Pergamon

0277-5387(94)00271-1

Polyhedron Vol. 14, No. 4, pp. 563–566, 1995

0277–5387/95 $9.50+0.00

STRUCTURE OF AQUABIS-(PICOLINATO)SCANDIUM HYDROXIDE DIHYDRATE

MA JIAN-FANG,* JIN ZHONG-SHENG and NI JIA-ZUAN

Laboratory of Rare Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

(*Received* 12 *April* 1994; *accepted* 3 *July* 1994)

Abstract—The crystal structure of the title complex was established by X-ray diffraction analysis. Each scandium ion is seven-coordinated by two oxygen atoms and two nitrogen atoms from the picolinato ions, one water oxygen atom and two hydroxide ions. The nitrogen atom and one carboxyl oxygen atom of each picolinato ion are coordinated to the same scandium ion to form a five-membered chelating ring. Each hydroxide ion is coordinated to two scandium ions to form hydroxide bridges and a dimeric molecule unit.

Picolinic acid, nicotinic acid and isonicotinic acid are three isomers. The structures and coordination modes of their complexes with the lanthanides are very interesting. In the reported crystal structures of lanthanide complexes with nicotinic acid and isonicotinic acid,[1–7] only the carboxyl groups are coordinated, and none of the nitrogen atoms is coordinated. Starynowicz reported the structures of two neodymium complexes with picolinic acid,[8,9] in which both the nitrogen atom and oxygen atom of picolinato ion were coordinated to the neodymium ion. So far, there are no structural reports about scandium complexes with the three acids. In this paper the title complex was synthesized, and its crystal structure was determined.

EXPERIMENTAL

Reagents

Picolinic acid (Fluka) was used as received. Scandium chloride was prepared by dissolving Sc_2O_3 (AR) in hydrochloric acid. All other chemicals were AR grade and used without further purification.

Chemical and physical measurements

The scandium was determined by EDTA titration using xylenol as an indicator. Carbon, nitrogen and hydrogen were determined using a Carlo-Erba 1106 elemental analyser. TGA experiments were performed on a Perkin–Elmer TGA-7 thermal analyser under a mobile air atmosphere. The final temperature was 650°C with a heating rate of 10°C min^{-1}. The crystal structure was determined on a Nicolet R3M/E four-circle X-ray diffractometer.

Synthesis

Aqueous scandium chloride (10 cm^3, 2 mmol) solution was added to 30 cm^3 of an aqueous solution of picolinic acid (6 mmol). The pH value of the mixture was adjusted to 4.5 by adding aqueous ammonia with stirring. Crystals of the title complex suitable for X-ray diffraction were obtained by evaporating the mixture at room temperature for several days. Found: Sc, 12.4; C, 40.2; H, 4.1; N, 7.6. Calc. for $Sc(C_5H_4NCO_2)_2(OH)\cdot 3H_2O$: Sc, 12.5; C, 40.0; H, 4.2; N, 7.8%.

Structure determination

A single crystal of dimensions 0.52 × 0.44 × 0.48 mm was selected for the data collection on a Nicolet R3M/E diffractometer with graphite-monochromated Mo-K_α radiation, using the ω–2θ scan mode. Twenty-five reflections were used for measuring lattice parameters and 5023 independent

---

* Author to whom correspondence should be addressed.

reflections were collected in the range of $3° < 2\theta < 70°$. Of these 2769 reflections with $I > 5.0\sigma(I)$ were used in the structure determination and refinement. Intensities were corrected for Lorentz and polarization factors. Empirical absorption correction using the ψ scan technique was applied. Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). The heavy-atom method and difference Fourier calculations were used for structure solution. Refinements were made by block-diagonal least-squares with anisotropic temperature factors for non-hydrogen atoms. The hydrogen atoms on pyridine rings were calculated theoretically assuming rigid groups. Hydrogen positions and isotropic thermal parameters were used in structure factor calculations without any further refinement. All calculations were performed on an Eclipse S/140 computer using the SHELXTL program package. Crystal data, data collection parameters and residuals from refinement are summarized in Table 1. Atomic coordinates, thermal parameters and a full set of bond lengths and angles are deposited with the Cambridge Crystallographic Data Centre as supplementary material.

