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Synthesis, Magnetism and Structure of μ-Oxamido Heterobinuclear Cu(II)–Ni(II) Complexes

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Abstract

Three heterobinuclear complexes have been synthesized, namely $[Cu(oxpn)Ni(L)_2](ClO_4)_2 \cdot xH_2O$ (L = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen), and 5-nitro-1,10-phenanthroline (NO_2-phen)), where oxpn is *N,N*′-bis(3-aminopropyl)oxamido. The crystal structure of $[Cu(oxpn)Ni(phen)_2](ClO_4)_2 \cdot CH_3OH \cdot H_2O$ has been determined. Crystal data: triclinic, space group $P\bar{1}$, with $a = 9.661(3)$, $b = 13.522(2)$, $c = 17.143(3)$ Å, $\alpha = 86.39(2)$, $\beta = 82.09(2)$ and $\gamma = 71.73(2)°$ at room temperature, $Z = 2$. The copper(II) ion is in a square environment and the nickel(II) is in an octahedral environment. The dihedral angle between the two metal equatorial planes is 5.40°. The Cu–Ni distance is 5.338 Å. The temperature dependence of the magnetic susceptibility of $[Cu(oxpn)Ni(phen)_2](ClO_2)_2 \cdot H_2O$ has been studied, giving the exchange integral $J = -47.22$ cm^{-1}. This indicates an antiferromagnetic interaction among the metal ions.

Introduction

Binuclear metal complexes containing two different metal ions are of current interest in connection with spin exchange and charge transfer between metal ions and in the domain of metalloenzymes and homogeneous catalysis [1].

It is known that mononuclear complex, *N,N*′-bis(3-aminopropyl)oxamido copper(II) (abbreviated Cu(oxpn)) acts as a bidentate chelating agent toward a second metal ion to form binuclear and trinuclear metal complexes, such as $[Cu(oxpn) \cdot Cu(bpy)] \cdot (ClO_4)_2$, $[Cu_3(oxpn)_2](ClO_4)_2$ and $[Cu_2Ni(oxpn)_2 \cdot (H_2O)_2] \cdot (ClO_4)_2$ [2]. However, no crystal structures of heterobinuclear complexes of this kind have been reported.

This paper deals with the syntheses, the structure, and the magnetic and EPR properties of three new complexes, $[Cu(oxpn)Ni(L)_2](ClO_4)_2 \cdot xH_2O$ (L = 2,2′-bipyridyl (bpy), 1,10-phenanthroline (phen) and 5-nitro-1,10-phenanthroline (NO_2-phen)). The crystal structure of $[Cu(oxpn)Ni(phen)_2](ClO_4)_2 \cdot CH_3OH \cdot H_2O$ has been solved and refined.

Experimental

Materials

Cu(oxpn) was synthesized by the literature method [3]. bpy, phen and NO_2-phen were of analytical grade.

Syntheses

$[Cu(oxpn)Ni(bpy)_2](ClO_4)_2 \cdot H_2O$. To 66 mg of Cu(oxpn) stirred in 20 ml of methanol were successively added a solution of 78.1 mg of bpy in 10 ml of methanol and 91.4 mg of $Ni(ClO_4)_2 6H_2O$ in 10 ml of methanol. The solution was then filtered. Violet microcrystals were obtained. *Anal.* Calc. for $C_{28}H_{32}O_{10}Cl_2CuNi \cdot H_2O$: C, 39.59; H, 4.03; N, 13.18; Cu, 7.47; Ni, 6.90. Found: C, 39.51; H, 3.84; N, 12.84; Cu, 7.10; Ni, 7.15%.

$[Cu(oxpn)Ni(phen)_2](ClO_4)_2 \cdot H_2O$ was prepared in the same way using phen instead of bpy. *Anal.* Calc. for $C_{32}H_{32}N_8O_{10}Cl_2CuNi \cdot H_2O$: C, 42.77; H, 3.81; N, 12.47; Cu, 7.07; Ni, 6.53. Found: C, 42.69; H, 3.64; N, 12.37; Cu, 6.82; Ni, 6.71%. In order to obtain a single crystal suitable for X-ray analysis the compound was dissolved in hot methanol and evaporated at room temperature. A wine-red crystal of $Cu(oxpn)Ni(phen)_2 \cdot (ClO_4)_2 \cdot CH_3OH \cdot H_2O$ was formed in a few days.

