

Cluster Compounds



DOI: 10.1002/ange.200600292

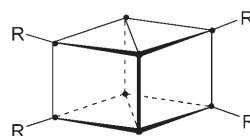
Higher-Nuclearity Group 14 Metalloid Clusters: $[\text{Sn}_9\{\text{Sn}(\text{NRR}')\}_6]$ **

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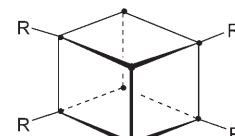
Dedicated to Professor Hansgeorg Schnöckel on the occasion of his 65th birthday

The term “metalloid cluster” was coined by Schnöckel and co-workers in the context of Al chemistry to designate those metal clusters in which “the number of metal–metal contacts

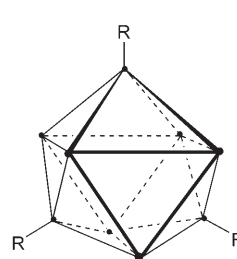
exceeds the number of metal–ligand contacts and by the presence of metal atoms which participate exclusively in metal–metal interactions”.^[1] Reviews of such Al and Ga clusters have appeared^[2] and were extended to those of the heavier Group 14 elements.^[3] Previously reported tin clusters $[\text{Sn}_x\text{R}_y]$ ($x > y$) include $[\text{Sn}_8\text{R}_4]$ (**I**),^[4] $[\text{Sn}_8\text{R}_6]^{2-}$ (**II**),^[5] $[\text{Sn}_9\text{R}_3]$ (**III**),^[6] $[\text{Sn}_{10}\text{R}_3]^-$ (**IV**),^[6] in each of which R represents an aryl or silyl ligand. In the spirit of Schnöckel’s definition, we now present data on the highest-nuclearity Group 14 “metalloid” clusters to be reported thus far, the isoelectronic compounds $[\text{Sn}_{15}\text{Z}_6]$ ($\text{Z} = \text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{SiMe}_2\text{X})$; $\text{X} = \text{Me}$ (**1**), Ph (**2**)). Compounds **1** and **2** are the first Group 14 metal clusters bearing amido ligands and are also unprecedented within this compound class for being body-centered and have as locus a tin atom with relatively close contacts (ca. 3.1 to 3.4 Å) to each of the remaining 14 tin atoms.



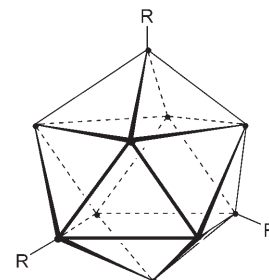
I $\text{R} = \text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\text{-}2,6$



II $\text{R} = \text{Si}t\text{Bu}_3$



III $\text{R} = \text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{IPr}_3\text{-}2,4,6)_2\text{-}2,6$



IV $\text{R} = \text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\text{-}2,6$

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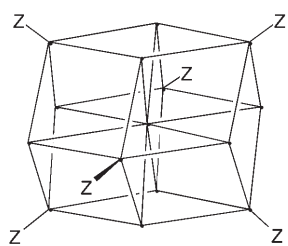
[**] We thank the EPSRC (A.V.P.) and the Royal Society (A.R.) for postdoctoral fellowships and the CRC Program of the U.S. National Science Foundation for financial support. $\text{R} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$; $\text{R}' = \text{SiMe}_3$ or SiMe_2Ph .

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

The best-known stable polyhedral clusters of the heavier Group 14 elements are the ligand-free Zintl anions, such as M_5^{2-} or M_9^{n-} ($\text{M} = \text{Ge}, \text{Sn}, \text{or Pb}$; $n = 2, 3, 4$).^[7] An intriguing aspect of progressively higher-nuclearity metalloid clusters $[\text{M}_x\text{R}_y]$ (where x is large and $x \gg y$) is that their morphology should increasingly resemble sections of the bulk metal. Detailed structural data for such species may provide insight into changes that occur at or near the surface of the metal compared with those within its bulk. For main-group chemistry, relevant information was previously available only for Group 13 metalloid clusters, as in $[\text{Al}_{77}\text{Z}_{20}]^{2-}$ ^[8a] or $[\text{Ga}_{84}\text{Z}_{20}]^{3-}$ ^[8b] ($\text{Z} = \text{N}(\text{SiMe}_3)_2$). The characterization of $[\text{Sn}_{15}\text{Z}_6]$ (**1**, **2**) is now a step along the same path for clusters of Group 14 elements. A recent contribution in this area relates to the synthesis and X-ray structure of $[\text{Si}_8(\text{Si}t\text{Bu}_3)_6]$.^[9]

