# μ-Dihydroxo-bis[2,6-pyridinedicarboxylatoaquachromium(III)]

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**Abstract.** $C_{14}H_8N_2O_{10}Cr_2.2H_2O$, monoclinic, $C2/m$, $a = 12.366$ (5), $b = 10.847$ (7), $c = 7.162$ (4) Å, $\beta = 117.5$ (3)°, $Z = 2$, $D_o = 1.95$ (1), $D_c = 1.965$ g cm$^{-3}$. The structure consists of $Cr(OH)[C_5H_3N(CO_2)_2]$-$(H_2O)$ dimers with $2/m$ symmetry. Each Cr atom has a distorted octahedral coordination geometry. Bridging hydroxyl ligands form planar $Cr_2(OH)_2^{4+}$ units [Cr–O, 1.955 (4), 1.939 (3), Cr···Cr, 2.999 (2) Å; Cr–O–Cr, 100.7 (2)°]. The antiferromagnetism of the title compound (78–299 K) agrees with a spin–spin coupling model using the $-2J\frac{3}{2}.\frac{3}{2}$ Hamiltonian with $J = -8.6$ cm$^{-1}$ and $g = 2.00$.

**Introduction.** Dark-green rhombohedral prisms of the title complex were prepared by heating an aqueous solution 0.01 $M$ in $CrCl_3.6H_2O$, 0.01 $M$ in 2,6-pyridinedicarboxylic acid, and 0.02 $M$ in urea for 48 h at 90°C, and were collected by filtration. Elemental analysis (calculated for $C_7H_6NO_6Cr$: C 33.35, H 2.40, N 5.55%; found: C 32.87, H 2.41, N 5.50%) was consistent with the formulation $\{Cr(OH)[C_5H_3N(CO_2)_2].H_2O\}_n$. A single crystal, 0.7 × 0.5 × 0.3 mm, mounted on the end of a glass rod, was used. Weissenberg and precession photographs revealed a monoclinic cell with the systematic absence $hkl$, $h + k = 2n + 1$ which is consistent with space groups $C2$, $Cm$ and $C2/m$. With the assumption of two dimeric units per unit cell ($n = 4$), the observed (gradient) and calculated densities agreed well.

Intensity data were collected at 20 ± 1°C on a CAD-3 automated diffractometer ($\theta$–$2\theta$ scan, $4 < 2\theta < 60$°) using graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å); 1011 reflections with $F^2 \geq 3\sigma(F^2)$ were considered observed, Lp-corrected, and used in

Table 2. *Interatomic distances* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Cr···Cr' | 2.999 (2) | O(1)–Cr–O(4) | 87.6 (1) |
| Cr–O(1) | 2.018 (3) | O(1)–Cr–N | 78.4 (1) |
| Cr–O(3) | 1.955 (4) | O(3)–Cr–O(3') | 79.3 (2) |
| Cr–O(3') | 1.939 (3) | O(3)–Cr–O(4) | 94.8 (2) |
| Cr–O(4) | 1.990 (4) | O(3')–Cr–N | 92.6 (2) |
| Cr–N | 1.978 (4) | O(4)–Cr–N | 93.3 (2) |
| O(1)–C(4) | 1.289 (6) | Cr–O(1)–C(4) | 117.3 (2) |
| O(2)–C(4) | 1.200 (5) | Cr–N–C(1) | 117.9 (2) |
| N–C(1) | 1.320 (4) | C(1)–N–C(1') | 124.0 (5) |
| C(1)–C(2) | 1.405 (6) | N–C(1)–C(2) | 119.4 (4) |
| C(1)–C(4) | 1.503 (6) | N–C(1)–C(4) | 112.5 (3) |
| C(2)–C(3) | 1.368 (7) | C(2)–C(1)–C(4) | 128.1 (4) |
| | | C(1)–C(2)–C(3) | 117.5 (5) |
| Cr–O(3)–Cr' | 100.7 (2) | C(2)–C(3)–C(2') | 122.2 (6) |
| O(1)–Cr–O(1') | 155.9 (2) | O(1)–C(4)–O(2) | 126.2 (5) |
| O(1)–Cr–O(3) | 101.9 (1) | O(1)–C(4)–C(1) | 113.6 (3) |
| O(1)–Cr–O(3') | 93.6 (1) | O(2)–C(4)–C(1) | 120.2 (5) |

