

Hexaamminechromium(III) Tetrachlorozincate(II) Chloride

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Abstract. $[\text{Cr}(\text{NH}_3)_6][\text{ZnCl}_4]\text{Cl}$, trigonal, $R\bar{3}c$; $a=7.5415$ (5), $c=44.959$ (3) Å (on hexagonal axes); $Z=6$, $D_o=1.78$, $D_c=1.785$ g cm⁻³. The compound was prepared in an attempt to produce the trigonal-bipyramidal $[\text{ZnCl}_5]^{3-}$ anion. The structure consists of $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{ZnCl}_4]^{2-}$ and Cl^- ions. The $[\text{ZnCl}_4]^{2-}$ ion is severely distorted from a regular tetrahedral geometry by the close approach of the Cl^- ion in the incipient formation of a fifth Zn-Cl bond. $[\text{Cr}(\text{NH}_3)_6][\text{CoCl}_4]\text{Cl}$ is isostructural.

Introduction. Initial cell dimensions for hexagonal axes were determined from precession photographs (Mo $K\alpha$ radiation). Systematic absences (hkl absent unless $-h+k+l=3n$, $h\bar{h}l$ absent unless $l=2n$) indicated space group $R\bar{3}c$ (No. 167) or $R3c$ (No. 161).

A yellow crystal displaying point-group symmetry $\bar{3}m$, with faces of the forms $\{001\}$ and $\{104\}$, was sealed in a Lindemann glass tube and mounted on a Hilger & Watts Y290 four-circle diffractometer in a general orientation. Unit-cell parameters and the orientation matrix were refined by least squares from 12 reflexions ($2\theta > 38^\circ$, Mo $K\alpha$ radiation, $\lambda=0.71069$ Å, Zr filter) (Busing & Levy, 1967). Intensities were collected for two equivalent sets of reflexions with $2\theta \leq 55^\circ$ ($\theta-2\theta$ scan mode, 4s count at each of 80 steps of 0.01° in θ , background counts of 80s at each end of the scan). Three standard reflexions showed $< 2\%$ intensity decay during the collection; linear decay functions were fitted and applied. The crystal was measured with a travelling microscope and absorption corrections applied by a Gaussian integration method ($\mu=33$ cm⁻¹, 312 grid points, transmission factors range from 0.411 to 0.716). 987 reflexions with positive net recorded intensity were merged to give 521 unique reflexions, with an internal consistency index $\sum(w_1 + w_2)(F_1 - F_2)^2 / 2\sum(w_1 F_1^2 + w_2 F_2^2) = 3.0\%$ [$w=1/\sigma^2(F)$, based on counting statistics]. The statistical distribution of E values indicated the centrosymmetric space group $R\bar{3}c$.

This would require the Cr and Zn atoms to lie on special positions with site symmetries $\bar{3}(S_6)$ and $32(D_3)$, which implies a regular trigonal-bipyramidal $[\text{ZnCl}_5]^{3-}$ anion. A Fourier synthesis phased by the metal atoms, however, showed the Zn atom to be disordered over two equal-weight symmetry-related sites close to the 32 position. All attempts to find a solution in lower-symmetry space groups were unsuccessful. With a twofold disorder model for Zn in $R\bar{3}c$, the Cl and N atoms were located, and the structure refined by full-matrix least squares to a minimum value of $\sum w\Delta^2$ ($\Delta=|F_o|-|F_c|$). Complex scattering factors for Cr^{3+} , Zn^{2+} , Cl^- , N and H were those of Cromer & Waber (1974) and Cromer & Ibers (1974). With anisotropic thermal parameters, R was reduced to 9.12% and $R_w=[(\sum w\Delta^2/\sum w|F_o|^2)^{1/2}]$ to 8.27%. It was then possible to resolve the 'equatorial' Cl atom [Cl(2)] into two half-weight symmetry-related components. Further refinement ($R=7.15$, $R_w=5.90\%$) followed by a difference map revealed the positions of the H atoms. These were also refined, with individual isotropic temperature factors, and the final values of R and R_w were 4.95 and 3.77%. The number of parameters refined was 41. All shift/e.s.d. ratios in the final cycle were < 0.005 . The weighting scheme was shown to be consistent by an analysis of variance (Hamilton, 1974). Atomic parameters are shown in Table 1. It was not possible to resolve Cl(1) into disorder components, and the reasonable U values indicate that any disorder for Cl(1) is insignificant. A final difference synthesis showed no significant features.*

