# Bimetallic Borate Derivatives of the Salen Ligands

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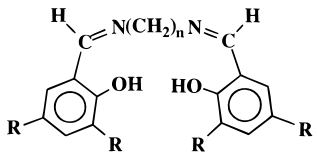
A series of bimetallic borate derivatives of the Salen ligands have been prepared. They are of the general formula Salen{$B(OR)_2$}$_2$ (where Salen = (*N*,*N*′-1,*n*-alkylenebis(salicylideneimine); alkylene = ethylene [R = Me (**1**), Et (**6**)], propylene [Me (**2**), Et (**7**)], butylene [Me (**3**), Et (**8**)], pentylene [Me (**4**), Et (**9**)], and hexylene [Me (**5**), Et (**10**)]) and the analogous Salen($^t$Bu) derivatives (where Salen($^t$Bu) = *N*,*N*′-1,*n*-alkylenebis(3,5-di-*tert*-butylsalicylideneimine); alkylene = ethylene [R = Me (**11**), Et (**16**)], propylene [Me (**12**), Et (**17**)], butylene [Me (**13**), Et (**18**)], pentylene [Me (**14**), Et (**19**)], and hexylene [Me (**15**), Et (**20**)]). All of the compounds were characterized by spectroscopic ($^1$H NMR, IR) and physical (mp, analyses) techniques. X-ray crystallographic data are presented for **1**, **4**, **7**, **10**, **12**, and **16**. Differences among these structures were found to be dependent upon the length of the ligand alkylene "backbone".

## Introduction

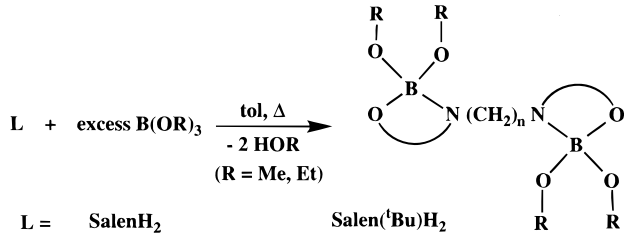
The Salen class of ligands has been used extensively to support transition metal bonding schemes[1] and to a much lesser extent those of the main group elements.[2] Some group 13 examples include those incorporating aluminum[3] and gallium[4] alkyls, aluminum alkoxides,[5] and aluminum cations.[6] These are primarily monomeric and monometallic and, in rare instances, bimetallic. Since the first reported bimetallic derivative, Salpen-$(GaMe_2)_2$, was formed under forcing conditions,[4] it appeared that bimetallic derivatives would be difficult to obtain. Recent attempts to prepare such complexes with indium lead to the isolation of dimeric methoxide derivatives and one unique complex having a ligand:metal stoichiometry of 3:2.[7] These were distinctive when compared to the related aluminum and gallium Salen complexes. Since going to a larger group 13 element produced unusual products, it seemed likely that using the lightest member of the group 13 elements, boron, might also reveal some unique chemistry. Moreover, it had previously been demonstrated that azomethines form boron chelate complexes.[8] Furthermore, the isolation of such boron derivatives might lead to their subsequent use in important catalytic applications such as has been demonstrated for chelated aluminum.[6a]




| | R = H | $^t$Bu |
|---|---|---|
| n = 2 | $SalenH_2$ | $Salen(^tBu)H_2$ |
| = 3 | $SalpenH_2$ | $Salpen(^tBu)H_2$ |
| = 4 | $SalbenH_2$ | $Salben(^tBu)H_2$ |
| = 5 | $SalptenH_2$ | $Salpten(^tBu)H_2$ |
| = 6 | $SalhenH_2$ | $Salhen(^tBu)H_2$ |

**Figure 1.** Depiction of the $SalenH_2$ and Salen($^t$Bu)$H_2$ ligands.

**Scheme 1.** General Syntheses of the Bimetallic Borate Derivatives **1**−**20**




| L = | $SalenH_2$ | Salen($^t$Bu)$H_2$ |
|---|---|---|
| | n = 2; R = Me (1), Et (6) | n = 2; R = Me (11), Et (16) |
| | n = 3; R = Me (2), Et (7) | n = 3; R = Me (12), Et (17) |
| | n = 4; R = Me (3), Et (8) | n = 4; R = Me (13), Et (18) |
| | n = 5; R = Me (4), Et (9) | n = 5; R = Me (14), Et (19) |
| | n = 6; R = Me (5), Et (10) | n = 6; R = Me (15), Et (20) |

The present work will detail the successful syntheses of a series of bimetallic boron derivatives supported by two types of Salen ligands. These represent the majority of known bimetallic group 13 complexes of these ligands. The primary and secondary structures of the complexes are dictated by intermolecular hydrogen bonding and the length of the ligand backbone.

## Results and Discussion

**Synthesis and Characterization.** The bimetallic borates are prepared by combining the ligand with an excess of the respective boron reagent in toluene (Scheme 1). The compounds are soluble and can be isolated in reasonable yields by precipitation after concentration of the solution or crystallization after cooling to −30 °C for a few days. Those prepared with the underivatized Salen ligands are less soluble than those

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**Table 1.** Selected $^1$H NMR Data for Compounds **1**−**20**[a]

