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Synthesis and Characterization of Oxa-azamacrocyclic Dinuclear Ni(II) Complex Containing $\mu(O, S)$ - $S_2O_3^{2-}$ Ion

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Nickel(II) is recognized as a transition metal of considerable biological importance forming the active site of a variety of metalloproteins such as hydrogenase, carbon monoxide dehydrogenase, methyl-S-coenzyme-M methyl-reductase and urease.¹⁻³ Discoveries of dinuclear cores at the active sites of some metalloproteins have aroused interest in the investigation of multimetallic systems.^{4,5} Dinucleating macrocyclic ligands which are designed to bind two similar or dissimilar metal ions in close proximity have received considerable attention.^{6,7} This is particularly fascinating for a family of phenol-based macrocyclic ligands, derived from the [2 + 2] template condensation of 2,6-diformyl-*p*-cresol (DFPC) with a diamine (e.g. 2,2-dimethyl-1,3-propanediamine) in the presence of metal ions.⁸

Thiosulfate ion is a common auxiliary ligand in transition metal complexes. The thiosulfate ion forms a wide range of transition metal complexes with several modes of ligation. Monodentate bonding through S only (**A**), bridging monodentate bonding through S (**B**) and bidentate bonding through O and S (**C**), etc. are known for cobalt(III) or nickel(II) complexes.^{9,10} Octahedral complex $(N(CH_3)_4)_2-[Ni(II)(H_2O)_4(S_2O_3)_2]$ ^{10,11} and tetranuclear $[Ag_4(\mu_3-S_2O_3)(\mu-S_2O_3)(\mu-dppm)_4]$ {dppm = bis(diphenyl-phosphino)methane}¹² have been reported related to a bridging $S_2O_3^{2-}$ anion (type **C**). To our knowledge, work has never been carried out on the preparation and characterization of the phenol-based dinucleating macrocyclic Ni(II) complex $[Ni(II)_2([22]-HMTADO)(L_a)]$ with auxiliary ligands ($L_a = S_2O_3^{2-}$, NCS^- , ClO_4^- and citrate ion, etc.).

With these facts in mind and in continuation of our work on dinuclear macrocyclic complexes,^{13,14} in this paper, we describe the synthesis and physicochemical characterization of the five-coordinate oxa-azamacrocyclic Ni(II) species $[Ni_2([22]-HMTADO)(H_2O)_2]Cl_2 \cdot H_2O$ (**1**) and $[Ni_2([22]-HMTADO)(\mu(O, S)-S_2O_3)]$ (**2**). And we also report the crystal structure of a new dinuclear macrocyclic complex **2**.

Experimental Section

Measurements. Microanalyses of C, H, and N were carried out using LECO CHN-900 analyzer. Conductance measurements of the complexes were performed in DMF at 25 ± 1 °C using an ORION 162 conductivity temperature meter. IR spectra were recorded with a Bruker FSS66 FT-IR spectrometer as KBr pellets. FAB-mass spectra were obtained on a JEOL JMS-700 Mass Spectrometer using argon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and glycerol was used as the matrix. The mass spectrometer was operated in positive ion mode and mass spectra were calibrated by Alkali-CsI positive.

Synthesis of $[Ni_2([22]-HMTADO)(OH)_2]Cl_2 \cdot H_2O$ (1**).**¹⁴ A methanolic solution (50 mL) of 2,6-diformyl-*p*-cresol (1.64 g) was added to a suspension of the 2,2-dimethyl-1,3-propanediamine (1.03 g) and the nickel chloride hexahydrate (4.80 g) in methanol (100 mL). The mixture was refluxed for 4 h, and then allowed to stand at room temperature until a green precipitate separated. This was collected by filtration, thoroughly washed with cold methanol, and dried *in vacuo*. Yield: 42%. Anal. Calcd (Found) % for $C_{28}H_{40}N_4O_5Cl_2Ni_2$: C, 47.98 (47.99); H, 5.75 (5.02); N, 7.99 (7.66). λ_M (water): 205 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

