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Rare-Earth Nicotinates: Structures of Tetra-μ-nicotinato-*O,O′*-bis[diaqua(nicotinato-*O,O′*)holmium(III)], $[Ho(C_5H_4NCO_2)_3(H_2O)_2]_2$, and Tetra-$\mu$-nicotinato-*O,O′*-bis[diaqua(nicotinato-*O,O′*)thulium(III)], $[Tm(C_5H_4NCO_2)_3(H_2O)_2]_2$

By Keith Prout and José M. Marín*

*Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX*1 3*PD, England*

and Clyde A. Hutchison Jr

Department of Chemistry, The University of Chicago, Chicago, Illinois 60637, *USA*

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Abstract. The isomorphous Ho and Tm compounds (I) and (II) are monoclinic, $P2_1/c$. (I): $M_r = 1134{\cdot}5$, $a = 9{\cdot}567\,(6)$, $b = 11{\cdot}596\,(2)$, $c = 17{\cdot}811\,(4)$ Å, $\beta = 91{\cdot}42\,(5)°$, $V = 1975$ Å^3, $Z = 2$, $D_x = 1{\cdot}91$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 4·26 mm^{-1}, $F(000) = 1104$, room temperature, $R = 0{\cdot}027$ for 4687 observed reflections. (II): $M_r = 1142{\cdot}6$, $a = 9{\cdot}498\,(7)$, $b = 11{\cdot}561\,(2)$, $c = 17{\cdot}847\,(4)$ Å, $\beta = 91{\cdot}60\,(4)°$, $V = 1959$ Å^3, $Z = 2$, $D_x = 1{\cdot}94$ Mg m^{-3}, μ(Mo $K\alpha$) = 4·73 mm^{-1}, $F(000) = 1112$, room temperature, $R = 0{\cdot}038$ for 3170 observed reflections. The molecules of (I) and (II) are centrosymmetric dimers disposed about the inversion centres (0,0,0) and (0,0·5,0·5). In each complex the metal atom in a general position is coordinated to eight O atoms. There are four bridging and two terminal nicotinate groups per dimer. For the chelating terminal carboxylate ligands the average Ln—O (Ln=Ho,Tm) distances are considerably longer than for the bridging ligands. Adjacent dimers are linked together by hydrogen bonds involving the N atoms of the nicotinate groups and the water molecules.

Introduction. X-ray crystallographic studies by Moore, Glick & Baker (1972) have shown that the monoclinic crystals of the dimeric lanthanoid nicotinates, $[Ln(C_5H_4NCO_2)_3(H_2O)_2]_2$, have a structure with space-group symmetry $P2_1/c$. In addition to the La complex, the structures of the species containing the ions Sm^{3+} (Moore *et al.*, 1972), Nd^{3+} Gd^{3+} and Er^{3+} (Glick, private communication) have been determined. In these structures the rare-earth ions occur in relatively isolated pairs, thus affording an opportunity for studies, by magnetic resonance and optical spectroscopy, of the pair-wise interactions between rare-earth ions that are relatively free of the complicating presence of the single-ion and triple-ion systems that occur when paramagnetic ions are dilutely substituted at La sites in ionic crystals.

In view of (*a*) the necessity of precise structural data for the interpretation of such magnetic and optical measurements, and (*b*) the interest in the rare-earth nicotinates with respect to the determination of proton coordinates by magnetic resonance methods (Hutchison & Mckay, 1977; Hutchison & Orlowski, 1980), the structures of the Ho and Tm complexes have been determined.

