub>c</sub> (1)-C(9)	120 (1)	C <sub>a</sub> (2)-C <sub>a</sub> (3)-N <sub>a</sub>	123
C <sub>c</sub> (1)-C <sub>c</sub> (2)-C <sub>c</sub> (3)	121 (1)	N <sub>a</sub> -C <sub>a</sub> (4)-C <sub>a</sub> (5)	126
C <sub>c</sub> (2)-C <sub>c</sub> (3)-N <sub>c</sub>	126 (2)	C <sub>a</sub> (4)-C <sub>a</sub> (5)-C <sub>a</sub> (1)	120

carboxylate carbon and the ligand ring. In order to account for the disordering, partial occupancy models and group least-squares refinement were used, but both approaches did not improve the description of the structure. Six cycles of full-matrix anisotropic refinement resulted in an  $R$  value of 0.038, a  $wR$  value of 0.062, and an error of fit of 3.00. Three of the bonding distances (two in ring c and one in ring a) are unrealistically short, with the smallest distance being 1.18 (2) Å.

### Description of Structures

The three-dimensional X-ray analysis of the two compounds leads to the formulations  $\{[\text{Ho}(\text{C}_5\text{H}_4\text{NCOOH})_3(\text{H}_2\text{O})_2(\text{NCS})_6\text{Cr} \cdot 2\text{H}_2\text{O}]_2\}_\infty$  and  $\{[\text{La}(\text{C}_5\text{H}_4\text{NCOOH})_3(\text{H}_2\text{O})_2]_2\}_\infty$ .

In both compounds adjacent metal ions are alternately bridged by four and two carboxylate groups (Figure 1). The fundamental difference between these structures and those of the lanthanide(III)-nicotinate complexes<sup>6</sup> is the polymeric configuration with all bridging carboxylates, rather than the dimeric configuration, with both bridging and chelating carboxylates. Two waters of coordination result in a coordination number of eight for all of these complexes. Atomic parameters, distances, and angles are given in Tables II-IV.

**Diaquotri(nicotinic acid)holmium(III) Hexa(isothiocyanato)chromate(III) Dihydrate.**—This compound can be described in terms of three structural species: a  $\text{Cr}[\text{NCS}]_6^{3-}$  anion, two waters of hydration, and a  $[\text{Ho}(\text{C}_5\text{H}_4\text{NCOOH})_3(\text{H}_2\text{O})_2]^{3+}$  cation in the configuration of a chain polymer. The cation and anion are linked *via* hydrogen bonding.

Holmium ions in the polymeric chain repeat every 4.459 and 5.141 Å. As seen in Figure 1a, the shorter metal-metal distance is bridged by four nicotinic acid groups (a and b and their inversion equivalents), and the longer distance is bridged only by nicotinic acid group c and its inversion equivalent. The distance between the further separated holmium ions accommodates four waters of coordination; there are no waters of coordination between the closer spaced metals. The configuration of the polymer can be described by "building" the chain from structurally resultant inversion operators at  $(0, 0, \frac{1}{2})$  and at  $(\frac{1}{2}, 0, \frac{1}{2})$ . These operations result in the separation of 5.141 and 4.459 Å. By continuous application of the center of inversion operator to holmium, water, and to the three nicotinic acid groups in the chemical formula, one forms the polymer chain configuration  $\{[\text{Ho}(\text{C}_5\text{H}_4\text{NCOOH})_3(\text{H}_2\text{O})_2]_2\}_\infty$ . Application of the  $c$  glide plane operator to any chain will generate four adjacent, parallel chains. The polymeric configuration can then be approximated by straight chains (the actual angle formed by holmium and its two inversion equivalents is  $172.1^\circ$ ) parallel to the crystallographic  $a$  axis at  $y = 1, 0, \frac{1}{2}$  and intersecting the  $c$  axis at  $z = 1, 0, \frac{1}{2}$ .

