C24—O1	1.160 (8)	C14—C8	1.399 (9)
C25—O2	1.160 (8)	C10—C9	1.548 (8)
C12—O3	1.356 (8)	C11—C9	1.416 (9)
C21—O3	1.420 (9)	C20—C10	1.528 (10)
C19—O4	1.406 (8)	C12—C11	1.411 (9)
C22—O4	1.410 (9)	C13—C12	1.397 (10)
C2—C1	1.523 (10)	C14—C13	1.379 (10)
C10—C1	1.531 (9)		
C24—Cr—C23	85.6 (3)	C14—C8—C9	117.8 (7)
C25—Cr—C23	85.7 (3)	C10—C9—C8	121.2 (6)
C25—Cr—C24	88.2 (3)	C11—C9—C8	118.9 (6)
C21—O3—C12	117.2 (6)	C11—C9—C10	119.6 (6)
C22—O4—C19	112.2 (6)	C5—C10—C1	109.6 (6)
C10—C1—C2	112.6 (6)	C9—C10—C1	111.4 (5)
C3—C2—C1	111.6 (7)	C9—C10—C5	108.3 (5)
C4—C3—C2	114.8 (6)	C20—C10—C1	108.6 (6)
C5—C4—C3	107.7 (5)	C20—C10—C5	114.8 (6)
C18—C4—C3	107.4 (6)	C20—C10—C9	103.9 (5)
C18—C4—C5	108.4 (5)	C12—C11—C9	121.3 (7)
C19—C4—C3	110.9 (6)	C11—C12—O3	115.4 (6)
C19—C4—C5	113.3 (6)	C13—C12—O3	125.7 (6)
C19—C4—C18	108.8 (6)	C13—C12—C11	118.8 (7)
C6—C5—C4	113.8 (6)	C14—C13—C12	118.9 (6)
C10—C5—C4	117.0 (5)	C13—C14—C8	123.8 (7)
C10—C5—C6	110.1 (5)	C4—C19—O4	108.5 (6)
C7—C6—C5	110.6 (6)	S—C23—Cr	176.0 (5)
C8—C7—C6	114.6 (6)	O1—C24—Cr	176.2 (8)
C9—C8—C7	122.6 (6)	O2—C25—Cr	176.1 (7)
C14—C8—C7	119.6 (7)		

A solution of hexacarbonylchromium(0) (6.21 mmol) and 12,19-dimethoxypodocarpa-8,11,13-triene (5.18 mmol) in dibutyl ether/THF (162 ml, 12:1) was heated under reflux for 24 h. Workup gave a mixture (7.3:1) of the α and β diastereoisomers of tricarbonyl[(8,9,11,12,13,14-η)-12,19-dimethoxypodocarpa-8,11,13-triene]chromium(0) (98%). A solution of this mixture (0.19 mmol) and *cis*-cyclooctene (7.68 mmol) in benzene (8 ml) was irradiated (366 nm) under nitrogen at room temperature for 25 min. A solution of Ph_3P (0.23 mmol) in CS_2 (2 ml) was then added to the red solution and the mixture was left standing without irradiation overnight. Filtration through Celite followed by flash chromatography (silica gel, hexane/diethyl ether) gave what is now established as the α diastereoisomer of dicarbonyl[(8,9,11,12,13,14-η)-12,19-dimethoxypodocarpa-8,11,13-triene]thiocarbonylchromium(0) (63%) in the form of orange needles; m.p. 378-380 K.

The infrared spectrum showed strong absorptions at 1941 and 1889 cm^{-1} (CO), and at 1194 cm^{-1} (CS). The NMR spectra confirmed the presence of a single stereoisomer: $\delta_H(CDCl_3)$ 1.05, H(3 ax.); 1.08, H(18)$_3$; 1.27, H(20)$_3$; 1.25-1.32, H(1 ax.), H(5); 1.62-1.72, H(2 ax.), H(2 eq.), H(6 ax.); 1.83, H(3 eq.); 1.93-2.01, H(1 eq.), H(6 eq.); 2.61, H(7 ax.); 2.63, H(7 eq.); 3.24, H(19); 3.31, 19-OCH_3; 3.41, H(19); 3.68, 12-OCH_3; 5.28, H(13); 5.44, H(11); 5.60, H(14); δ_C 18.3, C(2); 18.7, C(6); 27.0, C(20); 27.3, C(7); 27.5, C(18); 35.5, C(3); 36.6, C(1); 37.4, C(10); 37.8, C(4); 47.7, C(5); 56.0, 12-OCH_3; 59.3, 19-OCH_3; 76.1, C(19); 81.6, C(11); 81.8, C(13); 99.3, C(14); 105.9, C(8); 131.8, C(9); 143.5, C(12); 231.8, 231.9, (CO); 345.9, (CS). *m/z* 440 (*M*, 14), 384 (*M*—2CO, 100), 340 (*M*—2CO—CS, 63), 288 [*M*—$Cr(CO)_2CS$, 80].

