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Intramolecular Hydrogen Bonding: Synthesis and Crystal Structure of Nickel(II) and Copper(II) Complexes of a Tetradentate Amine Oxime*

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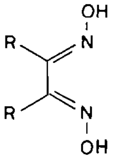
Abstract

In the reaction of the tetradentate ligand 3,3′-(1,4-butanediyldiamino)bis(3-methyl-2-butanone)-dioxime (BnAO) with nickel(II) and copper(II), the monomeric [Ni(BnAO-H)]I$\cdot H_2O$ and a mixed monomer/dimer salt [Cu(BnAO-H)H_2O]$_2$[(Cu-(BnAO-H))$_2$]$(ClO_4)_4$, respectively, are formed, and all complexes have an intramolecular hydrogen bond between *cis* oxime groups. The O–H–O bonds give the characteristic infrared absorptions as well as the downfield proton-NMR signal (Ni complex). [Ni-(BnAO-H)]I$\cdot H_2O$ crystallizes in space group $P2_1/a$ with $a = 13.511(2)$, $b = 10.599(2)$, $c = 14.096(2)$ Å, $\beta = 97.52°$, $Z = 4$ and $D_c = 1.623$ g/cm^3. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques to a final R of 0.021 for 2124 reflections with $I > 2\sigma(I)$. The nickel(II) atom in the complex has slightly distorted square planar geometry with an intramolecular O···O contact of 2.417(7) Å. The copper(II) complex crystallizes in space group $P2_1/c$ with $a = 13.425(2)$, $b = 21.446(3)$, $c = 14.349(4)$ Å, $\beta = 104.4(5)°$, $Z = 8$ (monomers) and $D_c = 1.485$ g/cm^3. The final R value for this complex was 0.053 for 3033 reflections with $I > 2\sigma(I)$. This structure contains a monomeric [Cu(BnAO-H)H_2O]$^+$ ion and a dimeric [(Cu(BnAO-H))$_2$]$^{2+}$ ion, having intramolecular O···O hydrogen bonds of 2.421(5) and 2.531(5) Å, respectively. The copper(II) ions have square-pyramidal coordination with the axial positions occupied by an oxygen of the water of hydration in the monomer and by an oxime oxygen atom in the dimer. A center of symmetry relates the two halves of the dimer. The copper atom in each case is out of the plane of the four nitrogen atoms toward the axial site. The copper(II) complex is unusual in that the crystal contains both a monomer and a dimer.

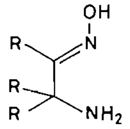
Introduction

It is now well established that vic-dioximes (I) and bidentate or tetradentate amine oximes (II and III) coordinate with transition metal ions to form complexes having strong intramolecular hydrogen bond(s) between *cis* oxime group(s) [e.g., 1–4]. Generally, mononuclear species are formed in which the O···O distance varies as a function of: (1) the size of the metal ion, (2) the constraint imposed by the methylene carbons bridging the amine nitrogen atoms, and (3) changing from an sp^3 amine nitrogen to an sp^2 imine nitrogen. Dinuclear species are formed: (a) by dimerization of the monomers through oxime oxygen [5], (b) by connecting two monomers, having an heterocyclic metal containing aromatic ring, at the carbon site with highest electron density [6], and (c) by bridging two metal ions with halides or tetradentate amine oxime ligands [7]. The [Rh(BnAO-H)Cl_2]$_2$ complex [7] is the



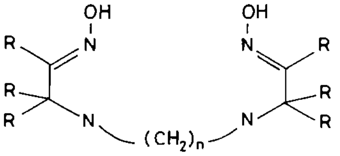
I

a: afdo, R = $-C_4H_4O$
b: dmg, R = CH_3



II

a: AO, R = CH_3



III

a: EnAO, $n = 2$, R = $-CH_3$
b: PnAO, $n = 3$, R = $-CH_3$
c: BnAO, $n = 4$, R = $-CH_3$

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only known example of the type (c) dimer in which two metal ions are bridged by two BnAO ligands (3,3′-(1,4-butanediyldiamino)bis(3-methyl-2-butanone)dioxime). Because of this unique behavior of BnAO towards Rh(III), we have extended our investigations on BnAO to other metal ions. Synthesis, spectroscopic studies and the molecular structures by X-ray diffraction for the Ni(II) and Cu(II) complexes of BnAO are reported here.

Experimental

Synthesis and Crystal Growth

The ligand 3,3′-(1,4-butanediyldiamino)bis(3-methyl-2-butanone)dioxime, BnAO was prepared by the procedure reported earlier [8].

[Ni(BnAO-H)]I·H_2O, I

To 3.0 mmol (0.870 g) of hydrated nickel(II) nitrate in 15 ml of water was added 3.0 mmol (0.825 g) of solid BnAO. The mixture was stirred at room temperature to obtain a clear solution. This was followed by addition of potassium iodide to precipitate yellow colored complex which was recrystallized from hot water. The yellow single crystals were obtained by cooling a saturated aqueous solution of the complex from 60 °C down to room temperature. Other salts can be obtained, but suitable X-ray diffraction crystals were only obtained with iodide.

[(Cu(BnAO-H))$_2$][Cu(BnAO-H)·H_2O]$_2$(ClO_4)$_4$, II

A solution of 3.0 mmol (0.825) of BnAO in 7.5 ml of water was added to an aqueous solution of 3.0 mmol (0.725 g) of copper(II) nitrate. The mixture was stirred at room temperature to obtain a dark purple solution. The solution was filtered after its pH was adjusted to 6 with solid Na_2CO_3. A purple colored solid product was precipitated from the clear solution by adding an excess of solid $NaClO_4$. Dark purple crystals of the complex were obtained by slowly cooling a saturated aqueous solution of the product.

