

## 단 신

### *cis*-[Cr(cyclam)(ONO)<sub>2</sub>]<sub>2</sub>NO<sub>2</sub>의 결정구조 및 IR 특성

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### Crystal Structure and IR Spectroscopy of *cis*-[Cr(cyclam)(ONO)<sub>2</sub>]<sub>2</sub>NO<sub>2</sub>

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## INTRODUCTION

The ligand behavior of the nitrite anion (NO<sub>2</sub><sup>-</sup>) is of interest because it can bond the metal through a number of different coordination modes, as shown in Fig. 1.<sup>1</sup>

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-NO<sub>2</sub>) and either monodentate (nitrito-O) or chelating bidentate (nitrite-O,O') (Cr-ONO) binding modes.<sup>2</sup> 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.<sup>3</sup> 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.<sup>4</sup> We previously described the spectroscopic and ligand-field properties of *cis*-[Cr<sup>III</sup>(cyclam)L<sub>2</sub>]<sup>n+</sup> system (L=en/2, pn/2, NH<sub>3</sub>, F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, NCS<sup>-</sup>, N<sub>3</sub><sup>-</sup>, ONO<sup>-</sup>, ox<sup>2-</sup>/2).<sup>5-15</sup> The electronic absorption and infrared spectra can be used diagnostically to identify the geometric isomers of chromium(III) complexes with various mixed ligands.<sup>16-18</sup> However, it should be noted that the assignments based on spectroscopic investigations are not always conclusive.<sup>19</sup> 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)<sub>2</sub>]<sub>2</sub>NO<sub>2</sub>.

## 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)<sub>2</sub>]<sub>2</sub>NO<sub>2</sub> was prepared as described in the literature.<sup>20</sup> The far-infrared spectrum in the

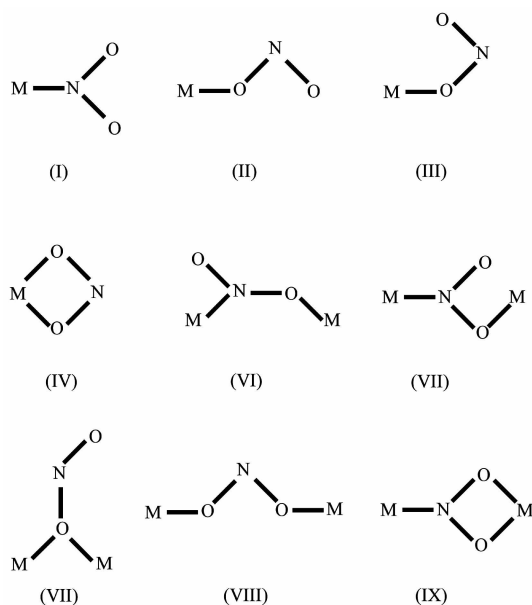


Fig. 1. Nine possible types of metal-nitrite coordination.

region 530-50 cm<sup>-1</sup> was recorded with a Bruker I13v spectrometer on a microcrystalline sample pressed into a polyethylene pellet. The mid-infrared spectrum was obtained with a Mattson Infinity 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.<sup>21</sup> 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)<sub>2</sub>]NO<sub>2</sub> · C<sub>10</sub>H<sub>24</sub>N<sub>4</sub>O<sub>6</sub>: 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)<sub>2</sub>]NO<sub>2</sub>.<sup>22</sup> The structural analysis showed the space group *C*2/*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)<sub>2</sub>]<sup>+</sup> cation together with the atomic

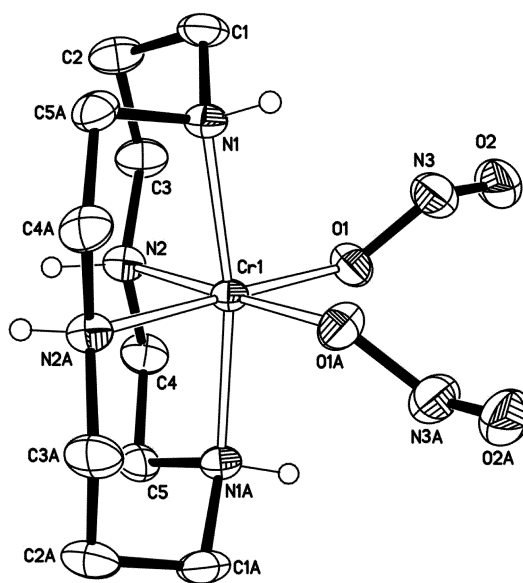


Fig. 2. Perspective view (30% probability level) of *cis*-[Cr(cyclam)(ONO)<sub>2</sub>]<sup>+</sup> cation.

