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The unit-cell dimensions and space groups of nickel(II) and palladium(II) 5-chlorosalicylaldoximates.

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Long needles of nickel(II) and palladium(II) 5-chlorosalicylaldoximate, obtained by slow cooling to room temperature of butyrolactone solutions saturated at 80° C., were used for a preliminary X-ray examination. The unit-cell dimensions were measured from rotation, Weissenberg, and precession photographs; the space groups were determined uniquely by the systematic extinctions; and densities were measured by flotation. The results are given in Table 1.

Table 1. *Unit-cell dimensions*

	Nickel(II) 5-chlorosalicylaldoximate	Palladium(II) 5-chlorosalicylaldoximate
a_0	5·90 Å	5·94 Å
b_0	25·96 Å	26·30 Å
c_0	4·65 Å	4·66 Å
β	93° 00′	93° 05′
Space group	$P2_1/n$	$P2_1/n$
Density, measured	1·868 g.cm.$^{-3}$	2·031 g.cm.$^{-3}$
Density, X-ray	1·882 g.cm.$^{-3}$	2·043 g.cm.$^{-3}$
Molecules per unit cell	2	2

The symmetry and two molecules per unit cell require that the metal atoms occupy centers of symmetry. The *c* axis is the needle axis. Infra-red studies indicate that the hydrogen bonds between the phenolic oxygen and oxime OH are essentially the same as in the corresponding nickel(II) and palladium(II) compounds of the unsubstituted salicylaldoxime.

Intensity data are being collected for structure determinations of these compounds, and full details will be reported at a later date.

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The distribution of phase angles for structures containing heavy atoms. I. Space group *P*1 with one heavy atom in the asymmetric unit.

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The use of the heavy-atom technique in structure analysis depends on the phase angles calculated on the basis of the heavy-atom contributions approximating to the true phase angles. In an earlier communication (Sim, 1957), the extent to which the signs of a set of structure factors are determined by the contributions to the structure factors of a heavy atom, or group of atoms, has been discussed for the case of the space group $P\bar{1}$.

In the present paper the phase-angle distribution corresponding to a unit cell of space group *P*1, containing a molecule with *m* light atoms of scattering factor f_L and one heavy atom of scattering factor f_H, is derived in terms of a parameter *r*, which is defined by the equation

$$r = f_H/f_L\sqrt{m}\,.$$

As the choice of origin in this space group is arbitrary. the heavy-atom coordinates have been chosen as origin.

The phase angle of a given structure factor is defined by the equations

$$\tan\alpha = \sum_{i=1}^{m} f_L \sin 2\pi\theta_i \Big/ \left\{ f_H + \sum_{i=1}^{m} f_L \cos 2\pi\theta_i \right\}$$
$$= \sqrt{\frac{2}{m}} \cdot \sum_{i=1}^{m} \sin 2\pi\theta_i \Big/ \left\{ \sqrt{2}.r + \sqrt{\frac{2}{m}} \cdot \sum_{i=1}^{m} \cos 2\pi\theta_i \right\}$$
$$= B'/\{\sqrt{2}.r + A'\}\,.$$

Also, if $x = R\cos\alpha$ and $y = R\sin\alpha$, then $\tan\alpha = y/x$.

The probability of obtaining a phase angle between α and $\alpha+d\alpha$ is equal to the joint probability of obtaining a value of B' between y and $y+dy$, and of A' between $(x-\sqrt{2}.r)$ and $(x+dx-\sqrt{2}.r)$, integrated over all values of y. Since

$$p(y)dy = (1/\sqrt{(2\pi)}) \exp(-\tfrac{1}{2}y^2)dy$$

and

$$p(x-\sqrt{2}.r)dx = (1/\sqrt{(2\pi)}) \exp[-\tfrac{1}{2}(x-\sqrt{2}.r)^2]dx\,,$$

it follows that on transforming to polar coordinates (R, α) we obtain

$$p(\alpha)d\alpha = \frac{1}{2\pi}\int_{R=0}^{\infty} R \exp[-\tfrac{1}{2}(R\cos\alpha - \sqrt{2}.r)^2] \times \exp[-\tfrac{1}{2}(R\sin\alpha)^2]dR\,d\alpha.$$