Spectroscopic Measurements

Solid state infrared spectra were measured on a Beckman IR10 Grating Infrared Spectrophotometer using fluorolube mulls and sodium chloride plates. The proton NMR spectra were recorded in d_6-DMSO on a Varian Model EM-360 NMR spectrometer with Me_4Si as an internal standard.

Crystallographic Studies

Diffraction data were collected at room temperature 21 °C on an Enraf-Nonius CAD4 automated diffractometer using graphite-monochromated Mo Kα radiation. Details of the procedure used for X-ray data collection, data reduction and structure refinement are described earlier [1,2]. Both structures were solved by usual Patterson and Fourier methods. The full-matrix least-squares refinement minimized the function $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/(\sigma^2(F_o))$, $\sigma(F_o{}^2) = [(\sigma(I_{raw}))^2 + (0.05\ I_{raw})^2]^{1/2}/Lp$, $\sigma(F_o) = \sigma(F_o{}^2)/2F_o$, F_c is the calculated structure factor, and I_{raw} is the background corrected intensity. The cutoff for inclusion in the refinement is $F_o > 2\sigma(F_o)$. Atomic scattering factors were taken from ref. 9 and included anomalous scattering contributions. Hydrogen atoms were included at chemically reasonable positions from difference Fourier syntheses and/or geometric calculations and were refined in the nickel complex.

A summary of the crystal data, data collection parameters and results of refinement is given in Table I.

Results and Discussion

The mixing of equimolar aqueous solutions of the ligand (BnAO) and the metal ion results in the formation of the expected monomeric complex [Ni(BnAO-H)]I·H_2O in the case of nickel(II) but a mixed salt of the formula [Cu(BnAO-H)H_2O]$_2$-[(Cu(BnAO-H))$_2$](ClO_4)$_4$ constituting a monomer/dimer mixture is obtained for copper(II) at a pH of 6. A similar binuclear copper(II) complex but without cocrystallizing with a monomer was reported earlier [5] for EnAO. However, nickel(II) complexes of the types **II** and **III** ligands studied to date are always mononuclear. The present synthetic behavior is consistent with the tendency of d^8 metal ions to form stable 4-coordinate species and preference for the formation of 5- and 6-coordinate distorted square-pyramidal or octahedral species by d^9 metal systems.

Spectroscopic Results

The infrared spectra of both compounds (Table II) show the characteristic broad, weak band in the region 1700–1800 cm^{-1} normally observed for the strong intramolecular hydrogen bond in the chelate structures [2–4]. A decrease in the O···O distance tends to shift the ν(OHO) band to a high energy: e.g. [Ni(dmg)$_2$] and [Pd(afdo)$_2$] have O···O distance of 2.462(2) and 2.583(4) Å with ν(OHO) at 1770 and 1730 cm^{-1}, respectively as compared to [Ni(PnAO-H)]Cl with an O···O distance of 2.409(3) Å and ν(OHO) of 1800 cm^{-1}. The proton NMR spectrum of the Ni(II) compounds shows all methyl proton resonances with the expected chemical shifts and integrated intensities. The O···H···O proton resonance appears at 18.5 ppm in the nickel(II) complex. This downfield chemical shift value fits into the general trend observed for the various

TABLE I. Cell Parameters and Details of Data Collection and Refinement

	Compound I	Compound II
Formula	$C_{14}H_{31}N_4O_3I$	$C_{28}H_{60}N_8O_{13}Cl_2Cu_2$
Formula weight	489.0	914.8
Space group	$P2_1/a$	$P2_1/c$
a (Å)	13.511(2)	13.425(2)
b (Å)	10.599(2)	21.446(3)
c (Å)	14.096(2)	14.349(4)
β (deg)	97.52(1)	104.41(5)
V (Å^3)	2001(1)	4001(3)
Z	4	4
D_c (g/cm^3)	1.623	1.518
F(000)	992	1872
Crystal dimensions (mm)	~0.33 × 0.27 × 0.15	~0.35 × 0.30 × 0.20
λ (Mo Kα) (Å)	0.7107	0.7107
Monochromator	graphite	graphite
μ (cm^{-1})	25.17	12.63
Absorption correction	none (estimated transmission range 0.97–0.99 based on ψ scans)	empirical absorption correction made on the basis of ψ scan
Scan method	θ–2θ step	θ–2θ step
Scan range (θ deg)	0.60 + 0.35 tan θ	0.80 + 0.35 tan θ
Scan speed	variable to obtain counting statistics of 2%, to a maximum scan time of 120 s	variable to obtain 2% counting statistics to a maximum scan time of 120 s
Number of reflections measured	5484	4330
Number of unique reflections	2616	3703
Number of reflections above 2σ	2124	3033
Number of variables	332	478
$R(F) = \Sigma\lvert F_o\rvert - \lvert F_c\rvert/\Sigma F_o$	0.021	0.053
$R_\omega(F) = [\Sigma_\omega(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma_\omega F_o^2]^{1/2}$	0.029	0.078
Maximum shift/error on last cycle	0.04	0.05

TABLE II. Infrared Stretching Frequencies (ν_{OHO}) and Chemical Shifts for the bridged Proton with Varying of O•••O Distance

Compound	O•••O (Å)	ν_{OHO} (cm^{-1})	δ_{OHO} (ppm)	Reference
$[Ni(dmg)_2]$	2.462(3)	1770		
$[Ni(PnAO\text{-}H)]Cl\cdot H_2O$	2.409(3)	1800	18.6	10
$[Ni(AO)_2\text{-}H]Cl_2$	2.420(3)	1802	18.7	11
$[Rh(BnAO\text{-}H)Cl_2]_2$	2.387(5)	1792	19.5	7
$[Ni(EnAO\text{-}H)]ClO_4$	2.478(5)	1750		12
$[Ni(BnAO\text{-}H)]I\cdot H_2O$	2.417(7)	1798	18.5	this work
$[Cu(BnAO\text{-}H)H_2O]ClO_4$	2.421(5)	1790		this work

α-amine oxime complexes of the same metal. Generally the smaller the O•••O distance the further downfield is the δ value for the bridged proton (Table I).

