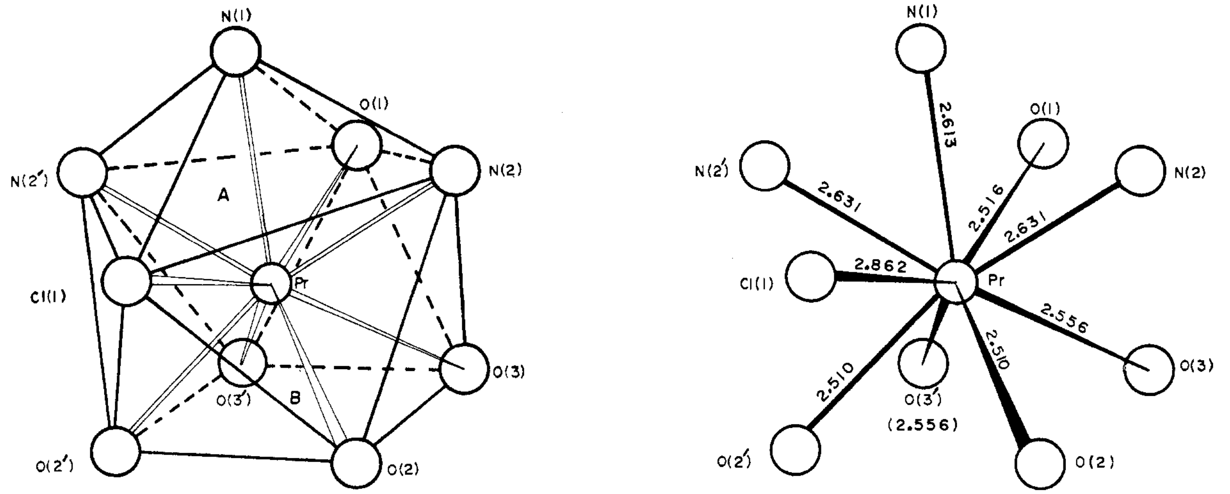

Figure 4.—The coordination polyhedron about the Pr(III) ion showing the monocapped square-antiprismatic configuration.

is bent down toward plane B as can be seen in Figure 3. Since this complex contains constraints of chelating as well as three different kinds of atoms in the coordination sphere, it does not lend itself to detailed analysis of the coordination polyhedron. Day and Hoard[25] have noted that the quasi-$C_4$ axis [N(1)–Pr] corresponding to the $C_{4v}$ symmetry of the idealized monocapped square antiprism must generate four axes [Pr–N(1), Pr–N(2), Pr–N(2)$^{I}$, and Pr–Cl(1)] normal to which are observed one-five-three layering of the ligated atoms. Examination of the model does show such layering.

A reasonable pattern of three-dimensional hydrogen bonding (Table III) can be proposed as

$$\mathrm{O}(1) \longrightarrow \mathrm{Cl}(1)^{\mathrm{VI}} \text{ and } \mathrm{O}(5)$$
$$\mathrm{O}(2) \longrightarrow \mathrm{Cl}(2) \text{ and } \mathrm{O}(4)$$
$$\mathrm{O}(3) \longrightarrow \mathrm{Cl}(2) \text{ and } \mathrm{Cl}(1)^{\mathrm{VI}}$$
$$\mathrm{O}(4) \longrightarrow \mathrm{Cl}(2)^{\mathrm{II}} \text{ and } \mathrm{Cl}(2)^{\mathrm{III}}$$
$$\mathrm{O}(5) \longrightarrow \mathrm{Cl}(2)^{\mathrm{IV}} \text{ and } \mathrm{Cl}(2)^{\mathrm{V}}$$

This scheme thus links each complex ion to all six of its neighboring ions *via* hydrogen bonding. This three-dimensional hydrogen bonding is manifested in the excellent crystals corresponding to the octahydrated complex.

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# The Crystal and Molecular Structure of Tris(glycinato)chromium(III) Monohydrate, $Cr(C_2H_4NO_2)_3 \cdot H_2O$

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*Received October 29, 1970*

The crystal and molecular structure of tris(glycinato)chromium(III) monohydrate, $Cr(C_2H_4NO_2)_3 \cdot H_2O$, has been determined by single-crystal X-ray analysis. The cell constants are $a = 6.256$ (1), $b = 14.649$ (1), $c = 12.267$ (1) Å, and $\beta = 100.39$ (1)°. The space group is $P2_1/c$ and with $Z = 4$ the calculated density is 1.755 g/cm$^3$ compared to the observed 1.76 (1) g/cm$^3$. Scintillation counter diffractometry was used to measure the intensities of 2631 independent reflections significantly above background. The phase problem was solved by the application of direct methods and the structural parameters refined by a block-diagonal least-squares procedure to a final $R$ of 0.0266. All hydrogen atoms in the structure were located and their positional parameters were refined. Anisotropic thermal parameters were used for all atoms except hydrogen. The chromium ion is octahedrally coordinated by three glycinato ligands so that the three nitrogen atoms are mutually cis. Average bond lengths are as follows (Å): Cr–N, 2.068 (5); Cr–O, 1.965 (2); N–C, 1.479 (3); C–C, 1.517 (2); C–O (coordinated), 1.290 (9); C–O(carbonyl), 1.223 (6). Individual molecules in the crystal are held together by a three-dimensional network of strong hydrogen bonds, including an unusual bifurcated linkage. The uv and visible spectra of the complex are presented and discussed.

## Introduction

No crystal structure analysis has been reported for any amino acid complex of chromium(III) though many amino acid complexes with other metal ions have been extensively studied.[1] We give here the results of an accurate three-dimensional single-crystal X-ray analysis of the structure of tris(glycinato)chromium(III) monohydrate and present and discuss the uv and visible spectra of the compound.

