Acta Cryst. (1957). **10**, 536

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

By S. H. Simonsen and C. E. Pfluger,* *Department of Chemistry, The University of Texas, Austin, Texas, U.S.A.*

(*Received* 5 *June* 1957)

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.

The authors are greatly indebted to the Robert A. Welch Foundation for support of this project.

* American Viscose Fellow in Chemistry, 1956–7.

Acta Cryst. (1957). **10**, 536

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

By G. A. Sim, Chemistry Department, The University, *Glasgow W.* 2, *Scotland*

(*Received* 9 *May* 1957)

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

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

Consequently,

$$p(\alpha) = \frac{1}{2\pi}\exp(-r^2\sin^2\alpha)\int_0^\infty R \times \exp[-\tfrac{1}{2}(R-\sqrt{2}.r\cos\alpha)^2]dR\,.$$

Let $u = R-\sqrt{2}.r\cos\alpha$, so that

$$\begin{aligned} p(\alpha) &= \frac{1}{2\pi}\exp(-r^2\sin^2\alpha)\left[\int_{-\sqrt{2}.r\cos\alpha}^\infty u\exp(-\tfrac{1}{2}u^2)du + \sqrt{2}.r\cos\alpha\int_{-\sqrt{2}.r\cos\alpha}^\infty \exp(-\tfrac{1}{2}u^2)du\right] \\ &= \frac{1}{2\pi}\exp(-r^2\sin^2\alpha)\left[\exp(-r^2\cos^2\alpha) + \sqrt{2}.r\cos\alpha\int_{-\sqrt{2}.r\cos\alpha}^\infty \exp(-\tfrac{1}{2}u^2)du\right] \\ &= \frac{1}{2\pi}\exp(-r^2) + \frac{r\cos\alpha}{\sqrt{\pi}}\exp(-r^2\sin^2\alpha)[\tfrac{1}{2}+\varphi(\sqrt{2}.r\cos\alpha)]\,, \end{aligned}$$

where

$$\varphi(z) = \frac{1}{\sqrt{(2\pi)}}\int_0^z \exp(-\tfrac{1}{2}t^2)dt\,.$$

The fraction $N(\alpha)$ of structure factors with phase angles between $-\alpha$ and α is then given by

$$N(\alpha) = \int_{-\alpha}^{\alpha} p(\alpha)d\alpha = 2\int_0^\alpha p(\alpha)d\alpha\,.$$

For various values of r, values of $p(\alpha)$ have been computed at 5° intervals of α between 0° and 180°, and from these ordinates values of $N(\alpha)$ have been obtained by numerical integration. These are listed in Table 1.

Table 1. *Values of $N(\alpha)$ for various values of r*

α (°)	r=0·0	r=0·1	r=0·5	r=1·0	r=2·0	r=3·0
0	0·000	0·000	0·000	0·000	0·000	0·000
10	0·056	0·066	0·118	0·199	0·377	0·539
20	0·111	0·132	0·231	0·382	0·667	0·854
30	0·167	0·196	0·337	0·536	0·843	0·966
40	0·222	0·260	0·434	0·658	0·931	0·994
50	0·278	0·323	0·520	0·750	0·970	0·999
60	0·333	0·384	0·594	0·817	0·987	1·000
70	0·389	0·443	0·659	0·864	0·993	1·000
80	0·444	0·501	0·713	0·897	0·996	1·000
90	0·500	0·556	0·760	0·921	0·998	1·000
100	0·556	0·611	0·800	0·939	0·998	1·000
120	0·667	0·714	0·865	0·963	0·999	1·000
140	0·778	0·813	0·917	0·978	0·999	1·000
160	0·889	0·907	0·960	0·990	1·000	1·000
180	1·000	1·000	1·000	1·000	1·000	1·000

In Fig. 1 curves of constant $N(\alpha)$ are shown as functions of r and α.

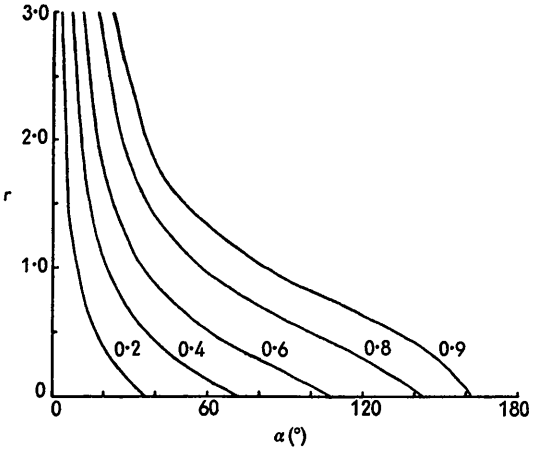

Fig. 1. $N(\alpha)$ as a function of (α, r). The curves shown are for $N(\alpha)$ = 0·2, 0·4, 0·6, 0·8 and 0·9.

In the corresponding case for space group $P\bar{1}$, where the unit cell contains one heavy atom at the origin and two centrosymmetrically related groups of atoms, each containing $\frac{1}{2}m$ atoms, the fraction of structure factors which are positive is given by

$$N = \tfrac{1}{2}+\varphi(r)\,.$$

Values of N are given in Table 2, along with values of α such that $N(\alpha) = N$.

Table 2. *Values of N, and of α such that $N(\alpha) = N$*

r	0·0	0·1	0·5	1·0	2·0	3·0
N	0·500	0·540	0·691	0·841	0·977	0·999
α (°)	90	87	76	65	53	49

When r = 1, for example, 84% of the signs of the structure factors for the centred case are given correctly by the heavy-atom sign (+), whereas in the non-centred case 84% of the phase angles are distributed over the range ±65° about the heavy-atom phase angle (0°). These results emphasize that, even apart from the inherent ambiguity in the non-centred case of introducing a pseudo-centre of symmetry at the origin when the heavy-atom phase angle is used initially, the situation with regard to structure determination is much less favourable in the non-centred unit cell.

I am indebted to the University of Glasgow for an I.C.I. Research Fellowship during the tenure of which this work was carried out. I am grateful to Dr S. D. Silvey and Mr J. Aitchison for discussing this subject with me.

Reference

Sim, G. A. (1957). *Acta Cryst.* **10**, 177.