Steric Control over Molecular Structure and Supramolecular Association Exerted by Tin- and Ligand-Bound Groups in Diorganotin Carboxylates

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Structural data (X-ray and solution and solid-state ^{119}Sn NMR) show that skew-trapezoidal-bipyramidal diorganotin compounds of 2-quinaldate are invariably monomeric, owing to the steric bulk of the carboxylate ligand. In contrast, most of the analogous compounds of 2-picolinate (2-pic) can increase their coordination number by polymerization or the incorporation of solvent in their coordination sphere in the solid state. The exceptional compound is $tBu_2Sn(2\text{-pic})_2$ (**3**), for which no increase in coordination number is apparent, a result that is correlated with the bulky *tert*-butyl groups. Thus, judicious choice of tin or ligand substituents can be exploited to dictate coordination number and/or the degree of supramolecular aggregation in the investigated systems.

Introduction

The importance of organotin compounds may be judged by their many and varied applications in diverse fields such as catalysis and PVC stabilization,[1] and more recently, their potential use as antitumor agents has been explored.[1e] Underpinning the understanding of organotin chemistry is a knowledge of their chemical structure, and arguably, the most important technique for structure determination is single-crystal X-ray crystallography. However, a difficulty with results obtained in the solid state is that extrapolation to the solution phase can be problematic. In this connection, while it is widely acknowledged that differences may exist between solution and solid-state structures, less well understood is the influence of intermolecular forces, i.e. crystal-packing effects, on molecular geometry. Indeed, recent bibliographic reviews have demonstrated that *significant* differences may exist for certain organotin systems, and indeed other main-group-element systems, for which different coordination geometries and even coordination numbers may exist for very closely related compounds: e.g., compounds that may differ in the nature of a remote R substituent of a ligand.[2] Allied to this, systematic research[3−5] on organotin systems and surveys[6−8] of certain transition-metal complexes have demonstrated that geometric parameters show a dependence on the crystalline environment. The inescapable conclusion of the above is that intermolecular forces can and do significantly influence molecular geometry and interatomic parameters in structures involving heavy-atom centers. Viewed in a different manner, molecules may be thought of as being somewhat malleable and molecular geometry reliant, to a greater or lesser extent, upon global crystal-packing considerations. In other words, molecules are *syntactic* with their host crystalline manifold.[8]

The structural chemistry of organotin carboxylates is as rich as it is diverse, owing to a variety of factors, one of the more important being the capacity of the Lewis acidic tin centers to increase their coordination numbers by *intra*- and/or *inter*molecular hypervalent interactions.[9] Thus, whereas the valency requirements of tin are satisfied by four bonds, coordination numbers up to 7 are commonly encountered in organotin carboxylates, for example.[2a,c] In the quest to determine the factors dictating the appearance of different structural

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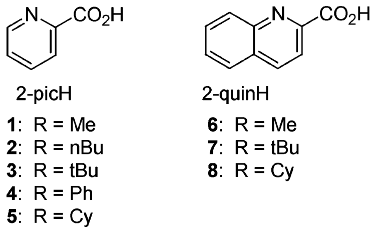
Chart 1



motifs for these compounds, this contribution reports a systematic study of two classes of diorganotin carboxylates for which systematic variations have been introduced in the tin- and ligand-bound R groups. This study has been conducted in order to ascertain whether it is possible to control the coordination geometry at tin and, intricately related to this, whether it is possible to direct supramolecular association between molecular entities, via steric control, a principle that has been demonstrated recently for related 1,1-dithiolate structures.[10] Herein, we report the preparation and crystallographic characterization, where possible, and solution and solid-state ^{119}Sn NMR data of a series of diorganotin bis(carboxylates) where the carboxylate is derived from 2-picolinic acid and 2-quinaldic acid and the tin-bound group is varied from small methyl to bulky cyclohexyl groups.

Results and Discussion

The diorganotin bis(carboxylates) (Chart 1) studied herein were prepared from the reaction between the respective diorganotin oxide and acid in a 1:2 molar ratio. The compounds are generally highly crystalline and air-stable and demonstrated the expected spectroscopic characteristics (see the Supporting Information).

