CRYSTAL PROPERTIES OF COPPER (II) AND NICKEL (II) CHLORIDE COORDINATION COMPLEXES WITH DIETHYLENETRIAMINE

A. G. BROOK*

University of Toronto, Toronto, Canada.

ABSTRACT

The crystal properties of the complexes of copper (II) and nickel (II) chloride with diethylenetriamine (dn) indicate that the complex $[Cudn_2]Cl_2 \cdot H_2O$ is isostructural with the analogous nickel compound $[Nidn_2]Cl_2 \cdot H_2O$ and that in each case the metal ion is probably in 6-fold covalent coordination. The complex $[CudnCl]Cl \cdot \frac{1}{2}H_2O$ was also studied.

Considerable interest has been shown in recent years in the complexes formed by metallic ions such as Cu^{++} and Ni^{++} with various organic compounds of basic character. This paper reports the crystal properties (morphology, optics, and unit cell dimensions) of three of these complexes formed from copper (II) or nickel (II) chloride and the organic base diethylenetriamine ($dn = NH_2\text{-}CH_2\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}NH_2$). These compounds, reported by Breckenridge (1948) have the formulae $[Cudn_2]Cl_2 \cdot H_2O$, $[Nidn_2]Cl_2 \cdot H_2O$ and $[CudnCl]Cl \cdot \frac{1}{2}H_2O$.

In complexes of this type it has been well established that nickel is in 6-fold covalent coordination (Mann & Pope, 1926; Mann, 1934; Haendler 1942). On the other hand, copper is more commonly in 4-fold coordination. However, since both metals form complexes of similar formulae, it might be expected that the coordination number of the metal ion would be the same in each compound.

A study of the crystal properties of these two complexes does indeed show that the complexes $[Cudn_2]Cl_2 \cdot H_2O$ and $[Nidn_2]Cl_2 \cdot H_2O$ are isostructural and hence that the states of coordination are identical. From chemical considerations, it seems probable therefore that both the copper and nickel ions are in 6-fold covalent coordination.

The complex $[CudnCl]Cl \cdot \frac{1}{2}H_2O$ has quite different crystal properties from the above complexes. It seems probable that the copper ion in this complex is in 4-fold covalent coordination.

Crystalline samples of these three complexes were donated by Dr. J. G. Breckenridge of the Department of Chemical Engineering of this University. These crystals were regrown from 95% ethanol to a size suitable for morphological, optical and *x*-ray studies (1–2 mm.). The

---

* Teaching Assistant, Department of Chemistry. The morphological and optical observations were made in the Mineralogical Laboratory, Department of Geological Sciences, under the supervision of Professor M. A. Peacock.

complex $[\mathrm{CudnCl}]\mathrm{Cl}\cdot\frac{1}{2}\mathrm{H_2O}$ would not crystallize from this solvent until acetone was added, which caused its rapid precipitation as fine needle-like prisms. *X*-ray powder photographs established the identity of these needles with the original material.

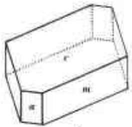
An examination with a two-circle reflecting goniometer was first made of each of the compounds. Since the crystal faces were in most cases very poor, the morphology was determined graphically with reference to the unit cells later found by *x*-ray measurements. Typical crystals of the three complexes (Figs. 1–3) show the similarity between the copper and nickel complexes of similar formulae.

An investigation of the optical properties of the compounds was made with the polarizing microscope and the universal stage using immersion technique (Table 1).

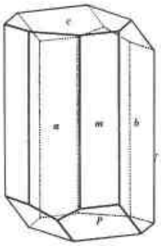
TABLE 1. CRYSTAL PROPERTIES OF COPPER AND NICKEL COMPLEXES WITH DIETHYLENETRIAMINE

$[\mathrm{Cudn_2}]\mathrm{Cl_2}\cdot\mathrm{H_2O}$		
Monoclinic, $P2_1/a$		
$a=13.96$, $b=8.80$, $c=13.62$ A, $\beta=102°\ 40'$, Z=4		
$a{:}b{:}c=1.586{:}1{:}1.548$ (*x*-ray)		
Forms: $c(001)$, $a(100)$, $m(110)$. Habit: tabular c		
Physical Properties: m.p. 197°. $d=1.459$—1.467 (meas.), 1.460 (calc.)		
Optical Properties:	n(Na)	
X (light blue): $c=+84°$	1.582 ± 0.001	Positive
Y (purplish blue): $c=-6°$	1.592 ± 0.001	$2V=81\frac{1}{2}°$ (meas.)
Z (dark blue) $=b$	1.607 ± 0.001	$r>v$ perceptible
$[\mathrm{Nidn_2}]\mathrm{Cl_2}\cdot\mathrm{H_2O}$		
Monoclinic, $P2_1/a$		
$a=13.91$, $b=8.67$, $c=13.50$ A, $\beta=102°\ 15'$, Z=4		
$a{:}b{:}c=1.604{:}1{:}1.557$ (*x*-ray)		
Forms: $c(001)$, $a(100)$, $m(110)$, $d(011)$. Habit: tabular c		
Physical Properties: m.p. 232°. $d=1.468$ (meas.), 1.478 (calc.)		
Optical Properties:	n(Na)	
X (reddish): $c=-65°$	1.591 ± 0.001	Positive
Y (purplish): $c=+25°$	1.596 ± 0.001	$2V=89°$ (meas.)
Z (bluish) $=b$	1.601 ± 0.001	Dispersion not perceptible
$[\mathrm{CudnCl}]\mathrm{Cl}\cdot\frac{1}{2}\mathrm{H_2O}$		
Monoclinic, $P2/m$		
$a=7.32$, $b=10.27$, $c=6.72$ A, $\beta=95°\ 56'$, Z=2		
$a{:}b{:}c=0.713{:}1{:}0.654$		
Forms: $c(001)$, $a(100)$, $b(010)$, $m(110)$, $p(\bar{1}11)$. Habit: prismatic [001]		
Physical Properties: m.p. 205° (decomposed). $d=1.633$ (meas.), 1.628 (calc.)		
Optical Properties:	n(Na)	
X (bluish): $c=-54°$	1.555 ± 0.002	Negative
Y (bluish purple) $=b$	1.600 ± 0.002	$2V=66°$ (meas.)
Z (reddish purple): $c=+36°$	1.625 ± 0.002	$r>v$ perceptible