Description of the structures

The final positional parameters for the non-hydrogen atoms are listed in Tables III and IV for compounds I and II, respectively. The bond distances and angles for both compounds are given in Table V (see also 'Supplementary Material').

$[Ni(BnAO\text{-}H)]I\cdot H_2O$

This structure consists of discrete, distorted square planar $[Ni(BnAO\text{-}H)]^+$ complex cations (Fig. 1), iodide anions and water of hydration. The square plane about the nickel is distorted slightly towards tetrahedral geometry in that the *trans* N(1) and N(4) are below the best plane through the nickel and four nitrogens while the *trans* N(2) and N(3) are above the plane. Both oxime oxygens are above the NiN_4 plane. There are no unusually short intermolecular contacts. The shortest contacts are the hydrogen bonds between the N(4) and O(w) atoms at 2.980(5) Å and between I and O(w) at 3.464(5) Å.

$[Cu(BnAO\text{-}H)H_2O]_2[(Cu(BnAO\text{-}H))_2](ClO_4)_4$

The structure of this mixed salt consists of both monomeric and dimeric copper(II) complex ions.

TABLE III. Atomic Positional Parameters for Compound I[a]

Atom	x	y	z	B_{A2}[b]
I	0.28664(2)	0.25204(2)	0.39537(2)	4.333(6)
Ni	−0.09234(3)	−0.36054(4)	0.19175(2)	2.300(7)
O(w)	0.2370(3)	−0.0685(3)	0.3952(2)	6.53(7)
O(1)	−0.0650(2)	−0.3331(2)	−0.0033(1)	3.81(5)
O(2)	−0.0180(2)	−0.1523(3)	0.0971(2)	4.69(6)
N(1)	−0.1048(2)	−0.4034(3)	0.0527(2)	2.82(5)
N(2)	−0.0538(3)	−0.1940(3)	0.1775(2)	3.11(5)
N(3)	−0.1255(2)	−0.5343(3)	0.2047(2)	2.70(5)
N(4)	−0.0863(2)	−0.3137(3)	0.3243(2)	2.57(5)
C(1)	−0.1568(2)	−0.5011(3)	0.0360(2)	3.21(7)
C(2)	−0.0603(2)	−0.1166(3)	0.2459(2)	3.29(7)
C(3)	−0.1955(2)	−0.5712(4)	0.1165(2)	3.38(7)
C(4)	−0.1061(2)	−0.1729(3)	0.3286(2)	2.85(7)
C(5)	−0.1984(3)	−0.5413(4)	−0.0652(2)	4.50(9)
C(6)	−0.0327(3)	0.0185(4)	0.2429(3)	5.5(1)
C(7)	−0.1998(3)	−0.7136(4)	0.1009(3)	4.98(9)
C(8)	−0.2995(3)	−0.5209(5)	0.1292(3)	4.85(9)
C(9)	−0.2187(3)	−0.1525(3)	0.3099(2)	3.44(7)
C(10)	−0.0658(3)	−0.1155(4)	0.4244(3)	4.26(8)
C(11)	−0.0306(3)	−0.6085(3)	0.2179(2)	3.12(7)
C(12)	0.0526(2)	−0.5390(3)	0.2779(2)	3.31(7)
C(13)	0.0297(2)	−0.4932(3)	0.3758(2)	3.30(7)
C(14)	0.0093(2)	−0.3537(3)	0.3812(2)	3.20(7)

[a] Estimated standard deviations from the least-squares refinement are given in parentheses in this and subsequent tables.

[b] $B_{eq} = (4/3)[a^2\beta 11 + b^2\beta 22 + c^2\beta 33 + ab \cos \delta\beta 12 + ac \cos \beta\beta 13 + bc \cos \alpha\beta 23]$.

The monomer is a discrete five coordinated square pyramidal $[Cu(BnAO\text{-}H)H_2O]^+$ cation (Fig. 2) with the apical position occupied by the water molecule. The copper atom is 0.27 Å out of the plane defined by the four nitrogens of BnAO and the copper atom. The short intramolecular O···O hydrogen bond distance is 2.421(5) Å.

The dimer is a $[(Cu(BnAO\text{-}H))_2]^{2+}$ binuclear copper(II) dipositive ion. Each copper atom in the dimer has near square-pyramidal geometry (Fig. 3). The two oxime nitrogen atoms and the two amine nitrogen atoms of one BnAO have a near square planar arrangement about one copper atom while an oxime oxygen atom of the second BnAO moiety occupies the apical position of that square pyramid (Fig. 3). A center of symmetry relates the two halves of the dimer. The copper atom is out of the plane of the four nitrogen atoms toward the coordinated oxime oxygen atom as is usually the case in square pyramidal copper complexes. The intramolecular hydrogen bond has an O···O distance of 2.528(5) Å. There are two symmetry independent perchlorate ions in the unit cell. Extensive hydrogen bonding exists among the perchlorate oxygens and the amine hydrogen atoms. The perchlorate oxygens have quite high thermal motion and probably have some disorder.

