

단 신

cis-[Cr(cyclam)(ONO)₂]NO₂의 결정구조 및 IR 특성

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Crystal Structure and IR Spectroscopy of *cis*-[Cr(cyclam)(ONO)₂]NO₂

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INTRODUCTION

The ligand behavior of the nitrite anion (NO₂⁻) is of interest because it can bond the metal through a number of different coordination modes, as shown in Fig. 1.¹

Monodentate coordination may occur either through nitrogen to give a nitro complex or through oxygen to give a nitrite complex. Bidentate coordination is known to take place either by chelation or by forming a bridge. In general, three types of ligand binding modes are possible for mononuclear chromium (III) complexes. These are the nitro (Cr-NO₂) and either monodentate (nitrito-O) or chelating bidentate (nitrite-O,O') (Cr-ONO) binding modes.² Moreover, the cyclam (1,4,8,11-tetraazacyclotetradecane) ligand is moderately flexible structure, and can adopt both planer (*trans*) and folded (*cis*) configurations. There are five configurational *trans* isomers for the cyclam which differ in the chirality of the *sec*-NH centers. The *trans*-V configuration which is symmetrical about the diagonal can fold to form *cis*-V isomer.³ The 14-membered cyclam ligand and its derivatives are involved in diverse application

fields such as catalysis, enzyme mimics, selective metal recovery, therapy and diagnosis.⁴ We previously described the spectroscopic and ligand-field properties of *cis*-[Cr^{III}(cyclam)L₂]ⁿ⁺ system (L=en/2, pn/2, NH₃, F⁻, Cl⁻, Br⁻, NCS⁻, N₃⁻, ONO⁻, ox²⁻/2).⁵⁻¹⁵ The electronic absorption and infrared spectra can be used diagnostically to identify the geometric isomers of chromium(III) complexes with various mixed ligands.¹⁶⁻¹⁸ However, it should be noted that the assignments based on spectroscopic investigations are not always conclusive.¹⁹ The present investigation was undertaken in order to supply additional details of IR spectral criteria used to distinguish nitrite and nitro linkage isomers, and to confirm stereochemical structure of [Cr(cyclam)(ONO)₂]NO₂.

EXPERIMENTAL SECTION

The free ligand cyclam was purchased from Strem Chemicals. All chemicals were reagent grade materials and used without further purification. The *cis*-[Cr(cyclam)(ONO)₂]NO₂ was prepared as described in the literature.²⁰ The far-infrared spectrum in the

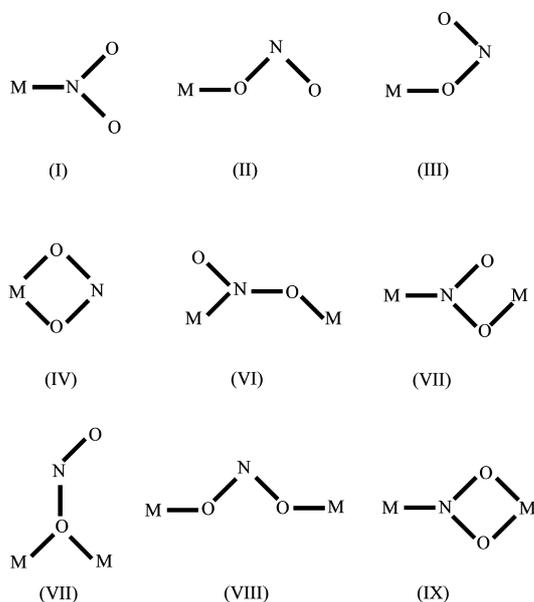


Fig. 1. Nine possible types of metal-nitrite coordination.

region 530-50 cm⁻¹ was recorded with a Bruker 113v spectrometer on a microcrystalline sample pressed into a polyethylene pellet. The mid-infrared spectrum was obtained with a Mattson Infinities series FT-IR spectrometer using a KBr pellet. The IR measurements were carried out at a room temperature and spectral data were analyzed with the GRAMS/32 software package.²¹ Analyses for C, H, and N were determined on a Carlo Erba 1108 Elemental Vario EL analyzer. The room-temperature visible absorption spectrum was recorded with a HP 8453 diode array spectrophotometer. Elemental analysis for [Cr(cyclam)(ONO)₂]NO₂ = C₁₀H₂₄CrN₇O₆; Found (Calc.): C, 30.12 (30.77); H, 5.98 (6.19); N, 24.53 (25.12)%.