The carboxylate oxygen-holmium distances range from 2.266 to 2.345 Å with an average value of 2.304 Å, and the two aquo oxygens have an average bonding distance of 2.489 Å. The coordination polyhedron (Figure 2) is a slightly distorted square antiprism. The polygon formed by O(1), ..., O(4) (carboxylate oxygens) is very close to a square. The internal angles range from 88.5 to  $91.3^\circ$ , averaging to  $90.0^\circ$ ; the sides of this "square" have lengths in the interval [2.775, 2.920] Å with a mean value of 2.835 Å. The figure formed by O(5), ..., O(8) is more distorted with internal angles

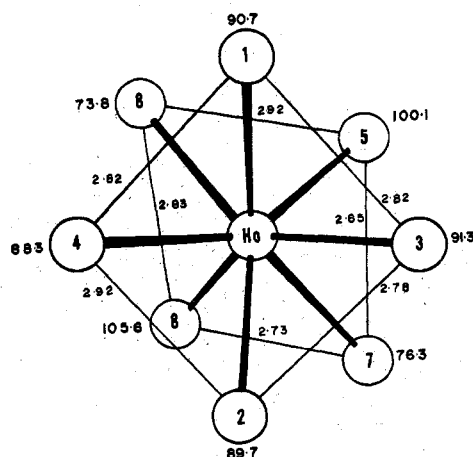


Figure 2.—Diaquotri(nicotinic acid)holmium(III) hexa(isothiocyanato)chromate(III) dihydrate, coordination polyhedron about holmium(III).

in the range  $73.8$ – $105.6^\circ$  and sides from 2.725 to 2.917 Å. The distortion results from the fact that the negatively charged carboxylate oxygens are 0.18 Å (av) closer to the metal than the neutral water oxygens. Least-squares planes analyses (Table V) shows that O(1), ..., O(4) are essentially coplanar and that the maximum deviation from planarity of O(5), ..., O(8) is 0.20 Å. The holmium ion is very nearly centered between these two planes, with metal to plane distances of 1.14 and 1.33 Å, respectively. The dihedral angle between the two planes is  $1.5^\circ$ .

The three nicotinic acid ligands do not exhibit any large anomalies in structural parameters. The ranges of carbon-carbon bonding distances in rings a, b, and c are [1.36, 1.41] Å, [1.39, 1.42] Å, and [1.33, 1.41] Å, with average values of 1.38, 1.40, and 1.37 Å. The range and average value for all carbon-carbon bond lengths are [1.33, 1.42] and 1.38 Å as compared with [1.35, 1.41] and 1.37 Å for the carbon-nitrogen bond lengths in nicotinic acid. All three rings exhibit only minor deviations from planarity, with ring c showing the greatest distortions (0.03 Å from the mean plane). The dihedral angles between the mean planes of the nicotinic acid rings and their respective carboxylate groups are  $7.7$ ,  $5.4$ , and  $16.9^\circ$  for rings a, b, and c. Again ring c shows the greatest distortions from ideality. These distortions will be discussed later.

Although the extremes for the holmium(III)-oxygen bond distances differ by more than nine standard deviations, it cannot be inferred that the acidic proton is bonded to one of the oxygen atoms of the ligand. The nicotinate dihydrates<sup>6</sup> of both lanthanum and samarium show similar effects, as does the lanthanum isonicotinate. Also, when corrected for the lanthanide contraction, the average metal to bridging oxygen bond lengths for all four compounds are in the interval [2.47, 2.50] Å. Chupakhina and Serebrennikov<sup>5</sup> report band frequencies in the infrared spectra of the rare earth nicotinic acid compound characteristic of the NH functional group. Thus the evidence suggests that the zwitterionic form of nicotinic acid predominates in this complex.

The coordination sphere about the chromium in the  $\text{Cr}[\text{NCS}]_6^{3-}$  anion is an octahedron with only minor distortions from ideality (Figure 3). The average

TABLE V  
 LEAST-SQUARES PLANES ANALYSIS<sup>a</sup>

Diaquotri(nicotinic acid)holmium(III) Hexa(isothiocyanato)chromate(III) Dihydrate