Synthesis of $[Ni_2([22]-HMTADO)(\mu(O, S)-S_2O_3)]$ (2**).** To an aqueous solution (30 mL) of $[Ni_2([22]-HMTADO)(H_2O)_2]Cl_2 \cdot H_2O$ (0.701 g), sodium thiosulfate (1.240 g) in water (30 mL) was added dropwise with stirring. The resulting mixture was refluxed for 2 h, then evaporated under reduced pressure until a green precipitate separated. This was collected by filtration, thoroughly washed with cold water, and dried *in vacuo*. Yield 13%. Anal. Calcd (Found) % for $C_{28}H_{34}N_4O_5S_2Ni_2$: C, 48.87 (48.70); H, 4.98 (4.76); N, 8.14 (8.15). λ_M (methanol): 4 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$.

X-ray Crystallography of Complex. Pale green crystals of **2** suitable for X-ray diffraction study were grown by slow evaporation of hot aqueous solution of the title complex. A

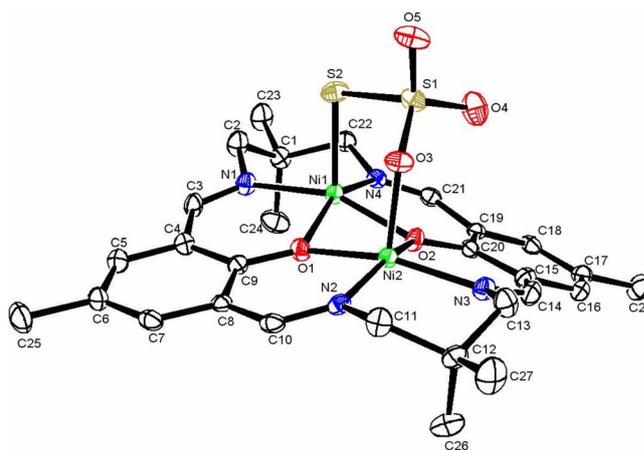
Table 1. Crystal data and details of the structure determination for complex **2**

Empirical formula	C ₂₈ H ₃₄ N ₄ Ni ₂ O ₅ S ₂
Temperature, K	173(2)
Crystal system, Space group	Monoclinic, <i>P2(1)/n</i>
<i>a</i> , Å	15.4796(11)
<i>b</i> , Å	13.0076(9)
<i>c</i> , Å	15.9632(12)
<i>Z</i>	4
Density (calculated)	1.538 g/cm ³
Absorption coefficient	1.453 mm ⁻¹
<i>F</i> (000)	1432
Theta range for data collection, °	2.09 to 28.29.
Reflections collected	18648
Independent reflections	6987 [<i>R</i> (int) = 0.0513]
Goodness-of-fit on <i>F</i> ²	1.021
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0395, <i>wR</i> ₂ = 0.0889
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0700, <i>wR</i> ₂ = 0.1009

single crystal of complex was attached to glass fibers and mounted on a Bruker SMART diffractometer equipped with a graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Cell constants and an orientation matrix were obtained by least-squares refinement of the data for 6987 reflections of the 18648 unique reflections measured, in the range $2.09^\circ \leq 2\theta \leq 28.29^\circ$ for complex. The data were corrected for Lorentz and polarization effects during data reduction. The structure was solved by the direct method,¹⁵ and refined by full-matrix least-squares refinement with use of the SHELXS program of the SHELXTL package.¹⁶ All non-hydrogens atoms of the nickel(II) complex were refined on *F*² by the full matrix least-squares procedure using anisotropic displacement parameters. Hydrogen atoms were inserted in the calculated positions, assigned fixed isotropic thermal parameters at 1.2 times the equivalent isotropic *U* of the atoms to which they are attached [*U*_{iso} = 1.2*U*_{eq} (parent atom)] and allowed to ride on their respective parent atoms. The summary of the crystal data, experimental details and refinement results for complex **2** is listed in Table 1.

