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Crystal and Molecular Structure of Tetracyclohexylsilane. A Sterically Crowded Molecule

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The crystal structure of tetracyclohexylsilane, $(C_6H_{11})_4Si$, has been determined from three-dimensional single-crystal x-ray diffraction data collected by counter methods on a computer-automated diffractometer. The compound crystallizes in the monoclinic space group C_{2h}^6-$C2/c$ with unit cell dimensions a = 17.646 (13) Å, b = 8.533 (8) Å, c = 17.793 (16) Å, β = 120.86 (3)°, and Z = 4. The structure was solved by direct methods and refined by a full-matrix least-squares procedure to a conventional R index of 0.063 for 942 reflections. The $(C_6H_{11})_4Si$ molecule lies on a site of crystallographic C_2 symmetry which leads to two independent cyclohexyl groups in the asymmetric unit. The cyclohexyl rings, which are in the chair form, are bonded equatorially to the silicon and have normal C–C distances and C–C–C angles. Because of the four bulky substituents the environment about the silicon atom is "crowded" resulting in Si–C bond distances of 1.909 (5) and 1.914 (5) Å and C–Si–C valency angles (those bisected by the C_2 axis) of 114.8 (3) and 114.1 (3)°. The observed C_2 conformation differs from the S_4 conformations reported for symmetrical tetra(aryl) group 4A derivatives and arises from enhanced nonbonded repulsions between adjacent cyclohexyl groups.

Introduction

Tetracyclohexylsilane was first prepared by the hydrogenation of tetraphenylsilane at 50–100 atm pressure and 100 °C.[1] Although initial efforts to synthesize $(C_6H_{11})_4Si$ by organometallic condensation reactions were unsuccessful,[2-4] Spialter[5] showed in 1967 that $(C_6H_{11})_4Si$ made from the reaction of $C_6H_{11}Li$ and $(C_6H_{11})_3SiF$ was identical with the product obtained from the hydrogenation of $(C_6H_5)_4Si$.

The sterically hindered nature of the $(C_6H_{11})_4Si$ moiety was anticipated from the early difficulties encountered in its synthesis,[1-4] observations of molecular models which suggested restricted rotation of the cyclohexyl rings,[1] suggestions of possible boat–chair cyclohexyl conformers,[1,2] and even the possible existence of rotational isomers.[3]

Although tetraaryl derivatives of group 4A elements have been the object of many structural investigations,[6-20] there has not been any structural characterization of the corresponding tetracyclohexyl derivatives. Particular interest in tetrasubstituted group 4A compounds has been their static and dynamic stereochemistry, molecular symmetry and crystal packing, and energetics.[17-20] This paper reports on the crystal structure of $(C_6H_{11})_4Si$ which exhibits a molecular conformation not observed previously for this class of compounds.

Experimental Section

Suitable crystals of tetracyclohexylsilane were kindly supplied by Dr. Leonard Spialter.[5] A crystal of approximate dimensions 0.14 × 0.14 × 0.20 mm was mounted along the longest crystal dimension which corresponded to the b^* direction. Preliminary indexed Weissenberg photographs revealed monoclinic symmetry and systematic absences, $h + k$ odd for hkl and $l = 2n + 1$ for all $h0l$ leading to the possible space groups $C2/c$ and Cc. The unit cell parameters were determined from a least-squares refinement of the angular settings of 12 carefully centered reflections on a Picker FACS-1 four-circle automated (PDP-8/L) diffractometer using Mo Kα radiation (λ 0.71069 Å).

Crystal Data for $(C_6H_{11})_4Si$: monoclinic; space group $C2/c$; a = 17.646 (13), b = 8.533 (8), c = 17.793 (16) Å; β = 120.86 (3)°; V = 2300 Å^3; Z = 4; d_{measd} = 1.08 (1) (by flotation), d_{calcd} = 1.04 g cm^{-3}; mol wt 360.70; $F(000)$ = 808; μ(Mo Kα) = 1.1 cm^{-1}.

