solve as the solution is neutralized carefully to pH = 7.0. Evaporation in a rotary evaporator at aspirator vacuum and temperature less than 30 °C left a solid that was then pumped under high vacuum for several hours to remove traces of water. The solid was extracted with chloroform and the solvent removed under high-vacuum pumping to leave a semisolid. Stirring with a few drops of water caused crystallization to white crystals that were then dried under high vacuum, giving 1.20 g (80%) of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCONH_2$ (**4**). A sublimed sample (65–70 °C/high vacuum) melted sharply at 158–159 °C as opposed to a melting range beginning at 127 °C for the product as obtained, even though the infrared spectra were identical. NMR data: ^1H NMe_2 2.85, 2.69, 2.65, 2.61; NH_2 broad doublet 5.5 and 5.4; CH_2 broad ca. 1:3:3:1 quartet 2.42, broad ca. 1:2:1 triplet 1.90; ^{11}B unsymmetrical and shouldered triplet −8.4, −9.4, −10.0 decouples to a singlet −8.9. GC/MS data: one major GC peak and one minor one; *m/e* 184 (21%) and 183 (11%) parent − 1 with $^{11}B_2$ and $^{10}B^{11}B$ isotopic composition; 141 (100%) and 140 (52%) parent − 1 for **1**. Infrared data (cm^{-1}): NH 3435, 3282, 3166 s; BH 2343/2313 s with multiple shoulders; amide carbonyl 1621, 1575 s; 1306 w with shoulders, 1235 w, 1175 w, 1330–1320 m doublet, 1070 m multiplet, 1030–1010 m doublet, 966 m, 930 m, 889 w, 852 m, 830 w, 734 m.

If the basic hydrolysis solution is treated with 1 M HCl to approximately 0.15 M H^+, the carboxylate derivative $Me_2\overline{NCH_2BH_2CH_2NMe_2B}HCO_2H$ (**3**) settles slowly from the solution after a few minutes induction. Yields were better than 80%; for example, from 25.9 mmol of $Me_2\overline{NCH_2BH_2CH_2NMe_2B}HI$ and 25.8 mmol of $Me_3N{\cdot}BH_2N{\equiv}C$ precursors was obtained 3.96 g of **3**, 82%. Recrystallization from 30% methanol in water gives recovery of better than 70% as white needles, mp 196 °C/sealed capillary. Anal. Calcd for $C_7H_{20}B_2N_2O_2$: C, 45.23; H, 10.84; N, 15.07. Found: C, 45.52; H, 10.89; N, 14.93. **3** can be sublimed at 80 °C/high vacuum. Infrared data (cm^{-1}): OH under mineral oil CH stretch; BH 2373, 2353, 2328 s (shouldered); CO 1651 s; 1301 w, 1244 s, 1175 s (1195 m shoulder), 1128/1118 w doublet, 1074 s, 1025 w, 1004 m, 966 m, 928 m, 887 w, 855 w, 746 m. NMR data: ^{13}C NMe_2 57.56, 56.02, 48.08, 43.54; ^1H NMe_2 2.81, 2.77, 2.66, 2.61; CH_2 (broad multiplets) 2.47, 2.28, 2.20, 1.87; ^{11}B unsymmetrical triplet −8.1, −9.4, −10.4 decoupled to unsymmetrical doublet −9.1, −9.9.

$Me_3N{\cdot}BH_2CO_2H$. A solution of 297 mg (0.94 mmol) of $(Me_3NBH_2)_2C{\equiv}N^+PF_6^-$ [7] in 8 mL of degassed 1 M NaOH was heated to 40 °C to initiate hydrolysis and then allowed to stir overnight. Noncondensible gas at −196 °C amounted to 1.8 mmol (100% of theory). The solution was filtered and adjusted to pH 4 and evaporated and the solid extracted with chloroform. Removal of solvent left a solid with amide infrared bands present, so it was dissolved in 5 mL of 0.3 M HCl and evaporated under high vacuum. Extraction with chloroform, followed by evaporation and sublimation, gave 58 mg (53%) of $Me_3N{\cdot}BH_2CO_2H$ identified by its infrared spectrum.[4a]