RESULTS AND DISCUSSION

Structural properties. We previously reported the X-ray crystal structure of *cis*-[Cr(cyclam)(ONO)₂]NO₂.²² The structural analysis showed the space group *C2/c* of the monoclinic system with a cell of dimensions *a*=9.878 (2), *b*=11.813 (2), *c*=14.837 (3) Å and *Z*=4. A perspective drawing of *cis*-[Cr(cyclam)(ONO)₂]⁺ cation together with the atomic

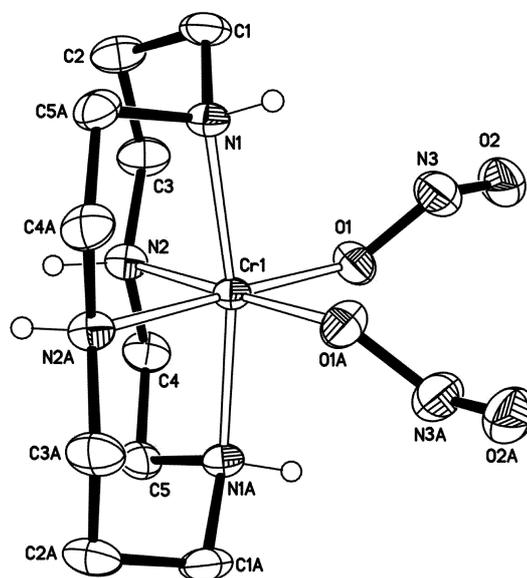


Fig. 2. Perspective view (30% probability level) of *cis*-[Cr(cyclam)(ONO)₂]⁺ cation.

labeling is depicted in Fig. 2 for convenience.

The coordinated nitrite anions are each bound to chromium ion via only one oxygen atom. The macrocyclic cyclam ligand is folded the N(2) and N(2A) direction with four N atoms coordinate to the Cr atom. The two nitrito ligands coordinate to the remaining positions of Cr atom in a *cis* configuration. But the non-bonded nitrite oxygen atoms are located *trans* to the Cr metal in monodentate nitrite coordination. The crystal consists of dinitrito(cyclam)-chromium(III) monocation and nitrite anion in a molecular ratio of 1:1, so that it can be formulated as *cis*-[Cr(cyclam)(ONO)₂]NO₂. This is in agreement with elemental analysis. The complex cation has its central Cr atom in a distorted octahedral coordination with four nitrogen atoms and two nitrite oxygen atoms in a *cis* position. The crystals are held together by hydrogen bonds between secondary NH groups and nitrite ligands. The geometry of title compound was found to be *cis* configuration with respect to monodentate nitrito oxygens. The complex cation has its central Cr atom in a slightly distorted octahedral coordination with two Cr-O and four Cr-N bonds. The mean Cr-N and Cr-O bond distances are 2.0895(14) and 1.9698(14) Å while the

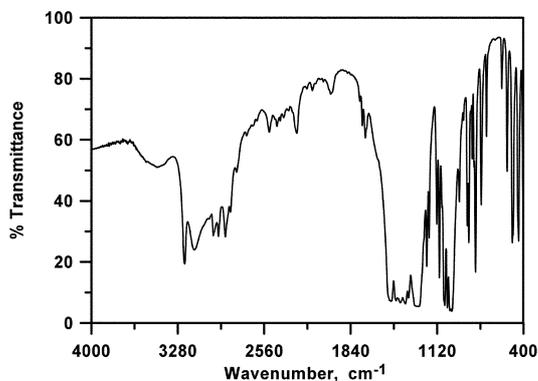


Fig. 3. Mid-infrared spectrum of *cis*-[Cr(cyclam)(ONO)₂]NO₂ at 298 K.

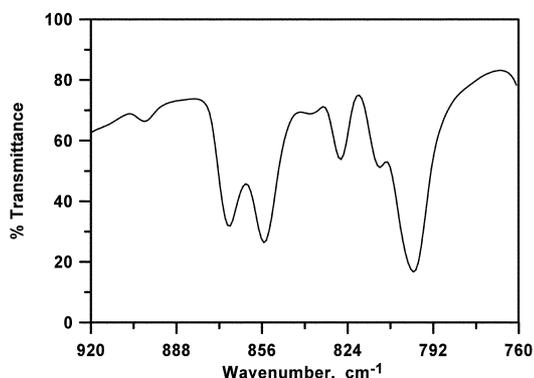


Fig. 4. Expanded portion of mid-infrared spectrum in the range 920-760 cm⁻¹.

O(1)-Cr-O(1A) angle is 94.03(9)°.

IR spectral properties. The mid-infrared spectrum of *cis*-[Cr(cyclam)(ONO)₂]NO₂ recorded at room temperature is presented in Fig. 3.