Data Collection. A complete set ($h\bar{k}\bar{l}$, $\bar{h}\bar{k}l$) of three-dimensional intensity data was collected out to 41° in 2θ using zirconium-filtered Mo Kα radiation. The $\theta/2\theta$ scan mode with a fixed scan rate of 1°/min and a scan range of 2θ(Mo Kα) − 1.0° to 2θ(Mo Kα_2) + 1.0° was used. Stationary crystal, stationary counter background counts were measured for 20 s at each end of the scan. The intensities of three standard reflections were monitored after each 50 measurements to check on crystal and electronic instability and these showed no significant variation during the data collection. Absorption corrections were judged to be negligible in view of the small absorption coefficient and dimensions of the crystal. The raw intensity data were assigned estimated standard deviations and reduced to values of F_o and $\sigma(F_o)$ using $I = C - (t_c/2t_b)(B_1 + B_2)$, $F_o = (I/Lp)^{1/2}$, $\sigma(I) = [C + (t_c/2t_b)^2(B_1 + B_2) + (pI)^2]^{1/2}$ and $\sigma(F_o) = (2F_o)^{-1}(Lp)^{-1}\sigma(I)$. In these expressions C is the total count accumulated during the scan in time t_c, B_1 and B_2 are the background counts observed at each extreme of the scan each in a time t_b, and p[21] was taken to be 0.04. A total of 942 reflections had $I > \sigma(I)$ and these were used in subsequent calculations.

Solution and Refinement of the Structure. An analysis of the distribution of normalized structure factors clearly indicated a centrosymmetric structure. Hence, the space group $C2/c$ was initially assumed and was subsequently confirmed by successful refinement of the structure. The structure was solved by direct methods using MULTAN.[22] The positions of the silicon and all 12 of the carbon atoms in the asymmetric unit were readily evident from an E map generated from the solution with the highest figure of merit and lowest residual. After isotropic refinement of the heavy atoms the positions of the hydrogen atoms were introduced at their calculated positions assuming tetrahedral H–C–H angles. All C–H bond lengths were adjusted to the true internuclear value of 1.08 Å so that the coordinates would later establish the accurate intermolecular and intramolecular contact distances involving hydrogen atoms.[23] The structure was refined by full-matrix least squares assuming anisotropic motion for the silicon and carbon atoms. Each hydrogen atom was assigned the average isotropic[24] temperature factor calculated from the anisotropic thermal parameters of the carbon atom to which it was attached; however, hydrogen atom coordinates and temperature factors were not varied. A total of 114 parameters was refined yielding a data–parameter ratio of 8.3:1. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight w applied to each observation was taken to be $[\sigma(F_o)]^{-2}$. New hydrogen parameters were calculated after each least-squares cycle. The structure refinement converged to a conventional R_1 index, $\sum||F_o| - |F_c||/\sum|F_o|$, of 0.063 and a weighted R_2 index, $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, of 0.078. In the final least-squares cycle no parameter varied by more than 0.03 of its estimated standard deviation. The error in an observation of unit weight was 2.46 electrons. An analysis of $w(|F_o| - |F_c|)^2$ as a function of $|F_o|$ or $(\sin\theta)/\lambda$ revealed no dependence on these quantities suggesting the weighting scheme used was adequate. A final three-dimensional Fourier map showed no residual electron density greater than 0.20 e Å^{-3} or less than −0.30 e Å^{-3}. The neutral scattering factors for all atoms were taken from Cromer and Waber and included corrections for the real and imaginary dispersion of the silicon atom.[25] A listing of the final observed and calculated structure factors as $10|F_o|$ and $10|F_c|$ in electrons is available.[26] Final positional and thermal parameters are given in Tables I and II.

Discussion

The molecular symmetry of $(C_6H_{11})_4Si$ in the crystalline state is constrained by the space group to be C_2. A view of the molecular structure and atom-labeling scheme is presented in Figure 1. Intramolecular bond distances and angles are given in Table III.