It was expected that the stereochemistry of the single monothiocarbonyl isomer isolated from the ligand-exchange reaction would reflect the stereochemistry of the major α isomer present in the precursor mixture of $Cr(CO)_3$ complexes, so confirmation was sought by determination of the crystal structure.

An analogous refinement with inverted coordinates refined to $R = 0.0471$. Therefore the published atomic positions represent the true absolute structure of the molecule.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71286 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HL1032]

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Structure of Ethylenediammonium *catena*-Poly[tris(2-pyridinecarboxylato-κ*N*,κ*O*)holmate-μ-2-pyridinecarboxylato-κ*N*,κ*O*:κ*O*′] Hexahydrate

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Abstract

The structure consists of polymeric complex anions, ethylenediammonium cations and waters of crystallization. The Ho atoms are surrounded by four N atoms and five carboxylic O atoms. The compound is isomorphous with a previously published neodymium complex.

Comment

The title compound is isomorphous with a neodymium compound, whose structure has been published previously (Starynowicz, 1991). This work was undertaken to obtain precise information about bond lengths within the holmium coordination sphere and their variation with a change of lanthanide cation.

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The crystals were grown in the same manner as the analogous Nd compound, using freshly precipitated holmium hydroxide as the source of lanthanide. For the refinement, the coordinates of the non-H atoms were taken from the isomorphous complex; the C-bonded H atoms were placed geometrically and the N- and O-bonded atoms were located from a $\Delta\rho$ map; not all were found. For the refinement, the crystal structure orientation which produced the best R value with respect to the polar axes was chosen.

The refinement results are presented in Tables 1 and 2; the latter also presents the differences between the Ho-ligand bond lengths and the relevant lengths of the isomorphous Nd complex and the ratio of these differences to the ionic radius decrement. The values of the ionic radii used were obtained from those of the appropriate nine-coordinate lanthanide(3+) cations published by Shannon (1976); the difference is 0.091 Å. The overall trends in bond-length contraction are indicated by values of ρ (see Table 2 for definition). For all bonds the average value is approximately 103 (33)%, which indicates that the lanthanide-ion radius contraction is very well matched by the bond shortening. The mean values of ρ for Ho—O and Ho—N bonds are 102 (15) and 104 (49)%, respectively, and are essentially the same. The difference in the e.s.d. values may indicate that the Ho—N bonds are weaker and easier to change compared with the Ho—O bonds.

The coordination figure of Ho1 may be described better as a capped square antiprism (CSA) with N1 as the cap and O28, O11, N3, O13 and O15, N5, O27, N7 as the capped and non-capped bases, respectively, rather than as a tricapped trigonal prism (TCTP) with O13, O28, O15 and N3, O11, O27 spanning the bases and N1, N5, N7 being the caps. The Δ parameter, defined as $\Sigma d_i^2/9$, where d_i is the distance between the ith atom and the relevant vertex of the ideal least-squares-fitted polyhedron, was 0.068 Å^2 in the first case and 0.087 Å^2 in the latter (Drew, 1977). The coordination environment of Ho2 approaches a TCTP shape (with O12, N4, O17 and N6, N8, O16 as the bases, O18, O14, N2 as the caps and Δ = 0.068 Å^2) more than CSA (with O14, O16, N2, O17 as the non-capped bases, N8, N6, O12, N4 as the capped bases, O18 as the cap and Δ = 0.095 Å^2).

ORTEP views (Johnson, 1976) of the polymer fragment and the ethylenediammonium cation, together with the numbering scheme, are given in Fig. 1. The overall description of the Nd complex is also valid in the present case and will not be repeated here for the sake of brevity.