Experimental. Block-shaped single crystals of (I) (0·30 × 0·35 × 0·35 mm) and (II) (0·25 × 0·29 × 0·35 mm). Enraf–Nonius CAD-4F diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell constants obtained by the least-squares refinement of $\sin^2\theta/\lambda^2$ values for 25 accurately centred reflections. 6672 independent reflections with $2\theta \leq 58°$ and 4513 independent reflections with $2\theta \leq 54°$ measured for (I) and (II), respectively, using $\omega/2\theta$ scans. Three standard reflections checked periodically, intensity variation within 6% for (I) and (II). Data corrected for Lorentz, polarization and (compound I) absorption effects (North, Phillips & Mathews, 1968), range of A 1–1·3. 4687 reflections considered observed $[I \geq 3\sigma(I)]$ for (I), index range ±13, 0→15, 0→24 and 3170 for (II), index range ±12, 0→14, 0→21. Structures solved by Patterson and Fourier methods and refined by least squares with anisotropic thermal parameters using a large-block approximation to the normal matrix. The refinements, based on F's, converged at $R = 0{\cdot}027$ (compound I) and $R = 0{\cdot}038$ $[(\Delta/\sigma)_{\max} = 0{\cdot}25]$ (compound II). All H atoms located by means of difference Fourier maps and included in the refinements with fixed contributions [except the water H atoms of compound (II), whose coordinates were refined]. In the last stages of the refinement each reflection given a weight computed from a Chebyshev series with three coefficients: 10·3, 15·2 and 3·1 for complex (I), and 45·4, 60·6 and 11·4 for complex (II) (Carruthers & Watkin, 1979); final R_w values 0·031 and 0·055, respectively. Scattering factors from Cromer & Mann (1968), f' and f'' for Ho and Tm from *International Tables for X-ray Crystallography*

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* Present address: Departamento de Química Inorgánica, Facultad de Química, Universidad, Sevilla, Spain.

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* $[Ho(C_5H_4NCO_2)_3(H_2O)_2]_2$

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
Ho(1)	0·18972 (2)	0·10487 (2)	0·00511 (2)	0·0157
O(2)	−0·0194 (2)	0·2068 (2)	0·0037 (1)	0·0283
O(3)	−0·2087 (2)	0·0926 (2)	−0·0121 (1)	0·0315
O(4)	0·0726 (3)	0·0358 (3)	−0·0997 (1)	0·0418
O(5)	−0·1050 (3)	−0·0818 (2)	−0·1257 (1)	0·0344
O(6)	0·2526 (2)	0·2380 (2)	−0·0984 (1)	0·0318
O(7)	0·3923 (2)	0·0922 (2)	−0·0755 (1)	0·0282
O(8)	0·3926 (2)	0·0678 (2)	0·0814 (1)	0·0287
O(9)	0·2551 (2)	0·2804 (2)	0·0632 (1)	0·0279
N(10)	−0·4712 (3)	0·3516 (3)	0·0528 (2)	0·0370
N(11)	0·1585 (3)	0·0644 (3)	−0·3254 (2)	0·0437
N(12)	0·4824 (3)	0·3409 (3)	−0·2813 (2)	0·0424
C(13)	−0·1466 (3)	0·1864 (2)	0·0060 (1)	0·0225
C(14)	−0·2406 (2)	0·2836 (2)	0·0314 (2)	0·0198
C(15)	−0·3846 (3)	0·2703 (3)	0·0295 (2)	0·0276
C(16)	−0·4161 (4)	0·4497 (3)	0·0796 (2)	0·0395
C(17)	−0·2743 (4)	0·4703 (3)	0·0830 (2)	0·0403
C(18)	−0·1832 (3)	0·3851 (3)	0·0591 (2)	0·0301
C(19)	−0·0006 (3)	−0·0236 (3)	−0·1434 (1)	0·0262
C(20)	0·0389 (2)	−0·0260 (2)	−0·2245 (1)	0·0216
C(21)	−0·0037 (3)	−0·1155 (3)	−0·2706 (2)	0·0319
C(22)	0·0396 (4)	−0·1160 (3)	−0·3447 (2)	0·0402
C(23)	0·1206 (4)	−0·0233 (4)	−0·3682 (2)	0·0422
C(24)	0·1200 (3)	0·0619 (3)	−0·2538 (2)	0·0329
C(25)	0·3610 (3)	0·1827 (3)	−0·1119 (1)	0·0235
C(26)	0·4557 (3)	0·2235 (3)	−0·1722 (1)	0·0261
C(27)	0·5924 (3)	0·1855 (4)	−0·1767 (2)	0·0357
C(28)	0·6736 (4)	0·2282 (4)	−0·2341 (2)	0·0414
C(29)	0·6147 (4)	0·3060 (4)	−0·2845 (2)	0·0398
C(30)	0·4056 (3)	0·3005 (3)	−0·2262 (2)	0·0359

Table 2. *Atomic coordinates and* U_{eq} *values* (Å^2) *for* $[Tm(C_5H_4NCO_2)_3(H_2O)_2]_2$

