distances observed between perchlorate O atoms, water O atoms and the ligand N atoms.

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Structure of Tris{2'-[α-(2-pyridyl)benzylidene]salicylohydrazido}samarium(III), [Sm(C₁₉H₁₄N₃O₂)₃]

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Abstract. $M_r = 1099.4$, orthorhombic, $P2_12_12_1$, $a = 10.889\ (2)$, $b = 19.765\ (5)$, $c = 23.702\ (4)$ Å, $V = 5101\ (2)$ Å^3, $Z = 4$, $D_m = 1.45$ (by flotation in xylene/chloroform), $D_x = 1.433$ Mg m^{-3}, $\lambda(Mo\ K\alpha) = 0.71073$ Å, $\mu(Mo\ K\alpha) = 1.213$ mm^{-1}, $F(000) = 2228$, $T = 294$ K, final $R = 0.057$ and $wR = 0.055$ for 3776 observed diffractometer data. The three non-planar $C_{19}H_{14}N_3O_2$ ligands are chemically identical but crystallographically different and display bond lengths and angles close to expected values. They are stabilized by intramolecular O—H···N hydrogen bonds. The Sm atom is surrounded by three pyridine (py) N [Sm—N(py) = 2.636 (10), 2.659 (10), 2.632 (10) Å], three azo N [Sm—N(azo) = 2.572 (11), 2.583 (10), 2.580 (10) Å] and three enolic O atoms which define a distorted tricapped trigonal prism. The Sm—O distances range from 2.345 (8) to 2.392 (9) Å. Differences in SM→N back-donation may explain the shortness of Sm—N(azo) bonds compared with the Sm—N(py) distances.

Introduction. The tridentate ligand 2'-[α-(2-pyridyl)-benzylidene]salicylohydrazide (pbs H), synthesized by

Dutta & Hossain (1984), is capable of functioning as a neutral tridentate (NNO) donor in the keto form or as a monobasic (NNO) donor in the enol form and has an added special feature in having a phenolic OH group *ortho* to the hydrazone group. Several complexes of this ligand with transition and non-transition elements [Ni, Co, Cu, Zn, Cd, Mg (Dutta & Hossain, 1984)] and with lanthanides [La, Pr, Nd, Sm, Gd, Tb, Dy, Y (Dutta & Das, 1984)] have also been synthesized. The crystal structure of [Sm^{III}(pbs)₃] presented here permits the metal coordination and the nature of the Sm—N bonding to be discussed.
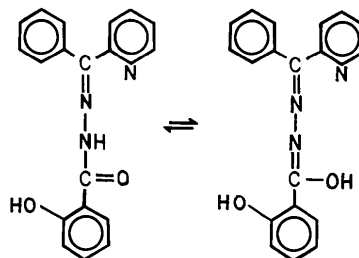
Experimental. The title compound was synthesized by refluxing an aqueous solution of samarium acetate with

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an ethanolic solution of the Schiff's base ligand pbs H. Thin plate-shaped yellow crystals obtained by slow evaporation of a saturated dimethyl sulfoxide solution at room temperature; approximate lattice constants from rotation and Weissenberg photographs, accurate values by least-squares treatment of 25 randomly chosen reflections with $11 \cdot 6 < \theta < 12 \cdot 2°$; Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation; crystal dimensions ca $0 \cdot 21 \times 0 \cdot 12 \times 0 \cdot 10$ mm; intensity data for $4 \cdot 0 \leq 2\theta \leq 52 \cdot 0°$, index range $0 \leq h \leq 13$, $0 \leq k \leq 24$, $0 \leq l \leq 29$, $\omega{-}2\theta$ scans; three standard reflections monitored periodically, no significant variation; intensities were corrected for Lorentz, polarization and absorption effects (min. and max. correction factors $= 0 \cdot 9627$, $0 \cdot 9987$); 5548 independent reflections, 3776 observed $[I \geq 2\sigma(I)]$.