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TABLE 1. Physical data of the complexes

Compound[a]	Colour	Λ_m (Ω^{-1} cm^2 mol^{-1})	IR, $\bar{\nu}$ (cm^{-1})				UV (cm^{-1})		μ_{eff} (BM)
			$>C=O$	$-NH_2$	Cyclic $-N=C$	ClO_4^-	d–π	d–d	
1	rose		1585	3175					
2	violet–red	192	1600	3175	1440	1100	33333	18181	3.127
3	violet–red	175	1600	3175	1510	1100	29411, 30959 31250	18181	3.350
4	violet–red	162	1610	3175	1520	1100	29411	18181	3.237

[a] 1: Cu(oxpn); 2: $[Cu(oxpn)Ni(bpy)_2](ClO_4)\cdot H_2O$; 3: $[Cu(oxpn)Ni(phen)_2](ClO_4)_2\cdot H_2O$; 4: $[Cu(oxpn)Ni(NO_2\text{-}phen)_2](ClO_4)_2\cdot 2H_2O$.

$[Cu(oxpn)Ni(NO_2\text{-}phen)_2](ClO_4)_2\cdot 2H_2O$ was obtained in the same way by replacing bpy with NO_2-phen. *Anal.* Calc. for $C_{32}H_{30}N_{10}O_{14}Cl_2CuNi\cdot 2H_2O$: C, 38.14; H, 3.37; N, 13.91; Cu, 6.31; Ni, 5.83. Found: C, 38.19; H, 2.89; N, 13.62; Cu, 6.03; Ni, 5.87%.

Measurements

Analyses for C, H and N were carried out on a Perkin-Elmer analyzer model 240, and metal contents were determined by EDTA titration. The infrared spectra were recorded with an IR-408 infrared spectrophotometer on KBr disks. The electronic spectra were measured on a Perkin-Elmer Hitachi-240 spectrophotometer. Molar conductances were measured with a DDS-11A conductometer. The crystal was mounted on a CAD-4 Enraf-Nonius PDP8/M computer-controlled single-crystal diffractometer. Variable-temperature magnetic susceptibility was measured on a vibrating-sample magnetometer model CF. Diamagnetic corrections were made with Pascal's constants [4] for all the constituent atoms, and the magnetic moments were calculated by the equation $\mu_{eff} = 2.828(XT)^{1/2}$.

Results and Discussion

Elemental analyses have indicated that the reaction of Cu(oxpn) with $Ni(ClO_4)_2\cdot 6H_2O$ and bpy, phen or NO_2-phen yielded the heterobinuclear complexes. For all $[Cu(oxpn)Ni(L)_2](ClO_4)_2\cdot xH_2O$ complexes, the molar conductance values (see Table 1) fall in the expected range for 1:2 electrolytes [5]. The significant bands from the IR spectra for the complexes are given in Table 1. It is noted that the $>C=O$ (carbonyl) stretching vibration at 1585 cm^{-1} for Cu(oxpn) and the $-N=C-$ stretching vibration at 1450–1500 cm^{-1} for terminal ligands bpy, phen or the NO_2-phen ring were shifted to higher frequencies in their binuclear complexes. In addition, the $-NH_2$ vibration at 3175 cm^{-1} for Cu(oxpn) and the ClO_4^- group vibration at 1100 cm^{-1} were present for all complexes. The data of electronic absorption spectra of methanol solutions of these complexes are shown in Table 1. A strong absorption in the ultraviolet range and only a weak absorption in visible range can be observed. The former may be attributed to the charge transfer absorption bands (d–π) and the latter to the d–d transition.

