Pergamon

0277–5387(94)00370–X

Polyhedron Vol. 14, No. 9, pp. 1241–1243, 1995
Copyright © 1995 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0277–5387/95 $9.50+0.00

MOLECULAR STRUCTURE OF MESO-TETRA(4-PYRIDYL) PORPHYRINATOTHALLIUM(III) ACETATE, Tl(tpyp)(OAc)

SUH-SHING TANG, YUN-HUIN LIN, MING-TORNG SHEU, CHU-CHIEH LIN and JYH-HORUNG CHEN*

Department of Chemistry, National Chung-Hsing University,
Taichung 40227, Taiwan, R.O.C.

and

SHIN-SHIN WANG

Union Chemical Laboratories, Hsin-Chu 30034, Taiwan, R.O.C.

(*Received* 13 *July* 1994; *accepted* 12 *September* 1994)

Abstract—The molecular structure of meso-tetra(4-pyridyl)porphyrinatothallium(III) acetate, Tl(tpyp)(OAc), has been determined by X-ray analysis. The displacement of the thallium atom from the porphyrin mean plane was 0.858 Å. The geometry around the thallium centre of the Tl(tpyp)(OAc) molecule has Tl—O(1) = 2.266(10), Tl—O(2) = 2.512(9) and average Tl—N = 2.224(8) Å. This X-ray diffraction data provides evidence for an asymmetric pseudo-chelating acetato group coordinated to the thallium(III) atom. This might explain why intermolecular acetate exchange is the chief exchange mechanism for Tl(tpyp)(OAc).

Recently, Fuh *et al.*[1] reported the synthesis, characterization and dynamic NMR studies of meso-tetra(4-pyridyl)porphyrinato thallium(III) acetate, Tl(tpyp)(OAc). Suen *et al.*[2] reported the molecular structure and dynamic NMR studies of thallium meso-tetraphenylporphyrin acetate, Tl(tpp)(OAc). It turned out that the acetato ligand exchange for Tl(tpyp)(OAc) in CD_2Cl_2 solvent was intermolecular, whereas the exchange for Tl(tpp)(OAc) in the same solvent was intramolecular. However, what is not clear is why the exchange for Tl (tpyp)(OAc) is intermolecular when a very similar complex, Tl(tpp)(OAc), apparently exhibited intramolecular exchange? In order to elucidate the exchange mechanism, we now report the molecular structure of the crystalline Tl(tpyp)(OAc) by X-ray analysis.

EXPERIMENTAL

Crystal data

$C_{42}H_{27}N_8O_2Tl$, $M = 880.1$, monoclinic purple crystal, space group $C2/c$, $a = 29.495(6)$, $b = 14.777(3)$, $c = 17.887(4)$ Å, $\beta = 99.99(3)^\circ$, $Z = 8$, $V = 7678(3)$ Å^3, $D_c = 1.523$ g cm^{-3}, $\mu = 42.53$ cm^{-1}, $F(000) = 3456$. Intensities were collected for a crystal of dimensions $0.4 \times 0.6 \times 0.8$ mm on a Siemens R3 m/V diffractometer using monochromatized Mo-K_α radiation ($\lambda = 0.71073$ Å) via the θ–2θ scan technique. Absorption correction was not applied. The structure was solved by direct methods and each molecule was refined by full-matrix least-square refinement methods (see Table 1 for important crystal information and details on data collection). All non-hydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were refined isotropically and included in the structure factor cal-

---

* Author to whom correspondence should be addressed.

Table 1. Crystal data

Formula	$C_{42}H_{27}N_8O_2Tl$
Formula weight	880.1
a (Å)	29.495(6)
b (Å)	14.777(3)
c (Å)	17.887(4)
β (°)	99.99 (3)
V (Å^3)	7678(3)
Z	8
D_c (g cm^{-3})	1.523
Space group	$C2/c$
F(000)	3456
μ (cm^{-1})	42.53
R[a] (%)	4.72
R_w[b] (%)	6.22
GOF	1.76
A[b]	1
B[b]	5×10^{-4}
Crystal size (mm)	$0.4 \times 0.6 \times 0.8$
Data collected	10475
$2\theta_{max}$ (°)	45
Temperature (K)	293
Data used	4007
Discrimination	$I > 4\sigma(I)$

[a] $R = [\Sigma||F_o|-|F_c||/|F_o|]$.