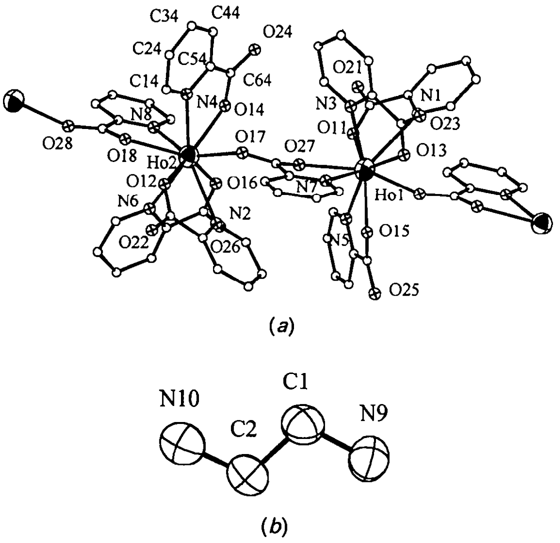

Fig. 1. (*a*) A fragment of the complex polymer and (*b*) the ethylenediammonium cation. The numbering scheme for the 2-pyridinecarboxylate C atoms follows that for the atoms C14-C64.

Experimental

Crystal data

$[C_2H_{10}N_2][Ho_2(C_6H_4NO_2)_8].6H_2O$
M_r = 5907.6
Monoclinic
Cc
a = 13.518 (9) Å
b = 21.496 (10) Å
c = 20.055 (10) Å
β = 99.56 (4)°
V = 5747 (6) Å^3
Z = 4

D_x = 1.707 (2) Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 15 reflections
θ = 8.5 - 12°
μ = 2.93 mm^{-1}
T = 299 (1) K
Parallelepiped
0.4 × 0.35 × 0.3 mm
Yellow

Data collection

Syntex $P2_1$ computer-controlled four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF
T_{min} = 0.500, T_{max} = 1.213
6109 measured reflections
6109 independent reflections

5417 observed reflections $[F > 6\sigma(F)]$
R_{int} = 0.0251
θ_{max} = 30°
$h = -28 \rightarrow 27$
$k = 0 \rightarrow 30$
$l = 0 \rightarrow 18$
2 standard reflections monitored every 50 reflections
intensity variation: 2.6%

Refinement

Refinement on F
Final R = 0.0308
wR = 0.0305
5401 reflections
786 parameters
Only coordinates of H atoms refined
Calculated weights $w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.496 e Å^{-3}
$\Delta\rho_{min}$ = −0.853 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Syntex $P2_1$ software (Syntex, 1973). Data reduction: locally modified *XTL*/*XTLE* programs (Syntex, 1976). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976).