The work herein was begun at the University of Sussex in 2003.^[10] The crystalline compound **1** was isolated as small black crystals of space group $Pnnm$ (**1** ($Pnnm$)) by treatment of the colorless compound $[\{\text{Sn}(\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3))(\mu\text{-Cl})\}_2]$ (**3**)^[11] with KC_8 in Et_2O at about -30°C and successive filtering, concentration of the filtrate, addition of PhMe , and prolonged storage at -27°C . By this procedure compound

1 (*Pnnm*) was obtained in very low yield together with unreacted **3**.^[10] A subsequent experiment, in which the crystallization was carried out at ambient temperature, furnished **1** (*R $\bar{3}$*) in very low yield as black (or dark red in thin layers) hexagonal prisms. The new crystalline amidotin(II) chloride **3**^[11] was prepared in Et₂O from SnCl₂ and one equivalent of Li[N(2,6-*i*Pr₂C₆H₃)(SiMe₃)]^[12a] (76 %) or [Sn{N(2,6-*i*Pr₂C₆H₃)(SiMe₃)₂}]^[12b] (93 %). Attempted reduction of three other amidotin(II) compounds failed to yield isolable clusters. Reaction of [Sn{N(SiMe₃)₂}]₂ or [Sn{N(SiMe₃)₂}(μ-Cl)]₂ with KC₈ or NaC₁₀H₈ gave elemental tin, and reaction of [Sn(tmp)(μ-Cl)]₂ (tmp = 2,2,6,6-tetramethylpiperidinato) with KC₈ yielded a tar of unidentified content.



1 Z = N(C₆H₃/*i*Pr₂-2,6)(SiMe₃)
2 Z = N(C₆H₃/*i*Pr₂-2,6)(SiMe₂Ph)

Complementary experiments were subsequently carried out at the University of California, Davis, where a new synthetic strategy was introduced, namely the use of a reductive elimination from a precursor metal chloride with Li[BHsBu₃] (L-selectride). Thus, the cluster **1** (ca. 5 %) was obtained by treatment of the in situ generated amidotin(II) chloride **3** with a less-than-stoichiometric amount of Li[BHsBu₃] at –78 °C. Two forms of **1** were obtained by this route; crystallization from PhMe or hexane yielded X-ray-quality crystals **1** (*R $\bar{3}$ c*) or **1** (*P2₁/n*), respectively. Compound **2** (7 %) was obtained similarly from an analogue of **3** (prepared in situ from [Sn{N(2,6-*i*Pr₂C₆H₃)(SiMe₂Ph)}]₂ and SnCl₂) and Li[BHsBu₃]. It is likely that a transient amidotin(II) hydride is an intermediate in these syntheses. In support of this postulate, we note that i) treatment of **3** with an equivalent of [Cu(μ-H)(PPh₃)₆] in C₆D₆ resulted in evolution of H₂ (NMR experiment) and ii) thermolysis of the sterically hindered Sn(II) hydride [Sn{2,6-(2,4,6-*i*Pr₃C₆H₂)₂C₆H₃}(μ-H)]₂^[13] in toluene afforded the [Sn₉R₃] cluster **III**.^[6]

Although single crystals of **1** were obtained in four different space groups (*Pnnm*, *R $\bar{3}$* , *R $\bar{3}$ c*, *P2₁/n*),^[14] the molecular structures that were deduced from each are essentially identical, and the various Sn–Sn distances are also closely similar to those of **2** (Table 1).^[15] The structures of **1** and **2** are illustrated in Figure 1. The most striking feature of each structure is the body-centered arrangement of the 15 tin atoms, an architecture previously unknown for metalloid clusters of the Group 14 elements. The ligand-free tin atoms in **1** and **2** form a body-centered distorted cube, and each of the six faces is capped by an {Sn(NRR')} moiety, as shown in Figure 2.

