

Syntheses and Structural Studies of 1:1 (M:L) Silver(I) and 1:2 Nickel(II) Complexes with Tripodal Amide Ligand

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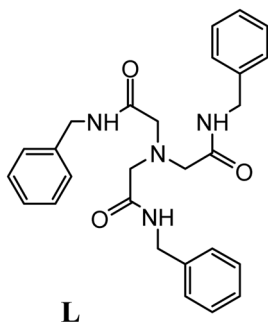
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Due to their central role in both coordination and organometallic chemistry as well as metalloenzyme, tripodal ligands have attracted the attention of researchers from various backgrounds.¹ Parallel to this, amide-type ligands are of considerable importance in the extraction and separation of wide range of metal ions such as transition metal, lanthanide and actinide ions.² In addition, the coordinating properties of the amide-group are also interest in the relation to the other oxygen donors such as alcoholic and ether oxygen donors. Tripodal amide ligands³ as the fusion of tripode and amide units enable the divergent conformational changes of their complexes to accommodate a variety of metal ions as guests. Taking this reason into account, our group^{3a} and others^{3b-d} have reported lead(II), Pr(III) and Nd(III) complexes of the tripodal amide ligands including **L**^{3d} which is a versatile tetradentate ligand. As a part of our ongoing efforts, we employed **L** as the amide-type tripodal ligand and synthesized its silver(I) and nickel(II) complexes with different stoichiometries and coordination numbers.



Results and Discussion

The tripodal amide **L** was synthesized according to the procedure previously reported.^{3d} To investigate the metal center with different coordination geometry on the structures of resulting complexes, the reactions of **L** with silver(I) and nickel(II) as nitrate salts were carried out, respectively, and complexes **1** and **2** were isolated.

Preparation and Crystal Structure of L Complex with AgNO₃ (1). Complex **1** has been synthesized by reacting equimolar amounts of **L** and AgNO₃ in ethanol/water mixed solvent. Slow evaporation of the resulting solution gave an

X-ray quality crystalline product **1**. The IR spectrum of **1** shows strong bands at 1382 cm⁻¹ due to NO₃⁻ ion, in addition to the ligand peaks. The crystallographic analysis reveals that **1** is a 1:1 (M:L) complex of formula [Ag(**L**)NO₃] with an inclusion structure (Figure 1). The Ag atom in **1** is six-coordinated by one tertiary amine N atom (N1), three carbonyl O atoms and two O atoms of one bidentate nitrate ion. Three secondary amine N atoms remain uncoordinated. In fact, the narrow bite angle [O4-Ag-O5: 51.0(2)°] of the bidentate nitrate ion for Ag atom allows the pseudo-trigonal bipyramidal geometry, in which the three carbonyl O atoms define the equatorial plane. The potential threefold symmetry of **1** seems to be broken due to the anion coordination and/or crystal packing. The Ag atom is deflected out of the trigonal plane by 0.930 Å toward the nitrate ion. Three benzyl end-groups spread out and no interactions were observed between them. The bond lengths of Ag to carbonyl O atoms are different each other. For example, the Ag-O1 bond length [2.740(5) Å] is considerably longer than those of Ag-O2 [2.551(6) Å] and Ag-O3 [2.663(5) Å], with the latter being quite close to that observed for a related system reported previously.⁴ The Ag-N1 bond length [2.357(6) Å] is also comparable with those reported previously for such bonds.⁵ The bidentate nitrate group is bonded asymmetrically to the Ag atom, with bond lengths [Ag-O4 2.352(6), Ag-O5 2.565(6) Å] that fall within the range observed for

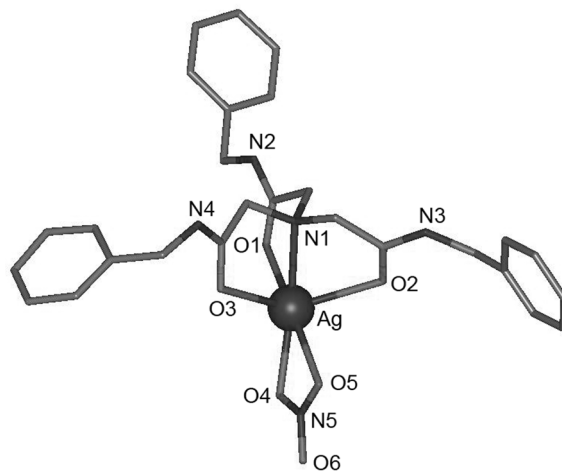


Figure 1. Molecular structure of **1**, [Ag(**L**)NO₃]. Hydrogen atoms are omitted for clarity.

