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# The Crystal Structure of the Ammonium Salt of Catena-di- $\mu$ -chromato-diamminezincate(II), $(NH_4)_2[Zn(NH_3)_2(CrO_4)_2]$

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Received January 22, 1968

The crystal structure of the ammonium salt of the polymeric anion catena-di- $\mu$ -chromato-diamminezincate(II),  $(NH_4)_2$ -[Zn(NH<sub>3</sub>)<sub>2</sub>(CrO<sub>4</sub>)<sub>2</sub>], has been determined by three-dimensional X-ray diffraction procedures. The yellow prismatic crystals are monoclinic with a = 12.85 ( $\sigma = 0.02$ ) Å, b = 5.912 ( $\sigma = 0.008$ ) Å, c = 7.434 ( $\sigma = 0.008$ ) Å, and  $\beta = 111.2^{\circ}$  ( $\sigma = 0.2^{\circ}$ ). The space group is C2/m; there are two monomeric units in the unit cell with measured and calculated densities of 2.29 and 2.316 g cm<sup>-3</sup>, respectively. The data consist of 484 unique observed intensities on zero and upper level Weissenberg photographs prepared with Cu K $\alpha$  radiation about the b and c axes. The trial structure was refined by least-squares procedures to a conventional R index of 11.6%. The polymeric anions consist of infinite chains parallel to the b axis. The chains are made up of Zn octahedra linked to each other through pairs of Cr tetrahedra. Each Zn atom is bonded at the corners of a square to four oxygen atoms, each from a different CrO<sub>4</sub> tetrahedron, and to two NH<sub>3</sub> molecules in axial positions. The Cr atoms are bonded to four oxygen atoms, two of which are shared with Zn atoms and two of which are unshared. The observed distances are: Zn-O, 2.23 ( $\sigma = 0.02$ ) Å; Zn-N, 2.00 ( $\sigma = 0.03$ ) Å; Cr-O, 1.67 ( $\sigma = 0.02$ ) Å for shared oxygen atoms and 1.65 ( $\sigma = 0.03$ ) Å for the unshared oxygen atoms. The bond angles about Zn range from 89 to 91° ( $\sigma = 2^{\circ}$ ) while about Cr there are four angles of 109° ( $\sigma = 2^{\circ}$ ) and two of 110° ( $\sigma = 2^{\circ}$ ).

### Introduction

One of the laboratory assignments under development for the first-year General Chemistry Course at UCLA involves the preparation of a group of metal-ammine complexes with compositions presumably unknown to the student. In a subsequent assignment, the basic equivalent weight of the unknown complex is determined by titration with standardized hydrochloric acid.

In an attempt to prepare a novel animine complex of zinc, the synthetic procedure given in the Experimental Section was evolved. Although the resulting crystalline compound did not prove to be satisfactory as an equivalent weight unknown (owing to both the color and the basic properties of the chromate ion), there was considerable interest in the composition and structure of the complex. Thus a series of undergraduate research projects followed which resulted in a complete structure determination.

#### **Experimental Section**

**Preparation of the Complex.**—A solution of 11 g of fine-crystal reagent  $ZnSO_4 \cdot 7H_2O$  in 20 ml of concentrated ammonium hydroxide (28% NH<sub>3</sub>) was prepared in a 125-ml conical flask. To this, a hot solution of 10 g of fine-crystal reagent (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 15 ml of water was added and the combination was thoroughly mixed. As the solution slowly cooled, yellow crystals of the complex formed. These were filtered, washed with 5 ml of cold water and then with 5 ml of acetone, and allowed to dry in air. The yield was about 5 g. *Anal.* Calcd for (NH<sub>4</sub>)<sub>2</sub>Zn(NH<sub>3</sub>)<sub>2</sub>-(CrO<sub>4</sub>)<sub>2</sub>: Zn, 17.8; Cr, 28.3; N, 15.3. Found: Zn, 17.6; Cr, 28.3; N, 15.1.