Table 1. *Final atomic parameters*

Estimated standard deviations, obtained from the least-squares refinement, are given in parentheses. Fractional coordinates are ×10⁴ for nonhydrogen atoms and ×10³ for hydrogen atoms. Anisotropic $\beta$ values are ×10⁴. The form of the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

| | $x$ | $y$ | $z$ | $\beta_{11}$ or $B$ (Å²) | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cr | 1224.7 (6) | 0 | 1908 (1) | 37.2 (4) | 82.4 (7) | 122 (1) | 0 | 40.0 (4) | 0 |
| O(1) | 1606 (3) | 1819 (3) | 2145 (4) | 112 (2) | 80 (2) | 196 (5) | 46 (2) | 91 (2) | 35 (3) |
| O(2) | 3034 (4) | 3175 (3) | 2500 (4) | 246 (4) | 61 (3) | 266 (5) | −27 (3) | 175 (3) | −21 (3) |
| O(3) | −512 (3) | 0 | 1138 (5) | 40 (2) | 176 (6) | 140 (5) | 0 | 50 (2) | 0 |
| O(4) | 1781 (4) | 0 | 4996 (5) | 97 (3) | 73 (4) | 126 (6) | 0 | 58 (3) | 0 |
| N | 2906 (3) | 0 | 2250 (5) | 38 (2) | 54 (3) | 120 (6) | 0 | 32 (2) | 0 |
| C(1) | 3415 (3) | 1073 (4) | 2280 (4) | 60 (2) | 75 (3) | 120 (5) | −18 (2) | 39 (2) | −4 (3) |
| C(2) | 4563 (3) | 1104 (5) | 2325 (5) | 65 (3) | 153 (6) | 156 (6) | −54 (3) | 49 (3) | −23 (5) |
| C(3) | 5101 (5) | 0 | 2341 (8) | 43 (3) | 207 (11) | 173 (9) | 0 | 44 (4) | 0 |
| C(4) | 2650 (4) | 2142 (4) | 2314 (5) | 126 (3) | 58 (3) | 138 (5) | 4 (3) | 82 (3) | 6 (3) |
| H[C(2)] | 487 (4) | 185 (5) | 233 (7) | 1.9 | | | | | |
| H[C(3)] | 580 (9) | 0 | 234 (15) | 5.6 | | | | | |
| H[O(3)] | −93 | 0 | 206 | 3.8 | | | | | |
| H[O(4)] | 183 (4) | 67 (4) | 565 (6) | 1.6 | | | | | |

the structure solution and refinement. Absorption corrections were not applied ($\mu$ for Mo $K\alpha$ = 13·7 cm$^{-1}$).

The structure was solved by the heavy-atom method and refined by full-matrix least-squares techniques. The space group was assumed initially to be $C2/m$ and approximate coordinates for the unique Cr atom were obtained from a normal sharpened Patterson map. A difference map revealed the coordinates of the remaining non-hydrogen atoms. The quantity $\Sigma w(|F_o| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2(F_o)$. Neutral-atom scattering factors were obtained from Cromer & Waber (1965); both real and imaginary parts of the anomalous dispersion corrections (*International Tables for X-ray Crystallography*, 1962) were applied to Cr.

After several anisotropic refinement cycles, the coordinates of the pyridine ring and ligand water H atoms were located on a difference Fourier map. Heavy-atom residuals obscured the position of the hydroxyl group H atom; this atom was placed at an idealized position. Further refinement, including the



Fig. 1. *ORTEP* view of the title complex showing the atom-numbering scheme; 50% equiprobability ellipsoids are shown.

coordinates of all but the latter H atom, led to convergence with $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0\cdot0483$ and $R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2} = 0\cdot061$. H atom thermal parameters were set equal to the final isotropic values of the heavy atoms to which the H atoms are attached; they were not refined. For all anisotropic refinement cycles, weights were chosen by an analysis of variance (Ricci, Eggers & Bernal, 1972) to make $\Delta F/\sigma(F_o)$ independent of $|F_o|$. This led to the following final assignments: $\sigma(F_o) = 1\cdot73 + 0\cdot049|F_o|$, $|F_o| \leq 126$; $\sigma(F_o) = 1\cdot46 + 0\cdot053|F_o|$, $|F_o| > 126$. For the final cycle, all parameter changes were within their estimated standard deviation. A final difference map showed no peaks above a general background of $\pm0\cdot3$ e Å$^{-3}$. Atomic parameters are given in Table 1, while views of the structure and packing are shown in Figs. 1 and 2 respectively.* Interatomic distances and angles are listed in Table 2.