$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OH$. A solution of 53 mg (0.285 mmol) of **3** in about 3 mL of dry glyme was added to 0.57 mL of 0.5 M $LiAlH_4$ in glyme under nitrogen. Brisk gas evolution occurred, resulting in a clear solution. After the solution was stirred overnight, 1 mL of 2-propanol and 1 mL of saturated aqueous NaF were added sequentially with stirring. The solid was removed by filtration and the filtrate evaporated to dryness under vacuum. Extraction with methylene chloride followed by solvent removal and sublimation at 55 °C/high vacuum, gave 73 mg, 62%, of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OH$, mp 85–86 °C sealed cap under nitrogen. Anal. Calcd for $C_7H_{22}N_2OB_2$: C, 48.91; H, 12.90; N, 16.29. Found: C, 49.21; H, 12.35; N, 16.38. Infrared data (cm^{-1}): OH 3470 m, BH 2391 m shoulder, 2347 s, 2300 s, 2260 m shoulder; 1308 w, 1293 m, 1237, 1179, 1135/1125 m doublet, 1095 s (1085 shoulder), 1026 m, 1001 s, 975 s, 956 w, 926 m, 877 m, 857 m, 816 m, 774 m, 734. Mass spectral data: 172, P + 1; 171, P; 169, P − 2. NMR data: ^1H NMe_2 2.68, 2.65, 2.58, 2.56; CH_2OH broad ab-type quartet, 3.18, 3.15, 3.08, 3.04; CH_2 broad triplet 2.18, broad doublet 1.89, 1.85; ^{11}BH 1:1 doublet −5.6 and −6.6 (J_{BH} = 96 Hz); BH_2 1:2:1 triplet −9.0, −10.1, −11.0 (J_{BH} = 96 Hz).

$Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$. A solution of 73 mg (0.42 mmol) of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OH$ in 1 mL of $CHCl_3$ was treated with 0.2 mL of hexamethyldisilazane under nitrogen and allowed to stir overnight. Evaporation of solvent left an oil characterized as $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OSiMe_3$. To this was added 1 mL of $CHCl_3$ containing 0.1 mL of Me_3SiI, and the mixture was allowed to stand overnight. Removal of solvent under vacuum followed by sublimation (80 °C/high vacuum) gave 64 mg, 54%, of $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$ as a cream white solid. NMR data for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OSiMe_3$: ^1H NMe_2 2.61, 2.59, 2.52, 2.50; ^{11}B BH doublet −5.8, −6.7 (J_{BH} = 87 Hz); BH_2 triplet −8.0, −9.0 −10.0 (J_{BH} = 96 Hz). NMR data for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$: ^1H NMe_2 2.87, 2.74, 2.54, 2.43, NCH_2 broad 2.3, 1.65, BCH_2I broad −0.5; ^{11}B unsymmetrical triplet −4.6, −5.9, −6.9 decouples to unsymmetrical doublet −5.3, −6.4. Mass spectral data for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2OSiMe_3$: 1 Gc/Ms peak *m/e* 245 (1%), 244 (3%) parent, 243 (4%) parent − 1; 141 (100%) and 140 (54%), $^{11}B_2$, $^{10}B^{11}B$ $Me_2\overline{NCH_2BH_2NMe_2CH_2B}H^+$. Mass spectral data for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$: one GC peak *m/e* 281 (12.8%) and 280 (6.4%), parent − 1, $^{11}B_2$, $^{10}B^{11}B$ distribution, 155 (100%), 154 (52%) parent − iodine, $^{11}B_2$, $^{10}B^{11}B$. Infrared data (cm^{-1}) for $Me_2\overline{NCH_2BH_2NMe_2CH_2B}HCH_2I$: BH 2445 m, 2362 m doublet with multiplet shoulders, 1402 w, 1295 m, 1191 s, 1171 m, 1120 m, 1093 m, 1024 m, 1003 m, 988 s, 955 m, 878 m, 847 s, 820 w, 749 w, 684 m.

Acknowledgment. Support for this research by a Cottrell College Science Grant (No. C-2595) from the Research Corp. and an in part matching grant from the Future Fund of the State of South Dakota is gratefully acknowledged. NSF grants and matching South Dakota Future Fund grants for GC/MS, NMR, and FTIR instrumentation at the University of South Dakota are also acknowledged. High-resolution mass spectral data were obtained from the Midwest Center for Mass Spectrometry at the Department of Chemistry, University of Nebraska/Lincoln.

