Synthesis and Structure of a Complex of Bismuth(III) with a Nitrogen Donor Macrocycle

Robert Luckay,[a] **Joseph H. Reibenspies**[b] **and Robert D. Hancock***[a]

[a] *Department of Chemistry, University of the Witwatersrand, WITS 2050, Johannesburg, South Africa*
[b] *Department of Chemistry, Texas A & M University, College Station, Texas 77843, USA*

The synthesis and structure of the first example of a bismuth(III) complex of a nitrogen donor macrocycle is reported, with the pendant-donor cyclen-based tetraaza macrocycle 1,4,7,10-tetrakis[(*S*)-2-hydroxypropyl]-1,4,7,10-tetraazacyclo-dodecane; the complex is eight-coordinate with approximately square antiprismatic coordination geometry.

The chemistry of bismuth has been rather neglected, as seen in the small number of pages devoted to it in the compilation in ref. 1, compared to other metals. Bismuth has of late increased in importance because of its potential medical applications, such as the use of ^{212}Bi in cancer therapy[2] and of bismuth compounds in treating gastric ulcers.[3] Particularly lacking is information on compounds of bismuth that might be useful in aqueous solution, which are needed for biomedical applications. Until recent studies[4] of polyamine complexes of Bi^{III} in solution, one could not even have surmised whether it would be advantageous to incorporate nitrogen donors into ligands designed for coordinating Bi^{III}. We report here the first example of a complex of Bi^{III} with a nitrogen donor macrocycle L^1, based on cyclen.

The ligand L^1 was synthesized as described previously,[5] except that the optically resolved (*S*)-(−)-propylene oxide (Aldrich) was used so as to obtain the (*S,S,S,S*)-enantiomer of L^1, and avoid the problems of disorder found with a crystallographic[5] study of the Pb^{II} complex, where two enantiomers were present. The Bi^{III} complex was synthesized by dissolving Bi_2O_3 in 70% $HClO_4$, and then adding a stoichiometric quantity of (*S,S,S,S*)-L^1. Na_2CO_3 was used to raise the pH to about 0. Colourless cubic crystals were deposited, which gave satisfactory elemental analyses for $C_{20}H_{40}BiO_4N_4(ClO_4)_3{\cdot}H_2O$. The X-ray crystal structure of the $[Bi\{(S,S,S,S)\text{-}L^1\}]^{3+}$ complex cation is shown in Fig. 1.† The Bi^{III} is eight-coordinate, and the structure is similar to that found[5] for the isoelectronic Pb^{II}, except for the shorter Bi–N (*ca.* 253 pm) and Bi–O (*ca.* 258 pm) bond lengths, as compared to[5] Pb–N (264 pm) and Pb–O (275 pm), which is to be expected from the smaller octahedral ionic radius[6] of Bi^{III} (103 pm) as compared to Pb^{II} (119 pm). In both Pb^{II} and Bi^{III} structures, a point of interest is[5] the presence of a stereochemically active lone pair of electrons.[7] The criteria for a stereochemically active lone pair are:[8,9] (*i*) a gap in the coordination sphere, which is present in both structures, and (*ii*) short M–L bond lengths on the side of the complex away from the proposed position of the lone pair. In the present complex the nitrogen donors are on the side away from the lone pair, and the M–N bond lengths can be regarded as short because they are shorter than the M–O bond lengths, whereas M–O bond lengths are usually about 6 pm shorter than M–N bond lengths, which correlates with the smaller covalent radius[10] of oxygen (66 pm) than nitrogen (70 pm). The gaps in the coordination spheres of both the Pb^{II} and Bi^{III} complexes of L^1 may well correspond to the presence of stereochemically active lone pairs. It is of interest that O(13) from one of the perchlorates is 334(1) pm from the Bi^{III}, directly above the gap in the coordination sphere where the lone pair of electrons on the Bi^{III} is expected to be situated. It appears that this is a very weak interaction between the perchlorate and the Bi^{III} in the direction of the lone pair on the Bi^{III}. It is not clear what the forces are that are involved in interactions of this type, except that they frequently occur in Pb^{II} complexes. For example, in $[Pb(L^1)](ClO_4)_2{\cdot}Me_2CHOH$,[11] the oxygen of the propan-2-ol molecule is situated directly over the gap in the coordination geometry, analogous to the placement of the perchlorate oxygen in $[Bi(L^1)]^{3+}$, with a Pb–O distance of 350 pm.

On the basis of the present work, Bi^{III} should have an extensive chemistry with nitrogen donor macrocycles, as rich as that of its isoelectronic analogue Pb^{II}, which we are in the process of exploring with the synthesis of complexes such as $[Bi(cyclen)(H_2O)(ClO_4)_3]$. One should note the remarkably high stability of these complexes of Bi^{III} with tetraaza macrocycles, which can form at pH 0.

The authors thank the University of the Witwatersrand and Texas A & M University, as well as the Foundation for Research Development, for generous financial support for this work.