## Experimental Section

The complex was prepared by refluxing an aqueous solution of

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[1] For a recent review of metal complexes with amino acids and peptides see H. C. Freeman, *Advan. Protein Chem.*, **22**, 258 (1967).

$CrCl_3 \cdot 6H_2O$, glycine, and NaOH, in the molar ratio 1:3:3, for 24 hr. The solution was allowed to stand at room temperature for about 1 month, at the end of which time it was noted that large crimson platelets of the complex had separated from the mother liquor.

Unit cell constants, and their estimated standard deviations, were derived from a least-squares refinement of preliminary values obtained from precession photographs against the observed values of $\pm 2\theta$ for 17 strong, general reflections measured on the diffractometer as the mean values of $2\theta$ at half-height both left and right of the peak maxima. Monochromatic Mo K$\alpha$ radiation with a wavelength of 0.71069 Å was obtained by Bragg reflection of the direct beam from the (002) planes of a highly oriented graphite single crystal mounted in the Picker incident-beam monochromator assembly. The cell constants are $a$ = 6.256 (1), $b$ = 14.649 (1), $c$ = 12.267 (1) Å, and $\beta$ = 100.39 (1)°. From systematic absences, ($h0l$) with $l$ odd and ($0k0$) with $k$ odd, the space group was uniquely defined as $P2_1/c$. The density of the crystals, as measured by pycnometry with a bromoform-acetone mixture, was 1.76 (1) g/cm$^3$ while that calculated on the basis of four formula weights per unit cell is 1.755 g/cm$^3$. This places no restrictions on the symmetry of the molecule, while the presence of a center of symmetry in the crystal lattice ensures that both possible enantiomeric forms of this potentially asymmetric molecule will be present.

A crystal ground mechanically to a near sphere of radius 0.25 mm was used for intensity measurements. The crystal was mounted on a glass fiber with the $h0\bar{h}$ reciprocal axis parallel to the fiber axis and aligned parallel to the $\phi$ axis of a Picker four-circle diffractometer operated under the control of an XDS Sigma 2 computer. Crystal monochromated Mo K$\alpha$ radiation was used. Reflected intensity was measured using the $\theta$–$2\theta$ scanning technique with symmetrical scan ranges of 2° and a scan speed of 2°/min. Scintillation counting, with pulse height analysis, was employed with source to crystal and crystal to counter distances of 30 cm. The counter receiving apertures were set to 4 mm$^2$ and linearity of counter response was established for all count rates occurring during the experiment. By means of $\omega$ scans the mosaicity of the crystal was demonstrated to be satisfactory with peak widths, at half-height, of around 0.4°. Background measurements were made left and right of the scan range by the stationary-counter, stationary-crystal method for 10-sec intervals, and true background was assumed to be linear between these points.

Three reference reflections, monitored after every 50 measurement cycles, showed no significant variation in intensity during the course of the experiment. For this particular crystal, $\mu R$ = 0.28 and the variation of transmission factor with scattering angle is negligible. No absorption corrections were therefore applied.

About 3500 independent reciprocal lattice points within a single quadrant were surveyed out to $2\theta = 60°$, and scattered intensity significantly above background was observed at 2631 of these. A reflection was taken to have significant intensity if $I > 3.0\sigma(I)$, where $I = N - (t_s/2t_b)(B_1 + B_2)$, $\sigma^2(I) = N + (t_s/2t_b)^2(B_1 + B_2)$, and $N$ and $B$ are the counts accumulated during $t_s$ and $t_b$, the times taken in scan and background measurements, respectively.

Standard errors were assigned to the reflections as $\sigma^2(I) = [N + (t_s/2t_b)^2(B_1 + B_2) + (pI)^2]$ where $p$ is a factor introduced to take account of effects of a nonstatistical nature.[2]

## Determination and Refinement of the Structure

All calculations described were carried out using programs written in this laboratory for the 16K Sigma 2 computer.

The 2631 significant reflections were placed on an absolute scale by the use of Wilson's method,[3] ignoring randomly absent data, and converted to normalized structure amplitudes ($E$ values). (Experience with a number of structure analyses carried out in our laboratory has shown that the answers derived from a Wilson treatment of the data are not significantly affected by omission of the randomly absent intensities, if a spherical distribution of significant intensities is used. Clearly, this need not always be the case where unusual intensity distributions are involved.) The phase problem was solved by a direct methods program, PHAGEN, based on procedures outlined by Hall.[4] Two alternative sets of phases were generated for the top 500 $E$ values, corresponding to a choice of positive or negative phase for the reflection 1,2,6 ($E$ = 2.65) interacting with the origin-determining phases. The set with 1,2,6 positive had fewer inconsistencies and a higher average probability, and an $E$ map generated with this set revealed the locations of all nonhydrogen atoms in the structure with no spurious additional peaks. A structure factor calculation based on these atomic sites and assuming an overall thermal parameter $B$ of 2.5 Å$^2$ gave a conventional $R$ of 0.24 for all 2631 significant structure amplitudes.

Refinement of the positional and individual isotropic thermal parameters of the atoms by means of a block-diagonal least-squares procedure minimizing $\Sigma w(|F_o| - |F_c|)^2$ and using unit weights, $w$, gave convergence at $R$ = 0.078. Individual anisotropic thermal parameters were then assumed for all atoms and after 16 cycles of refinement led to $R$ = 0.042. For the last 8 cycles of this process and thereafter, $w$ was taken as $4LI/\sigma^2(I)$, where $L$ denotes the Lorentz–polarization factor and $p$, the factor already defined, was given a value about twice the current value of $R$.