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Table I. Positional[a] and Thermal Parameters[b] for $(C_6H_{11})_4Si$

atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Si	0	0.1946 (2)	1/4	28 (1)	100 (4)	26 (1)	0	15.5 (8)	0
C(1)	0.0790 (3)	0.3152 (6)	0.3505 (3)	33 (2)	89 (9)	31 (2)	−3 (4)	18 (2)	−5 (4)
C(2)	0.1357 (4)	0.4319 (7)	0.3344 (3)	50 (3)	185 (12)	45 (3)	−38 (5)	32 (3)	−36 (5)
C(3)	0.2077 (3)	0.5085 (8)	0.4204 (4)	46 (3)	193 (12)	58 (3)	−43 (5)	29 (3)	−31 (5)
C(4)	0.1672 (3)	0.5898 (7)	0.4674 (3)	51 (3)	145 (11)	36 (3)	−15 (5)	15 (3)	−16 (4)
C(5)	0.1094 (4)	0.4770 (7)	0.4837 (3)	57 (3)	167 (11)	36 (3)	−23 (5)	25 (3)	−30 (5)
C(6)	0.0381 (3)	0.4003 (6)	0.3978 (3)	42 (3)	171 (11)	40 (3)	−21 (5)	25 (3)	−27 (4)
C(7)	−0.0703 (3)	0.0727 (5)	0.2818 (3)	33 (3)	87 (8)	30 (2)	−2 (4)	17 (2)	−1 (4)
C(8)	−0.1492 (3)	−0.0152 (7)	0.2075 (3)	36 (3)	181 (11)	34 (3)	−27 (5)	16 (2)	2 (4)
C(9)	−0.2068 (3)	−0.0911 (7)	0.2392 (3)	38 (3)	170 (12)	50 (3)	−23 (5)	23 (3)	7 (5)
C(10)	−0.1522 (3)	−0.2017 (7)	0.3166 (4)	51 (3)	143 (10)	65 (3)	−8 (5)	37 (3)	12 (6)
C(11)	−0.0731 (4)	−0.1176 (7)	0.3910 (4)	55 (3)	211 (13)	48 (3)	−16 (6)	28 (3)	30 (5)
C(12)	−0.0161 (3)	−0.0409 (6)	0.3584 (3)	38 (3)	162 (11)	39 (3)	−15 (5)	16 (2)	19 (5)

[a] The estimated standard deviations in the least significant figures are given in parentheses here and in other tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table II. Positional and Thermal Parameters for Hydrogen Atoms

atom	x	y	z	B, Å^2
H(1)	0.1198	0.2196	0.3907	2.60
H(2)	0.0934	0.5226	0.2906	4.07
H(3)	0.1671	0.3703	0.3046	4.07
H(4)	0.2433	0.5937	0.4054	4.76
H(5)	0.2527	0.4190	0.4626	4.76
H(6)	0.2194	0.6336	0.5296	4.26
H(7)	0.1270	0.6864	0.4278	4.26
H(8)	0.0777	0.5412	0.5124	4.14
H(9)	0.1508	0.3864	0.5284	4.14
H(10)	−0.0063	0.4901	0.3552	3.77
H(11)	0.0017	0.3165	0.4127	3.77
H(12)	−0.0940	0.1685	0.3039	2.54
H(13)	−0.1890	0.0665	0.1556	3.98
H(14)	−0.1249	−0.1056	0.1828	3.98
H(15)	−0.2351	−0.0003	0.2595	4.22
H(16)	−0.2590	−0.1571	0.1861	4.22
H(17)	−0.1935	−0.2455	0.3404	4.51
H(18)	−0.1290	−0.2984	0.2947	4.51
H(19)	−0.0964	−0.0279	0.4172	4.91
H(20)	−0.0335	−0.2012	0.4418	4.91
H(21)	0.0370	0.0232	0.4118	3.97
H(22)	0.0111	−0.1317	0.3369	3.97

Table III. Interatomic Distances (Å) and Angles (deg)