Structure of $[Cu(oxpn)Ni(phen)_2](ClO_4)_2\cdot CH_3OH\cdot H_2O$

Information concerning the crystallographic data collection and the refinement conditions is given in Table 2. The structure was solved by the direct

TABLE 2. Information concerning the crystallographic data collection and refinement conditions for $[Cu(oxpn)Ni(phen)_2](ClO_4)_2\cdot CH_3OH\cdot H_2O$

Formula	$C_{33}H_{38}Cl_2CuN_8NiO_{12}$
Crystal system	triclinic
M_r	926.83
Space group	$P\bar{1}$
Temperature at cryst.	room temperature
Unit cell	
a (Å)	9.661(3)
b (Å)	13.522(2)
c (Å)	17.143(3)
α (°)	86.39(2)
β (°)	82.09(2)
γ (°)	71.73(2)
V (Å^3)	2094.91
Z	2
$F(000)$	956
D_x (g cm^{-1})	1.469
μ(Mo Kα) (cm^{-1})	11.519
Crystal size (mm)	0.2 × 0.3 × 0.2
Instrument	CAD-4
Scan type	ω
Radiation	monochromated Mo Kα (λ = 0.71073 Å)
Max. 2θ (°)	36
No. measured reflections	3013
No. observed reflections (NO)	2335
Agreement factors	
R	0.078
R_w	0.082

TABLE 3. Atomic parameters for non-hydrogen atom of $[Cu(oxpn)Ni(phen)_2](ClO_4)_2 \cdot CH_3OH \cdot H_2O$

Atom	x	y	z	B_{eq} (Å^2)
Cu	0.1314(2)	1.0242(1)	0.2441(1)	4.57(5)
Ni	0.1014(2)	1.4244(1)	0.2526(1)	3.43(5)
Cl1	0.2321(5)	0.8683(4)	0.8506(3)	7.7(1)
Cl2	0.4329(5)	0.6923(4)	0.3213(3)	7.8(1)
O	0.450(2)	0.333(1)	0.0820(9)	10.8(5)
O′	0.360(3)	0.959(2)	0.336(2)	24(1)
O1	0.2032(9)	1.2950(7)	0.1831(5)	3.6(2)
O2	0.0219(9)	1.3148(6)	0.3183(5)	3.8(2)
O11	0.226(3)	0.778(1)	0.821(2)	22.0(9)
O12	0.095(2)	0.934(3)	0.858(2)	27(1)
O13	0.312(3)	0.898(2)	0.789(1)	19.2(9)
O14	0.311(2)	0.853(2)	0.908(1)	20.7(9)
O21	0.474(3)	0.733(2)	0.251(1)	23(1)
O22	0.499(2)	0.587(1)	0.323(1)	13.0(6)
O23	0.463(3)	0.735(2)	0.379(1)	22.6(8)
O24	0.289(2)	0.713(1)	0.318(2)	16.8(8)
N1	0.212(2)	0.910(1)	0.1648(9)	8.0(5)
N2	0.217(1)	1.1211(8)	0.1816(7)	3.8(3)
N3	0.036(1)	1.1418(7)	0.3130(6)	3.6(3)
N4	0.048(1)	0.9238(9)	0.3115(8)	5.5(4)
N11	0.026(1)	1.5342(8)	0.3385(7)	4.0(3)
N12	0.281(1)	1.3903(8)	0.3156(6)	3.5(3)
N21	−0.081(1)	1.4669(8)	0.1884(6)	4.0(3)
N22	0.166(1)	1.5294(8)	0.1727(6)	3.1(3)
C′	0.413(5)	1.037(3)	0.383(3)	22(2)
C1	0.174(1)	1.211(1)	0.2096(7)	2.9(3)
C2	0.071(1)	1.223(1)	0.2865(7)	3.1(3)
C11	−0.022(2)	0.953(1)	0.395(1)	7.5(6)
C12	−0.134(2)	1.026(1)	0.397(1)	6.4(5)
C13	−0.068(2)	1.155(1)	0.3857(9)	5.3(4)
C21	0.327(3)	0.916(1)	0.094(1)	10.3(7)
C22	0.321(4)	1.017(2)	0.065(2)	12.3(1)
C23	0.316(2)	1.105(1)	0.108(1)	6.0(5)
C31	−0.101(2)	1.607(1)	0.3451(9)	5.5(4)
C32	−0.160(2)	1.681(1)	0.407(1)	6.5(5)
C33	−0.061(2)	1.669(1)	0.465(1)	6.7(5)
C34	0.080(2)	1.589(1)	0.4595(8)	4.5(4)
C35	0.185(2)	1.570(1)	0.5158(9)	5.5(4)
C36	0.308(2)	1.493(1)	0.508(1)	5.7(5)
C37	0.354(2)	1.427(1)	0.4370(9)	4.5(4)
C38	0.483(2)	1.351(1)	0.4240(9)	5.3(4)
C39	0.517(2)	1.294(1)	0.357(1)	6.5(5)
C40	0.407(2)	1.319(1)	0.3045(9)	4.9(4)
C41	0.250(1)	1.445(1)	0.3806(9)	3.9(4)
C42	0.115(1)	1.527(1)	0.3934(8)	3.1(3)
C51	−0.199(1)	1.434(1)	0.196(1)	5.0(4)
C52	−0.304(2)	1.467(1)	0.140(1)	5.8(5)
C53	−0.286(2)	1.533(1)	0.0804(9)	5.0(4)
C54	−0.163(2)	1.569(1)	0.0729(9)	4.8(4)
C55	−0.138(2)	1.642(1)	0.010(1)	6.2(5)
C56	−0.020(2)	1.678(1)	0.006(1)	6.6(5)
C57	0.092(2)	1.639(1)	0.0618(8)	5.5(5)
C58	0.221(2)	1.673(1)	0.058(1)	5.4(4)
C59	0.313(2)	1.633(1)	0.112(1)	5.5(4)
C60	0.280(2)	1.559(1)	0.1711(9)	4.3(4)
C61	0.061(2)	1.567(1)	0.1209(8)	3.8(4)
C62	−0.061(1)	1.532(1)	0.1291(8)	3.7(4)