**Crystallography.**—Most of the crystals appeared to be monoclinic and prismatic, with elongation on b. The unit cell dimensions were determined by use of zero-level Weissenberg and rotation photographs about the b axis prepared with Cu K $\alpha$  radiation and precession photographs of the hk0, h0l, and 0kl nets prepared with Mo K $\alpha$  radiation. A least-squares treatment of the measurements of these photographs based on  $\lambda$  1.5419 Å for Cu K $\alpha$  and  $\lambda$  0.7107 Å for Mo K $\alpha$  gave the following cell parameters at 23  $\pm$  2°: a = 12.85 (2) Å, b = 5.912 (8) Å, c = 7.434 (8) Å, and  $\beta = 111.2$  (2)°. The figures in parentheses represent the standard deviations in the least significant digits. This notation is used throughout the paper.

The photographs showed the systematic extinction of reflections with h + k odd with all other types of reflections present. The probable space group was therefore Cm, C2, or C2/m. Weissenberg photographs about b showed intensity relationships characteristic of structures having most or all of the atoms in mirror planes normal to b. Thus the intensity distribution on the second level was much like that on the zero level (but unlike that on the first level) and that on the third level was like the first. For this reason and the fact that the crystal symmetry appeared to be 2/m, the space group was taken as C2/m. No attempt was made to detect a piezoelectric effect.

The pycnometric density of the crystals was found to be 2.29 (1) g cm<sup>-3</sup>, while that computed for  $2(NH_4)_2Zn(NH_3)_2(CrO_4)_2$  in the unit cell was 2.316 (4) g cm<sup>-3</sup>.

Intensity Data.—The intensities were estimated visually on zero and upper level multiple-film Weissenberg photographs about the *b* and *c* axes, prepared with Cu K $\alpha$  radiation. The crystal used for the *b* axis data was approximately  $0.10 \times 0.30 \times 0.12$  mm along *a*, *b*, and *c*, respectively, while that used for the *c*-axis data was about  $0.11 \times 0.19 \times 0.25$  mm. The intensities used in the refinement were derived from 484 observed, unique reflections taken exclusively from the *b* axis photographs. These were corrected by the usual factors and for absorption by use of a modification of C. W. Burnham's GNABS program.  $\mu$  for Cu K $\alpha$  was taken as  $210 \text{ cm}^{-1}$ . The *c*-axis data were of low quality and were used only for the initial interlayer scaling. Within the geometric limits of the observed *b*-axis data, an additional 82 possible reflections were below the observational level.

# Determination and Refinement of the Structure

It was assumed that the correct space group was C2/m and all later developments supported this. With two formula units of  $(NH_4)_2Zn(NH_3)_2(CrO_4)_2$  in the unit cell, the zinc atoms were placed at 0, 0, 0 and 1/2, 1/2, 0. Examination of the k00 and 00l intensities in this light (with structural considerations in mind) suggested Cr positions near x = 0.16, y = 1/2, z = 0.22 and the three symmetry equivalents. A three-dimensional Patterson synthesis supported this suggestion with Cr at x = 0.15, y = 1/2, z = 0.21. A three-dimensional Fourier syn-

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thesis phased on Zn and Cr further confirmed the above data and served to locate the oxygen and nitrogen atoms which were distinguished from each other on chemical grounds. This structure was then refined isotropically by three-dimensional least-squares procedures to an Rvalue of 0.19 where  $R = \Sigma |\{|F_o| - |F_c|\}| / \Sigma |F_o|$ . An examination of the algebraic signs of  $|F_o|$  –  $|F_{
m c}|$  at this stage showed a drift from predominantly positive on the zero level to predominantly negative on the fifth level. This suggested errors in the scaling and adjustments were made, layer by layer, by use of the ratios  $\Sigma |F_{o}| / \Sigma |F_{c}|$  for the individual layers. Two cycles of least-squares refinement then reduced Rto 0.13. At this point, the thermal parameters of Zn and Cr were allowed to go partially anisotropic. Because of the way in which the interlayer scaling was adjusted,  $b_{22}$  was held fixed at its last isotropic equivalent and the  $b_{12}$  and  $b_{23}$  factors were set and held at zero. Two more cycles of least-squares then gave a final Rvalue of 0.116 for the observed reflections.