As in the structures of all Cu(II) α-amineoxime complexes studied to date [5, 14, 15], the fifth position of the square pyramid is occupied by a

TABLE IV. Atomic Positional Parameters for Compound II

Atom	x	y	z	B_{A2}	Atom	x	y	z	B_{A2}
Cu	−0.36652(7)	0.00706(4)	0.34956(6)	2.73(2)	C(3)	−0.3317(7)	−0.0986(4)	0.2329(6)	3.9(2)
Cu′	0.04911(7)	0.08591(4)	0.00389(6)	2.31(2)	C(4)	−0.3451(7)	0.1368(4)	0.4168(6)	3.7(2)
Cl(1)	0.8703(2)	0.6594(1)	0.0599(2)	5.56(7)	C(5)	−0.4865(8)	−0.1705(5)	0.2439(8)	5.9(3)
Cl(2)	−0.3756(2)	0.1582(1)	0.0901(2)	6.30(7)	C(6)	−0.5213(7)	0.1544(4)	0.4523(7)	4.6(2)
O(1)	−0.5473(4)	−0.0730(2)	0.3388(4)	3.7(1)	C(7)	−0.2695(7)	−0.1576(5)	0.2319(7)	6.8(3)
O(2)	−0.5670(4)	0.0346(2)	0.3821(4)	3.4(1)	C(8)	−0.3692(8)	−0.0703(5)	0.1327(6)	5.3(3)
O(3)	−0.3052(4)	−0.0279(3)	0.5038(4)	3.9(1)	C(9)	−0.3469(9)	0.2022(5)	0.3784(7)	6.1(3)
O(4)	0.8725(8)	0.6095(4)	0.1201(7)	11.3(3)	C(10)	−0.2792(8)	0.1318(5)	0.5199(7)	5.6(3)
O(5)	0.847(1)	0.7144(4)	0.0976(7)	13.8(4)	C(11)	−0.1856(7)	−0.0223(5)	0.2618(7)	5.4(3)
O(6)	0.800(1)	0.6507(6)	−0.0219(8)	18.3(5)	C(12)	−0.0988(7)	−0.0010(5)	0.3414(8)	6.5(3)
O(7)	0.9574(8)	0.6675(5)	0.035(1)	24.7(5)	C(13)	−0.1251(7)	0.0463(5)	0.4111(7)	5.6(3)
O(8)	−0.4086(8)	0.1155(5)	0.1445(7)	15.7(3)	C(14)	−0.1863(7)	0.1002(5)	0.3630(8)	5.5(3)
O(9)	−0.441(1)	0.1733(8)	0.023(1)	29.2(6)	C(1)′	−0.0931(6)	0.0572(4)	−0.1695(5)	2.5(2)
O(10)	−0.310(1)	0.1356(7)	0.057(2)	36.5(7)	C(2)′	0.2636(6)	0.0648(4)	0.0820(5)	2.8(2)
O(11)	−0.3205(9)	0.2067(6)	0.1384(7)	18.2(4)	C(3)′	−0.1168(6)	0.1246(4)	−0.1564(5)	3.0(2)
O(1)′	0.0105(4)	−0.0266(2)	−0.1122(3)	2.7(1)	C(4)′	0.2469(6)	0.1303(4)	0.1188(5)	3.0(2)
O(2)′	0.1942(4)	−0.0157(2)	−0.0133(4)	3.4(1)	C(5)′	−0.1511(7)	0.0218(4)	−0.2557(6)	3.9(2)
N(1)	−0.4576(4)	−0.0665(3)	0.3124(4)	3.0(1)	C(6)′	0.3641(6)	0.0328(4)	0.1085(6)	3.9(2)
N(2)	−0.4730(5)	0.0580(3)	0.3840(4)	2.7(1)	C(7)′	−0.2299(7)	0.1386(5)	−0.1880(7)	5.2(3)
N(3)	−0.2705(4)	−0.0514(3)	0.3002(4)	3.4(2)	C(8)′	−0.0578(8)	0.1624(4)	−0.2147(7)	5.5(3)
N(4)	−0.3006(5)	0.0928(3)	0.3526(5)	3.9(2)	C(9)′	0.3146(7)	0.1408(4)	0.2207(6)	4.8(2)
N(1)′	−0.0182(4)	0.0344(3)	−0.1056(4)	2.2(1)	C(10)′	0.2737(7)	0.1771(4)	0.0487(7)	4.8(2)
N(2)′	0.1815(4)	0.0419(3)	0.0261(4)	2.3(1)	C(11)′	−0.0725(8)	0.2049(4)	−0.0283(7)	5.7(3)
N(3)′	−0.0784(5)	0.1384(3)	−0.0513(4)	3.1(2)	C(12)′	−0.0824(7)	0.2198(5)	0.0723(8)	6.3(3)

(continued on facing page)

TABLE IV *(continued)*

Atom	x	y	z	B_{A2}	Atom	x	y	z	B_{A2}
N(4)	0.1354(5)	0.1340(3)	0.1173(4)	3.2(2)	C(13)′	−0.0145(7)	0.1893(5)	0.1485(6)	6.3(2)
C(1)	−0.4262(6)	−0.1113(4)	0.2684(6)	3.5(2)	C(14)′	0.1004(7)	0.1927(5)	0.1503(8)	5.2(3)
C(2)	−0.4518(6)	0.1131(4)	0.4140(5)	3.0(2)					