The absorption near 3468 cm⁻¹ and broadness of the band indicate that there are hydrogen bonds in this complex. The sharp peaks at 3223 cm⁻¹, and 3000-2800 cm⁻¹ regions are due to the symmetric and antisymmetric N-H and C-H stretching modes, respectively. The strong absorption band at 1512 cm⁻¹ and the two bands at 1445 and 1426 cm⁻¹ can be assigned to NH₂ and CH₂ bending modes, respectively. In the nitro ligand the charge is delocalized resulting in two N-O bonds formally of bond order 1.5. We would expect two N-O absorptions because there are two N-O bonds. Because the bonds are similar they will couple to give a symmetric and an antisymmetric stretching vibration with similar frequencies. In the case of the nitrito ligand one N-O bond can be viewed as a single bond and the other as a double bond which means we could expect to see on higher vibrational frequency and one lower one. The transition metal complexes containing an O-bound nitrite ligand exhibit an intense antisymmetric stretching frequency, $\nu_{as}(\text{ONO})$ at ~1460 cm⁻¹ and a symmetric mode, $\nu_s(\text{ONO})$ at ~1050 cm⁻¹ and deformation band, $\delta_w(\text{ONO})$ at ~820 cm⁻¹.² The three strong absorption peaks at 1464, 1056 and 826 cm⁻¹ are characteristic of the nitrito ligand toward chromium(III). It is noteworthy that nitrito complexes lack the wagging modes near 620 cm⁻¹

which appear in all nitro complexes. We have not been able to detect any band assignable to the N-bonded $\rho_w(\text{NO}_2)$ vibration in the 600-650 cm⁻¹ region.

The infrared spectroscopy is also very useful in assigning configuration of *cis* and *trans* isomers of cyclam chromium(III) complexes. It is well known that *cis* isomer exhibits at least three bands in the 890-830 cm⁻¹ region due to the N-H wagging modes while the methylene vibration splits into two peaks in the 830~790 cm⁻¹ region. However, *trans* isomer shows two groups of bands, a doublet near 890 cm⁻¹ arising from the secondary amine vibration and only one band near 810 cm⁻¹ due mainly to the methylene vibration.¹² Fig. 4 shows an expanded view of the IR spectrum in the region 920-760 cm⁻¹ of interest. The present complex exhibits three bands at 899, 868 and 855 in the N-H wagging frequency region. The CH₂ rocking bands at 812 and 799 cm⁻¹ are also observed. These vibrational modes are not affected by differing counteranions.

Meta-ligand stretching and ring-deformation bands occur in the far infrared range. The far-infrared spectrum (530-50 cm⁻¹) was measured in order to assign the Cr-ONO and Cr-N(cyclam) stretching vibrations. The far-IR spectrum is shown in Fig. 5.

The Cr-N and Cr-ONO stretching bands in the far-infrared spectrum to which we have assigned a *cis* dinitrito geometric configuration exhibit splitting, whereas the *trans* isomer shows no splitting of these bands, as would be expected from the lower

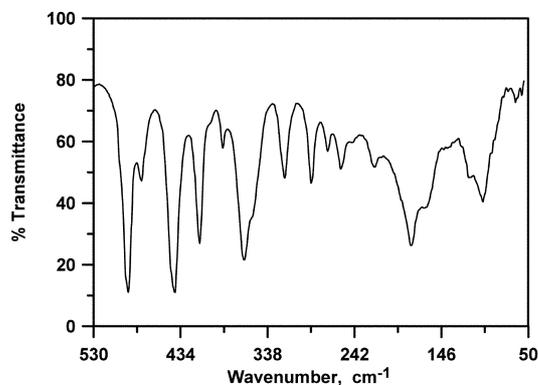


Fig. 5. Far-infrared spectrum of *cis*-[Cr(cyclam)(ONO)₂]NO₂ at 298 K.

symmetry of the Cr-N skeleton in the *cis* complex. For the *cis*-[CrN₄(ONO)₂]⁺ complex with C_{2v} symmetry, the group theoretical analysis predicts four Cr-N and two Cr-ONO infrared-active stretching vibrations, respectively. The four peaks in the range 495-410 cm⁻¹ can be assigned to the Cr-N(cyclam) stretching modes. Typically, all nitrito complexes exhibit absorption bands in the 370-340 cm⁻¹ region due to the n(M-ONO).¹ The two absorptions at 364 and 353 cm⁻¹ are assigned to the Cr-ONO stretching modes. The title complex was clearly consistent with the *cis* configuration. A number of absorption bands below 319 cm⁻¹ arise from the skeletal bending and lattice vibration modes.

The infrared spectral properties of the title complex are in agreement with the result of X-ray crystallography, which show that the NO₂ group is bonded to chromium(III) through the one O of its oxygen atoms and the cyclam ligand adopts the *cis*-V(RRRR) configuration.

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