Plane no.	Atoms defining plane	Dev, Å	a	b	c	d
1	O(1), O(2), O(3), O(4)	0.00	0.992	0.071	-0.103	0.431
2	O(5), O(6), O(7), O(8)	0.20	0.994	-0.078	-0.080	-1.868
3	C <sub>a</sub> (1), C <sub>a</sub> (2), C <sub>a</sub> (3), C <sub>a</sub> (4), C <sub>a</sub> (5), C(7), N <sub>a</sub> , O(1) <sup>I</sup> , O(2)	0.11	0.151	0.963	-0.225	-1.095
4	C <sub>b</sub> (1), C <sub>b</sub> (2), C <sub>b</sub> (3), C <sub>b</sub> (4), C <sub>b</sub> (5), C(8), N <sub>b</sub> , O(3) <sup>I</sup> , O(4)	0.08	0.119	-0.262	-0.958	-7.280
5	C <sub>c</sub> (1), C <sub>c</sub> (2), C <sub>c</sub> (3), C <sub>c</sub> (4), C <sub>c</sub> (5), C(9), N <sub>c</sub> , O(5), O(6) <sup>II</sup>	0.24	-0.301	0.326	-0.896	-6.595
6	C <sub>a</sub> (1), C <sub>a</sub> (2), C <sub>a</sub> (3), C <sub>a</sub> (4), C <sub>a</sub> (5), N <sub>a</sub>	0.01	0.194	0.954	-0.230	-0.975
7	C(7), O(1) <sup>I</sup> , O(2)	0.00	0.063	0.965	-0.256	-1.454
8	C <sub>b</sub> (1), C <sub>b</sub> (2), C <sub>b</sub> (3), C <sub>b</sub> (4), C <sub>b</sub> (5), N <sub>b</sub>	0.01	0.091	-0.284	-0.955	-7.458
9	C(8), O(3) <sup>I</sup> , O(4)	0.00	0.177	-0.243	-0.243	-7.056
10	C <sub>c</sub> (1), C <sub>c</sub> (2), C <sub>c</sub> (3), C <sub>c</sub> (4), C <sub>c</sub> (5), N <sub>c</sub>	0.03	-0.365	0.259	-0.894	-6.672
11	C(9), O(5), O(6) <sup>II</sup>	0.00	-0.140	0.447	-0.883	-6.666
12	N(1), N(2), N(3), N(5)	0.00	0.829	-0.242	-0.504	-4.956
13	N(1), N(2), N(4), N(6)	0.01	-0.263	-0.965	-0.003	-16.862
14	N(3), N(4), N(5), N(6)	0.07	-0.479	0.137	-0.867	-3.039

## Angles between Planes

Plane no.	Plane no.	Angle, deg	Plane no.	Plane no.	Angle, deg
1	2	1.4	8	9	5.4
3	4	91.1	10	11	16.9
3	5	61.9	12	13	89.0
4	5	42.6	12	14	89.6
6	7	7.7	13	14	90.3

## Diaquotris(isonicotinato)lanthanum(III)

Plane no.	Atoms defining plane	Dev, Å	a	b	c	d
1	O(6), O(5), C(9)	0.00	0.199	0.426	-0.883	1.385
2	C <sub>c</sub> (1), C <sub>c</sub> (2), C <sub>c</sub> (3), N <sub>c</sub> , C <sub>c</sub> (4), C <sub>c</sub> (5)	0.03	0.354	0.368	-0.860	2.159
3	O(3), O(4), C(8)	0.00	0.128	0.989	-0.068	9.731
4	C <sub>b</sub> (1), C <sub>b</sub> (2), C <sub>b</sub> (3), N <sub>b</sub> , C <sub>b</sub> (4), C <sub>b</sub> (5)	0.02	-0.557	-0.828	-0.061	-9.364
5	O(1), O(2), C(7)	0.00	0.252	0.421	-0.871	-0.952
6	C <sub>a</sub> (1), C <sub>a</sub> (2), C <sub>a</sub> (3), N <sub>a</sub> , C <sub>a</sub> (4), C <sub>a</sub> (5)	0.07	0.496	0.431	-0.754	0.147
7	O(6) <sup>VIII</sup> , O(5), O(7), O(8)	0.22	0.979	-0.008	-0.204	4.482
8	O(2) <sup>XI</sup> , O(4) <sup>XI</sup> , O(3), O(1)	0.06	0.962	-0.041	-0.271	1.082

## Angles between Planes

Plane no.	Plane no.	Angle, deg	Plane no.	Plane no.	Angle, deg
1	2	10	5	6	16
3	4	28	7	8	4

<sup>a</sup> The equation for a plane is  $aX + bY + cZ = d$ . The  $X$ ,  $Y$ , and  $Z$  are orthogonal unit vectors, directions defined by the equations:  $X = a$ ;  $Y = a \times c$ ;  $Z = a \times (a \times c)$ . Dev is the maximum deviation of any atom from its parent plane.

bond lengths for Cr-N, N-C, and C-S are 2.002, 1.144, and 1.619 Å, and the average bond angles about N and C are 164.3 and 176.6°. These values are in good agreement with those parameters reported in the literature<sup>14-16</sup> for similar metal isothiocyanates, and are seen as evidence in favor of the M-N<sup>+</sup>=C-S<sup>-</sup> resonance formulation.