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Crystal and Molecular Structure of $(2,2,2\text{-crypt-}K^+)_2Pb_2Te_3^{2-}$

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Received July 20, 1990

Introduction

In a recent publication[3] we reported the preparation of a new family of dilead(II) chalcogenide anions $Pb_2Ch_3^{2-}$ (Ch = Se, Te) by extraction of the appropriate ternary or quaternary Zintl phases $KPb_{0.5}Se_{1-x}Te_x$ (where $x \approx 0.3$ or 0.71) with ethylenediamine (en) in the presence of 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) and their characterization in solution by ^{207}Pb, ^{125}Te, and ^{77}Se NMR spectroscopy and by the X-ray analysis of a representative example, $(2,2,2\text{-crypt-}K^+)_2Pb_2Se_3^{2-}$. The NMR findings showed that the structures of the anions are all based upon a trigonal-bipyramidal structure[5] having axial Pb atoms bonded to three chalcogen atoms in the equatorial plane. Moreover, after the nuclear dependence had been removed and allowances for relativistic effects had been applied to the observed coupling constants $^1J(^{207}Pb-^{125}Te)$ and $^1J(^{207}Pb-^{77}Se)$ to give relativistically corrected reduced coupling constants $^1K_{RC}$, it was proposed that the effects of increasing Te substitution in the series $Pb_2Se_{3-n}Te_n^{2-}$ (n = 0–3) was additive and that the structure of the $Pb_2Te_3^{2-}$ anion would be "flatter" than that of the $Pb_2Se_3^{2-}$ anion with angles Se–Pb–Se < Te–Pb–Te and Pb–Se–Pb > Pb–Te–Pb.

In the present note, the structure of $(2,2,2\text{-crypt-}K^+)_2Pb_2Te_3^{2-}$ has been determined by X-ray crystallography at room temperature. The structures of the $Pb_2Te_3^{2-}$ and $Pb_2Se_3^{2-}$ anions are

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Table I

Positional Parameters and Their Estimated Standard Deviations for $(2,2,2\text{-crypt-K}^+)_2Pb_2Te_3^{2-}$

atom	x	y	z	B_{eq}, Å$^{2\,a}$
Pb(1)	0.0000	0.0000	0.17580 (9)	7.85 (3)
Te	0.0000	0.2075 (2)	0.2500	13.14 (8)
K(1)	0.3333	0.6666	0.9518 (3)	3.28 (8)
N(11)	0.3333	0.6666	0.820 (1)	4.4 (5)*
C(12)	0.453 (2)	0.672 (2)	0.7969 (8)	5.5 (4)*
C(13)	0.498 (2)	0.596 (2)	0.8303 (8)	4.8 (4)*
O(14)	0.5178 (9)	0.6219 (9)	0.8933 (5)	4.0 (2)*
C(15)	0.638 (2)	0.739 (2)	0.9089 (8)	5.4 (4)*
C(16)	0.661 (2)	0.734 (1)	0.9759 (8)	4.7 (4)*
O(17)	0.5660 (9)	0.7468 (8)	1.0091 (4)	3.3 (2)*
C(18)	0.563 (2)	0.716 (2)	1.0726 (7)	4.4 (4)*
C(19)	0.469 (1)	0.743 (1)	1.1080 (6)	4.2 (3)*
N(110)	0.3333	0.6666	1.086 (1)	3.4 (4)*

General Temperature Factor Expressions (B's, Å^2)^b

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{eq}
Pb(1)	6.27 (4)	B_{11}	9.5 (1)	$-B_{11}/2$	0	0	7.85 (3)
Te	15.0 (1)	2.71 (5)	20.1 (2)	$-B_{22}/2$	−111 (1)	0	13.14 (8)
K(1)	3.0 (1)	B_{11}	2.9 (2)	$-B_{11}/2$	0	0	3.28 (8)

Root-Mean-Square Amplitudes of Thermal Vibrations (Å)

atom	min	intmed	max
Pb(1)	0.261	0.332	0.347
Te	0.151	0.268	0.636
K(1)	0.178	0.190	0.238