Crystal and Molecular Structures. The first motif to be described is that of $Bu_2Sn(2\text{-pic})_2$ (**2**). As shown in Figure 1, the tin atom is seven-coordinate, existing in a distorted-pentagonal-bipyramidal geometry with the butyl groups occupying axial positions. The pentagonal plane is defined by donor atoms derived from three separate 2-pic anions. One 2-pic ligand chelates by employing the nitrogen and one oxygen atom, and the other 2-pic ligand coordinates in a similar fashion, except that the second oxygen atom of the carboxylate bridges a symmetry-related tin atom. The Sn−O distances are systematically shorter than the Sn−N distances, and the Sn−O distances involving the bridging carboxylate are longer than that formed by the monodentate 2-pic ligand. Whereas the same structural motif is found in $Me_2Sn(2\text{-pic})_2$ (**1**),[11] the isomeric *tert*-butyl analogue $tBu_2Sn(2\text{-pic})_2$ (**3**) adopts a very different motif.[12]

The tin atom in mononuclear **3** is six-coordinated in a geometry best described as skew-trapezoidal bipyramidal. The basal plane is defined by a N_2O_2 donor set, defined by two chelating 2-pic ligands, with the Sn−N bond distances significantly longer than the Sn−O bond distances.[12] Similarly, no molecular aggregation is observed in the structure of $Ph_2Sn(2\text{-pic})_2$ (**4**), which has crystallographic 2-fold symmetry and features a similar $C_2N_2O_2$ donor set and mode of coordination for the 2-pic ligands as for **3**.[13] In this case, the great disparity in the Sn−N and Sn−O bond distances noted above no longer pertains and the oxygen atoms are trans to each other.[13] The coordination geometry is therefore best described as distorted octahedral. The final 2-pic structure to be described incorporates solvent in its coordination sphere.

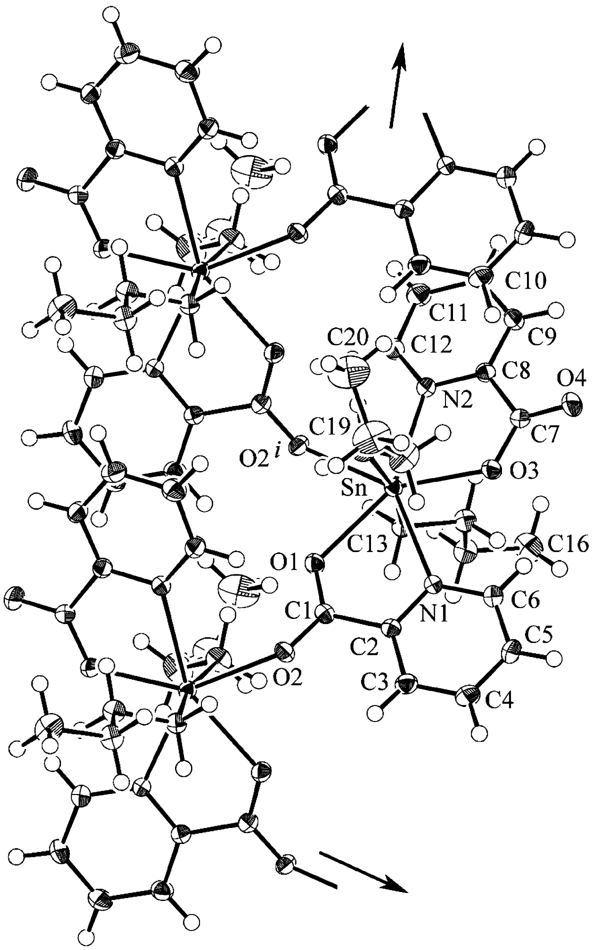


Figure 1. Molecular aggregation operating in the crystal structure of $Bu_2Sn(2\text{-pic})_2$ (**2**). Selected geometric parameters (distances in Å and angles in deg): Sn−O1 = 2.3824(19), Sn−O3 = 2.191(2), Sn−N1 = 2.478(2), Sn−N2 = 2.470(2), Sn−O2^i = 2.3653(19); C13−Sn−C17 = 167.82(11). Symmetry operation i: $-x, -^1/_2 + y, ^1/_2 - z$.