$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}$.

	x	y	z	U_{eq}
Tm(1)	0·18979 (4)	0·10502 (4)	0·00514 (3)	0·0148
O(2)	−0·0190 (3)	0·2060 (3)	0·0026 (3)	0·0244
O(3)	−0·2086 (4)	0·0904 (3)	−0·0130 (2)	0·0297
O(4)	0·0782 (5)	0·0355 (4)	−0·0989 (2)	0·0387
O(5)	−0·1021 (5)	−0·0818 (4)	−0·1234 (2)	0·0330
O(6)	0·2531 (4)	0·2382 (3)	−0·0970 (2)	0·0304
O(7)	0·3937 (4)	0·0904 (3)	−0·0741 (2)	0·0293
O(8)	0·3921 (3)	0·0701 (4)	0·0809 (2)	0·0229
O(9)	0·2516 (4)	0·2809 (4)	0·0620 (3)	0·0285
N(10)	−0·4731 (5)	0·3515 (5)	0·0528 (3)	0·0364
N(11)	0·1563 (6)	0·0660 (5)	−0·3246 (3)	0·0397
N(12)	0·4808 (5)	0·3405 (6)	−0·2805 (3)	0·0393
C(13)	−0·1469 (4)	0·1847 (4)	0·0048 (3)	0·0171
C(14)	−0·2401 (5)	0·2823 (4)	0·0318 (3)	0·0175
C(15)	−0·3847 (5)	0·2701 (4)	0·0293 (3)	0·0235
C(16)	−0·4155 (6)	0·4482 (5)	0·0796 (4)	0·0383
C(17)	−0·2722 (6)	0·4713 (5)	0·0819 (4)	0·0394
C(18)	−0·1824 (6)	0·3843 (4)	0·0571 (4)	0·0313
C(19)	0·0009 (5)	−0·0251 (5)	−0·1423 (2)	0·0235
C(20)	0·0393 (5)	−0·0261 (4)	−0·2231 (2)	0·0196
C(21)	−0·0021 (6)	−0·1168 (5)	−0·2690 (3)	0·0306
C(22)	0·0399 (7)	−0·1173 (5)	−0·3430 (4)	0·0359
C(23)	0·1168 (7)	−0·0235 (6)	−0·3672 (4)	0·0449
C(24)	0·1198 (6)	0·0617 (5)	−0·2538 (3)	0·0341
C(25)	0·3610 (5)	0·1815 (4)	−0·1115 (3)	0·0212
C(26)	0·4550 (5)	0·2218 (4)	−0·1724 (3)	0·0227
C(27)	0·5931 (5)	0·1837 (5)	−0·1775 (4)	0·0323
C(28)	0·6728 (6)	0·2274 (6)	−0·2347 (4)	0·0396
C(29)	0·6138 (6)	0·3060 (6)	−0·2842 (3)	0·0368
C(30)	0·4045 (6)	0·2992 (5)	−0·2256 (3)	0·0332

(1974). Final difference Fourier maps showed no feature greater than ±0·3 e Å^{-3}. All computations carried out with the Oxford *CRYSTALS* package (Watkin & Carruthers, 1981).

Discussion. Final atomic parameters are given in Tables 1 and 2 for (I) and (II) respectively.* Tables 3 and 4 give the corresponding bond distances and angles.

The individual molecules of $[Ho(C_5H_4NCO_2)_3(H_2O)_2]_2$ (I) and $[Tm(C_5H_4NCO_2)_3(H_2O)_2]_2$ (II) are centrosymmetric dimers with four bridging and two terminal nicotinate (3-pyridinecarboxylate) ligands. The coordination sphere of each metal atom is completed by two molecules of water, thus leading to octacoordination with no point symmetry at the metal sites (see Fig. 1).

The geometry about each metal ion can be described in terms of a distorted square antiprism (ideal point symmetry D_{4d}), with the O atoms of the water molecules and of the terminal nicotinate ligand occupying the vertices of one of the quadrilateral faces of the O_8 polyhedron. The O*M*O angles (*M* = Ho, Tm) involving O atoms occupying opposite positions within the quadrilateral faces range from 96 to 125° (see Tables 3 and 4), while in the ideal D_{4d} polyhedron these angles are all 118·5°.