A three-dimensional difference electron density synthesis, calculated at this point, clearly revealed the 14 hydrogen atoms in the complex and the water molecule as the most significant features of the map. Peak heights for the hydrogen atoms ranged from 0.6 to 0.8 e$^-$/Å$^3$. Inclusion of the hydrogen atom contributions in the structure factors, with the isotropic thermal parameters taken equal to the equivalent isotropic thermal parameters of the atoms to which the hydrogens were attached, significantly reduced $R$ to 0.031. Before continuing the refinement, we now removed 36 reflections for which $(|F_o| - |F_c|)/\sigma(|F_o|) > 4.0$ by assigning them zero weight. Of these, one low-order reflection, 0,2,0, seemed to be affected by extinction error, having a calculated value substantially greater than its observed amplitude, while the others were very weak. The least-squares refinement was continued with the positional parameters of the hydrogen atoms allowed to vary but their thermal parameters being held fixed. Shifts in the positional parameters of nonhydrogen atoms of up to $10\sigma$ were noted during the course of these cycles. At the conclusion of the refinement with all parameters convergent, $R$ was 0.0266 and $wR$, defined as $[\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, was 0.0337. The standard deviation of an observation of unit weight was 1.06 with a final ratio of observations to variable parameters of 13:1.

A final three-dimensional residual electron density map had no structurally significant features apart from a negative volume at the site of the chromium ion, with a peak height of $-0.5$ e$^-$/Å$^3$, indicative of the inadequacy of the scattering curve used for the chromium ion. No other peak had an amplitude greater than 0.3 e$^-$/Å$^3$.

The scattering functions used were those for the

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(2) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).

(3) A. J. C. Wilson, *Acta Crystallogr.*, **2**, 318 (1949).

(4) S. R. Hall in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 66.

TABLE I

ATOMIC PARAMETERS DEFINING THE CRYSTAL STRUCTURE OF TRIS(GLYCINATO)CHROMIUM(III) MONOHYDRATE

Positional Parameters[a]

| Atom | $x/a$ | $y/b$ | $z/c$ | $X$ | $Y$ | $Z$ |
|---|---|---|---|---|---|---|
| Cr | 1029.7 (3) | 2614.4 (1) | 4085.4 (2) | −0.259 | 3.830 | 4.929 |
| N(1) | 2334 (2) | 2944 (1) | 5712 (1) | 0.203 | 4.313 | 6.892 |
| N(2) | −2052 (2) | 3100 (1) | 4116 (1) | −2.194 | 4.541 | 4.967 |
| N(3) | 362 (2) | 1268 (1) | 4411 (1) | −0.749 | 1.858 | 5.322 |
| O(1) | 1920 (2) | 3870 (1) | 3840 (1) | 0.352 | 5.670 | 4.633 |
| O(2) | 2479 (2) | 5237 (1) | 4616 (1) | 0.530 | 7.672 | 5.569 |
| O(3) | −206 (2) | 2434 (1) | 2509 (1) | −0.684 | 3.566 | 3.027 |
| O(4) | −2939 (2) | 2808 (1) | 1165 (1) | −2.096 | 4.113 | 1.405 |
| O(5) | 3810 (2) | 2074 (1) | 3888 (1) | 1.524 | 3.038 | 4.691 |
| O(6) | 5567 (2) | 800 (1) | 3661 (1) | 2.673 | 1.171 | 4.418 |
| O(7) | 3130 (2) | 4241 (1) | 1630 (1) | 0.972 | 6.212 | 1.967 |
| C(1) | 2344 (2) | 4410 (1) | 4691 (1) | 0.429 | 6.460 | 5.660 |
| C(2) | 2650 (3) | 3946 (1) | 5812 (1) | 0.373 | 5.780 | 7.013 |
| C(3) | −2038 (2) | 2834 (1) | 2132 (1) | −1.746 | 4.152 | 2.573 |
| C(4) | −3001 (2) | 3382 (1) | 2978 (1) | −2.536 | 4.955 | 3.593 |
| C(5) | 3935 (2) | 1205 (1) | 3831 (1) | 1.614 | 1.766 | 4.622 |
| C(6) | 1899 (3) | 680 (1) | 3943 (1) | 0.316 | 0.996 | 4.758 |
| H(1) | 155 (3) | 422 (1) | 623 (2) | −0.409 | 6.179 | 7.517 |
| H(2) | 391 (3) | 414 (1) | 622 (2) | 1.069 | 6.059 | 7.507 |
| H(3) | −451 (3) | 333 (1) | 279 (1) | −3.439 | 4.885 | 3.364 |
| H(4) | −264 (3) | 398 (1) | 288 (1) | −2.288 | 5.835 | 3.479 |
| H(5) | 113 (3) | 49 (1) | 316 (2) | 0.009 | 0.713 | 3.813 |
| H(6) | 236 (3) | 16 (1) | 438 (2) | 0.511 | 0.230 | 5.280 |
| H(7) | 157 (3) | 275 (1) | 624 (2) | −0.399 | 4.035 | 7.524 |
| H(8) | 360 (3) | 267 (1) | 586 (1) | 0.956 | 3.914 | 7.072 |
| H(9) | −288 (3) | 274 (1) | 431 (1) | −2.752 | 4.008 | 5.198 |
| H(10) | −214 (3) | 357 (1) | 456 (1) | −2.348 | 5.234 | 5.501 |
| H(11) | −103 (3) | 108 (1) | 412 (1) | −1.553 | 1.585 | 4.972 |
| H(12) | 49 (3) | 119 (1) | 515 (1) | −0.830 | 1.740 | 6.213 |
| H(13) | 306 (3) | 472 (1) | 160 (2) | 1.560 | 6.911 | 1.934 |
| H(14) | 206 (3) | 419 (1) | 231 (2) | 0.777 | 6.135 | 2.785 |