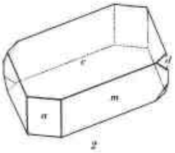
The unit cell dimensions were found using a Weissenberg camera and copper radiation ($CuK\alpha_1 = 1.5405$ A). In each case rotation and Weissenberg photographs were taken about the *b*-axis and one other direction of the crystal. The space groups were derived from a consideration of the systematically missing reflections on the zero and first layer-line Weissenberg exposures. Table 1 summarizes the observed crystallographic data of the three compounds in the form recently proposed by Peacock (1945, p. 558).



1



3



2

FIG. 1. [Cudn$_2$]Cl$_2$·H$_2$O; forms *c* (001), *a* (100), *m* (110).
FIG. 2. [Nidn$_2$]Cl$_2$·H$_2$O; forms *c* (001), *a* (100), *m* (110), *d* (011).
FIG. 3. [CudnCl]Cl·$\frac{1}{2}$H$_2$O; forms *c*(001), *a* (100), *b* (010), *m* (110), *p* ($\bar{1}$11).

TABLE 2. OBSERVED INTENSITIES AND SPACINGS (A) OF POWDER PATTERNS

[Cudn$_2$]Cl$_2$·H$_2$O				[Nidn$_2$]Cl$_2$·H$_2$O				[CudnCl]Cl·$\frac{1}{2}$H$_2$O			
I	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*	*I*	*d*
1	8.19	1	2.57	10	7.37	2	2.47	5	8.43	1	2.34
10	7.31	1	2.47	9	6.66	2	2.37	10	7.31	1	2.30
9	6.71	1	2.39	1	6.19	1	2.30	10	6.71	1	2.21
1	6.19	1	2.32	3	5.64	1	2.21	10	5.44	1	2.15
2	5.61	1	2.20	5	5.33	1	2.19	3	5.13	2	2.12
5	5.31	2	2.09	3	4.67	3	2.08	1	4.53	1	2.05
3	4.67	1	2.02	2	4.37	1	2.03	4	4.42	1	1.982
2	4.29			2	4.13	$\frac{1}{2}$	2.01	2	4.25		
1	4.15			2	3.90	1	1.941	3	3.63		
1	3.87			2	3.72	$\frac{1}{2}$	1.906	1	3.45		
1	3.74			2	3.68	$\frac{1}{2}$	1.848	2	3.34		
1	3.66			2	3.45	$\frac{1}{2}$	1.762	1	3.20		
1	3.49			3	3.27	1	1.692	8	3.10		
3	3.29			10	3.15	$\frac{1}{2}$	1.664	1	3.04		
10	3.15			2	3.02	$\frac{1}{2}$	1.634	1	2.94		
1	3.02			3	2.85	$\frac{1}{2}$	1.595	1	2.70		
3	2.85			3	2.67	$\frac{1}{2}$	1.570	2	2.53		
2	2.68			1	2.56	$\frac{1}{2}$	1.441	1	2.43		

Table 2 lists the principal interplanar spacings and visually estimated intensities of the *x*-ray powder patterns of the three complexes, using filtered copper radiation, CuKα = 1.5418 A.

REFERENCES

BRECKENRIDGE, J. G. (1948): Copper (II) and nickel (II) coordination compounds with diethylenetriamine and hydroxyethylethylenediamine—*Can. J. Research*, **26**B, 11–19.

HAENDLER, H. M. (1942): Copper (II) and nickel (II) complex ions of ethylenetriamine—*J. Am. Chem. Soc.*, **64**, 686–688.

MANN, F. G. (1934): The constitution of complex metallic salts. Part II. The platinum derivatives of β,β'-diaminodiethylamine—*J. Chem. Soc.*, 466–474.

—— & POPE, W. J. (1926): The configuration of the bistriaminopropane metallic complexes—*J. Chem. Soc.*, 2675–2681.

PEACOCK, M. A. (1945): Determination of crystal form—*Physical methods of organic chemistry*, ed. 1, **1**—New York.