TABLE V. Intramolecular Bond Distances (Å) and Angles (deg) in Compounds I and II

	Compound I [Ni(BnAO-H)]I	Compound II[a]	
		$[Cu(BnAO)H_2O]^+$	$[(Cu(BnAO\text{-}H))_2]^{2+}$
Bond distances			
M–N(1)	1.862(2)	1.986(4)	1.950(4)
M–N(2)	1.859(3)	1.958(4)	1.967(4)
M–N(3)	1.910(3)	2.047(7)	2.038(4)
M–N(4)	1.924(2)	2.036(4)	2.029(4)
N(1)–O(1)	1.356(4)	1.356(5)	1.373(5)
N(1)–C(1)	1.279(4)	1.278(5)	1.277(5)
N(2)–O(2)	1.363(4)	1.353(5)	1.387(5)
N(2)–C(2)	1.278(4)	1.264(5)	1.288(5)
N(3)–C(3)	1.511(4)	1.496(7)	1.498(6)
N(3)–C(11)	1.496(4)	1.518(7)	1.461(7)
N(4)–C(4)	1.519(4)	1.540(7)	1.494(6)
N(4)–C(14)	1.489(4)	1.512(7)	1.463(7)
C(1)–C(3)	1.507(5)	1.505(7)	1.502(7)
C(1)–C(5)	1.483(5)	1.502(8)	1.494(7)
C(2)–C(4)	1.511(5)	1.512(8)	1.536(7)
C(2)–C(6)	1.483(5)	1.487(8)	1.478(7)
C(3)–C(7)	1.525(6)	1.519(8)	1.503(8)
C(3)–C(8)	1.536(5)	1.526(8)	1.521(8)
C(4)–C(9)	1.525(5)	1.505(8)	1.533(7)
C(4)–C(10)	1.525(5)	1.527(8)	1.527(8)
C(11)–C(12)	1.508(4)	1.486(8)	1.516(9)
C(12)–C(13)	1.532(5)	1.526(9)	1.409(8)
C(13)–C(14)	1.508(5)	1.485(9)	1.541(8)
Cu–O(3)		2.287(4)	
Cu′–O(1)″			2.300(4)
Bond angles			
N(1)–M–N(2)	96.7(1)	94.1(2)	94.55(2)
N(1)–M–N(3)	82.3(1)	79.6(2)	79.9(2)
N(1)–M–N(4)	177.2(1)	163.4(2)	172.9(2)
N(2)–M–N(3)	177.1(1)	172.5(2)	164.9(2)
N(2)–M–N(4)	83.3(1)	80.3(2)	78.6(2)
N(3)–M–N(4)	97.8(1)	104.6(2)	106.7(2)
M–N(1)–O(1)	122.9(2)	122.5(3)	120.9(3)
M–N(1)–C(1)	117.4(2)	118.3(4)	119.1(3)
O(1)–N(1)–C(1)	119.6(2)	119.0(4)	119.9(4)
M–N(2)–O(2)	122.2(2)	121.6(3)	123.9(3)
M–N(2)–C(2)	118.7(2)	119.4(4)	119.4(4)
O(2)–N(2)–C(2)	119.1(3)	118.9(4)	114.9(4)
M–N(3)–C(3)	107.5(2)	110.2(3)	109.1(3)
M–N(3)–C(11)	108.1(2)	117.9(4)	117.3(4)
M–N(4)–C(4)	107.9(2)	109.6(3)	110.8(3)
M–N(4)–C(14)	111.9(2)	121.4(4)	122.1(3)
C(3)–N(3)–C(11)	113.6(2)	112.64(4)	114.1(4)
C(4)–N(4)–C(14)	113.7(2)	114.30(5)	115.3(4)
N(1)–C(1)–C(3)	114.1(3)	116.13(5)	115.5(4)

(continued overleaf)

TABLE V *(continued)*

	Compound I [Ni(BnAO-H)]I	Compound II[a]	
		$[Cu(BnAO)H_2O]^+$	$[(Cu(BnAO\text{-}H))_2]^{2+}$
C(3)–C(1)–C(5)	122.0(3)	121.9(6)	120.6(5)
N(2)–C(2)–C(4)	113.8(3)	117.0(5)	112.7(4)
N(2)–C(2)–C(6)	123.8(3)	125.3(5)	124.7(5)
C(4)–C(2)–C(6)	122.3(3)	117.8(5)	122.6(5)
N(3)–C(3)–C(1)	104.5(3)	106.1(4)	106.6(4)
N(3)–C(3)–C(7)	112.5(3)	110.8(5)	109.5(4)
N(3)–C(3)–C(8)	107.3(3)	109.8(5)	110.6(4)
C(1)–C(3)–C(7)	113.0(3)	111.3(5)	112.7(5)
C(1)–C(3)–C(8)	109.3(3)	106.5(5)	106.8(4)
C(7)–C(3)–C(8)	110.0(3)	112.1(5)	110.7(5)
N(4)–C(4)–C(2)	105.4(3)	106.5(4)	106.0(4)
N(4)–C(4)–C(9)	108.0(3)	109.0(5)	111.1(4)
N(4)–C(4)–C(10)	113.4(3)	108.6(5)	110.7(4)
C(2)–C(4)–C(9)	108.1(3)	112.1(5)	111.1(4)
C(2)–C(4)–C(10)	112.7(3)	108.6(5)	107.1(4)
C(9)–C(4)–C(10)	109.0(3)	111.9(5)	110.5(5)
N(3)–C(11)–C(12)	112.1(3)	111.3(5)	114.0(6)
C(11)–C(12)–C(13)	115.9(3)	116.3(5)	117.4(6)
N(4)–C(14)–C(13)	113.8(3)	113.3(5)	111.1(5)
N(1)–Cu–O(3)		92.8(2)	
N(2)–Cu–O(3)		92.8(2)	
O(1)″–Cu′–N(1)′			93.6(2)
O(1)″–Cu′–N(2)			94.5(2)
O(1)″–Cu′–N(3)′			99.7(2)
O(1)″–Cu′–N(4)			87.9(2)

