

Preparation and crystal structure of azido bridged one-dimensional polymeric cadmium(II) complex, $[\text{Cd}(\text{N}_3)_2(2\text{-ethylimidazole})_2]$

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요약 : $[\text{Cd}(\text{N}_3)_2(2\text{-ethylimidazole})_2]$ 착물을 합성하고 단결정 X-선 회절법으로 구조를 규명하였다. 이 착물은 단사정계, 공간군 Cc , $a = 16.200(3)$, $b = 12.926(3)$, $c = 7.007(1)$ Å, $\beta = 102.29(3)^\circ$, $V = 1433.7(5)$ Å³, $Z = 4$ 로 결정화되었으며, 1874 개의 독립적인 회절반점에 대한 최종 신뢰도 인자 R_1 및 ωR_2 값은 각각 0.0239 및 0.0604 이었다. Cd(II) 금속 원자는 4개의 azido 리간드와 2개의 2-ethylimidazole 리간드의 질소 원자가 배위되어 약간 찌그러진 팔면체 구조를 나타낸다. c 축 방향으로 배열되어 있는 Cd(II) 금속 원자 사이를 azido 리간드가 end-on (μ -1,1) 형태로 bridge 하고 2-ethylimidazole 리간드가 시스 형태로 결합하여 이 착물은 1차원의 zigzag 사슬 구조를 형성한다.

Abstract : The title complex, $[\text{Cd}(\text{N}_3)_2(2\text{-ethylimidazole})_2]$, **I**, has been prepared and characterized by X-ray single crystallography. The complex **I** crystallizes in the monoclinic system, Cc space group with $a = 16.200(3)$, $b = 12.926(3)$, $c = 7.007(1)$ Å, $\beta = 102.29(3)^\circ$, $V = 1433.7(5)$ Å³, $Z = 4$, $R_1 = 0.0239$ and $\omega R_2 = 0.0604$ for 1874 independent reflections. Cd(II) atom has a slightly distorted octahedral coordination geometry, with four end-on (μ -1,1) bridging azido ligands and two 2-ethylimidazole ligands bonding through nitrogen atom. The central cadmium(II) atoms are run in parallel to the c -axis and are doubly bridged with neighboring cadmium(II) atoms by the end-on (μ -1,1) bridging azido ligands. Thus, this complex has a one-dimensional zigzag chain structure in which the 2-ethylimidazole is in the *cis* conformation.

Key words : cadmium complex, azide, 2-ethylimidazole, crystal structure

1. Introduction

The supramolecular architecture of one- (1D), two- (2D), and three-dimensional (3D) frameworks with organic-inorganic hybrid compositions has become of great interest recently.^{1,2} It has been reported that they have useful properties as catalytic, electronic, magnetic

and optical materials.³ For designing infinite multi-dimensional frameworks, one of us⁴ and other workers^{5,6} have used the coordination properties of various pseudohalide ions such as CN^- , SCN^- , OCN^- , SeCN^- , N_3^- , and the complementary organic ligands. Generally, they are known to build up one-, two-, and three-dimensional framework linking one metal atom

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M to another metal atom M' alternately.⁷

Among these pseudohalide metal complexes, transition metal thiocyanato and cyano complexes with various amine ligands such as aliphatic amines, aromatic amines, and cyclic amines have been intensively studied by X-ray single crystallography.⁸⁻¹³ However, the frameworks of metal azido complexes have been considerably less investigated compared with metal thiocyanato and cyano complexes. The pseudohalide azide anion has been demonstrated to be an extremely versatile ligand and also an excellent magnetic coupler.¹⁴ Thus, the crystal structures of metal-azide systems show from dimers to 3D compounds with azide ligands act as terminal and/or bridging coordination modes to metal ions.¹⁵ When the azide group acts as a end-on (μ -1,1) bridging ligand to transition metal atoms, the metal complex usually show ferromagnetic behaviour. In contrast, when it is bridged end-to-end (μ -1,3) fashion, anti-ferromagnetic coupling results.¹⁴ On the other hand, one of us has studied using imidazole as a complementary ligand for designing novel supramolecular frameworks, and reported⁴ the variations of ligating behavior of the imidazole and host topology in the multi-dimensional structures.

As an extension study of the supramolecular architecture with novel framework structures, we have also applied the coordination behaviour of the azide ligand as pseudohalide ions and the imidazole derivatives as a complementary organic ligands. In this paper, we report the preparation and crystal structure of the azido bridged cadmium(II) complex I with 2-ethylimidazole ligands (*Scheme 1*).