Results and Discussion

Description of Crystal Structure. The structure of the discrete neutral complex **2** shows that the two nickel(II) centers are bridged by the two phenolate oxygens as well as by a thiosulfate ion as shown in Figure 1. Both the metal centers are five-coordinated with irregular square pyramidal geometries and have N₂O₂ equatorial donors provided by the oxa-azamacrocyclic ligand. The remaining apical position of the nickel(II) centres is occupied by a thiosulfate oxygen and sulfur. The methyl groups {C(24) and C(26)} attached to each lateral chain C(1) and C(12) are situated trans to an axially coordinated thiosulfato ligand with respect to the mean NiN₂O₂ plane. The dimethyl trimethylene lateral chain in the six-membered chelate rings involving Ni(1), N(1), C(2), C(1), C(22) and N(4), and Ni(2), N(2), C(11), C(12),

**Figure 1.** ORTEP drawing with atom-labelling scheme for [Ni₂([22]-HMTADO)(μ(O, S)-S₂O₃)] complex.

C(13) and N(3) adopt a near chair conformation.

Selected bond lengths and angles of **2** are listed in Table 2. The relevant metal-donor distances are generally in accord with those reported for the [Ni₂L_{m1}(NC₅)₂(H₂O)₂]:2(CH₃)₂-NCHO (L_{m1} = tetraamino diphenolic macrocycle) complex with an average bond lengths {Ni-N = 2.071(3) Å; Ni-O = 2.040(3)} in complex **1**.¹⁷ The Ni(II)-O_{thi}sul and -S_{thi}sul bond lengths {1.984(2) and 2.3319(9) Å} by a thiosulfato ligand are dissimilar and the Ni(II)-O_{thi}sul bond length is close to the other metal-donor distances.¹⁷ The shortest Ni(2)-O(3) bond length involves the O atom of thiosulfate anion, which suggests that interaction between the Ni²⁺ cation and the thiosulfate anion is strong. The thiosulfate anion is thus a good competitor for Ni²⁺ cation and might also be able to form complexes with higher S₂O₃²⁻ to Ni²⁺ ratios. Because of the thiosulfate bridge, the two N(imine)₂O₂ least-square

Table 2. Selected bond lengths (Å) and angles (°) for [Ni₂([22]-HMTADO)(μ(O, S)-S₂O₃)] complex

Ni(1)-N(1)	2.004(2)	Ni(2)-N(2)	2.003(2)
Ni(1)-N(4)	2.005(2)	Ni(2)-N(3)	2.000(2)
Ni(1)-O(1)	2.024(2)	Ni(2)-O(1)	2.008(2)
Ni(1)-O(2)	2.0093(19)	Ni(2)-O(2)	1.999(2)
Ni(1)-S(2)	2.3319(9)	Ni(2)-O(3)	1.984(2)
S(1)-S(2)	2.0482(11)	S(1)-O(3)	1.504(2)
S(1)-O(4)	1.452(2)	S(1)-O(5)	1.453(2)
N(1)-Ni(1)-N(4)	96.16(10)	N(3)-Ni(2)-N(2)	96.14(10)
N(1)-Ni(1)-O(1)	90.22(9)	N(2)-Ni(2)-O(1)	90.93(9)
N(4)-Ni(1)-O(1)	155.37(9)	N(3)-Ni(2)-O(1)	159.90(9)
N(1)-Ni(1)-O(2)	157.69(9)	N(2)-Ni(2)-O(2)	159.09(9)
N(4)-Ni(1)-O(2)	90.38(9)	N(3)-Ni(2)-O(2)	91.17(9)
O(1)-Ni(1)-O(2)	75.63(8)	O(1)-Ni(2)-O(2)	76.22(8)
Ni(1)-O(1)-Ni(2)	97.80(8)	Ni(1)-O(2)-Ni(2)	98.56(9)
N(1)-Ni(1)-S(2)	93.93(8)	N(2)-Ni(2)-O(3)	100.61(9)
N(4)-Ni(1)-S(2)	104.86(7)	N(3)-Ni(2)-O(3)	95.65(9)
O(2)-Ni(1)-S(2)	105.00(6)	O(2)-Ni(2)-O(3)	98.12(8)
O(1)-Ni(1)-S(2)	98.37(6)	O(1)-Ni(2)-O(3)	101.51(8)
Ni(1)-S(2)-S(1)	102.02(4)	Ni(2)-O(3)-S(1)	127.70(13)

