Preparation and Properties of Dinickel(II) Complexes Bridged with μ-Oxalato Ligand: X-Ray Structure of (μ-Oxalato)bis((*N*,*N'*-bis(2-aminoethyl)-1,3-propanediamine)nickel(II))

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Study on the structure and properties of dinuclear transition metal complexes is important not only because it can help understanding the role of multinuclear enzymes but also it can open a new perspective in the field of low-dimensional electronic and magnetic systems as well.[1-4] Dinuclear oxalate-bridged nickel(II) complexes with NiN_4O_2 chromophore, where N_4 is tetraazamacrocycles, linear tetraamines or two diamine molecules, have been studied relating to the structure and properties.[5-13] It has been revealed that their properties are strongly depend on the nature of the terminal aza ligands.[14-15] In this study, we used linear tetraamines, 2,3,2-tet (*N*,*N'*-bis(2-aminoethyl)-1,3-propanediamine) and 3,2,3-tet (*N*,*N'*-bis(2-aminopropyl)-1,2-ethylenediamine), and diamine molecule, dach (1,2-diaminocyclohexane), as the terminal ligands to get the dimeric complexes of Ni(II). Syntheses and properties of dimeric complexes of nickel(II), $[(2,3,2\text{-tet})Ni(II)(ox)Ni(2,3,2\text{-tet})](ClO_4)_2$ (**1**), $[(3,2,3\text{-tet})Ni(II)(ox)Ni(3,2,3\text{-tet})](ClO_4)_2$ (**2**), and $[(dach)Ni(II)(ox)Ni(dach))](ClO_4)_2$ (**3**), where ox is oxalate, are discussed along with the X-ray structure of **1**.

Experimental Section

Physical Measurements. IR spectra were recorded on a Midac FT-IR spectrometer. Electronic absorption spectra were measured with a SLM DW-2000 spectrophotometer. The magnetic susceptibilities were measured by the Faraday method using a Johnson Matthy MK-1 magnetic susceptibility balance at 25 °C. Molar susceptibilities were corrected for diamagnetism of the ligands and the anion by use of Pascal's constants. Molar conductivities were measured with a Jenway 4020 conductivity meter. Elemental analyses were performed at Basic Science Research Institute. Cyclic voltammograms were recorded using a Bas CW-50 potentiost t in oxygen-free 0.1 mol · cm^{-3} $(t\text{-}Bu)_4NClO_4$ acetonitrile solution at 25 °C. FAB-mass spectra were recorded at Korea Research Institute of Chemical Technology.

Materials. All chemicals used in syntheses were of reagent grade. Reagents for spectrochemical and electrochemical studies were purified according to the literature.[16]

Caution! Perchlorate salts should be handled with great caution as they are potentially explosive.

Syntheses. $[(3,2,3\text{-tet})Ni(ox)Ni(3,2,3\text{-tet})](ClO_4)_2$ (1). 97% 2,3,2-tet (1.92 g, 1.16×10^{-2} mol) was added to aqueous solution (50 mL) of $NiCl_2 \cdot 6H_2O$ (2.87 g, 1.16×10^{-2} mol) with stirring. Sodium oxalate monohydrate (1.08 g, 5.81×10^{-3} mol) dissolved in water (20 mL) was added dropwise to the dark blue solution. During this reaction, dark blue color of the solution changed to violet. The solution was filtered and excess amount of sodium perchlorate dissolved in water was added to the filtrate. Violet crystals were formed from the solution in a few hours at room temperature. The crystals were filtered, washed with methanol, and recrystallized from hot water. Yield: ~75%. Anal. Calcd for $C_{16}H_{40}N_8Ni_2Cl_2O_{12}$: C, 26.51; H, 5.56; N, 15.46. Found: C, 26.48; H, 5.51; N, 14.83. FAB mass: $[(2,3,2\text{-tet})Ni(ox)Ni(2,3,2\text{-tet})]ClO_4^+$ (m/z = 623).