Table 1: Comparison of average bond lengths (Å) in clusters **1** and **2**.^[a]

Compound	Sn1–Sn _A	Sn1–Sn _B	Sn _A –Sn _B	Sn _A –Sn _A
1 (<i>Pnnm</i>)	3.18 ± 0.03	3.36 ± 0.02	3.01 ± 0.03	3.67 ± 0.07
1 (<i>R$\bar{3}$</i>)	3.15 ± 0.03	3.40 ± 0.01	3.02 ± 0.02	3.64 ± 0.02
1 (<i>R$\bar{3}$c</i>)	3.16 ± 0.03	3.40 ± 0.01	3.02 ± 0.02	3.64 ± 0.03
1 (<i>P2₁/n</i>)	3.18 ± 0.02	3.33 ± 0.04	2.99 ± 0.02	3.67 ± 0.06
2 (<i>P2₁/n</i>)	3.15 ± 0.03	3.41 ± 0.02	3.02 ± 0.04	3.64 ± 0.04

[a] Sn1: central Sn atom; Sn_A: Sn atoms at cube apices; Sn_B: ligand-bound Sn atoms.

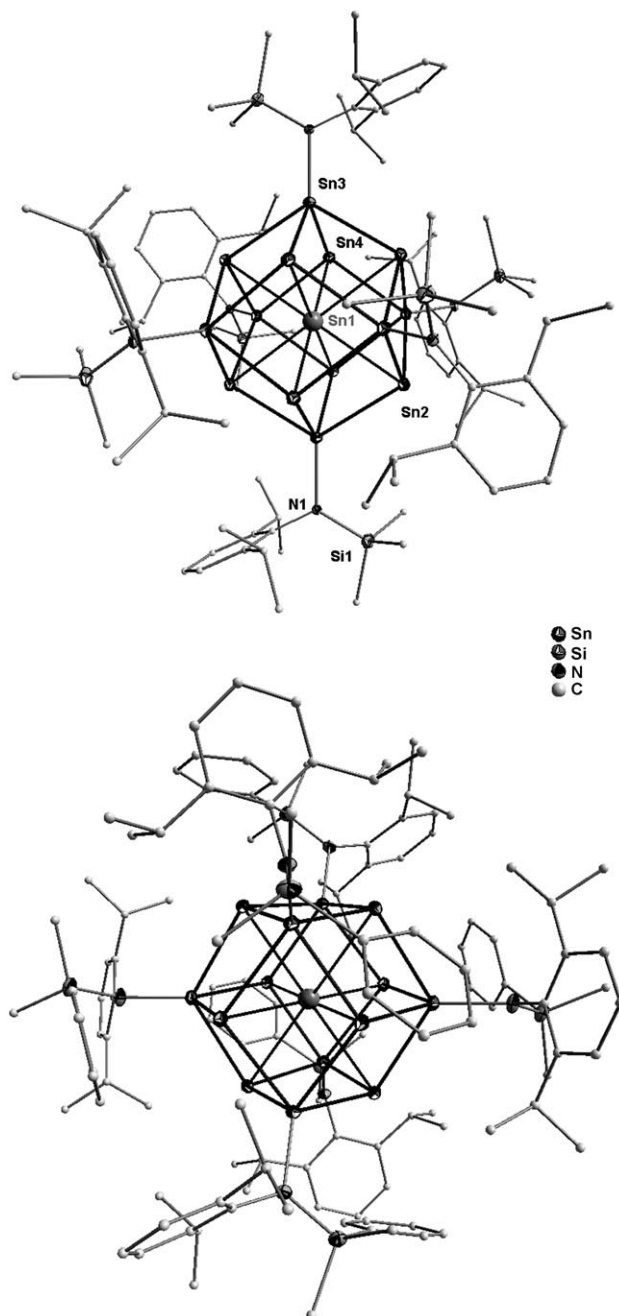


Figure 1. Thermal-ellipsoid plot (ellipsoids set at 50% probability) of **1** (*R $\bar{3}$ c*) (upper) and **2** (lower) with isotropic representation of the C atoms and the central Sn atoms (H atoms are omitted for clarity).