[a] Starred values indicate atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter B_{eq} defined as $(4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. [b] The form of the anisotropic thermal parameter is $\exp[-0.25(h^2a^2B_{11} + k^2b^2B_{22} + l^2c^2B_{33} + 2hkabB_{12} + 2hlacB_{13} + 2klbcB_{23})]$ where a, b, and c are reciprocal lattice constants.

consistent with the trends previously predicted on the basis of solution NMR data.[3]

Experimental Section

An ethylenediamine solution of the title material was prepared from $KPb_{0.65}Te$ and 2,2,2-crypt as has already been described.[3] Crystalline material formed in the NMR sample over a period of several weeks. The mother liquor was decanted, and crystals were dried under dynamic vacuum. The large well-formed dark red crystals were cleaved into smaller fragments and sealed in 0.2–0.3-mm Lindemann glass capillaries in a dry (<1 ppm), nitrogen-filled drybox equipped with a microscope. Further work was done on an Enraf-Nonius CAD4 diffractometer and a plate-shaped crystal, bound by the forms {001} and {100} and faces (012), $(01\bar{2})$, $(\bar{1}1\bar{2})$, $(\bar{1}12)$, and $(1\bar{2}1)$, 0.0056, 0.0152, 0.0080, 0.0080, 0.0080, 0.0080, and 0.0068 cm from an origin within the crystal. Least-squares refinement of the diffracting positions of 25 reflections ($9.5° < \theta < 17.6°$) using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) indicated that the title compound crystallizes in the centric trigonal space group $P\bar{3}c1$ (No. 165) with $a = 11.828$ (3) Å, $c = 21.889$ (4) Å, $V = 2650$ Å^3, $D_x = 2.30$ g cm^{-3} for $Z = 2$, and $F(000) = 1540$.

Intensity data was collected by the use of ω–2θ scans over $(0.65 + 0.35 \tan\theta)°$ and scan rates were chosen to give $I/\sigma(I) \geq 25$ within a maximum scan time of 52 s. In initial work it was apparent that throughout the data set reflections $hkil$ with $l = 2n$ were much stronger than those with $l = 2n + 1$, and thus, since absorption effects and space group assignments would also be better with extra data available, all 10717 reflections (including standards) in the octants $h,\pm k,\pm l$ with $2\theta \leq 52°$ were measured. Three standard reflections collected after every 6200 s of exposure time showed some slight losses in intensities.

Lorentz, polarization, and, at a later stage in the refinements, absorption corrections (program ABSCOR, $\mu = 82.2$ cm^{-1}, 12 × 8 × 6 grid, above crystal faces, range of transmission coefficients 0.340–0.527) were applied to all the collected data. With $Z = 2$, both the expected $Pb_2Te_3^{2-}$ anion and 2,2,2-crypt-K$^+$ moieties have at least crystallographic symmetry 3. However, $N(Z)$ tests and the program NORMAL did not give a clear distinction between the experimental and theoretical centric/acentric E distributions.[4] A solution in the acentric space group $P3c1$, however, was attempted since, after rejecting 2575 systematically absent $h\bar{k}0l$ and zero F_o data, the merging index [$R_{int}(F) = 0.067$] when subsequently averaging 4511 symmetry-equivalent reflections was better than that in $P\bar{3}c1$ ($R_{int} = 0.091$ for 6108 symmetry-equivalent data—but 269 reflections were also omitted during this calculation as being too dissimilar in intensity). However, least-squares refinements gave high temperature factors for the two Pb atoms on the 3-fold axis and the Te atom on the general position 6(d). Introduction of anisotropic thermal parameters for these atoms markedly improved the crystallographic residual, since the anisotropy of the three heavy atoms is quite extreme. Similar effects have been observed for the isostructural $Pb_2Se_3^{2-}$ anion, which crystallizes in a monoclinic space group with a long b axis.[3] However, there was not a large difference in the refinement of the alternative orientation of the structure with respect to the polar z axis[5] although some thermal parameters of opposite ends of the crypt entities were more equivalent in one refinement compared to the other. Moreover, convergence in the least-squares refinement was slow, since an origin shift in Z meant that many of the atoms were approximately centrosymmetrically related. An exception was Te, which was slightly displaced from position 6(f) with 2-fold symmetry in $P\bar{3}c1$. Nonetheless, reaveraging of the absorption-corrected data [$R_{int} = 0.080$ for 6100 symmetry-equivalent data—but fewer (133) reflections were omitted during the calculation (cf. above)] and shifting the atoms to correspond to space group $P\bar{3}c1$ gave improved residuals, and refinement was normal although the Te and Pb atoms still had significant anisotropic thermal parameters. (Root-mean-square displacements for the anisotropic atoms are given in Table I.)