In this compound there is evidence for the presence of hydrogen bonds. The nitrogen associated with nicotinic acid ring a is located 2.781 (17) Å from O(10). The angles C<sub>a</sub>(2)-N<sub>a</sub>-C<sub>a</sub>(3), C<sub>a</sub>(2)-N<sub>a</sub>...O(10), C<sub>a</sub>(3)-N<sub>a</sub>...O(10) have respective values of 121.8 (13), 116.6 (9), and 120.7 (11)°; the sum of these angles being 359.1°. The oxygen atom is displaced 0.5 Å from the mean plane of the ring. Hydrogen bonding is possible between the hydrogen of N<sub>c</sub> and O(9). The O(9)-N<sub>c</sub> distance is 2.654 (19) Å. The angles C<sub>c</sub>(3)-N<sub>c</sub>-C<sub>c</sub>(2), C<sub>c</sub>(3)-N<sub>c</sub>...O(9), and C<sub>c</sub>(2)-N<sub>c</sub>...O(9) are 120.4 (14), 131.4 (12), and 103.5 (9)° with a sum value of 354.9°. The oxygen atom is displaced 1.03 Å normal to the mean plane of nicotinic acid ring c. Weak

hydrogen bonding might occur between O(7) and S(4) (3.339 (10) Å) and between O(9) and S(6) (3.349 (15) Å). The sum of the van der Waals radii for oxygen and sulfur is 3.25 Å. It is seen from these distances (and from the assumption of hydrogen bonding between O(9) and N<sub>c</sub> and O(10) and N<sub>a</sub>) that hydrogen bonds could contribute to the overall stability of the compound in the crystalline state.

It is possible to relate hydrogen bonding to distortions in the nicotinic acid system. The difference in the holmium-oxygen bond length for O(7) and O(8) can be related to the participation of the former oxygen in hydrogen bonding. It has been suggested that the nitrogen atoms on rings a and c are hydrogen bonded to water hydrogens. These two rings show greater dihedral angles with the plane of their respective carboxylate functional groups. Ring b (which exhibits the smallest such distortion) does not show evidence of hydrogen bonding. The relationship of this type of dihedral angle to hydrogen bonding schemes has been already discussed.<sup>6</sup>

In a projection onto the  $bc$  plane the ligands (nicotinic acid rings a, b, and c) project out as spokes on a wheel with the holmium chain appearing as its hub (Figure 4). The mean planes of rings a and b are

(14) Y. Takeuchi and Y. Saito, *Bull. Chem. Soc. Jap.*, **30**, 319 (1957).(15) J. R. Knox and K. Eriks, *Inorg. Chem.*, **7**, 84 (1968).(16) J. L. Martin, L. C. Thompson, L. J. Radonovich, and M. D. Glick, *J. Amer. Chem. Soc.*, **90**, 4493 (1968).

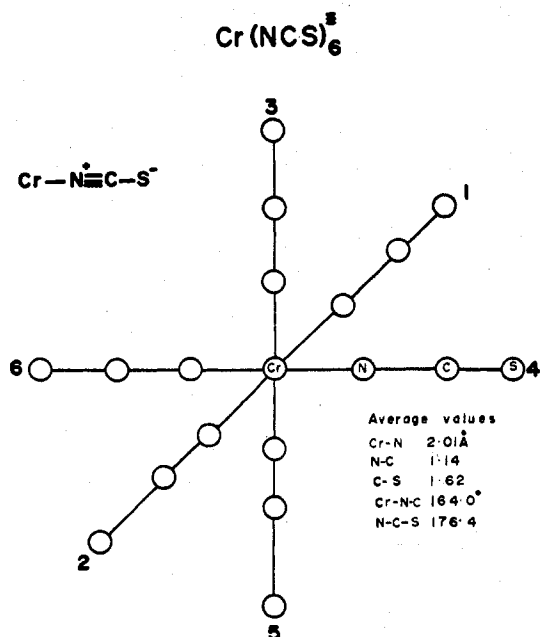


Figure 3.—Diaquotri(nicotinic acid)holmium(III) hexa(iso-thiocyanato)chromate(III) dihydrate, coordination polyhedron about chromium(III).