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 dinitro(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)<sub>2</sub>]NO<sub>2</sub>. 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

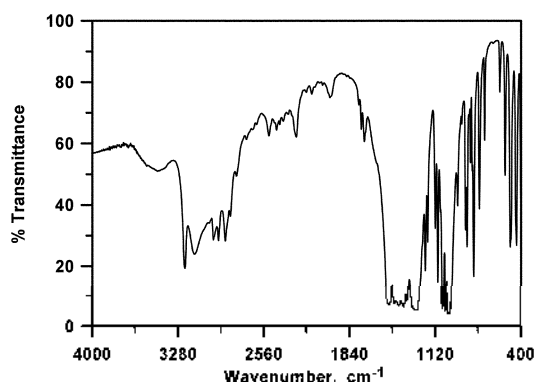


Fig. 3. Mid-infrared spectrum of *cis*-[Cr(cyclam)(ONO)<sub>2</sub>]<sub>2</sub>NO<sub>2</sub> at 298 K.

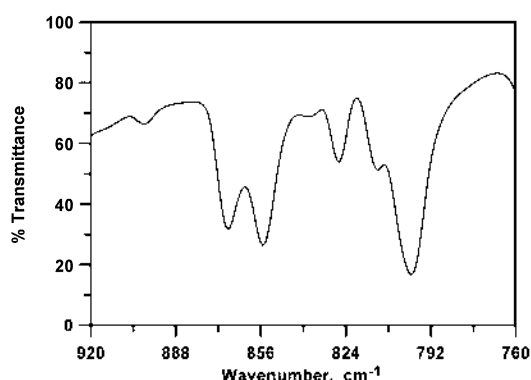


Fig. 4. Expanded portion of mid-infrared spectrum in the range 920-760 cm<sup>-1</sup>.

O(1)-Cr-O(1A) angle is 94.03(9)°.

**IR spectral properties.** The mid-infrared spectrum of *cis*-[Cr(cyclam)(ONO)<sub>2</sub>]<sub>2</sub>NO<sub>2</sub> recorded at room temperature is presented in Fig. 3.

The absorption near 3468 cm<sup>-1</sup> and broadness of the band indicate that there are hydrogen bonds in this complex. The sharp peaks at 3223 cm<sup>-1</sup>, and 3000-2800 cm<sup>-1</sup> regions are due to the symmetric and antisymmetric N-H and C-H stretching modes, respectively. The strong absorption band at 1512 cm<sup>-1</sup> and the two bands at 1445 and 1426 cm<sup>-1</sup> can be assigned to NH<sub>2</sub> and CH<sub>2</sub> 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 one 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<sup>-1</sup> and a symmetric mode,  $\nu_s(\text{ONO})$  at ~1050 cm<sup>-1</sup> and deformation band,  $\delta_{as}(\text{ONO})$  at ~820 cm<sup>-1</sup>.<sup>2</sup> The three strong absorption peaks at 1464, 1056 and 826 cm<sup>-1</sup> are characteristic of the nitrito ligand toward chromium(III). It is noteworthy that nitrito complexes lack the wagging modes near 620 cm<sup>-1</sup>

which appear in all nitro complexes. We have not been able to detect any band assignable to the N-bonded  $\rho_u(\text{NO}_2)$  vibration in the 600-650 cm<sup>-1</sup> 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<sup>-1</sup> region due to the N-H wagging modes while the methylene vibration splits into two peaks in the 830~790 cm<sup>-1</sup> region. However, *trans* isomer shows two groups of bands, a doublet near 890 cm<sup>-1</sup> arising from the secondary amine vibration and only one band near 810 cm<sup>-1</sup> due mainly to the methylene vibration.<sup>12</sup> Fig. 4 shows an expanded view of the IR spectrum in the region 920-760 cm<sup>-1</sup> of interest. The present complex exhibits three bands at 899, 868 and 855 in the N-H wagging frequency region. The CH<sub>2</sub> rocking bands at 812 and 799 cm<sup>-1</sup> 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<sup>-1</sup>) 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