[a]The atom numbering in this Table for the dimeric cation $[(Cu(BnAO\text{-}H))_2]^{2+}$ corresponds to identical primed numbers in Table IV and Fig. 3.

more weakly coordinated atom. In $[Cu(PnAO\text{-}H)(ReO_4)]$ [14] the Cu–O distance is the longest (2.40(1) Å) while the shortest distance is observed [5] in dinuclear $[(Cu(EnAO\text{-}H))_2]^{2+}$ where the oxime oxygen is 2.185(4) Å from the copper. In the present case both the monomeric and dimeric complex ion have intermediate distances of 2.287(4) and 2.300(4) Å, respectively.

Intramolecular hydrogen bonds

The distances and angles involving the intramolecular hydrogen bonds in the present compounds along with some related compounds are given in Table VI.

The hydrogen bonded O···O distances are 2.417(7) Å in $[Ni(BnAO\text{-}H)]^+$, 2.421(5) Å in the monomeric $[Cu(BnAO\text{-}H)H_2O]^+$ and 2.531(5) Å in the dimeric $[(Cu(BnAO\text{-}H))_2]^{2+}$ cation. Among the monomeric complexes there is an increase of about 0.04–0.06 Å in the O···O distance and of about 2° in the M–N–O angle for copper(II) complexes over those in the nickel(II) complexes consistent with the larger size of copper(II). The degree of constraint (based on O···O distance) caused by the amine–oxime ligands in nickel(II) monomeric complexes follows the order: PnAO < BnAO < AO < PreH < EnAO. The ethylene bridge in EnAO, opposite the intramolecular hydrogen bond imposes the greatest constraint resulting in significant elongation of the O···O distance. The steric constraint of the butylene bridge in BnAO with O···O distance of 2.417(7) Å, is essentially equal to that with the propylene bridge in PnAO (O···O = 2.409(10) Å). Among the monomeric copper(II) complexes the effects of constraints imposed by the 3- or 4-carbon chains on the O···O distances are similar. Dimerization through an hydrogen bonded oxime oxygen in copper(II) tends to elongate the O···O separation. For example O···O distances in $[(Cu(BnAO\text{-}H))_2]_2^{2+}$ and $[Cu(EnAO\text{-}H))_2]^{2+}$ dimeric cations are 2.531(5) and 2.698(6) Å, respectively. In the case of the latter, the constraint due to ethylene bridge also contributes towards the elongation of the O···O distance.

The O–H distance varies with the O···O separation. A nearly symmetric hydrogen bond appears in the complexes with O···O separation of less than 2.46 Å but with O···O distance greater than 2.46 Å, more unsymmetric hydrogen bonds are observed. However, an exact correlation between O–H bond distance and O···O separation cannot be established without a comparison between isolated O–H–O bond systems where oxygen atoms are not involved