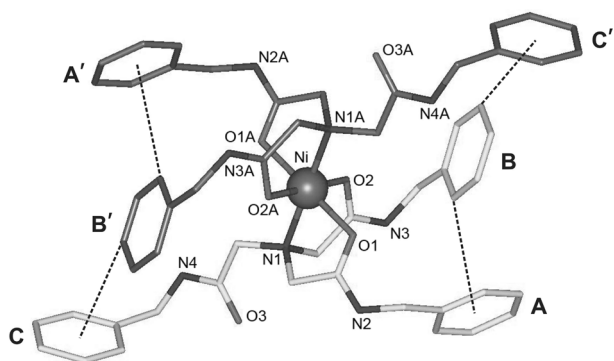


Figure 2. Molecular structure of **2**, $[\text{Ni}(\text{L})_2](\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$. Hydrogen atoms, noncoordinating anions and solvent molecules are omitted for clarity. [Symmetry operation: (A): $-x, -y + 2, -z$.]

other bidentate nitrate complexes of silver.⁶

Preparation and Crystal Structure of L Complex with $\text{Ni}(\text{NO}_3)_2$ (2**).** Complex **2** has been synthesized by reacting equimolar amounts of **L** and $\text{Ni}(\text{NO}_3)_2$ in ethanol/water mixed solvent. Slow evaporation of the resulting solution gave an X-ray quality crystalline product **2**. The IR spectrum of **2** shows strong bands at 1384 cm^{-1} due to NO_3^- ion. The crystallographic analysis reveals that **2** is an interesting 1:2 (M:L) complex of formula $[\text{Ni}(\text{L})_2](\text{NO}_3)_2 \cdot 2\text{C}_2\text{H}_5\text{OH} \cdot 2\text{H}_2\text{O}$, in which two ligand molecules sandwich the metal center (Figure 2). In the coordination sphere of **2**, the asymmetric unit contains one **L** and half of one Ni atom. The structural unit in Figure 2 is generated through an inversion symmetry. The six-coordinated Ni center adopts a distorted octahedral geometry by coordinating to one tertiary amine N atom and two carbonyl O atoms from each ligand. One carbonyl O atom and three amide N atoms in each ligand remain uncoordinated. The four carbonyl O atoms from two **L**s define the equatorial plane, with the axial positions occupied by two tertiary amine N atoms [N1-Ni-N1A 180.0°]. No deviation of the four O donors from the mean square plane was observed, with four O-Ni-O bond angles ranging from 89.8 – 90.2° . Thus, the Ni atom locates exactly on the square plane. However, the angles between the axis and plane vary from 79.74° (O1-Ni-N1) to 100.26° (O1A-Ni-N1). These large deviations of the angles from the regular octahedron are due to formation of the pentagonal ring *via* Ni-O1 bond. The Ni-N1 bond length [$2.114(2)\text{ \AA}$] is comparable with those reported previously for such bonds.⁷ Additionally, the edge-to-face type π - π stacking interaction⁸ between benzyl-end groups (dashed lines, centroid of A-to-edge of B: 3.595 \AA and centroid of C-to-edge of B': 3.724 \AA) also stabilizes the structure. The particular sandwich-type complex **2** seems to be obtained because of high affinity of the carbonyl O atoms toward the Ni atom which favors hexa-coordinate. Consequently, the metal center in **2** is completely shielded by two **L**s and therefore, unlike the complex **1**, is unable to contact the anion or solvent. Comparing the structures between **1** and **2** afforded a good case for metal ion effect. As described, the higher coordination affinity of NO_3^- to silver(I) than to Ni(II) leads the structural discrimination.

IR spectra of silver(I) and nickel(II) complexes **1** and **2** are

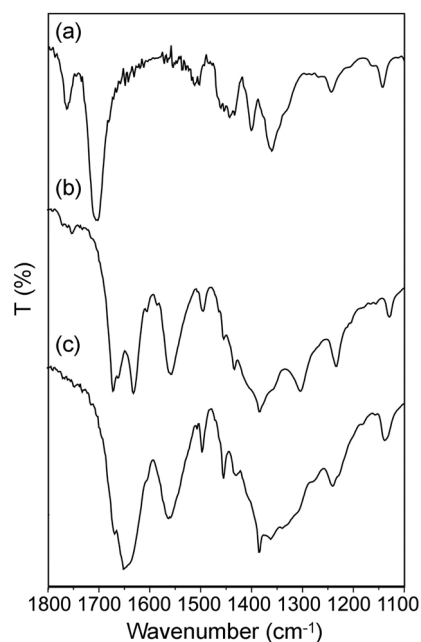


Figure 3. IR spectra of (a) **L**, (b) **1** and (c) **2**.

similar in pattern to those of the ligands (Figure 3). As mentioned, respective strong bands at 1382 (for **1**) and 1384 (for **2**) cm^{-1} due to NO_3^- ion were observed in addition to the ligand peaks. From the comparative IR spectra of the free **L** and its amide-type complexes, we also observed the spectral shifts toward the lower energy for the characteristic carbonyl bands [from 1708 (for **L**) to 1668 cm^{-1} (for **1**) or to 1677 cm^{-1} (for **2**)] due to the complexation. In addition, the molar conductivity of complexes **1** and **2** (60 and $250\text{ S}\cdot\text{cm}^2\cdot\text{mol}^{-1}$, respectively) confirms their mono- and dicationic characters as expected.

Experimental Section

All commercial reagents including solvents were of analytical reagent grade where available. NMR spectra were recorded on a Bruker DRX-300 spectrometer (300 MHz). Infrared spectra were measured with a Mattson Genesis Series FT-IR spectrophotometer. The mass spectra were obtained on a JEOL JMS-700 spectrometer (FAB) at the Central Instrument Facility of Gyeongsang National University. Melting points are uncorrected.