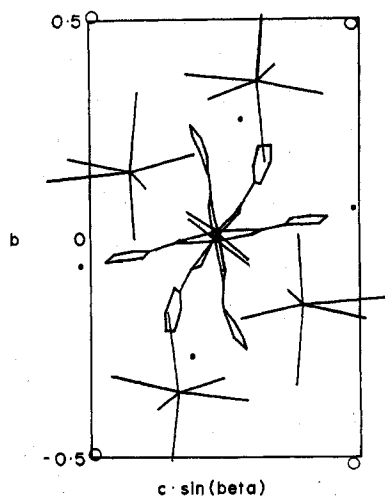


Figure 4.—Diaquotri(nicotinic acid)holmium(III) hexa(iso-thiocyanato)chromate(III) dihydrate, unit cell packing.

nearly orthogonal and the plane of ring *c* nearly bisects the angle between these planes. The dihedral angle between planes consisting of the carboxylate functional group and holmium(III) for each ligand are the following:  $ab = 87.3$ ,  $ac = 47.4$ , and  $bc = 40.3^\circ$ . The  $\text{Cr}(\text{NCS})_6^{3-}$  ion occupies the spaces between these spokes along the polymeric chain. The deviations from linearity of the bonding angles in the  $\text{Cr}(\text{NCS})_6^{3-}$  system may result from packing restraints and other resonance structures. Significant nonbonded distances are given in Table III.

**Diaquotris(isonicotinato)lanthanum(III).**—The distances between adjacent lanthanum ions in the chains are 4.302 (3) and 5.453 (4) Å. The 4.302 (3) Å distance is bridged by four isonicotinate carboxylates (isonicotinates *a* and *b* and their inversion equivalents). The 5.454 (4) Å distance is bridged in a similar

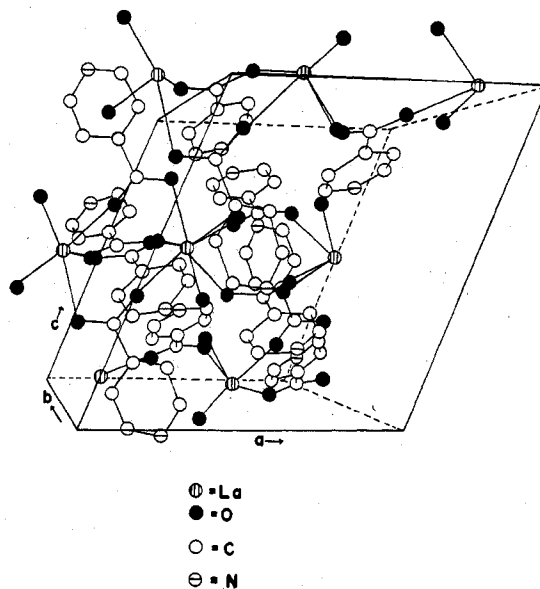


Figure 5.—Diaquotris(isonicotinato)lanthanum(III), unit cell packing.

fashion by two isonicotinate ligands (isonicotinate *c* and its inversion equivalent). The individual La-O bridging distances in the isonicotinate range from 2.465 (6) Å [La-O(6)] to 2.536 (6) Å [La-O(4)] and each metal is bound to six bridging oxygens (Figure 5). Eight-coordination of each metal is completed by two waters of hydration at distances of 2.59 Å (av).

If we describe the polyhedron as that of a distorted square antiprism, none of the sides of either "square" are defined by two carboxylate oxygens of the same isonicotinate group. Atoms O(5), O(6), O(7), and O(8) form one "square" with the greatest deviation of any of the atoms from the best plane formed by the four atoms being 0.22 Å. Atoms O(1), O(2), O(3), and O(4) form the other "square" with the greatest deviation of any atom from the best plane being 0.06 Å. The dihedral angle formed by the two planes is  $4^\circ$ .

Hydrogen bonding occurs between different chains. The O(7)...N<sub>b</sub> and O(7)...N<sub>c</sub> distances are 2.772 (9) and 2.78 (1) Å. The O(8)...N<sub>a</sub> distance is 2.80 (1) Å.

The anisotropic ellipsoids of the ring carbons ortho and meta to the nitrogen atoms in rings *a* and *c* are much larger than the ellipsoids of the other atoms. The largest axes of these ellipsoids are in the direction normal to the pyridine rings. This is consistent with thermal disordering or free rotation of the pyridine rings about the carboxylate carbon-ring carbon single bond. Isonicotinate *b* does not display the thermal disordering. This is probably due to steric factors. The C<sub>b</sub>(2)...N<sub>b</sub><sup>1</sup>, C<sub>b</sub>(3)...C<sub>b</sub>(3)<sup>1</sup>, and C<sub>b</sub>(3)...N<sub>b</sub><sup>1</sup> distances are 3.36 (1), 3.23 (2), and 3.38 (1) Å, respectively. They are so situated that if the *b*-type rings were to rotate, the C<sub>b</sub>(3)...C<sub>b</sub>(3)<sup>1</sup> and C<sub>b</sub>(3)...C<sub>b</sub>(2) [3.52 (1) Å] distances would become prohibitively small during the rotations. The C<sub>b</sub>(3)...N<sub>b</sub><sup>1</sup> and C<sub>b</sub>(2)...N<sub>b</sub><sup>1</sup> distances would not appreciably decrease on rotation so they do not represent critical distances. Consequently, the C<sub>b</sub>(3)...C<sub>b</sub>(3)<sup>1</sup> distance of 3.23 (2) Å