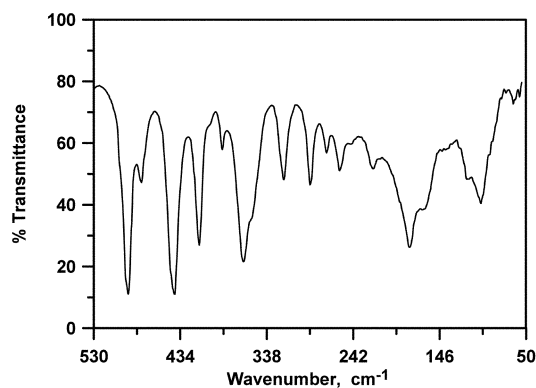


Fig. 5. Far-infrared spectrum of *cis*-[Cr(cyclam)(ONO)]·NO at 298 K.

symmetry of the Cr-N skeleton in the *cis* complex. For the *cis*-[CrN<sub>4</sub>(ONO)<sub>2</sub>]<sup>+</sup> complex with C<sub>2v</sub> 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<sup>-1</sup> can be assigned to the Cr-N(cyclam) stretching modes. Typically, all nitrito complexes exhibit absorption bands in the 370–340 cm<sup>-1</sup> region due to the n(M-ONO).<sup>1</sup> The two absorptions at 364 and 353 cm<sup>-1</sup> 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<sup>-1</sup> 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 NO<sub>2</sub> group is bonded to chromium(III) through the one O of its oxygen atoms and the cyclam ligand adopts the *cis*-V(RRRR) configuration.

## REFERENCES

1. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*; 5th Ed., John Wiley & Sons: New York, 1997.
2. Hitchman, M.; Rowbottom, G. L. *Coord. Chem. Rev.* **1982**, *42*, 55.
3. Sosa, M. F.; Tobe, M. L. *J. Chem. Soc. Dalton Trans.* **1986**, 427.
4. Hunter, T. M.; Paisey, S. J.; Park, H. S.; Cleghorn, L.; Parkin, A.; Parsons, S.; Sadler, P. J. *J. Inorg. Biochem.* **2004**, *98*, 713.
5. Choi, J. H. *Bull. Korean Chem. Soc.* **1993**, *14*, 118.
6. Choi, J. H.; Oh, I. G. *Bull. Korean Chem. Soc.* **1993**, *14*, 348.
7. Choi, J. H. *J. Korean Chem. Soc.* **1995**, *39*, 501.
8. Choi, J. H. *Bull. Korean Chem. Soc.* **1997**, *18*, 819.
9. Choi, J. H. *J. Photosci.* **1997**, *4*, 127.
10. Choi, J. H. *Spectrochim. Acta* **2000**, *56A*, 1653.
11. Choi, J. H. *Chem. Phys.* **2000**, *256*, 29.
12. Choi, J. H.; Hong, Y. P.; Park, Y. C.; Ryoo, K. S. *J. Photosci.* **2000**, *7*, 21.
13. Choi, J. H.; Hong, Y. P.; Park, Y. C. *Bull. Korean Chem. Soc.* **2003**, *24*, 384.
14. Choi, J. H.; Oh, I. G.; Linder, R.; Schönherr, T. *Chem. Phys.* **2004**, *297*, 7.
15. Choi, J. H.; Oh, I. G.; Suzuki, T.; Kaizaki, S. *J. Mol. Struct.* **2004**, *694*, 39.
16. Choi, J. H.; Hoggard, P. F. *Polyhedron* **1992**, *11*, 2399.
17. Choi, J. H.; Hong, Y. P.; Park, Y. C. *Spectrochim. Acta* **2002**, *58A*, 1599.
18. Choi, J. H.; Hong, Y. P.; Park, Y. C.; Lee, S. H.; Ryoo, K. S. *Bull. Korean Chem. Soc.* **2001**, *22*, 107.
19. Stearns, D. M.; Armstrong, W. H. *Inorg. Chem.* **1992**, *31*, 5178.
20. Ferguson, J.; Tobe, M. L. *Inorg. Chim. Acta* **1970**, *4*, 109.
21. GRAMS/32 V5.21. Galactic Industries Corporation, Salem, NH 03079, USA.
22. Choi, J. H.; Oh, I. G.; Lim, W. T.; Park, K. M. *Acta Cryst.* **2004**, *C60*, m238.
23. Poon, C. K.; Pun, K. C. *Inorg. Chem.* **1980**, *19*, 568.