| compd | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** |
|---|---|---|---|---|---|---|---|---|---|---|
| BO*R* | 3.30 (s) | 3.23 (s) | 3.21 (s) | 3.18 (s) | 3.21 (s) | 1.19 (m)<br>3.50 (m)<br>3.59 (m) | 1.19 (m)<br>3.23 (m)<br>3.47 (m) | 1.15 (m)<br>3.30 (m)<br>3.44 (m) | 1.15 (m)<br>3.29 (m)<br>3.44 (m) | 1.13 (m)<br>3.27 (m)<br>3.44 (m) |
| N=C*H* | 8.40 (s) | 8.40 (s) | 8.27 (s) | 8.21 (s) | 8.25 (s) | 8.51 (s) | 8.38 (s) | 8.23 (s) | 8.22 (s) | 8.20 (s) |
| compd | **11** | **12** | **13** | **14** | **15** | **16** | **17** | **18** | **19** | **20** |
| BO*R* | 3.29 (s) | 3.27 (s) | 3.22 (s) | 3.22 (s) | 3.22 (s) | 1.15 (m)<br>3.45 (m)<br>3.62 (m) | 1.11 (m)<br>3.26 (m)<br>3.51 (m) | 1.12 (m)<br>3.29 (m)<br>3.50 (m) | 1.12 (m)<br>3.25 (m)<br>3.48 (m) | 1.12 (m)<br>3.24 (m)<br>3.45 (m) |
| N=C*H* | 8.34 (s) | 8.38 (s) | 8.18 (s) | 8.18 (s) | 8.18 (s) | 8.47 (s) | 8.38 (s) | 8.16 (s) | 8.16 (s) | 8.14 (s) |
| Ph−$^t$Bu | 1.22 (s)<br>1.45 (s) | 1.24 (s)<br>1.47 (s) | 1.27 (s)<br>1.45 (s) | 1.27 (s)<br>1.42 (s) | 1.28 (s)<br>1.43 (s) | 1.22 (s)<br>1.44 (s) | 1.24 (s)<br>1.42 (s) | 1.27 (s)<br>1.44 (s) | 1.27 (s)<br>1.43 (s) | 1.29 (s)<br>1.42 (s) |

[a] Samples were run in $CDCl_3$ at 270 MHz. The terms "s" and "m" refer to peaks that are singlets and multiplets, respectively.

**Table 2.** Selected Bond Distances (Å) and Angles (deg) for **1**, **4**, **7**, **10**, **12**, and **16**

Salen[B(OMe)$_2$]$_2$ (**1**)

| | | | |
|---|---|---|---|
| B(1)−N(1) | 1.615(2) | B(1)−O(1) | 1.495(2) |
| B(1)−O(2) | 1.426(2) | B(1)−O(3) | 1.417(2) |
| N(1)−B(1)−O(1) | 106.7(1) | N(1)−B(1)−O(2) | 102.8(1) |
| O(1)−B(1)−O(2) | 113.2(1) | N(1)−B(1)−O(3) | 111.3(1) |
| O(1)−B(1)−O(3) | 109.9(1) | O(2)−B(1)−O(3) | 112.7(1) |
| B(1)−N(1)−C(1) | 118.7(1) | B(1)−N(1)−C(2) | 121.8(1) |
| B(1)−O(1)−C(8) | 123.5(1) | B(1)−O(2)−C(9) | 117.8(1) |
| B(1)−O(3)−C(10) | 120.1(1) | | |

Salpten[B(OMe)$_2$]$_2$ (**4**) (One Molecule Only)

| | | | |
|---|---|---|---|
| B(1)−O(1) | 1.413(8) | B(1)−O(2) | 1.442(8) |
| B(1)−O(5) | 1.475(8) | B(1)−N(1) | 1.622(8) |
| B(2)−O(4) | 1.414(8) | B(2)−O(3) | 1.430(8) |
| B(2)−O(6) | 1.486(7) | B(2)−N(2) | 1.607(7) |
| O(1)−B(1)−O(2) | 106.6(5) | O(1)−B(1)−O(5) | 112.6(5) |
| O(2)−B(1)−O(5) | 112.3(5) | O(1)−B(1)−N(1) | 110.1(5) |
| O(2)−B(1)−N(1) | 108.6(5) | O(5)−B(1)−N(1) | 106.6(4) |
| O(4)−B(2)−O(3) | 106.4(5) | O(4)−B(2)−O(6) | 114.4(5) |
| O(3)−B(2)−O(6) | 110.0(5) | O(4)−B(2)−N(2) | 108.7(5) |
| O(3)−B(2)−N(2) | 110.5(5) | O(6)−B(2)−N(2) | 106.9(4) |
| C(17)−N(2)−B(2) | 122.9(5) | C(16)−N(2)−B(2) | 115.7(4) |
| C(11)−N(1)−B(1) | 123.3(5) | C(12)−N(1)−B(1) | 120.4(4) |
| B(1)−O(1)−C(1) | 117.4(5) | C(2)−O(2)−B(1) | 117.7(5) |
| C(3)−O(3)−B(2) | 118.6(5) | C(4)−O(4)−B(2) | 119.2(5) |
| C(5)−O(5)−B(1) | 126.2(4) | C(23)−O(6)−B(2) | 123.0(4) |

Salpen[B(OEt)$_2$]$_2$ (**7**)

| | | | |
|---|---|---|---|
| B(1)−O(1) | 1.409(6) | B(1)−O(2) | 1.435(6) |
| B(1)−O(5) | 1.480(6) | B(1)−N(1) | 1.616(6) |
| B(2)−O(3) | 1.410(6) | B(2)−O(4) | 1.421(5) |
| B(2)−O(6) | 1.478(6) | B(2)−N(2) | 1.623(5) |
| O(1)−B(1)−O(2) | 113.0(4) | O(1)−B(1)−O(5) | 110.7(4) |
| O(2)−B(1)−O(5) | 112.9(4) | O(1)−B(1)−N(1) | 111.4(4) |
| O(2)−B(1)−N(1) | 102.8(4) | O(5)−B(1)−N(1) | 105.5(4) |
| O(3)−B(2)−O(4) | 107.1(4) | O(3)−B(2)−O(6) | 112.7(4) |
| O(4)−B(2)−O(6) | 112.8(4) | O(3)−B(2)−N(2) | 108.4(4) |
| O(4)−B(2)−N(2) | 108.8(3) | O(6)−B(2)−N(2) | 106.8(3) |
| B(1)−O(1)−C(1) | 120.8(4) | C(3)−O(2)−B(1) | 118.4(4) |
| B(2)−O(3)−C(5) | 117.6(4) | C(7)−O(4)−B(2) | 118.1(4) |
| C(9)−O(5)−B(1) | 120.0(4) | C(21)−O(6)−B(2) | 126.9(3) |
| C(15)−N(1)−B(1) | 119.7(4) | C(16)−N(1)−B(1) | 121.1(4) |
| C(19)−N(2)−B(2) | 122.7(4) | C(18)−N(2)−B(2) | 117.6(4) |