[b] $R_w = [(\Sigma w(||F_o|-|F_c||^2/\Sigma w|F_o|^2)^{1/2}]$; $w = A/(\sigma^2 F_o + BF_o^2)$.

culation. The final agreement factors were $R = 4.72\%$ and $R_w = 6.22\%$ for 478 variables and 4007 unique reflections with $I > 4\sigma(I)$. The GOF was 1.76. A selection of bond distances and angles is given in Table 2.

Preparation of the complex

This complex was prepared as reported previously[1] and crystals were grown by diffusion of ether vapour into a $CHCl_3$ solution.

RESULTS AND DISCUSSION

The skeletal framework of Tl(tpyp)(OAc) is illustrated in Fig. 1. It reveals the six-coordination of the thallium atom with the four nitrogen atoms (N_p) of the porphyrinato group and the asymmetric pseudo-chelating COO^-; the coordination polyhedra were: Tl—O(1) = 2.266(10), Tl—O(2) = 2.512(9), O(1)—C(21) = 1.201(14), O(2)—C(21) = 1.212(15), C(21)—C(22) = 1.463(18) and the mean Tl—N_p = 2.224(8) Å. The thallium atom lies 0.858 Å above the plane ($C_{20}N_4$) defined by the porphyrin ring system, and the O(1)—Tl—O(2) bond angle is 51.7(3)°. The dihedral angles between the mean plane of the porphyrin skeleton and the mean planes of four pyridine groups are 85.5 [C(31), C(32), C(33), N(34), C(35), C(36)], 105.8 [C(41), C(42), C(43), N(44), C(45), C(46)], 84.8 [C(51), C(52), C(53), N(54), C(55), C(56)] and 70.5° [C(61), C(62), C(63), N(64), C(65), C(66)], respectively.

The acetate exchange of Tl(tpyp)(OAc) in CD_2Cl_2 is intermolecular when a very similar complex, Tl(tpp)(OAc), apparently exhibited intermolecular exchange. This might correlate to the different types of thallium–carboxylate binding modes in Tl(tpyp)(OAc) and Tl(tpp)(OAc). The complex Tl(tpp)(OAc) is chelated in bidentate

Table 2. Selection of bond distances (Å) and angles (°)

Tl—O(1)	2.266(10)	Tl—N(4)	2.228(8)
Tl—O(2)	2.512(9)	O(1)—C(21)	1.201(14)
Tl—N(1)	2.212(7)	O(2)—C(21)	1.212(15)
Tl—N(2)	2.235(8)	C(21)—C(22)	1.463(18)
Tl—N(3)	2.220(7)		
O(1)—Tl—O(2)	51.7(3)	N(1)—Tl—N(3)	141.3(3)
O(1)—Tl—N(1)	120.8(3)	N(1)—Tl—N(4)	83.6(3)
O(1)—Tl—N(2)	95.2(3)	N(2)—Tl—N(3)	83.6(3)
O(1)—Tl—N(3)	96.4(3)	N(2)—Tl—N(4)	139.2(3)
O(1)—Tl—N(4)	124.5(3)	N(3)—Tl—N(4)	83.4(3)
O(2)—Tl—N(1)	89.5(3)	Tl—O(1)—C(21)	100.0(8)
O(2)—Tl—N(2)	134.8(3)	Tl—O(2)—C(21)	87.6(7)
O(2)—Tl—N(3)	124.8(3)	O(1)—C(21)—O(2)	120.5(12)
O(2)—Tl—N(4)	83.3(3)	O(1)—C(21)—C(22)	117.0(11)
N(1)—Tl—N(2)	82.9(3)	O(2)—C(21)—C(22)	122.5(10)