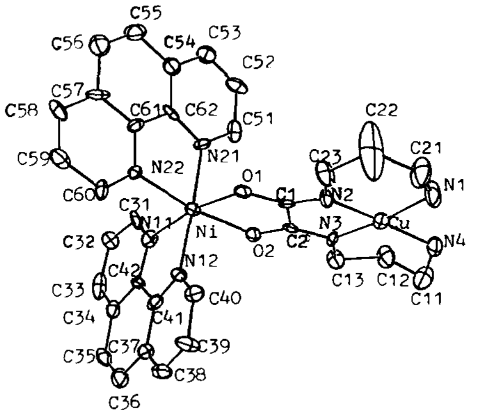

Fig. 1. Perspective view of the $[Cu(oxpn)Ni(phen)_2]^{2+}$ cation; the hydrogen atoms are not shown.

method. The positions of Cu and Ni atoms were found in the *E* map. All the remaining non-hydrogen atoms were located by Fourier and difference Fourier maps and least-squares refinement. The highest peak on the final difference Fourier map is 0.77 e/Å^3. Final atomic positional parameters for the non-hydrogen atoms are collected in Table 3.

A perspective view of $[Cu(oxpn)Ni(phen)_2]^{2+}$ cation is shown in Fig. 1. Selected bond distances and angles are collected in Table 4. In the $[Cu(oxpn)Ni(phen)_2]^{2+}$ cation, nickel(II) and copper(II) are linked by μ-oxamido and the separation is 5.338 Å. The copper(II) ion is four coordinate and lies only 0.0378 Å away from the least-squares plane through the N1, N2, N3 and N4 atoms. The nickel(II) ion is six coordinated and displaced by 0.0273 Å from the least-squares plane through the O1, O2, N11 and N22 atoms. The dihedral angle between the CuN_4 plane and the NiO_2N_2 plane is 5.40°. The actual symmetry of the cation is very close to C_{2v}.

