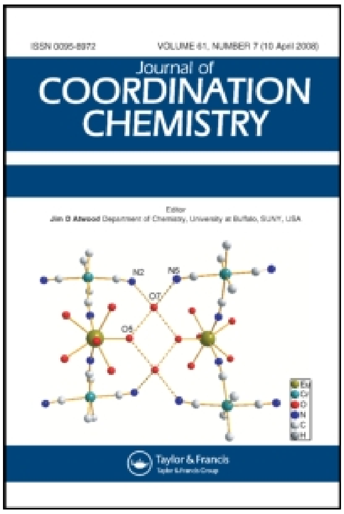

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SYNTHESIS, STRUCTURE AND SPECTROSCOPIC STUDIES OF ETHYLENEDIAMINE-*N, N*-BIS[1'-METHYL-3'-OXO-3'-(2''-HYDROXY-5''-METHYLPHENYL)PROPENYL] AND ITS MONO AND HOMOBINUCLEAR COMPLEXES WITH NICKEL(II) AND COPPER(II)

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SYNTHESIS, STRUCTURE AND SPECTROSCOPIC STUDIES OF ETHYLENEDIAMINE-*N,N'*-BIS[1'-METHYL-3'-OXO-3'-(2''-HYDROXY-5''-METHYLPHENYL)PROPENYL] AND ITS MONO AND HOMOBINUCLEAR COMPLEXES WITH NICKEL(II) AND COPPER(II)

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The title compound and its mono and homobinuclear complexes with Ni(II) and Cu(II) have been prepared. Spectroscopic and magnetic studies and crystal X-ray structure determinations show a slightly distorted square planar geometry for the mononuclear Cu(II) and Ni(II) complexes with the metals in the N_2O_2 compartment. Both compounds crystallize in the monoclinic space group $P2_1/n$, with $a = 8.382(1)$, $b = 15.435(1)$, $c = 17.216(1)$Å, $\beta = 100.62(1)°$; $R = 0.077$, with 1228 reflections for the Ni(II) complex and $a = 8.405(1)$, $b = 15.324(2)$, $c = 17.483(2)$Å, $\beta = 101.96(10)°$; $R = 0.075$, with 1255 reflections for the Cu(II) complex. The presence of Cu(II) causes slight changes in the structure and conformation of the complex. The spectroscopic and magnetic study for the dinuclear Ni(II) complex is consistent with an octahedral environment for the metal occupying the O_2O_2 site and a square planar geometry for that occupying the N_2O_2 site, whereas the spectroscopic and magnetic data for the dinuclear Cu(II) complex indicate a square planar structure that is slightly distorted around the metal occupying the N_2O_2 site and a square pyramid for that which occupies the O_2O_2 site.

Key words: Nickel, copper, Schiff base, x-ray structure

INTRODUCTION

The reaction of an α, β-diamine with a terminal keto function belonging to a β-triketone, ketophenol or ketocarboxylic acid leads to the formation of a Schiff base with two adjacent but non-equivalent coordination sites; one of these bases resembles a Schiff base and is referred to as N_2O_2, and the other can be compared with a β-diketone, a ketophenol or a ketocarboxylic acid and is therefore referred to as O_2O_2. The complexation of a ligand of this type to form a mononuclear complexes leads to the possible existence of two isomers, according to whether the coordination site occupied is N_2O_2 or the O_2O_2. The preference for either site depends upon hardness or softness of the cation, and also upon its size. The mononuclear complex can be treated with a second metallic cation to give a dinuclear complex.[1-3]

Thus for the mononuclear complexes of the Schiff base obtained by reaction of *o*-acetoacetylphenol with ethylenediamine it was shown that Ni(II) occupies the N_2O_2 site, while the much harder and larger UO_2^{2+} cation occupies the O_2O_2 site; with Cu(II), either isomer is obtained, according to the synthetic conditions.[4]

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Here, we report the preparation of the dinucleating acyclic Schiff base ethylenediamine-N,N'-bis[1'-methyl-3'-oxo-3'-(2"-hydroxy-5"-methylphenyl)-propenyl] (aacen) resulting from the condensation of ethylenediamine with 4-methyl-2-acetoacetylphenol. Mononuclear and homodinuclear complexes of Ni(II) and Cu(II) were prepared with the aacen ligand.

EXPERIMENTAL

Preparation of the ligand

To a solution of 4-methyl-2-acetoacetylphenol (1.92 g, 0.01 mol), previously obtained by the Baker method[5] from *p*-cresol, in ethanol (50 cm^3) was added dropwise ethylenediamine (0.33 cm^3, 0.005 mol). The resulting yellow solution was refluxed for half an hour, transferred to a vessel and after 3 days, the polycrystalline yellow solid was filtered off, then recrystallized from the minimum amount of chloroform. The compound melted with decomposition at 240°C, is insoluble in water, partially soluble in ethanol, cyclohexane and benzene, and soluble in chloroform and DMSO. *Anal.*: Calcd. for $C_{24}H_{28}N_2O_4$: C, 70.57; H, 6.96; N, 6.86%. Found: C, 70.34; H, 7.02; N, 6.68%.