Thermal Parameters[b]

| Atom | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Cr | 898 (4) | 174 (1) | 216 (1) | −40 (2) | 106 (2) | −4 (1) |
| N(1) | 1294 (28) | 303 (5) | 255 (7) | −54 (10) | 87 (11) | 8 (5) |
| N(2) | 1106 (25) | 227 (5) | 270 (7) | −22 (9) | 184 (10) | −23 (4) |
| N(3) | 1200 (27) | 220 (5) | 398 (8) | −76 (9) | 183 (12) | 31 (5) |
| O(1) | 1879 (27) | 220 (4) | 299 (6) | −136 (9) | 224 (10) | −15 (4) |
| O(2) | 2771 (38) | 232 (5) | 682 (10) | −140 (11) | 456 (15) | −91 (5) |
| O(3) | 1317 (23) | 301 (5) | 256 (5) | 31 (8) | 134 (9) | −53 (4) |
| O(4) | 2198 (35) | 795 (9) | 281 (7) | 249 (15) | −91 (12) | −122 (7) |
| O(5) | 1054 (22) | 245 (4) | 460 (7) | −47 (8) | 185 (10) | −15 (4) |
| O(6) | 1574 (30) | 384 (6) | 862 (12) | 177 (11) | 364 (15) | −97 (7) |
| O(7) | 2545 (36) | 461 (7) | 390 (8) | −335 (12) | −16 (13) | 98 (5) |
| C(1) | 1186 (31) | 255 (6) | 392 (9) | −67 (11) | 236 (13) | −59 (6) |
| C(2) | 2345 (46) | 329 (7) | 313 (9) | −205 (15) | 68 (16) | −101 (6) |
| C(3) | 1220 (31) | 334 (7) | 255 (8) | −30 (12) | 87 (12) | −29 (6) |
| C(4) | 1318 (32) | 291 (6) | 308 (8) | 129 (12) | 117 (13) | 15 (6) |
| C(5) | 1232 (32) | 266 (6) | 341 (8) | 45 (11) | 114 (13) | −22 (6) |
| C(6) | 1803 (39) | 208 (6) | 602 (12) | −47 (12) | 374 (17) | −20 (7) |

| Atom | $B$ | Atom | $B$ | Atom | $B$ |
|---|---|---|---|---|---|
| H(1) | 2.83 | H(6) | 2.67 | H(11) | 2.10 |
| H(2) | 2.83 | H(7) | 2.09 | H(12) | 2.10 |
| H(3) | 2.20 | H(8) | 2.09 | H(13) | 3.42 |
| H(4) | 2.20 | H(9) | 1.82 | H(14) | 3.42 |
| H(5) | 2.67 | H(10) | 1.82 | | |

[a] Fractional coordinates $\times 10^4$ (hydrogen atom coordinates $\times 10^3$); estimated standard deviations in parentheses; Cartesian coordinates in ångströms. The transformation from fractional to Cartesian coordinates is given by $X = x + z \cos \beta$, $Y = y$, and $Z = z \sin \beta$. [b] The anisotropic thermal parameters, $\beta$, are multiplied by $10^5$ and the exponent has the form: $-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$. The isotropic $B$ values assumed for the hydrogen atoms correspond to the equivalent isotropic $B$ values of the atoms to which they are attached as calculated at the time of inclusion of hydrogens in the refinement. $B$ is given in square ångströms.

neutral atoms,[5] that for hydrogen being taken from the calculation of Stewart, *et al.*[6] The curve for chromium was corrected for the real part of the anomalous dispersion term.[7]

TABLE II

INTERATOMIC DISTANCES AND ANGLES[a]

Bond Lengths, Å

| | | | |
|---|---|---|---|
| Cr–N(1) | 2.073 (1) | Cr–O(1) | 1.962 (1) |
| Cr–N(2) | 2.062 (1) | Cr–O(3) | 1.967 (1) |
| Cr–N(3) | 2.069 (1) | Cr–O(5) | 1.966 (1) |
| N(1)–C(2) | 1.482 (2) | C(1)–C(2) | 1.516 (2) |
| N(2)–C(4) | 1.475 (2) | C(3)–C(4 | 1.520 (2) |
| N(3)–C(6) | 1.481 (2 | C(5)–C(6) | 1.516 (2) |
| O(1)–C(1) | 1.298 (2) | O(2)–C(1) | 1.219 (2) |
| O(3)–C(3) | 1.296 (2 | O(4)–C(3 | 1.219 (2) |
| O(5)–C(5) | 1.277 (2) | O(6)–C(5) | 1.231 (2) |
| C(1)–C(2) | 1.516 (2) | O(7)–H(13) | 0.91 (2) |
| C(3)–C(4) | 1.520 (2) | O(7)–H(14) | 0.85 (2) |
| C(5)–C(6) | 1.516 (2) | | |
| N(1)–H(7) | 0.92 (2) | C(2)–H(1) | 1.01 (2) |
| N(1)–H(8) | 0.87 (2) | C(2)–H(2) | 0.90 (2) |
| N(2)–H(9) | 0.81 (2) | C(4)–H(3) | 0.93 (2) |
| N(2)–H(10) | 0.89 (2) | C(4)–H(4) | 0.92 (2) |
| N(3)–H(11) | 0.92 (2) | C(6)–H(5) | 1.03 (2) |
| N(3)–H(12) | 0.90 (2) | C(6)–H(6) | 0.95 (2) |