The Patterson and Fourier summations were computed to use of UCLAFOUR and the least-squares refinement was carried out by use of UCLALS4 which minimizes the weighted sum of the squares of the quantity  $(KF_{o} - GF_{c})$  by a full-matrix routine, where K and G are scale factors. The weighting scheme used for observed reflections was that of Hughes<sup>2</sup> and unobserved reflections were omitted from the refinement. The atomic scattering factors were those for  $Zn^{2+}$ , Cr<sup>2+</sup>, O<sup>-</sup>, and N<sup>-</sup> given in Table 3.3.1A of ref 3, corrected for dispersion for Cu K $\alpha$  radiation by use of the  $\Delta f'$  values given in Table 3.3.2B of the same reference.

The final positional and thermal parameters with their standard deviations are given in Table I and the

TABLE I Atomic Positional and Isotropic Thermal PARAMETERS WITH THEIR STANDARD DEVIATIONS<sup>a</sup> B & 2

	~	2	-	1, 11
Zn	0	0	0	b
Cr	0.1533(4)	1/2	0.2142(6)	ь
O(1)	0.130(1)	0.269(2)	0.077(1)	2.9(2)
O(2)	0.069(2)	$^{1}/_{2}$	0.339(2)	2.7(3)
O(3)	0.284(2)	1/2	0.361(3)	3.2(3)
N(1)	0.001(2)	0	0.270(3)	3.3(4)
N(2)	0.328(1)	0	0.263(2)	2.8(3)

<sup>a</sup> Numbers in parentheses here and in succeeding tables are the standard deviations in the least significant digits. <sup>b</sup> Anisotropic thermal parameters (Å<sup>2</sup>)  $B_{11}$ ,  $B_{22}$ ,  $B_{33}$ , and  $B_{13}$ , respectively, for Zn: 4.2 (1), 3.4 (1), 2.6 (1), 1.3 (1); for Cr: 2.3 (1), 2.2 (1), 2.2(1), 0.9(1). The anisotropic temperature ellipsoid was of the form  $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$ . The b values in this expression are related to the tabulated B's as follows:  $B_{11} = 4a^2(\sin^2 \beta)b_{11}$ .  $B_{22} = 4b^2b_{22}$ ,  $B_{33} = 4a^2(\sin^2 \beta)b_{33}$ , and  $B_{13} = 2ac(\sin^2 \beta)b_{13}$ .

structure factors computed from them are compared with the observed values in Table II.

# Discussion of the Structure

Projections of the structure down the crystallographic b and c\* axes are shown in Figures 1 and 2, respectively,

(2) E. W. Hughes, J. Am. Chem. Soc., 63, 1737 (1941). (3) "International Critical Tables for X-Ray Crystallography," Vol. III,

The Kynoch Press, Birmingham, England, 1962.

TABLE II					
OBSERVED AND	CALCULATED	STRUCTURE	FACTORS		

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<sup>a</sup> The data are separated into groups having common values of h and k. The three columns in each group list values of l,  $F_{o}$ , and  $F_{\rm e}$  in that order. Unobserved reflections are indicated by asterisks and the values of  $F_o$  given correspond to  $\sqrt{2}/2$  times the minimum observable values.



Figure 1.—Projection of the structure of (NH<sub>4</sub>)<sub>2</sub>[Zn(NH<sub>3</sub>)<sub>2</sub>- $(CrO_4)_2$ ] down the *b* axis. The parallelogram outlines one unit cell.



Figure 2.—Projection of the structure of  $(NH_4)_2[Zn(NH_3)_2-(CrO_4)_2]$  down  $c^*$ . Only those atoms in the region  $z = \pm 1/2$  are shown.

and the structurally interesting distances and angles are given in Tables III and IV.