Preparation of the complexes

The four complexes were prepared by a method described by Fenton *et al.* for complexes of a similar ligand.[4]

The complex Cu(aacen) is a bright brown solid that crystallized as needles, is soluble in chloroform, pyridine and dichloromethane, slightly soluble in methanol and ethanol, and insoluble in water, cyclohexane, carbon tetrachloride and benzene. *Anal.*: Calcd. for $C_{24}H_{26}N_2O_4Cu$: C, 61.33; H, 5.58; N, 5.96; Cu, 13.52%. Found: C, 61.42; H, 5.80; N, 6.35; Cu, 13.44%.

Cu_2(aacen) is a green solid, insoluble in water and in most common organic solvents, except in pyridine in which it takes on a brownish tone upon dissolving. *Anal.*: Calcd. for $C_{24}H_{24}N_2O_4Cu_2$: C, 54.23; H, 4.55; N, 5.27; Cu, 23.91%. Found: C, 54.17; H, 4.80; N, 5.27; Cu, 23.14%.

Ni(aacen) is a dark green solid that crystallized as needles, is soluble in chloroform, pyridine and dichloromethane, slightly soluble in methanol and ethanol, and insoluble in water, carbon tetrachloride, hexane, cyclohexane and benzene. *Anal.*: Calcd. for $C_{24}H_{26}N_2O_4Ni$: C, 61.91; H, 5.63; N, 6.02; Ni, 12.62%. Found: C, 62.25; H, 5.64; N, 6.14; Ni, 12.48%.

Ni_2(aacen) is a light green solid and is insoluble in water and in most common organic solvents. *Anal.*: Calcd. for $C_{24}H_{24}N_2O_4Ni_2$: C, 55.23; H, 4.63; N, 5.37; Ni, 22.50%. Found: C, 54.91; H, 4.30; N, 5.05; Ni, 22.63%.

The four complexes decompose without melting above 300°C.

Instruments and methods

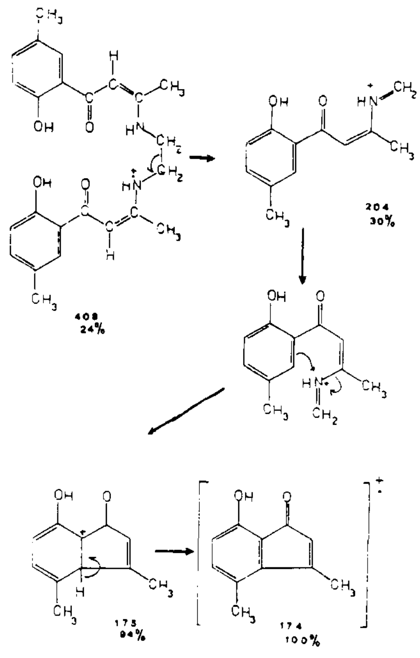
The C, H and N analyses were performed using a Carlo Erba I-102 analyser and Ni and Cu using a Perkin Elmer 305-B atomic absorption spectrophotometer. The mass spectra were measured on a VG Micromass ZAB-IF spectrometer, with direct introduction of the sample. The ^{1}H NMR spectra were run on a Bruker WP-200SY instrument using $CDCl_3$ as solvent and TMS as internal standard. IR spectra were obtained with a Beckman 20-AX spectrophotometer in the range 250–4000 cm^{-1}, in KBr pellets. Electronic spectra in the solid state were recorded on a Beckman DU-2 spectrophotometer (dispersing the products in $BaSO_4$) and in solutions on a Perkin Elmer 550S spectrophotometer. Magnetic susceptibility measurements were recorded at room temperature following the Gouy method using Hg[Co(NCS)$_4$] as the calibrating substance. The diamagnetic corrections were carried out according to Selwood.[6]

The X-ray data were collected on a computer-controlled Siemens AED-4 four-circle diffractometer, using graphite-monochromated CuK_α radiation in the ω:2θ scan mode.

RESULTS

Mass spectra

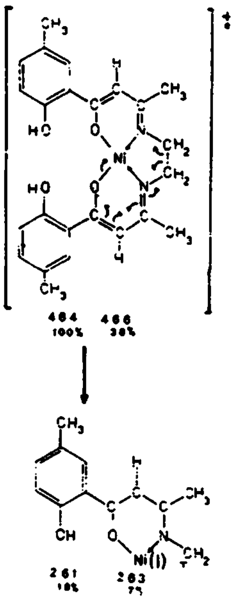
The mass spectrum of the ligand showed the peak corresponding to the molecular ion, *m/e* 408, 24% r.i., confirmed by high resolution mass spectrometry (experimental *m/e* 408.2000; theoretical *m/e* for $C_{24}H_{28}N_2O_4$, 408.2046). The base peak of the spectrum appeared at *m/e* 174, a fragment that in accordance with high resolution data (exp. *m/e* 174.0690; theor. *m/e* for $C_{11}H_{10}O_2$, 174.0680) could be explained by the mechanism proposed in Scheme I.