Table 3. *Bond lengths* (Å) *and angles* (°) *for* (I)

Ho(1)–O(2)	2·323 (2)	N(10)–C(16)	1·338 (5)
Ho(1)–O(3′)	2·300 (2)	N(11)–C(23)	1·316 (5)
Ho(1)–O(4)	2·298 (2)	N(11)–C(24)	1·336 (4)
Ho(1)–O(5′)	2·329 (2)	N(12)–C(29)	1·331 (5)
Ho(1)–O(6)	2·490 (2)	N(12)–C(30)	1·327 (4)
Ho(1)–O(7)	2·445 (2)	C(13)–C(14)	1·518 (3)
Ho(1)–O(8)	2·380 (2)	C(14)–C(15)	1·385 (3)
Ho(1)–O(9)	2·361 (2)	C(14)–C(18)	1·385 (4)
O(2)–C(13)	1·241 (3)	C(16)–C(17)	1·377 (5)
O(3)–C(13)	1·277 (3)	C(17)–C(18)	1·391 (4)
O(4)–C(19)	1·242 (4)	C(19)–C(20)	1·502 (3)
O(5)–C(19)	1·252 (4)	C(20)–C(21)	1·379 (4)
O(6)–C(25)	1·248 (3)	C(20)–C(24)	1·391 (4)
O(7)–C(25)	1·265 (3)	C(21)–C(22)	1·393 (5)
O(8)–N(12^{i})	2·781 (4)	C(22)–C(23)	1·395 (6)
O(9)–N(10^{ii})	2·756 (3)	C(25)–C(26)	1·499 (3)
O(9)–N(11^{i})	2·850 (4)	C(26)–C(27)	1·384 (4)
N(10)–C(15)	1·328 (4)	C(26)–C(30)	1·389 (4)
		C(27)–C(28)	1·390 (4)
		C(28)–C(29)	1·383 (6)
O(7)–Ho(1)–O(9)	95·95 (7)	O(4)–C(19)–C(20)	117·4 (3)
O(6)–Ho(1)–O(8)	109·02 (8)	O(5)–C(19)–C(20)	117·0 (3)
O(4)–Ho(1)–O(5′)	122·4 (1)	C(19)–C(20)–C(21)	120·6 (3)
O(2)–Ho(1)–O(3′)	125·02 (8)	C(19)–C(20)–C(24)	120·3 (3)
O(6)–Ho(1)–O(7)	52·60 (7)	C(21)–C(20)–C(24)	119·1 (3)
O(8)–Ho(1)–O(9)	72·66 (8)	C(20)–C(21)–C(22)	118·5 (3)
Ho(1)–O(2)–C(13)	138·1 (2)	C(21)–C(22)–C(23)	117·4 (3)
Ho(1′)–O(3)–C(13)	143·0 (2)	C(22)–C(23)–N(11)	124·7 (3)
Ho(1)–O(4)–C(19)	163·4 (2)	N(11)–C(24)–C(20)	123·0 (3)
Ho(1′)–O(5)–C(19)	126·3 (2)	O(6)–C(25)–O(7)	121·0 (2)
Ho(1)–O(6)–C(25)	92·3 (2)	O(6)–C(25)–C(26)	119·7 (3)
Ho(1)–O(7)–C(25)	94·0 (1)	O(7)–C(25)–C(26)	119·3 (2)
C(15)–N(10)–C(16)	118·2 (3)	C(25)–C(26)–C(27)	122·0 (3)
C(23)–N(11)–C(24)	117·2 (3)	C(25)–C(26)–C(30)	119·7 (3)
C(29)–N(12)–C(30)	117·9 (3)	C(27)–C(26)–C(30)	118·3 (3)
O(2)–C(13)–O(3)	127·1 (2)	C(26)–C(27)–C(28)	118·4 (3)
O(2)–C(13)–C(14)	117·2 (2)	C(27)–C(28)–C(29)	118·9 (3)
O(3)–C(13)–C(14)	115·6 (2)	C(28)–C(29)–N(12)	122·9 (3)
C(13)–C(14)–C(15)	120·4 (2)	N(12)–C(30)–C(26)	123·5 (3)
C(13)–C(14)–C(18)	120·3 (2)		
C(15)–C(14)–C(18)	119·3 (2)		
C(14)–C(15)–N(10)	122·7 (3)		
N(10)–C(16)–C(17)	122·8 (3)		
C(16)–C(17)–C(18)	119·2 (3)		
C(17)–C(18)–C(14)	117·8 (3)		
O(4)–C(19)–O(5)	125·6 (3)		

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

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, and distances and angles involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39797 (61 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Bond lengths* (Å) *and angles* (°) *for* (II)

For symmetry code see Table 3.

