

Table 4. Coordination distances of the sodium cation in Å

| $\text{Na}^+ \cdots X$ | Symmetry operation for X |
|------------------------------------|----------------------------|
| $\text{Na}^+ \cdots \text{O}(1W)$ | 2.415 (7) |
| $\text{Na}^+ \cdots \text{O}(1W)$ | 2.491 (5) |
| $\text{Na}^+ \cdots \text{O}(2W)$ | 2.386 (7) |
| $\text{Na}^+ \cdots \text{O}(2W)$ | 2.482 (5) |
| $\text{Na}^+ \cdots \text{O}(4W1)$ | 2.332 (6) |
| $\text{Na}^+ \cdots \text{O}(4W2)$ | 2.482 (6) |
| $\text{Na}^+ \cdots \text{O}(71)$ | 2.685 (5) |
| | x, y, z |
| | $1-x, 1-y, 1-z$ |
| | x, y, z |
| | $1-x, -y, 1-z$ |
| | x, y, z |
| | x, y, z |
| | x, y, z |

Table 5. Hydrogen bridges, distances in Å

| $X-\text{H} \cdots Y$ | $X \cdots Y$ | $X-\text{H}$ | $\text{H} \cdots Y$ | Symmetry operation for Y |
|--|--------------|--------------|---------------------|----------------------------|
| $\text{O}(1W)-\text{H}(11W) \cdots \text{O}(3)$ | 2.840 (4) | 0.952 (6) | 1.906 (6) | $-x, 1-y, 2-z$ |
| $\text{O}(1W)-\text{H}(21W) \cdots \text{O}(3W1)$ | 2.983 (9) | 0.969 (7) | 2.06 (1) | $x, y, 1+z$ |
| $\text{O}(2W)-\text{H}(12W) \cdots \text{O}(3W1)$ | 3.36 (1) | 0.953 (8) | 1.70 (1) | x, y, z |
| $\text{O}(2W)-\text{H}(22W) \cdots \text{N}(2)$ | 3.034 (4) | 0.962 (8) | 2.074 (7) | $-x, 1-y, 1-z$ |
| $\text{O}(3W1)-\text{H}(23W1) \cdots \text{N}(2)$ | 2.87 (1) | 0.95 (2) | 1.94 (1) | $1+x, -1+y, -1+z$ |
| $\text{O}(4W1)-\text{H}(14W1) \cdots \text{O}(11)$ | 2.638 (6) | 0.92 (1) | 1.73 (1) | $1+x, -1+y, z$ |
| $\text{O}(4W1)-\text{H}(24W1) \cdots \text{O}(3)$ | 2.851 (7) | 0.96 (2) | 1.93 (2) | $1+x, y, -1+z$ |
| $\text{O}(1W)-\text{H}(21W) \cdots \text{O}(3W2)$ | 2.72 (1) | 0.97 (7) | 1.76 (1) | $x, y, 1+z$ |
| $\text{O}(2W)-\text{H}(12W) \cdots \text{O}(3W2)$ | 2.998 (9) | 0.953 (8) | 2.07 (1) | $x, y, 1+z$ |
| $\text{O}(3W2)-\text{H}(23W2) \cdots \text{N}(2)$ | 3.12 (1) | 0.98 (1) | 2.17 (1) | $1+x, -1+y, -1+z$ |
| $\text{O}(4W2)-\text{H}(14W2) \cdots \text{O}(11)$ | 2.93 (6) | 0.96 (1) | 1.97 (1) | $1+x, -1+y, z$ |
| $\text{O}(4W2)-\text{H}(24W2) \cdots \text{O}(3)$ | 2.512 (6) | 0.95 (1) | 1.62 (1) | $1+x, y, -1+z$ |

the title compound [1.395 (3) Å] than in UH-AF 50 NA [1.411 (5) Å]. The bond angles are given in Table 3. The Na^+ ion is sixfold coordinated. The coordination polyhedron is a distorted octahedron, consisting of five O atoms from the water molecules and one from the NO_2 group. The coordination distances can be seen in Table 4. There are seven intermolecular hydrogen bridges, two between water molecules, the others

between one water molecule and the 6-nitrosaccharin molecule (Table 5). The disordered water molecules are involved in five of the hydrogen bridges.