Salhen[B(OEt)$_2$]$_2$ (**10**) (One Molecule Only)

| | | | |
|---|---|---|---|
| B(1)−O(3) | 1.41(2) | B(1)−O(2) | 1.42(2) |
| B(1)−O(1) | 1.49(1) | B(1)−N(1) | 1.62(2) |
| B(2)−O(4) | 1.40(2) | B(2)−O(5) | 1.38(2) |
| B(2)−O(4) | 1.50(2) | B(2)−N(2) | 1.61(2) |
| O(3)−B(1)−O(2) | 107.0(14) | O(3)−B(1)−O(1) | 112(2) |
| O(2)−B(1)−O(1) | 110.8(14) | O(3)−B(1)−N(1) | 112.4(13) |
| O(2)−B(1)−N(1) | 110(2) | O(1)−B(1)−N(1) | 105.0(13) |
| O(6)−B(2)−O(5) | 109.8(14) | O(5)−B(2)−O(4) | 113.1(13) |
| O(6)−B(2)−O(4) | 111(2) | O(5)−B(2)−N(2) | 110.6(14) |
| O(6)−B(2)−N(2) | 107.9(12) | O(4)−B(2)−N(2) | 104.0(12) |
| C(11)−N(1)−B(1) | 125.5(13) | C(12)−N(1)−B(1) | 114.5(13) |
| C(18)−N(2)−B(2) | 125.9(13) | C(17)−N(2)−B(2) | 116.9(13) |
| C(5)−O(1)−B(1) | 127.0(13) | C(24)−O(4)−B(2) | 127.9(12) |
| C(3)−O(2)−B(1) | 119.3(14) | C(1)−O(3)−B(1) | 122.2(2) |
| C(25)−O(5)−B(2) | 118.1(13) | C(27)−O(6)−B(2) | 119.7(14) |

Salpen($^t$Bu)[B(OMe)$_2$]$_2$ (**12**)

| | | | |
|---|---|---|---|
| B(1)−O(3) | 1.411(7) | B(1)−O(4) | 1.414(7) |
| B(1)−O(1) | 1.498(7) | B(1)−N(1) | 1.600(7) |
| B(2)−O(6) | 1.416(11) | B(2)−O(5) | 1.448(10) |
| B(2)−O(2) | 1.463(9) | B(2)−N(2) | 1.578(8) |
| O(3)−B(1)−O(4) | 112.0(5) | O(3)−B(1)−O(1) | 111.1(4) |
| O(4)−B(1)−O(1) | 111.4(5) | O(3)−B(1)−N(1) | 106.2(5) |
| O(4)−B(1)−N(1) | 109.6(4) | O(1)−B(1)−N(1) | 106.4(4) |
| O(6)−B(2)−O(5) | 109.3(7) | O(6)−B(2)−O(2) | 112.1(6) |
| O(5)−B(2)−O(2) | 111.3(7) | O(6)−B(2)−N(2) | 109.4(6) |
| O(5)−B(2)−N(2) | 104.6(6) | O(2)−B(2)−N(2) | 109.9(5) |
| C(19)−N(1)−B(1) | 123.4(4) | C(20)−N(1)−B(1) | 117.1(4) |
| C(23)−N(2)−B(2) | 120.5(5) | C(22)−N(2)−B(2) | 116.3(5) |
| C(5)−O(1)−B(1) | 126.2(4) | C(37)−O(2)−B(2) | 126.3(4) |
| C(1)−O(3)−B(1) | 116.1(5) | C(2)−O(4)−B(1) | 119.4(5) |
| C(3)−O(5)−B(2) | 128.7(6) | C(4)−O(6)−B(2) | 116.1(5) |

Salen($^t$Bu)[B(OEt)$_2$]$_2$ (**16**)

| | | | |
|---|---|---|---|
| B(1)−O(2) | 1.42(2) | B(1)−O(1) | 1.42(2) |
| B(1)−O(5) | 1.485(14) | B(1)−N(1) | 1.60(2) |
| B(2)−O(4) | 1.419(14) | B(2)−O(3) | 1.421(14) |
| B(2)−O(6) | 1.508(14) | B(2)−N(2) | 1.572(14) |
| O(2)−B(1)−O(1) | 112.9(11) | O(2)−B(1)−O(5) | 111.0(12) |
| O(1)−B(1)−O(5) | 112.8(12) | O(2)−B(1)−N(1) | 110.9(12) |
| O(1)−B(1)−N(1) | 103.5(11) | O(5)−B(1)−N(1) | 105.2(9) |
| O(4)−B(2)−O(3) | 113.0(10) | O(4)−B(2)−O(6) | 108.7(11) |
| O(3)−B(2)−O(6) | 111.2(10) | O(4)−B(2)−N(2) | 105.3(11) |
| O(3)−B(2)−N(2) | 111.0(11) | O(6)−B(2)−N(2) | 107.2(9) |
| C(1)−O(1)−B(1) | 118.6(9) | C(3)−O(2)−B(1) | 122.1(10) |
| C(5)−O(3)−B(2) | 117.1(9) | C(7)−O(4)−B(2) | 119.6(9) |
| C(9)−O(5)−B(1) | 125.5(9) | C(40)−O(6)−B(2) | 127.0(9) |
| C(23)−N(1)−B(1) | 121.1(10) | C(24)−N(1)−B(1) | 120.5(11) |

prepared with the *tert*-butylated version. Attempts to prepare the Salophan (*N*,*N*′-1,2-phenylenebis(salicylideneimine)) and Salomphan (*N*,*N*′-1,2-(4,5-dimethylphenylene)bis(salicylideneimine)) derivatives under similar conditions were not successful. The enforced cis geometry of these two ligands apparently precludes the formation of bimetallic derivatives.