# $\label{eq:Table III} TABLE III \\ INTERATOMIC DISTANCES (IN Å) IN (NH_4)_2 Zn(NH_8)_2 (CrO_4)_2 \\ WITH THEIR STANDARD DEVIATIONS$

	(a) Bon	ded Distances	
Zn-O(1)	2.23(2)	Cr-O(1)	1.67(2)
Zn-N(1)	2.00(3)	Cr-O(2)	1.65(3)
		CrO(3)	1.65(3)

## (b) Nonbonded Distances within Coordination Polyhedra Zn octahedron Cr Tetrahedron

O(1) - O(1)    to b	3.18 (3)	O(1)-O(1)	2.74(3)
$O(1)-O(1) \perp to b$	3.12(3)	O(1)-O(2)	2.71(4)
O(1) - N(1)	2.99(4)	O(1)-O(3)	2.70(4)
O(1) - N(1)	3.00(4)	O(2) - O(3)	2.70(5)

(c) N-O Packing Distances<sup>a</sup>

About NH <sub>3</sub>	About NH <sub>4</sub> +
2 N(1)-O(2) at 3.08 (4)	1 N(2)-O(2) at 2.78 (3)
1 N(1)-O(3) at 3.08 (4)	2 N(2)-O(1) at 2.90 (3)
	1 N(2)-O(2) at 2.95 (3)
	2 N(2)-O(1) at 3.09 (3)
	2 N(2)-O(3) at 3.15 (4)

<sup>a</sup> The digit before the atom designations gives the multiplicity.

#### TABLE IV

#### Bond Angles (deg) in $(NH_4)_2 Zn(NH_8)_2 (CrO_4)_2$ with Their Standard Deviations

O(1)-Zn- $O(1)'    to b$	91(2)	O(1)-Cr-O(1)	110(2)
$O(1)$ -Zn- $O(1)'' \perp$ to	b 89 (2)	O(1)-Cr-O(2)	109(2)
N(1)–Zn– $O(1)$	90(2)	O(1)-Cr- $O(3)$	109(2)
N(1)-Zn-O(1)'	90(2)	O(2)-Cr-O(3)	110(2)
	Zn-O(1)-Cr	134(1)	

Zinc is octahedrally coordinated by four equivalent oxygen atoms at the corners of a square and two ammonia molecules in the axial positions. The Zn–O distance is 2.23 (2) Å, the Zn–N distance 2.00 (3) Å,

and all angles about Zn are  $90^{\circ}$  within their respective standard deviations. Although the crystallographic symmetry about Zn is actually 2/m, the coordination polyhedron has the symmetry 4/mmm within the accuracy of the determination.

As expected, the coordination about Cr is tetrahedral. In this case the true point group symmetry is m but the observed symmetry of the coordination polyhedron does not deviate significantly from that of a regular tetrahedron. There are two equivalent Cr-O distances of 1.67 (2) Å (for the oxygen atoms shared with Zn) and two independent values of 1.65 (3) Å for the unshared oxygen atoms. The six O-Cr-O bond angles consist of two equivalent values at 109 (2)°, two additional equivalent values at 109 (2)°, and two nonequivalent values at 110 (2)°.

Each Zn octahedron is linked to its two neighboring octahedra through pairs of Cr tetrahedra to form infinite anionic chains along the *b* axis. Each of the four oxygen atoms about a given Zn atom is from a different  $CrO_4$  group and each  $CrO_4$  group, in turn, shares oxygen atoms with two different Zn atoms. The chains thus contain eight-membered rings of alternating metal and oxygen atoms which are joined by sharing Zn atoms between neighboring rings. The electric charges on the polymeric anions are balanced by  $NH_4^+$  ions distributed between the chains.

Most of the packing contacts appear to be between the chains and the ammonium ions. For example, the N–O distances about NH<sub>4</sub>+ consist of one value of 2.78 Å with O(2), two equivalent values of 2.90 Å with O(1), one of 2.95 Å with O(2), two equivalent values of 3.09 Å with O(1), and two equivalent values of 3.15 Å with O(3). In contrast, the only apparent contacts between chains are those of coordinated NH3 molecules with O(3) for which the two independent N–O distances are each 3.08 Å. Some of the above N-O separations about NH4+ suggest the possibility of strong  $N-H \cdots O$  bonds and it is probable that some are formed. However, the angular distribution of the oxygen atoms about nitrogen appears to be unfavorable for the simultaneous formation of more than one or possibly two good hydrogen bonds on a given nitrogen atom.

Acknowledgments.—The authors are pleased to acknowledge the financial assistance of the National Science Foundation, both through Research Grant NSF-GP-6356 and through the Summer Undergraduate Research Program.