Tm(1)–O(2)	2·300 (3)	N(10)–C(15)	1·337 (6)
Tm(1)–O(3′)	2·270 (4)	N(10)–C(16)	1·328 (8)
Tm(1)–O(4)	2·261 (4)	N(11)–C(23)	1·331 (8)
Tm(1)–O(5′)	2·307 (4)	N(11)–C(24)	1·322 (7)
Tm(1)–O(6)	2·474 (4)	N(12)–C(29)	1·328 (7)
Tm(1)–O(7)	2·435 (4)	N(12)–C(30)	1·324 (7)
Tm(1)–O(8)	2·353 (3)	C(13)–C(14)	1·521 (4)
Tm(1)–O(9)	2·340 (4)	C(14)–C(15)	1·380 (6)
O(2)–C(13)	1·242 (6)	C(14)–C(18)	1·372 (7)
O(3)–C(13)	1·274 (6)	C(16)–C(17)	1·387 (7)
O(4)–C(19)	1·264 (7)	C(17)–C(18)	1·398 (7)
O(5)–C(19)	1·232 (6)	C(19)–C(20)	1·497 (4)
O(6)–C(25)	1·249 (6)	C(20)–C(21)	1·381 (7)
O(7)–C(25)	1·280 (6)	C(20)–C(24)	1·392 (6)
O(8)–N(12^{i})	2·791 (7)	C(21)–C(22)	1·390 (8)
O(9)–N(10^{ii})	2·748 (6)	C(22)–C(23)	1·383 (8)
O(9)–N(11^{i})	2·855 (6)	C(25)–C(26)	1·501 (4)
		C(26)–C(27)	1·389 (6)
		C(26)–C(30)	1·380 (7)
		C(27)–C(28)	1·384 (7)
		C(28)–C(29)	1·375 (8)
O(7)–Tm(1)–O(9)	96·8 (1)	O(4)–C(19)–C(20)	116·2 (4)
O(6)–Tm(1)–O(8)	108·6 (1)	O(5)–C(19)–C(20)	118·4 (5)
O(4)–Tm(1)–O(5′)	122·5 (2)	C(19)–C(20)–C(21)	120·3 (4)
O(2)–Tm(1)–O(3′)	124·9 (1)	C(19)–C(20)–C(24)	121·6 (5)
O(6)–Tm(1)–O(7)	53·2 (1)	C(21)–C(20)–C(24)	118·1 (5)
O(8)–Tm(1)–O(9)	73·1 (1)	C(20)–C(21)–C(22)	118·8 (5)
Tm(1)–O(2)–C(13)	137·9 (3)	C(21)–C(22)–C(23)	117·5 (6)
Tm(1′)–O(3)–C(13)	143·3 (3)	C(22)–C(23)–N(11)	125·0 (6)
Tm(1)–O(4)–C(19)	162·1 (4)	N(11)–C(24)–C(20)	124·4 (6)
Tm(1′)–O(5)–C(19)	128·4 (4)	O(6)–C(25)–O(7)	120·8 (4)
Tm(1)–O(6)–C(25)	92·5 (3)	O(6)–C(25)–C(26)	119·6 (4)
Tm(1)–O(7)–C(25)	93·5 (3)	O(7)–C(25)–C(26)	119·5 (4)
C(15)–N(10)–C(16)	116·7 (5)	C(25)–C(26)–C(27)	122·0 (5)
C(23)–N(11)–C(24)	116·1 (6)	C(25)–C(26)–C(30)	119·8 (4)
C(29)–N(12)–C(30)	118·0 (5)	C(27)–C(26)–C(30)	118·2 (4)
O(2)–C(13)–O(3)	127·3 (4)	C(26)–C(27)–C(28)	118·0 (5)
O(2)–C(13)–C(14)	116·2 (4)	C(27)–C(28)–C(29)	119·6 (5)
O(3)–C(13)–C(14)	116·5 (4)	C(28)–C(29)–N(12)	122·5 (5)
C(13)–C(14)–C(15)	120·1 (4)	N(12)–C(30)–C(26)	123·7 (5)
C(13)–C(14)–C(18)	120·8 (4)		
C(15)–C(14)–C(18)	119·1 (4)		
C(14)–C(15)–N(10)	123·5 (5)		
N(10)–C(16)–C(17)	124·5 (5)		
C(16)–C(17)–C(18)	117·4 (6)		
C(17)–C(18)–C(14)	118·7 (5)		
O(4)–C(19)–O(5)	125·4 (4)		