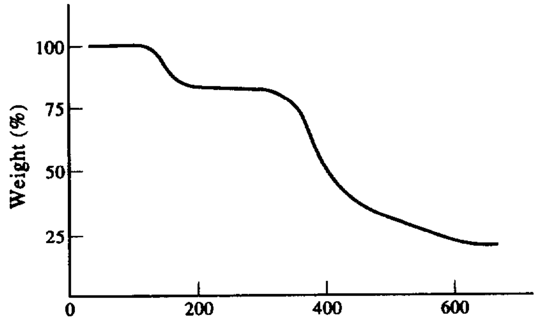

Fig. 1. TGA curve of the complex.

RESULTS AND DISCUSSION

Thermal decomposition

The TGA curve is shown in Fig. 1. Water molecules are lost in one step (134–169°C) to form $Sc(C_5H_4NCO_2)_2(OH)$ (**I**) with a weight loss of 15.4% (calc. 15.0%). Compound (**I**) gradually decomposes into $Sc(C_5H_4NCO_2)_2O_{0.5}$ (**II**) from 169 to 346°C with a weight loss of 2.7% (calc. 2.5%). The large weight loss of 346°C can be correlated with the departure of picolinato ligands. Eventually, Sc_2O_3 is obtained at 635°C with a residual weight of 19.0% (calc. 19.1%). The following scheme can be proposed for the thermal decomposition:

$$Sc(C_5H_4NCO_2)_2(OH)\cdot 3H_2O \longrightarrow$$

$$Sc(C_5H_4NCO_2)_2(OH)\ (\mathbf{I}) \longrightarrow$$

$$Sc(C_5H_4NCO_2)_2O_{0.5}\ (\mathbf{II}) \longrightarrow Sc_2O_3.$$

The compounds **I** and **II** were not separated and identified. An accurate interpretation of the details

Table 1. Crystallographic data

Formula	$Sc_2(C_5H_4NCO_2)_4(OH)_2(H_2O)_2\cdot 4H_2O$
Formula weight	720.42
Space group	$P2_1/a$
a (Å)	12.940(4)
b (Å)	10.616(3)
c (Å)	11.408(2)
β (°)	110.62(2)
V (Å^3)	1466.8(6)
Z	2
D_c (g cm^{-3})	1.63
Radiation	$\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å
μ (cm^{-1})	5.6
$F(000)$	744
Temperature (°C)	25
h, k, l max	21, 18, 19
δ max/σ	0.12
$\delta\rho_{max}$ (e Å^{-3})	0.29
$\delta\rho_{min}$ (e Å^{-3})	−0.48
$R = [\Sigma\lVert F_o\rvert - \lvert F_c\rVert]/\Sigma\lvert F_o\rvert$	0.037
$R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$	0.043
$w = [\sigma^2(F_o)+0.0641(F_o)^2]^{-1}$	

Table 2. Selected bond lengths (Å) and angles (°)

Sc—N(1)	2.405(1)	Sc—N(2)	2.407(1)
Sc—O(11)	2.176(1)	Sc—O(21)	2.156(1)
Sc—O	2.063(2)	Sc—Ow(1)	2.175(2)
Sc—Oa	2.080(1)	O(11)—C(1)	1.261(2)
O(12)—C(1)	1.251(2)	O(21)—C(2)	1.276(2)
O(22)—C(2)	1.238(2)		
N(1)—Sc—N(2)	141.8(1)	N(1)—Sc—O(11)	69.2(1)
N(2)—Sc—O(11)	141.8(1)	N(1)—Sc—O(21)	145.5(1)
N(2)—Sc—O(21)	69.7(1)	O(11)—Sc—O(21)	76.3(1)
N(1)—Sc—O	93.3(1)	N(2)—Sc—O	106.7(1)
O(11)—Sc—O	87.5(1)	O(21)—Sc—O	86.3(1)
N(1)—Sc—Ow(1)	80.5(1)	N(2)—Sc—Ow(1)	79.0(1)
O(11)—Sc—Ow(1)	89.5(1)	O(21)—Sc—Ow(1)	98.4(1)
O—Sc—Ow(1)	173.7(1)	N(1)—Sc—Oa	78.1(1)
N(2)—Sc—Oa	76.9(1)	O(11)—Sc—Oa	141.2(1)
O(21)—Sc—Oa	133.9(1)	O—Sc—Oa	73.7(1)
Ow(1)—Sc—Oa	105.5(1)	Sc—O—Sca	106.3(1)
Sc—O(11)—C(1)	123.8(1)	Sc—O(21)—C(2)	126.0(1)
O(11)—C(1)—O(12)	125.5(2)	O(21)—C(2)—O(22)	125.4(2)