Bond Angles, Deg

| | | | |
|---|---|---|---|
| Cr–N(1)–C(2) | 109.5 (1) | N(2)–C(4)–H(3) | 116 (1) |
| Cr–N(2)–C(4) | 107.3 (1) | N(2)–C(4)–H(4) | 109 (1) |
| Cr–N(3)–C(6) | 108.2 (1) | N(3)–C(6)–C(5) | 110.8 (1) |
| Cr–N(1)–H(7) | 116 (1) | N(3)–C(6)–H(5) | 107 (1) |
| Cr–N(1)–H(8) | 106 (1) | N(3)–C(6)–H(6) | 114 (1) |
| Cr–N(2)–H(9) | 115 (1) | O(1)–C(1)–O(2) | 123.4 (1) |
| Cr–N(2)–H(10) | 116 (1) | O(3)–C(3)–O(4) | 123.9 (1) |
| Cr–N(3)–H(11) | 115 (1) | O(5)–C(5)–O(6) | 123.4 (1) |
| Cr–N(3)–H(12) | 109 (1) | O(1)–C(1)–C(2) | 115.5 (1) |
| Cr–O(1)–C(1) | 118.0 (1) | O(2)–C(1)–C(2) | 121.1 (1) |
| Cr–O(3)–C(3) | 117.1 (1) | O(3)–C(3)–C(4) | 115.4 (1) |
| Cr–O(5)–C(5) | 118.2 (1) | O(4)–C(3)–C(4) | 120.7 (1) |
| N(1)–Cr–N(2) | 96.4 (1) | O(5)–C(5)–C(6) | 116.1 (1) |
| N(1)–Cr–N(3) | 95.5 (1) | O(6)–C(5)–C(6) | 120.4 (1) |
| N(1)–Cr–O(1) | 81.7 (1) | C(1)–C(2)–H(1) | 107 (1) |
| N(1)–Cr–O(3) | 174.2 (1) | C(1)–C(2)–H(2) | 109 (1) |
| N(1)–Cr–O(5) | 90.3 (1) | C(3)–C(4)–H(3) | 107 (1) |
| N(2)–Cr–N(3) | 95.9 (1) | C(3)–C(4)–H(4) | 106 (1) |
| N(2)–Cr–O(1) | 88.4 (1) | C(5)–C(6)–H(5) | 108 (1) |
| N(2)–Cr–O(3) | 82.0 (1) | C(5)–C(6)–H(6) | 106 (1) |
| N(2)–Cr–O(5) | 173.0 (1) | C(2)–N(1)–H(7) | 109 (1) |
| N(3)–Cr–O(1) | 175.1 (1) | C(2)–N(1)–H(8) | 110 (1) |
| N(3)–Cr–O(3) | 90.3 (1) | C(4)–N(2)–H(9) | 107 (1) |
| N(3)–Cr–O(5) | 81.6 (1) | C(4)–N(2)–H(10) | 108 (1) |
| O(1)–Cr–O(3) | 92.7 (1) | C(6)–N(3)–H(11) | 108 (1) |
| O(1)–Cr–O(5) | 94.4 (1) | C(6)–N(3)–H(12) | 111 (1) |
| O(3)–Cr–O(5) | 91.4 (1) | H(7)–N(1)–H(8) | 107 (2) |
| N(1)–C(2)–C(1) | 112.1 (1) | H(9)–N(2)–H(10) | 103 (2) |
| N(1)–C(2)–H(1) | 110 (1) | H(11)–N(3)–H(12) | 105 (2) |
| N(1)–C(2)–H(2) | 116 (1) | H(1)–C(2)–H(2) | 102 (2) |
| N(2)–C(4)–C(3) | 110.9 (1) | H(3)–C(4)–H(4) | 108 (2) |
| H(5)–C(6)–H(6) | 110 (2) | H(13)–O(7)–H(14) | 105 (2) |

Torsion Angles, Deg

| | | | |
|---|---|---|---|
| Cr–N(1)–C(2)–C(1) | 11.0 (5) | N(1)–C(2)–C(1)–O(1) | 1.4 (5) |
| Cr–N(2)–C(4)–C(3) | 27.9 (5) | N(2)–C(4)–C(3)–O(3) | 19.2 (5) |
| Cr–N(3)–C(6)–C(5) | 23.6 (5) | N(3)–C(6)–C(5)–O(5) | 16.0 (5) |

[a] Esd's (in parentheses) include the contribution of the cell constant errors and correlations between the parameters of a given atom. No account has been taken of possible correlations between the parameters of different atoms.

## Results and Discussion

The atomic parameters defining the crystal structure of the complex are given, together with their estimated standard deviations, in Table I. The estimated standard deviations were obtained, as part of the least-squares calculation, from the formula $\sigma(j) = [a^{jj} \cdot \Sigma w(|F_o| - |F_c|)^2/(n - m)]^{1/2}$, where $a^{jj}$ is obtained by inversion of the matrix $a_{ij}$, $w$ is the least-squares weight, $n$ is the number of observations, and $m$ is the number of variable parameters.

Bond lengths and angles and torsion angles of interest appear in Table II. A projection of the molec-

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(5) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(6) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(7) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

ular structure, viewed down the approximate threefold axis of the complex and having the numbering scheme adopted for the atoms, is shown in Figure 1.

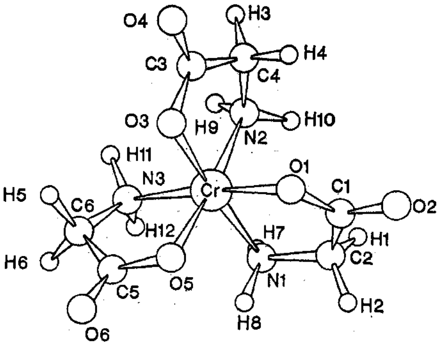

Figure 1.—View of the tris(glycinato)chromium(III) molecule showing the numbering scheme adopted for the atoms.

The crystal structure of tris(glycinato)chromium(III) monohydrate consists of discrete molecules of the complex linked together by a three-dimensional arrangement of strong hydrogen bonds also involving the water molecule. As has been mentioned, the presence of a center of symmetry in the crystal means that both enantiomers of the complex are present.

**Coordination of the Chromium Ion.**—The three glycinato residues form chelate rings at the chromium ion through their nitrogen atoms and one oxygen atom so so to give octahedrally coordinated chromium. The arrangement is such that the three nitrogen atoms are mutually cis.