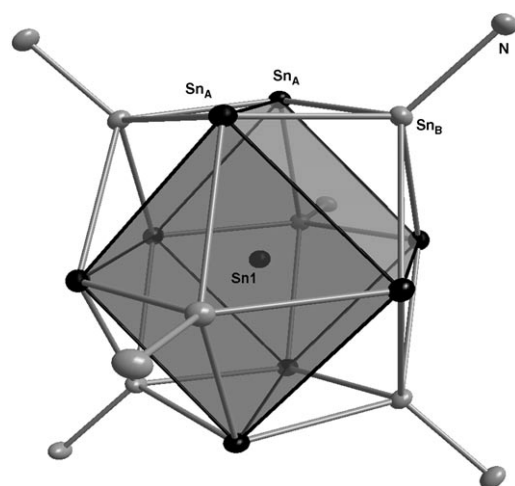


Figure 2. Polyhedral representation of the cluster core in **1** and **2** (unsubstituted Sn_A atoms black, N atoms and ligand-bound Sn_B atoms gray; only the N atoms of the amido ligands shown).

The metalloid character of **1** and **2** is revealed in the Sn–Sn interactions between the central tin atom (Sn1) and the eight tin atoms at the cube apices (Sn_A ; Figure 2) of an Sn_8 cube. The Sn1 – Sn_A distances have an average value close to 3.15 Å,^[15] which is considerably longer than the average value of 2.81 Å in white tin (β -Sn), but closer to the average value of 3.10 Å in gray tin (α -Sn, diamond lattice). The Sn_A – Sn_B bonds between the amido-substituted tin atoms (Sn_B ; Figure 2) and those at the apices of the cube (Sn_A) have an average length of 3.02 Å. The Sn_B –N bonds have an average length of 2.09 Å (for **1**) and 2.11 Å (for **2**), and are unexceptional (for comparison, Sn–N bond length in **3**: 2.068(2) Å).^[11] The slightly larger average Sn_B –N bond length in **2** is probably a result of the greater steric demand of the silyl group of the ligand. The only main-group-metal cluster that possesses a structure similar to that of **1** and **2** is the neutral-atom cluster $[\text{SiAl}_8(\text{AlCp}^*)_6]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$), which has a bcc arrangement of Al atoms in which the central aluminum atom is replaced by a silicon atom and the faces are capped by $\{\text{AlCp}^*\}$ units.^[16]

The structural motif of the Sn-centered core in **1** or **2** is similar to that of typical metallic structures. Thus, the bcc arrangement of the nine central tin atoms in **1** (black Sn atoms in Figure 2) corresponds to that in the α -iron structure, but not to those of white or gray tin. The bcc structure is observed for elemental tin only at high pressure, above 45 ± 5 GPa.^[17] This relationship between the number of associated metal atoms in a molecular structure and high-pressure modifications of the corresponding bulk metal has also been observed in large clusters of Group 13 elements.^[2]

Attempts to record solution ^{119}Sn NMR spectra of **1** and **2** failed possibly because of their very low solubility at ambient temperature as a result of their high symmetry and molecular weight. Heating the complex **1** ($Pnnm$) in $[\text{D}_8]$ toluene led to precipitation of metallic tin. Moreover, the tin nuclei are in a rigid cage structure that forms part of a relatively large

molecule, thus making NMR relaxation very slow, and the sample is thus quickly saturated.

Temperature-dependent ^{119}Sn Mössbauer spectroscopic experiments on a sample of **1** were carried out^[18] to complement the above X-ray structural data. A representative spectrum is shown in Figure 3. Two distinct quadrupole-

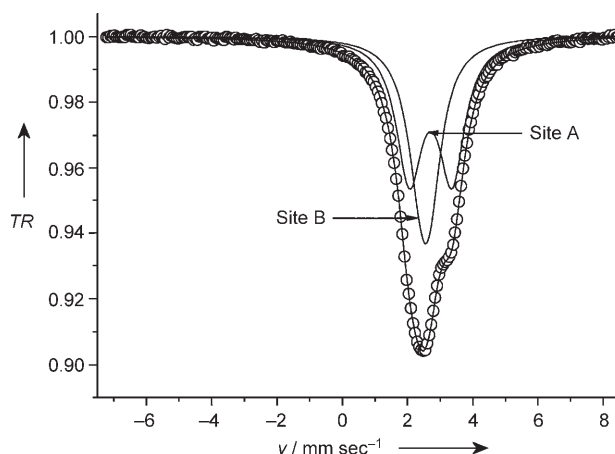


Figure 3. ^{119}Sn Mössbauer spectrum of **1** at 89 K (TR = relative transmission). The velocity scale is with respect to the centroid of a room-temperature BaSnO_3 -absorber spectrum. The A site is ascribed to the core Sn_9 atoms, and the B site to the six ligand-bound Sn atoms.