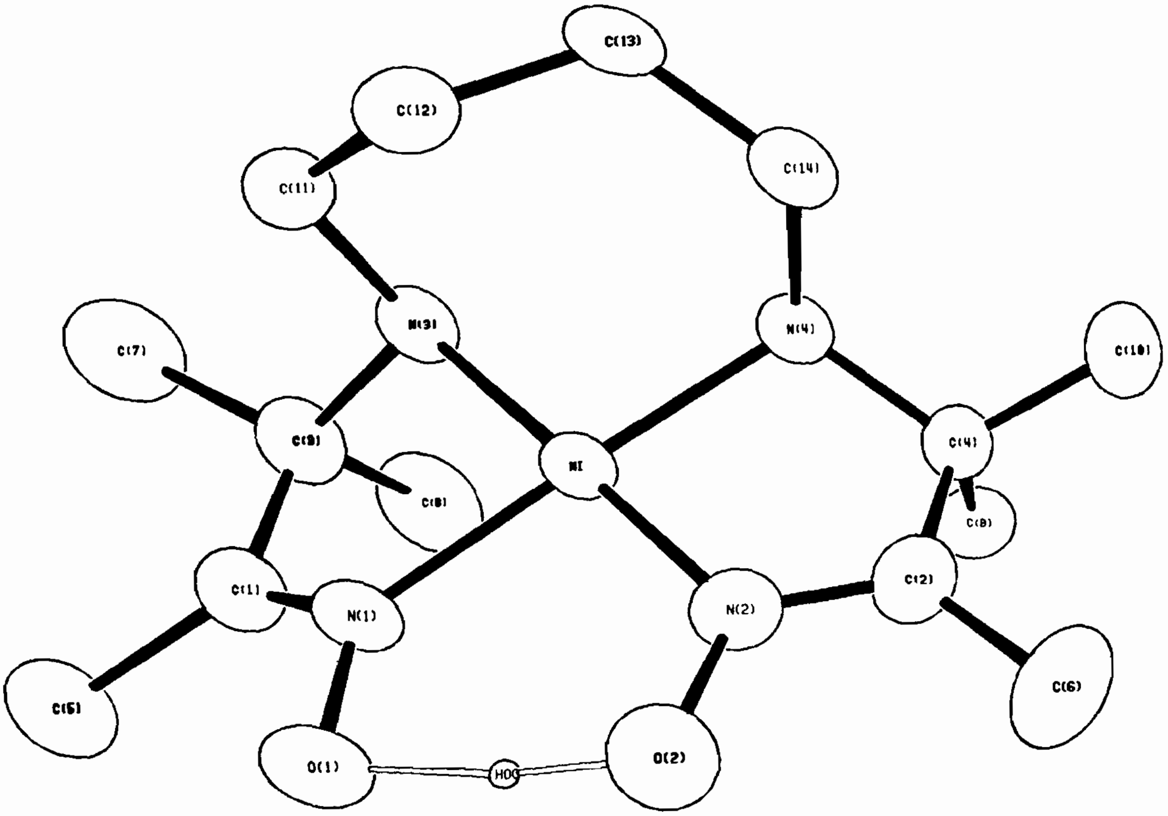

Fig. 1. Perspective view of the [Ni(BnAO-H)]$^+$ ion showing the atom labelling scheme and thermal ellipsoids.

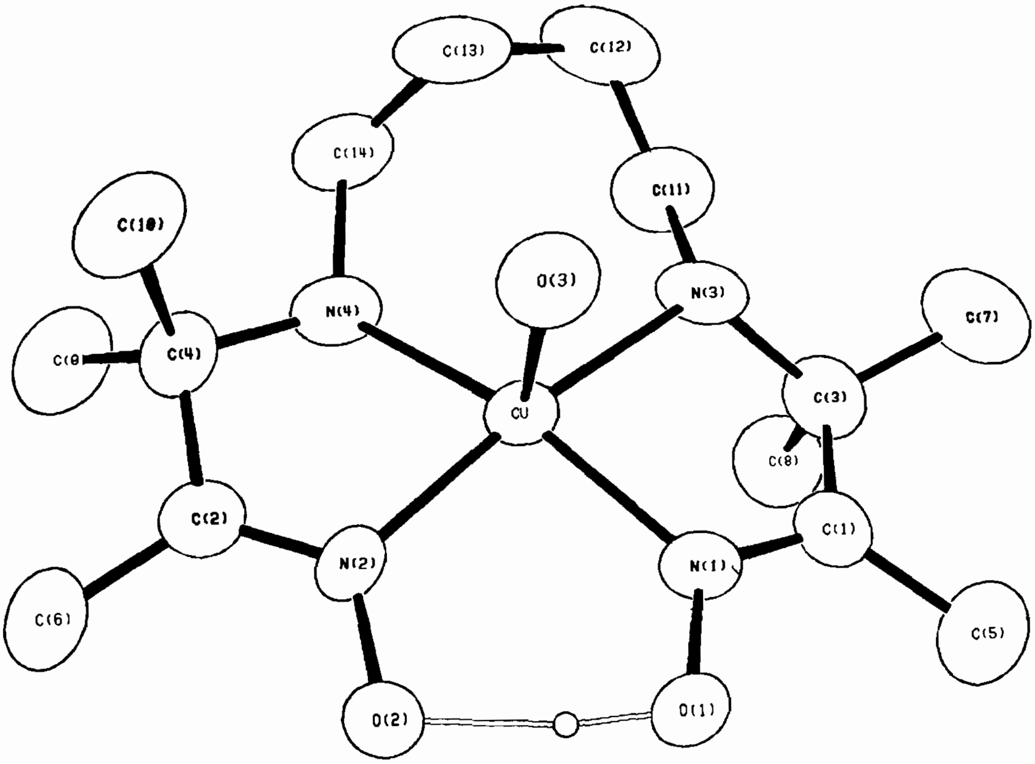

Fig. 2. Perspective view of the [Cu(BnAO-H)(H_2O)]$^+$ ion showing the atom labelling scheme and thermal ellipsoids.