Si–C(1)	1.909 (5)	C(5)–C(6)	1.541 (7)
Si–C(7)	1.914 (5)	C(7)–C(8)	1.536 (6)
C(1)–C(2)	1.540 (1)	C(7)–C(12)	1.542 (7)
C(1)–C(6)	1.542 (7)	C(8)–C(9)	1.535 (7)
C(2)–C(3)	1.545 (7)	C(9)–C(10)	1.534 (7)
C(3)–C(4)	1.519 (7)	C(10)–C(11)	1.522 (8)
C(4)–C(5)	1.533 (7)	C(11)–C(12)	1.541 (7)
C(1)–Si–C(1)[a]	114.8 (3)	C(3)–C(4)–C(5)	111.3 (5)
C(1)–Si–C(7)	106.8 (2)	C(4)–C(5)–C(6)	111.3 (4)
C(1)–Si–C(7)[a]	107.3 (1)	C(5)–C(6)–C(1)	111.6 (4)
C(7)–Si–C(7)[a]	114.1 (3)	C(6)–C(1)–C(2)	109.2 (4)
Si–C(1)–C(2)	113.9 (3)	C(7)–C(8)–C(9)	111.6 (4)
Si–C(1)–C(6)	116.3 (3)	C(8)–C(9)–C(10)	111.1 (4)
Si–C(7)–C(8)	116.8 (3)	C(9)–C(10)–C(11)	111.3 (5)
Si–C(7)–C(12)	113.6 (3)	C(10)–C(11)–C(12)	111.0 (4)
C(1)–C(2)–C(3)	111.8 (4)	C(11)–C(12)–C(7)	111.8 (4)
C(2)–C(3)–C(4)	111.0 (4)	C(12)–C(7)–C(8)	109.3 (4)

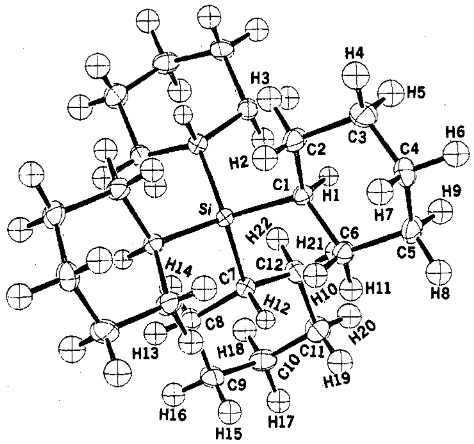

Figure 1. Molecular structure of $(C_6H_{11})_4Si$ showing the labeling of atoms. This view is down the molecular C_2 axis.

Table IV. Dihedral Angles[b] in $(C_6H_{11})_4Si$

i	j	k	l	dihedral angle, deg
C(1)	C(2)	C(3)	C(4)	−56.7
C(2)	C(3)	C(4)	C(5)	55.1
C(3)	C(4)	C(5)	C(6)	−55.1
C(4)	C(5)	C(6)	C(1)	56.1
C(5)	C(6)	C(1)	C(2)	−56.2
C(6)	C(1)	C(2)	C(3)	56.5
C(7)	C(8)	C(9)	C(10)	−56.4
C(8)	C(9)	C(10)	C(11)	55.3
C(9)	C(10)	C(11)	C(12)	−55.1
C(10)	C(11)	C(12)	C(7)	56.3
C(11)	C(10)	C(9)	C(8)	−56.4
C(12)	C(11)	C(10)	C(9)	56.4
Si	C(1)	C(2)	C(3)	−171.6
Si	C(7)	C(8)	C(9)	−172.8
C(2)	C(1)	Si	C(1^a)	−56.2
C(8)	C(7)	Si	C(7^a)	−71.0

[a] Symmetry transformation $\bar{x}, y, 1/2 - z$. [b] A positive angle represents a clockwise rotation of the bond kl with respect to the bond ij, when viewed along the bond jk.

There are two cyclohexyl groups in the asymmetric unit and their molecular characteristics are practically identical. The variation in C–C bond lengths of 1.519–1.545 Å in ring A (C1–C2–C3–C4–C5–C6) and 1.522–1.542 Å in ring B (C7–C8–C9–C10–C11–C12) compare favorably with those found in other cyclohexyl derivatives.[27,28] The average[29] of the 12 C–C bond lengths in $(C_6H_{11})_4Si$ is 1.536 ± 0.002 Å which is slightly larger than the 1.520 ± 0.003 Å found from an electron diffraction study of cyclohexane.[30] Similarly, the ranges in the C–C–C angles of rings A and B agree with those found in previously reported cyclohexyl compounds.[27,28,30] In particular, it is worthy of note that the two C–C–C angles at the apex carbon atoms, C(2)–C(1)–C(6) 109.2 (4)° and C(8)–C(7)–C(12) 109.3 (4)°, are significantly smaller than the other ten endocyclic valency angles (Table III). Similar skeletal deformations occur in substituted benzene derivatives[31,32] and it is likely that substituent electronic effects are operative in cyclohexyl rings also.