2. Experimental

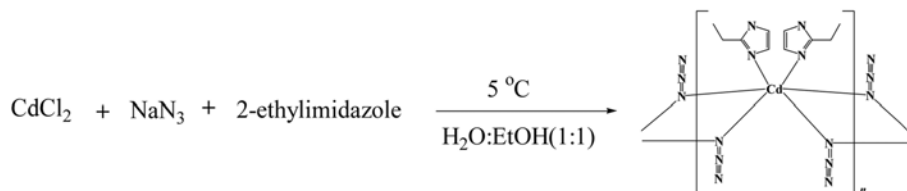
2.1. Preparation and characterization of [Cd(N₃)₂(2-ethylimidazole)₂], I

10 ml water-ethanolic (1:1) solution of sodium azide (2 mmol, 0.13 g) was added to 10 ml water-ethanolic (1:1) solution of CdCl₂·2.5H₂O (1 mmol, 0.23 g). To this mixture solution, 10 ml water-ethanolic (1:1) solution of 2-ethylimidazole (1 mmol, 0.10 g) was introduced with stirring. The resulting solution had a small amount of white precipitates and the precipitate was filtered off. The filtered water-ethanolic solution was allowed to stand in a refrigerator at 5°C. After a few days the colourless plate crystals suitable for X-ray analysis were obtained.

IR spectrum of the crystal was recorded with a BioRad Digilab FTS-155 infrared spectrophotometer. The 2-ethylimidazole and azido ligand were confirmed to assignment of the relevant IR absorption bands, respectively.¹⁵ The EDS spectrum obtained on a Philips XL-30S FEG scanning electron microscope/EDAX Phoenix energy-dispersive X-ray spectrometer showed the presence of C, N and Cd. The contents of the carbon, hydrogen and nitrogen were analyzed by a CE EA-1110 elemental analyzer. The content of the cadmium was analyzed by a Jobin-Yvon Ultima-C inductively coupled plasma-atomic emission spectrometer.

2.2. X-ray crystallography

A colourless plate crystal (0.48×0.40×0.10 mm) was coated with epoxy glue in order to prevent



Scheme 1. Preparation of complex I.

degradation of the specimen under ambient conditions. The epoxy coated crystal was mounted on a Enraf-Nonius CAD4 X-ray diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The intensity data were collected in the ω - 2θ scan mode with operating 40 kV, 30 mA at a temperature $289 \pm 2 \text{ K}$. The cell parameters and an orientation matrix were determined from the least-squares fit of 25 accurately centered reflections with θ range of 11.15 to 14.55° .¹⁶ One orientation reflection was checked every 200 reflections and three standard reflections were monitored every 300 minutes. The intensity variation was less than 0.3% over the course of data collection. Lorentz and polarization corrections were applied to the intensity data, and a semi-empirical absorption correction based on the ψ -scans was applied.

All calculations were carried out using the Siemens SHELXTL crystallographic software programs.¹⁷ Space group was assigned based on the systematic absences and intensity statistics, and was confirmed by successful refinements. The structure was solved by the direct method¹⁸ and refined by successive least-squares method followed by difference Fourier map. All the non-hydrogen atoms were refined anisotropically; all the hydrogen atoms fixed at the calculated positions with the isotropic thermal parameters were included in the final structure factor calculations. Final difference of electron density maps contained no significant features.

3. Results and discussion

As shown in Fig. 1, the IR spectrum of the complex I exhibits strong absorption bands in the regions 2070 cm^{-1} , which is identified as $\nu_{\text{asym}}(\text{N}_3)$ mode of the azide ligand. This peak is due to the end-on (μ -1,1) bridged structure and is in good agreement with those of similar modes in transition metal complexes.¹⁵ The typical peaks in the 1562 , 1462 , 1122 , 1055 and 775 cm^{-1} indicate the presence of 2-ethylimidazole ligand. The composition of the crystal I was deduced from the elemental analyses; the

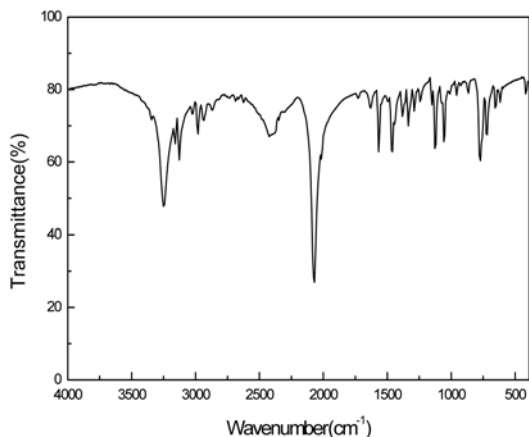


Fig. 1. Infrared spectrum of complex I.