Discussion. Although $[\text{CuCl}_5]^{3-}$ (Raymond, Meek & Ibers, 1968), $[\text{CdCl}_5]^{3-}$ (Long, Herlinger, Epstein &

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31844 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Atomic coordinates ($\times 10^4$) and anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁ or <i>U</i>	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Zn	0	0	2386.6 (2)	412 (4)	<i>U</i> ₁₁	560 (7)	0	0	<i>U</i> ₁₁ /2
Cl(1)	0	0	1827.6 (3)	489 (4)	<i>U</i> ₁₁	755 (9)	0	0	<i>U</i> ₁₁ /2
Cl(2)	2551 (2)	-590 (3)	2526.8 (6)	656 (11)	1078 (23)	471 (11)	-128 (16)	-67 (11)	619 (15)
Cr	0	0	0	371 (3)	<i>U</i> ₁₁	255 (5)	0	0	<i>U</i> ₁₁ /2
N	1831 (6)	-675 (6)	265.1 (7)	540 (16)	593 (19)	413 (15)	16 (13)	-47 (13)	323 (17)
H(1)	2714 (83)	258 (87)	300 (10)	1000 (208)					
H(2)	1329 (61)	-1239 (64)	430 (11)	820 (124)					
H(3)	2247 (68)	-1327 (70)	174 (11)	932 (154)					

Bernal, 1970; Epstein & Bernal, 1971) and $[\text{HgCl}_5]^{3-}$ (Clegg, Greenhalgh & Straughan, 1975a) exist as regular trigonal-bipyramidal ions stabilized in the solid state by large counter-ions, the complex originally formulated as $[\text{Co}(\text{NH}_3)_6][\text{ZnCl}_5]$ was shown to contain $[\text{ZnCl}_4]^{2-}$ and separate Cl^- ions (Meek & Ibers, 1970). It has been found that salts of empirical formula $[\text{M}(\text{NH}_3)_6][\text{M}'\text{Cl}_5]$ with $\text{M}=\text{Cr}, \text{Co}$ are often not isostructural (Clegg, Greenhalgh & Straughan, 1975a, b). An attempt was therefore made to crystallize $[\text{ZnCl}_5]^{3-}$ as the $[\text{Cr}(\text{NH}_3)_6]^{3+}$ salt. Preliminary X-ray photographs, together with a density measurement, indicated that the Zn atom lay on a special position of site symmetry 32, and thus made trigonal-bipyramidal $[\text{ZnCl}_5]^{3-}$ the probable result of the structure determination. As in the $[\text{Co}(\text{NH}_3)_6]^{3+}$ salt, however, this was not to be.

The crystal structure consists of $[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{ZnCl}_4]^{2-}$ and Cl^- ions, held together by ionic forces and by a network of weak $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds [four independent $\text{N}\cdots\text{Cl}$ distances are $< 3.5 \text{ \AA}$, with corresponding $\text{H}\cdots\text{Cl} < 2.6 \text{ \AA}$ and $\text{N}-\text{H}\cdots\text{Cl}$ between 145 and 175° when the $\text{N}-\text{H}$ bonds are extended to 1.01 \AA (Churchill, 1973)]. The coordination of Cr is not significantly different from regular octahedral [$\text{Cr}-\text{N} 2.071(3) \text{ \AA}$, $\text{N}-\text{Cr}-\text{N}' 90.2(2)^\circ$].