The $^1$H NMR data are fairly consistent throughout the entire series (Table 1). The imine CH resonances appear as singlets in the range $\delta$ 8.14−8.51 ppm. There is no evidence for hydrogen bonding involving this group in solution although there is in the solid state (see below). Likewise, there is, in general, only one set of resonances which can be attributed to the BO*R*

**Table 3.** Data Collection and Processing Parameters for the Bimetallic Borates

| | complex | | | | | |
|---|---|---|---|---|---|---|
| | **1** | **4** | **7** | **10** | **12** | **16** |
| formula | $C_{10}H_{13}NO_{3B}$ | $C_{46}H_{64}N_4O_{12}B_4$ | $C_{25}H_{36}N_2O_6B_2$ | $C_{82}H_{124}B_6N_6O_{18}$ | $C_{40.5}H_{63.5}N_2O_6B_2$ | $C_{40}H_{66}N_2O_6B_2$ |
| fw | 206.0 | 908.25 | 482.18 | 1546.73 | 696.05 | 692.58 |
| color, habit | pale yellow prism | pale yellow block | pale yellow prism | colorless prism | pale yellow block | pale yellow prism |
| cryst size ($mm^3$) | 0.50 × 0.25 × 0.20 | 0.10 × 0.18 × 0.22 | 0.06 × 0.20 × 0.35 | 0.08 × 0.12 × 0.20 | 0.10 × 0.18 × 0.22 | 0.06 × 0.20 × 0.35 |
| cryst system | monoclinic | triclinic | triclinic | triclinic | triclinic | triclinic |
| Space group | $P2_1/n$ | $\bar{P}1$ | $\bar{P}1$ | $\bar{P}1$ | $\bar{P}1$ | $\bar{P}1$ |
| $a$ (Å) | 10.682(1) | 6.199(1) | 8.671(1) | 8.4718(7) | 9.576(1) | 10.474(1) |
| $b$ (Å) | 6.721(1) | 13.885(1) | 13.231(1) | 18.598(2) | 14.950(1) | 11.162(1) |
| $c$ (Å) | 15.549(1) | 28.576(2) | 13.326(1) | 30.832(3) | 15.032(1) | 19.861(2) |
| α (deg) | 90 | 88.97(1) | 109.31(1) | 88.285(3) | 83.53(1) | 81.38(1) |
| $\beta$ (deg) | 109.22(1) | 83.82(1) | 98.54(1) | 82.218(2) | 78.19(1) | 82.56(1) |
| $\gamma$ (deg) | 90 | 77.11(1) | 104.56(1) | 76.892(2) | 87.05(1) | 70.79(1) |
| $V$ ($Å^3$) | 1054.1(1) | 2384.1(3) | 1351.0(2) | 4687.8(7) | 2092.3(3) | 2160.1(4) |
| Z | 4 | 2 | 2 | 2 | 2 | 2 |
| $F$(000) | 436 | 968 | 516 | 1664 | 757 | 760 |
| $D$(calcd) (g $cm^{-3}$) | 1.298 | 1.265 | 1.185 | 1.096 | 1.105 | 1.068 |
| $\mu$ ($mm^{-1}$) | 0.094 | 0.089 | 0.083 | 0.075 | 0.072 | 0.069 |
| $2\theta_{max}$ (deg) | 45 | 45 | 45 | 45 | 45 | 45 |
| unique data measd | 2458 | 5832 | 3289 | 11404 | 3792 | 2623 |
| obsd data | 2158 [$F \geq 4\sigma(F)$] | 5776 [$F \geq 4\sigma(F)$] | 3260 [$F \geq 4\sigma(F)$] | 6942 [$F \geq 4\sigma(F)$] | 3633 [$F \geq 4\sigma(F)$] | 2573 [$F \geq 4\sigma(F)$] |
| no. of variables, | 136 | 595 | 316 | 1027 | 442 | 448 |
| *R1* (%)[a] | 5.08 | 8.18 | 7.19 | 12.65 | 9.67 | 9.06 |
| *R (all data)* (%) | 5.66 | 11.67 | 10.64 | 19.64 | 11.83 | 13.12 |

[a] $R = (\sum \| |F_o| - |F_c| \|)/\sum |F_o|$.

and Ph-$^t$*Bu* groups. This is indicative of a symmetrical solution-state geometry. There is no systematic difference in the spectroscopic data for either the Salen or Salen($^t$Bu) ligands.

**Structural Characterization of 1, 4, 7, 10, 12, and 16.** Selected bond distances and angles for these compounds are listed in Table 2. Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 3. In general, the intramolecular arrangement of the $B(OR)_2$ groups within these structures is trans. The exception to this is the structure of **16** where these groups adopt a cis orientation. In **1** there is a center of symmetry equating the two halves of the molecule (Figure 2a). The B−N (1.615(2) Å) and B−O (chelate) (1.495(2) Å) bond lengths compare closely to other related four-coordinate boron compounds. For instance, these distances in two diarylboroxazolidines average 1.65(5) and 1.477(4) Å, respectively.[9] By comparison, three-coordinate boron complexes of chelating (N,O) ligands demonstrate much shorter B−N distances. This distance in the 2-aminophenol portion of a boronato-functionalized ferrocenylphosphine ligand is 1.428(6) Å.[10] The difference in these values may be partially attributed to an increase in bond distance on going from $sp^2$ (three-coordinate) to $sp^3$ (four-coordinate) hybridization. The B−OMe distances (1.426(2) and 1.417(2) Å) in **1** are somewhat shorter than the B−O(chelate) distance (1.495(2) Å).

The angles around boron approximate tetrahedral. They range in value from 102.8(1)° (N(1)-B(1)-O(2)) to 113.2(1)° (O(1)-B(1)-O(2)). A similar situation is observed for the bond lengths and angles in the structures of **4** (Figure 3, top), **7** (Figure 4, top), **10** (Figure 5, top), and **12** (Figure 6, top). Overall, the B−N and B−O distances do not increase as a consequence of an increase in steric bulk of the alkoxide ligand (Me to Et) or of the chelate (on going from Salen to Salen($^t$Bu)).