The approximate position of the Sm atom was obtained from unsharpened three-dimensional Patterson function and positions of the remaining non-H atoms from successive weighted Fourier syntheses. Block-diagonal least-squares refinement with anisotropic thermal parameters for C, N, O and Sm atoms converged at $R = 0 \cdot 057$ and $wR = 0 \cdot 055$ for 3776 observed reflections (maximum shift/e.s.d. $= 0 \cdot 41$); function minimized was $\sum w(|F_o| - |F_c|)^2$, $w = [1/\sigma(F_o)]^2$ (from counting statistics). No correction for secondary extinction was attempted, $(|F_o| - |F_c|)$ values for strong low-order reflections being randomly positive and negative. No allowance was made for the scattering of the H atoms. Function values in the final difference Fourier synthesis were within the range $-1 \cdot 9$ to $+1 \cdot 2$ e Å^{-3}. The thermal motion of the molecule is strongly anisotropic with U_{11} larger than the other components for most of the atoms. The X-ray scattering factors for the non-H atoms and anomalous-dispersion corrections for Sm were taken from *International Tables for X-ray Crystallography* (1974). All computations were performed using Burroughs B6700 computer of the Regional Computer Centre, Jadavpur University Campus, Calcutta, using program system *XRAYARC* (Vickery, Bright & Mallinson, 1971). Programs *EXFFT* and *SEARCH* of *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) were used for weighted Fourier synthesis.

Discussion. The final positional coordinates and equivalent isotropic thermal parameters for the non-H atoms are given in Table 1,* selected bond angles about Sm in Table 2. The atom numbering is given in Fig. 1. Due to

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* Lists of structure factors, anisotropic thermal parameters, selected torsion angles, interatomic distances and angles involving non-H atoms, and least-squares-planes calculations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51723 (47 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

the high atomic number of Sm, refinement of the lighter atoms in the ligands was not as satisfactory as in the case of the corresponding Ni complex (Seth &

Table 1. *Final fractional atomic coordinates ($\times 10^4$, for Sm $\times 10^5$) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters for the non-H atoms*