Received, 24th April 1995; Com. 5/02589C

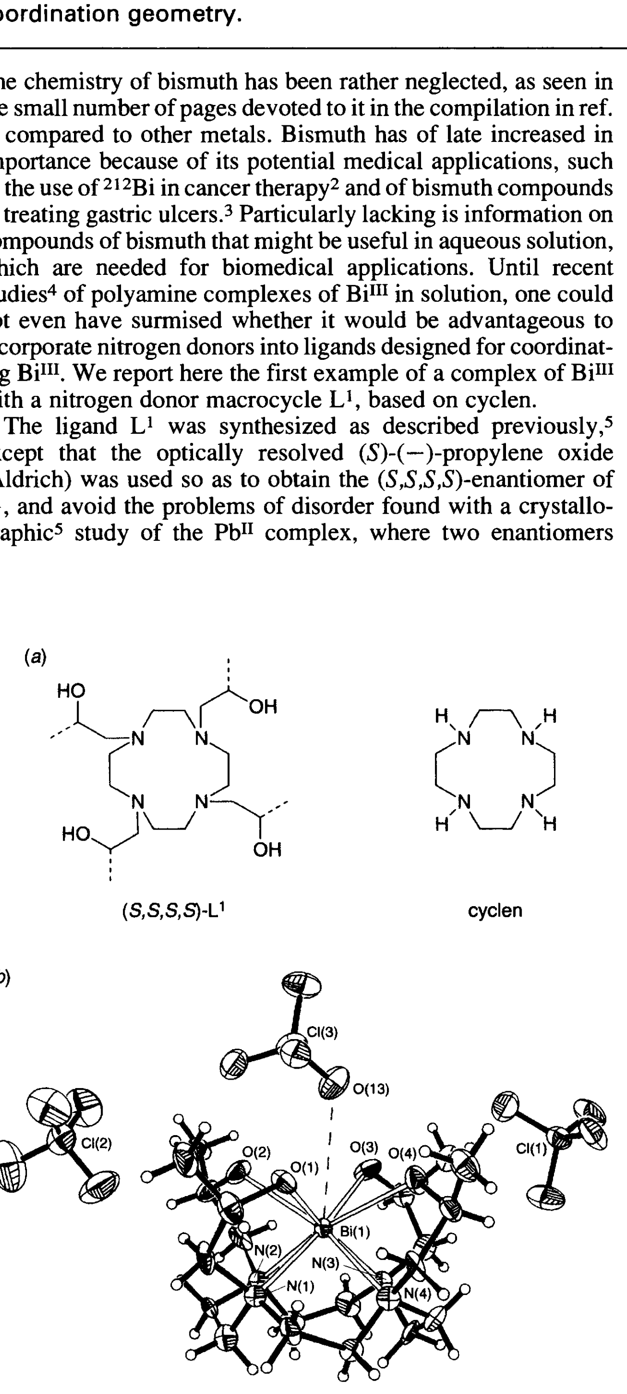

Fig. 1 (*a*) The macrocycles (*S,S,S,S*)-L^1 and cyclen. Note that the chiral carbons of the 2-hydroxypropyl groups of L^1 are all (*S*). (*b*) Structure of $[Bi(L^1)](ClO_4)_3{\cdot}H_2O$, showing the numbering scheme. The water molecule, which is far from Bi^{III} in the crystal lattice, is omitted for clarity. Bond lengths: Bi–O(1) 258.8, Bi–O(2) 253.3, Bi–O(3) 258.1, Bi–O(4) 257.7, Bi–N(1) 254.4, Bi–N(2) 253.3, Bi–N(3) 252, Bi–N(4) 251, Bi–O(13) 334 pm. Angles: N(1)–Bi–N(2) 71.4, N(1)–Bi–N(3) 112.3, N(1)–Bi–O(1) 64.0, O(1)–Bi–O(2) 79.90°.

Footnote

† *Crystal data*: $[Bi\{(S,S,S,S)\text{-}L^1\}](ClO_4)_3{\cdot}H_2O$, orthorhombic, space group $P2_12_12_1$, a = 1093.6(2), b = 1596.8(2), c = 1851.9(3) pm, Z = 4, 3208

independent reflections, $R1$ [$I > 2\sigma(I)$] 0.043, $wR2$ (on F^2, all data) 0.27, absolute configuration confirmed by Flack's method. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, London, 1987, vols. 1–7.
2 R. W. Kozak, T. A. Waldmann, R. W. Atcher and O. A. Gansow, *Trends Biotechnol.*, 1985, **4**, 259.
3 G. F. Baxter, *Chem. Br.*, 1992, **28**, 445.
4 R. D. Hancock, I. Cukrowski and J. Mashishi, *J. Chem. Soc., Dalton Trans.*, 1993, 2895.
5 R. D. Hancock, M. S. Shaikjee, S. M. Dobson and J. C. A. Boeyens, *Inorg. Chim. Acta*, 1988, **154**, 229.
6 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
7 R. J. Gillespie and R. S. Nyholm, *Q. Rev., Chem. Soc.*, 1957, **11**, 339.
8 S. L. Lawton and G. T. Kokotailo, *Inorg. Chem.*, 1972, **11**, 363.
9 K. Wieghardt, M. Kleine-Boymann, B. Nuber, J. Weiss and L. Zsolnai, *Inorg. Chem.*, 1986, **25**, 1647.
10 L. Pauling, *The Nature of the Chemical Bond*, 3rd edn., Cornell University Press, New York, 1960, p. 224.
11 R. Luckay, J. H. Reibenspies and R. D. Hancock, to be published