Each cyclohexyl ring is in a chair conformation. The endocyclic dihedral angles are given in Table IV. The average value[29] of the absolute magnitudes for these 12 torsion angles is 56.0 ± 0.2° which is identical with that reported for cyclohexane.[30] Both rings are equatorially attached to the silicon atom which can be succinctly shown by the torsion angles Si–C(1)–C(2)–C(3) of −171.6° and Si–C(7)–C(8)–C(9) of −172.8°.

The parameters presented above indicate there is relatively little distortion of the individual cyclohexyl ring geometry compared to free cyclohexane. The "crowded" nature of this molecule is shown by examining parameters nearer the silicon atom. Thus, the Si–C(1), 1.909 (5) Å, and Si–C(7), 1.914 (5) Å, bond lengths are significantly larger than the accepted[33] alkyl–Si bond length of 1.870 ± 0.005 Å, indicating some bond stretching in order to accomodate the four bulky substituents around the silicon. Furthermore, the $(C_6H_{11})_4Si$ molecule is compressed along the molecular C_2 axis. The two C–Si–C valency angles bisected by the C_2 axis C(1)–Si–C(1) ($\bar{x}, y, {}^1/_2 - z$) 114.8 (3)° and C(7)–Si–C(7) ($\bar{x}, y, {}^1/_2 - z$) 114.1 (3)° indicate considerable flattening of the molecule from idealized "tetrahedral" symmetry. The corresponding angle in tetraphenylsilane is 109.5°.

The crystal structure consists of discrete $(C_6H_{11})_4Si$ molecules separated by normal van der Waals distances. The shortest intermolecular H···H and H···C distances are H(3)···H(17) (${}^1/_2 + x, {}^1/_2 + y, z$) 2.412 Å, H(9)···H(17) ($\bar{x}, \bar{y}, \bar{z}$) 2.379 Å, H(6)···C(8) (${}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$) 2.981 Å, and H(3)···C(9) (${}^1/_2 + x, {}^1/_2 + y, z$) 3.011 Å while the corresponding shortest intramolecular van der Waals contacts between adjacent rings are H(1)···H(13)^a 2.215 Å, H(2)···H(10)^a 2.254 Å, H(14)···H(22)^a 2.219 Å, H(3)···H(12)^a 2.409 Å, H(14)···C(12)^a 2.984 Å, H(1)···C(8)^a 2.876 Å, H(13)···C(1)^a 2.916 Å where in each of the foregoing the symmetry operation indicated by superscript a refers to the transformation $\bar{x}, y, {}^1/_2 - z$.

The molecular symmetry of tetracyclohexylsilane is C_2 and $(C_6H_{11})_4Si$ represents the first example of a symmetric tetrasubstituted group 4A derivative to have this symmetry in the crystalline state. The tetraphenyl derivatives of C,[12,13] Si,[6] Ge,[7,8] Sn,[9,10] and Pb[11] ($P\bar{4}2_1c$), the tetra-2-thienyl derivatives of Si,[14] Ge,[15] Sn,[15] and Pb[15] ($P\bar{4}2_1c$), the tetrakis(pentafluorophenyl) compounds of Si,[34] Ge,[18] and Sn[18] ($I4_1/a$), tetrakis(3-methylphenyl)tin[17] ($I4_1/a$), and tetrakis(4-methylphenyl)tin[16] ($I\bar{4}$) all crystallize in tetragonal space groups and each exhibits S_4 molecular symmetry in the crystalline state. This apparent preference of S_4 symmetry in crystalline tetrasubstituted group 4A derivatives has been previously noted and results in very efficient packing for such molecules.[19–20] The S_4 molecular conformation has also been determined to be energetically favored for an isolated $(C_6H_5)_4Si$ molecule on the basis of empirical force field calculations.[20] We are not exactly certain why $(C_6H_{11})_4Si$ does not adopt a S_4 conformation. Examination of inter- and intramolecular contact distances for a $(C_6H_{11})_4Si$ species forced into a S_4 conformation (keeping molecular dimensions as found in the C_2 structure) does not reveal any unusually close contacts which would necessarily negate a S_4 conformation. A more accurate assessment would involve an analysis and comparison of the crystal lattice energies for both C_2 and S_4 conformations. Such a study is currently underway.