The mean Cr–O distance is 1.965 Å, with an rms deviation of 0.002 Å. This bond length may be compared with the distance of 1.951 (7) Å found for Cr–O in tris(acetylacetonato)chromium(III)[8] and the length of 1.955 (9) Å noted in di-$\mu$-diphenylphosphinato-acetylacetonatochromium(II).[9] The bond distance for Cr–O in the tris(oxalato)chromate(III) ion is shorter, 1.90 (2) Å.[10]

The mean of the Cr–N bond distances is 2.068 Å, with an rms deviation from this mean of 0.005 Å. This mean compares well with the mean values of 2.075 (2) and 2.081 (5) Å found in the tris(ethylenediamine)chromium(III) salts of the $Ni(CN)_5^{3-}$ and $Co(CN)_6^{3-}$ anions, respectively.[11,12]

There are apparently significant differences among the lengths of the individual Cr–N bonds, even if the standard deviations are underestimated by a factor of as much as 3. (Experience has shown[13] that esd's calculated in the manner described, from the block-diagonal matrices, are generally underestimated by a factor of 1.5–2.0 if only random errors are assumed.) While it is possible that, through minor differences in the chemical environment, the three bonds are not equivalent, it is far more likely that there remains some systematic error in the intensity measurements which causes us to underestimate the standard deviations. Alternatively, the absence of any correction for the effects of anisotropic thermal motion of the atoms involved upon the bond distance found may be responsible for the apparent differences.

**Geometry of the Glycine Residues.**—The mean values of the bond lengths and angles found in the glycinato ligands are close to those observed in bis(glycinato)copper(II) monohydrate[14] and in $\alpha$-glycine[15] itself. In the crystal structure of glycine, the two C–O bonds are equivalent and the mean C–O distance is 1.253 (2) Å, uncorrected for the effects of anisotropic thermal behavior of the atoms, and 1.263 (2) Å, with the correction applied. On coordination, however, the C–O carbonyl distance is reduced to about 1.22 Å while the C–O bond to the atom attached to the metal ion is lengthened. The C–O bond lengths involving C(5) are significantly different (6–10$\sigma$) from those at the other two carbon atoms. The other two pairs of distances are, by contrast, in excellent agreement. We believe this effect to be physically significant and to derive from the participation by O(6) in two strong hydrogen bonds while the others are involved in only one. This would result in a different distribution of electron density about O(6) carrying over, in its effects, to the rest of the carboxyl group.

The equations of the least-squares mean planes through the three chelate rings are given in Table III.

TABLE III

EQUATIONS OF LEAST-SQUARES MEAN PLANES THROUGH SELECTED GROUPS OF ATOMS[a]

| Plane | $l$ | $m$ | $n$ | $p$ |
|---|---|---|---|---|
| 1 | −0.97314 | 0.21844 | 0.07267 | 1.3479 |
| 2 | −0.47794 | −0.87049 | 0.11758 | −2.5055 |
| 3 | 0.23207 | 0.00239 | 0.97270 | 4.8508 |
| 4 | −0.99623 | 0.08666 | 0.00448 | 0.1604 |
| 5 | −0.54740 | −0.81193 | 0.20277 | −1.9034 |
| 6 | 0.14618 | −0.05465 | 0.98775 | 4.6944 |

Distances of Atoms from the Planes, Å

1: Cr, −0.099; N(1), 0.103; O(1), 0.115; C(1), −0.057; C(2), −0.062
2: Cr, 0.124; N(2), −0.185; O(3), −0.084; C(3), −0.029; C(4), 0.173
3: Cr, 0.107; N(3), −0.157; O(5), −0.024; C(5), −0.024; C(6), 0.147
4: O(1), −0.001; O(2), −0.001; C(1), 0.003; C(2), −0.001
5: O(3), 0.003; O(4), 0.004; C(3), −0.010; C(4), 0.003
6: O(5), 0.004; O(6), 0.004; C(5), −0.011; C(6), 0.003

[a] The equation of a plane is expressed as $lX + mY + nZ = p$, where $X$, $Y$, and $Z$ are the Cartesian coordinates of the atoms in the axial system defined in Table I. All atoms were given equal weight.

The rings are all significantly nonplanar and the degree of nonplanarity may be seen from the torsion angles listed in Table II. The puckering of each chelate ring is different and arises, most probably, from packing considerations. However, even the planes defined by C(4)–C(3)–O(3)–O(4) and C(6)–C(5)–O(5)–O(6) are significantly nonplanar, with the central carbon atom in each case lying about 0.01 Å out of the plane.

The mean N–H and C–H bond distances found are 0.88 (4) and 0.96 (5) Å, respectively. These are close to the values expected, bearing in mind the distortion in the electron density distribution for hydrogen atoms normally encountered in X-ray studies.[16]

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[8] B. Morosin, *Acta Crystallogr.*, **19**, 131 (1965).

[9] C. E. Wilkes and R. A. Jacobson, *Inorg. Chem.*, **4**, 99 (1965).

[10] J. N. van Niekerk and F. R. L. Shoening, *Acta Crystallogr.*, **5**, 196 (1952).

[11] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).

[12] K. N. Raymond and J. A. Ibers, *ibid.*, **7**, 2333 (1968).

[13] R. F. Bryan, *J. Chem. Soc. B*, 1311 (1967).

[14] H. C. Freeman, M. R. Snow, I. Nitta, and K. Tomita, *Acta Crystallogr.*, **17**, 1463 (1964).

[15] R. E. Marsh, *ibid.*, **11**, 654 (1958).

[16] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, p 64.

