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On the Synthesis and Crystal Structure of Dodecabismuth Tetradecachloride, $Bi_{12}Cl_{14}$

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An improved synthesis has been developed for $Bi_{12}Cl_{14}$ based on its crystallization from a reduced KCl-$BiCl_3$ melt, and the previously reported crystal structure[1] for the compound confirmed. Peak height diffraction data were collected on an automatic diffractometer usying MoKα radiation. A total of 1705 data above the $3\sigma_F$ threshold were refined by full matrix least squares methods to a conventional residual of 0.169 using anisotropic and isotropic thermal parameters for bismuth and chlorine respectively. Some further refinement of the original data set was also carried out varying the same parameters ($R = 0.148$). The results confirm the previously reported structure in detail but none of the refinements give a more precise description, all positional and distance parameters falling within a 3σ range of one another.

Introduction

The correct stoichiometry of the so-called bismuth monochloride was first established to be $BiCl_{1.167}$ about twelve years ago through a crystal structure determination[1] using one of about 100 crystals which had been isolated. Sufficient pure material for an analytical confirmation could not be obtained. Even long equilibrations in the $BiCl_3$-Bi system gave a poor yield of the phase; the viscosity of the melts, the incongruent melting of the subchloride (323°) and the large difference between the compositions of the metal-saturated salt (45 mol % Bi in $BiCl_3$)[2] and the compound (61%) all restricted a substantial conversion.[3] Earlier attempts to prepare larger amounts suitable for chemical analysis through fractionation of the polycrystalline mixture of the normal and subchlorides were also unsatisfactory in that partial decomposition evidently led to a product contaminated with excess metal.[3]

The present study was undertaken with the intent of producing $BiCl_{1.167}$ in good yields by crystallization from a reduced MCl-$BiCl_3$ melt, the analytical composition of the product being corrected for solvent retention through knowledge of the concentration of M in the crystals and in the final solvent.[4] Although the necessary accuracy for this analytical procedure turned out to be precluded by large changes in the composition of the solvent during the process of crystallization the method did give good yields of high quality single crystals. The previous crystal structure work had employed film methods, CuKα radiation, and less extensive computing facilities, and the refinement had been carried out only with isotropic thermal parameters even though there was considerable evidence of highly anisotropic thermal motion in the final difference map. Some small uncertainties in the exact location if not the number of the lighter chloride atoms naturally remained. Therefore diffraction data were recollected and refined by more modern methods in order to confirm in detail the previous stoichiometry and structure, *viz.*, $Bi_9^{5+}(BiCl_5^{2-})_2(Bi_2Cl_8^{2-})_{1/2}$. Some additional refinements were also carried out with the original data set.

The system KCl-$BiCl_3$ was chosen from among a number of possibly binary solvent systems.[5] The selection was made primarily on the basis of the wide composition and temperature ranges available in the probable presence of the desired chlorobismuthate(III) anions. These variations offered the most favorable conditions for a suitable reduction and isolation of the desired phase at temperatures below its decomposition point.

Experimental Section

The addition of small amounts of KCl to the Bi-$BiCl_3$ system was found to increase the yield of cry-

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stals, while large concentrations of base prevented any reduction from occurring. These observations are consistent with a common ion effect of the $BiCl_4^-$ and $BiCl_5^{2-}$ species which evidently[5,6] form on addition of chloride ions to $BiCl_3$. At higher chloride concentrations most of the bismuth in the melt is strongly complexed thus increasing the stability of the Bi^{III} state and decreasing the reduction to the Bi_9^{5+} ion. The best preparative conditions appeared to be equilibration of melts containing 20 to 30 mol% KCl in $BiCl_3$ with excess metal for several hours at *ca.* 315° followed by slow cooling to 285° and then filtration.