(17) Primed atoms are related to unprimed atoms by the transformation  $x, y, z \rightarrow 1-x, 1-y, -z$ . Doubly primed atoms are related to unprimed atoms by the transformation  $x, y, z \rightarrow 1-x, 1/2+y, 1/2-z$ .



probably represents the closest possible approach of the two rings. This value roughly approximates twice the half thickness (3.4 Å) of the pyridine ring.<sup>18</sup> Although the C<sub>a</sub>(3)...C<sub>a</sub>(5)<sup>11</sup> distance is 3.40 (2) Å, rotations of rings a and c do not decrease this value.

Another effect related to the positions of C<sub>b</sub>(2), C<sub>b</sub>(3), and C<sub>b</sub>(3)<sup>I</sup> is the dihedral angle of 28° (Table V) formed between the planes defined by the carboxylate group and the pyridine ring of isonicotinate b. The corresponding dihedral angles for isonicotinates a and c are 16 and 10°, respectively. Atoms N<sub>c</sub> and N<sub>b</sub> are displaced from the planes of their respective carboxylate groups by 0.16 and 0.25 Å, respectively; N<sub>c</sub> lies 0.04 Å from the plane of its carboxylate group. This bending distortion is probably an effect of hydrogen bonding.

### Conclusions

Some comparative data between the four structures representing trivalent rare earth complexes of the nicotinates,<sup>6</sup> isonicotinates, and nicotinic acid are summarized in Tables VI and VII.

TABLE VI  
COMPARATIVE DISTANCES (Å) IN THE RARE EARTH NICOTINATE,<sup>6</sup>  
ISONICOTINATE, AND NICOTINIC ACID COMPLEXES

Species	Ionic radius	Distances, Å			
		M-M	M-O		
			Bridg- ing	Chelat- ing	Aquo
La (nicotinate)	1.061	4.23	2.50	2.61	2.51
Sm (nicotinate)	0.964	4.30	2.38	2.53	2.43
La (isonicotinate)	1.061	4.38, 5.36	2.50		2.59
Ho (nicotinic acid)	0.894	4.46, 5.14	2.30		2.40

TABLE VII  
COMPARATIVE DISTANCES (Å) IN THE RARE EARTH NICOTINATE,<sup>6</sup>  
ISONICOTINATE, AND NICOTINIC ACID COMPLEXES, WHEN  
CORRECTED FOR THE LANTHANIDE CONTRACTION

Metal-oxygen	Corrected to La		
	Bridged	Chelated	Aquo
La (nicotinate)	2.50	2.61	2.51
Sm (nicotinate)	2.48	2.62	2.52
La (isonicotinate)	2.50		2.59
Ho (nicotinic acid)	2.47		2.66

When corrected for the lanthanide contraction the metal-bridging oxygen distances are in an interval 0.031 Å wide, and the interval for the carbon-carboxylate oxygen distances is 0.018 Å in width. The similarity in distances in the compounds suggests that these oxygens are chemically similar, implying the acid hydrogen in the nicotinic acid ligand is at the nitrogen position. The aromatic nitrogen-carbon bond lengths are found to be longest on the holmium nicotinic acid in agreement with this conclusion. The quadruply bridged metal-metal distances in the two polymeric structures are longer than the quadruply bridged metal-metal distances in the two dimeric compounds. This difference may result from the fact that the coordination sphere of the dimers contains a chelating carboxylate group. The small "bite" of this group occupies less volume than two oxygens from different ligands. When these chelating groups are replaced by bridging groups, the metals must get further apart in order to

(18) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

compensate for van der Waals repulsive forces. This argument could also be used to explain why the metal-aquo oxygen distances are smaller in the dimers than in the polymers.