$$B_{eq} = (B_{11} + B_{22} + B_{33})/3.$$

	x	y	z	B_{eq}(Å²)
Sm	56051 (8)	35008 (4)	84585 (4)	3·0
O(1)	4891 (8)	2384 (4)	8534 (4)	4·0
O(2)	2759 (9)	1418 (5)	7301 (4)	5·9
O(3)	3926 (8)	3685 (4)	9091 (4)	4·1
O(4)	3198 (9)	5501 (4)	9922 (4)	5·0
O(5)	6322 (8)	3297 (4)	7541 (3)	3·8
O(6)	8407 (9)	1648 (5)	7005 (4)	5·2
N(1)	4416 (10)	4466 (5)	7919 (4)	3·2
N(2)	3798 (10)	3164 (5)	7819 (4)	3·8
N(3)	3601 (10)	2467 (5)	7759 (4)	3·6
N(4)	7614 (9)	4265 (5)	8439 (5)	3·7
N(5)	5756 (10)	4557 (5)	9097 (4)	3·7
N(6)	4667 (10)	4723 (5)	9395 (4)	3·5
N(7)	6752 (10)	3085 (5)	9372 (4)	3·1
N(8)	7378 (10)	2649 (5)	8328 (4)	3·6
N(9)	7524 (10)	2393 (5)	7797 (4)	3·7
C(1)	4582 (13)	5146 (6)	8017 (5)	4·1
C(2)	3911 (14)	5652 (7)	7747 (6)	4·9
C(3)	2999 (15)	5458 (7)	7372 (6)	5·4
C(4)	2725 (14)	4782 (7)	7278 (6)	4·9
C(5)	3483 (12)	4291 (6)	7566 (5)	3·4
C(6)	3249 (12)	3557 (7)	7476 (5)	3·8
C(7)	2407 (14)	3341 (7)	7026 (6)	4·6
C(8)	1367 (17)	2974 (9)	7145 (7)	8·0
C(9)	577 (17)	2780 (9)	6675 (8)	9·1
C(10)	1003 (18)	2962 (9)	6125 (8)	9·1
C(11)	2030 (17)	3330 (8)	6006 (7)	7·9
C(12)	2767 (14)	3527 (9)	6470 (6)	6·4
C(13)	4187 (11)	2126 (5)	8155 (5)	2·8
C(14)	3957 (11)	1371 (6)	8149 (5)	3·3
C(15)	4526 (13)	988 (6)	8575 (5)	3·9
C(16)	4353 (15)	258 (7)	8580 (6)	5·8
C(17)	3617 (14)	−30 (7)	8162 (6)	5·2
C(18)	3077 (14)	374 (7)	7744 (6)	5·2
C(19)	3257 (13)	1075 (6)	7726 (6)	3·8
C(20)	8572 (13)	4112 (7)	8090 (6)	4·6
C(21)	9674 (14)	4503 (8)	8059 (6)	5·3
C(22)	9717 (14)	5070 (8)	8409 (7)	6·4
C(23)	8773 (14)	5229 (8)	8772 (6)	5·6
C(24)	7735 (13)	4820 (7)	8775 (6)	4·1
C(25)	6642 (12)	4947 (6)	9141 (5)	3·3
C(26)	6685 (13)	5526 (7)	9568 (6)	4·8
C(27)	6723 (16)	5350 (8)	10137 (6)	5·9
C(28)	6731 (17)	5879 (9)	10542 (7)	7·7
C(29)	6777 (15)	6524 (9)	10368 (7)	7·4
C(30)	6736 (17)	6726 (8)	9809 (8)	8·3
C(31)	6733 (16)	6183 (8)	9368 (7)	6·3
C(32)	3790 (12)	4270 (6)	9341 (5)	3·6
C(33)	2582 (12)	4416 (6)	9561 (5)	3·8
C(34)	1624 (15)	3937 (8)	9477 (6)	5·4
C(35)	431 (15)	4071 (8)	9699 (6)	5·9
C(36)	229 (14)	4705 (7)	9956 (6)	5·3
C(37)	1123 (14)	5186 (7)	10038 (6)	5·3
C(38)	2294 (14)	5038 (7)	9842 (5)	4·8
C(39)	6493 (14)	3384 (7)	9876 (5)	4·9
C(40)	7219 (14)	3184 (7)	10360 (6)	4·6
C(41)	8169 (14)	2732 (7)	10305 (6)	4·6
C(42)	8403 (13)	2434 (7)	9772 (5)	4·0
C(43)	7650 (12)	2621 (6)	9326 (5)	2·9
C(44)	7904 (12)	2344 (6)	8745 (5)	3·3
C(45)	8635 (12)	1715 (6)	8699 (5)	3·8
C(46)	8271 (13)	1151 (6)	8991 (6)	4·1
C(47)	8972 (15)	523 (8)	8918 (7)	6·3
C(48)	9958 (15)	534 (8)	8562 (7)	6·7
C(49)	10305 (15)	1071 (8)	8263 (7)	7·3
C(50)	9649 (14)	1707 (7)	8327 (6)	5·5
C(51)	6909 (14)	2756 (7)	7433 (6)	4·3
C(52)	6826 (13)	2491 (6)	6845 (5)	3·8
C(53)	5966 (12)	2782 (7)	6483 (6)	4·5
C(54)	5846 (16)	2491 (7)	5928 (6)	5·7
C(55)	6529 (17)	1953 (8)	5739 (7)	6·6
C(56)	7419 (15)	1674 (7)	6094 (6)	5·2
C(57)	7546 (14)	1948 (7)	6662 (6)	5·1