A total of 2881 three-dimensional data contained in one octant of a 2θ sphere of 50° were measured at room temperature using an automated diffractometer[7] with Zr-filtered MoKα radiation ($\lambda = 0.71069$ Å), a take-off angle of 4.5°, and with the spindle axis collinear with the crystal c-axis. The peak height intensity data were collected together with stationary crystal-stationary counter background measurements on both sides of the peak along a θ-2θ path. The choice of space group Pnnm (D_{2h}^{12}, No. 58) or Pnn2 (C_{2v}^{10}, No. 34) was confirmed by examination of the distribution of the net intensities of symmetry-extinct data, $h+\ell = 2n+1$ for $h0\ell$ and $k+\ell = 2n+1$ for $0k\ell$, which were found to be arranged in a Gaussian distribution about zero counts. The lattice parameters of the orthorhombic crystal system were redetermined from the ω-arc settings of the Freidel-related pairs of three independent reflections whose peaks were centered by top-bottom, left-right beam splitting in the alignment of the crystal. The results compare favorably with those reported earlier (counter, film[1]): a = 23.067(6), 23.057(2); b = 14.992 (19), 15.040(7); and c = 8.772(8), 8.761(3) Å.

The peak height data were converted to integrated intensities by the method of Alexander and Smith,[8] then corrected for Lorentz, polarization, and absorption effects. Programs used in this work, ABCOR, OMEGA, ALFF, ORFLS, and ORFFE, are referenced elsewhere.[9] The transmission factors, calculated for a cylindrical crystal shape (0.237×0.167 mm dia.) using a linear absorption coefficient of 678.2 cm^{-1}, ranged from 0.0011 to 0.0127. The standard deviations of the structure factors were estimated by the method of finite differences[10] with the fractional random errors in the total count, background count, and absorption factor arbitrarily assigned values of 0.10, 0.10, and 0.15, respectively. A total of 1705 reflections exceeded the $3\sigma_F$ threshould chosen for consideration as observable. The square of the reciprocal of the standard deviation was used as the weight of each structure factor in the least-squares refinement. Concomitant refinements were carried out using these data and the original 1956 observed data[1] with atomic scattering factors for neutral Bi and Cl taken from Hanson, et al.,[11] and corrections applied for real imaginary parts of anomalous dispersion.[12]

Results and Discussion

The earlier film data had been collected by the equi-inclination Weissenberg technique supplemented by precession photographs. The present refinement of the corrected data was begun with unit weights and a different scale factor for each of the six layers, hk0 through hk5. If a complete anisotropic refinement is attempted with film data collected about only one axis and a different variable scale factor allowed for each layer, the least-squares equations will generate a singular matrix. In order to determine a single common scale factor several cycles of least-squares were therefore performed using isotropic thermal parameters and unit weighting of each observed reflection and noting that the positional parameters did not change [$R_1 = 0.183 = \Sigma(|\Delta|/|F_o|)$, $\Delta = |F_o| - |F_c|$]. After the data were then converted to the same scale, the thermal parameters of the bismuth atoms were allowed to vary anisotropically. The weights of the refletions were subsequently adjusted by alternately plotting $\omega\Delta^2$ ($\omega = \sigma^{-2}$) for groups of 100 reflections versus F_o and $\sin\theta/\lambda$ and adjusting ω such that $\omega\Delta^2$ for the groups were constant.[9] Successive iterations of least-squares yielded a conventional residual of 0.148 and R_ω of 0.206. Attempts to vary the thermal parameters for the chlorine atoms anisotropically gave non-positive definite, i.e., physically unreal, results. Since the earlier isotropic refinement using these data with seven-tenths as many parameters had resulted in values of 0.151 and 0.187 for R_1 and R_ω respectively, it is obvious that the adjusted weighting scheme used was not as good as the original weights chosen to reflect the experimental uncertainties in the data.

A difference Fourier revealed peaks of ±9 e/Å^3 in the neighborhood of the Bi_9^{5+} cation and ±4 e/Å^3 in the region of the chlorine atoms on a scale of 186 and 35 e/Å^3 for the bismuth and chlorine atoms, respectively; peaks remaining near bismuth in the earlier isotropic refinement were $\leqslant 28$ e/Å^3 on the present scale.