Scheme I

In the mass spectra of the mononuclear complexes, recorded at 70eV, the peaks corresponding to the molecular ions were observed at 464, 100% r.i. (exp. *m/e*, 464.1243; theor. *m/e* for $C_{24}H_{26}N_2O_4{}^{58}Ni$, 464.1243) and 469, 20% r.i. (exp. *m/e*, 469.1219; theor. *m/e* for $C_{24}H_{26}N_2O_4{}^{63}Cu$, 469.1188). The lower stability of the complex Cu(II) against electron impact was manifested by the lower intensity of the peak corresponding to the molecular ion, the presence in the spectrum of the base peak of the free ligand (*m/e*, 174, 100% r.i.) and by the appearance of the same fragments as in the Schiff base spectrum, which do not appear in the case of the Ni(II) complex.

In the Ni(II) complex, a fragment is observed corresponding to the peaks at *m/e* 261, 18% r.i., and 263, 7% r.i., for ^{58}Ni and ^{60}Ni, respectively, comprised of half the ligand and the metal, as observed in Schiff base complexes containing a chain of the ethylenediamine type (exp. *m/e*, 261.0299; theor. *m/e* for $C_{12}H_{13}N_2O^{58}Ni$, 261.0298). This cleavage can be explained by the fragmentation mechanism in Scheme II.



Scheme II

In the mass spectrum of the dinuclear Ni(II) complex, measured at 15 eV, the peak corresponding to the molecular ion is observed at *m/e* 520, 2% r.i. The remaining peaks of the spectrum are the same, with identical relative intensity, as those appearing in the corresponding mononuclear complex.

The peak corresponding to the molecular ion could not be detected for the dinuclear Cu(II) complex, even when a chemical ionization (methane) method was employed.

Magnetic behaviour of the complexes

The mononuclear Ni(II) complex is diamagnetic, while that of Cu(II) is paramagnetic with $\mu_{eff} = 1.80$ B.M. at room temperature. For the dinuclear Cu(II) complex, the effective magnetic moment for each Cu ion is 1.17 B.M. at room temperature, a value obtained by considering that the two metal ions contribute in the same measure to the magnetic behaviour of the complex.

For the dinuclear Ni(II) complex, by considering one metal to be paramagnetic and the other diamagnetic, the effective magnetic moment at room temperature is 3.46 B.M. (T.I.P. = 196×10^{-6} emu mol^{-1}), of the order obtained by other authors for dinuclear Ni(II) complexes of this type.[4,7]

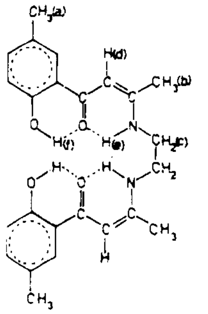


FIGURE 1 Schiff base aacen.

^1H NMR spectra

The ^{1}H nmr spectrum run in deuterated chloroform, showed for the ligand (Fig. 1) signals at 2.24δ (6H, s, methyls "a"), 2.06δ (2H, s, methyls "b"), 3.60δ (4H, d, methylene), 5.68δ (2H, s, vinyl), 6.8-7.5δ (6H, m, φ), 11.11δ (2H, broad, N-H .. O), 13.10δ (2H, s, O-H). This last signal disappeared after adding D_2O. The signal at 11.11δ disappeared when the spectrum was recorded 24 hours after adding the D_2O.

The spectrum of the ligand in deuterated chloroform was also measured. By irradiating at *11.11δ, the signal at 3.60δ collapsed to a singlet.*

The ^{1}H NMR spectrum of the diamagnetic complex Ni(aacen), in $CDCl_3$, showed signals at 2.19δ (6H, s, methyls "a"), 1.88δ (6H, s, methyls "b"), 3.04δ (4H, s, methylene), 5.54δ (2H, s, vinyls), 6.8-7.5δ (6H, s, φ) and 10.32δ (2H, s, O-*H*). This last signal disappeared immediately after addition of D_2O.

IR spectra

The IR spectrum of the ligand shows bands at 3200-2800 cm^{-1} that are broad and weak, ν(O-H .. O) and ν(N-H .. O); 1605 cm^{-1}, medium, ν(C=O); 1580^{-1}, strong, $\nu(C\doteq C)$;

TABLE I
Electronic spectral data.

Compound	λ/nm in solvent† D.R.	Chloroform	Pyridine
aacen	~420sh		
	365, 380	365, 380	365, 380
		(40000)	(38000)
Cu(aacen)	540	540	575
	~650sh	~650sh	
Cu_2(aacen)	580, 650		
	750sh		
Ni(aacen)	570	570	570
		(160)	(160)
Ni_2(aacen)	570	570	570
		(160)	(160)
	~1000	~1000	~1000

†D.R. = Difuse Reflectance; sh = shoulder; Extinction coefficients in parentheses, M^{-1} cm^{-1}.

TABLE II

Atomic positional parameters with estimated standard deviations for the mononuclear complexes.

