Space group and cell dimensions of nickel(II) and copper(II) NN'-disalicylidene-o-phenylenediamine.

By H. MONTGOMERY and B. MOROSIN,* *University of Washington, Seattle, Wn., U.S.A.*

The stability and magnetic properties of the nickel (II) and copper (II) complex of NN'-disalicylidene-o-phenylenediamine have been measured by several investigators (Calvin & Bailes, 1946; Duffield & Calvin, 1946; Hall & Willeford, 1951; Mellor, 1942; Klemm & Raddatz, 1942). However, the only crystallographic data reported for these compounds is that by v. Stackelberg (1947) and this data differs from our results.

The compounds were prepared by reacting bissalicylaldehydatonickel (II) or -copper (II) in warmed chloroform with an o-phenylenediamine methanol solution. After standing several hours, the crystals were filtered off, purified by recrystallization from chloroform, and finally grown from dimethylformamide. The nickel complex crystallized as needle-like rods with a flattened hexagonal cross section and appeared deep red by transmitted light while the copper complex crystallized as flat, reddish-brown needles.

Rotation and zero, first and second level Weissenberg photographs were taken about the needle axis (b_0) and a zero level Weissenberg about the c_0 axis using Cu $K\alpha$ ($\lambda = 1.5418$ Å) radiation. Visual inspection of the intensities of similar Weissenberg photographs indicate the two complexes are isomorphous. The following cell dimensions were obtained by superimposing NaCl rotation photographs ($a_0 = 5.6387$ Å) on rotation and zero level Weissenberg photographs:

	Ni complex	Cu complex	Cu (v. Stackelberg, 1947)
$a_0 =$	$17.41_1 \pm 0.015$ Å	$17.79_9 \pm 0.010$ Å	19.2 ± 0.2 Å
$b_0 =$	$5.45_5 \pm 0.005$	$5.34_1 \pm 0.005$	9.3 ± 0.1
$c_0 =$	$16.72_6 \pm 0.010$	$16.87_6 \pm 0.010$	18.2 ± 0.1

Systematic extinctions for $h00$, $0k0$, and $00l$ of h, k, and l (respectively) indicate the space group to be $P2_12_12_1$. The measured densities were 1.58 and 1.59 g.cm.$^{-3}$ for the nickel and copper complex respectively compared to 1.56 calculated with four molecules per cell.

It is interesting to compare these two isomorphous complexes with the NN'-disalicylidene-ethylenediamine complexes of nickel (II) and copper (II). With the replacement of the o-phenylenediimino group by the ethylenediimino group, the two metal complexes are no longer isomorphous.

Waters, Hall & Llewellyn (1958) and v. Stackelberg (1947) both report the olive brown copper (II) complex belongs to the monoclinic space group $C2/c$ with the following cell dimensions (8 molecules per cell):

	Waters, Hall & Llewellyn	v. Stackelberg
$a_0 =$	26.55 ± 0.10 Å	26.5 ± 0.1 Å
$b_0 =$	6.93 ± 0.02	7.05 ± 0.1
$c_0 =$	14.60 ± 0.05	14.8 ± 0.15
$\beta =$	$82.5 \pm 0.5°$	$82.1°$

Lingafelter & Morosin (unpublished) found that the

corresponding light red nickel (II) complex had a somewhat similar over-all packing, but belonged to the orthorhombic system. The following cell dimensions were obtained by Weissenberg and rotation photographs (Cu $K\alpha$ radiation) and precession photographs (Mo $K\alpha$ radiation):

$$a_0 = 26.11 \pm 0.12, \quad b_0 = 7.49 \pm 0.03, \quad c_0 = 13.80 \pm 0.07 \text{ Å}$$
$$(a_0, \text{NaCl}, = 5.6387 \text{ Å}).$$

With eight molecules per cell the calculated density is $\varrho = 1.60$ g.cm.$^{-3}$. Systematic extinctions for h odd in $hk0$'s, k odd in $0kl$'s and l odd in $h0l$'s indicate the space group to be $Pbca$. One notes, however, that intensities corresponding to $h+k$ odd for hkl are generally very weak compared to $h+k$ even, corresponding to a pseudo C centering similar to that found in the copper (II) complex. This suggests that probably the nickel (II) complex has the dimer structure similar to that recently reported by Hall & Waters (1960) for the copper (II) complex.

Whereas the b_0 axis of about 7 Å allows the ethylenediimine complexes to form partial or full octahedral coordination (oxygen or nitrogen of adjacent molecules filling one or both of the two remaining positions of a somewhat distorted configuration) as is observed with the copper complex (Hall & Waters, 1960) and with other greenish brown copper (II) complexes (Simmons, 1959), the extraordinarily short distance of about 5.5 Å as the repeat distance and packing considerations in the phenylenediimine complexes strongly indicates in agreement with the magnetic measurements that these complexes are square planar. The 5.5 Å repeat distance requires either adjacent molecules at 2.8 Å which appears too short for the van der Waals distance required by benzene rings (radius about 1.7 Å) or adjacent metal atoms at 5.5 Å with inclined molecules which results in either greatly distorted bond angles or loose packing of about 5 Å perpendicular distance between adjacent molecules. Contrary to the latter requirement, Hall & Waters (1960), have suggested the densities corresponding to those observed with the above complexes result from close stacking in the crystals.

References

CALVIN, M. & BAILES, R. H. (1946). *J. Amer. Chem. Soc.* **68**, 949.

DUFFIELD, R. B. & CALVIN, M. (1946). *J. Amer. Chem. Soc.* **68**, 557.

HALL, D. & WATERS, T. N. (1960). *J. Chem. Soc.* p. 2644.

HALL, N. F. & WILLEFORD, B. R., Jr. (1951). *J. Amer. Chem. Soc.* **73**, 5419.

KLEMM, W. & RADDATZ, K. H. (1942). *Z. anorg. Chem.* **250**, 207.

LINGAFELTER, E. C. & MOROSIN, B. (Unpublished.)

MELLOR, D. P. (1942). *J. Proc. Roy. Soc.* **75**, 157.

SIMMONS, G. (1959). Ph.D. thesis, Univ. of Wash.

STACKELBERG, M. VON (1947). *Z. anorg. Chem.* **253**, 136.

WATERS, T. N., HALL, D. & LLEWELLYN, F. J. (1958). *Chem. and Ind.* p. 1203.

* Now with Hughes Research Laboratories, Malibu, California, U.S.A.