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# Crystal and Molecular Structure of Hexaimidazolidone Chromium(III) Nitrate, $[Cr(OC_3H_6N_2)_6](NO_3)_3 \cdot 4H_2O$

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# Hexaimidazolidonechromium(III) Nitrate, $[Cr(OC_3H_6N_2)_6](NO_3)_3 \cdot 4H_2O$의 결정 및 분자 구조

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Abstract

The title compound, $[Cr(OC_3H_6N_2)_6](NO_3)_3 \cdot 4H_2O$, was crystallized in the centrosymmetric space group $P\bar{1}$ with two half molecules in an asymmetric unit, and the two complete molecules are generated by inversion symmetry located at Cr atoms. Therefore, the Cr atoms are coordinated to six imidazolidone ligands through the oxygen atoms, and both $CrO_6$ units have a slightly distorted octahedral geometry.

요 약

$[Cr(OC_3H_6N_2)_6](NO_3)_3 \cdot 4H_2O$는 중심대칭적 공간군인 $P\bar{1}$로 결정화되며 비대칭 단위 내의 두 개의 반분자로 구성되어 Cr 원자에 위치한 반전중심으로 대칭되게 분자 구조를 이룬다. Cr 금속은 6개의 imidazolidone의 산소와 결합하여서 $CrO_6$ 단위는 약간 일그러진 팔면체 구조를 가진다.

## 1. Introduction

Phosphorescence and fluorescence of dual emission from hexaurachromium(III) complex has lead to an extensive investigation for spectroscopy and ligand field analysis. The imidazolidone complex which shows similar emission behavior is closely related to the urea complex and the two ligands differ only at the nitrogen end of the molecules.[1] The knowledge of its crystal structure is therefore important in interpreting spectroscopic properties and ligand field analysis for complexes of this type.

## 2. Experimental Section

Crystals of the title compound were prepared according to the method of Chatterjee and Porter.[1] Successive recrystallizations from aqueous solution yielded dark green, needle-shaped crystals. Sample purity was checked by 12 K luminescence spectroscopy. Data collection, cell refinement, and data reduction were carried out with CAD-4 EXPRESS[2] and XCAD4.[3] The structure was solved by direct methods by SHELX86.[4] Refinement was performed by SHELXL97.[5] All H atoms except for water H atoms were added at calculated positions and given isotropic displacement parameters equal to 1.2 times the equivalent isotropic displacement parameter of the carrier atom in a riding model. Molecular graphics were prepared using ORTEP-3.[6] Crystallographic data and refinement details are summarized in Table 1. Atomic coordinates, bond distances and angles for

**Table 1. Experimental details**

| | |
|---|---|
| Crystal data | |
| Chemical formula | $C_{18}H_{44}CrN_{15}O_{19}$ |
| Chemical formula weight | 826.68 |
| Cell setting | Triclinic |
| Space group | $P\bar{1}$ |
| a (Å) | 10.373(2) |
| b (Å) | 13.020(3) |
| c (Å) | 15.608(3) |
| α (°) | 103.872(19) |
| β (°) | 109.111(18) |
| γ (°) | 98.861(17) |
| V (Å) | 1870.5(7) |
| Z | 2 |
| Radiation Type | Mo Kα |
| Wavelength (Å) | 0.71069 |
| No. of reflectins for cell parameters | 22 |
| θ range (°) | 11.339~13.315 |
| μ ($mm^{-1}$) | 0.389 |
| Temperature (K) | 293(2) |
| Crystal form | needle |
| Crystal size | 0.5×0.3×0.3 |
| Crystal color | dark green |
| Data collection | |
| Diffractometer | Enraf-Nonius CAD4 |
| Data collection method | ω-2θ scan |
| Absorption correction | None |
| No. of measured reflections | 6071 |
| No. of reflections with I > 2σ | 5830 |
| $R_{int}$ | 0 0362 |
| $\theta_{max}$ | 24.97 |
| Range of $h$, $k$, $l$ | $-12 \rightarrow h \rightarrow 1$, $-15 \rightarrow k \rightarrow 15$, $0 \rightarrow l \rightarrow 18$ |
| Refinement | |
| Refinement on F | |
| $R$ | 0.0693 |
| $\omega R$ | 0.1633 |
| $S$ | 0.905 |
| No. of reflections used for refinement | 5830 |
| No. of parametets used | 475 |
| Weighting scheme | $\omega = 1/[(\sigma 2(F_0^2)+(0.1160p)^2+0.0000p]$ where $P=(F_o^2+2F_c^2)/3$ |
| Extinction method | none |
| Source of atomic scattering factors | SHELXL-97 |

**Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameter(Å$^2$)**

| | x | y | z | $U_{eq}$ |
|---|---|---|---|---|
| Cr | 0.0000 | 0.0000 | 0.5000 | 0.0205(2) |
| O1 | 0.1775(3) | -0.0072(2) | 0.48384(18) | 0.0269(6) |
| O2 | 0.0987(3) | 0.0573(2) | 0.63887(19) | 0 0297(6) |
| O3 | 0.0208(3) | 0.1494(2) | 0.49101(19) | 0.0292(6) |
| O4 | 0.5422(3) | 0.6351(2) | 0.10196(18) | 0.0295(6) |
| O5 | 0.6075(3) | 0.5764(2) | -0.05871(19) | 0.0275(6) |
| O6 | 0.6678(3) | 0.4602(2) | 0.07329(19) | 0.0321(7) |
| N1 | 0.3049(4) | -0.0707(3) | 0.6036(3) | 0.0437(10) |
| N2 | 0.3400(4) | -0.1062(3) | 0.4696(3) | 0.0474(11) |
| N3 | 0.0373(4) | 0.2162(3) | 0.6867(2) | 0.0399(9) |
| N4 | 0.1284(4) | 0 1403(3) | 0.7920(3) | 0.0460(10) |
| N5 | 0.1454(5) | 0.1653(3) | 0.3961(3) | 0.0474(11) |
| N6 | 0.0395(4) | 0.2914(3) | 0.4325(3) | 0.0402(9) |
| N7 | 0.5587(5) | 0.7495(3) | 0.2433(3) | 0 0480(11) |
| N8 | 0.6134(4) | 0.5935(3) | 0.2436(2) | 0.0427(10) |
| N9 | 0.6727(5) | 0.6924(3) | -0.1347(3) | 0.0490(11) |
| N10 | 0.5754(4) | 0.7520(3) | -0.0333(2) | 0.0381(9) |
| N11 | 0.8150(5) | 0.3471(4) | 0.0835(3) | 0.0623(13) |
| N12 | 0.7923(4) | 0.4300(3) | -0.0247(3) | 0.0476(10) |
| C1 | 0.2661(4) | -0.0587(3) | 0.5178(3) | 0 0273(9) |
| C2 | 0.3993(6) | -0.1420(4) | 0.6158(3) | 0.0475(12) |
| C3 | 0.4386(5) | -0.1525(4) | 0.5296(4) | 0.0488(13) |
| C4 | 0.0881(4) | 0.1340(3) | 0.7011(3) | 0.0233(8) |
| C5 | 0.0354(6) | 0.2894(4) | 0.7750(3) | 0.0501(13) |
| C6 | 0.0918(5) | 0.2321(4) | 0.8463(3) | 0.0498(13) |
| C7 | 0.0642(4) | 0.1970(3) | 0.4409(3) | 0.0231(8) |
| C8 | 0.1709(6) | 0.2387(4) | 0.3391(4) | 0.0544(14) |
| C9 | 0.1092(7) | 0.3347(4) | 0.3770(4) | 0.0584(15) |
| C10 | 0.5699(4) | 0.6567(3) | 0.1914(3) | 0.0233(8) |
| C11 | 0.5843(6) | 0.7515(4) | 0.3401(3) | 0.0535(14) |
| C12 | 0.6393(5) | 0.6471(4) | 0.3458(3) | 0.0441(12) |
| C13 | 0.6159(4) | 0.6674(3) | -0.0734(3) | 0.0290(9) |
| C14 | 0 6612(7) | 0.7982(4) | -0.1446(4) | 0.0651(17) |
| C15 | 0.6133(7) | 0 8477(4) | -0.0635(4) | 0.0584(15) |
| C16 | 0.7523(4) | 0.4163(3) | 0.0453(3) | 0.0330(10) |
| C17 | 0.9101(6) | 0.3084(5) | 0.0384(5) | 0.0710(18) |
| C18 | 0.8746(6) | 0.3542(4) | -0.0453(4) | 0.0573(15) |

the molecular unit are listed Table 2 and 3.

## 3. Results and Discussion

An asymmetric unit of this complex is composed of two half molecules of $[Cr(OC_3H_6N_2)_6]^{+3}$, three $NO_3$ groups, and four water molecules, and the two mol-