The $[\text{ZnCl}_4]^{2-}$ and Cl^- ions are disordered across a position of 32 symmetry (Fig. 1). The $[\text{ZnCl}_4]^{2-}$ ion is severely distorted from tetrahedral symmetry by the fairly close approach of the Cl^- ion along one three-fold axis, which is retained in the crystal structure (Fig. 2). The $\text{Cl}(2)\cdots\text{Cl}^-$ distance (2.630 \AA) is rather longer than $\text{Zn}\cdots\text{Cl}^-$ (2.533 \AA), and this, together with the lengthening of the $\text{Zn}-\text{Cl}(1)$ bond relative to $\text{Zn}-\text{Cl}(2)$ and the reduction of the $\text{Cl}(1)-\text{Zn}-\text{Cl}(2)$ angles from the tetrahedral value of 109.5 to 106.1° , may indicate that the distortion is caused by incipient coordination of Zn by the fifth Cl ligand rather than steric crowding between $\text{Cl}(2)$ and the Cl^- ion. The nature of the distortion from tetrahedral $[\text{ZnCl}_4]^{2-}$ and a separate Cl^- ion fits in well with the treatment of distorted five-coordinate Cd complexes by Bürgi (1973) in terms of the reaction coordinate for a nucleophilic displacement reaction at a tetrahedrally coordinated metal ion. The experimental points for this complex ($\Delta x = 0.21$, $\Delta y = 1.23$, $\Delta z = 0.63 \text{ \AA}$) lie reasonably close to Bürgi's $\Delta x, \Delta y = g(\pm \Delta z)$ curve, even with a different metal and different ligands, if Pauling's (1960) covalent radii of 1.31 (Zn) and 0.99 \AA (Cl) are used to bring the 'axial' distances to the same basis.

The corresponding complex, $[\text{Cr}(\text{NH}_3)_6][\text{CoCl}_4]\text{Cl}$, obtained by a similar method as green hexagonal plates, is isostructural with the Zn complex: $a = 7.543(5)$, $c = 44.95(3) \text{ \AA}$, and corresponding precession photographs of the two complexes are almost indistinguishable.

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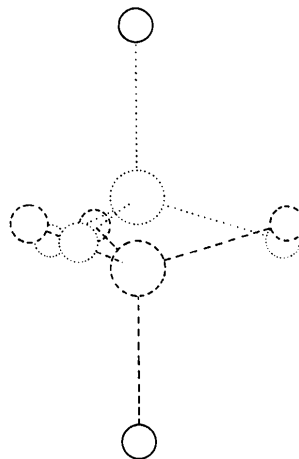


Fig. 1. Disorder of the anions. One component is shown dashed, the other dotted. The 'axial' chlorine atom $\text{Cl}(1)$, shown full, is ordered.

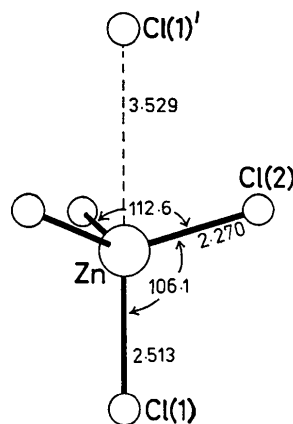


Fig. 2. Geometry of the anions (perspective view). E.s.d.'s in distances are 0.002 \AA , in angles 0.1° . The $\text{Cl}(1)\cdots\text{Zn}-\text{Cl}(1)$ line is a crystallographic threefold rotation axis.