splitting (QS) sites were revealed in a ratio of 1.5:1 at 90 K. These are assigned to the nine “naked” tin atoms Sn1 and Sn_A (site A) and the six ligand-bound atoms Sn_B (site B), respectively. Thus, the QS values of the A and B sites were determined to be 1.341 ± 0.012 (at 90 K) and 0.13 ± 0.01 mm s^{-1} (essentially temperature-independent), respectively.

The isomer shifts (IS) were found at 2.733 ± 0.011 and 2.63 ± 0.01 mm s^{-1} at 90 K for the A and B sites, respectively. These values are close to that of gray tin (α -Sn, 2.56 ± 0.02 mm s^{-1} at room temperature) or white tin (β -Sn, 2.68 mm s^{-1} ^[19]), and are within the range for bivalent tin compounds. For example, $[\text{Sn}(\text{N}(\text{SiMe}_3)_2)(\mu\text{-Cl})_2]$ has IS and QS values of 3.28 and 3.10 mm s^{-1} , respectively.^[20] The IS values for quadrivalent organic tin compounds are substantially lower; for example, $\text{SnCl}[\text{CH}(\text{SiMe}_3)_2]_3$ has IS and QS values of 1.27 ± 0.03 and 2.18 ± 0.05 mm s^{-1} , respectively.^[21]

Detailed analysis of the temperature dependence of the Mössbauer spectra is provided in the Supporting Information, which shows that the ratio of the two tin sites B and A is 0.66 (ca. 6/9) in the temperature range 120–230 K. It has not been possible to analyze the Mössbauer data in terms of three distinct tin atom types, and the resonance associated with the larger quadrupole-splitting site includes that from the central tin atom, which is located in a distorted cubic environment.

The geometry optimization of the model tin cluster $[\text{Sn}_9(\text{Sn}(\text{NH}_2))_6]$ (**M1**) was performed in the gaseous phase by using DFT calculations. The geometry optimization was performed at the B3LYP/LanL2DZ level of theory by using the Gaussian03 package.^[22] The calculations reproduced the

main features of the experimentally observed Sn_{15} cluster with the optimized bond lengths being about 3 % larger than those observed in the crystal structures of complexes **1** and **2**. In the polyhedral representation of the cluster core, the symmetrically inequivalent tin atoms became fully symmetric after optimization. The calculated $\text{Sn}_A\text{--Sn}_A$ distances are 3.78 Å, and the corresponding distances in the crystal structures of **1** and **2** vary over the range 3.60–3.74 Å (see Table 1). The Sn_B atoms are symmetrically distant from the central cube vertices by 3.15 Å (in contrast to the slightly asymmetric distribution of distances in the X-ray structures, 2.97 to 3.06 Å).

In conclusion, we report the crystalline metalloid clusters **1** and **2**, the first examples of a body-centered cluster of Group 14 elements.^[23] Compounds **1** and **2** are also noteworthy for being i) the highest-nuclearity Group 14 clusters to be described, ii) unprecedented in this compound class for being body-centered, and iii) the first Group 14 metal clusters to have amido ligands. The inner cube of eight tin atoms (Sn_A) have the closer contacts to Sn1, and the distances between Sn1 and the remaining six tin atoms (Sn_B) are longer. The preferred method of synthesis of **1** and **2** involved a novel route, namely the reduction of the appropriate amidotin(II) chloride by the reducing agent $\text{Li}[\text{BHsBu}_3]$. DFT calculations on the model cluster $[\text{Sn}_9\{\text{Sn}(\text{NH}_2)\}_6]$ reasonably reproduced the experimental Sn1--Sn_A , Sn1--Sn_B , $\text{Sn}_A\text{--Sn}_B$, and $\text{Sn}_A\text{--Sn}_A$ distances. Mössbauer spectra of **1** are consistent with the X-ray structure in showing that there are two distinct quadrupole-splitting sites in the ratio 1.5:1, which correspond to the Sn_9 core and the six $\{\text{Sn}(\text{NRR}')\}$ moieties, but the Mössbauer data do not distinguish the Sn1 atom from the Sn_A atoms. The isomer shift of the atoms in the Sn_9 core is almost identical to that for β-tin.