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Structure of Bis[μ -*N,N'*-(*o*-phenylene)thiourea-*S*]-bis[*N,N'*-(*o*-phenylene)thiourea-*S*]-selenium(II)}* Perchlorate Hexahydrate

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Abstract. $[\text{Se}_2(\text{C}_7\text{H}_6\text{N}_2\text{S})_6](\text{ClO}_4)_4 \cdot 6\text{H}_2\text{O}$, $M_r = 1564$, monoclinic, $P2_1$, $a = 17.089$ (3), $b = 10.741$ (2), c

* *N,N'*-(*o*-Phenylene)thiourea is 2(3*H*)-benzimidazolethione.

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$= 17.506$ (4) Å, $\beta = 108.2$ (1)°, $V = 3053.0$ Å³, $Z = 2$, $D_x = 1.70$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 54.79$ cm⁻¹, $F(000) = 1584$, $T = 283$ K, final $R = 0.069$ for 3980 observed reflections. A dinuclear complex formation with planar SeS_4 groups sharing two

unequal bridging S atoms is observed. Each Se atom exhibits planar trapezoidal four-coordination from two terminal Se—S bonds [average Se—S = 2.287 (5) Å] and two weak bridging Se—S bonds [average Se—S = 2.916 (5) Å]. The average overall Se—S bond distance [2.602 (5) Å] is close to the value reported for four-coordinated selenium(II)—sulfur ligand complexes.

Introduction. Selenium(IV)—sulfur ligand interaction has been found to be biochemically important (Ganther, 1968). With sulfur ligands, selenium(IV) undergoes either reductive complexation to give selenium(II) complexes or reduction to elemental selenium, the latter occurring mostly with ligands of the thiourea type. The only known thiourea complexes, *cis*-dichloro- and *cis*-dibromobis(thiourea)selenium(II), were prepared under anhydrous conditions and are unstable (Bjørnevåg & Hauge, 1983). With a substituted thiourea, namely *o*-phenylenethiourea (ptu), stable selenium(II) complexes form. Recently the structures of tetrakis-, tris- and bis(ptu)selenium(II) complexes have been reported from our laboratory (Sowrirajan, Aravamudan, Seshasayee & Rout, 1985; Chidambaram, Aravamudan, Rout & Seshasayee, 1986; Chidambaram, Aravamudan, Ganesh, Seshasayee, Sibanova & Simonov, 1989). The structure of the title compound is interesting and unexpectedly different from that reported for the bromide [Se(ptu)₃]Br₂·5H₂O (Chidambaram *et al.*, 1986).

Experimental. The preparation of the complex was similar to that of the bromide, 4 M perchloric acid being used instead of 2 M hydrobromic acid.

An orange-yellow needle-shaped crystal 0.53 × 0.16 × 0.1 mm was selected and mounted on an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Cu K α radiation was used. Unit-cell parameters and their standard deviations were obtained by least-squares analysis of 20 high-angle reflections. Intensity data were collected by the $\omega/2\theta$ scan technique for $2 < \theta < 60^\circ$ (h —19 to 19; k 0 to 12; l 0 to 20). The check reflection $\bar{2}37$ showed no significant variation in its intensity during data collection. Out of 5868 reflections collected, 4045 satisfied the condition $I > 3\sigma(I)$ and were used for structure determination. Out of 4045 total reflections, 65 weak reflections with $|F_o - F_c| > 3\sigma(F)$ were omitted. The data were corrected for absorption using the Gaussian method [SHELX76 (Sheldrick, 1976)]. The structure was solved by the heavy-atom method. All the non-H atoms, except the O atoms, were refined anisotropically. Since the thermal parameters of the O atoms were found to be high, they were refined isotropically. Owing to SHELX76 program constraints, it was not possible to refine all the 88 non-H atoms together. The minimum attainable residual factor was 0.069 for 3980 observed reflections (including anisotropic non-H

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters of the non-H atoms of [Se₂(ptu)₆](ClO₄)₄·6H₂O