**Hydrogen Bonding.**—It has been demonstrated by Skinner and Jones[17] that tris(glycinato)chromium(III) monohydrate is very insoluble in all common solvents and that is has an unusually high heat of sublimation. On the basis of these observations it was suggested that some unusual bonding forces were present in this complex, either that a polymeric species was present or that the intermolecular forces were unusually strong, or both. The results of this crystal structure analysis show clearly that only monomeric units are present and that the unusual physical properties result from an elaborate network of hydrogen bonds in the crystal involving bonds between monomeric units and through the water molecule.

The intermolecular hydrogen bonds detected in the crystal structure are listed in Table IV. The water molecule serves to link two molecules of the complex together through O(1) and O(6). All of the hydrogen atoms attached to nitrogen atoms are involved as donors to oxygen atoms. Perhaps the most interesting feature of the hydrogen-bonding pattern is an apparent bifurcated hydrogen bond linking three molecules of the complex. The arrangement of atoms involved is shown in Figure 2. N(2) is situated 2.982 (2) Å from O(4) and 2.963 (1) Å from O(5) and forms a bifurcated hydrogen bond with each through H(9). H(9) is about 0.1 Å removed from the plane of these three atoms.

TABLE IV

HYDROGEN BONDS OF THE TYPE A–H···B IN THE CRYSTAL STRUCTURE OF TRIS(GLYCINATO)CHROMIUM(III) MONOHYDRATE[a]

| A–H···B | A···B | A–H | H···B | A–H···B |
|---|---|---|---|---|
| O(7)–H(14)···O(1) | 2.790 (2) | 0.85 (2) | 1.95 (2) | 171 (2) |
| O(7)–H(13)···O(6)$^{\mathrm{I}}$ | 2.757 (2) | 0.91 (2) | 1.86 (2) | 167 (2) |
| N(1)–H(7)···O(3)$^{\mathrm{II}}$ | 2.996 (2) | 0.92 (2) | 2.09 (2) | 170 (2) |
| N(1)–H(8)···O(4)$^{\mathrm{III}}$ | 3.104 (2) | 0.87 (2) | 2.24 (2) | 170 (2) |
| N(2)–H(9)···O(4)$^{\mathrm{II}}$ | 2.982 (2) | 0.81 (2) | 2.42 (2) | 128 (2) |
| N(2)–H(9)···O(5)$^{\mathrm{IV}}$ | 2.963 (1) | 0.81 (2) | 2.26 (2) | 146 (2) |
| N(2)–H(10)···O(2)$^{\mathrm{V}}$ | 2.928 (2) | 0.89 (2) | 2.05 (2) | 172 (2) |
| N(3)–H(11)···O(6)$^{\mathrm{IV}}$ | 3.053 (2) | 0.92 (2) | 2.14 (2) | 170 (2) |
| N(3)–H(12)···O(7)$^{\mathrm{II}}$ | 2.847 (2) | 0.90 (2) | 2.02 (2) | 152 (2) |

[a] A–B distances <3.2 Å. All distances are in ångströms; all angles, in degrees. Roman superscripts refer to the following translations of the acceptor atom from the coordinates listed in Table I: (I) $1 - x, 0.5 + y, 0.5 - z$; (II) $x, 0.5 - y, 0.5 + z$; (III) $1 + x, 0.5 - y, 0.5 + z$; (IV) $x - 1, y, z$; (V) $-x, 1 - y, 1 - z$.

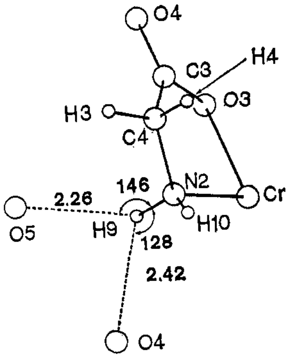

Figure 2.—Diagrammatic illustration of the possible bifurcated hydrogen bond. The projection is onto the plane of N(2) and the symmetry-related equivalents of O(4) and O(5). The donor hydrogen atom is about 0.1 Å out of this plane.

Whether a bond of this type really exists depends very much on one's interpretation of the X-ray data and one's concept of the hydrogen bond. If only the true internuclear separations are held to be important, then the actual O···H separations are less than those implied by taking the *observed* center of the electron density distribution for the hydrogen atom as the true nuclear center since it is well known that the electron density observed for hydrogen atoms in X-ray studies is always polarized toward the atom to which hydrogen is attached. The true internuclear separations will therefore be less than those noted in Table IV and certainly less than the conventional sum of the van der Waals radii for oxygen and hydrogen, 2.5 Å. On the other hand, if the electron density cloud is held to be the active agent in the hydrogen bond, then the withdrawal of density on the hydrogen atom toward the nitrogen atom to which it is attached has the effect of making the O···H separations much more comparable to the sum of the van der Waals radii and so, presumably, reducing the strength of the bonding. A number of other examples of this type of environment for a hydrogen atom have been reported[16] and are subject to the same considerations.

**Other Intermolecular Contacts.**—A view of the arrangement of a single layer of molecules in the crystal lattice, seen in projection down *a*, is given in Figure 3. The shortest contacts between molecules, other than hydrogen-bonded interactions, involve H···H separations of 2.45–2.47 Å, O···O contacts of 3.12–3.20 Å, an O···H–C separation of 2.62 Å, and an O···C approach of 3.12 Å.

**Thermal Behavior.**—The rms amplitudes of vibration along the principal axes of the thermal ellipsoids are given, for the nonhydrogen atoms, in Table V. The atoms are not markedly anisotropic in their thermal behavior and so the direction cosines of the principal axes of the thermal ellipsoids are ill defined. They are not given. The overall thermal vibration is low, consistent with the strong intermolecular hydrogen bonding and the very extensive scattering of X-rays by crystals of the complex even at very high Bragg angles.