The molecular structure of $Cy_2Sn(2\text{-pic})_2(OH_2)\cdot MeOH$ (**5**) is illustrated in Figure 2, from which it can be seen that the arrangement of two chelating 2-pic ligands is similar to that found for **3**. A pentagonal-bipyramidal coordination geometry similar to that in **1** and **2** is found, but through the agency of a coordinated water

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[9] E.g.: (a) Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Lahcini, M.; Jaumier, P.; Jousseaume, B. *Organometallics* **1996**, *15*, 2237. (b) Jaumier, P.; Jousseaume, B.; Tiekink, E. R. T.; Biesemans, M.; Willem, R. *Organometallics* **1997**, *16*, 5124. (c) Dakternieks, D.; Jurkschat, K.; Tozer, R.; Hook, J.; Tiekink, E. R. T. *Organometallics* **1997**, *16*, 3696. (d) Biesemans, M.; Willem, R.; Damoun, S.; Geerlings, P.; Tiekink, E. R. T.; Jaumier, P.; Lahcini, M.; Jousseaume, B. *Organometallics* **1998**, *17*, 90. (e) Caruso, F.; Bol-Schoenmakers, M.; Penninka, A. H. *J. Med. Chem.* **1993**, *36*, 1168.

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[13] Gielen, M.; Bouâlam, M.; Tiekink, E. R. T. *Main Group Met. Chem.* **1993**, *16*, 251.

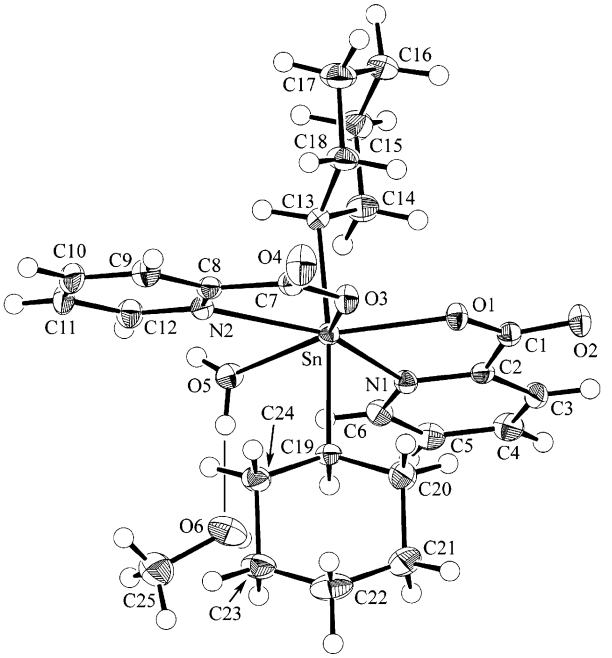

Figure 2. Molecular structure of Cy$_2$Sn(2-pic)$_2$(OH$_2$)·MeOH (**5**), showing the atomic numbering scheme. Selected geometric parameters (distances in Å and angles in deg): Sn−O1 = 2.250(2), Sn−O3 = 2.225(2), Sn−N1 = 2.550(3), Sn−N2 = 2.495(3), Sn−O5 = 2.4603(11) Å; C13−Sn−C19 = 171.50(12).

molecule rather than via a bridging carboxylate. A solvent methanol molecule is associated with the coordinated water molecule, and the symmetry-related Cy$_2$Sn(2-pic)$_2$(OH$_2$)·MeOH entities thus formed aggregate into a chain, as illustrated in Figure 3. Thus, both water-bound hydrogen atoms form hydrogen-bonding interactions: one, as just described, to the methanol molecule (O5−H···O6 = 1.85 Å, O5···O6 = 2.697(3) Å, and angle at H 173°) and another to a coordinated carboxylate oxygen (O5−H···O3^i = 1.99 Å, O5···O3^i = 2.818(3) Å, and angle 164° for symmetry operation i (x, $^1/_2 - y$, $^1/_2 + z$)). The acidic proton of methanol forms a donor interaction to a noncoordinating carbonyl oxygen atom (O6−H···O2^i = 1.83 Å, O6···O2^i = 2.663(4) Å, and angle 174°). In this way a ten-membered [H−O−H···O−H···O−C−O−Sn−O···] ring is formed, serving to connect the organotin residues into chains. While all other compounds prepared in this study were solvent-free, even without taking special precautions, in our hands it was not possible to generate anhydrous, solvent-free crystals of Cy$_2$Sn(2-pic)$_2$.[14] Attention is now directed to the structures of a series of 2-quin analogues.