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} (Å ²) |
|-------|--------------|--------------|--------------|--|
| Se(1) | 0.2777 (1) | 0.1152 (2) | 0.2590 (1) | 0.037 (1) |
| Se(2) | 0.2125 (1) | 0.5000 | 0.2430 (1) | 0.036 (1) |
| S(1) | 0.3861 (3) | 0.0070 (6) | 0.3428 (3) | 0.047 (3) |
| S(2) | 0.2038 (3) | −0.0535 (5) | 0.1938 (3) | 0.045 (3) |
| S(3) | 0.1377 (3) | 0.2759 (6) | 0.1660 (3) | 0.048 (3) |
| S(4) | 0.3600 (3) | 0.3421 (6) | 0.3174 (3) | 0.043 (3) |
| S(5) | 0.1042 (3) | 0.6138 (6) | 0.1712 (2) | 0.043 (2) |
| S(6) | 0.2883 (3) | 0.6610 (5) | 0.3194 (3) | 0.042 (3) |
| Cl(1) | 0.2833 (3) | 0.0880 (6) | 0.0153 (3) | 0.065 (3) |
| Cl(2) | 0.3182 (3) | −0.1544 (7) | 0.5370 (3) | 0.073 (3) |
| Cl(3) | 0.2172 (3) | −0.4348 (6) | 0.0015 (3) | 0.062 (3) |
| Cl(4) | 0.2523 (4) | 0.2560 (7) | 0.4911 (3) | 0.084 (4) |
| C(1) | 0.4592 (10) | 0.0242 (19) | 0.2943 (9) | 0.042 (10) |
| N(1) | 0.4489 (8) | 0.0432 (14) | 0.2170 (7) | 0.042 (8) |
| N(2) | 0.5389 (8) | 0.0210 (16) | 0.3326 (7) | 0.045 (8) |
| C(11) | 0.5249 (11) | 0.0482 (17) | 0.2017 (10) | 0.044 (10) |
| C(12) | 0.5852 (10) | 0.0331 (15) | 0.2785 (10) | 0.040 (10) |
| C(13) | 0.6877 (13) | 0.0439 (21) | 0.2166 (14) | 0.070 (14) |
| C(14) | 0.6659 (11) | 0.0336 (15) | 0.2861 (12) | 0.052 (11) |
| C(15) | 0.6288 (12) | 0.0602 (19) | 0.1384 (13) | 0.060 (12) |
| C(16) | 0.5428 (11) | 0.0629 (19) | 0.1306 (10) | 0.049 (11) |
| C(2) | 0.1305 (8) | −0.0592 (16) | 0.2448 (9) | 0.031 (12) |
| N(3) | 0.0524 (10) | −0.0555 (15) | 0.2062 (10) | 0.051 (9) |
| N(4) | 0.1482 (9) | −0.0769 (15) | 0.3234 (8) | 0.047 (8) |
| C(21) | 0.0112 (10) | −0.0755 (17) | 0.2633 (10) | 0.044 (10) |
| C(22) | 0.0706 (9) | −0.0842 (16) | 0.3382 (11) | 0.041 (10) |
| C(23) | 0.0546 (11) | −0.0986 (22) | 0.4069 (9) | 0.054 (11) |
| C(24) | −0.0318 (14) | −0.1079 (22) | 0.4025 (19) | 0.068 (18) |
| C(25) | −0.0881 (4) | −0.0938 (21) | 0.3302 (13) | 0.067 (14) |
| C(26) | −0.0759 (12) | −0.0706 (24) | 0.2495 (14) | 0.079 (15) |
| C(3) | 0.0687 (11) | 0.2706 (19) | 0.2195 (9) | 0.033 (9) |
| N(5) | −0.0149 (8) | 0.2806 (16) | 0.1863 (8) | 0.040 (9) |
| N(6) | 0.0868 (9) | 0.2387 (15) | 0.2956 (8) | 0.042 (9) |
| C(31) | 0.0122 (11) | 0.2404 (16) | 0.3183 (10) | 0.038 (10) |
| C(32) | −0.0495 (11) | 0.2701 (16) | 0.2468 (10) | 0.047 (11) |
| C(33) | 1.1330 (12) | −0.2290 (21) | −0.2410 (14) | 0.062 (13) |
| C(34) | 1.1473 (12) | −0.2453 (19) | −0.3134 (19) | 0.083 (16) |
| C(35) | 1.0824 (13) | −0.2687 (23) | −0.3892 (13) | 0.065 (14) |
| C(36) | −0.0005 (12) | 0.2278 (18) | 0.3907 (11) | 0.058 (11) |