The stereochemistry of eight-coordination has been discussed in depth elsewhere.<sup>19-22</sup> Lippard<sup>22</sup> has established a set of procedures for choosing between the two eight-coordinate polyhedra, the square antiprism and the trigonal dodecahedron. The square antiprism is described by two parallel squares of  $D_{4h}$ - $\bar{8}2m$  symmetry. Ideally the four atoms of each square are planar and the normal distances of the metal to each plane are equal. The trigonal dodecahedron can be described by two mutually perpendicular trapezoids of  $D_{2d}$ - $\bar{4}2m$  symmetry. In the ideal case the metal should lie in the intersection of these two planes.

In trying to assign a label to the coordination polyhedra for the nicotinate, isonicotinate, and nicotinic acid complexes, a three-dimensional model of each coordination polyhedron was constructed. Two sets of two planes each were designated for each complex. One set of planes corresponded to the best visually observable square antiprism, while the other set of planes corresponded to the trigonal dodecahedron. Least-squares planes analysis was then carried out for the planes of the designated coordination polyhedra. Referring to Table VIII, it can be seen that all of the

TABLE VIII  
COMPARATIVE DATA FOR THE COORDINATION SPHERES OF THE  
RARE EARTH NICOTINATE,<sup>6</sup> ISONICOTINATE, AND  
NICOTINIC ACID COMPLEXES<sup>a</sup>

	Dev 1	Dev 2	Dist 1	Dist 2	Angle
La (nicotinate)	0.21	0.12	1.62 (0.28)	1.06	17.1
	0.21	0.06	0.58 (0.59)	0.13	96.3
Sm (nicotinate)	0.13	0.05	1.54 (0.23)	1.08	10.2
	0.23	0.20	0.39 (0.42)	0.15	95.1
La (isonicotinate)	0.21	0.06	1.45 (0.14)	1.18	4.4
	0.24	0.23	0.15 (0.32)	0.28	94.9
Ho (nicotinic acid)	0.00	0.19	1.14 (0.10)	1.33	1.5
	0.24	0.26	0.16 (0.23)	0.17	94.3

<sup>a</sup> The first row of figures for each complex refer to the square antiprism. The second row of figures refer to the trigonal dodecahedron. The numbers under "Dev 1" and "Dev 2" give the maximum deviation from planarity for each of the planes appropriate to the particular coordination sphere. The normal distance of the rare earth ion to each plane is given by "Dist 1" and "Dist 2." The numbers in parentheses refer to the displacement of the metal from the center of each polyhedron. All numbers are in Å. The dihedral angle (deg) between the planes referred to under "Dist 1" and "Dist 2" is given by "Angle."

possible coordination polyhedra show distortions from ideality. The polymeric complexes, however, seem to be better described in terms of the antiprism.

The four compounds studied, representing polymeric and dimeric species, are based upon neutral and charged ligands and contain different uncoordinated species. Nonetheless the coordination polyhedra are virtually indistinguishable. Indeed, the inherent stability of the coordination geometry is demonstrated by the consistency of these parameters.

(19) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

(20) D. L. Kepert, *J. Chem. Soc.*, 4736 (1965).

(21) R. V. Parish, *Coord. Chem. Rev.*, **1**, 439 (1966).

(22) S. J. Lippard and B. J. Russ, *Inorg. Chem.*, **7**, 1686 (1968).

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## Models for the Interaction of Nitrogen with Transition Metals. I.

### Crystal and Molecular Structure of Carbonylbis(triphenylphosphine)(1,4-*p*-fluorophenyltetrazene)iridium Tetrafluoroborate

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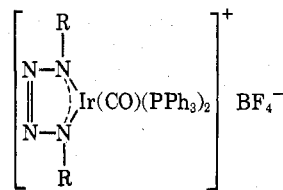
The reaction of *p*-fluorophenyldiazonium fluoroborate with Vaska's complex *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>] yields the title compound, the crystal and molecular structure of which are reported here. The compound crystallizes in the space group *P* $\bar{1}$  with two formula units in a unit cell of dimensions  $a = 13.669$  (5) Å,  $b = 17.423$  (7) Å,  $c = 10.852$  (4) Å,  $\alpha = 104.57$  (3)°,  $\beta = 98.02$  (5)°,  $\gamma = 88.43$  (3)°. The calculated density is 1.549 g cm<sup>-3</sup> and measured density 1.53 g cm<sup>-3</sup>. Full-matrix least-squares refinement of 3252 observed three-dimensional X-ray counter measured intensities led to a final conventional *R* index of 0.049. The principal feature in the structure of the complex cation is the presence of a five-membered iridium-nitrogen ring, and the cation may alternately be described as the 1-carbonyl-1,1-bis(triphenylphosphino)iridio-2,5-di-*p*-fluorophenyltetrazolium ion. The uncoordinated nitrogen atoms are 1.270 (16) Å apart, and bound to the coordinated nitrogen atoms by essentially single bonds of dimensions 1.400 (16) and 1.350 (16) Å.