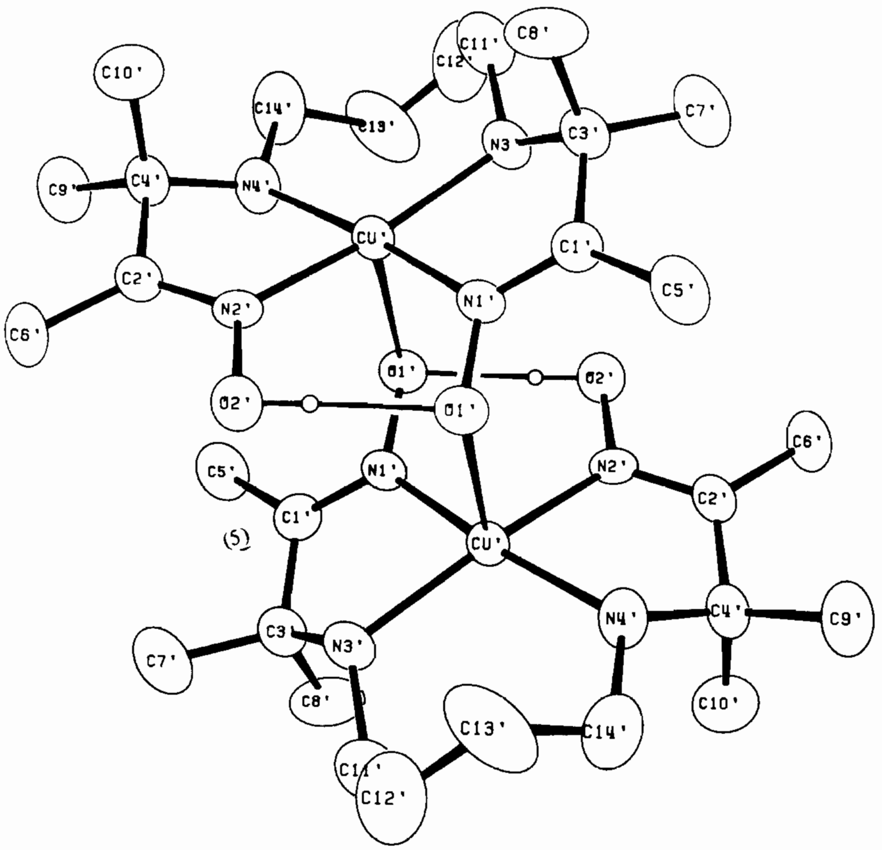

Fig. 3. Perspective view of the [(Cu(BnAO-H))$_2$] binuclear ion showing the atom labelling scheme and thermal ellipsoids.

TABLE VI. Bond Distances and Angles Involving the Hydrogen Bond in α-Amine Oxime Complexes of Ni(II) and Cu(II)

Compound	O···O (Å)	O(2)–H (Å)	O(1)–H (Å)	O(1)··HOO··O(2) (deg)	N–O(1) (Å)	N–O(2) (Å)	Reference
[Ni(BnAO-H)]I·H_2O	2.417(7)	1.116(5)	1.307(6)	172(5)	1.356(4)	1.363(4)	this work
[Ni(PnAO-H)]·Cl·H_2O	2.409(10)	1.16(2)	1.26(2)	170(1)	1.337(7)	1.338(7)	10
[Ni(AO)$_2$-H]Cl·H_2O	2.420(3)	1.187(5)	1.242(5)	169(3)	1.335(2)	1.346(2)	11
[Ni(EnAO-H)]ClO_4	2.478(5)	1.171(7)	1.316(8)	170(1)	1.349(2)	1.352(2)	12
[Ni(PreH)]ClO_4	2.425(5)	1.04(13)	1.45(13)	155(12)	1.339(8)	1.347(9)	13
[Cu(BnAO-H)H_2O]ClO_4	2.421(5)	1.437(3)	0.991	171(1)	1.356(5)	1.353(5)	this work
[(Cu(BnAO-H))$_2$](ClO_4)$_2$	2.531(5)	0.840	1.695	173(2)	1.373(5)	1.387(5)	this work
[Cu(PnAO-H)(ReO_4)]	2.46(2)	1.23(2)	1.23(2)	180.0	1.37(2)	1.37(2)	14
[Cu(PnAO-H)(CN)]·$\frac{1}{2}CH_3CN$	2.475(4)			175.1	1.367(4)	1.367(4)	15
[Cu(PreH)H_2O](ClO_4)·H_2O	2.49(2)				1.35(2)	1.33(2)	16
[(Cu(EnAO-H))$_2$](ClO_4)$_2$	2.698(6)	0.75	1.95		1.368	1.398	5

in any other intermolecular contacts. In addition X-ray located hydrogen atom positions are not sufficiently accurate for meaningful comparison.

Other aspects of the structures

The bond distances and angles of these compounds are similar to those in other α-amine oxime Ni(II) and Cu(II) complexes. The average M–N (amine) bond distances are significantly longer than the M–N (oxime) bond distances. The average Cu–N (amine) bond distance in [Cu(BnAO-H)H_2O]$^+$ is the longest among Cu(II) α-amine oxime complexes. This is probably indicative of weaker metal–ligand interaction in the BnAO complex compared with EnAO, PreH, AO or PnAO complexes. All C–C and C–N distances in the ligand moieties are quite reasonable in both complexes studied here. The average C–N (oxime) bond distances (1.280 and 1.278 Å, respectively) are close to those expected for a double bond and are similar to those observed in other amine oxime metal complexes. The difference in the two Ni–N (amine) distances in $[Ni(BnAO\text{-}H)_2]I \cdot H_2O$ is associated with the presence of hydrogen bonding between the water oxygens and an amine hydrogen. A similar difference is also observed for $[Cu(BnAO\text{-}H)H_2O]^+$ due to the hydrogen bonding between the perchlorate oxygens and the amine nitrogens.

The N–M–N angles in all of the Cu(II) and Ni(II) α-amine oxime complexes are distorted from ideal square planar values, depending upon the steric constraints of the ligand and the size of the metal ion. The largest deviation is observed in dimeric $[(Cu(BnAO\text{-}H))_2](ClO_4)_2$ where the N(amine)–M–N(amine) angle is found to be 106.70(2)°. The corresponding angles for the monomeric $[Cu(BnAO\text{-}H)H_2O]^+$ and $[Ni(BnAO\text{-}H)]^+$ species are 104.64(2) and 97.83(3) Å, respectively.

Conclusions

In contrast to the dinuclear complex with two bridging BnAO ligands observed [7] for Rh(III), BnAO acts as a normal tetradentate ligand with Ni(II) and Cu(II). The complexes studied here are analogous to those observed with other α-amine oxime ligands. The structure of the copper complex shows the usual five coordination and reveals a wide range of Cu–O distances for the fifth position in the Cu α-amine oxime complexes. The most unusual feature observed in this study is the cocrystallization of the monomeric and dimeric Cu(II) complexes. This strongly suggests an equilibrium between these two in aqueous media with the mixed salt being the least soluble.

Supplementary Material

Position parameters for the hydrogen atoms, thermal parameters, least-squares planes, and listing of structure factors for both compounds are available from the authors on request.

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