The most remarkable intramolecular structural feature of these compounds is displayed in **16** (Figure 7). The cis configuration is observed despite the apparent steric effects of the Ph−$^t$Bu groups. This can be attributed to intramolecular hydrogen bonding between the two imine CH groups and the oxygens of two borate groups. This is unusual since the non-*tert*-butylated derivative, **1** (Figure 2a), adopts the expected trans arrangement and demonstrates *intermolecular* hydrogen bonding. Further-

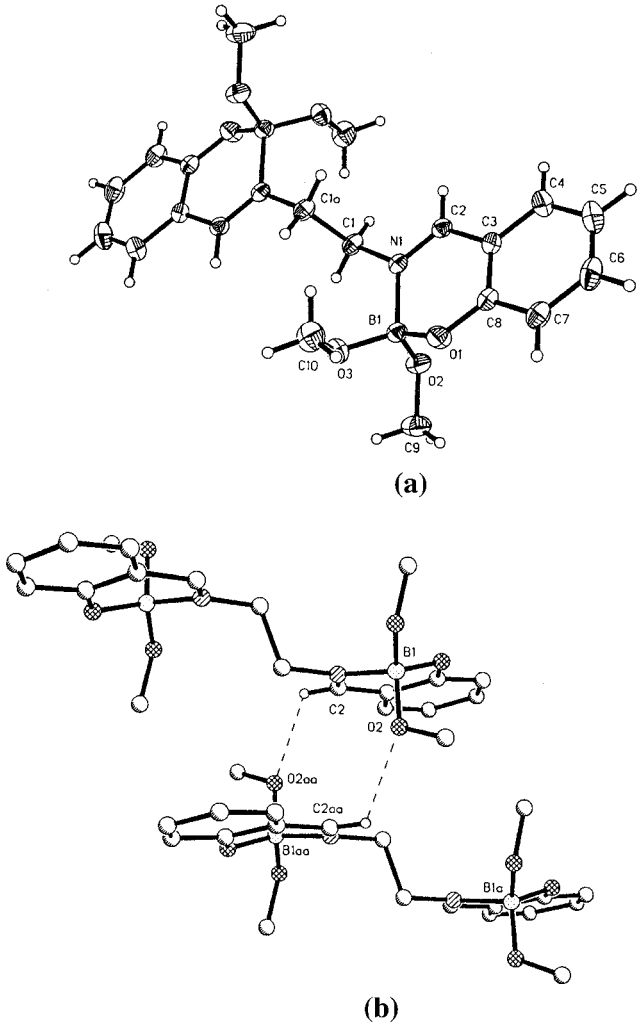


**Figure 2.** Molecular structure and atom-numbering scheme (a) and view of the hydrogen bonding (b) for Salen{$B(OMe)_2$}$_2$ (**1**).

(10) Kimmich, B. F. M.; Landis, C. R.; Powell, D. R. *Organometallics* **1996**, *15*, 4141.
(11) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

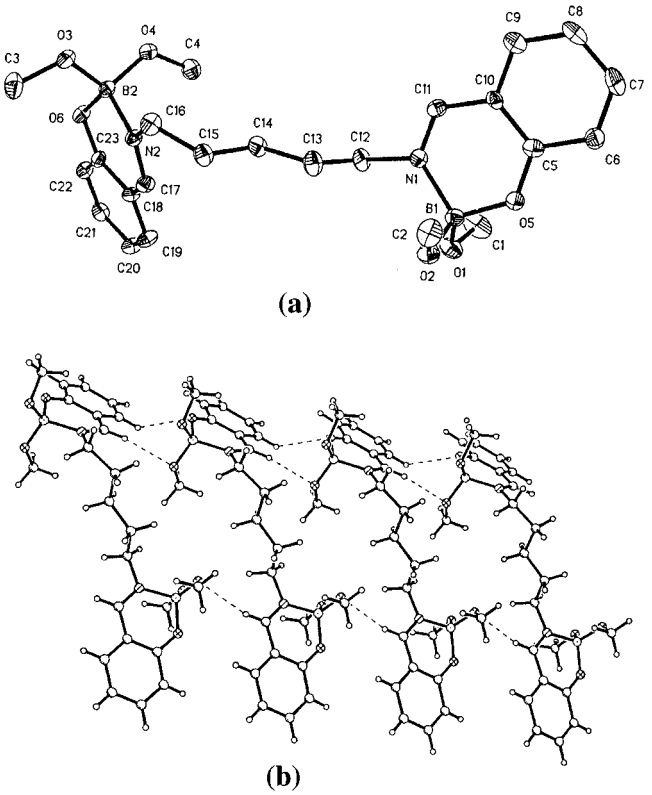


**Figure 3.** Molecular structure and atom-numbering scheme (a) and view of the hydrogen bonding (b) for Salpen{$B(OMe)_2$}$_2$ (**4**).

more, the propyl derivative, **12** (Figure 6b), also possesses intermolecular hydrogen bonding.

Intermolecular hydrogen bonding is a common feature in these molecules and is observed in the solid-state structures of **1**, **4**, **7**, **10**, and **12**. The hydrogen bonding usually occurs between the imine hydrogen (N═CH) and an oxygen of one of the borates. This situation is best exemplified in part of the packing diagram for **1** (Figure 2b). The contact occurs between H2 and O2aa at 2.48 Å. The full packing diagram consists of an infinite array of such molecules. This is also the case for **4** and **10**. In **4** (Figure 3b) the borate−oxygen−imine distances are 2.38 and 2.48 Å, while for **10** (Figure 5b) they are 2.48 Å to one borate oxygen and 2.50 and 2.52 Å to the two borate oxygens. There is also a contact between a Ph−H hydrogen and a ligand−oxygen atom of 2.57 Å for **4** and two such contacts at 2.44 and 2.54 Å for **10**. In **7** (Figure 4b) and **12** (Figure 6b) the imine−borate interaction forms at 2.34 and 2.42 Å, respectively.

The hydrogen atoms in these complexes were placed in ideal positions with a C−H distance of 0.90 Å. Being involved in hydrogen bonding, these distances could conceivably be somewhat longer, but in the absence of neutron diffraction data they cannot be quantitatively determined. However, they are clearly within the sum of the van der Waals radii for hydrogen (1.20 Å) and oxygen (1.50 Å)[11] and in keeping with distances observed in other systems containing such hydrogen bonds.[12]

An additional factor influencing the long-range structures is the length of the backbone in the ligand. As the length increases, the packing diagrams are observed to demonstrate layered structures. For the structures currently available the transition to this type of structure occurs for the pentyl backbone (**4**), which forms a two-dimensional layered structure. The