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Cytidine Nitrate

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Abstract. $C_9H_{14}N_3O_5^+NO_3^-$, monoclinic, $P2_1$; $a = 7.818$ (3), $b = 7.514$ (3), $c = 11.095$ (5) Å, $\beta = 108.35$ (5)°, $U = 618.6$ Å³; $M = 306.2$, $Z = 2$, $D_x = 1.644$ g cm⁻³. The structure has been determined by direct methods and refined to an R of 0.026 for 1319 unique X-ray diffractometer data. The sugar residue is best described by the envelope conformation, with C(1'), C(2'), C(4') and O(1') defining the best plane through the ring. The glycosidic torsion angle, C(2)–N(1)–C(1')–O(1'), is -163.6° .

Introduction. Crystals of cytidine nitrate (Fig. 1) were grown by accident in the course of a study of metal complexes of nucleic acid components. In view of the interesting pattern of hydrogen bonding we have completed the structure determination.

Intensities were determined with an automated Stoe STADI-2 two-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation, and two crystals (layers $h0-8l$ and $hk0-12$ respectively). Cell dimensions were determined by least squares from 357 diffractometer zero-layer ω measurements. L_p (but not absorption, $\mu = 0.98$ cm⁻¹) corrections were applied, and inter-layer scale factors obtained by a linear least-squares analysis of common reflexions. Equivalent reflexions were averaged to yield the 1319 unique observed data employed in structure refinement.

The structure (Fig. 2) was solved by multiresolution tangent refinement with the program *SHELX*. A starting set of nine reflexions was chosen on the basis of a convergence map; this defined the origin and enantiomorph and generated 2⁸ phase permutations. One of the two phase sets with lowest figure of merit ($R_\alpha = 0.037$) revealed all but two of the non-hydrogen atoms. The structure was refined by full-matrix least squares

with anisotropic temperature factors for C, N and O and an overall H atom isotropic temperature factor (which refined to $U = 0.048$ Å²). C–H vectors were constrained to lie in geometrically idealized orientations with C–H = 1.01 Å; the coordinates of all other H atoms were allowed to refine freely. The weights were

Table 1. *Atom coordinates* ($\times 10^4$)

	<i>x</i>	<i>y</i>	<i>z</i>
N(1)	8243 (3)	6733 (4)	3508 (2)
C(2)	7957 (4)	5226 (6)	4128 (3)
O(2)	8120 (3)	3730 (4)	3768 (2)
N(3)	7506 (4)	5558 (5)	5210 (3)
C(4)	7243 (5)	7186 (5)	5644 (3)
N(4)	6808 (4)	7305 (6)	6690 (3)
C(5)	7451 (4)	8662 (5)	4929 (3)
C(6)	7962 (4)	8398 (5)	3893 (3)
C(1')	8863 (4)	6414 (5)	2383 (3)
C(2')	7349 (4)	5843 (4)	1215 (3)
O(2')	8159 (3)	4672 (4)	541 (2)
C(3')	6796 (4)	7589 (4)	511 (2)
O(3')	6068 (3)	7359 (4)	-824 (2)
C(4')	8556 (4)	8584 (5)	825 (3)
C(5')	8474 (5)	10592 (4)	814 (3)
O(5')	7479 (3)	11188 (4)	1625 (2)
O(1')	9566 (2)	8008	2086 (2)
N(10)	6464 (3)	2391 (5)	7218 (2)
O(10)	6431 (3)	3807 (4)	7799 (2)
O(11)	6672 (3)	2437 (4)	6144 (2)
O(12)	6258 (4)	949 (4)	7684 (2)
H(1)	7247 (45)	4693 (50)	5525 (31)
H(2)	6556 (43)	8361 (54)	6917 (33)
H(3)	6732 (42)	6396 (55)	7081 (31)
H(4)	7219	9905	5189
H(5)	8143	9460	3388
H(6)	9785	5426	2615
H(7)	6287	5221	1362
H(8)	7346 (44)	4585 (44)	-281 (34)
H(9)	5820	8215	766
H(10)	5063 (42)	6988 (45)	-959 (29)
H(11)	9101	8301	135
H(12)	7858	11020	-81
H(13)	9737	11089	1128
H(14)	7902 (42)	12016 (50)	2021 (30)

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