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The Crystal Structure of the Ammonium Salt of Catena-di- μ -chromato-diamminezincate(II), $(\text{NH}_4)_2[\text{Zn}(\text{NH}_3)_2(\text{CrO}_4)_2]$

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The crystal structure of the ammonium salt of the polymeric anion catena-di- μ -chromato-diamminezincate(II), $(\text{NH}_4)_2[\text{Zn}(\text{NH}_3)_2(\text{CrO}_4)_2]$, 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⁻³, respectively. The data consist of 484 unique observed intensities on zero and upper level Weissenberg photographs prepared with Cu K α 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 CrO₄ tetrahedron, and to two NH₃ 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 ammine 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 ZnSO₄·7H₂O in 20 ml of concentrated ammonium hydroxide (28% NH₃) was prepared in a 125-ml conical flask. To this, a hot solution of 10 g of fine-crystal reagent (NH₄)₂Cr₂O₇ 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 (NH₄)₂Zn(NH₃)₂(CrO₄)₂: 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 α radiation and precession photographs of the $hk0$, $h0l$, and $0kl$ nets prepared with Mo K α radiation. A least-squares treatment of the measurements of these photographs based on λ 1.5419 Å for Cu K α and λ 0.7107 Å for Mo K α gave the following cell parameters at $23 \pm 2^\circ$: $a = 12.85$ (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⁻³, while that computed for 2(NH₄)₂Zn(NH₃)₂(CrO₄)₂ in the unit cell was 2.316 (4) g cm⁻³.

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 α radiation. The crystal used for the b axis data was approximately 0.10 × 0.30 × 0.12 mm along a , b , and c , respectively, while that used for the c -axis data was about 0.11 × 0.19 × 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. μ for Cu K α was taken as 210 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 (NH₄)₂Zn(NH₃)₂(CrO₄)₂ in the unit cell, the zinc atoms were placed at 0, 0, 0 and 1/2, 1/2, 0. Examination of the $h00$ 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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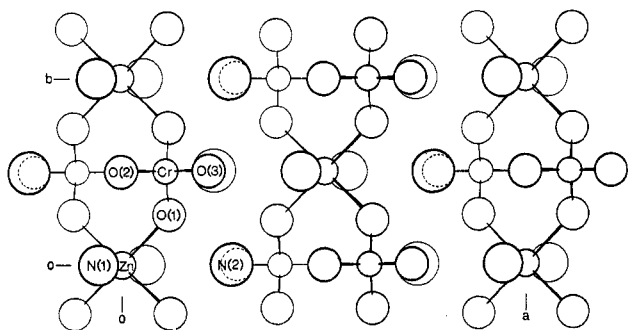


Figure 2.—Projection of the structure of $(\text{NH}_4)_2\text{Zn}(\text{NH}_3)_2(\text{CrO}_4)_2$ down c^* . Only those atoms in the region $z = \pm 1/2$ are shown.

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

TABLE III

INTERATOMIC DISTANCES (IN Å) IN $(\text{NH}_4)_2\text{Zn}(\text{NH}_3)_2(\text{CrO}_4)_2$ WITH THEIR STANDARD DEVIATIONS

(a) Bonded 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)
		Cr-O(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^a

About NH_3		About NH_4^+	
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)

^a The digit before the atom designations gives the multiplicity.

TABLE IV

BOND ANGLES (DEG) IN $(\text{NH}_4)_2\text{Zn}(\text{NH}_3)_2(\text{CrO}_4)_2$ 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° 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_4^+ 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 NH_3 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 NH_4^+ suggest the possibility of strong N-H...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.

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