#### Introduction

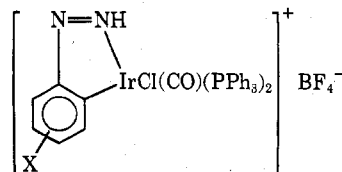
In this series of papers<sup>1-4</sup> we shall report the synthesis and characterization of compounds formed in the reactions of transition metal compounds with ligands which are closely related to dinitrogen. It is anticipated that the results will shed further light upon the unresolved question as to the factors which influence metal-dinitrogen interaction, and in this regard we hope to obtain information pertinent to the problem of the role of the transition metals iron and molybdenum in the nitrogen-fixing enzyme *nitrogenase*. In particular, we shall be concerned with the question of whether, and under what circumstances, facile reduction and eventual fission of the N≡N bond can be achieved by the participation of transition metal intermediates. Thus we hope to provide information as to whether direct coordination of dinitrogen to a transition metal ion is indeed (as presently appears to be the case on circumstantial evidence) a likely factor in the mechanism of dinitrogen reduction by enzyme systems.

For our initial experiments we have chosen to examine the interaction of the aryldiazonium ion with various metals. The significance of this ion as a promising dinitrogen model is suggested by Parshall's demonstration<sup>5</sup> that it will insert into the metal-hydrogen bond in PtHCl(PET<sub>3</sub>)<sub>2</sub> to produce the substituted diimide complex ArN=NHPTCl(PET<sub>3</sub>)<sub>2</sub><sup>+</sup>. This then undergoes facile reduction to the substituted hydrazine complex ArNH·NH<sub>2</sub>PtCl(PET<sub>3</sub>)<sub>2</sub><sup>+</sup> and eventual N-N bond fission to give ArNH<sub>2</sub> and NH<sub>3</sub> and regenerate PtHCl(PET<sub>3</sub>)<sub>2</sub>. Rather than pursue this type of insertion reaction, we decided to attempt the synthesis of arylazo complexes ArN=NM by straightforward oxidative addition reactions of aryldiazonium salts to suitable

low-oxidation-state metal complexes. In view of the published synthesis and structure<sup>6</sup> of the nitrosyl complex [Ir(NO)(CO)Cl(PPh<sub>3</sub>)<sub>2</sub>]BF<sub>4</sub> and similarity in the electronic structures of N≡O<sup>+</sup> and (ArN≡N)<sup>+</sup>, the first such reaction attempted was that of para-substituted aryldiazonium salts with Vaska's complex *trans*-[IrCl(CO)(PPh<sub>3</sub>)<sub>2</sub>]. To date we have been able to isolate and identify two principal products from these reactions. The first is the compound I, an example of a complex involving the uncommon heterocyclic system of four nitrogen atoms and one metal atom.

I, R = *p*-XC<sub>6</sub>H<sub>4</sub>; X = H, F, Cl, Br, CF<sub>3</sub>, OCH<sub>3</sub>

The synthesis and characterization of this compound have been reported briefly<sup>2</sup> and the details of the X-ray crystallographic determination of its crystal and molecular structure are presented here. The second product, II, is a cyclic diimide complex whose crystal structure has also been determined.<sup>3</sup> A full description of this compound and a discussion of the interrelationship of these products and their chemical properties will be presented at a later date.

II, X = H; *o*-, *m*-, and *p*-F, -Cl, -Br, -NO<sub>2</sub>;  
*p*-CF<sub>3</sub>; *m*- and *p*-CH<sub>3</sub>; *m*-OCH<sub>3</sub>

(1) For preliminary communications of the results of this study see ref 2-4.

(2) A. B. Gilchrist, F. W. B. Einstein, G. W. Rayner-Canham, and D. Sutton, *J. Amer. Chem. Soc.*, **83**, 1826 (1971).(3) A. B. Gilchrist, F. W. B. Einstein, G. W. Rayner-Canham, and D. Sutton, *ibid.*, **84**, 645 (1972).(4) A. B. Gilchrist, G. W. Rayner-Canham, and D. Sutton, *Nature (London)*, **235**, 42 (1972).(5) G. W. Parshall, *J. Amer. Chem. Soc.*, **87**, 2133 (1965); **89**, 1822 (1967).(6) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); **8**, 1282 (1969).