The Crystal Structure and Magnetic Properties of Cu^{II}-Ni^{II} Heterodinuclear Complex with *N,N'*-Bis(2-pyridyl-ethyl)-oxamide Dianion

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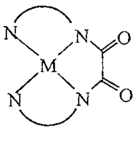
A new Cu^{II}-Ni^{II} heterodinuclear complex [Cu(PEoxd) $Ni(bpy)_2](ClO_4)_2 \cdot 1/2H_2O$ has been synthesized and its structure determined by single crystal X-ray analysis. Crystal data: space group $P2_1/c$ with a = 9.226(2) Å, b = 30.857(6) Å, c = 14.241(3) Å, and β = 97.36(3)°, V= 4021(2) $Å^3$, Z = 4. Magnetic measurement indicates that the overall magnetic behavior is weakly antiferromagnetic.

Symmetrically N, N'-disubstituted oxamides are versatile ligands for the design and preparation of polynuclear systems.[1] One of the most outstanding character of these ligands is the easy transformation of cis-trans conformations,[2] which favours the formation three type of complexes: in the mononuclear complexes (I) these oxamides coordinate as simple linear quadridenate ligands, while in the complexes (II) and (III) they bridge two metal ions either symmetrically or unsymmetrically leads to the formation of homo-and heteropolynuclear complexes.[3-6]



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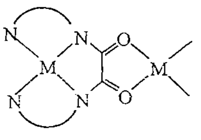

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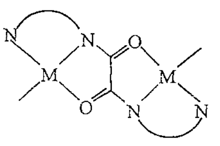

III

Ojima and Nonoyama first utilized N,N'-bi(2-pyridyl-ethyl)-oxamide dianion (PEoxd) as a bridged ligand to prepare the binuclear copper(II) complexes in 1977,[7] however its detailed physicochemical properties and crystal structure have not been reported. Recently, Vigato et al attempted to synthesize Cu^{II}-Ni^{II} heterodinuclear complex with μ -PEoxd bridge,[8] but failed and led only to the formation of dicopper(II) complexes under different experimental conditions.

In this paper, we report the synthesis, crystal structure and magnetism of Cu^{II}-Ni^{II} heterodinuclear complex $[Cu(PEoxd)Ni(bpy)_2](ClO_4)_2 \cdot 1/2H_2O$, where PEoxd = N,N'-bis(2-pyridyl-ethyl)-oxamide dianion.

The titled compound was synthesized by two steps: (1). The mononuclear complex [Cu(PEoxd)] has been prepared by the modified literature method from 2-(2-aminoethyl)-pyridine, diethyl oxalate and copper hydroxide;[7] (2). Cu(PEoxd) was used as "ligands" to synthesis heterodinuclear complex. A solution of 2,2'-bipyridine (bpy; 63 mg, 0.4 mmol) in ethanol (10 ml) as added dropwise to a stirred aqueous solution (15 ml) of $Ni(ClO_4)_2 \cdot 6H_2O$ (73 mg, 0.2 mmol); then a solution of Cu(PEoxd) (0.2 mmol) in water was added slowly. After the mixture was stirred for 6 h at room temperature, the violet-red microcrystals obtained were washed several times with absolute ethanol and absolute diethyl ether, and dried under vacuum. The elemental analysis result was consistent with the formula $[Cu(PEoxd)Ni(bpy)](ClO_4)_2 \cdot 2H_2O$.[9] Finally, a violet-red crystals suitable for X-ray investigations were obtained by the slow evaporation of the filtrate at room temperature over one week.[10]

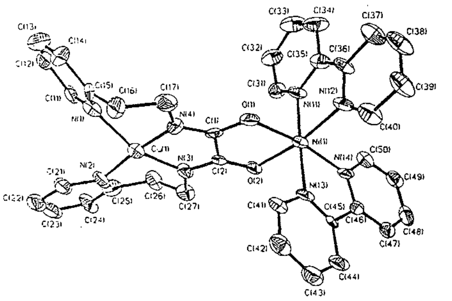

Figure 1. The ORTEP drawing of [Cu(PEoxd)Ni(bpy)] $\cdot 1/2H_2O$. Selected interatomic bond distance (Å) And angles (°): Cu(1)-N(1) 2.009(12), Cu(1)-N(2) 2.014(10) , Cu(1)-N(3) 1.952(10), Cu(1)-N(4) 1.923(9), Ni(1)-O(1) 2.070(9), Ni(1)-O(2) 2.067(7), Ni(1)-N(11) 2.080(9), Ni(1)-N(12) 2.037(9), Ni(1)-N(13) 2.092(9), Ni(1)-N(14) 2.073(10), N(1)-Cu(1)-N(2) 94.7(4), N(1)-Cu(1)-N(3) 156.5(5), N(2)-Cu(1)-N(3) 93.6(4), N(1)-Cu(1)-N(4) 90.4(4), N(2)-Cu(1)-N(4) 173.8(5), N(3)-Cu(1)-N(4) 83.0(4), O(1)-Ni(1)-O(2) 81.3(3), O(1)-Ni(1)-N(11) 90.5(4), O(2)-Ni(1)-N(11) 91.4(3), O(1)-Ni(1)-N(12) 92.7(4), O(2)-Ni(1)-N(12) 168.8(4), N(11)-Ni(1)-N(12) 79.1(4), O(1)-Ni(1)-N(13) 91.6(4), O(2)-Ni(1)-N(13) 90.8(3), N(11)-Ni(1)-N(13) 177.2(4), N(12)-Ni(1)-N(13) 98.9(4), O(1)-Ni(1)-N(14) 168.8(3), O(2)-Ni(1)-N(14) 94.3(3), N(11)-Ni(1)-N(14) 100.0(4), N(12)-Ni(1)-N(14) 93.3(4), N(13)-Ni(1)-N(14) 78.1(4)