The appearance of the lower C_2 molecular symmetry in $(C_6H_{11})_4Si$ further substantiates the crowded nature of this molecule and implicates a large steric requirement for the cyclohexyl group. The unfavorable repulsive nonbonded interactions between adjacent cyclohexyl rings (A and B) are not alleviated by just stretching of the Si–C bonds or opening of the C–Si–C and C-C-Si angles or by relaxing the cyclohexyl ring torsions. In this instance, further molecular distortion occurs such that the two pairs of cyclohexyl rings which are no longer symmetry related can help relax the repulsive strain by adjusting independently from each other. This relaxation mode is not available to conformers with S_4 symmetry. The magnitude of this independent adjustment may be seen from the C(2)–C(1)–Si–C(1^a) and C(8)–C(7)–Si–C(7^a) dihedral angles given in Table IV. For a molecule of S_4 symmetry these two dihedral angles would be equal. For $(C_6H_{11})_4Si$ these angles are −56.2 and −71.0°, respectively, which means the rings A and B are twisted by about 15° from an "idealized" S_4 conformation.

Although the tetragonal space groups commonly observed for tetra(aryl) compounds, $P\bar{4}2_1c$, $I\bar{4}$, and $I4_1/a$, can accomodate molecules of C_2 site symmetry, this has, in fact, never been found to occur. For $(C_6H_{11})_4Si$ the crystal system is lowered to monoclinic in order to accomodate the lowered molecular symmetry of the $(C_6H_{11})_4Si$ molecule. This observation is consistent with Kitaigorodsky's[35] findings from an analysis of close-packing based on symmetry considerations that the C_2 sites in the listed tetragonal space groups are not favored for occupancy by symmetric tetrasubstituted group 4A compounds.

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Supplementary Material Available: A listing of structure factor amplitudes (5 pages). Ordering information is given on any current masthead page.

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Structural Studies of Precursor and Partially Oxidized Conducting Complexes. 19. Synthesis and Crystal Structure of $Cs_2[Pt(CN)_4]Cl_{0.30}$, the First Anhydrous One-Dimensional Tetracyanoplatinate Chloride Complex[1]

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The preparation and single-crystal x-ray structural characterization of a new, partially oxidized tetracyanoplatinate (POTCP), $Cs_2[Pt(CN)_4]Cl_{0.30}$, CsCP(Cl), has been carried out. This one-dimensional conducting salt crystallizes with four formula units in the tetragonal unit cell $I4/mcm$, with cell constants a = 13.176 (2) Å, c = 5.718 (1) Å, and V = 992.7 Å^3. A total of 3112 observed data were averaged to yield 427 independent reflections. The structure was solved by standard heavy-atom methods and was refined by full-matrix least squares to a final $R(F_o^2) = 0.045$ and $R_w(F_o^2) = 0.059$. Pertinent structural features include perfectly linear chains of Pt atoms with Pt–Pt separations crystallographically constrained to a value of $(c/2)$ = 2.859 (2) Å and interchain Pt–Pt distances of 9.317 Å. Separations between the Cs^+ and Cl^- ions are significantly shorter than the sum of the ionic radii. A discussion of these unusually short interionic distances and the absence of hydration as determined from the structural study and thermogravimetric analyses is given.

Introduction

The one-dimensional tetracyanoplatinate (TCP) conductors have received a great deal of attention in recent years.[2] The interest in these systems has been generated in no small measure by the search for high-temperature excitonic superconductors. The one-dimensional properties of partially oxidized tetracyanoplatinates are presently under extensive study in our laboratory.[3] These polynuclear systems with infinitely long metal atom arrays offer a suitable series on which to test further details and applicability of one-dimensional band theory[4] in a comprehensive manner. Structural studies of these systems are a necessary prerequisite for the development of meaningful interpretive models. By incrementally varying such parameters as cation and anion site occupancy, size, and charge ratios, theoretical predictions may be tested in minute detail. With this in mind we have undertaken the synthesis and structural characterization of a new one-dimensional conducting salt, cesium tetracyanoplatinate chloride, $Cs_2[Pt(CN)_4]Cl_{0.30}$.