Atom	*x/a*	*y/b*	*z/c*
Ni(aacen)			
Ni	0.7981(3)	0.4959(1)	0.1662(1)
O(1)	0.6749(10)	0.4311(4)	0.9859(4)
O(2)	0.6751(10)	0.4387(4)	0.2306(4)
O(3)	0.5125(11)	0.2926(6)	0.0717(4)
O(4)	0.3775(12)	0.4011(5)	0.2095(5)
N(1)	0.8930(13)	0.5641(6)	0.0990(5)
N(2)	0.9396(14)	0.5458(6)	0.2501(5)
C(1)	0.4976(17)	0.3056(7)	−0.0080(6)
C(2)	0.4042(17)	0.2450(8)	−0.0565(6)
C(3)	0.3846(18)	0.2513(8)	−0.1379(6)
C(4)	0.4561(17)	0.3172(7)	−0.1720(6)
C(5)	0.5444(16)	0.3789(7)	−0.1235(6)
C(6)	0.5671(16)	0.3749(7)	−0.0406(6)
C(7)	0.6662(16)	0.4404(7)	0.0093(6)
C(8)	0.7435(17)	0.5075(7)	−0.0217(6)
C(9)	0.8502(17)	0.5681(7)	0.0224(6)
C(10)	0.9120(18)	0.6398(8)	−0.0249(7)
C(11)	1.006(2)	0.6313(8)	0.1422(7)
C(12)	1.072(29)	0.5920(8)	0.0223(7)
C(13)	0.9389(18)	0.5358(7)	0.3247(6)
C(14)	1.074(21)	0.5735(8)	0.3869(7)
C(15)	0.8122(18)	0.4920(7)	0.3528(6)
C(16)	0.6840(18)	0.4496(7)	0.3075(6)
C(17)	0.5490(18)	0.4133(7)	0.3393(6)
C(18)	0.5580(17)	0.4019(7)	0.4211(6)
C(19)	0.4290(19)	0.3693(7)	0.4517(7)
C(20)	0.2846(20)	0.3486(8)	0.4028(8)
C(21)	0.2692(20)	0.3598(9)	0.3210(8)
C(22)	0.4035(20)	0.3912(8)	0.2901(7)
C(23)	0.4383(18)	0.3221(8)	−0.2611(7)
C(24)	0.4437(18)	0.3573(8)	0.5409(7)
Cu(aacen)			
Cu	0.7902(1)	0.4938(1)	0.1666(1)
O(2)	0.6593(6)	0.4397(3)	0.2317(2)
O(1)	0.6776(6)	0.4238(3)	0.0823(2)
O(3)	0.2915(3)	0.0614(2)	0.0614(2)
O(4)	0.3686(6)	0.3938(4)	0.2112(2)
N(1)	0.8921(7)	0.5652(3)	0.1006(3)
N(2)	0.9386(7)	0.5443(4)	0.2541(3)
C(1)	0.4898(9)	0.3058(4)	−0.0164(4)
C(2)	0.3960(9)	0.2464(4)	−0.0675(4)
C(3)	0.3816(9)	0.2550(5)	−0.1475(4)
C(4)	0.4595(9)	0.3210(4)	−0.1784(4)
C(5)	0.5488(8)	0.3804(4)	−0.1270(4)
C(6)	0.5673(8)	0.3749(4)	−0.0456(4)
C(7)	0.6673(8)	0.4391(4)	0.0076(4)
C(8)	0.7432(8)	0.5081(4)	−0.0199(4)
C(9)	0.8499(9)	0.5698(4)	0.0250(4)
C(10)	0.9137(10)	0.6418(5)	−0.0205(4)
C(11)	1.005(1)	0.6298(5)	0.1467(4)
C(12)	1.070(1)	0.5899(5)	0.2275(4)
C(13)	0.9369(9)	0.5339(4)	0.3275(4)
C(14)	1.071(1)	0.5710(5)	0.3907(4)
C(15)	0.0802(9)	0.4896(4)	0.3531(4)
C(16)	0.6766(9)	0.4485(4)	0.3076(4)
C(17)	0.5415(9)	0.4122(4)	0.3399(4)
C(18)	0.5525(9)	0.4028(4)	0.4204(4)
C(19)	0.4276(10)	0.3707(4)	0.4514(4)
C(20)	0.2823(10)	0.3468(5)	0.4026(5)
C(21)	0.2659(11)	0.3564(6)	0.3223(5)
C(22)	0.3965(10)	0.3876(5)	0.2902(4)
C(23)	0.4488(10)	0.3272(5)	−0.2653(4)
C(24)	0.4453(10)	0.3600(5)	0.5397(4)

1515 cm^{-1}, medium, $\nu(\mathrm{C}\doteq\mathrm{N})$ and $\nu(\mathrm{C}\doteq\mathrm{C})$; and 1280^{-1}, strong, $\nu(\mathrm{C{-}O})$. Bands are present at 1590 cm^{-1} in the spectra of the four complexes; strong, $\nu(\mathrm{C}\doteq\mathrm{O}$ and $\nu(\mathrm{C}\doteq\mathrm{C})$; 1515 cm^{-1}, medium, $\nu(\mathrm{C}\doteq\mathrm{N})$ and $\nu(\mathrm{C}\doteq\mathrm{C})$. The broad and weak band at 3200–2800 cm^{-1} that persists in the IR spectra of the mononuclear complexes, disappears in those of the dinuclear complexes. The band at 1280 cm^{-1} remains in the same position in the spectra of the mononuclear complexes, but is displaced to higher frequencies, around 1305 cm^{-1}, in those of the dinuclear complexes.[4,8,9]

Electronic spectra

The most significant bands in solid state and in solution, of the ligand and its Ni(II) and Cu(II) complexes prepared in this work are given in Table I.