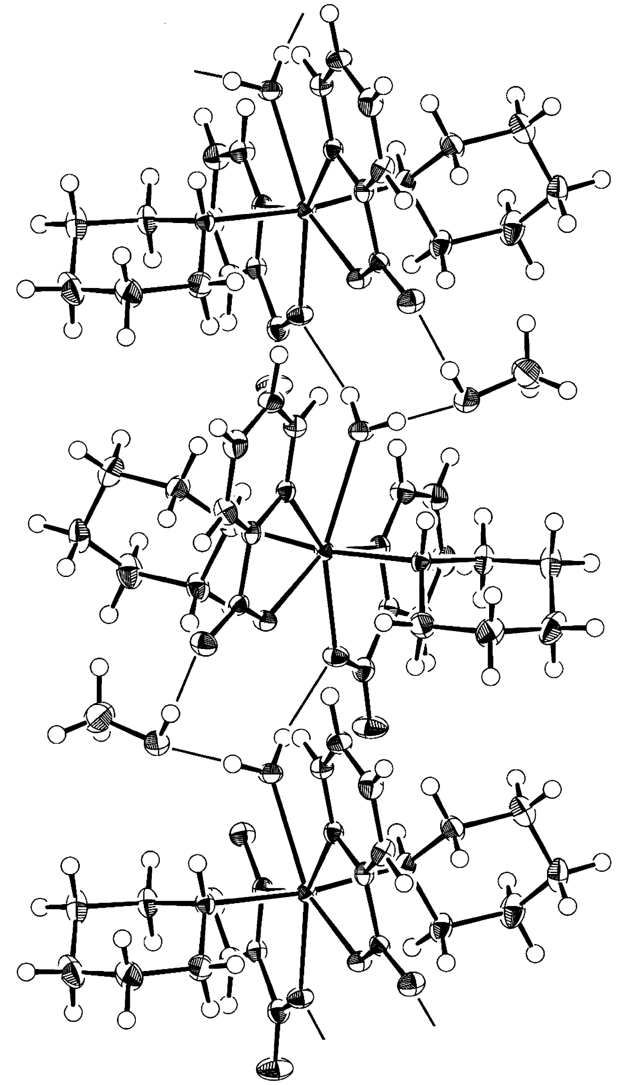

Figure 3. Supramolecular association in the crystal structure of Cy$_2$Sn(2-pic)$_2$(OH$_2$)·MeOH (**5**).

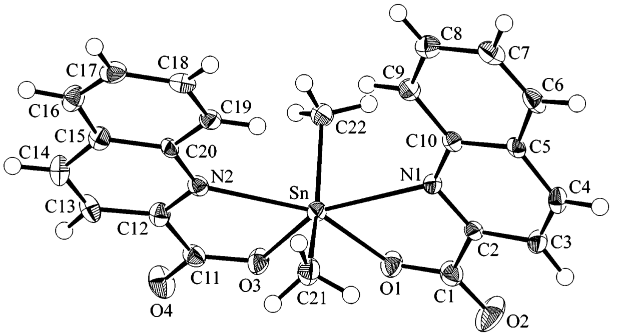

Figure 4. Molecular structure of Me$_2$Sn(2-quin)$_2$ (**6**), showing the atomic numbering scheme. Selected geometric parameters (distances in Å and angles in deg): Sn−O1 = 2.085(3), Sn−O3 = 2.090(3), Sn−N1 = 2.594(3), Sn−N2 = 2.473(4); O1−Sn−O3 = 80.80(12); N1−Sn−N2 = 138.25(11), C21−Sn−C22 = 147.33(18).