Table 1. Crystallographic and experimental data for complex I

Formula	$\text{C}_{10}\text{H}_{16}\text{N}_{10}\text{Cd}$
Formula weight	388.73
Crystal system	monoclinic
Space group	Cc
a (\AA)	16.200(3)
b (\AA)	12.926(3)
c (\AA)	7.007(1)
β ($^\circ$)	102.29(3)
V (\AA^3)	1433.7(5)
Z	4
D_c (g/cm^3)	1.801
μ (Mo- $K\alpha$) (mm^{-1})	1.535
$F(000)$	776
θ range for data collection ($^\circ$)	2.0–25.0
Index range	$-12 \leq h \leq 19, -15 \leq k \leq 12, -8 \leq l \leq 8$
Reflections collected/unique	2608/1874 [$R_{\text{int}} = 0.0372$]
Data/restraints/parameters	1874/2/190
Goodness-of-fit on F^2	1.130
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.024, \omega R_2 = 0.060$

formula of $[\text{Cd}(\text{N}_3)_2(2\text{-ethylimidazole})_2]$ is consistent with the results of X-ray single crystallography. *Anal. Found*: C, 30.60; H, 4.15; N, 36.03; Cd, 28.7%. *Calc. for* $\text{C}_{10}\text{H}_{16}\text{N}_{10}\text{Cd}$: C, 30.90; H, 4.15; N, 36.03; Cd, 28.92%.

The crystallographic and experimental data are summarized in Table 1. The selected bond distances and bond angles are listed in Table 2. Asymmetric unit with the atomic numbering scheme and a perspective view of the complex I are shown in Fig.

Table 2. Selected bond distances (Å) and angles (°) for complex I

Cd-N(1)	2.423(1)	Cd-N(4)	2.388(1)
Cd-N(11)	2.320(1)	Cd-N(21)	2.283(1)
N(1)-N(2)	1.158(2)	N(2)-N(3)	1.135(2)
N(4)-N(5)	1.235(2)	N(5)-N(6)	1.177(2)
N(11)-C(12)	1.296(1)	C(12)-N(13)	1.426(1)
N(13)-C(14)	1.319(1)	C(14)-C(15)	1.342(2)
C(15)-N(11)	1.445(1)	C(12)-C(16)	1.399(2)
C(16)-C(17)	1.440(2)	N(21)-C(22)	1.363(1)
C(22)-N(23)	1.354(2)	C(25)-N(21)	1.327(2)
C(24)-C(25)	1.276(1)	N(23)-C(24)	1.393(1)
C(22)-C(26)	1.570(1)	C(26)-C(27)	1.581(2)
N(1)-Cd-N(4)	102.5(1)	N(1)-Cd-N(11)	86.3(4)
N(1)-Cd-N(21)	163.4(3)	N(4)-Cd-N(11)	161.4(3)
N(4)-Cd-N(21)	85.2(4)	N(11)-Cd-N(21)	90.7(1)
Cd-N(1)-N(2)	119.0(8)	Cd-N(4)-N(5)	114.3(9)
Cd-N(11)-C(12)	130.3(8)	Cd-N(11)-C(15)	119.3(8)
Cd-N(21)-C(22)	131.4(8)	Cd-N(21)-C(25)	126.1(9)
N(1)-N(2)-N(3)	177.2(1)	N(4)-N(5)-N(6)	176.0(1)
N(11)-C(12)-N(13)	105.1(9)	C(12)-N(13)-C(14)	110.1(9)
N(13)-C(14)-C(15)	109.2(9)	C(14)-C(15)-N(11)	105.3(1)
C(15)-N(11)-C(12)	110.3(1)	N(11)-C(12)-C(16)	131.6(1)
N(13)-C(12)-C(16)	122.9(1)	C(12)-C(16)-C(17)	118.7(1)
N(21)-C(22)-N(23)	113.9(9)	C(22)-N(23)-C(24)	107.5(8)
N(23)-C(24)-C(25)	103.0(1)	C(24)-C(25)-N(21)	114.0(1)
C(25)-N(21)-C(22)	101.5(1)	N(21)-C(22)-C(26)	122.8(1)
N(23)-C(22)-C(26)	123.2(8)	C(22)-C(26)-C(27)	108.8(1)

2 and Fig. 3, respectively.