Crystal data for the Ni(II) complex

Crystals of $C_{24}H_{26}N_2NiO_4$ (M = 438.98) are monoclinic, space group $P2_1/n$ with $a = 8.382(1)$, $b = 15.435(1)$, $c = 17.216(1)$Å, $\beta = 100.62(1)°$, $V = 2189.15(41)$Å^3, $Z = 4$. Of the 1266 independent reflections with $2\theta < 110°$, 1228 were considered observed with $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization factors but no absorption (μ = 15.1 cm^{-1}) correction was applied. The structure was solved by direct methods[10] and Fourier synthesis. Refinement by full-matrix least-squares with anisotropic temperature factors for the metal atom and isotropic factors for the light atoms[11] was carried out. Most of the H atoms were found in a difference synthesis map and the remainder placed in calculated positions[12] and included in subsequent refinements with fixed isotropic thermal contribution. Final R = 0.077 and Table II lists atomic positions. The molecular structure[13] is shown in Fig. 2.

Crystal data for Cu(II) complex

Crystals of $C_{24}H_{26}N_2CuO_4$ (M = 406.02) are monoclinic, space group $P2_1/n$ with $a = 8.405(1)$, $b = 15.324(2)$, $c = 17.483(2)$Å, $\beta = 101.96(10)°$, $V = 2202.82(90)$Å^3, $Z = 4$. Of

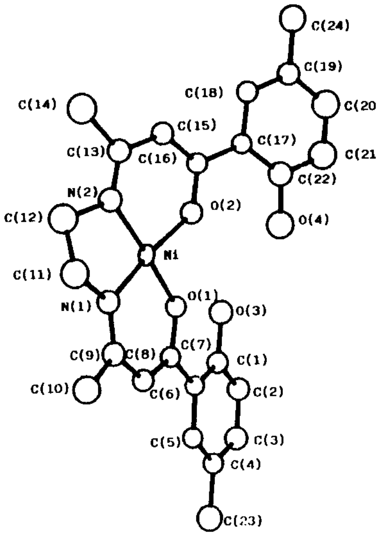


FIGURE 2 Molecular structure of Ni(aacen).

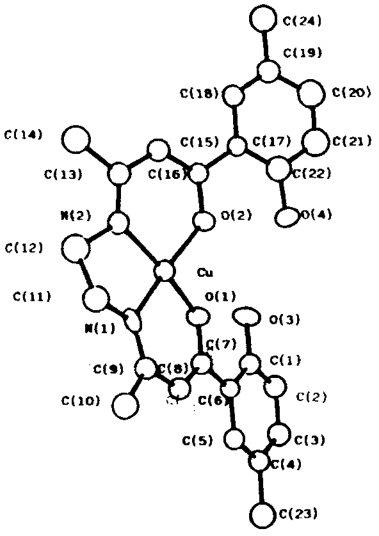


FIGURE 3 Molecular structure of Cu(aacen).

TABLE III
Bondlengths (Å) with estimated standard deviations for the mononuclear complexes.

Cu(aacen)		*Ni(aacen)*	
Cu-O(2)	1.926(5)	Ni-O(1)	1.859(7)
Cu-O(1)	1.908(4)	Ni-O(2)	1.869(8)
Cu-N(1)	1.916(6)	Ni-N(1)	1.850(10)
Cu-N(2)	1.926(6)	Ni-N(2)	1.859(9)
O(2)-C(16)	1.312(8)	O(1)-C(7)	1.314(12)
O(1)-C(7)	1.311(8)	O(2)-C(16)	1.323(13)
O(3)-C(1)	1.364(8)	O(3)-C(1)	1.369(13)
O(4)-C(22)	1.355(9)	O(4)-C(22)	1.374(14)
N(1)-C(9)	1.299(8)	N(1)-C(9)	1.302(13)
N(1)-C(11)	1.489(9)	N(1)-C(11)	1.506(16)
N(2)-C(12)	1.467(11)	N(2)-C(12)	1.475(19)
N(2)-C(13)	1.295(9)	N(2)-C(13)	1.294(15)
C(1)-C(2)	1.398(9)	C(1)-C(2)	1.395(16)
C(1)-C(6)	1.394(10)	C(1)-C(6)	1.385(17)
C(2)-C(3)	1.385(10)	C(2)-C(3)	1.384(16)
C(3)-C(4)	1.374(10)	C(3)-C(4)	1.367(18)
C(4)-C(5)	1.385(9)	C(4)-C(5)	1.387(15)
C(4)-C(23)	1.506(10)	C(4)-C(23)	1.515(16)
C(5)-C(6)	1.402(9)	C(5)-C(6)	1.405(14)
C(6)-C(7)	1.488(9)	C(6)-C(7)	1.479(15)
C(7)-C(8)	1.373(10)	C(6)-C(8)	1.380(17)
C(8)-C(9)	1.422(9)	C(8)-C(9)	1.415(16)
C(9)-C(10)	1.521(10)	C(9)-C(10)	1.520(18)
C(11)-C(12)	1.532(10)	C(11)-C(12)	1.516(17)
C(13)-C(14)	1.518(10)	C(13)-C(14)	1.524(18)
C(13)-C(15)	1.418(11)	C(13)-C(15)	1.417(20)
C(15)-C(16)	1.380(9)	C(15)-C(16)	1.371(17)
C(16)-C(17)	1.477(10)	C(16)-C(17)	1.458(20)
C(17)-C(18)	1.384(9)	C(17)-C(18)	1.406(15)
C(17)-C(22)	1.395(10)	C(17)-C(22)	1.393(19)
C(18)-C(19)	1.368(11)	C(18)-C(19)	1.382(21)
C(19)-C(20)	1.385(10)	C(19)-G(20)	1.379(20)
C(19)-C(24)	1.530(10)	C(19)-C(24)	1.528(17)
C(20)-C(21)	1.390(12)	C(20)-C(21)	1.401(19)
C(21)-C(22)	1.416(13)	C(21)-C(22)	1.416(20)