Refinement of the counter data starting with the previously determined positional parameters yielded values of $R_1 = 0.208$ and $R_\omega = 0.232$ with isotropic thermal parameters and $R_1 = 0.169$ and $R_\omega = 0.192$ with anisotropic thermal parameters for the bismuth atoms. The final data are given in Table I. Again the chlorine thermal parameters could not be varied anisotropically. That the absorption corrections were not totally correct was manifest in the observation that structure factors for 186 symmetry-equivalent reflections differed from each other by an average of 16%. The final difference map showed peaks of ±5 e/Å^3 near the bismuth positions and ± 6 e/Å^3 near the chlorine positions on a scale of 195 and 28 e/Å^3 for bismuth and chlorine, thereby indicating

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Table I. Final positional and thermal parameters for $Bi_{12}Cl_{14}$, counter data.[a]

Atom	x/a	y/b	c/z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Bi(1)[c]	.0461(3)	.2230(3)	.1870(6)	24(1)	40(2)	86(7)	—4(1)	13(3)	—13(4)
Bi(2)	.2004(2)	.1546(3)	.1822(7)	24(1)	29(2)	101(8)	—4(1)	—11(3)	17(3)
Bi(3)	.4103(3)	.4545(4)	0	17(1)	18(2)	89(10)	1(1)	0	0
Bi(4)	.0984(3)	.0694(4)	0	19(1)	23(3)	114(12)	—7(2)	0	0
Bi(5)	.0733(4)	.3981(5)	0	36(2)	24(3)	135(14)	11(2)	0	0
Bi(6)	.4132(4)	.1014(5)	0	32(2)	34(3)	61(10)	—15(2)	0	0
Bi(7)	.3576(3)	.1918(3)	0.5	12(1)	20(2)	81(9)	0(1)	0	0
Bi(8)	.2386(3)	.3297(5)	0	20(2)	28(3)	119(11)	4(2)	0	0
Bi(9)	.1528(3)	.3422(4)	.2672(7)	24(1)	48(3)	108(8)	0(2)	—3(3)	—42(4)

Atom	x/a	y/b	c/z	B, Å^2
Cl(10)	0	0	.278(6)	3.5(9)
Cl(11)	.049(2)	.417(3)	0.5	4.3(10)
Cl(12)	.111(2)	.125(3)	0.5	3.1(8)
Cl(13)	.264(2)	.293(3)	0.5	4.2(10)
Cl(14)	.283(2)	.056(3)	0.5	4.1(10)
Cl(15)	.314(2)	.020(3)	0	4.2(10)
Cl(16)	.339(1)	.214(2)	.193(4)	3.4(6)
Cl(17)	.333(1)	.444(2)	.212(4)	2.8(5)
Cl(18)	.436(2)	.338(3)	0.5	2.3(6)
Cl(19)	.441(1)	.084(2)	.302(5)	4.0(7)
Cl(20)	.465(2)	.274(3)	0	2.9(8)

[a] Standard deviations of least significant figures are given in parentheses. [b] The form of the anisotropic ellipsoid is exp$[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$. The β values have been multiplied by 10^4. [c] Positions as defined in Ref. 1.

that the bismuth atoms accounted for the counter data somewhat "better" than with film data, and the chlorines, somewhat poorer.

The most significant result of this study is that it fully confirms the structure reported earlier. The final Fourier difference functions calculated with the two independent data sets showed no apparent similarity. which strongly suggests that the residual peaks reflect errors associated with the data and are not a consequence of any systematic error in the structure. On the other hand the collection of new and presumably better data and attempted refinements of both sets did not improve the agreement between the model and the data; all alternatives yielded comparable results. Differences in the positional coordinates and distances between all refinements were within the associated (3σ) error, with the largest differences involving the anions and the lighter chlorine atoms which are most affected by the quality of the data. The overall agreement in accuracy of the two determinations by different techniques is in accord with expectations,[13] particularly since the inherent limitation appears to lie in the large and critical absorption corrections applied to the data taken on the two crystals. The advantages of shaping of the crystal used in the older study thus about compensate for limitations in earlier data collection and refinement methods.

Finally, the credibility of the conclusions is strengthened by note of the obvious relationship between the Bi_9^{5+} ion found here with C_s symmetry and the more symmetrical tricapped trigonal prismatic (C_{3h}) ion recently found[9] in $Bi^+Bi_9^{5+}(HfCl_6^{2-})_3$. The *average* for each of the three types of independent Bi-Bi distances within the cluster in $Biy_{12}Cl_{14}$[1] and $Bi_{10}Hf_3Cl_{13}$[9] are, respectively prism prism height 3.796(7) and 3.747(4), triangular face of prism 3.202(11) and 3.241(3), and prism to waist 3.103(6) and 3.094(3)Å.

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