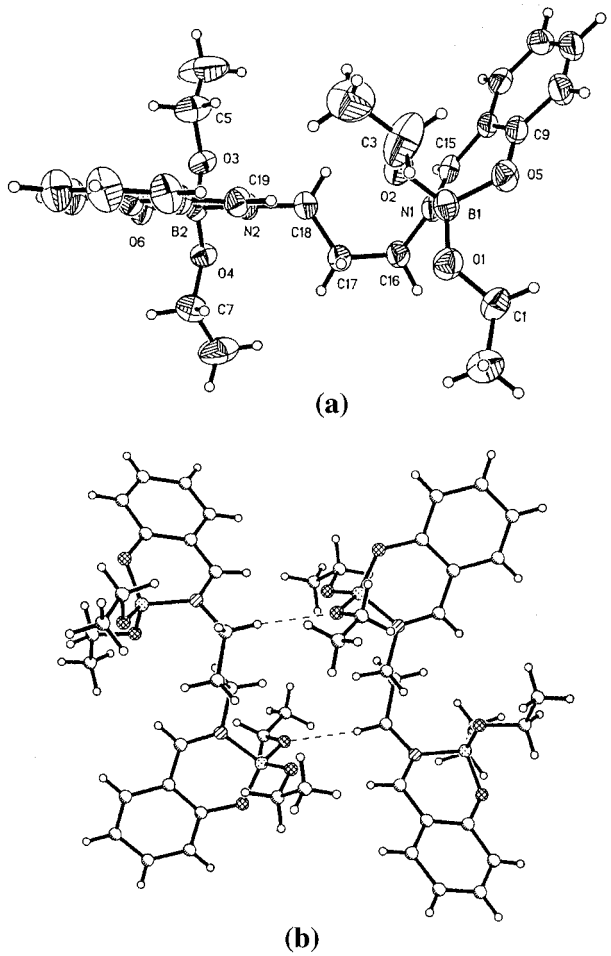


**Figure 4.** Molecular structure and atom-numbering scheme (a) and view of the hydrogen bonding (b) for Salpen{$B(OEt)_2$}$_2$ (**7**).

extreme manifestation of this backbone effect occurs for the hexyl-based ligand (**10**). Each molecule is oriented in an extended trans configuration (Figure 8) which maintains a staggered arrangement for the methylenes making up the backbone. The bimetallic units orient themselves such that the packing diagram consists of an infinite spiral of molecules. Each molecule is arranged normal to the translation of the spiral. Hydrogen bonding in bis(formamides) connected by alkyl chains have been demonstrated to be related to the number of methylenes in the alkyl.[13] Maximal hydrogen bonding was found for even-numbered alkyls. This is apparently not the case for the present compounds as both the pentyl and hexyl derivatives feature extended structures. In order to make definite statements about the trends in hydrogen bonding for these molecules additional structural data will be needed.

## Conclusion

Under the conditions employed in this report, the Salen ligands adopt exclusively bimetallic compounds with boron. The bimetallic nature of these limits their formation to only those ligands possessing an alkyl backbone. For the structurally characterized derivatives the intramolecular bond lengths and angles are fairly consistent (B−N(av) = 1.61(1) Å, B−O (Salen)(av) = 1.47(3) Å, B−OR (av) = 1.42(2) Å). The secondary and long-range structures for these compounds are dependent upon intermolecular hydrogen bonding and to a lesser extent upon the chain length in the ligand backbone. Three

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(13) Chaney, J. D.; Goss, C. R.; Folting, K.; Santarsiero, B. D.; Hollingsworth, M. D. *J. Am. Chem. Soc*. **1996**, *118*, 9432.
(14) Casiraghi, G.; Casnati, G.; Puglia, G.; Sartori, G.; Terenghi, G. *J. Chem. Soc., Perkin Trans*. **1980**, 1862.

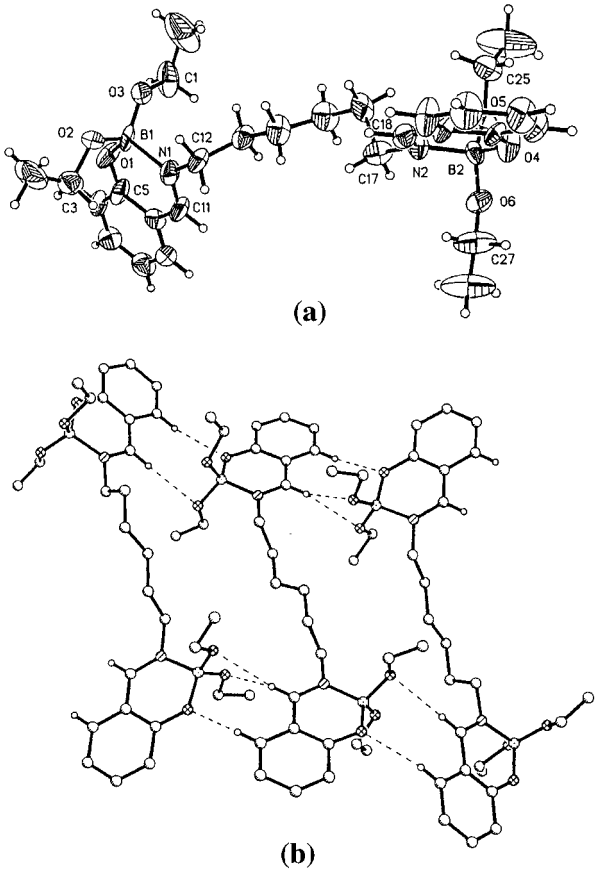


**Figure 5.** Molecular structure and atom-numbering scheme (a) and view of the hydrogen bonding (b) for Salhen{$B(OMe)_2$}$_2$ (**10**).

types of C−H···O hydrogen bonding to a borate oxygen were observed: inter- and intramolecularly with the N=CH group and intermolecularly with a Ph−H group.

## Experimental Section

**General Considerations.** All manipulations were conducted using Schlenk techniques in conjunction with an inert-atmosphere glovebox. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and -270 instruments at 270.17 ($^1$H) and are reported relative to $SiMe_4$ and in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 analyzer and were satisfactory for all compounds. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm$^{-1}$. The reagent 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde was prepared according to the literature.[14] X-ray data for **1** were collected on a Siemens P4 diffractometer while the data for the others were collected on a Siemens SMART-CCD unit. There were two molecules in the independent unit of **4** and three in **10**. Except where indicated pale yellow solids were obtained for the compounds by removal of the solvent following the reaction.