| C(4) | 0.4199 (10) | 0.3616 (19) | 0.2566 (11) | 0.038 (10) |
| N(7) | 0.3961 (9) | 0.3614 (16) | 0.1759 (8) | 0.044 (8) |
| N(8) | 0.5024 (8) | 0.3682 (16) | 0.2825 (8) | 0.043 (9) |
| C(41) | 0.4632 (11) | 0.3686 (19) | 0.1461 (11) | 0.049 (11) |
| C(42) | 0.4697 (13) | 0.3827 (23) | 0.0707 (11) | 0.057 (13) |
| C(43) | 0.5468 (16) | 0.3929 (21) | 0.0669 (14) | 0.068 (15) |
| C(44) | 0.6152 (13) | 0.3951 (22) | 0.1368 (13) | 0.058 (13) |
| C(45) | 0.6111 (11) | 0.3812 (21) | 0.2122 (15) | 0.066 (14) |
| C(46) | 0.5317 (11) | 0.3750 (18) | 0.2175 (12) | 0.047 (11) |
| C(5) | 0.0342 (8) | −0.3948 (16) | 0.2229 (8) | 0.032 (8) |
| N(9) | 0.0473 (7) | −0.4167 (12) | 0.3025 (7) | 0.034 (7) |
| N(10) | 0.0487 (8) | 0.1157 (15) | 0.8140 (7) | 0.044 (8) |
| C(51) | 0.0288 (9) | 0.0839 (15) | 0.6827 (9) | 0.037 (9) |
| C(52) | 0.0870 (9) | 0.1082 (17) | 0.7566 (9) | 0.042 (9) |
| C(53) | 0.1738 (10) | 0.1167 (20) | 0.7662 (12) | 0.059 (11) |
| C(54) | −0.1917 (13) | 0.5967 (19) | 0.3066 (12) | 0.070 (13) |
| C(55) | −0.1273 (16) | 0.5715 (19) | 0.3844 (12) | 0.073 (15) |
| C(56) | 0.0454 (11) | 0.0687 (17) | 0.6123 (10) | 0.050 (10) |
| C(6) | 0.3613 (10) | 0.6807 (16) | 0.2731 (8) | 0.036 (9) |
| N(11) | 0.4438 (8) | 0.6933 (14) | 0.3102 (8) | 0.045 (9) |
| N(12) | 0.3514 (8) | 0.6899 (15) | 0.1922 (9) | 0.050 (9) |
| C(61) | 0.4853 (9) | 0.7035 (15) | 0.2572 (9) | 0.036 (9) |
| C(62) | 0.4307 (11) | 0.7025 (17) | 0.1831 (11) | 0.052 (11) |
| C(63) | 0.4563 (14) | 0.7099 (19) | 0.1133 (15) | 0.064 (14) |
| C(64) | 0.5275 (13) | 0.7170 (22) | 0.1186 (13) | 0.069 (14) |
| C(66) | 0.5723 (12) | 0.7182 (19) | 0.2703 (14) | 0.065 (13) |
| C(65) | 0.5951 (13) | 0.7187 (21) | 0.1979 (15) | 0.066 (14) |
| O(1) | 0.224 (1) | 0.040 (1) | −0.045 (1) | 0.101 (9) |
| O(2) | 0.334 (2) | 0.139 (2) | −0.026 (1) | 0.159 (14) |
| O(3) | 0.253 (1) | 0.194 (2) | 0.057 (1) | 0.084 (10) |
| O(4) | 0.320 (1) | −0.004 (2) | 0.073 (1) | 0.104 (16) |
| O(5) | 0.242 (2) | −0.216 (2) | 0.542 (1) | 0.200 (19) |
| O(6) | 0.383 (1) | −0.248 (1) | 0.548 (1) | 0.170 (19) |
| O(7) | 0.291 (1) | −0.096 (2) | 0.458 (1) | 0.154 (10) |
| O(8) | 0.297 (2) | −0.069 (3) | 0.591 (2) | 0.191 (17) |
| O(9) | 0.201 (2) | −0.405 (2) | −0.075 (1) | 0.156 (12) |
| O(10) | 0.296 (1) | −0.489 (2) | 0.032 (1) | 0.113 (11) |
| O(11) | 0.209 (1) | −0.335 (1) | 0.055 (1) | 0.100 (9) |
| O(12) | −0.172 (1) | −0.037 (2) | −0.036 (1) | 0.185 (17) |
| O(13) | 0.256 (2) | 0.345 (2) | 0.431 (2) | 0.113 (12) |
| O(14) | 0.246 (2) | 0.293 (2) | 0.561 (2) | 0.189 (16) |
| O(15) | 0.341 (2) | 0.218 (2) | 0.523 (1) | 0.166 (12) |