[Ag(L)NO₃] (1**).** AgNO_3 (29 mg , 0.117 mmol) was dissolved in water and was added to the solution of **L** (30 mg , 0.107 mmol) in ethanol. The reaction mixture was stirred for 1 hr and filtered. The slow evaporation of the filtrate afforded colorless crystals. M.p. (decomp.) 165 – 167°C . IR (KBr, cm^{-1}): 3292 , 3087 , 1668 (C=O), 1631 , 1558 , 1494 , 1382 (NO_3^-), 1303 , 1234 , 1128 , 1031 , 727 , 700 , 619 . MS (FAB): $m/z = 565$ ($[\text{Ag}(\text{L})]^+$, $[\text{C}_{27}\text{H}_{30}\text{AgN}_4\text{O}_3]^+$).

[Ni(L)₂]NO₃·2C₂H₅OH·2H₂O (2**).** $\text{Ni}(\text{NO}_3)_2$ (20 mg , 0.107 mmol) was dissolved in water and was added to the solution of **L** (25 mg , 0.105 mmol) in ethanol. The reaction mixture was stirred for 1 hr and filtered. The slow evaporation of the filtrate afforded purple color crystals. M.p.

Table 1. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **1**, [Ag(L)NO₃]

Ag1-O1	2.740(5)	Ag1-O2	2.551(6)
Ag1-O3	2.663(5)	Ag1-O4	2.352(6)
Ag1-O5	2.565(6)	Ag1-N1	2.357(6)
O4-Ag1-N1	171.9(2)	O4-Ag1-O2	115.0(2)
N1-Ag1-O2	69.29(19)	O4-Ag1-O5	51.0(2)
N1-Ag1-O5	125.5(2)	O2-Ag1-O5	81.2(2)

Table 2. Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **2**, [Ni(L)₂]NO₃·2C₂H₅OH·2H₂O

Ni1-O1	2.072(1)	Ni1-O2	2.015(1)
Ni1-N1	2.114(2)	N5-O4	1.250(2)
N5-O5	1.241(2)	N5-O6	1.251(2)
O1-Ni1-O1A	180.00(8)	O1-Ni1-N1	79.74(6)
O1-Ni1-N1A	100.26(6)	O2A-Ni1-O1	89.82(6)
O2-Ni1-O1	90.18(6)	O2A-Ni1-O2	180.0
O2-Ni1-N1	83.64(6)	O2-Ni1-N1A	96.36(6)
N1-Ni1-N1A	180.0		

Symmetry codes A: $-x + 2, -y, -z$.**Table 3.** Crystal data and structural refinement

	1	2
Formula	C ₂₇ H ₃₀ AgN ₅ O ₆	C ₅₈ H ₇₆ Ni ₁₀ NiO ₁₆
M	628.43	1228.00
T/K	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> /Å	16.674(2)	18.9369(8)
<i>b</i> /Å	9.1394(13)	9.8402(4)
<i>c</i> /Å	17.512(2)	18.7102(8)
β /°	94.018(3)	118.7690(10)
<i>V</i> /Å ³	2662.1(7)	3056.2(2)
Z	4	2
μ (Mo-K α)/mm ⁻¹	0.809	0.393
Crystal size/mm	0.35 × 0.20 × 0.10	0.50 × 0.40 × 0.30
Absorption correction	SADABS	
Reflections collected	10518	18555
Independent reflections	5652	6912
Goodness-of-fit on <i>F</i> ²	0.969	1.084
Final <i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)]	0.0553, 0.1363	0.0446, 0.1081
(all data)	0.1524, 0.2118	0.0680, 0.1237

(decomp.) 172–174 °C. IR (KBr, cm⁻¹): 3406, 3253, 3091, 2935, 1677 (C=O), 1633, 1581, 1515, 1454, 1384 (NO₃⁻), 1323, 1257, 1107, 1029, 952, 892, 827, 725, 698. MS (FAB): *m/z* = 973 ([Ni(L)₂-H]⁺, [C₅₄H₅₉NiN₈O₆]⁺).

A crystal suitable for X-ray diffraction was mounted on a Bruker SMART diffractometer equipped with a graphite monochromated Mo-K α (λ = 0.71073 Å) radiation source and a CCD detector and 45 frames of two-dimensional diffraction images were collected and processed to deduce the cell parameters and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected. The frame data were processed to give structure factors by the program SAINT.⁹ The intensity data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for complexes using the

program SADABS.¹⁰ The structures were solved by a combination of the direct method and the difference Fourier methods provided by the program package SHELXTL, and refined using a full matrix least square against *F*² for all data. All the non-H atoms were refined anisotropically. All hydrogen atoms were included in calculated positions with isotropic thermal parameters 1.2 times those of attached atoms. Crystallographic data are summarized in Table 3.

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Supplementary material. Supplementary crystallographic data associated to complexes **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 656966 and 656967. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk), or electronically via www.ccdc.cam.ac.uk/data_request/cif.

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