Coordination Chemistry

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On the Molecular Structure and Bonding in a Lithium Bismuth Porphyrin Complex: LiBi(TPP)$_2$**

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Abstract: *A new Bi–Li porphyrin sandwich compound, LiBi(TPP)$_2$ has been synthesized and characterized (TPP = tetraphenylporphyrin). The unique molecular structure of LiBi(TPP)$_2$ is such that the Bi sits between the porphyrins and is directed towards the Li. This complex was shown to remain intact in solution by temperature-dependent 2D NMR spectroscopy. In order to investigate the potential interaction between these two metals, DFT calculations were used and showed a Bi 6s orbital polarized towards Li which could be indicative of a Bi–Li dative bond. This bond is remarkably short, 2.87 Å, and is among the shortest Bi–Li distances seen in a small molecule.*

Ring-opening polymerization of lactides (L, *rac* and *meso*) by coordination complexes is a topic of considerable current interest with regard to stereocontrol by the metal center with its attending set of ligands.[1–3] A limitation of the majority of these catalyst systems lies in their mortality because of side reactions with minor impurities such as water, oxygen, and carbon dioxide and ligand scrambling.[4,5] In this regard the commercial employment of tin(II) octanoate as a catalyst is superior though it offers no stereoselectivity.[6–8] In looking for an alternative, we found that bismuth(III) in the form of bismuth subsalicylate was comparable and that salen bismuth alkoxides were more active though not immortal being subject to ligand scrambling.[5] This prompted us to investigate the reactions of porphyrin bismuth alkoxides thinking that the porphyrin ligand would be more chemically inert compared to the Schiff base salen ligands. These findings will be reported elsewhere, but during the course of these studies we discovered the interesting green crystalline complex that can be formed in high yield according to the reaction shown in Equation (1). We report here on the molecular structure and bonding in this complex, LiBi(TPP)$_2$, where TPP is tetraphenylporphyrin (Figure 1).

$$\begin{aligned}&\mathrm{BiCl_3} + 2\,\mathrm{TPPH_2} + 4\,\mathrm{LiN(SiMe_3)_2} \xrightarrow{\text{THF, RT, 12 h}} \\ &\quad \mathrm{BiLi(TPP)_2} + 3\,\mathrm{LiCl} + 4\,\mathrm{HN(SiMe_3)_2}\end{aligned} \qquad (1)$$

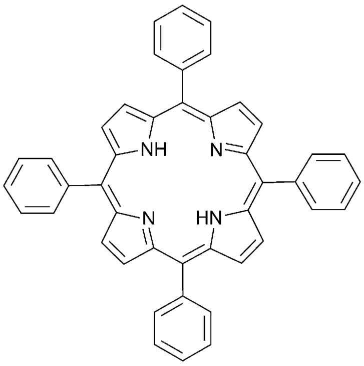

Figure 1. Tetraphenylporphyrin (TPP).

The optimized synthesis of the titled compound, LiBi(TPP)$_2$ (**1**), involves the stochiometric reaction given in Equation (1).

The reaction must be carried out in a dry and oxygen-free N_2 or Ar atmosphere with similarly purified solvents because of the reactive nature of the reagents. The green crystals are soluble in $CHCl_3$, CH_2Cl_2, and tetrahydrofuran (THF) but not appreciably soluble in hydrocarbons. Crystals suitable for single-crystal X-ray studies were grown from CH_2Cl_2 in a refrigerator at −25 °C. MALDI-TOF mass spectrometry operating in the positive and negative ion modes gave the Bi(TPP)$^+$ and Li(TPP)$^-$ ions as parent ions, respectively. In addition the molecular ion LiBi(TPP)$_2^{+/-}$ was observed.

NMR and UV/Vis spectral data are given in the Supporting Information. Elemental analyses were not performed because partial loss of solvent molecules of crystallization visibly occurs in a dynamic vacuum.

The solid-state structure of compound **1** crystallized in the space group *C*2/*c*; there is one unique LiBi(TPP)$_2$ ion pair and CH_2Cl_2 disordered molecules of solvent within the unit cell. A view of the molecular structure looking down the Li–Bi axis, and a view of the central portion of the molecule (lacking phenyl substituents for clarity) looking perpendicular to the Li–Bi axis can be seen in Figure 2a and b, respectively.