TABLE V

RMS AMPLITUDES OF VIBRATION (Å) ALONG THE PRINCIPAL AXES OF THE THERMAL ELLIPSOIDS[a]

| Atom | | | |
|---|---|---|---|
| Cr | 0.1225 (7) | 0.1287 (13) | 0.1419 (4) |
| N(1) | 0.137 (2) | 0.156 (2) | 0.184 (2) |
| N(2) | 0.128 (2) | 0.148 (2) | 0.162 (2) |
| N(3) | 0.135 (2) | 0.164 (2) | 0.175 (2) |
| O(1) | 0.143 (2) | 0.147 (2) | 0.197 (1) |
| O(2) | 0.150 (2) | 0.206 (2) | 0.247 (1) |
| O(3) | 0.130 (2) | 0.159 (1) | 0.186 (1) |
| O(4) | 0.134 (2) | 0.205 (2) | 0.304 (2) |
| O(5) | 0.138 (2) | 0.164 (2) | 0.185 (1) |
| O(6) | 0.149 (3) | 0.211 (2) | 0.258 (2) |
| O(7) | 0.160 (2) | 0.185 (2) | 0.266 (2) |
| C(1) | 0.140 (3) | 0.152 (2) | 0.187 (2) |
| C(2) | 0.132 (3) | 0.192 (2) | 0.226 (2) |
| C(3) | 0.136 (2) | 0.153 (2) | 0.192 (2) |
| C(4) | 0.147 (3) | 0.151 (3) | 0.188 (2) |
| C(5) | 0.150 (3) | 0.157 (2) | 0.175 (2) |
| C(6) | 0.149 (2) | 0.172 (3) | 0.217 (2) |

[a] The footnote to Table II applies here also.

**The Absorption Spectrum.**—The visible and uv spectrum of the complex is shown in Figure 4. Because

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[17] C. E. Skinner and M. M. Jones, *Inorg. Nucl. Chem. Lett.*, **3**, 185 (1968).

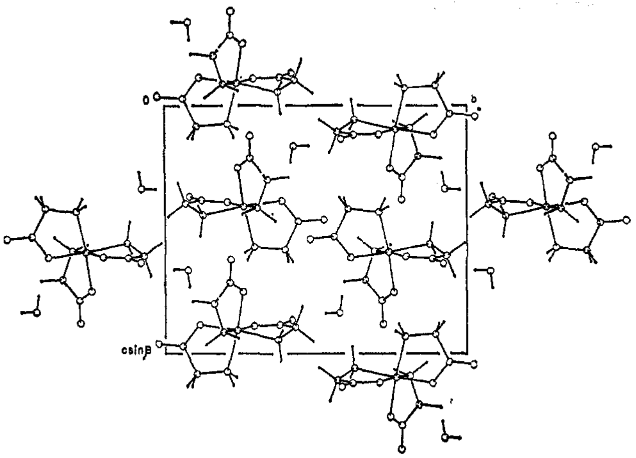

Figure 3.—View of a single layer of molecules in the crystal seen in projection down the *a* axis.

of the remarkable insolubility of the crystals, the spectrum was obtained from a mineral oil mull. The two major peaks in the visible region are assigned ${}^4A_2 \rightarrow {}^4T_2$ for the 503-nm transition and ${}^4A_2 \rightarrow {}^4T_1$ (F) for the 384-nm transition. Values of 19.9 kK and 570 $cm^{-1}$ are obtained for $10Dq$ and $\beta$, respectively. From these values a band is predicted at 237 nm for the ${}^4A_2 \rightarrow {}^4T_1$ transition. A band is observed at 223 nm, in reasonable agreement with expectation, but its relative intensity is too large for this to be the sole component of this absorption.

Besides these three bands discussed, both single-crystal and mineral oil mull spectra show three weak bands above 630 nm at room temperature. Only the lowest energy band of this series, which is about 25 times lower in intensity than the first, is assigned as the ${}^4A_2 \rightarrow {}^2E$ spin-forbidden transition at 689 nm. The other two bands are of uncertain origin, possibly a ${}^4A_2 \rightarrow {}^2T_1$ transition or vibrational overtones of the ${}^2E$ band. All three of these bands are further resolved in the single-crystal spectrum at liquid nitrogen temperature into multiple peaks. The E level is split into bands at 686.8 and 690.4 nm, corresponding to a difference of 80 $cm^{-1}$.[18]

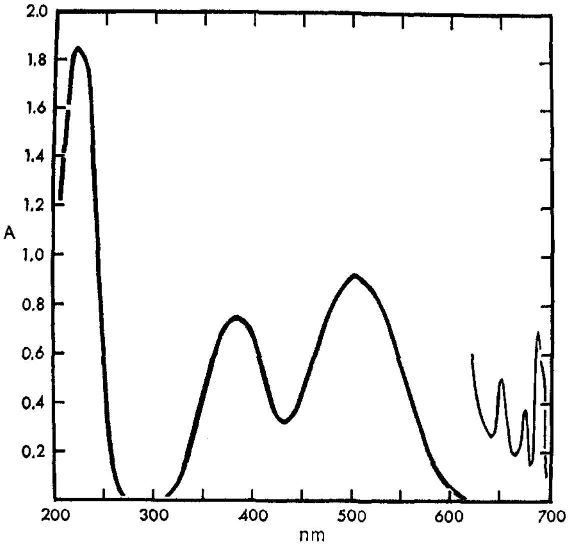

Figure 4.—Mineral oil mull absorption spectrum of tris(glycinato)chromium(III) monohydrate. The curve above 630 nm has the absorbance scale enlarged 25 times relative to the rest of the spectrum.

**Acknowledgments.**—This research was supported by a grant from the National Science Foundation (GU 1531) to the Center for Advanced Studies of the University of Virginia. We thank Dr. John Spencer, of this department, for taking the single-crystal spectrum at liquid nitrogen temperature.

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(18) A listing of structure factor amplitudes will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit $3.00 for photocopy or $2.00 for microfiche.