Short Communications

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Crystallographic data for some ditertiary arsine–metal carbonyl complexes of Group VI elements.

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Crystallographic data are reported for three complexes of the type M(CO)$_4$(diarsine), where M = Cr, Mo, or W and diarsine = *o*-phenylenebisdimethylarsine $C_6H_4[As(CH_3)_2]_2$, the preparation of which has been described (Nigam, Nyholm & Stiddard, 1960). Single crystals were obtained by slow evaporation of solutions in sodium-dried benzene, the solutions being kept in an atmosphere of dry nitrogen. Unit-cell dimensions were measured from Weissenberg and oscillation photographs (Cu $K\alpha$ radiation, $\lambda = 1{\cdot}542$ Å), the crystals being sealed in thin Formvar envelopes during the exposures to prevent possible hydrolysis by atmospheric moisture. Crystal densities were measured by flotation in mixtures of carbon tetrachloride and trimethylene dibromide.

Cr(CO)$_4$(diarsine)

Monoclinic, $a = 17{\cdot}4$, $b = 9{\cdot}0$, $c = 12{\cdot}9$ Å, $\beta = 117{\cdot}6°$. Measured density 1·67 g.cm^{-3}, 4 molecules in the unit cell, calculated density 1·67 g.cm^{-3}. Systematic absences of X-ray reflexions: *h*0*l* when *h* is odd, 0*k*0 when *k* is odd. Space group $P2_1/a$.

Mo(CO)$_4$(diarsine)

Orthorhombic, $a = 17{\cdot}1$, $b = 16{\cdot}3$, $c = 12{\cdot}8$ Å. Measured density 1·80 g.cm^{-3}, 8 molecules in the unit cell, calculated density 1·84 g.cm^{-3}. Systematic absences of X-ray reflexions: *hk*0 when *h* is odd, *h*0*l* when *l* is odd, 0*kl* when *k* is odd. Space group *Pbca*.

W(CO)$_4$(diarsine)

Isomorphous with Mo(CO)$_4$(diarsine) with same unit-cell dimensions. The only detectable differences in the X-ray photographs of W(CO)$_4$(diarsine) and Mo(CO)$_4$(diarsine) were in the intensities.

No further work on these substances is contemplated.

I thank Dr H. L. Nigam for providing samples of the three substances.

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Properties of the small angle X-ray scattering from rods.

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The diameter of the cross section of elongated colloidal rods has been obtained from the position of the maximum of the quantity $\theta^2 I(\theta)$, where $I(\theta)$ is the relative intensity of the small angle X-ray scattering from an assembly of identical, independent, randomly oriented rods with uniform electron density at a scattering angle θ (Fedorov & Ptitsyn, 1963). In their calculation Fedorov & Ptitsyn assumed that the rods had a circular cross section. However, this maximum in $\theta^2 I(\theta)$ occurs not only for a circular cross section but is a general property of the small angle X-ray scattering from elongated rods.

Miller & Schmidt (1962) expressed the scattered intensity from an assembly of identical independent, randomly oriented rods with uniform electron density as the sum of terms proportional to different negative powers of the axial ratio $\nu = H/L$, where H is the length of the rod, and L is the maximum diameter of the cross section — tnat is, the length of the longest straight line that can be drawn inside the cross section. For elongated rods, $\nu \gg 1$, and for sufficient elongation, only the term proportional to ν^{-1} need be retained. The resulting approximate expression for $I(\theta)$ is

$$I(\theta) = \frac{\pi}{h\nu L}\, i_c(hL) \tag{1}$$

where

$$i_c(hL) = \frac{2\pi L^2}{A}\int_0^1 ds\,.\, s\beta_o(s) J_o(hLs)$$

and where $h = 4\pi\lambda^{-1}\sin(\theta/2)$, λ is the X-ray wavelength, $J_o(X)$ is the zero-order Bessel function of the first kind, A is the area of the cross section, and $\beta_o(s)$ is the characteristic function for the cross section. This approximate form of the scattered intensity has also been obtained by Porod (1948) and by Stokes (1957). Luzzati (1960) developed an expression which is equivalent to (1) when hL is not large.

Since $\beta_o(s)$ is never negative, $i_c(hL)$ will have its largest value for $hL = 0$. Also, because of the properties of $\beta_o(s)$, for $hL \gg 1$, $i_c(hL)$ is proportional to $(hL)^{-3}$. Therefore, one can expect at least one maximum in $hLi_c(hL)$ and consequently in $\theta^2 I(\theta)$.

The location of the maximum depends on the shape of the cross section. When there is sufficient information about the scattering sample, reasonable assumptions can be made about the form of the cross section. Once a shape has been chosen, $\beta_o(s)$ can be calculated, either analytically or numerically, and the maximum in $hLi_c(hL)$ can be found numerically.