$[(3,2,3\text{-tet})Ni(ox)Ni(3,2,3\text{-tet})](ClO_4)_2$ (2). This complex was prepared by a method similar to that for **1** except that 3,2,3,-tet instead of 2,3,2-tet was used. Yield: ~82%. Anal. Calcd for $C_{18}H_{44}N_8Ni_2Cl_2O_{12}$: C, 28.72; H, 5.89; N, 14.89. Found: C, 27.83; H, 6.10; N, 13.85. FAB-mass: $[(3,2,3\text{-tet})Ni(ox)Ni(3,2,3\text{-tet})]ClO_4^+$ (m/z = 651)

$[(dach)Ni(ox)Ni(dach)](ClO_4)_2$ (3). 99% dach (2.61 g, 2.26×10^{-2} mol) was added to aqueous solution (50 mL) of $NiCl_2 \cdot 6H_2O$ (2.58 g, $1,13 \times 10^{-2}$ mol) with stirring. Sodium oxalate monohydrate (1.05 g, 5.66×10^{-3} mol) dissolved in water (20 mL) was added dropwise to the dark blue solution. The solution was filtered and excess amount of sodium perchlorate dissolved in water was added to the filtrate. Violet crystals were formed from the solution in a few hours at room temperature. The crystals were filtered, washed with methanol, and recrystallized from hot water. Yield: 63%. Anal. Calcd for $C_{26}H_{56}N_8Ni_2Cl_2O_{12}$: C, 29.34; H, 5.34; N, 14.42. Found: C, 28.93; H, 5.58; N, 15.02. FAB-mass: $[(dach)Ni(ox)Ni(dach)]ClO_4^+$ (m/z = 759)

Crystallography for $[(2,3,2\text{-tet})Ni(ox)Ni(2,3,2\text{-tet})](ClO_4)_2$ (1). Violet crystals of $[(2,3,2\text{-tet})Ni(ox)Ni(2,3,2\text{-tet})](ClO_4)_2$ were obtained from water. Intensity data were collected on an Enraf-Nonius CAD4 diffractometer equipped with monochromated MoK_α radiation. Crystallographic parameters and information related to the data collection and structural refinements are given in Reference 17. The data were corrected for Lorenz and polarization effects. Empirical Ψ absorption correction was also applied. The SHELXS-86 program was utilized for the heavy atom method.[18] The structure refinements were performed with the SHELXS-93 program on F^2 data.[19] Heavy atoms (Ni and Cl) were located by use of heavy atom method. Other non-hydrogen atoms were found by successive difference Fourier synthesis. All oxygen atoms of discovered perchlorate anions were refined with fixed site occupancy factor 0.5. Anistropic thermal parameters for all non-hydrogen atoms were included in the refinements. All hydrogen atoms bonded to carbon atoms were included in calculated positions. This C-H bond was fixed at 1.00 Å and U values were assigned based on the U values of the attached atom. The other hydrogens (N-H) were located with U = 0.08 Å^2.

Results and Discussion

Syntheses and Identification of the Complexes. The oxalate anions have been known to function as a bis-bidentate ligand, and its coordination to two metal ions affords a wide variety of polynuclear compounds.[4] Stoichiometric amount of the reactants were used in the syntheses. Tetraaza ligands had shown to coordinate metal ions in square-planar fashion in many cases.[20-25] Therefore, there are possibilities that di- or poly-nuclear complexes are resulted from two oxalate ions coordinated to one nickel(II) ion which is coordinated with four nitrogen donors in equatorial plane. However, resulting products have dimeric octahedral geometry in which two oxygen atoms of oxalato ligand locate at *cis* position.

The infrared spectra of the complexes (Table 1) show bands of primary NH at ~3300 cm^{-1}, ClO_4^- at ~1100 cm^{-1}, and coordinated oxalate at ~1650 cm^{-1}. The ν (C=O) value of bis-bidentate oxalato ligand is lower than that of the bidentate oxalato ligand.[26] The value of molar conductances for the complexes (Table 1) in water indicates that the complexes are 1 : 2 electrolytes.[27] Three absorption maxima in electronic spectra (Table 1) of the complexes indicate that these complexes have d^8-octahedral geometries around the Ni(II) metal ions. From these spectral data together with elemental analysis data and FAB-mass, we confirm the products.

Crystal Structure of [(2,3,2-tet)Ni(ox)Ni(2,3,2-tet)]-(ClO_4)$_2$ (1). The structure consists of binuclear [(2,3,2-tet)Ni(ox)Ni(2,3,2-tet)]$^{2+}$ cations and perchlorate anions. The ORTEP drawing of the complex cation is shown in Figure 1, with the atomic labeling scheme for the non-hydrogen atoms. Selected bond lengths and bond angles are listed in Table 2.