Lastly, we comment on the choice of space group. The thermal ellipsoids for the pyridinedicarboxylate ligand atoms in Fig. 1 suggest that this ligand is vibrating as a unit about an axis roughly normal to the pyridine plane and passing through the N atom. Such an effect could also arise from symmetry-enforced overlap of mirror images if the true space group was $C2$. To test this, block refinement was performed for $C2$ and $Cm$ (full-matrix refinement gave singular matrices). Refinement in either noncentrosymmetric space group gave significantly lower values of $R_F$ and $R_{wF}$ (0·0443, 0·055 for $C2$ and 0·0437, 0·055 for $Cm$) but did not lead to the expected changes in the thermal parameters; similar observations have been made by Sletten & Ruud (1975). Indeed, based on the weighted $R$ values, it is impossible to distinguish between $C2$ and $Cm$. In view of this, parameters are reported for space group $C2/m$.
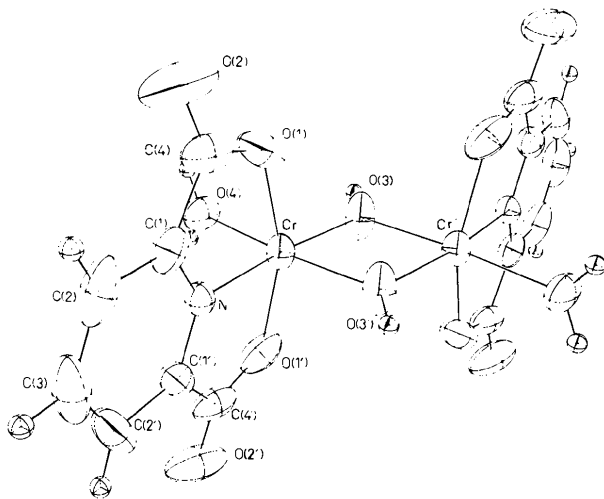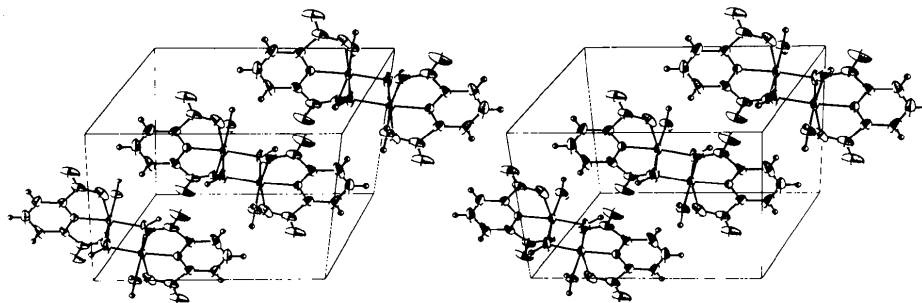
Fig. 2. Stereoscopic packing diagram for the title complex.

**Discussion.** To help define and better understand the vibrational, magnetic and related features of $Fe_2(OH)_2^{4+}$ units, we have prepared and characterized analogous dimeric complexes with $Cr_2(OH)_2^{4+}$ and $Al_2(OH)_2^{4+}$ units (Thich *et al.*, 1976). Powder diffraction data showed that the title complex and its $Al^{III}$ analog were isomorphous, but were different from the $Fe^{III}$ analog. The present study was undertaken to verify the existence of $Cr_2(OH)_2^{4+}$ units and to help facilitate structural/magnetic correlations being explored for these dimers (Scaringe, Singh, Eckberg, Hatfield & Hodgson, 1975).

The structure consists of $Cr(OH)[C_5H_3N(CO_2)_2]$-$(H_2O)$ dimers with $2/m$ symmetry. Crystallographically equivalent $Cr^{III}$ ions are bridged by two OH groups to form $Cr_2(OH)_2^{4+}$ units. A tridentate 2,6-pyridinedicarboxylate ligand and a $H_2O$ molecule complete the distorted octahedral Cr coordination geometry. The major distortion from octahedral symmetry results from the limited 'bite' of the tridentate ligand [O(1)—Cr—O(1'), 155·9°]. Structural parameters for the planar $Cr_2(OH)_2^{4+}$ units [Cr—O, 1·955 (4), 1·939 (3) Å, Cr···Cr, 2·999 (2) Å; Cr—O—Cr, 100·7 (2)°] fall within ranges reported for this group in other species (Kaas, 1976). The Cr—N distance [1·978 (4) Å] is 0·08–0·10 Å shorter than those in similar dimers with ethylenediamine (Kaas, 1976) or phenanthroline (Scaringe *et al.*, 1975) non-bridging ligands. A possible consequence of this result is that the longest Cr—OH bond in the title complex is *trans* to the Cr—N bond whereas, with the $Fe^{III}$ analog (Thich *et al.*, 1976), the reverse is true. The remaining structural parameters are comparable with those reported for the $Fe^{III}$ analog.

Preliminary susceptibility data were obtained using a Faraday balance, corrected for diamagnetism (209 × $10^{-6}$ c.g.s.u. per $Cr^{III}$) and fit using least-squares methods to the expression

$$\mu^2 = 12 \cdot 006 \left( \frac{14 + 5Z^6 + Z^{10}}{7 + 5Z^6 + 3Z^{10} + Z^{12}} \right)$$

Table 3. *Magnetic properties of the title complex*

Observed magnetic moments per $Cr^{III}$ were obtained from the experimental $\chi$ values and the relationship $\mu_o = 2 \cdot 828(\chi T)^{1/2}$: calculated magnetic moments were obtained from the expression given in the text for $J = -8 \cdot 6$ cm$^{-1}$.

| $T$ (K) | $\mu_o$ | $\mu_c$ |
|---|---|---|
| 299 | 3·66 | 3·68 |
| 240 | 3·57 | 3·63 |
| 186 | 3·50 | 3·55 |
| 103 | 3·26 | 3·25 |
| 78 | 3·11 | 3·05 |

where $Z = \exp(-J/kT)$ (Earnshaw, 1968). The antiferromagnetism of the title complex (Table 3) is consistent with $J \simeq -8 \cdot 6$ cm$^{-1}$ for the temperature range investigated.

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