Short Communication

The Crystal Structure of Heptakis(4-picoline-*N*-oxide)ytterbium(III) Trifluoromethanesulfonate

C. Rodellas,[a,*] G. Vicentini[b] and L. B. Zinner[b]

[a]Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, SF-02150 Espoo, Finland and [b]Institute of Chemistry, University of São Paulo, C.P. 20.780, CEP 01498, São Paulo, Brazil

Rodellas, C., Vicentini, G. and Zinner, L. B., 1987. The Crystal Structure of Heptakis(4-picoline-*N*-oxide)ytterbium(III) Trifluoromethanesulfonate. – Acta Chem Scand., Ser. A 41: 294–298.

The trifluoromethanesulfonate (triflate) anion is a weakly coordinating anion which has been used, for instance, as a counterion in the synthesis of lanthanoid complexes with organic ligands.[1] Recently, the preparation of two series of 4-picoline-*N*-oxide (4-picNO) complexes was described, and an X-ray study of a representative of the first series (Ln = La–Gd) showed the complexes to be octacoordinated.[2] The stoichiometry of the second series, $Ln(4\text{-picNO})_7(CF_3SO_3)_3$ (Ln = Tb–Lu, Y) pointed to heptacoordination, which has now been corroborated by an investigation of the ytterbium complex.

Experimental

The complexes were precipitated by addition of triethylorthoformate (teof) to an ethanolic solution of 4-picNO and hydrated lanthanoid trifluoromethanesulfonate (molar ratio 7:1).[2] The unit cell dimensions were obtained by least-squares refinements of setting angles for 25 reflections measured with a Syntex $P2_1$ four-circle diffractometer. The interpretation of the Patterson map gave the position of the heavy atom. Successive Fourier syntheses[3] and electron density difference maps revealed the remaining atoms of the structure. The structure was refined by full-matrix least-squares methods using anisotropic temperature factors for Yb and S atoms and isotropic temperature factors for the rest of the atoms. Due to disorder in the three $CF_3SO_3^-$ ions, rigid refinement for C–F, S–O and C–S was used. All hydrogen atoms were located in a difference map but they were not included in the refinement. No absorption correction was applied. Details of crystal data and structure refinement are given in Table 1. The final positional parameters and equivalent or isotropic temperature factors are presented in Table 2. Lists of observed and calculated structure factors and anisotropic thermal parameters for Yb and S are obtainable from one of the authors (C.R.) on request.

Results

The Yb^{3+} ion is coordinated by seven oxygen atoms belonging to the 4-picNO groups. The structure of the complex corresponds thus to the formula $[Yb(4\text{-picNO})_7](CF_3SO_3)_3$. The Yb–O distances are in a rather narrow range of 2.22–2.32 Å. Fig. 1 shows a perspective view of the coordination around Yb, where it is possible to see that the configuration is a nearly regular pentagonal bipyramid. The edges between the axial site of a pentagonal bipyramid and the equatorial site should be 20 % longer than the edges connecting equatorial sites, but in this case the difference is slightly larger (around 25 %). The ideal and observed angles for the ML_7 structure are

*To whom correspondence should be addressed.

Table 1. Summary of crystal data, intensity collection and structure refinement for $[Yb(4\text{-picNO})_7](CF_3SO_3)_3$.

(a) Crystal data

Formula	$YbC_{45}H_{49}S_3N_7O_{16}F_9$
Crystal system	Triclinic
a/Å	14.673(4)
b/Å	15.256(7)
c/Å	16.122(9)
α/°	83.82(4)
β/°	63.52(4)
γ/°	62.99(3)
V/Å^3	2857(2)
Space group	$P\bar{1}$
Z	2
M.W.	1384.1
D_c/g cm^{-3}	1.607
Radiation	Mo*K*α(λ=0.71069 Å)
μ(Mo*K*α)/cm^{-1}	19.3

(b) Data collection and structure refinement[a]

Scan mode	ω
Range 2θ/°	3–50
Scan speed/° min^{-1}	2–29.30
Total no. of refl.	10036
No. of refined refl. [$I>3\sigma(I)$]	9574
R	0.090
$R_w(w=1/\sigma^2)$	0.088

[a]Computations were performed with the programs MITHRIL[3] and SHELX-76.[4]

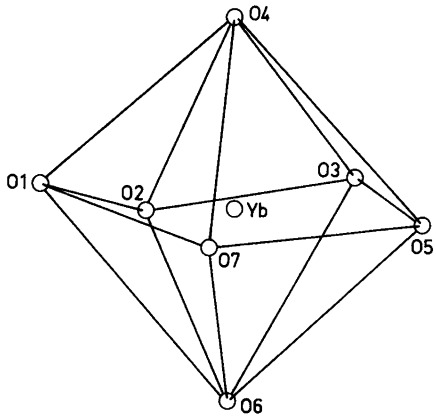

Fig. 1. Coordination polyhedron around Yb with atomic numbering.

given in Table 3, where (*a*) and (*b*) are the results of separate calculations of the δ angles for the upper and lower parts of the observed polyhedron based on pentagonal bipyramidal geometry (D_{5h}).[5,6] The symmetry of the complex is distorted from D_{5h}, as can be seen from Table 3. The angles are different for the upper and lower parts of the polyhedron, and deviate from the ideal value of 54.4°.