EPR Spectra

The X-band powder EPR spectra at 110 K for the three complexes are given in Fig. 2. Each of them only exhibits a broad band [6] which can be simulated with $g_{\parallel} = 2.59$, $g_{\perp} = 2.05$ (for bpy); $g_{\parallel} = 2.51$, $g_{\perp} = 2.05$ (for phen) and $g_{\parallel} = 2.17$, $g_{\perp} = 2.05$ (for NO_2-phen). The EPR of $[Cu(oxpn)Ni(bpy)_2](ClO_4)_2$ is substantially attributable to the ground doublet state ($^2A_1$). Since at 110 K, the population in the $^4A_2$ state is about 14%, estimated on the basis of Boltzmann distribution by using $J = -47.2$ cm^{-1} (see below) [7], the signals would be expected to be very weak, and not observed in the EPR spectra.

Magnetic Properties

The observed magnetic moment per binuclear complex at room temperature shown in Table 1, is considerable less than the spin-only value (3.61 BM). This suggests the operation of an antiferromagnetic spin-exchange interaction in these complexes.

TABLE 4. Main bond lengths and bond angles for $[Cu(oxpn)Ni(phen)_2](ClO_4)_2 \cdot CH_3OH \cdot H_2O$

(a) Bond lengths (Å)

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Cu	N1	2.02(2)	Cu	N2	1.95(1)
Cu	N3	1.95(2)	Cu	N4	2.02(1)
Ni	O1	2.08(1)	Ni	O2	2.08(3)
Ni	N11	2.05(2)	Ni	N12	2.08(2)
Ni	N21	2.11(2)	Ni	N22	2.08(2)
O1	C1	1.29(2)	O2	C2	1.31(4)
N2	C1	1.27(2)	N3	C2	1.29(2)

(b) Bond angles (°)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	Cu	N2	94.2(7)	N1	Cu	N3	173.5(7)
N1	Cu	N4	86.5(7)	N2	Cu	N3	84.6(7)
N2	Cu	N4	177.9(8)	N3	Cu	N4	94.9(7)
O1	Ni	O2	80.0(1)	O1	Ni	N11	168.1(6)
O1	Ni	N12	91.3(5)	O1	Ni	N21	90.7(5)
O1	Ni	N22	95.2(9)	O2	Ni	N11	94.0(1)
O2	Ni	N12	91.0(1)	O2	Ni	N21	91.0(2)
O2	Ni	N22	171.0(2)	N11	Ni	N12	78.2(6)
N11	Ni	N21	100.0(6)	N11	Ni	N22	92.0(1)
N12	Ni	N21	177.1(2)	N12	Ni	N22	96.4(7)
N21	Ni	N22	81.50(7)	O1	C1	N2	131.0(2)
O2	C2	N3	126.0(2)	Ni	O1	C1	115.0(2)
Ni	O2	C2	112.0(3)	Cu	N3	C2	111.0(1)
Cu	N2	C1	113.0(2)				

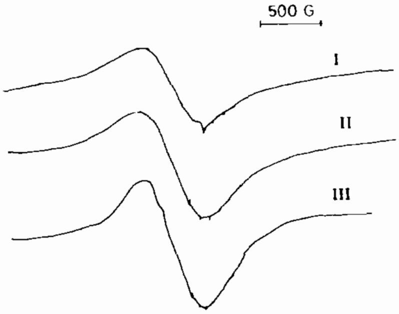

Fig. 2. Powder X-band EPR spectra of the complexes: I, bpy; II, phen; III, NO_2-phen.