Experimental Section

Crystal Preparation. The preparation of $Cs_2[Pt(CN)_4]Cl_{0.30}$, CsCP(Cl) hereafter, was carried out by the direct interaction of $Cs_2[Pt(CN)_4]$, $Cl_2(g)$, and CsCl in aqueous solution. A 15-mL aqueous solution containing 0.5 g of $Cs_2[Pt(CN)_4]$ was saturated with $Cl_2(g)$ at 1 atm. After driving off excess Cl_2 at 100 °C, an additional 2.5 g of $Cs_2[Pt(CN)_4]$ was added. The resulting solution was concentrated to a volume of 5 mL and cooled to 0 °C. A mass of microcrystalline brown product was collected and redissolved in 50 mL of a 2.0 M CsCl solution. This step was found to be necessary in the preparation of $Rb_2[Pt(CN)_4]Cl_{0.3}\cdot 3H_2O$ in order to avoid formation of the cation-deficient material.[5] After 24 h at room temperature, bronze colored crystals of CsCP(Cl), suitable for a detailed x-ray structural analysis, were collected. Anal. Calcd for $Cs_2[Pt(CN)_4]Cl_{0.30}$: C, 8.35; N, 9.73; Cl, 1.85. Found (Midwest Microlab Inc., Indianapolis, Ind.): C, 8.34; N, 9.49; Cl, 1.87, 1.90, 2.05 (average = 1.94). The presence of Cs and Pt was confirmed by emission spectrographic analyses.[16]

Collection of X-Ray Diffraction Data. A well-formed crystal of approximate dimensions 0.06 × 0.10 × 0.22 mm was sealed in a glass capillary and mounted on a Syntex $P2_1$ diffractometer equipped with a molybdenum x-ray tube and a graphite monochromator. From the observed Laue symmetry ($4/mmm$) and the systematic absences (hkl for $h + k + l = 2n + 1$ and $h0l$ ($0kl$) for $l = 2n + 1$) a body-centered tetragonal cell was indicated. The same results were obtained for three different crystals. The centrosymmetric space group $I4/mcm$ [D_{4h}^{18}, No. 140] was chosen initially and confirmed by the satisfactory least-squares refinement. The refined cell parameters, determined from 25 diffractometer-centered reflections with $2\theta \geq 22.5°$, are a = 13.176 (2) Å, c = 5.718 (1) Å, and V = 992.7 Å with Z = 4 and a calculated density of 3.88 g cm^{-3}. Intensity data were collected using a coupled ω–2θ scan for 3112 reflections in the region $+h,\pm k,\pm l$ with $5° \leq 2\theta \leq 60°$. The reflection scan ranges were from $[2\theta(K\alpha_1) - 1.0]°$ to $[2\theta(K\alpha_2) + 1.0]°$ with scan rates from $2.0°(2\theta)$/min to $29.3°(2\theta)$/min. The actual scan rate was determined from a preliminary peak intensity measurement for each reflection. Stationary background counts were taken at each extremity of the scan such that the total background counting time was equal to half of the total scan time. Three standard reference reflections (600, 060, 004) were measured after every 50 reflections and showed an average decrease in intensity of 9% during the course of data collection. An isotropic correction was applied to the intensity data to account for this effect. Net intensities (I) were calculated as

$$I = \left(P - \frac{t_P}{t_B}(B_1 + B_2)\right)SR$$

where P is the total scan count, B_1 and B_2 are the background counts, SR is the scan rate, and t_P and t_B are the counting times for the peak and background, respectively. The value of $\sigma(I)$ was evaluated as

$$\sigma(I) = \left[I + \left(\frac{t_P}{t_B}\right)^2(B_1 + B_2) + (cI)^2\right]^{1/2} SR$$

where c, a factor to account for errors other than those arising from counting statistics, was assigned a value of 0.05.

The 3112 reflections were averaged to yield 427 symmetry-independent data. The "agreement index"

$$R(F_o^2) = \sum(F_{av}^2 - F_o^2)/\sum F_o^2$$

between averaged reflections was 0.121 before application of absorption corrections and 0.048 after the data were corrected for absorption (μ_c = 185.4 cm^{-1}).

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