A list of bond lengths in the 4-picNO ligands is given in Table 4. The geometry of the ligands ap-

Table 2. Atomic coordinates (×10^4) and isotropic temperature factors (×10^2). $U_{eq} = \frac{1}{3}U_{ij}\sum_i\sum_j a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$ for the Nd and S atoms.

Atom	*x*	*y*	*z*	U_{iso} or U_{eq}/Å^2
Yb	2880(1)	2438(1)	2637(1)	5.9(1)
O1	2459(8)	3678(7)	1744(7)	6.7(3)
N1	2817(9)	4367(8)	1445(7)	5.3(3)
C12	3081(13)	4499(11)	533(10)	6.6(4)
C13	3383(15)	5298(13)	198(12)	8.5(5)
C14	3398(13)	5866(11)	782(11)	7.1(4)
C141	3693(16)	6744(14)	445(13)	9.5(6)
C15	3116(14)	5713(12)	1702(11)	7.6(5)
C16	2789(13)	4925(11)	2030(10)	6.6(4)
O2	4419(8)	2770(7)	1889(6)	6.3(3)
N2	5274(10)	2597(8)	2039(8)	6.1(3)
C22	6303(14)	1802(12)	1567(11)	7.5(4)
C23	7218(16)	1739(14)	1701(3)	9.3(5)
C24	7107(15)	2364(13)	2263(12)	8.4(5)
C241	8169(23)	2223(20)	2423(19)	15.4(9)
C25	6086(17)	3165(15)	2732(14)	10.1(6)

contd

Table 2. (contd)

Atom	*x*	*y*	*z*	U_{iso} or U_{eq}/Å^2
C26	5115(18)	3338(13)	2627(12)	8.5(5)
O3	3954(9)	1763(8)	3456(8)	8.3(3)
N3	4090(11)	940(9)	3892(9)	6.9(3)
C32	5086(14)	110(3)	3424(12)	8.2(5)
C33	5219(20)	−761(15)	3872(14)	10.0(6)
C34	4330(17)	−738(14)	4747(13)	9.5(6)
C341	4505(20)	−1714(17)	5233(16)	12.2(7)
C35	3361(16)	169(14)	5215(13)	9.3(5)
C36	3286(14)	1006(12)	4733(11)	7.6(4)
O4	1905(9)	3715(7)	3737(7)	7.4(3)
N4	1497(10)	3712(8)	4667(8)	6.2(3)
C42	2137(15)	3810(14)	5046(13)	9.2(5)
C43	1716(15)	3850(13)	6043(12)	8.6(5)
C44	618(13)	3856(12)	6565(11)	7.1(4)
C441	184(16)	3978(14)	7653(13)	9.7(6)
C45	107(14)	3741(12)	6133(12)	8.0(5)
C46	545(14)	3706(12)	5152(11)	7.5(4)
O5	2185(18)	1476(7)	3617(7)	7.0(3)
N5	1707(10)	904(8)	3609(8)	5.8(3)
C52	588(13)	1336(11)	3907(10)	6.6(4)
C53	93(15)	688(13)	3917(12)	8.7(5)
C54	764(15)	−314(13)	3632(12)	8.3(5)
C541	223(19)	−953(16)	3707(15)	11.6(7)
C55	1920(15)	−679(13)	3371(12)	8.2(5)
C56	2413(13)	−83(11)	3337(10)	6.8(4)
O6	3813(9)	1198(8)	1481(7)	8.1(3)
N6	4914(10)	821(18)	832(8)	6.1(3)
C62	5220(4)	1273(12)	83(11)	7.6(5)
C63	6363(13)	831(11)	−604(10)	6.8(4)
C64	2842(12)	29(10)	475(10)	6.1(4)
C641	1567(15)	501(13)	1231(12)	9.0(5)
C65	3185(13)	460(11)	9677(11)	7.1(4)
C66	5646(13)	−26(11)	962(10)	6.8(4)
O7	1361(8)	2566(7)	2515(7)	7.0(3)
N7	826(9)	3024(8)	1961(7)	5.5(3)
C72	1470(12)	2837(11)	1031(10)	6.1(4)
C73	868(12)	3311(12)	481(11)	7.7(5)
C74	9667(13)	3934(11)	922(11)	7.0(4)
C741	9019(19)	4343(16)	336(15)	11.2(7)
C75	9093(14)	4087(12)	1894(12)	7.7(5)
C76	9703(12)	3637(11)	2426(10)	6.2(4)
S1	7622(4)	3794(4)	5432(3)	9.1(1)
O11	8627(12)	3735(10)	4676(10)	11.9(5)
O12	7142(15)	4561(13)	6170(12)	15.0(6)
O13	7639(18)	2856(16)	5729(15)	18.6(8)
C1	6709(17)	4167(19)	4847(15)	19.2(13)
F11	6528(19)	5089(18)	4677(16)	24.5(9)
F12	5674(19)	4380(15)	5533(15)	22.0(8)
F13	6806(35)	3354(22)	4514(28)	44.7(23)
S2	4253(8)	2605(4)	8229(4)	17.1(2)
O21	3449(10)	2829(11)	9204(15)	12.7(5)
O22	4926(11)	1611(16)	7754(10)	13.0(5)
O23	5056(23)	2947(26)	8158(24)	33.0(17)