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions.

1 ($Pnnm$, $R\bar{3}$): KC_8 (0.11 g, 0.81 mmol) was added with stirring to a solution of **3** (0.47 g, 0.55 mmol) in Et_2O (40 mL) at about -30°C . The mixture was stirred for 5 h and filtered. The dark red-brown filtrate was concentrated to about 3 mL, toluene (10 mL) was added, and the mixture was stored at -27°C for 3 months (initially, a black powder precipitated, which was filtered off and discarded) to yield several small black crystals of compound **1** ($Pnnm$) along with large pale crystals of unreacted **3**. In another experiment, when the crystals of unreacted **3** had precipitated, the remaining solution was decanted, concentrated again, and stored at room temperature to produce black (or dark red in thin layers) hexagonal prisms of compound **1** ($R\bar{3}$).

1 ($R\bar{3}c$, $P2_1/n$): $[\text{Sn}\{\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)_2\}]_2$ (1.23 g, 2 mmol) and SnCl_2 (0.38 g, 2 mmol) were mixed in freshly degassed THF (50 mL) at room temperature and stirred for 6 h. The reaction mixture was cooled to about -78°C , and $\text{Li}[\text{BHsBu}_3]$ (L-selectride) (3.0 mL, 1.0 M solution in THF, 3.0 mmol) was added quickly. After slowly warming to room temperature, the solution was stirred for 48 h. The solvent was removed in vacuo, and the black residue was extracted into toluene (50 mL). The deep-black extract was filtered, and the filtrate was concentrated (ca. 30 mL). Storage of the solution at room temperature for 5 days afforded crystalline **1** ($R\bar{3}c$) (0.045 g, 5 %). The synthesis of **1** ($P2_1/n$) was identical to that of **1** ($R\bar{3}c$), except that the residue was extracted with hexane. Crystals of compound **1** were only sparingly soluble in hydrocarbons or ethers.

2: $[\text{Sn}\{\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)(\text{SiMe}_3)_2\}]_2$ (1.25 g, 1.75 mmol) and SnCl_2 (0.332 g, 1.75 mmol) were mixed in freshly degassed THF (40 mL) at room temperature and stirred for 6 h. The reaction mixture was cooled to about -78°C , and $\text{Li}[\text{BHsBu}_3]$ (2.8 mL, 1.0 M solution in THF, 2.8 mmol) was added quickly. After slowly warming to room temperature, the solution was stirred for 24 h. The solvent was removed in vacuo, and the black residue was extracted into hexanes (30 mL). The deep-black extract was filtered, and the filtrate was concentrated (ca. 20 mL). Storage of the solution at room temperature for 2 days afforded crystalline **2** (0.057 g, 7 %).

Received: January 23, 2006

Revised: April 25, 2006

Keywords: amide ligands · cluster compounds · Mössbauer spectroscopy · tin · X-ray diffraction

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- 6, $R1(\text{obs. data}) = 0.0262$, $wR2(\text{all data}) = 0.0560$. Crystal data for **1** ($P2_1/n$) with $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) at 90(2) K: black plate, monoclinic, space group $P2_1/n$, $a = 16.2048(6)$, $b = 24.0255(9)$, $c = 16.6026(6) \text{ \AA}$, $\beta = 113.159(1)^\circ$, $V = 5943.0(4) \text{ \AA}^3$, $Z = 2$, $R1(\text{obs. data}) = 0.0224$, $wR2(\text{all data}) = 0.0549$. Crystal data for **2**-hexane with $\text{MoK}\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) at 90(2) K: black block, monoclinic, space group $P2_1/n$, $a = 17.5916(6)$, $b = 18.8745(6)$, $c = 21.7499(7) \text{ \AA}$, $\beta = 90.904(1)^\circ$, $V = 7220.8(4) \text{ \AA}^3$, $Z = 2$, $R1(\text{obs. data}) = 0.0249$, $wR2(\text{all data}) = 0.0693$. CCDC-295619–295624 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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