The X-ray structure analysis shows that the nickel(II) and the copper(II) ions are linked by cis-configuration μ-oxamido and the separation is 5.340 Å in the [Cu(PEoxd) $Ni(bPy)_2]^{2+}$ cation. The coordination environment of copper ion can be described as a distorted square quadrilateral (CuN_4). The Cu-N(1) and Cu-N(2) (pyridine) bond distance are longer [2.009(12) Å and 2.014(10) Å] than that of Cu-N(3) and Cu-N(4) (amidic) [1.952(10) Å and 1.923(9) Å]; this is because the amidic nitrogen are negatively charged. The copper atom is 0.1529 Å above the mean plane formed by four nitrogen atoms. The two pyridine rings of oxamido are not in a plane. The dihedral angle between the two pyridine rings is 65.5°. The coordination environment of nickel (II) ion can be considered as a distorted octahedral. Nickel (II) ion is coordinated with two carbonyl oxygen atoms and four nitrogen atoms of the bipyridine ligands as shown in Figure 1. The nickel atom is 0.0101 Å above the mean plane formed by two oxygen [O(1) and O(2)] and two nitrogen atoms [N(12) and N(14)]. The actual symmetry of the cation is very close to C_{2V}.

Variable-temperature susceptibility data was collected for this complex. The observed magnetic moment for the binuclear complex at room temperature (3.20 B.M.) is considerably less than the spin-only value (3.32 B.M.). This suggests the operation of an antiferromagnetic spin-exchange interaction in this complex. The magnetic analysis was performed using the susceptibility equation based on the Heisenberg spin operator ($\mathbf{H} = -2JS_AS_B$, $S_A = 1/2$ $S_B = 1$).[1c]

$$\chi_M = \frac{N\beta^2}{4kT}\left[\frac{10g_{3/2}^2 + g_{1/2}^2\exp(-3J/kT)}{2+\exp(-3J/kT)}\right] + N\alpha \qquad (1)$$

Where χ_M denotes the susceptibility the Cu^{II}-Ni^{II} heterodinuclear complex and $g_{1/2}$ and $g_{3/2}$ are g factors associated with the doublet and the quartet states. respectively. They are related to the local g factors g_{Ni} and g_{Cu}, assumed to be isotropic through $g_{1/2} = (4g_{Ni}-g_{Cu})/3$, $g_{3/2} = (2g_{Ni} + g_{Cu}) / 3$. $N\alpha$ is temperature independent paramagnetism (200×10^{-6} cm^3 mol^{-1}) and the remaining symbols have their usual meanings. As shown in Figure 2, good fits to the experimental data were attained with Eq 1, giving $J = -42.70$ cm^{-1}, $g_{Ni} = 2.21$, $g_{Cu} = 2.08$. The agreement factor F defined here as $F = \Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2 / \Sigma(\chi_M)_{obs}$ is then equal to 2.48×10^{-5}.

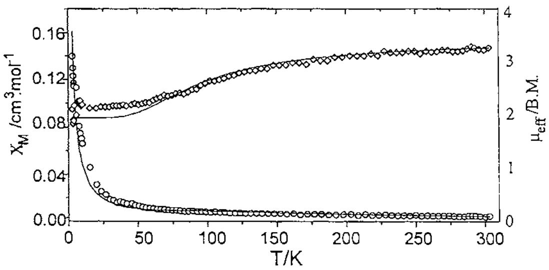

Figure 2. Variable-temperature magnetic susceptibility and magnetic moment of complex.

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9 Anal. Found: C, 44.48; H, 3.70; N, 11.24, Cu, 6.89; Ni, 5.97%. Calcd. for $CuNiC_{36}H_{38}N_8O_{12}Cl_2$: C, 44.77; H, 3.76; N, 11.60; Cu, 6.58; Ni, 6.08%. *IR* (cm^{-1}): $\nu_{C=O} = 1625$, $\nu_{C=N} = 1570$, $\nu_{ClO_4^-} = 1095$.

10 Crystal data: $C_{36}H_{35}N_8O_{10.5}Cl_2CuNi$, Mr = 940.89, triclinic space group $P2_1/c$, a = 9.226(2) Å, b = 30.857(6) Å, c = 14.241(3) Å, β = 97.36(3)°, V = 4021(2) Å^3 , Z = 4, D_X = 1.554 Mg m^{-3}, μ = 1.1993 mm^{-1}, F(000) = 1928, R = 0.076 and wR = 0.075. Determination of the unit cell and data collection were performed with Mo-k_α radiation (λ = 0.7107 Å) on a computer controlled Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal monoclinic situated in the incident beam. A total of 5914 independent reflections was collected by the $\omega/2\theta$ scan technique, θ_{max} = 23° at room temperature, of which 4542 reflections [$I \geqslant 3\sigma(I)$] were considered to be observed and used in the succeeding refinement. Intensity data were corrected for Lorentz and polarization factors. The structure was solved by direct methods. The copper atom positions were located from an E-map. The other non-hydrogen atoms were determined with successive difference-Fourier syntheses. The final refinement by the full-matrix least-squares method with anisotropic thermal parameters for the non-hydrogen atoms converged with the unweighted and weighted agreement factor 0.076 and 0.075, respectively. The highest peak on the final difference Fourier map had a height of 0.73 eÅ^{-3}. All calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.