of the decomposition of II to Sc_2O_3 would be difficult.

Crystal structure

Selected bond lengths and angles are given in Table 2. Figure 2 shows the structure and numbering scheme for the complex. Figure 3 shows the packing arrangement in the unit cell.

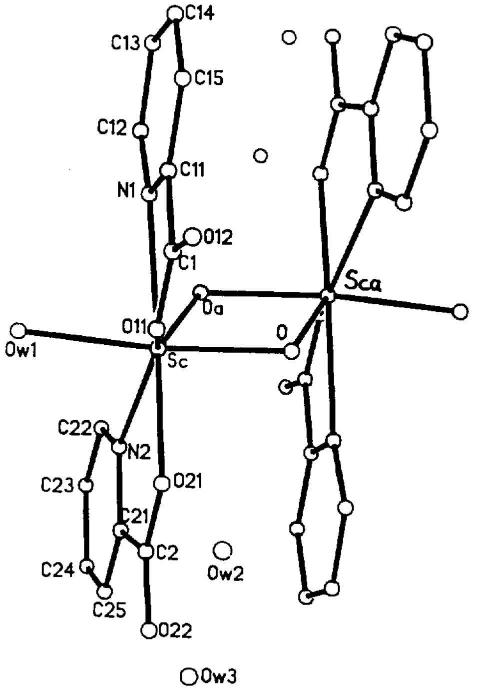

Fig. 2. Structure of $[Sc(C_5H_4NCO_2)_2(OH)(H_2O)]_2 \cdot 4H_2O$.

Each scandium ion is coordinated by two carboxyl oxygen atoms [O(11), O(21)] and two nitrogen atoms [N(1), N(2)] from two picolinato ions, two hydroxide ions [O, O(a)] and one water molecule [Ow(1)]. There are two lattice water molecules [Ow(2), Ow(3)] which are not coordinated to scandium ions. Each picolinato ion coordinates one scandium ion via its nitrogen atom and one of its carboxyl oxygen atoms to form a five-membered ring, as in the neodymium complexes.[8,9] The dihedral angle between the chelating ring [ScO(11)C(1)C(11)N(1)] plane and the pyridine ring [C(11)N(1)C(12)C(13)C(14)C(15)] plane is 9.0°, and that between the plane [ScO(21)C(2)C(21)N(2)] and the plane [C(21)N(2)C(22)C(23)C(24)C(25)] is 2.1°. For the lanthanide complexes with nicotinic acid and isonicotinic acid,[1–7] the carboxyl oxygen atoms coordinate to the metal ions, but the nitrogen atoms cannot coordinate because of the steric disadvantage resulting from the relative position between the nitrogen atom and carboxyl group. Each hydroxide ion is bonded to two scandium ions to form a hydroxide bridge. Two scandium ions are bridged by two hydroxide ions to form a dimeric structure, and the Sc—Sca distance is 3.315 Å. The Sc—O distances of different oxygen atoms increase in the following order: hydroxide (2.072 Å), carboxyl (2.166 Å) and water (2.175 Å) oxygen atoms. The average Sc—N distance (2.406 Å) is longer than that of Sc—O (2.130 Å).