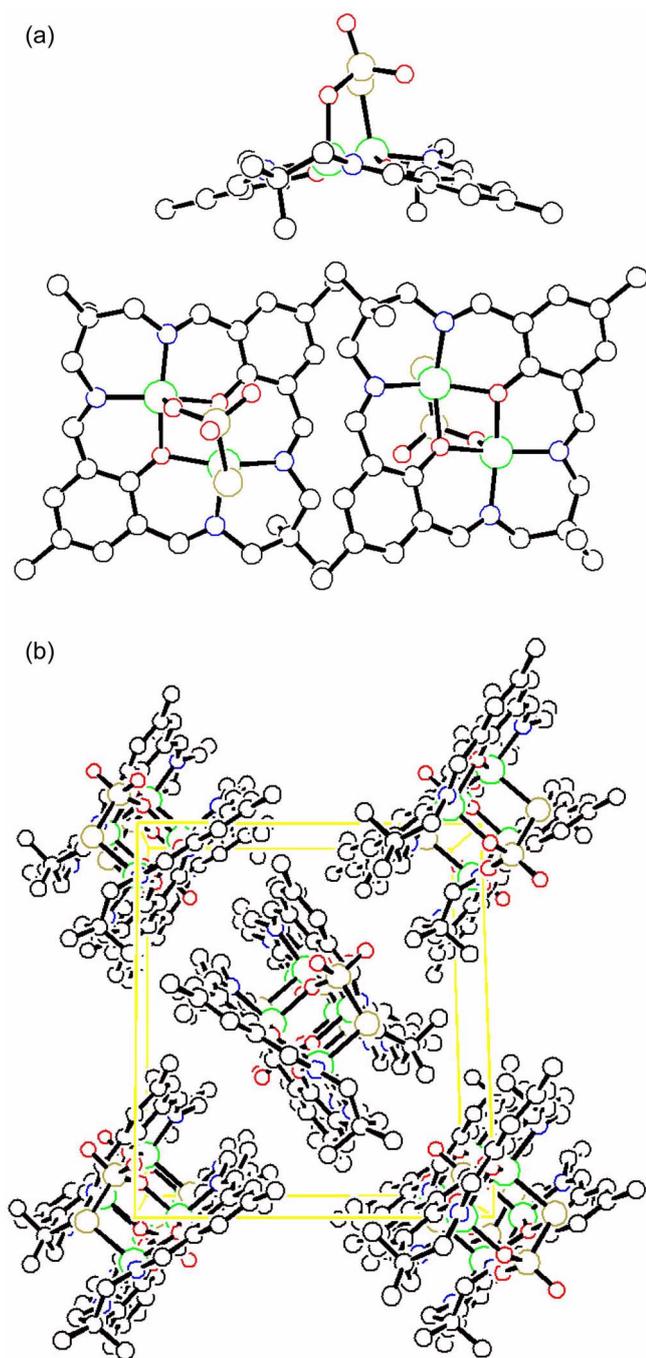


Figure 2. (a) View of the important intermolecular interactions in a five-coordinate oxa-azamacrocyclic Ni(II) species. (b) The molecular packing diagram of dinuclear nickel (II) complex **2** along the *a*-axis.

planes are bent at the O1...O2 edge with a dihedral angle of 9.04°. And the planes of the two phenyl rings are inclined by 14.04°. The {Ni₂([22]-HMTADO)} unit is of concave shape when viewed down the thiosulfate moiety. The nonbonded Ni...Ni distance {3.0382(2) Å} is very similar to that of Ni...Fe distance {3.03 Å} in [Fe(III)Ni(II) L_{m1}(μ-OAc)(OAc)-(H₂O)]ClO₄·2H₂O.¹⁸ The bridging angles Ni-O-Ni within the binuclear complex are equal to 97.80(8) {Ni(1)-O(1)-Ni(2)} and 98.56(9) {Ni(1)-O(2)-Ni(2)}. The bond angles

Ni(1)-S(2)-S(1) and Ni(2)-O(3)-S(1) are 102.02(4) and 127.70(13)°, respectively.