Table 1. Spectral and Conductance Data for Dimeric Nickel(II) Complexes

complex	IR,[a] cm^{-1}	electronic spectra[b] λ_{max}, nm (ε, M^{-1} cm^{-1})$^{-1}$	Λ_M,[b] Ω^{-1}cm^{-2} M^{-1}
1	ν_{N-H}; 3356, 3277 $\nu_{oxalate}$; 1646 $\nu_{ClO_4^-}$; 1088	351(34), 550(14), 886(10)	242
2	ν_{N-H}; 3348, 3299 $\nu_{oxalate}$; 1651 $\nu_{ClO_4^-}$; 1098	347(33), 551(17), 880(11)	267
3	ν_{N-H}; 3364, 3312 $\nu_{oxalate}$; 1643 $\nu_{ClO_4^-}$; 1100	354(39), 569(22), 895(11)	230

[a]Nujol mull. [b]Measured in aqueous solution at 25 °C.

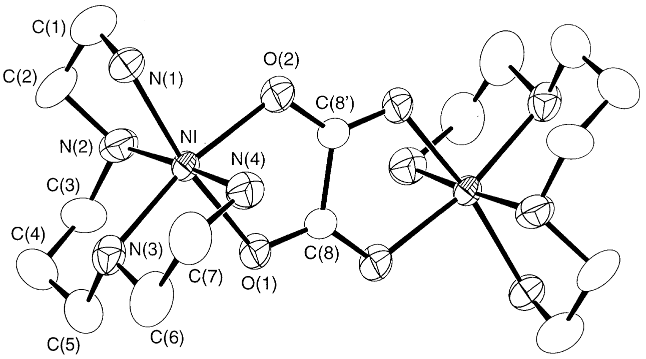
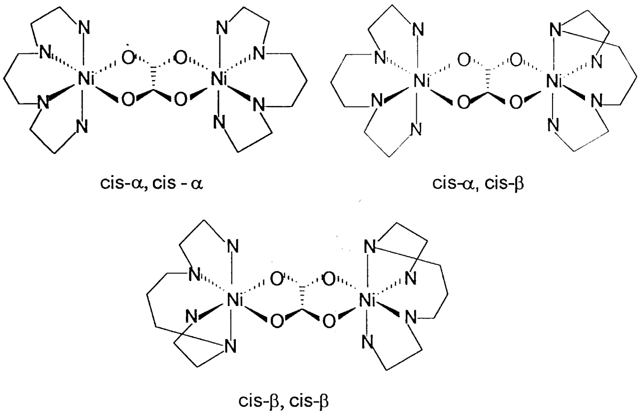


Figure 1. ORTEP drawing for the cation of **1** with the atomic labelling scheme.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for the Cation of **1**

Ni(1)--O(1)	2.090(3)	Ni(1)--O(2)	2.083(3)
Ni(1)--N(1)	2.103(4)	Ni(1)--N(2)	2.100(4)
Ni(1)--N(3)	2.103(4)	Ni(1)--N(4)	2.103(4)
O(1)--C(8)	1.250(5)	O(2)--C(8`)	1.251(5)
O(2)-Ni(1)-O(1)	80.2(1)	O(2)-Ni(1)-O(2)	93.2(1)
O(1)-Ni(1)-N(2)	92.4(1)	O(2)-Ni(1)-N(3)	169.3(1)
O(1)-Ni(1)-N(3)	89.9(1)	N(2)-Ni(1)-N(3)	91.5(2)
O(2)-Ni(1)-N(1)	89.8(1)	O(1)-Ni(1)-N(1)	169.1(1)
N(2)-Ni(1)-N(1)	83.5(2)	N(3)-Ni(1)-N(1)	100.2(1)
O(2)-Ni(1)-N(4)	92.0(2)	O(1)-Ni(1)-N(4)	89.6(1)
N(2)-Ni(1)-N(4)	174.6(2)	N(3)-Ni(1)-N(4)	83.5(2)
N(1)-Ni(1)-N(4)	95.2(2)	C(8)-O(1)-Ni(1)	112.6(2)
C(8)-O(2)-Ni(1)	112.9(3)		