TABLE IV
Bond angles (°) with estimated standard deviations for the mononuclear complexes.

Cu(aacen)		*Ni(aacen)*	
N(1)-Cu-N(2)	87.2(3)	N(1)-Ni-N(2)	87.9(4)
O(1)-Cu-N(2)	167.4(3)	O(2)-Ni-N(2)	94.5(4)
O(1)-Cu-N(1)	93.9(2)	O(2)-Ni-N(1)	171.2(4)
O(2)-Cu-N(2)	93.3(2)	O(1)-Ni-N(2)	171.4(4)
O(2)-Cu-N(1)	169.3(2)	O(1)-Ni-N(1)	94.8(3)
O(2)-Cu-O(1)	87.8(2)	O(1)-Ni-O(2)	84.0(3)
Cu-O(2)-C(16)	126.6(5)	Ni-O(1)-C(7)	127.5(7)
Cu-O(1)-C(7)	126.0(4)	Ni-O(2)-C(16)	126.7(7)
Cu-N(1)-C(11)	111.7(4)	Ni-N(1)-C(11)	112.7(7)
Cu-N(1)-C(9)	125.6(5)	Ni-N(1)-C(9)	126.2(9)
C(9)-N(1)-C(11)	121.6(6)	C(9)-N(1)-C(11)	119.9(9)
Cu-N(2)-C(13)	126.8(6)	Ni-N(2)-C(13)	127.0(9)
Cu-N(2)-C(12)	110.3(4)	Ni-N(2)-C(12)	111.1(7)
C(12)-N(2)-C(13)	122.5(7)	C(12)-N(2)-C(13)	121.9(11)
O(3)-C(1)-C(6)	123.5(6)	O(3)-C(1)-C(6)	123.5(10)
O(3)-C(1)-C(2)	116.2(6)	O(3)-C(1)-C(2)	116.1(10)
C(2)-C(1)-C(6)	120.4(6)	C(2)-C(1)-C(6)	120.4(10)
C(1)-C(2)-C(3)	120.2(7)	C(1)-C(2)-C(3)	120.5(11)
C(2)-C(3)-C(4)	121.2(6)	C(2)-C(3)-C(4)	120.5(11)
C(3)-C(4)-C(23)	120.4(6)	C(3)-C(4)-C(23)	120.2(10)
C(3)-C(4)-C(5)	117.9(6)	C(3)-C(4)-C(5)	118.7(10)
C(5)-C(4)-C(23)	121.7(6)	C(5)-C(4)-C(23)	121.2(10)
C(4)-C(5)-C(6)	123.3(6)	C(4)-C(5)-C(6)	122.6(10)
C(1)-C(6)-C(5)	117.1(6)	C(1)-C(6)-C(5)	117.2(10)
C(5)-C(6)-C(7)	121.6(6)	C(5)-C(6)-C(7)	121.1(9)
C(1)-C(6)-C(7)	121.3(6)	C(1)-C(6)-C(7)	121.6(9)
O(1)-C(7)-C(6)	114.6(6)	O(1)-C(7)-C(6)	115.5(9)
C(6)-C(7)-C(8)	122.2(6)	C(6)-C(7)-C(8)	122.8(9)
O(1)-C(7)-C(8)	123.2(6)	O(1)-C(7)-C(8)	121.7(9)
C(7)-C(8)-C(9)	127.2(6)	C(7)-C(8)-C(9)	125.8(11)
N(1)-C(9)-C(8)	122.3(6)	N(1)-C(9)-C(8)	122.7(10)
C(8)-C(9)-C(10)	116.4(6)	C(8)-C(9)-C(10)	116.0(9)
N(1)-C(9)-C(10)	121.4(6)	N(1)-C(9)-C(10)	121.3(10)
N(1)-C(11)-C(12)	107.5(6)	N(1)-C(11)-C(12)	105.4(10)
N(2)-C(12)-C(11)	109.4(7)	N(2)-C(12)-C(11)	108.4(11)
N(2)-C(13)-C(15)	122.4(7)	N(2)-C(13)-C(15)	122.5(11)
N(2)-C(13)-C(14)	121.0(7)	N(2)-C(13)-C(14)	120.8(11)
C(14)-C(13)-C(15)	116.6(6)	C(14)-C(13)-C(15)	116.7(10)
C(13)-C(15)-C(16)	127.6(6)	C(13)-C(15)-C(16)	126.2(10)
O(2)-C(16)-C(15)	122.5(7)	O(2)-C(16)-C(15)	121.6(11)
C(16)-C(17)-C(22)	120.4(6)	C(15)-C(16)-C(17)	123.4(10)
C(15)-C(16)-C(17)	122.6(6)	O(2)-C(16)-C(17)	115.0(9)
C(16)-C(17)-C(18)	121.9(7)	C(16)-C(17)-C(22)	121.2(10)
C(18)-C(17)-C(22)	117.8(7)	C(16)-C(17)-C(18)	121.5(12)
C(17)-C(18)-C(19)	122.6(7)	C(18)-C(17)-C(22)	117.2(11)
C(18)-C(19)-C(24)	121.1(8)	C(17)-C(18)-C(19)	121.8(11)
C(18)-C(19)-C(20)	120.2(7)	C(18)-C(19)-C(24)	120.2(12)
C(20)-C(19)-C(24)	118.7(8)	C(18)-C(19)-C(20)	120.7(11)
C(19)-C(20)-C(21)	118.9(9)	C(20)-C(19)-C(24)	119.1(13)
C(20)-C(21)-C(22)	120.9(8)	C(19)-C(20)-C(21)	119.6(14)
C(17)-C(22)-C(21)	119.6(7)	C(20)-C(21)-C(22)	119.2(13)
O(2)-C(16)-C(17)	114.6(6)	C(17)-C(22)-C(21)	121.5(11)
O(4)-C(22)-C(21)	116.4(7)	O(4)-C(22)-C(21)	115.4(11)
O(4)-C(22)-C(17)	124.0(7)	O(4)-C(22)-C(17)	123.1(11)