The central cadmium(II) atom has a slightly distorted octahedral coordination geometry as shown in Fig. 2, and is hexa-coordinated by four end-on (μ -1,1) bridging azido ligands and by two nitrogen atoms of 2-ethylimidazole ligands in the *cis* conformation. The average Cd-N_{azide} bond length of 2.406(1) Å is longer than the average Cd-N_{2-ethylimidazole} bond length of 2.302(1) Å. The bond angles of N_{azide}-Cd-N_{azide} and N_{2-ethylimidazole}-Cd-N_{2-ethylimidazole} are 102.5(1) and 90.7(1)°, respectively. The average bond angles of N_{azide}-Cd-N_{2-ethylimidazole} are 85.8(3) and 162.4(3)°. All bond distances and angles of 2-ethylimidazole ligands are similar to other reported compound, tetrakis(2-ethylimidazole)bis(isothiocyanato)nickel(II) complex.¹³

A perspective view of complex I along the *b*-axis is shown in Fig. 3. The octahedral cadmium atoms make an array in parallel to the *c*-axis, and each pair of adjacent cadmium atoms are doubly bridged by the end-on (μ -1,1) bridging azido ligands. The azide ligands take the end-on (μ -1,1) structure with the $\nu_{\text{asym}}(\text{N}_3)$ at 2070 cm⁻¹ are nearly linear [177.2(1) and 176.0(1)°] as reported in the literature.¹⁴ Repeating unit of the cadmium(II) atom-azido group formed -Cd-N₃-Cd-N₃- four membered ring in a diamond-shape. Thus, this complex has a one-dimensional zigzag chain structure in which the 2-ethylimidazole is in the *cis* conformation. The one-dimensional zigzag chain lies on an array in parallel to the *ac*-plane. Uncoordinated nitrogen atoms of the end-on (μ -1,1) bridging azido ligands and nitrogen atoms of

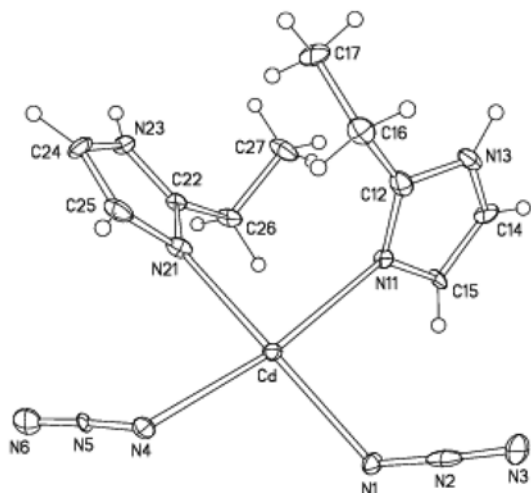


Fig. 2. Asymmetric unit of complex I with the atomic numbering scheme and displacement ellipsoids at the 30% probability level.

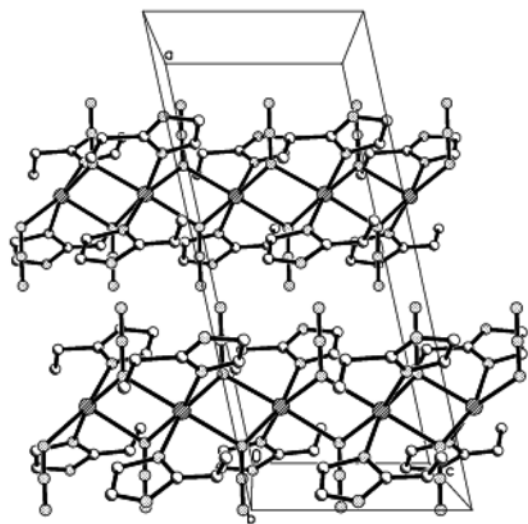


Fig. 3. Perspective view of complex I along the *b* axis.

the 2-ethylimidazole ligands are linked together in intermolecular hydrogen bonding along *ac*-plane by the weak N-H...N hydrogen bond: N(13)-H(13a)...N(6), 3.05(2) Å, 179.7°; N(23)-(23a)...N(3), 3.01(2) Å, 171.1°. These N₂-ethylimidazole-H...N_{azide} hydrogen bonding networks contribute to stabilization of the crystal structure.

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