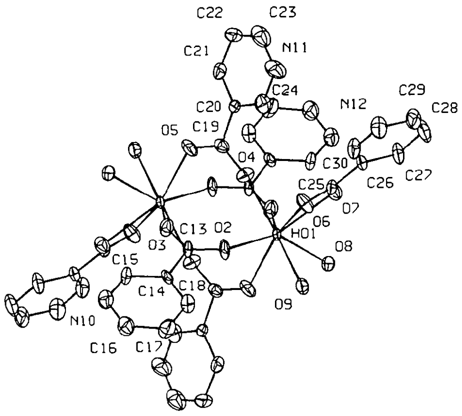

Fig. 1. *ORTEP* (Johnson, 1965) perspective view of the molecule of $[Ho(C_5H_4NCO_2)_3(H_2O)_2]_2$ and atom-labelling scheme. The corresponding view for $[Tm(C_5H_4NCO_2)_3(H_2O)_2]_2$ is entirely similar and is therefore not shown separately.

Table 5. *Comparison of relevant bond distances* (Å) *in the complexes* $[Ln(C_5H_4NCO_2)_3(H_2O)_2]_2$ (Ln = La, Nd, Sm, Gd, Ho, Er *and* Tm)

	M—O(bridge)	*M*—O(chelate)	*M*—O(H_2O)	*M*—*M*	Ionic radii
La	2·501	2·607	2·513	4·221	1·061
Nd	2·439	2·558	2·467	4·227	0·995
Sm	2·380	2·526	2·425	4·297	0·964
Gd	2·356	2·509	2·409	4·360	0·938
Ho	2·312	2·468	2·370	4·369	0·894
Er	2·304	2·461	2·366	4·369	0·881
Tm	2·284	2·454	2·346	4·346	0·869

Data for the La and Sm compounds taken from Moore *et al.* (1972), for the Nd, Gd and Er compounds provided by M. D. Glick (private communication). The *M*—O distances are average values. Ionic radii taken from Cotton & Wilkinson (1980).

Comparison of the crystal and molecular parameters of (I), (II) and the other structurally characterized lanthanoid nicotinates (Moore *et al.*, 1972; Glick & Ilsley, private communication) shows the compounds to be isomorphous and isostructural.

In general, and as a consequence of the lanthanoid contraction, a lowering in the coordination number of the metal atom is to be expected for a series of analogous complexes when moving from La to Lu (Cotton & Wilkinson, 1980). No difference of this sort is observed in the nicotinates of La, Nd, Sm, Gd, Ho, Er and Tm, even though these elements cover a considerable range of the lanthanoid series.

A significant difference between the metal—O bond lengths of the terminal and bridging carboxylate ligands exists in the lanthanoid nicotinates (Table 5). The average *M*—O distance is 0·106–0·170 Å longer for the terminal groups. The difference is large enough for a stronger metal—O(bridge) interaction to be assumed.

The effect of the lanthanoid contraction can be seen (Table 5) as a shortening of the metal—O bond distances when passing from the La to the Tm nicotinate. In relative terms (*i.e.* comparing the differences in *M*—O distances with the differences in ionic radii for each pair of Ln^{3+} ions), there occurs a shortening of the average metal—O(bridge) distance (by 0·025 Å) and a lengthening of the *M*—O(terminal carboxylate) (by 0·039 Å) and *M*—O(H_2O) (by 0·025 Å), when moving from La to Tm.

The metal—metal intramolecular separation steadily increases from La to Ho, but a shortening takes place from Er to Tm (Table 5). In contrast to the La and Sm nicotinates (Moore *et al.*, 1972), no appreciable bending of the pyridine rings about the ring-carboxylate bonds is found in compounds (I) and (II). However, there is a considerable rotation of the ring relative to the carboxylate planes within each nicotinate ligand. These twists are thought to minimize the distances within the hydrogen-bonding network which involves the coordinated water molecules and the pyridine-ring N atoms of adjacent dimers (Moore *et al.*, 1972).