The binuclear cation consists of two [(2,3,2-tet)Ni]$^{2+}$ units bridged by an oxalate anion. Three kinds of stereo isomers can exist in this type of complexes (Scheme 1).[7] The Isomer with *cis-β* configuration at both metal ions is not common in the oxalate bridged bi-nuclear complexes with tetraamine open ring systems because this configuration induces strains in the secondary nitrogens. As can be seen in Figure 1, the isolated complex has *cis-β* configuration for both metal ions.



cis-α, cis - α

cis-α, cis-β

cis-β, cis-β

Scheme 1

Table 3. Redox Potentials and Magnetic Moments of Dimeric Ni(II) Complexes[a]

complex	E_{ox},[b] V	E_{red},[b] V	μ_{eff},[c]
	Ni(II)/Ni(III)	Ni(II)/Ni(I)	BM
1	0.62 V(irr)	–1.21 V(irr)	4.10
2	0.55 V(irr)	–1.20 V(irr)	3.89
3	0.87 V(irr)	undetectable	3.92
$[(bispicen)_2Ni_2(ox)]^{2+}$ [d]			4.2

[a]Measured in acetonitrile (0.1 M TBAP) against Ag/AgCl reference electrode. [b]Cathodic potential. [c]Measured at 298 K. [d]Reference 7, bispicen: *N,N'*-bis(2-pyridylmethyl)-1,3-propanediamine.

There is an inversion center in the middle of the cations, bisecting the C(8)-C(8') bond. The nickel atoms are surrounded by the four nitrogen atoms of the 2,3,2-tet ligand and the oxygen atoms of the bridging oxalate in *cis* arrangement. The geometry around nickel(II) ion is distorted octahedron. The bond angles involving Ni(II) ion range from 80.2(1) (O(1)-Ni(1)-O(2)) to 95.2(2)° (N(1)-Ni(1)-N(4)). The C-O bond lengths of 1.250(5) and 1.251(5) Å in the oxalate ion are consistent with that for bidentate coordination. As usual C_2O_4 fragment including two Ni(II) ions is approximately planar. Bond lengths of Ni-N(1) and Ni-N(3) are identical even if secondary amine is, electronically, more basic than primary amine. Bond length of Ni-O(1) trans to primary amine (N(1)) is nearly same as that of Ni-O(2) trans to secondary amine (N(3)). Bond lengths of four Ni-N bonds, two axial and two equatorial, are nearly identical (2.100 Å-2.103 Å). This indicates that there is no trans effect attributed to the oxalate oxygen atoms.

Properties. All dimeric complexes are soluble in water, actonitrile and DMSO, but insoluble in ether, nitromethane and chloroform, and slightly soluble in methanol. The value of 10 Dq[28] for **1** (11,290 cm^{-1}) or **2** (11,360 cm^{-1}) is larger than that for **3** (11,170 cm^{-1}). This indicates that ligand field of tetradentate chelates (2,3,3-tet and 3,2,3-tet) are stronger than that of bidentate chelate ligand (1,2-diamoinocyclohexane). In addition, the value of 10 Dq for **2** is larger than that of **1**, indicating that 3,2,3-tet exerts stronger ligand field than 2,3,2-tet. The values of B' for the complex **1**, **2** and **3** are 887, 873 and 814 cm^{-1}, respectively.[29] From these results, we can see that the nephelauxetic effect[30] of **1** is geater than that of **2** although 3,2,3-tet ligand is stonger than 2,3,2-tet in these complexes.

Cyclic voltammetry data of the complexes are listed in Table 3. The cyclic votammogram of the complexes displays an irreversible Cu(II)-Cu(I) couple and an irreversible Cu(II)-Cu(III) couple. Oxidation potentials of the complexes are increased in the order of **3**, **1** and **2**. More anodic oxidation potential of **3** compared with that of **1** or **2** may be related to the reduced ligand-field strength of 1,2-diaminocyclohexane ligand than the tetradentate ligands. This result is consistent with the reported results.[31,32]

The values of effective magnetic moment of the complexes measured at 293 K are summarized in Table 3. The values are in the range of 3.89-4.10 BM, close to the expected spin only magnetic moment of 4.0 BM.

The complexes are not stable in acidic aqueous solution. Each complex is decomposed completely to nickel(II) aqua complex in 0.1 M $HClO_4$ in a few min.

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Supplementary Material Available. Tables listing detailed crystallographic data, atomic coordinates, anisotropic thermal parameters and bond lengths and bond angles (12 pages) are available from corresponding author.

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