The molecular structure of Me$_2$Sn(2-quin)$_2$ (**6**) is illustrated in Figure 4. This structure and those of the *tert*-butyl analogue **7**, for which two molecules comprise the asymmetric unit, and cyclohexyl analogue **8** all conform to the same motif and resemble closely the skew-trapezoidal-bipyramidal geometry found for **3**. While it is not possible to compare with any level of confidence the derived geometric parameters for the methyl and cyclohexyl derivatives, as different motifs are found depending on the nature of the carboxylate ligand, the structures of the *tert*-butyl compounds conform to the same motif, so that a direct comparison of parameters is valid. An examination of the geometric data shows that the geometric parameters defining the tin atom geometries in **3** and **7** are virtually identical, indicating that the ligand donor strengths of 2-pic and 2-quin are similar. This key result indicates that any

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[14] Stapleton, C. P. D. B. Sc.(Hons) Thesis, The University of Adelaide, 2000.

Table 1. Solution and Solid State ^{119}Sn NMR Data (δ, ppm) for 1−8

	soln		
	$CDCl_3$	DMSO	solid state
1	*a*	−444.0	−458.5
2	−359.9	−465.1	−477.0
3	−374.6	−406.0	−394.6
4	−427.5	−603.8	−414.0
5	−364.4	−502.0	−510.4
6	*a*	−260.8	−265.2
7	*a*	−312.9	−369.7, −379.4
8	*a*	−338.1	−349.1

[a] Not measured due to poor solubility.

differences between the 2-pic and 2-quin structures are not related to differences in the electronic structures of the ligands. It was thought to be of some interest to investigate the solution structures of these compounds and make a comparison with the above crystal structures, and so both solution and solid-state ^{119}Sn NMR measurements were conducted.

^{119}Sn NMR Study. Table 1 summarizes the results of ^{119}Sn NMR data measured in a noncoordinating solvent ($CDCl_3$), in a coordinating solvent (DMSO), and in the solid state, where possible. The poor solubility of **1** precluded the measurement of a ^{119}Sn chemical shift in $CDCl_3$ solution, but in the case of **2**, data could be obtained. This indicates likely dissociation of **2** in $CDCl_3$ solution, a conclusion supported by the upfield shift in the ^{119}Sn resonance in DMSO solution that is comparable to the solid-state ^{119}Sn chemical shift, supporting the coordination of DMSO. Considering first the 2-pic series in $CDCl_3$ and DMSO solvents, the values of the chemical shifts moved significantly upfield in the coordinating solvent for **2**, **4**, and **5**, but no significant change in chemical shift was noted for **3**. This result indicates an increase in coordination number for **2**, **4**, and **5** and, therefore, the incorporation of DMSO in the coordination sphere. Although there is no aggregation for both **3** and **4** in the solid state, an increased coordination in DMSO is observed for the phenyl compound (**4**). This result is consistent with the known steric bulk of the *tert*-butyl group; e.g. the crystal structure of tBu_2SnCl_2 is the only one of the "common" R_2SnCl_2 compounds that does not feature intermolecular Sn···Cl interactions.[15] The chemical shifts of the *n*-butyl (**2**) and phenyl (**4**) compounds in the solid state is consistent with the seven- and six-coordinate coordination geometries observed crystallographically. The solid-state ^{119}Sn NMR spectrum of $Cy_2Sn(2\text{-pic})_2(OH_2)$.MeOH (**5**) is in harmony with an increase in coordination number, but by the inclusion of solvent rather than by carboxylate bridging. For the 2-quin series a very clear trend is evident in that no increase in coordination number in DMSO solution is possible, as judged by the similarity between the solution (DMSO) and solid-state ^{119}Sn NMR results (Table 1). The observation of two isotropic ^{119}Sn signals for $tBu_2Sn(2\text{-quin})_2$ (**7**) is consistent with there being two independent molecules in the unit cell, as shown by crystallography. In no case were crystals obtained from the DMSO solutions. On the basis of the above crystallographic and ^{119}Sn NMR results, the following conclusions may be drawn as to the steric control exerted by both the tin-bound substituents as well as by the carboxylate ligands.