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(2,2′-Bipyridine)bromo(triphenylphosphine)copper(I), $[CuBr(C_{10}H_8N_2)\{P(C_6H_5)_3\}]$

By J. Zukerman-Schpector, E. E. Castellano and G. Oliva

Instituto de Física e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13.560 – *São Carlos, São Paulo, Brazil*

and A. E. Mauro and M. R. Roveri

Instituto de Química de Araraquara, Caixa Postal 174, 14.800 – *Araraquara, São Paulo, Brazil*

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Abstract. $M_r = 561{\cdot}93$, monoclinic, $C2/c$, $a = 34{\cdot}089\,(5)$, $b = 9{\cdot}370\,(3)$, $c = 18{\cdot}863\,(3)$ Å, $\beta = 124{\cdot}50\,(1)°$, $V = 4965\,(4)$ Å^3, $Z = 8$, $D_x = 1{\cdot}50$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 2{\cdot}49$ mm^{-1}, $F(000) = 2264$, $T = 296$ K, $R = 0{\cdot}054$ for 1067 observed reflections. The metal atom is tetrahedrally coordinated to 2,2′-bipyridine [Cu—N 2·11 (1), 2·10 (1) Å; N—Cu—N 78·6 (5)°], Br [Cu—Br 2·428 (3) Å] and triphenylphosphine [Cu—P 2·206 (4) Å], and is distorted [N—Cu—Br 115·2 (3), 108·8 (4)°; N—Cu—P 116·2 (4), 114·8 (4)°; and Br—Cu—P 117·0 (2)°].

Introduction. Monodentate tertiary phosphines form many complexes with Cu^I that show a variety of stoichiometries and structures (Gill, Mayerle, Welcker, Lewis, Ucko, Barton, Stowens & Lippard, 1976). Considerable interest exists in structural studies of copper(I) derivatives, not only because of their stereochemistry but also for their importance in oxidation–reduction reactions in enzymes containing copper (Peisach, Aisen & Blumberg, 1966) and in organic synthesis (Tsuda, Fujii, Kawasaki & Saegusa, 1980). Some years ago Jardine, Rule & Vohra (1970) reported the preparation of halogenocopper(I) complexes using tertiary phosphines as ligands. We synthesized one of them, the title compound, and proceeded to its crystal-structure determination because the only characterizations in the Jardine *et al.* (1970) paper were analytical data and melting point.

Experimental. Prismatic yellow crystals from butanol at 277 K, 0·23 × 0·18 × 0·05 mm, Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, cell parameters by least squares on setting angles for 25 reflections, $16 < 2\theta < 30°$, ω–2θ scans, scan width $(0{\cdot}80 + 0{\cdot}14 \tan\theta)°$, scan speed 6·7° min^{-1} max., range of hkl: $h < 37$, $k < 10$, $-20 < l < 20$; standards $60\bar{6}$, $11,\bar{1},\bar{3}$, $0\bar{8}0$, varied ±2% of mean intensities over data collection; 3520 reflections measured, 3454 unique, $R_{\text{int}} = 0{\cdot}039$, 1068 observed above $3\sigma(I)$. Lp and absorption corrections (transmission factors 0·51–0·89); structure solved by direct methods, H atoms located in a difference map; least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$; 196 parameters refined: coordinates and anisotropic thermal parameters for non-H atoms, phenyl rings of triphenylphosphine as rigid bodies (C—C = 1·395, C—H = 1·08 Å, all angles 120°, H atoms with common $B = 6{\cdot}3$ Å^2), H atoms of bipyridine with fixed isotropic temperature factor $B = 4{\cdot}7$ Å^2; excluding unobserved and one reflection ($\bar{2}04$) $R = 0{\cdot}054$, $R_w = 0{\cdot}048$; max. $\Delta/\sigma = 0{\cdot}056$, $\Delta\rho$ excursions within $-0{\cdot}40$ and $0{\cdot}42$ e Å^{-3}, scattering factors for non-H atoms from Cromer & Mann (1968) with corrections

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