contd

Table 2. (contd)

Atom	*x*	*y*	*z*	U_{iso} or U_{eq}/Å^2
C2	3842(20)	3521(13)	7476(14)	55.2(53)
F21	3843(18)	4301(15)	7772(14)	22.5(8)
F22	4825(20)	3174(18)	6699(17)	26.2(10)
F23	3014(20)	3249(20)	7804(19)	30.1(13)
S3	1414(19)	1050(11)	7947(18)	27.4(4)
O31	1367(18)	1683(13)	7220(11)	18.3(8)
O32	2403(15)	440(17)	8101(18)	24.2(11)
O33	1107(44)	310(29)	7830(36)	48.3(34)
C3	31(16)	1580(26)	8974(16)	25.1(18)
F31	240(39)	2164(32)	9344(32)	51.7(28)
F32	−775(29)	1821(24)	8702(25)	35.0(16)
F33	144(27)	815(23)	9471(22)	33.0(15)

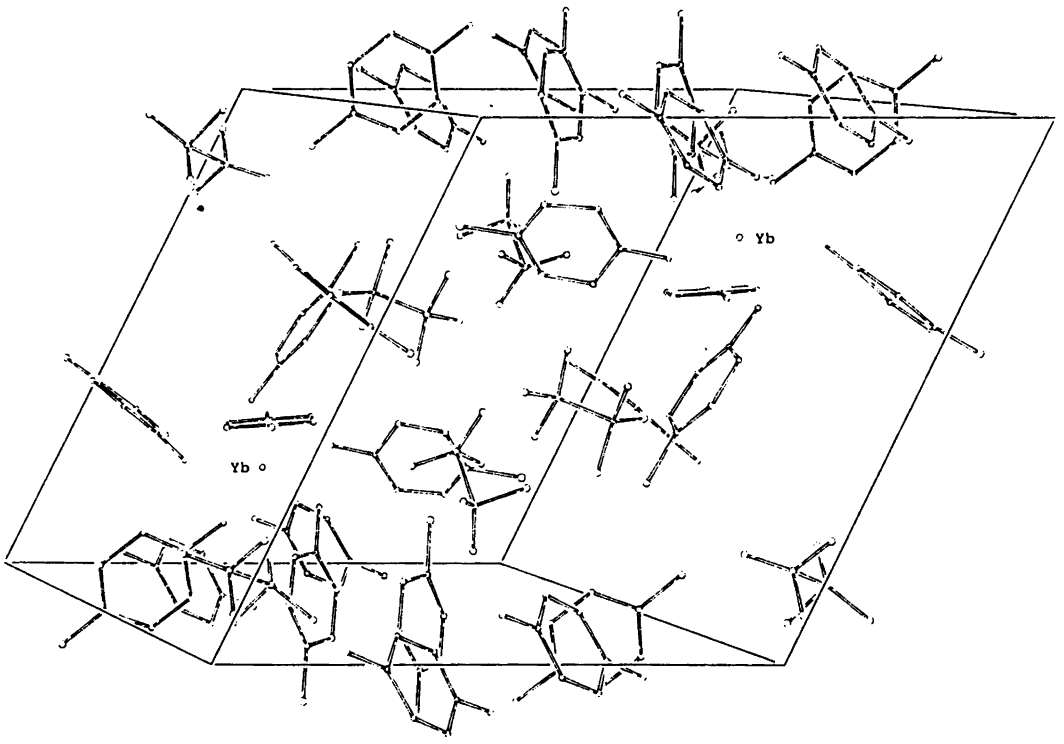

Fig. 2. A perspective view of the structure of $[Yb(4\text{-picNO})_7](CF_3SO_3)_3$ showing the unit cell.