In the final cycles of the full-matrix least-squares refinement minimizing $\sum w\Delta F^2$, anisotropic thermal parameters were introduced for the Pb, Te, and K atoms and H atoms in the crypt moieties were placed in calculated positions with fixed temperature factors ($U_H = 0.07$ Å^2) and then converged (max $\Delta/\sigma = 0.10$) to final residuals R (R_w) = 0.068 (0.103) for 686 observed [$I \geq 3\sigma(I)$] reflections. Weights were given by $w = 4F^2[\sigma^2(I) + (0.11F^2)^2]^{-1}$, and at convergence, S was 1.54. A final difference Fourier contained residual peaks of heights 2.20 e Å^{-3} close to the Pb atoms, somewhat high presumably due to the anisotropy of these atoms, reflecting some unresolved static disorder of the anion. Scattering factors were taken from ref 6.

The final atomic positional and thermal parameters are given in Table I. Tables of bond lengths and bond angles in the 2,2,2-crypt-K$^+$ cation and final structure factor amplitudes have been deposited as supplementary material.

Results and Discussion

Crystals of $(2,2,2\text{-crypt-K}^+)_2Pb_2Te_3^{2-}$ consist of discrete cryptated potassium ions and "flattened" trigonal-bipyramidal $Pb_2Te_3^{2-}$ anions with crystallographic symmetries 3 and 32, respectively. As expected on the basis of the previous NMR

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(6) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

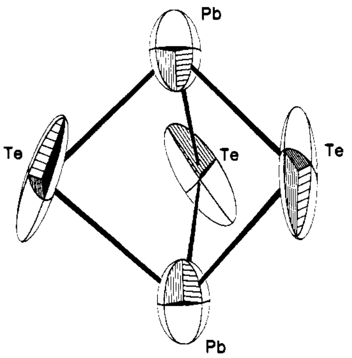

Figure 1. ORTEP view of the $Pb_2Te_3^{2-}$ anion. Ellipsoids are drawn at the 50% probability level.

studies,[3] the $Pb_2Te_3^{2-}$ anion is isostructural with the previously determined $Pb_2Se_3^{2-}$ anion, and their structural differences are in agreement with those proposed.[3] Thus, in the $Pb_2Te_3^{2-}$ anion the Pb–Te distance is 2.943 (2) Å, compared with an average Pb–Se bond length of 2.751 Å in $Pb_2Se_3^{2-}$, while the Te–Pb–Te angles [92.46 (4)° × 6] are significantly larger than the corresponding Se–Pb–Se bond angles [average 89.8 [15]°; range 87.1 (2)–92.4 (1)°] and the Pb–Te–Pb bond angles [67.01 (6)° × 3] correspondingly smaller than the analogous Pb–Se–Pb angles [70.4 (1)–70.9 (1)°]. However, the equatorial Te···Te contacts (4.25 Å) in $Pb_2Te_3^{2-}$ are slightly longer than van der Waals distances (4.12 Å)[7] by amounts very similar to those by which the Se···Se contacts in the $Pb_2Se_3^{2-}$ anion (3.81, 3.89, and 3.95 Å) exceed the Se van der Waals limit (3.8 Å). Finally, the Pb(1)···Pb(1′) distance (3.249 (2) Å) is again significantly less than the approximate van der Waals distances (4.0 Å) but is longer than the corresponding distance in the $Pb_2Se_3^{2-}$ anion (3.184 (3) Å).