**Synthesis of Salen[$B(OMe)_2$]$_2$ (1).** To a stirred toluene solution (25 mL) of $SalenH_2$ (1.00 g, 3.73 mmol) was added trimethyl borate (1.55 g, 14.92 mmol). The resulting solution was refluxed for 6 h. After filtration and concentration, pale yellow crystals were grown at −30 °C (0.94 g, 61%): mp 157 °C.

**Synthesis of Salpen[$B(OMe)_2$]$_2$ (2).** The procedure was as for **1** with toluene (25 mL), $SalpenH_2$ (1.00 g, 3.54 mmol), and trimethyl borate (1.47 g, 14.17 mmol): Yield 0.72 g, 48%; mp 158−162 °C (dec).

**Synthesis of Salben[$B(OMe)_2$]$_2$ (3).** The procedure was as for **1** with toluene (25 mL), $SalbenH_2$ (1.00 g, 3.37 mmol), and trimethyl borate (1.40 g, 13.50 mmol): Yield, 0.86 g, 58%: mp 169 °C.

**Synthesis of Salpten[$B(OMe)_2$]$_2$ (4).** The procedure was as for **1** with toluene (25 mL), $SalptenH_2$ (1.00 g, 3.22 mmol), and trimethyl borate (1.34 g, 12.90 mmol). After filtration and concentration, pale yellow crystals were grown at −30 °C (0.72 g, 50%); mp 136−140 °C.

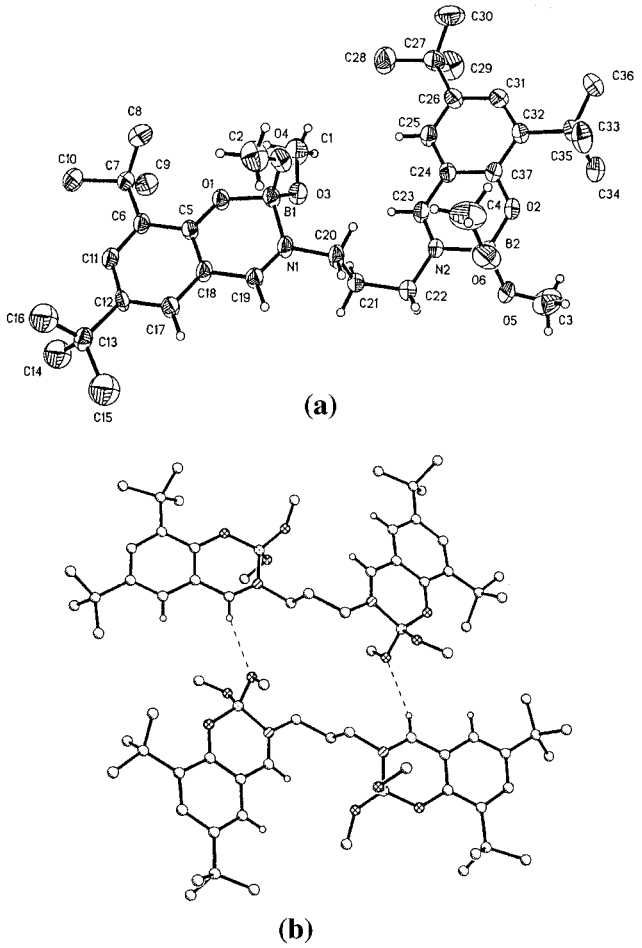


**Figure 6.** Molecular structure and atom-numbering scheme (a) and view of the hydrogen bonding (b) for Salpen($^t$Bu){$B(OMe)_2$}$_2$ (**12**).

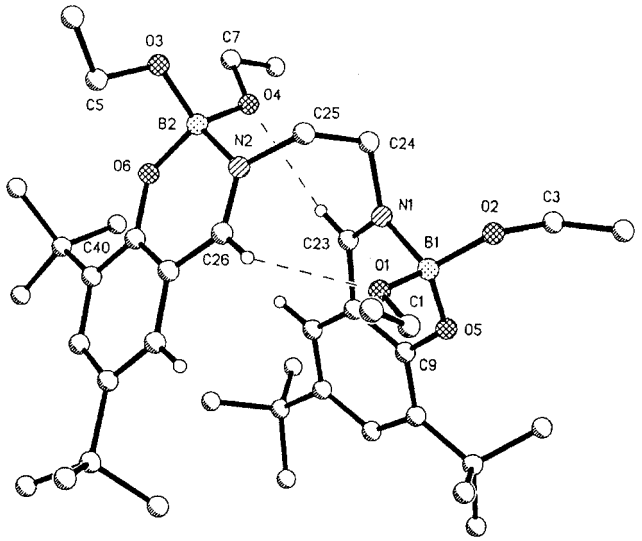


**Figure 7.** Molecular structure and atom-numbering scheme and view of the hydrogen bonding for Salen(tBu){$B(OEt)_2$}$_2$ (**16**).

**Synthesis of Salhen[$B(OMe)_2$]$_2$ (5).** The procedure was as for **1** with toluene (25 mL), $SalhenH_2$ (1.00 g, 3.08 mmol), and trimethyl borate (1.28 g, 12.34 mmol): Yield, 1.21 g, 84%; mp 158 °C.

**Synthesis of Salen[$B(OEt)_2$]$_2$ (6).** The procedure was as for **1** with toluene (25 mL), $SalenH_2$ (1.00 g, 3.73 mmol), and triethyl borate (2.18 g, 14.92 mmol). Yield, 1.3 g, 75%; mp 111−114 °C.

**Synthesis of Salpen[$B(OEt)_2$]$_2$ (7).** The procedure was as for **1** with toluene (25 mL), $SalpenH_2$ (1.00 g, 3.54 mmol), and triethyl borate (2.07 g, 14.17 mmol). After filtration and concentration, pale yellow crystals were grown at −30 °C (0.93 g, 55%); mp 144−147 °C.