Table 3. Analysis of the seven-coordination polyhedra.

Polyhedron ML_7		δ/°		
C_{2v} monocapped trigonal prism		0	0	41.5
C_{3v} capped octahedron		24.2	24.2	24.2
D_{5h} pentagonal bipyramid		54.4	54.4	
YbO_7	(*a*)[a]	49.9	42.2	
	(*b*)	56.7	66.1	

[a](*a*) and (*b*) are the results of separate calculations of δ angles for the upper and lower parts of the observed polyhedron based on pentagonal bipyramidal geometry.

pears to be normal.[7–10] Fig. 2 shows a perspective view of the unit cell.[11] There are no intermolecular contacts below 3Å.

Acknowledgements. The authors wish to thank Prof. Lauri Niinistö for valuable discussions during the work. Financial support from the Kemira Foundation to C.R. is gratefully acknowledged.

References

1. Lawrence, G. A. *Chem. Rev. 86* (1986) 17.
2. Fantin, C. A., Zinner, L. B., Vicentini, G., Rodellas, C. and Niinistö, L. *Acta Chem. Scand., Ser. A 41* (1987) 259 and references therein.
3. Gilmore, C. J. *MITHRIL: A Computer Program for the Automatic Solution of Crystal Structures from X-Ray Data,* Department of Chemistry, University of Glasgow, Glasgow 1983.
4. Sheldrick, G. M. *SHELX-76: Program for Crystal Structure Determination,* University of Cambridge, Cambridge 1976.
5. Muetterties, E. L. and Guggenberger, L. J. *J. Am. Chem. Soc. 96* (1974) 1748.
6. Kepert, D. L. *Inorganic Stereochemistry,* Springer-Verlag, Berlin 1982.
7. Wood, J. S., Day, R. O., Keijzers, C. P., de Boer, E., Yildirim, A. E. and Klaassen, A. A. K. *Inorg. Chem. 20* (1981) 1982.
8. Bertini, I., Dapporto, P., Gatteschi, P. and Scozzafava, A. *Inorg. Chem. 14* (1975) 1639.
9. Colye, B. A. and Ibers, J. A. *Inorg. Chem. 9* (1970) 767.

Table 4. Selected distances (Å) with estimated standard deviations in parentheses.

(a) YbO_7 coordination polyhedron			
Yb–O1	2.276(10)	Yb–O5	2.261(10)
Yb–O2	2.300(9)	Yb–O6	2.249(11)
Yb–O3	2.319(11)	Yb–O7	2.243(10)
Yb–O4	2.222(10)		
(b) C_6H_7NO (4-picNO)			
N1–O1	1.334(14)	N5–O5	1.349(15)
N1–C12	1.361(17)	N5–C52	1.320(19)
N1–C16	1.312(16)	N5–C56	1.361(18)
C12–C13	1.452(23)	C52–C53	1.466(23)
C13–C14	1.360(23)	C53–C54	1.377(25)
C14–C15	1.375(22)	C54–C55	1.386(25)
C14–C141	1.561(24)	C54–C541	1.479(28)
C15–C16	1.455(22)	C55–C56	1.380(23)
N2–O2	1.288(15)	N6–O6	1.347(16)
N2–C22	1.357(20)	N6–C62	1.324(20)
N2–C26	1.423(21)	N6–C66	1.323(19)
C22–C23	1.413(25)	C62–C63	1.404(22)
C23–C24	1.292(26)	C63–C64	1.376(20)
C24–C25	1.355(27)	C64–C65	1.372(21)
C24–C241	1.607(32)	C64–C641	1.561(22)
C25–C26	1.411(26)	C65–C66	1.408(21)
N3–O3	1.348(17)	N7–O7	1.377(14)
N3–C32	1.360(21)	N7–C72	1.344(18)
N3–C36	1.317(21)	N7–C76	1.342(18)
C32–C33	1.417(27)	C72–C73	1.439(21)
C33–C34	1.422(28)	C73–C74	1.422(22)
C34–C35	1.409(27)	C74–C75	1.394(23)
C34–C341	1.574(30)	C74–C741	1.524(27)
C35–C36	1.408(25)	C75–C76	1.417(22)
N4–O4	1.344(15)		
N4–C42	1.392(21)		
N4–C46	1.264(20)		
C42–C43	1.439(25)		
C43–C44	1.443(23)		
C44–C45	1.300(23)		
C44–C441	1.576(24)		
C45–C46	1.413(23)		

10. Razzak Al-Karaghouli, A. and Wood, J. S. *Inorg. Chem. 18* (1979) 1177.
11. Johnson, C. K. *ORTEP*: Report ORLN-3794, Oak Ridge National Laboratory, Oak Ridge, TN 1965.

Received April 23, 1987.