Few Pb–Te distances have been reported. Distances of 3.06 and 3.31 Å have been mentioned for the compound $PbBi_4Te_7$,[8] but no values in covalent species are known. The present distances are, however, substantially longer than the Pb(IV)–Te single-bond distance (2.81 Å) and are significantly longer than the Pb(II)–Te single-bond distance (2.86 Å) if the Te covalent radius of 1.32 Å given by Bondi[7] is utilized. However, the Pb-Te distance is in good agreement with the sum of the Te covalent radius (1.37 Å) and the metallic radius of Pb(II) (1.54 Å) of 2.97 Å as given by Pauling.[9] Likewise, the Pb–Se distances in the $Pb_2Se_3^{2-}$ anion correspond resonably well to the sum of the Se covalent radius (1.17 Å) and that of Pb(II) (1.54 Å) to give a value of 2.71 Å. The angle trends between the two anions $Pb_2Se_3^{2-}$, namely, Se–Pb–Se < Te–Pb–Te and Pb–Se–Pb > Pb–Te–Pb, can be rationalized from the electronegativity difference between Se and Te. As one would expect from the VSEPR rules[10] the Ch–Pb–Ch bond angle decreases and the corresponding Pb–Ch–Pb bond angle increases with the more electronegative chalcogen atom. Moreover, as Sanderson[11] has pointed out, the "inert-pair" effect has a substantial effect on electronegativity. Thus, whereas the electronegativities of Ge(IV), Sn(IV), and Pb(IV) are 2.62, 2.30, and 2.29, respectively, those of Ge(II), Sn(II), and Pb(II) are only 0.56, 1.49, and 1.92, respectively. This means that Pb(II) compounds are more polar than corresponding inorganic Pb(IV) compounds. As mentioned in the Introduction, the bond angle trends in the $Pb_2X_3^{2-}$ anions were readily apparent in the relativistically corrected reduced coupling constants $^1K_{RC}$ for these two species in solution.[3] For a fuller discussion of the bonding in the $Pb_2Ch_3^{2-}$ species and their comparisons to related structures, the reader is referred to ref 3, except that we wish to mention here the structural parameters for two other trigonal-bipyramidal molecules, $[(C_6F_5)_2Ge]_3Bi_2$[12] and $(t\text{-}BuO)_3Sn^{II}Tl^{I}$,[13] the former because the Bi···Bi separation of 4.005 Å in this compound is normal and considerably longer than that in $Bi_2[W(CO)_5]_3$.[14] However, in the $Sn^{II}Tl^{I}$ species the Sn···Tl separation of 3.306 (3) Å was considered relatively short.

In the (2,2,2-crypt-K^+) moieties, the K···N and K···O distances are 2.75 (2)–2.99 (4) Å.

Acknowledgments. The Natural Sciences and Engineering Research Council of Canada is thanked for providing operating grants (G.J.S.) and an equipment grant for the X-ray diffractometer (Chemistry Department, University of Toronto), and McMaster University and the Ontario Ministry of Colleges and Universities are acknowledged for the award of a fellowship and scholarships, respectively, to M.B.

Supplementary Material Available: Tables of crystal data and refinement results, complete bond lengths and bond angles, and positional parameters for the hydrogen atoms (5 pages); a listing of final structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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Models of Photosynthetic Chromophores. Molecular Structure of the Bacteriochlorin (2,3,12,13-Tetrahydro-5,10,15,20-tetraphenylporphinato)(pyridine)zinc(II)

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Received November 27, 1990

Recent X-ray studies of antenna[1] and reaction center[2] bacteriochlorophyll (BChl) proteins have elicited avid experimental and theoretical interest in the physical and chemical properties of bacteriochlorins, both to rationalize photosynthetic light harvesting and energy transduction and to model the efficient and rapid charge separation carried out by photosynthetic organisms.[3] In a different context, the successful use of porphyrin derivatives in phototherapy has prompted a search for chromophores that absorb at longer wavelengths than porphyrins themselves to allow deeper tissue penetration of incident light.[4]

Besides the low structural resolution of the chromophores inherent to BChl proteins,[1,2] few X-ray structures of the generic class of bacteriochlorins exist to guide experimental and theoretical studies. Indeed, only three high-precision structures of bacteriochlorins have been reported to date: a free base[5,6] and a nickel[7]

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