Absorption correction: locally modified *ABSORB* (Ugozzoli, 1987). Software used to prepare material for publication: locally modified *XTL/XTLE* programs.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ho1	0	0.2119 (1)	0	0.0577 (2)
Ho2	0.1898 (1)	0.4768 (1)	−0.0275 (1)	0.0555 (2)
O11	0.0642 (6)	0.2140 (4)	−0.1011 (4)	0.072 (3)
O21	0.1458 (10)	0.1838 (5)	−0.1808 (6)	0.116 (5)
O12	0.1813 (6)	0.5251 (4)	0.0758 (4)	0.065 (3)
O22	0.1044 (7)	0.5681 (5)	0.1534 (5)	0.089 (4)
O13	0.0264 (6)	0.1393 (4)	0.0873 (4)	0.068 (3)
O23	0.1314 (7)	0.0869 (5)	0.1652 (5)	0.089 (4)
O14	0.2603 (6)	0.3941 (4)	−0.0808 (4)	0.067 (3)
O24	0.3675 (7)	0.3153 (4)	−0.0794 (4)	0.085 (4)
O15	−0.1425 (6)	0.2442 (4)	0.0433 (4)	0.071 (3)
O25	−0.3040 (7)	0.2693 (5)	0.0308 (5)	0.086 (4)
O16	0.0686 (6)	0.4560 (4)	−0.1199 (4)	0.066 (3)
O26	−0.0660 (7)	0.4796 (5)	−0.1928 (5)	0.093 (4)
O17	0.1686 (7)	0.3888 (4)	0.0349 (4)	0.073 (3)
O27	0.0713 (6)	0.3105 (4)	−0.0086 (4)	0.068 (3)
O18	0.2983 (6)	0.5633 (4)	−0.0104 (4)	0.065 (3)
O28	0.3727 (7)	0.6452 (4)	−0.0443 (4)	0.073 (3)
O*W*1	−0.5050 (6)	0.1188 (4)	−0.7582 (4)	0.078 (3)
O*W*2	−0.7475 (8)	−0.1457 (5)	−0.7778 (5)	0.097 (4)
O*W*3	−0.7468 (7)	−0.0123 (5)	−0.7759 (5)	0.088 (4)
O*W*4	−0.1734 (8)	−0.1184 (5)	−0.3682 (5)	0.092 (4)
O*W*5	−0.0263 (12)	−0.0768 (7)	−0.2630 (8)	0.166 (7)
O*W*6	−0.0295 (11)	−0.1773 (8)	−0.1888 (9)	0.180 (8)
N1	0.0675 (8)	0.1011 (5)	−0.0488 (5)	0.073 (4)
N2	0.0144 (7)	0.4727 (4)	0.0152 (4)	0.069 (3)
N3	0.1800 (7)	0.1942 (4)	0.0424 (5)	0.064 (3)
N4	0.3631 (8)	0.4400 (5)	0.0329 (5)	0.066 (4)
N5	−0.1311 (7)	0.2748 (4)	−0.0822 (5)	0.069 (4)
N6	0.0845 (7)	0.5706 (5)	−0.0706 (5)	0.067 (4)
N7	0.0482 (7)	0.2720 (4)	0.1140 (5)	0.064 (3)
N8	0.2589 (7)	0.5188 (5)	−0.1350 (5)	0.069 (4)
N9	−0.2524 (8)	0.2356 (5)	−0.8385 (6)	0.081 (4)
N10	−0.3467 (8)	0.1800 (5)	−0.6838 (5)	0.077 (4)
C1	−0.3284 (9)	0.2146 (6)	−0.7976 (6)	0.072 (4)
C2	−0.2764 (10)	0.1901 (7)	−0.7305 (6)	0.085 (5)
C11	0.0624 (10)	0.0452 (6)	−0.0260 (7)	0.081 (5)
C21	0.0926 (12)	−0.0081 (7)	−0.0567 (9)	0.105 (7)
C31	0.1260 (15)	−0.0010 (7)	−0.1164 (10)	0.120 (8)
C41	0.1314 (14)	0.0581 (6)	−0.1424 (8)	0.104 (7)
C51	0.1033 (9)	0.1076 (6)	−0.1072 (6)	0.071 (4)
C61	0.1059 (11)	0.1732 (6)	−0.1319 (6)	0.076 (5)
C12	−0.0695 (10)	0.4392 (5)	−0.0112 (7)	0.079 (5)
C22	−0.1503 (10)	0.4319 (7)	0.0216 (8)	0.094 (6)
C32	−0.1488 (11)	0.4571 (8)	0.0822 (8)	0.103 (7)
C42	−0.0665 (11)	0.4926 (6)	0.1115 (7)	0.088 (6)
C52	0.0110 (9)	0.4989 (6)	0.0753 (6)	0.067 (4)
C62	0.1055 (10)	0.5339 (5)	0.1044 (6)	0.070 (4)
C13	0.2568 (8)	0.2213 (6)	0.0188 (6)	0.072 (4)
C23	0.3559 (11)	0.2084 (8)	0.0428 (8)	0.094 (6)
C33	0.3781 (12)	0.1644 (8)	0.0961 (8)	0.109 (7)
C43	0.2980 (10)	0.1358 (7)	0.1204 (7)	0.085 (5)
C53	0.2026 (9)	0.1518 (5)	0.0926 (6)	0.065 (4)
C63	0.1160 (10)	0.1230 (6)	0.1181 (6)	0.070 (4)
C14	0.4123 (10)	0.4659 (6)	0.0891 (6)	0.073 (5)
C24	0.5029 (10)	0.4395 (7)	0.1219 (7)	0.085 (5)
C34	0.5425 (9)	0.3892 (7)	0.0942 (7)	0.086 (5)
C44	0.4891 (10)	0.3632 (6)	0.0364 (7)	0.080 (5)
C54	0.3984 (8)	0.3889 (5)	0.0066 (6)	0.063 (4)
C64	0.3427 (9)	0.3646 (6)	−0.0554 (6)	0.066 (4)
C15	−0.1230 (10)	0.2935 (7)	−0.1436 (7)	0.089 (5)
C25	−0.1966 (12)	0.3201 (8)	−0.1872 (8)	0.103 (6)
C35	−0.2890 (12)	0.3291 (7)	−0.1678 (8)	0.103 (7)
C45	−0.3008 (11)	0.3112 (6)	−0.1037 (7)	0.078 (5)
C55	−0.2169 (9)	0.2829 (6)	−0.0609 (6)	0.069 (4)
C65	−0.2223 (10)	0.2625 (5)	0.0098 (6)	0.069 (4)
C16	0.0945 (10)	0.6290 (5)	−0.0464 (7)	0.075 (5)
C26	0.0287 (12)	0.6760 (7)	−0.0690 (7)	0.091 (6)
C36	−0.0543 (13)	0.6620 (7)	−0.1165 (8)	0.103 (6)
C46	−0.0626 (10)	0.6010 (7)	−0.1441 (7)	0.088 (5)
C56	0.0066 (9)	0.5589 (6)	−0.1193 (6)	0.065 (4)
C66	0.0013 (10)	0.4935 (6)	−0.1463 (6)	0.072 (4)
C17	0.0290 (10)	0.2556 (6)	0.1738 (6)	0.082 (5)
C27	0.0521 (11)	0.2909 (7)	0.2315 (6)	0.089 (5)
C37	0.1014 (12)	0.3473 (7)	0.2267 (6)	0.098 (6)
C47	0.1222 (11)	0.3636 (6)	0.1651 (7)	0.089 (5)
C57	0.0938 (9)	0.3256 (5)	0.1096 (6)	0.063 (4)
C67	0.1126 (8)	0.3424 (5)	0.0399 (6)	0.060 (4)
C18	0.2416 (11)	0.4916 (6)	−0.1953 (6)	0.081 (5)
C28	0.2817 (10)	0.5174 (7)	−0.2491 (6)	0.083 (5)
C38	0.3417 (11)	0.5689 (7)	−0.2388 (7)	0.090 (5)
C48	0.3560 (11)	0.5968 (7)	−0.1772 (6)	0.083 (5)
C58	0.3132 (8)	0.5687 (5)	−0.1257 (5)	0.061 (4)
C68	0.3313 (8)	0.5940 (6)	−0.0541 (6)	0.064 (4)