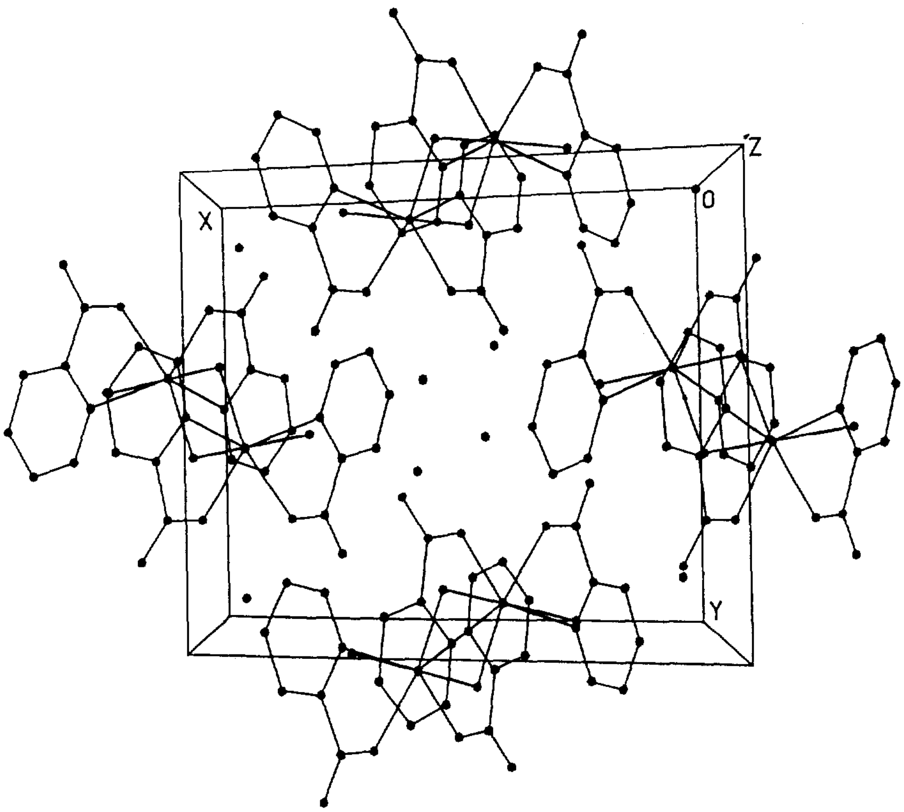

Fig. 3. Packing arrangement of the complex in the unit cell.

A noteworthy feature of the structure is the seven-coordinated polyhedron around the scandium ion. So far, only the six- or eight-coordinated scandium ions have been found in the reported structures of scandium carboxylates.[10-14]

REFERENCES

1. I. K. Abdul'minev, L. A. Aslanov, M. A. Porai-Koshits and R. A. Chupakhina, *Zh. Strukt. Khim.* 1973, **14**, 383.
2. L. A. Aslanov, I. K. Abdul'minev and M. A. Porai-Koshits, *Zh. Strukt. Khim.* 1972, **13**, 468.
3. L. A. Aslanov, I. D. Kiekbaev, I. K. Abdul'minev and M. A. Porai-Koshits, *Kristallografiya* 1974, **19**, 170.
4. J. Kay, J. W. Moore and M. D. Glick, *Inorg. Chem.* 1972, **11**, 2818.
5. J. W. Moore, M. D. Glick and W. A. Baker Jr., *J. Am. Chem. Soc.* 1972, **94**, 1858.
6. K. Prout, J. M. Marin and C. A. Hutchison Jr., *Acta Cryst.* 1985, **C41**, 201.
7. Z.-S. Zhang, J.-G. Wu and R.-W. Deng, *Gaodeng Xuexiao Huaxue Xuebao* 1990, **11**, 7.
8. P. Starynowicz, *Acta Cryst.* 1991, **C47**, 32.
9. P. Starynowicz, *Acta Cryst.* 1991, **C47**, 294.
10. R. Fuchs and J. Strahle, *Z. Naturfor.* 1984, **39b**. 1662.
11. M. K. Guseinova, A. S. Antsyshkina and M. A. Porai-Koshits, *Zh. Strukt. Khim* 1968, **9**, 1040.
12. E. Hansson, *Acta Chem. Scand.* 1972, **26**, 1337.
13. E. Hansson, *Acta Chem. Scand.* 1973, **27**, 2841.
14. Y. Sugita, Y. Ohki, Y. Suzuki and A. Ouchi, *Bull. Chem. Soc. Japan* 1987, **60**, 3441.