the 1661 independent reflections with $2\theta < 100°$, 1555 were considered observed with $I > 3\sigma(I)$. The data were corrected for Lorentz and polarization factors but no absorption correction ($\mu = 14.1\ \mathrm{cm}^{-1}$) was applied. Structure solution and refinement was carried out as above for the Ni(II) complex, with the difference that anisotropic thermal motion was included for copper, oxygen and nitrogen atoms. Again the contribution of H-atoms was fixed isotropic. Final $R = 0.075$. Atomic positions are listed in Table II. Figure 3 shows the molecular structure. Tables III and IV list bond lengths and angles for the complexes. Tables of thermal parameters and observed and calculated structure factors have been deposited with the Editor and are available upon request. Throughout refinement, unit weights were used and the function minimized was $\Sigma\Delta^2$. At the end of the refinement, the maximum shift on error values for any parameter were 0.25 and 0.12 for the nickel and copper complexes, respectively.

DISCUSSION

The appearance in the ^{1}H NMR spectrum of signal at 11.11δ assigned to the resonance of the N-H . . . O protons[4,14,15] is consistent with the ligand structure proposed in Fig. 1.

The value of the effective magnetic moment for the complex Cu(aacen), 1.89 B.M., seems to indicate that this is a complex with a basically square-planar geometry around the central ion[16]. The diamagnetic behaviour of the corresponding Ni(II) complex suggests a square planar environment for the central ion.

For the diamagnetic complex Ni(aacen), the disappearance of the signal in the free ligand at 11.11δ in the NMR spectrum is in agreement with the structure in Fig. 2 with the metal sited in the N_2O_2 compartment. This complex is green in colour and its electronic spectrum shows, both in solid state and in solution, Table I, an intense ligand field band at approximately 570 nm ($\varepsilon = 160$ M^{-1} cm^{-1}) assigned to the $^1A_{2g} \leftarrow {}^1A_{1g}$ transition with square-planar stereochemistry around Ni(II).[17,18] The fact that the spectrum in pyridine solution is quite comparable indicates the conservation of the square-planar structure in donor solvents. The behaviour would be different, were the Ni(II) to be found in the O_2O_2 site, since oligomerization should be expected through the ketonic oxygens.

TABLE V
Summary of data for planar fragments of the two mononuclear complexes.

