



Figure 1. Solid-state NMR spectrum of ^{13}C in $\text{CsZr}_6\text{I}_{14}\text{C}$ as a function of increasing shielding (Me_4Si at 0 ppm). Crosses are experimental points; the smooth line is a least-squares fit with axially symmetric shielding.

The Fourier transform of the FID of ^{13}C in $\text{CsZr}_6\text{I}_{14}\text{C}$ is shown in Figure 1. The shift scale has that for Me_4Si as the origin, and positive shifts are deshielded (downfield). Also shown is the fit of the theoretical expression to the NMR spectrum of the powdered sample that is achieved with a least-squares routine¹³ assuming axially symmetric shielding. The main features of the $\text{CsZr}_6\text{I}_{14}\text{C}$ spectra are as follows:

(a) There is only one ^{13}C shielding tensor, as expected. Since the ^{13}C is buried in the cluster, differences in bonding between clusters in different structures might be expected not to affect the ^{13}C electronic environment.

(b) The shielding is axially symmetric, in confirmation of the X-ray structure that shows a nearly square-bipyramidal zirconium environment about the carbon.

(c) σ_{\parallel} (15 ppm) is shielded (upfield) from σ_{\perp} (54 ppm), in agreement with the shorter Zr-C bonds along the approximate C_4 axis of the cluster. (One must still be cautious about interpreting chemical shifts in such a way; see ref 14.)

(d) The carbon is shielded relative to most carbon tensors in organic compounds, and in fact the isotropic value and anisotropy are very similar to those of carbon in a primary methyl group. The relatively small value of the anisotropy suggests that the bonding overlap is fairly symmetric and that perhaps the main difference between σ_{\parallel} and σ_{\perp} originates from the difference in bond lengths. The latter difference has been shown to depend in turn on the asymmetry of the bonding of the terminal iodine atoms at each zirconium vertex.⁹

(e) The spin-lattice relaxation time of carbon in the paramagnetic⁹ $\text{CsZr}_6\text{I}_{14}\text{C}$ was determined with use of an inversion-recovery experiment. The value of T_1 was found to be 4 ± 3 ms. This result is not in disagreement with that expected for carbon coupled to the quadrupolar zirconium and iodine nuclei. The electron spins close to the carbon must have spin-lattice transition rates so large that the electron spin is decoupled from the carbon nucleus.

Surprisingly, an accurate measurement of the shielding of ^{13}C in the structurally similar $\text{Zr}_6\text{I}_{12}\text{C}$ has not been obtained, mainly because of the extreme broadness of the signal. But it is clear that the pattern for a single-phase sample of $\text{Zr}_6\text{I}_{12}\text{C}$ runs from at least 28 to 480 ppm, with an isotropic value of 250–300 ppm. The value of 480 ppm is the greatest deshielding ever reported

for ^{13}C . Spin counting has confirmed that all the ^{13}C is being observed, and it appears that the signal is again more intense downfield than upfield (axial symmetry cannot be assigned yet).

For comparison, metal carbonyls exhibit isotropic shifts to 360 ppm, with a range of shifts >400 ppm,¹⁵ and inorganic carbides show shift values¹⁶ between +350 and -100 ppm, the largest anisotropy being in boron carbide, where the isotropic shift is about 300 ppm. A plausible source of the relative deshielding in $\text{Zr}_6\text{I}_{12}\text{C}$ is a substantial paramagnetic term in the chemical shift, an effect that is often seen in magnetic susceptibility measurements on such materials. However, the contrasting behavior of $\text{CsZr}_6\text{I}_{14}\text{C}$ vs. $\text{Zr}_6\text{I}_{12}\text{C}$ is not understood. No drastic differences in the carbide cluster bonding are indicated by the results of extended Hückel calculations⁹ on isolated $\text{Zr}_6\text{I}_{18}\text{C}^{2-}$ ($n = 5, 6$) clusters, that is, on Zr_6I_{12} units plus six terminal iodides with cluster geometries as found in $\text{CsZr}_6\text{I}_{14}\text{C}$ and $\text{Zr}_6\text{I}_{12}\text{C}$.

Registry No. $\text{CsZr}_6\text{I}_{14}\text{C}$, 98193-80-7; $\text{Zr}_6\text{I}_{12}\text{C}$, 98169-75-6.

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Crystal Structure of $[\text{Co}(\text{CoL}_3)_2]_2(\text{SO}_4)\text{Cl}_4$: Corrigendum

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Received April 17, 1985

The crystal structure of $(\text{Co}(\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)_3)_2)_2(\text{SO}_4)\text{Cl}_4$, reported⁴ in space group $P\bar{1}$ with cell constants $a = 11.803$ (3) Å, $b = 17.227$ (8) Å, $c = 17.239$ (4) Å, $\alpha = 83.24$ (2)°, $\beta = 69.98$ (2)°, and $\gamma = 69.99$ (3)°, has been recast and refined in a more appropriate space group. The matrix

$$\begin{pmatrix} 0 & 1 & -1 \\ -1 & 1 & 1 \\ 1 & 0 & 0 \end{pmatrix}$$

transforms the triclinic axes to the tetragonal axes $a = 22.892$ Å, $b = 22.907$ Å, and $c = 11.803$ Å, and the transformed coordinates are consistent with the space group $I4_1/a$ (No. 88, origin at $\bar{1}$) with $a = b = 22.900$ Å. The transformed reflection set generated 2724 independent reflections of which 2210 were observed ($I_0 \geq 3\sigma(I)$); the R value for averaging equivalent reflections was 0.031. The new symmetry requires $1/2$ cation per asymmetric unit and $Z = 4$ for the title formula. The central cobalt atom (Co2) occupies a crystallographic inversion center; the sulfato sulfur atom (S13) and one of the chloride anions (Cl1) occupy sites of $\bar{4}$ symmetry. All other atoms are in general positions. Refined atomic coordinates, thermal parameters, assumed hydrogen parameters, and structure factors have been deposited as supplementary material.

The tetragonal description refines to the same R values as does the triclinic description and yields no significantly different bond lengths or angles.

Supplementary Material Available: Listings of atomic positional parameters, thermal parameters, hydrogen positional parameters, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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