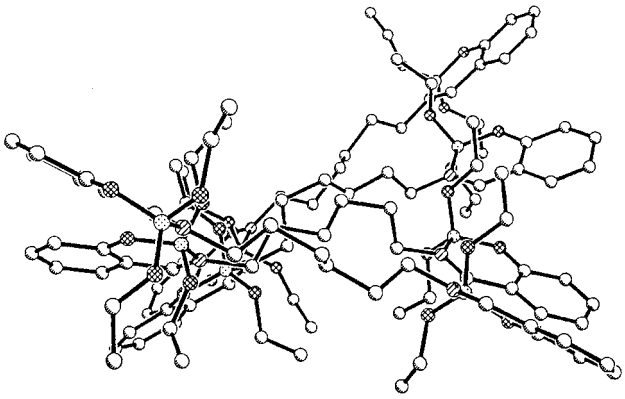

**Figure 8.** Partial packing diagram of **10** showing the staggered arrangement of the molecules.

**Synthesis of Salben[B(OEt)$_2$]$_2$ (8).** The procedure was as for **1** with toluene (25 mL), SalbenH$_2$ (1.00 g, 3.37 mmol), and triethyl borate (1.97 g, 13.50 mmol). Yield, 1.5 g, 90%; mp 170 °C (dec).

**Synthesis of Salpten[B(OEt)$_2$]$_2$ (9).** The procedure was as for **1** with toluene (25 mL), SalptenH$_2$ (1.00 g, 3.22 mmol), and triethyl borate (1.88 g, 12.89 mmol): Yield, 1.2 g, 73%; mp 126 −128 °C.

**Synthesis of Salhen[B(OEt)$_2$]$_2$ (10).** The procedure was as for **1** with toluene (25 mL), SalhenH$_2$ (1.00 g, 3.08 mmol), and triethyl borate (1.8 g, 12.34 mmol). After filtration and concentration, pale yellow crystals were grown at −30 °C (0.98 g, 58%); mp 142−146 °C.

**Synthesis of Salen($^t$Bu)[B(OMe)$_2$]$_2$ (11).** The procedure was as for **1** with toluene (25 mL), Salen($^t$Bu)H$_2$ (1.00 g, 2.02 mmol), and trimethyl borate (0.84 g, 8.08 mmol). Yield, 0.61 g, 47%; mp 243 °C.

**Synthesis of Salpen($^t$Bu)[B(OMe)$_2$]$_2$ (12).** The procedure was as for **1** with toluene (25 mL), Salpen($^t$Bu)H$_2$ (1.00 g, 1.97 mmol), and trimethyl borate (0.82 g, 7.90 mmol). After filtration and concentration, pale yellow crystals were grown at −30 °C (0.83 g, 64%); mp 208 °C.

**Synthesis of Salben($^t$Bu)[B(OMe)$_2$]$_2$ (13).** The procedure was as for **1** with toluene (25 mL), Salben($^t$Bu)H$_2$ (1.00 g, 1.92 mmol), and trimethyl borate (0.80 g, 7.69 mmol): Yield, 0.67 g, 51%; mp 208−210 °C.

**Synthesis of Salpten($^t$Bu)[B(OMe)$_2$]$_2$ (14).** The procedure was as for **1** with toluene (25 mL), Salpten($^t$Bu)H$_2$ (1.00 g, 1.87 mmol), and trimethyl borate (0.78 g, 7.48 mmol): Yield, 0.91 g, 72%; mp 202 −204 °C.

**Synthesis of Salhen($^t$Bu)[B(OMe)$_2$]$_2$ (15).** The procedure was as for **1** with toluene (25 mL), Salhen($^t$Bu)H$_2$ (1.00 g, 1.82 mmol), and trimethyl borate (0.76 g, 7.30 mmol): Yield, 0.72 g, 57%; mp 196 °C.

**Synthesis of Salen($^t$Bu)[B(OEt)$_2$]$_2$ (16).** The procedure was as for **1** with toluene (25 mL), Salen($^t$Bu)H$_2$ (1.00 g, 2.02 mmol), and triethyl borate (1.18 g, 8.08 mmol). After filtration and concentration, pale yellow crystals were grown at −30 °C (0.82 g, 59%); mp 150−152 °C.

**Synthesis of Salpen($^t$Bu)[B(OEt)$_2$]$_2$ (17).** The procedure was as for **1** with toluene (25 mL), Salpen($^t$Bu)H$_2$ (1.00 g, 1.97 mmol), and triethyl borate (1.15 g, 7.90 mmol): Yield, 1.1 g, 79%; mp 140−143 °C.

**Synthesis of Salben($^t$Bu)[B(OEt)$_2$]$_2$ (18).** The procedure was as for **1** with toluene (25 mL), Salben($^t$Bu)H$_2$ (1.00 g, 1.92 mmol), and triethyl borate (1.12 g, 7.69 mmol): Yield, 0.96 g, 70%; mp 130−136 °C.

**Synthesis of Salpten($^t$Bu)[B(OEt)$_2$]$_2$ (19).** The procedure was as for **1** with toluene (25 mL), Salpten($^t$Bu)H$_2$ (1.00 g, 1.87 mmol), and triethyl borate (1.09 g, 7.49 mmol). Removal of toluene under vacuum provided a pale yellow solid (0.86 g, 63%); mp 155 −156 °C.

**Synthesis of Salhen($^t$Bu)[B(OEt)$_2$]$_2$ (20).** The procedure was as for **1** with toluene (25 mL), Salhen($^t$Bu)H$_2$ (1.00 g, 1.82 mmol), and triethyl borate (1.07 g, 7.30 mmol). Yield, 0.97 g, 71%; mp 158 −162 °C.

**Attemted Synthesis of Salophen($^t$Bu)[B(OMe)$_2$]$_2$.** In a typical reaction B(OMe)$_3$ (0.83 g, 8.00 mmol) was added to a stirred solution of Salophen($^t$Bu)H$_2$ (1.08 g, 2.00 mmol) at room temperature. After being heated to reflux for 6 h, the solution was cooled and the solvent removed under vacuum to yield unreacted starting material as determined by $^1$H NMR. This procedure was also attempted with Salomphen($^t$Bu)H$_2$.

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**Supporting Information Available: Supporting Information available**. Text giving full experimental details for complexes **1**, **4**, **7**, **10**, **12**, and **16** (9 pages). X-ray crystallographic files, in CIF format, for complexes **1**, **4**, **7**, **10**, **12**, and **16** are available on the Internet only. Ordering and access information is given on any current masthead page.

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