Table 1 (cont.)

| | <i>x</i> | <i>y</i> | <i>z</i> | <i>U</i> _{eq} (Å ²) |
|-------|-----------|------------|-----------|--|
| O(16) | 0.195 (1) | 0.155 (2) | 0.454 (1) | 0.071 (10) |
| HO(1) | 0.908 (2) | 0.347 (3) | 0.028 (2) | 0.167 (15) |
| HO(2) | 0.496 (3) | 0.204 (2) | 0.525 (2) | 0.113 (9) |
| HO(3) | 0.014 (3) | 0.422 (3) | 0.075 (2) | 0.385 (23) |
| HO(4) | 1.073 (1) | 0.186 (1) | 0.971 (2) | 0.108 (16) |
| HO(5) | 0.172 (1) | -0.417 (1) | 0.439 (1) | 0.141 (12) |
| HO(6) | 0.995 (1) | 0.490 (2) | 0.956 (1) | 0.147 (14) |

Table 2. Principal bond lengths (Å) and bond angles (°) in [Se₂(ptu)₆](ClO₄)₄·6H₂O with their e.s.d.'s in parentheses

| | | | |
|------------------|------------|-----------------|------------|
| Se(1)–S(1) | 2.288 (5) | Se(1)–S(2) | 2.298 (5) |
| Se(1)–S(3) | 2.988 (5) | Se(1)–S(4) | 2.840 (5) |
| Se(2)–S(3) | 2.858 (6) | Se(2)–S(4) | 2.979 (5) |
| Se(2)–S(5) | 2.247 (5) | Se(2)–S(6) | 2.318 (5) |
| S(1)–C(1) | 1.726 (20) | S(2)–C(2) | 1.752 (17) |
| S(3)–C(3) | 1.719 (20) | S(4)–C(4) | 1.704 (21) |
| S(5)–C(5) | 1.715 (16) | S(6)–C(6) | 1.700 (19) |
| C(1)–N(1) | 1.325 (20) | C(1)–N(2) | 1.318 (19) |
| C(2)–N(3) | 1.295 (19) | C(2)–N(4) | 1.326 (21) |
| C(3)–N(5) | 1.369 (21) | C(3)–N(6) | 1.314 (21) |
| C(4)–N(7) | 1.343 (23) | C(4)–N(8) | 1.342 (21) |
| C(5)–N(9) | 1.362 (19) | C(5)–N(10) | 1.366 (17) |
| C(6)–N(11) | 1.363 (19) | C(6)–N(12) | 1.377 (21) |
| Se(1)–Se(1)–S(2) | 97.3 (3) | S(1)–Se(1)–S(3) | 173.2 (3) |
| Se(1)–Se(1)–S(4) | 89.7 (3) | S(2)–Se(1)–S(3) | 87.6 (3) |
| S(2)–Se(1)–S(4) | 171.4 (3) | S(3)–Se(1)–S(4) | 85.6 (3) |
| S(3)–Se(2)–S(4) | 85.3 (3) | S(3)–Se(2)–S(5) | 91.4 (3) |
| S(3)–Se(2)–S(6) | 170.9 (3) | S(4)–Se(2)–S(5) | 172.2 (3) |
| S(4)–Se(2)–S(6) | 85.8 (3) | S(5)–Se(2)–S(6) | 97.5 (3) |
| C(1)–S(1)–Se(1) | 101.3 (7) | C(2)–S(2)–Se(1) | 98.3 (6) |
| C(3)–S(3)–Se(1) | 104.6 (9) | C(4)–S(4)–Se(1) | 101.9 (9) |
| C(3)–S(3)–Se(2) | 93.1 (8) | C(4)–S(4)–Se(2) | 104.3 (9) |
| C(5)–S(5)–Se(2) | 105.3 (6) | C(6)–S(6)–Se(2) | 100.3 (7) |

atoms, except the O atoms, and isotropic O atoms). Unit weights. None of the H atoms appeared in the difference Fourier maps. Some of the ring H atoms were fixed geometrically, but they were not included in the residual-factor calculations. 659 parameters refined. $(\Delta/\sigma)_{\text{max}} = 1.9$. In the final difference Fourier map, the residual electron density corresponded to $1.1 \text{ e } \text{\AA}^{-3}$, in chemically meaningless positions. Atomic scattering factors for non-H atoms from Cromer & Mann (1968), for H atoms from Stewart, Davidson & Simpson (1965); anomalous-dispersion correction factors for non-H atoms from Cromer & Liberman (1970).