Table 2. *Selected bond angles* (°) *about* Sm *with e.s.d.'s in parentheses*

O(1)—Sm—O(3)	80·9 (3)	O(1)—Sm—O(5)	91·1 (3)
O(1)—Sm—N(1)	123·7 (3)	O(1)—Sm—N(2)	63·2 (3)
O(1)—Sm—N(4)	143·9 (3)	O(1)—Sm—N(5)	137·4 (3)
O(1)—Sm—N(7)	78·5 (3)	O(1)—Sm—N(8)	69·1 (3)
O(3)—Sm—O(5)	149·5 (3)	O(3)—Sm—N(1)	79·5 (3)
O(3)—Sm—N(2)	79·8 (3)	O(3)—Sm—N(4)	123·6 (3)
O(3)—Sm—N(5)	63·8 (3)	O(3)—Sm—N(7)	84·0 (3)
O(3)—Sm—N(8)	138·3 (3)	O(5)—Sm—N(1)	80·7 (3)
O(5)—Sm—N(2)	70·4 (3)	O(5)—Sm—N(4)	78·9 (3)
O(5)—Sm—N(5)	131·3 (3)	O(5)—Sm—N(7)	123·5 (3)
O(5)—Sm—N(8)	61·8 (3)	N(1)—Sm—N(2)	61·6 (3)
N(1)—Sm—N(4)	89·1 (3)	N(1)—Sm—N(5)	74·4 (3)
N(1)—Sm—N(7)	149·1 (3)	N(1)—Sm—N(8)	141·4 (3)
N(2)—Sm—N(4)	140·0 (3)	N(2)—Sm—N(5)	127·1 (3)
N(2)—Sm—N(7)	140·1 (3)	N(2)—Sm—N(8)	109·5 (3)
N(4)—Sm—N(5)	59·9 (3)	N(4)—Sm—N(7)	78·5 (3)
N(4)—Sm—N(8)	75·7 (3)	N(5)—Sm—N(7)	75·0 (3)
N(5)—Sm—N(8)	123·4 (3)	N(7)—Sm—N(8)	62·6 (3)
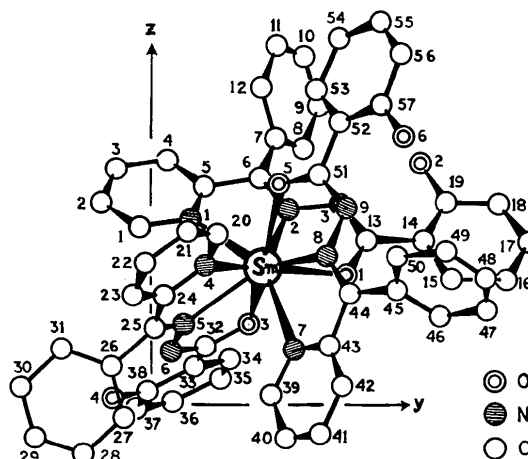
Fig. 1. View of the molecule projected on the (100) plane, showing the atom-numbering scheme.

Fig. 2. Perspective view of the coordination of the Sm atom, showing the distorted tricapped trigonal prism and the metal–ligand bond lengths (Å).

Chakraborty, 1984). The pyridine N, azo N and enolic O atoms of each tridentate ligand are coordinated to Sm^{III}, forming six five-membered chelate rings. The coordination polyhedron, shown in Fig. 2, is best described as a distorted tricapped trigonal prism. The two triangular faces of the prism itself are isosceles, the unique side being the longest. One trigonal base is formed by the two pyridine N atoms (N1, N4) and one enolic O atom (O5), the second by the two enolic O atoms (O1, O3) and one pyridine N atom (N7). The three capping azo N atoms (N2, N5 and N8) near the centres of the rectangular faces are equatorially positioned. Bond lengths and angles around the Sm atom suggest an appreciable distortion in the coordination polyhedron. The Sm—O bond lengths are normal, lying in the range 2·345 (8) to 2·392 (9) Å with a mean value of 2·369 Å and agree fairly well with those found in tetrakis(biuret)samarium(III) nitrate, [Sm(NH₂CONHCONH₂)₄](NO₃)₃ (Haddad, 1987).

The Sm—N(py) distances [2·632 (10) to 2·659 (10) Å] and Sm—N(azo) distances [2·572 (11) to 2·583 (10) Å] agree within experimental error with those reported for samarium complexes by Templeton, Templeton, Zalkin & Ruben (1982). The relative shortness of the Sm—N(azo) bonds compared to the Sm—N(py) distances accords with similar trends found in bis{2'-[α-(2-pyridyl)benzylidene]salicylohydrazide}nickel(II) monohydrate (Seth & Chakraborty, 1984) and also in two isomers of dichlorobis(2-phenylazopyridine)ruthenium(II) (Seal & Ray, 1984). This difference may arise from constraints involved in chelate-ring formation or from the differing positions which N(py) and N(azo) occupy in the coordination polyhedron, as well as from differential Sm→N back-donation.