Variable-temperature (4.2–300 K) magnetic susceptibility data were collected for $[Cu(oxpn)Ni(phen)_2](ClO_4)_2 \cdot H_2O$ (Table 5) and the magnetic analysis was carried out with the susceptibility equation based on the Heisenberg spin-exchange operator for a dimer ($\hat{H} = -2J\hat{S}_1\hat{S}_2$, $S_1 = \frac{1}{2}$, $S_2 = 1$) [6]

$$\chi_M = \frac{Ng^2\beta^2}{4KT}\,\frac{10 + \exp(-3J/KT)}{2 + \exp(-3J/KT)} + N\alpha \qquad (1)$$

where χ_M denotes the susceptibility per binuclear complex and the remaining symbols have their usual meanings. As shown in Fig. 3, good fits to the experimental data are attained with eqn. (1). Magnetic parameters thus determined are $J = -47.22$ cm^{-1}, $g = 2.15$, $N\alpha = 120 \times 10^{-6}$ cgs mol^{-1}. The agreement factor F defined here as $\Sigma[(\chi_M T)_{obs} - (\chi_M T)_{calc}]^2/(\chi_M T)_{obs}$ is then equal to $\sim 1 \times 10^{-3}$. The energy gap between doublet $^2A_1$ and quartet $^4A_1$ states ($\Delta E = -3J$) is equal to 141.66 cm^{-1}.

To describe the mechanism of the exchange interaction, several models have been proposed [8–10]. According to these models, strict orbital orthogonality results in ferromagnetism. For the present complex, if whole molecular symmetry is considered to be C_{2v}, the 3d metallic orbitals of Cu(II) and Ni(II) ions transform as a_1 (d_{z^2} and $d_{x^2-y^2}$), a_2 (d_{yz}), b_1 (d_{xy}) and b_2 (d_{zx}) [11]. Because there is not orthogonality between b_1 magnetic orbitals centered on Cu(II) ion and Ni(II) ion, the antiferromagnetic interaction should be observed.

We also investigated the magnetic behaviour of Cu(II)–Cu(II) and Cu(II)–Co(II) binuclear complexes with the same ligands and obtained the following sequence for the magnetic interaction: [CuCu] ($J = -231.46$ cm^{-1}) > [CuNi] ($J = -47.22$ cm^{-1}) > [CuCo] ($J = -23.47$ cm^{-1}) [12]*. This result is in accordance with Kahn's expectation [13].

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*For [CuCo], a more appropriate method was employed which includes isotropic exchange, zero-field splitting, and Curie-Weiss parameter, θ, in Hamiltonia.

TABLE 5. Temperature dependence of molar susceptibility (cgs mol^{-1}) and effective magnetic moment (BM) for [Cu(oxpn)Ni(phen)$_2$](ClO$_4$)$_2$·H$_2$O

T (K)	$\chi_M \times 10^6$	μ_{eff}
4.1	89091	1.70
5.5	74751	1.82
8.1	52818	1.85
11.8	36384	1.86
15.9	27824	1.88
20.8	21380	1.88
30.5	15180	1.97
39.2	12486	1.98
51.3	10443	2.07
60.4	9545	2.15
70.2	8893	2.23
80.9	8329	2.32
91.3	8038	2.43
101.6	7907	2.54
122.2	7835	2.65
132.8	7344	2.79
144.5	7185	2.88
156.9	6939	2.95
169.6	6604	2.99
182.5	6534	3.09
195.4	6287	3.14
207.5	5952	3.14
219.4	5882	3.21
231.3	5547	3.20
244.0	5388	3.24
256.4	5142	3.25
268.1	5054	3.29
279.6	4808	3.27
290.0	4738	3.31
298.1	4594	3.31

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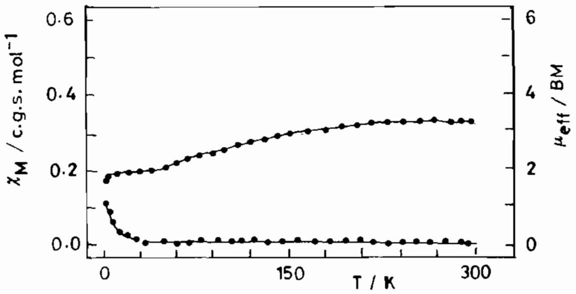

Fig. 3. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment per molecule, μ_{eff}, vs. temperature curves for [Cu(oxpn)Ni(phen)$_2$](ClO$_4$)$_2$·H$_2$O. The solid lines represent the best fitted technique fit of the data to the theoretical equation given in the text.

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