The former view of the molecule emphasizes the staggered nature of the porphyrin LiBi-N$_8$ core which minimizes steric hindrance of the eight phenyl groups. Figure 2b more clearly demonstrates the close porphyrin–porphyrin ring separation of about 3.5 Å. This is not surprising given the formal nature of the molecule as an ion pair involving [Li(TPP)]$^-$ and [Bi(TPP)]$^+$. The Bi atom lies significantly out of the N$_4$ plane of its porphyrin by 1.12 Å. Given the ionic radius of Bi^{3+} this is hardly surprising and is commonly seen

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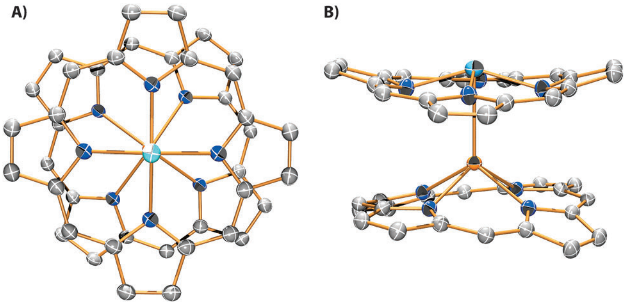

Figure 2. ORTEP representation of **1** viewed a) parallel and b) perpendicular to the Li–Bi bond. Figure drawn at 50% probability. (gray = carbon, dark blue = nitrogen, light blue = lithium, orange = bismuth) phenyl groups, hydrogen atoms, and solvent excluded for clarity.

for the heavier elements of the d block and the lanthanides. It is also immediately obvious from Figure 2b that the Li atom is also slightly out of the N_4 plane of its porphyrin by 0.58 Å. Bond distances around the Bi–Li core can be seen in Figure 3 and full details of the crystallographic data are given in the Supporting Information with a summary of details in the Experimental Section.

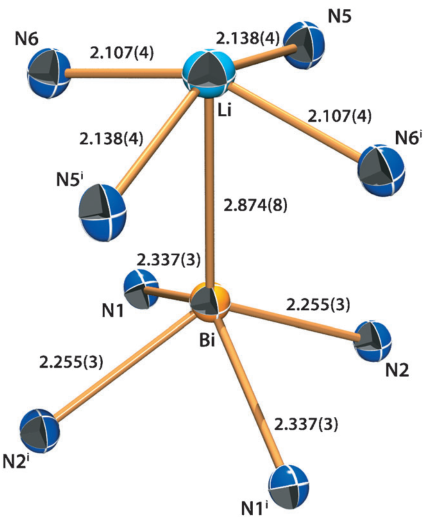

Figure 3. Bond distances in Å surrounding the Bi–Li core.

One point of immediate interest is the Bi–Li distance of 2.874(8) Å. Given that both Li and Bi are cations with formal charges of +1 and +3, respectively, one has to question whether or not this distance is imposed by the ionic nature of the ions Li(TPP)$^-$ and Bi(TPP)$^+$ or is there a dative Bi→Li bond involving the nonbonding Bi $6s^2$ orbital. To gain insight into this matter we undertook electronic structure calculations employing the commercial programs provided by Guassian.[9]

DFT calculations were carried out on the model compound involving the porphyrin-lacking phenyl substituents to save on computational time and resources. The highest energy occupied orbitals are associated with the Li(porphyrin)$^-$ ion not surprisingly given its negative charge and below these lie the frontier Bi(porphyrin)$^+$ orbitals. These sets of orbitals arise from the filled π systems of the porphyrins (see the Supporting Information). The HOMO-7, which is shown in Figure 4, contains a polarized Bi 6s filled orbital with some 6p mixing and is clearly directed at the Li$^+$ ion.