Out of six five-membered chelate rings only one [Sm—N(5)—C(25)—C(24)—N(4)] is planar. The average bite angle of the five-membered chelate ring is ~62°, introducing a distortion in the polyhedron. In the complex, the three non-planar ligands are chemically identical but crystallographically different. Pyridyl,
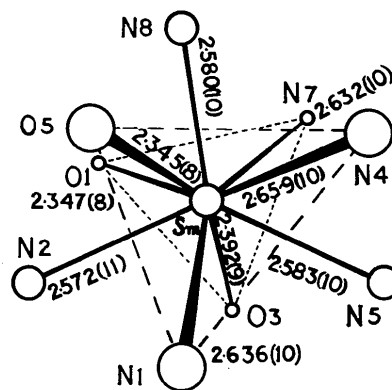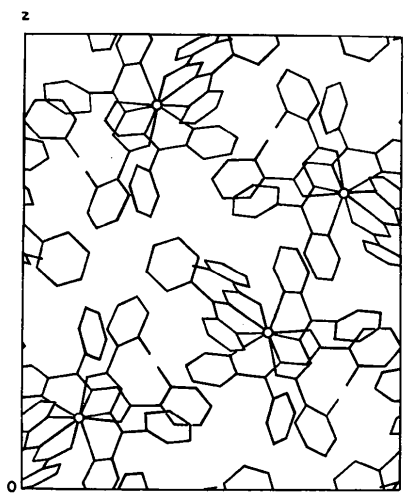

Fig. 3. The packing of the molecule in the crystal projected on the (100) plane.

salicyloyl and phenyl rings are reasonably planar and the first two rings are parallel while the third is twisted out of the plane of the associated chelate rings. Within the same ligand, a coplanar arrangement of the pyridine and phenyl rings is not possible due to steric effects.

Although H atoms were not located experimentally, non-bonded O···N distances [O(2)–N(3) = 2·51 (1), O(4)–N(6) = 2·55 (1) and O(6)–O(9) = 2·57 (1) Å] indicate that each ligand is stabilized by a strong intramolecular O—H···N hydrogen bond. Excluding its Ph substituent, each ligand consequently has two planar aromatic regions – pyridyl and salicyloyl. These two planes do not coincide [dihedral angles 16·0 (4), 16·3 (4) and 9·7 (4)°] because of twists about C—C bonds so that each ligand (minus Ph) is coplanar to within ±0·49 Å. Fig. 3 shows the content of the unit cell projected on the (100) plane. The molecules are packed in layers, but are displaced with respect to one another to relieve short intermolecular contacts, so that packing forces are unlikely to influence the geometry of the molecule to any appreciable extent.

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Das Isomerenpaar *tert*-Butylammoniumiodid und Tetramethylammoniumiodid

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Abstract. *tert*-Butylammonium iodide, [{(CH$_3$)$_3$C}-NH$_3$]I: $M_r = 201\cdot05$, orthorhombic, *Pbca*, $Z = 8$, $a = 19\cdot04$ (2), $b = 9\cdot547$ (9), $c = 9\cdot413$ (7) Å, $V = 1711\cdot1$ Å^3, $D_x = 1\cdot56$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 36\cdot8$ cm^{-1}, $T = 293$ K, $R = 4\cdot0\%$ for 845 observed independent reflexions. Crystals were obtained from {(CH$_3$)$_3$C}NH$_2$ and HI, m.p. 491–493 K. Tetramethylammonium iodide, [(CH$_3$)$_4$N]I: $M_r = 201\cdot05$, tetragonal, *P4/nmm*, $Z = 2$, $a = 7\cdot955$ (2), $c = 5\cdot747$ (1) Å, $V = 363\cdot7$ Å^3, $D_x = 1\cdot84$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $T = 293$ K, $R = 0\cdot9\%$ for 207 observed independent reflexions. Crystals (Merck) were recrystallized from methanol, m.p. 653 K (dec.). *tert*-Butylammonium iodide forms a distorted NaCl-type structure featuring a doubling in length of the *a* axis, which results in an antiferro-ordered arrangement of the ions. The N—H···I hydrogen-bond lengths range from 3·55 to 3·61 Å. Tetramethylammonium iodide can be considered to have a distorted NH$_4$Cl (=CsCl)-type structure in which the NH$_4^+$ group has been replaced by an N(CH$_3$)$_4^+$ group. The face-centred layers of the cations, with the N atoms located at $z = 0$, alternate with wavy face-centred layers of the anions, located at $z = 0\cdot5 \pm 0\cdot111$.

Einleitung. Bei vielen Ionenverbindungen haben Größe, Form und Ladungsverteilung der Kationen großen Einfluß auf die Anionenstruktur, so z.B. auch bei Halogenometallaten und speziell bei Iodometallaten. Bei unseren Strukturuntersuchungen von Iodocupraten(I) haben wir begonnen, diese Parameter systematisch zu variieren. So führte der Ersatz von Tetramethylammonium durch das isomere Kation *tert*-Butylammonium zu völlig verschiedenen Struk-