Discussion. Fractional atomic coordinates are given in Table 1, selected bond lengths and bond angles in Table 2.* Fig. 1 gives the *ORTEP* (Johnson, 1965) plot of the cation.

The structure is dinuclear with two Se atoms bridged by two sulfur ligands. Each Se atom exhibits planar

trapezoidal four-coordination from two strong equal Se–S terminal bonds and two weak unequal Se–S bridging bonds. Of the two bridging bonds, one is stronger than the other, which is reflected in their bond distances: Se(1)–S(3) = 2.988 (5), Se(2)–S(3) = 2.858 (6) Å. The average Se–S bond distance in the SeS_4 unit is 2.566 (5) Å, which is close to that observed in four-coordinated selenium(II)–sulfur ligand complexes (Sowrirajan *et al.*, 1985).

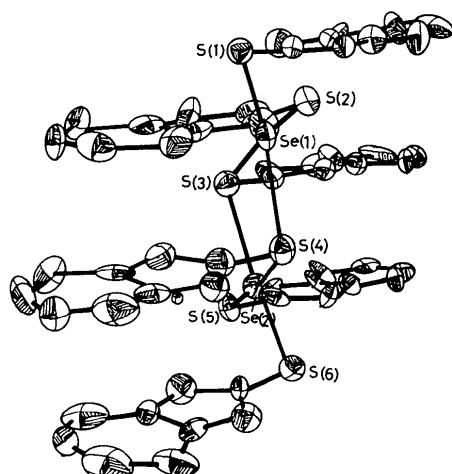
In tetrakis [Se(ptu)₄]Cl₂·2HCl, the S–Se–S bond angles were close to 90°. In tris complexes such as the bromide and the present complex, the S–Se–S bond angles vary substantially from 90°, 85.3 (3) to 97.5 (3)° in the present complex.

The two Se atoms and six ligand S atoms do not form a plane, unlike in the bromide. However, Se(1), S(1), S(2), S(3) and S(4) and Se(2), S(3), S(4), S(5) and S(6) form two approximate planes with maximum deviation of any atom being 0.115 (4) and 0.121 (4) Å respectively. The dihedral angle between the two SeS_4 planes is 8.8 (2)°. In addition, unlike in the bromide, the bridging S atoms are unsymmetrically bonded.

The average S–C bond distance, 1.72 (2) Å, is shorter than the single-bond distance, 1.81 Å. The C–N bond distances range from 1.30 (2) to 1.38 (2) Å, with an average 1.34 (2) Å. In each ligand the pairs of C–N bond distances do not vary much, indicating that in the present case the ligand is coordinating in its thione form, as observed in other selenium and tellurium complexes (Rout, Seshasayee, Aravamudan & Sowrirajan, 1984, 1985).

The ptu ligands are planar to within 0.06 (1) Å. The N–C and C–C bond distances and bond angles around N and C atoms are close to expected values.

An extensive hydrogen-bonding network stabilizes the lattice. The large number of water molecules contributes to this. There are 25 hydrogen-bonding

Fig. 1. Perspective view of the cation of [Se₂(ptu)₆](ClO₄)₄·6H₂O.

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles, least-squares-planes details and hydrogen-bonding distances have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51719 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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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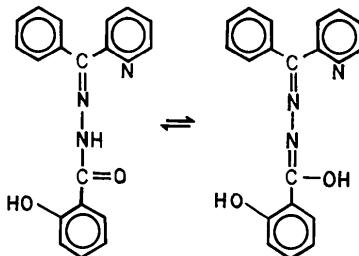
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Abstract. $M_r = 1099.4$, orthorhombic, $P2_12_12_1$, $a = 10.889$ (2), $b = 19.765$ (5), $c = 23.702$ (4) Å, $V = 5101$ (2) Å³, $Z = 4$, $D_m = 1.45$ (by flotation in xylene/chloroform), $D_x = 1.433$ Mg m⁻³, $\lambda(\text{Mo } \text{Ka}) = 0.71073$ Å, $\mu(\text{Mo } \text{Ka}) = 1.213$ 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 C₁₉H₁₄N₃O₂ 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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