The structure of the thiosulfato ligand itself has been reported.¹⁹ Comparison of structural parameters for free thiosulfate and transition metal nickel(II) complexes indicates that complexation of the metal ions causes changes in the bond angles and bond lengths.²⁰ The mean S-O bond length of 1.470(2) Å in the complex **2** is slightly similar to that of (N(CH₃)₄)₂[Ni(II)(H₂O)₄(S₂O₃)₂], and normal for the coordinated ligand. The Ni-S-S and the mean O-S-O bond angles {102.02(4) and 111.47(14)°} in the complex **2** are similar to those reported for (N(CH₃)₄)₂[Ni(II)(H₂O)₄(S₂O₃)₂] with 104.9(1) and 111.0(6)°, respectively.¹¹ The bond angles of C(21)-N(4)-Ni(1), C(10)-N(2)-Ni(2), N(1)-C(2)-C(1) and N(2)-C(11)-C(12) are 125.2(2), 124.4(2), 114.6(3) and 115.6(2), respectively. Additionally, the angles {C(2)-C(1)-C(22) = 111.3(3) and C(11)-C(12)-C(13) = 110.8(2)°} at the trimethylene lateral chains containing two methyl group are similar, as are bond angles of C(9)-O(1)-Ni(1) {130.48(18)} and C(20)-O(2)-Ni(2) {130.31(18)°}. Packing of complex **2** in the monoclinic cell is featured in Figure 2. The sheets are ulteriorly linked to be a 3-D network by [Ni₂([22]-HMTADO)(μ(O, S)-S₂O₃)] complex, as shown in Figure 2(b).

General Properties. Pale green complex **2** is soluble in hot water and methanol. The molar conductivity values, measured at room temperature using water or methanol, of the complexes **1** and **2** exhibit 205 ohm⁻¹cm²mol⁻¹ (water) and 4 ohm⁻¹cm²mol⁻¹ (methanol), respectively. These values for **1** and **2** suggest that the complexes are 2 : 1 electrolyte and non-electrolyte in each solvent, respectively.²¹ The formation of binuclear Ni(II) complex, inferable from elemental analysis and molar conductance of the complexes **1** and **2**, is evidenced by characteristic IR absorption bands and FAB mass spectrum. The most convincing evidence is the crystal structure of the complex **2**, which reveals entrapment of a pair of Ni²⁺ cations in the twin 22-membered coordination cavities of the compartmental chelate and ligation of thiosulfato ligand.

For complexes **1** and **2**, strong evidence that aldehyde groups had been completely converted into Schiff base residues was provided by the disappearance of the aldehydic C=O stretching band at 1680 cm⁻¹ and the appearance of a strong band at 1635 ± 5 cm⁻¹ assigned to ν(C=N) stretching band.⁸ For complex **1**, vibration associated with O-H stretching mode of coordinated and hydration water molecules is observed at 3196 and 3313 cm⁻¹, respectively. The vibrational spectrum of complex **2** features antisymmetric and symmetric stretching mode of bidentate S₂O₃²⁻ ion at 1225-1193 and 1121-1093 cm⁻¹, respectively. Other vibrational modes are found deformation bands at 1016, 652 and 644 cm⁻¹, and S-S stretching band of S₂O₃²⁻ at 550 cm⁻¹.²² Analysis of the FAB mass spectrum for **1** has been reported previously¹⁴ and is retained in this study. And in the complex **2** the important features of the FAB mass spectrum has three dominant ion peaks centered around *m/z* 664.5, 575.3 and 517.3, which are ascribed to the [Ni₂([22]-HMTADO)SO₄]⁺,

$[\text{Ni}_2([\text{22}]\text{-HMTADO})]^+$ and $[\text{Ni}([\text{22}]\text{-HMTADO})]^+$, respectively, a result that strongly supports the coordination between dinuclear nickel(II) and thiosulfate ion. The m/z 664.5 peak is produced by simple sulfur-sulfur bond fission of thiosulfato ligand and oxidation under the conditions of this analysis.²³

Supplementary Data. Crystallographic data for the structure reported here have been deposited with Cambridge Crystallographic Data Center (Deposition No. CCDC 271154). The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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