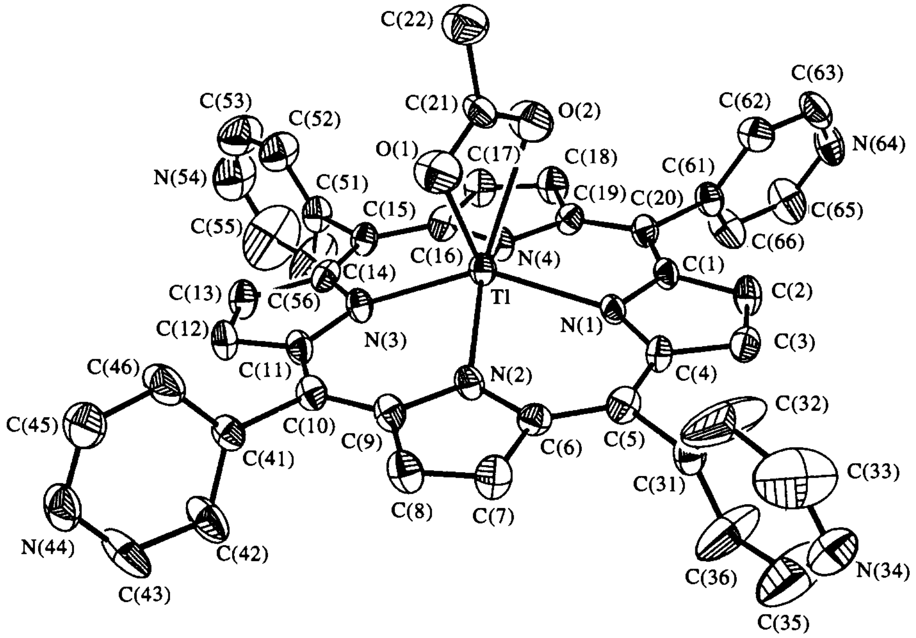

Fig. 1. Molecular configuration and scheme of labelling atoms for Tl(tpyp)(OAc) (hydrogen atoms are omitted for clarity).

fashion[1,3] (or symmetrically[4]) with Tl—O(1) = 2.361(9) and Tl—O(2) = 2.299(10) Å of comparable bond lengths. However, the complex Tl (tpyp)(OAc) contains asymmetric pseudo-chelating[1] (or bidentate, chelating, unsymmetrical;[5] asymmetric chelating[4]) acetate, with one Tl—O(1) [= 2.266(10) Å] distance normal, and the other Tl—O(2) [= 2.512(9) Å] significantly longer. It is easier to break Tl—O bonds for the asymmetric pseudo-chelating acetate in Tl(tpyp)(OAc) than for the bidentate-chelating acetate in Tl(tpp)(OAc). Furthermore, the easy formation of hydrogen bonding between the pyridine nitrogen of Tl(tpyp) (OAc) and the carboxyl hydrogen of HOAc, arising from the protonation of acetate, enhances the dissociation of Tl(tpyp)(OAc) into Tl(tpyp)$^+$ and OAc$^-$. However, such hydrogen bonding was absent for the Tl(tpp)(OAc) complex. Hence, the acetate exchange for the Tl(tpyp)(OAc) is intermolecular, while that for Tl(tpp)(OAc) is intramolecular.

Acknowledgements—Financial support of the National Research Councils of the R. O. C. under Grants NSC-83-0208-M-005-032 and NSC-84-0115-C005-01-089 M is gratefully acknowledged.

REFERENCES

1. J. J. Fuh, S. S. Tang, Y. H. Lin, J. H. Chen, T. S. Liu, S. S. Wang and J. C. Lin, *Polyhedron* 1994, **13**, 3031.
2. (a) S. C. Suen, W. B. Lee, F. E. Hong, T. T. Jong, J. H. Chen and L. P. Hwang, *Polyhedron* 1992, **11**, 3025; (b) J. C. Chen, H. S. Jang, J. H. Chen and L. P. Hwang, *Polyhedron* 1991, **10**, 2069.
3. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th edn, p. 232. John Wiley, New York (1986).
4. R. L. Rardin, W. B. Tolman and S. J. Lippard, *New J. Chem.* 1991, **15**, 417.
5. N. W. Alcock and V. M. Tracy, *J. Chem. Soc., Dalton Trans.* 1976, 2243.