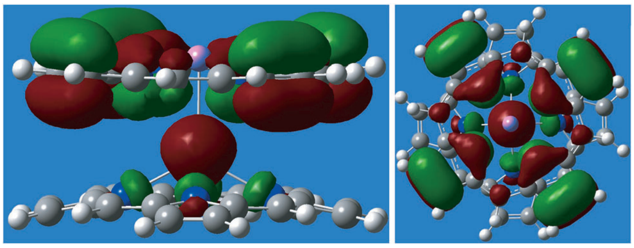

Figure 4. The filled frontier orbital HOMO-7 of model compound **1** from a side-on (left) and top-down (right) view.

This can be viewed as the dative Bi→Li bond which is primarily a Li$^+$ polarized Bi lone pair. The calculated Bi–Li distance of 2.81 Å is close to that seen in the crystal structure especially given the phenyl groups on the porphyrin were omitted in the calculation. The calculated structure still indicates that the Li$^+$ ion is out of the N_4 plane of the porphyrin and one may ask why if there is a Bi–Li bond. The answer lies in the fact that the porphyrin–porphyrin attraction is more than can be sustained for a Bi→Li dative bond. The repulsive energy curve of a bond rises much more steeply upon compression because of core–core repulsion than the attractive potential-energy curve rises with extension of the bond length. This is why the WW quadruple bond is nearly 0.1 Å longer than the MoMo quadruple bond in otherwise identical molecules[10] even though the atomic radii of Mo and W atoms are essentially identical because of the lanthanide contraction. So the Li$^+$ ion is pushed slightly out of the plane of its porphyrin by the repulsive core force of the Bi^{3+} ion. This notwithstanding the Bi–Li distance is remarkably short. We know of no other immediately relevant comparison that is available from crystallographic data banks. We do, however, recognize that there are lithium bismuthide complexes of formula $LiBiR_2$ where R is a bulky organic ligand. Here bismuth is formally Bi^{2+} and it is quite reasonable to envisage the bonding between Bi^{2+} and the Li$^+$ ion involves the use of a lone pair from bismuth in an sp^2 orbital with the BiR_2 group being related to its lighter congeners NR_2, PR_2, and AsR_2 that are well-known to form bonds to lithium. The Li-Bi distances in these complexes range from 2.90 to 3.19 Å.[11,12] Certainly, we would consider these as bonding distances and so in the case of the complex $LiBi(TPP)_2$ with a comparable distance it seems fair to invoke the presence of a Bi→Li bond though this may well not be the driving force for the formation of the complex.

The proton NMR spectrum of compound **1** in $CDCl_3$ is shown in Figure 5. The low-temperature spectrum is consistent with two different porphyrins and restricted rotation about the phenyl porphyrin carbon bonds as might be expected because of steric factors. DOSY spectra are also consistent with the LiTPP$^-$ and BiTPP$^+$ ions being associated

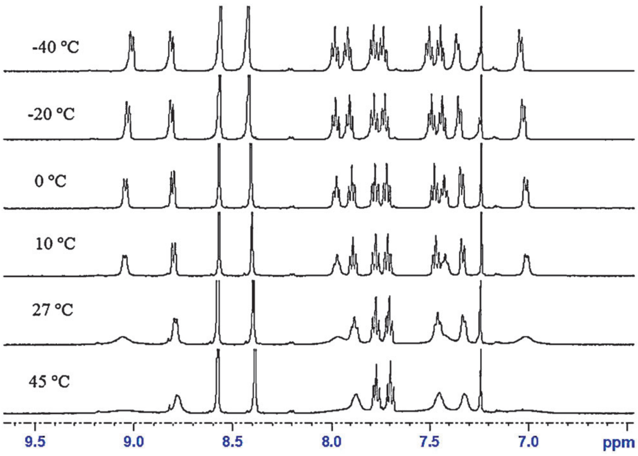

Figure 5. Variable-temperature ^{1}H NMR spectroscopy of **1** in $CDCl_3$.

in solution as a dinuclear species. ^{7}Li NMR spectroscopy reveals a sharp signal at δ −14.3 ppm. This signal is significantly shifted upfield, because of the ring current of TPP. This shift is typical in Li porphyrin complexes.[13]

In the MALDI mass spectrum the parent $LiBi(TPP)_2$ ion is seen in both the positive and negative ion modes along with $BiTPP^+$ and $LiTPP^-$ in the positive and negative ion modes, respectively. The latter constitute the most intense ions.