**Table 3. Bond distances (Å) and angles (deg) for $[Cr(OC_3H_6N_2)_6](NO_3)_3 \cdot 4H_2O$**

| | | | |
|---|---|---|---|
| Cr-O(1) | 1.952(3) | N2-C3 | 1.455(6) |
| Cr-O(2) | 1.959(3) | N3-C4 | 1.299(5) |
| Cr-O(3) | 1.968(3) | N3-C5 | 1.484(5) |
| O1-C1 | 1.270(5) | N4-C4 | 1.318(5) |
| O2-C4 | 1.262(4) | N4-C6 | 1.469(5) |
| O3-O7 | 1.256(4) | N5-C7 | 1.312(5) |
| N1-C1 | 1.323(5) | N5-C8 | 1.503(5) |
| N1-C2 | 1.449(6) | N6-C7 | 1.320(5) |
| N2-C1 | 1.355(5) | N6-C9 | 1.453(6) |
| O1-Cr-O1 | 180.0 | O1-C1-N1 | 127.0(3) |
| O1-Cr-O2 | 90.84(11) | O1-C1-N2 | 123.0(4) |
| O1-Cr-O2 | 89 16(11) | O2-C4-N3 | 126.4(4) |
| O1-Cr-O3 | 91.23(11) | O2-C4-N4 | 123.1(4) |
| O1-Cr-O3 | 88.77(11) | O3-C7-N5 | 125.9(3) |
| O2-Cr-O2 | 180.0 | O3-C7-N6 | 122.5(3) |
| O2-Cr-O3 | 90.84(11) | C1-N1-C2 | 112.3(3) |
| O2-Cr-O3 | 89.16(11) | C1-N2-C3 | 109.8(4) |
| O3-Cr-O3 | 180.0 | C4-N3-C5 | 112.3(3) |
| C1-O1-Cr | 128.8(2) | C4-N4-C6 | 111.4(4) |
| C4-O2-Cr | 131.9(3) | C7-N5-C8 | 111.5(4) |
| C7-O3-Cr | 134.1(2) | C7-N6-C9 | 112.6(4) |

ecules are generated by inversion symmetries located at Cr atoms (see Fig. 1), so that six imidazolidone ligands are coordinated to the central Cr metal through the oxygen atom. Each of the two $CrO_6$ chromophoric units is almost octahedral with Cr-O bond lengths ranging from 1.952(3)Å to 1.968(3)Å with the mean value of 1.958(1)Å and the bond angles about the Cr atom deviate by no more than 1.23° from ideal octahedral values of 90° and 180°.

The bond angles of Cr-O-C in the imidazolidone ligands range from 128.8(2)° to 134.1(2)°, which are relatively small and may be due to the π-orbital symmetry and its anisotropic π-bonding. Indeed, the luminescence spectrum of this complex suggests its symmetry is low since it shows the strongest zero phonon line with weak vibrational lines.

The geometry of six independent imidazolidone ligands (A, B, C, A', B', C') are very similar to one another; they are all planar with the maximum deviation from the mean plane by about 0.077(3)Å, their neighboring dihedral angles range from 26.4(3)° to 41.1(3)°, and homologous parameters present a very small dispersion, as seen in Table 3. In addition, all twelve nitrogen atoms in six imidazolidone ligands, all nine oxygen atoms in the three $NO_3$ molecules and all four water oxygen atoms are participating in intra- and intermolecular hydrogen bonds. These hydrogen bonds form a complete three-dimensional network and are presumably responsible for the stability of this complex.

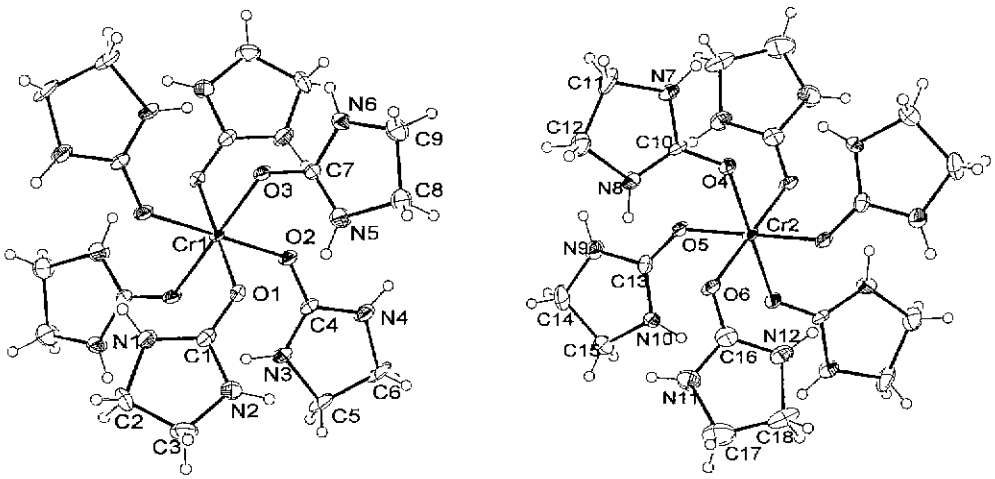


**Fig. 1. An ORTEP diagram of $[Cr(OC_3H_6N_2)_6](NO_3)_3 \cdot 4H_2O$ with 40% probability displacement ellipsoids. The asymmetric unit only is labeled.**

## References

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