		M = Ni	M = Cu
Plane 1 [O(1), O(2), N(1), N(2)]	M	0.004	0.012
Out-of-plane displacements	O(3)	−0.747	−0.634
	O(4)	1.360	1.296
Plane 2 [M, O(1), N(1)]	C(7)	−0.039	−0.174
Out of plane displacements	C(8)	−0.191	−10.338
	C(9)	−0.199	−0.274
	C(10)	−0.472	−0.536
Plane 3 [M, O(2), N(2)]	C(13)	−0.028	−0.059
Out-of-plane displacements	C(14)	−0.172	−0.182
	C(15)	0.111	0.016
	C(16)	0.184	0.093
Plane 4 [O(1), N(1), C(7)–C(9)]			
Out-of-plane displacement	M	−0.108	−0.225
Plane 5 O(2), N(2), C(13)–C(16)			
Out-of-plane displacement	M	0.091	0.023
Angles (°) between planes			
2-3		11.5	16.1
2-4		5.3	10.0
3-5		4.0	1.4
4-5		16.8	20.2

In the complex Cu(aacen), the ligand field band at 540 nm also suggests a basically square-planar environment for the central ion (N_2O_2 compartment).[4,7,17] The shoulder at 620–680 nm, in solid state and in chloroform solution, suggests a distorsion towards a tetrahedral structure.[23] This distortion is in agreement with the magnetic moment compared with that of the corresponding complex without the CH_3 in a *para* position with respect to the OH in the benzene ring (1.63 M.B.),[4] and could be due to the greater steric hindrance introduced in the molecule by these methyl groups. In pyridine solution, the position of the band at 575 nm indicates the possibility of coordination of two molecules of pyridine to the metal ion, with a structure close to octahedral.[19]

The X-ray results confirm the above conclusions, indicating that for both complexes the metal atom is coordinated in the inner compartment (N_2O_2). In the two compounds there is a substantial twist between the two *cis* M–O–N planes, 11.5° (M = Ni) and 16.1° (M = Cu), leading to distortion towards tetrahedral geometry but without any large displacement of the metal out of the N_2O_2 plane. Table V shows significant planar data for both compounds.

The molecular conformation in both compounds is similar. For the nickel complex, the metal is displaced in opposite directions from each of the two iminodiketone chelates leading to a "stepped"[17] arrangement about the nickel. For the copper complex the arrangement is again "stepped" but the metal is closer to the O(2), N(2), C(13)–C(16) iminoketone fragment than to the other one.

In both compounds the five membered ring metal atom, N(1), N(2), C(11), C(12) has a half-chair conformation with the C_2 symmetry axis through the metal atom as shown in Table VI using Altona[20] and Cremer[21] parameters. The two compounds exhibit intramolecular hydrogen bonding between the phenolic hydrogen groups and the coordinating oxygen atom on the same side of the outer compartment. Oxygen-oxygen distances are 2.52 and 2.52 Å for the Ni complex and 2.49 and 2.50 Å for the Cu complex.

The effective magnetic moment for the dinuclear Ni(II) complex, 3.46 B.M., obtained by considering one of the metal ions in a square-planar surrounding to be diamagnetic, falls within the usual range of values for octahedral complexes of this ion.[4,7,22]

The electronic spectrum, Table I, in the solid state of the complex Ni_2(aacen) is consistent with an octahedral surrounding for the Ni(II) ion in the O_2O_2 compartment; bands at approximately 570 nm and 1000 nm corresponding to the transitions ${}^3T_1(F) \leftarrow {}^2A_{2g}$ and ${}^3T_{2g} \leftarrow {}^3A_{2g}$. The bands due to the transition octahedral surrounding, ${}^3T_{1g}(P) \leftarrow {}^3T_{2g}$, and in a square-planar stereochemistry for the other ion Ni(II) in the N_2O_2 compartment are to be found in the region of the charge-transfer bands and of the internal transitions of the ligand, and are therefore difficult to locate. The electronic spectrum and magnetic behaviour are consistent with an oligomeric structure as suggested by other authors for Ni(II) complexes with ligands of the same type as employed here.[4,17]

In the complex Cu_2(aacen), the value of the effective magnetic moment at room temperature, 1.17 B.M., smaller than that expected for the spin-only contribution, is of

TABLE VI
Conformational parameters for the M-N(2)-C(12)-C(11)-N(1) rings in the mononuclear complexes.

	Altona's parameters†		Cremer's parameters	
	Δ	φ_m	φ_2	Q
M = Ni	8°	−39°	85°	0.35 Å
M = Cu	8°	−39°	85°	0.35 Å

†Taking τ_0 opposite to the metal atom and in the sense C(12) → C(11).

the order found by Fenton *et al.*,[17] in similar dinuclear complexes and may be explained by metal-metal interactions with antiferromagnetic coupling stabilised through bridge oxygens.[19]

The split ligand bands at 580 nm and 650 nm are attributed to the basically square-planar CuN_2O_2 chromophore, with a slight twist between the planes.[4,8,17] The shift to lower energies with respect to Cu(aacen) may be due to the fact that this band is effected by the presence of the other copper atom in the next compartment (O_2O_2 site). The shoulder at 750 nm is attributed to a square-planar CuO_2O_2 chromophore.[6] The appearance of this band in the same region of the spectrum as that found for Cu(sal-*N*-CH_3)[23] whose structure, determined by X-ray analysis, indicates a square-planar stereochemistry, would seem to confirm this. However, the possibility of dimerization of the type indicated in complexes with pentacoordinate ligands having a square pyramidal structure can not be ruled out, as discussed by us previously.[24]

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