Table 2. *Selected interatomic distances and comparison with those of the isomorphous* Nd *complex*

	Distance (Å)	δ (Å)*	ρ (%)†
Ho1—O11	2.334 (7)	−0.098 (10)	108
Ho1—O13	2.328 (7)	−0.097 (10)	107
Ho1—O15	2.346 (8)	−0.101 (11)	111
Ho1—O27	2.348 (7)	−0.076 (10)	84
Ho1—O28$^{\rm i}$	2.301 (8)	−0.081 (11)	89
Ho1—N1	2.785 (10)	−0.026 (13)	29
Ho1—N3	2.470 (9)	−0.129 (12)	142
Ho1—N5	2.592 (9)	−0.168 (12)	185
Ho1—N7	2.612 (9)	−0.069 (13)	76
Ho2—O12	2.338 (7)	−0.102 (10)	112
Ho2—O14	2.356 (7)	−0.098 (10)	108
Ho2—O16	2.304 (7)	−0.096 (10)	105
Ho2—O17	2.313 (7)	−0.111 (10)	122
Ho2—O18	2.358 (7)	−0.066 (10)	73
Ho2—N2	2.653 (9)	−0.092 (12)	101
Ho2—N4	2.576 (9)	−0.094 (12)	98
Ho2—N6	2.536 (9)	−0.123 (12)	135
Ho2—N8	2.647 (9)	−0.059 (12)	65

Symmetry code: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

* Ho-ligand distance minus relevant Nd-ligand distance.

† $\rho = \delta$ /(Ho ionic radius minus Nd ionic radius).

The author thanks Professor K. Bukietyńska for useful discussions and Professor T. Głowiak for help in performing the measurements.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71315 (42 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AB1068]

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