Table S1. Crystal data for compounds **1** and **2** and Experimental Details for the Crystallographic Analyses*.

Compound	1	2
Formula	$Ba_2CoSi_2O_7$	$BaCo_2Si_2O_7$
Formula weight	501.76	423.36
Crystal system	monoclinic	monoclinic
Color/Habit	blue/plates	blue/plates
a (Å)	8.450(1)	7.2131(6)
b (Å)	10.729(1)	12.781(1)
c (Å)	8.474(1)	13.762(1)
β (°)	111.365(8)	90.299(8)
V (Å³)	715.4(3)	1268.7(3)
Space group	$C2/c$ (#15)	$C2/c$ (#15)
Z value	4	8
ρ_{calc} (g/cm³)	4.66	4.43
μ (Mo Kα) (cm⁻¹)	135.1	116.7
Temperature (°C)	20	20
λ (Mo)	0.71069Å	0.71069Å
$2\Theta_{max}$ (°)	50.0	55.0
Octants	+h, +k, ±l	+h, +k, ±l
No. Obs. (I>3σ)	568	1370
Goodness of fit	1.85	2.91
Residuals: R; Rw	0.021; 0.026	0.042; 0.056
Abs. cor. (psi scans)	empirical	empirical
Largest peak in final diff. map	0.69	2.50

*$R = \Sigma_{hkl}(||F_{obs}|-|F_{calc}||/\Sigma_{hkl}|F_{obs}|$; $R_w = [\Sigma_{hkl}w(|F_{obs}|-|F_{calc}|^2)/\Sigma_{hkl}wF_{obs}^2]^{1/2}$, $w = 1/\sigma^2(F_{obs})$; $GOF = [\Sigma_{hkl}(|F_{obs}|-|F_{calc}|/\sigma(F_{obs})]/(n_{data} - n_{vari})$.

***Experimental Details for the Crystallographic Analyses.** Royal blue crystals of **1** and **2** were cleaved from the appropriate bulk samples. The crystals used for intensity measurements were mounted in thin-walled glass capillaries. The crystals were not measured. Diffraction

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measurements at 20°C were made on a Rigaku AFC6S four-circle diffractometer using graphite monochromated Mo Kα radiation. Unit cells were determined from 15 randomly selected reflections obtained by using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table 1. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz-polarization (Lp) and absorption corrections were applied to the data in each analysis. Neutral atom scattering factors were calculated by the standard procedures.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] No corrections for extinction were made. Full-matrix least-squares refinements minimized the function: $\Sigma_{hkl} w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$ and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02 I_{net})^2]^{1/2}/Lp$. The intensities of three standard reflections were measured every 150 reflections. These showed no significant deviations during the data collection process.

Both compounds crystallized in the monoclinic crystal system. For both compounds the patterns of systematic absences observed in the data were consistent with either of the space groups Cc or C2/c. The centric space group C2/c was assumed and confirmed by the successful solution and refinement of the structures in each case. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All atoms were refined with anisotropic thermal parameters.

Table S4. Anisotropic Thermal Parameters.

U values for Ba2CoSi2O7, 1.

ATOM	U11	U22	U33	U12	U13	U23
Ba	0.0093(02)	0.0084(02)	0.0084(02)	0.00012(14)	0.00320(16)	-0.00046(15)
Co	0.0096(06)	0.0099(06)	0.0072(06)	0	0.0030(05)	0
Si	0.0080(08)	0.0065(09)	0.0079(08)	-0.0003(07)	0.0031(07)	-0.0001(07)
O(1)	0.016(03)	0.013(04)	0.020(03)	0	0.010(03)	0
O(2)	0.009(02)	0.009(02)	0.013(02)	0.0003(17)	0.0028(18)	0.0024(18)
O(3)	0.013(02)	0.013(02)	0.007(02)	-0.0016(18)	0.0031(17)	0.0012(18)
O(4)	0.012(02)	0.008(02)	0.014(02)	-0.0006(18)	0.0047(19)	0.0009(18)

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Table S5. Anisotropic Thermal Parameters.

U values for BaCo2Si2O7, 2.

ATOM	U11	U22	U33	U12	U13	U23
Ba	0.0078(03)	0.0073(03)	0.0063(03)	-0.00028(15)	0.00006(17)	-0.00028(15)
Co(1)	0.0081(07)	0.0066(07)	0.0074(07)	0	-0.0002(05)	0
Co(2)	0.0086(07)	0.0075(07)	0.0059(06)	0	-0.0000(05)	0
Co(3)	0.0037(05)	0.0062(05)	0.0067(05)	0.0001(03)	0.0011(04)	-0.0004(04)
Si(1)	0.0041(09)	0.0025(09)	0.0074(09)	-0.0003(07)	0.0003(07)	-0.0004(07)
Si(2)	0.0032(09)	0.0036(09)	0.0066(09)	-0.0014(07)	-0.0001(07)	0.0001(07)
O(1)	0.012(03)	0.007(02)	0.008(02)	0.004(02)	0.000(02)	-0.0006(20)
O(2)	0.008(03)	0.010(03)	0.012(03)	0.005(02)	-0.002(02)	-0.003(02)
O(3)	0.007(03)	0.008(03)	0.008(02)	0.0006(20)	0.0030(20)	0.0007(20)
O(4)	0.006(03)	0.005(02)	0.006(02)	-0.0017(19)	0.0013(19)	0.0005(19)
O(5)	0.005(03)	0.003(02)	0.014(03)	0.0008(19)	0.004(02)	-0.0011(19)
O(6)	0.017(03)	0.012(03)	0.008(02)	-0.007(02)	-0.001(02)	0.001(02)
O(7)	0.006(02)	0.007(03)	0.015(03)	-0.0027(20)	0.004(02)	-0.001(02)

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