The location of the maximum can also be estimated from the approximation (Porod, 1948)

$$i_c(hL) = \exp\left(-h^2R_c^2/2\right) \tag{2}$$

where R_c is the radius of gyration of the cross section about an axis perpendicular to the cross section and passing through the center of mass of the cross section. This approximation is valid for an arbitrary cross section shape. According to (2), $hLi_c(hL)$ has a maximum for $hR_c = 1$.

The accuracy of the position of the maximum calculated from (2) was tested for circular and square cross sections and for a rectangular cross section for which one side of the rectangle was 10 times as long as the other. According to the approximate equation, the maxima for the three cross section shapes occur respectively for $hL = 2{\cdot}83$, 3·46, and 3·46, while the corresponding values from the exact expression are $hL = 2{\cdot}713$, 3·336, and 3·798. For square and circular cross sections, the agreement of the approximate and exact equations is good enough for analysis of many experimental curves, since high accuracy is often not necessary because of other approximations necessary for applying the theory to analysis of experimental data. For the elongated rectangular cross section a considerably greater error results from using the approximate expression. The tests of (2) thus suggest that while it may be sufficiently accurate for cross sections which are not elongated, for highly elongated cross sections, the exact equation probably should be used.

Since a maximum in $\theta^2I(\theta)$ can be expected for the small angle X-ray scattering from all elongated rods, plots of $\theta^2I(\theta)$ can be used to interpret the scattering data from samples consisting of long, rod-shaped particles. Fedorov & Ptitsyn obtained excellent results with the scattering data from a number of samples. Their experience suggests that the use of the $\theta^2I(\theta)$ plot may develop into a useful technique for the analysis of small angle X-ray scattering data.

As Mittelbach & Porod (1961) pointed out when discussing their numerical computations of the intensity of the small angle X-ray scattering from parallelpipeds, equation (1) may often be convenient for numerical calculations of the scattered intensity from highly elongated particles.

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Strain and particle size values from X-ray line breadths.

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The use of the breadth of the diffraction line for obtaining estimates of strain and particle size has the advantage of speed and convenience over the more elaborate analysis of line shapes (Warren, 1959). Therefore breadth analysis is frequently employed although its limitations are generally realized. However, in evaluating breadth data one of two assumptions is sometimes made, either of which is in most cases wrong. It is assumed either that the breadth due to strain and the breadth due to particle size are additive or that the squares of the breadths are additive. This is equivalent to assuming either a Cauchy line shape for particle and strain broadening or a Gauss shape for both broadenings. However, it is known that particle size broadening tends to give a Cauchy line and strain broadening a Gauss or $1/(1+K^2x^2)^2$ line (*cf.* Taylor, 1961). A method for using these more realistic profiles in a breadth analysis is given here.

The observed intensity profile $I_{\text{obs}}(x)$ is the convolution of the strain profile $I_s(x)$ and the particle size profile $I_p(x)$,

$$I_{\text{obs}}(x) = \int_{-\infty}^{+\infty} I_s(x-u)\, I_p(u)\, du\,.$$

The integral can be solved by using the Fourier transforms T of the functions, $T[I_{\text{obs}}(x)] = T[I_s(x)]T[I_p(x)]$. I_{obs} can be obtained by applying the inverse transformation. In the present case considerable simplification is possible because only the integral breadth

$$B_{\text{obs}} = \int_{-\infty}^{+\infty} I_{\text{obs}}(x)dx / I_{\text{obs}}(0)$$

is required. It is

$$\left.\begin{aligned} \int_{-\infty}^{+\infty} I_{\text{obs}}(x)dx &= \int_{-\infty}^{+\infty} T^{-1}\langle T[I_s(x)]T[I_p(x)]\rangle\, dx \\ &= \{T[I_s(x)] \times T[I_p(x)]\}_{u=0} \\ \text{and } I_{\text{obs}}(0) &= \{T^{-1}\langle T[I_s(x)]T[I_p(x)]\rangle\}_{x=0} \end{aligned}\right\} \tag{1}$$

where x and u are the variables in real and Fourier space respectively. Two cases were considered,

(*a*) $I_p = C_p/(1+K_p^2x^2)$ and $I_s = C_s/(1+K_s^2x^2)^2$
(*b*) $I_p = C_p/(1+K_p^2x^2)$ and $I_s = C_s \exp\{-K_s^2x^2\}$.

The transforms and the integral breadths B as function of particle size L and strain e are

(*a*) $T[I_p] = C_p\pi K_p^{-1} \exp\{-2\pi|u|/K_p\}$
$T[I_s] = \frac{1}{2}\pi C_sK_s^{-2}(K_s+2\pi u) \exp\{-2\pi u/K_s\}$
$B_p = \pi/K_p = \lambda/L \cos\theta$, $B_s = \pi/2K_s = e\tan\theta$