The electronic absorption spectrum is shown in the Supporting Information where it is compared with that of the free porphyrin. Electronic structure calculations on the model compound **1** indicate an expected absorption due to $LiTPP^-$ to $BiTPP^+$ charge transfer. There is some solvent dependence of the lower energy absorption at about 450 nm which red shifts and decreases in intensity upon dilution in CH_2Cl_2. This may reflect dissociation of the ion pair. See the spectra in the Supporting Information.

The complex $LiBi(TPP)_2$ which may be considered as a tight ion pair $[Bi(TPP)]^+[Li(TPP)]^-$ is present both in the solid state and in solution. The solid-state structure has a staggered porphyrin structure with virtual C_4 symmetry which affords the favorable packing of the phenyl groups. The variable temperature ^{1}H NMR spectra indicate a dynamic process at room temperature which is frozen out on the NMR time scale below 0 °C in $CDCl_3$. The short Li–Bi distance of 2.874(8) Å can be considered as a dative bond from the Bi^{3+} $6s^2$ lone pair to the Li^+ ion. Whether this is a result of the TPP–TPP ion pair formation or contributes significantly to the assembly of the structure as observed is a matter of conjecture at this time. However, attempts to prepare a related complex $NaBi(TPP)_2$ based on a reaction involving $NaN(SiMe_3)_2$ in place of $LiN(SiMe_3)_2$ failed to yield a related complex. The Na^+ ion is roughly 0.2 Å larger than the Li^+ ion and notably less electrophilic and polarizing as is well seen in their respective coordination chemistry with alkyl groups. Thus a Bi→Na bond would be expected not only to be longer but also weaker. We have not pursued the possible nature of the species that might be formed in the reaction mixture involving $NaN(SiMe_3)_2$, $BiCl_3$, and $TPPH_2$ but quite possibly a species of the form Na^+(solvent) $Bi(TPP)_2^-$ could be present. We have, however, obtained a similar structure to that of **1** for the compound $LiBi(salen)_2$ which is prepared in a related manner to **1**.[14] This also has a similarly short Bi–Li distance and this result would seem to discount the view that the short Bi–Li distance in **1** is due to the favorable π–π stacking of the porphyrin ligands.

Experimental Section

In 30.0 mL of tetrahydrofuran 0.500 g (1.59 mmol) of $BiCl_3$, 1.06 g (6.34 mmol) $LiN(SiMe_3)_2$, and 1.95 g (3.17 mmol) of tetraphenylporphyrin ($TPPH_2$) were dissolved and the solution was stirred at room temperature for 12 h. All the volatile components were removed in vacuum and the crude product was dissolved in benzene. The supernatant liquid was transferred to another Schlenk flask by cannula and the solvent was removed in vacuum. The resultant crude product was dissolved in a minimum amount of CH_2Cl_2 and placed in a freezer at −25 °C. Green crystals were obtained in 70 % yield. Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated CH_2Cl_2 solution in a freezer at −25 °C for one month.

^{1}H NMR ($CDCl_3$, 500 MHz, room temperature): δ = 7.01 (bs, 4 H, Ar*H*), 7.33 (d, 4 H, Ar*H*), 7.42 (bs, 4 H, Ar*H*), 7.46 (t, 4 H, Ar*H*), 7.70 (t, 4 H, Ar*H*), 7.77 (t, 4 H, Ar*H*), 7.88 (t, 4 H, Ar*H*), 7.96 (bs,4 H, Ar*H*), 8.40 (s, 8 H, pyrrole*H*), 8.57 (s, 8 H, pyrrole*H*), 7.78 (d, 4 H, Ar*H*), 9.05 ppm (bs, 4 H, Ar*H*). ^{7}Li NMR ($CDCl_3$, ppm): δ = −14.3 ppm.

MS(MALDI-TOF): Positive ion mode; *m/z* $[TPPBi]^+$ calculated 821.21; found 821.41 and $[BiLiTPP_2]^+$ calculated 1440.46; found 1440.43, Negative ion mode; *m/z* $[TPPLi]^-$ calculated 619.25; found 621.88 and $[BiLiTPP_2]^-$ calculated 1440.46; found 1439.83.

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