General Considerations. Crystallographic evidence shows that while an increase in coordination number at tin is possible for the 2-pic series, as exemplified by the solid-state structures of $^{n}Bu_2Sn(2\text{-pic})_2$ (**2**) and $Cy_2Sn(2\text{-pic})_2(OH_2)\cdot MeOH$ (**5**), via molecular aggregation and incorporation of solvent in the coordination sphere, respectively, no increase in coordination number is apparent for the 2-quin series. This evidence is supported by the ^{119}Sn NMR study, which indicated that no increase in coordination number was observed when the 2-quin compounds were dissolved in DMSO solution. Clearly, these results can be traced to the increased steric profile of the 2-quin ligand versus the 2-pic ligand in that, for the 2-quin ligand, the "bay" hydrogen atoms at C9 and C19 effectively block off a coordination site. Thus, steric control exerted by the 2-quin ligands is demonstrated so that, regardless of the nature of the tin-bound R group, a single motif is observed only. In contrast, arguably four motifs are observed for the 2-pic series.

There are major differences in the structures observed in the solid state for the $R_2Sn(2\text{-pic})_2$ series. For the molecules with smaller R groups, i.e. R = Me (**1**), ^{n}Bu (**2**), molecular aggregation occurs via the agency of a bridging carboxylate ligand. Such bridges are not present for the compounds with larger groups. However, increased coordination numbers are possible for the R = Ph (**4**), Cy (**5**) compounds but not for the R = tBu (**3**) species, as judged from the ^{119}Sn NMR results. The R = Cy (**5**) compound achieves an increase in coordination number by the incorporation of solvent in its coordination sphere, but the R = Ph (**4**) compound is monomeric in the solid state. The monomer formulation for the R = tBu (**3**) compound is entirely consistent with the known steric bulk of this ligand. The lack of molecular aggregation leading to an increase in coordination number of tin in the R = Ph (**4**) compound probably reflects the reduced Lewis acidity of tin in diphenyl species, a feature that is known to often result in novel structures. In the same way as steric effects globally reduced molecular aggregation in the 2-quin series compared with the 2-pic compounds, a clear profile of steric influence is exerted by the tin-bound alkyl groups, akin to related systematic crystallographic and theoretical studies for di- and triorganotins.[3−5]

Experimental Section

A literature procedure was employed for the synthesis of colorless and crystalline **1**−**8** that typically involved the reaction of freshly prepared R_2SnO and the respective carboxylic acid.[16] Characterization data (yield, melting point, elemental analysis, and IR) are given as Supporting Information.

^{1}H, $^{13}C\{^{1}H\}$, and $^{119}Sn\{^{1}H\}$ NMR spectra were obtained using a Varian BAX-300 FT/NMR spectrometer. ^{1}H, ^{13}C, and ^{119}Sn chemical shifts (δ) are given in ppm and are referenced against Me_4Si and Me_4Sn, respectively. The ^{119}Sn CP-MAS NMR spectra were obtained using a JEOL Eclipse+ 400 MHz

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NMR spectrometer operating at 149.05 MHz. An 8 μs (90°) pulse, 5 ms contact time, and recycle delay of 10 s were used. Spectra were recorded on 250−350 mg of sample packed into 6 mm diameter rotors. Chemical shifts are quoted relative to Me_4Sn, using c-Hex_4Sn (δ_{iso} −97.35 ppm) as a secondary external reference. Typically 15 000 transients were recorded in order to achieve a reasonable signal-to-noise ratio. At least two experiments with sufficiently different spinning rates, ranging from 4 to 7 kHz, were recorded in order to determine the isotropic chemical shift. Infrared spectra were recorded on a Perkin-Elmer BX FT spectrophotometer as KBr disks. The reported melting points are uncorrected.

Crystals of **1**, **2**, **5**, and **7** were grown by the slow evaporation of methanol solutions of the respective compounds. Crystals of **6** and **8** were grown similarly, but from ethanol solutions. Crystals of **3** were obtained by vapor diffusion of ether into a chloroform solution of the compound. Slow evaporation of an ethanol/benzene (5:1) solution containing **4** afforded suitable crystals. Intensity data for **1**−**8** were measured at 173 K on a Rigaku AFC7R diffractometer with Mo Kα radiation. The solution of the structures was by heavy-atom methods,[17a] and refinement (absorption-corrected data,[17b] anisotropic displacement parameters, H atoms in their calculated positions, and a weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3)$ was on F^2.[17c] Diagrams were drawn with ORTEP[17d] at the 50% probability level, and calculations were performed using teXsan.[17e]

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Supporting Information Available: Text giving characterization data and electronic files giving crystallographic data (CIF) for **1**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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