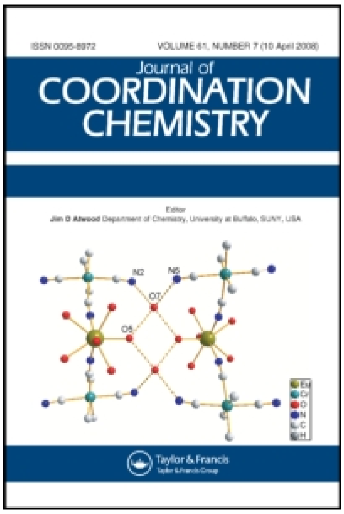

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NICKEL(II) AND EUROPIUM(III) COMPLEXES OF THE AMINOPHENOL LIGAND: 2-(DIETHYLAMINO)METHYLPHENOL (N~OH). CRYSTAL STRUCTURES OF THE $Ni(N{\sim}O)_2$ AND $[Eu(NO_3)_3(HN{\sim}O)_2]_2$ COMPLEXES

Abdelouahed Bouayad[a]; Nouzha Habbadi[b]; Fabienne Connac[c]; Michèle Dartiguenave[c]; Yolande Lucchese[c]; Lydia Lamandé[d]; Francine Bélanger-Gariépy[e]; André L. Beauchamp[e]; Yves Dartiguenave[c]; El Houssine El Ghadraoui[a]; Abdelaziz Souizi[b]
[a] Département de Chimie, Faculté des Sciences et Techniques, Université Sidi Mohamed Ben Abdellah, Saiss-Fes, Maroc [b] Laboratoire de Chimie, Organique et d'Agrochimie, Université Ibn Tofailm Faculté des Sciences, Kénitra, Maroc [c] Laboratoire de Chimie Inorganique, Université P. Sabatier, Narbonne, Toulouse, France [d] Laboratoire de Chimie et Physico-chimie, Organique (ESA CNRS 5068), Université P. Sabatier, Toulouse, France [e] Département de Chimie, Université de Montréal, Montréal, Québec, Canada

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NICKEL(II) AND EUROPIUM(III) COMPLEXES OF THE AMINOPHENOL LIGAND: 2-(DIETHYLAMINO)METHYLPHENOL (N ~ OH). CRYSTAL STRUCTURES OF THE $Ni(N\sim O)_2$ AND $[Eu(NO_3)_3(HN\sim O)_2]_2$ COMPLEXES

ABDELOUAHED BOUAYAD[a], NOUZHA HABBADI[b],
FABIENNE CONNAC[c], MICHÈLE DARTIGUENAVE[c,*],
YOLANDE LUCCHESE[c], LYDIA LAMANDÉ[d],
FRANCINE BÉLANGER-GARIÉPY[e], ANDRÉ L. BEAUCHAMP[e],
YVES DARTIGUENAVE[c], EL HOUSSINE EL GHADRAOUI[a]
and ABDELAZIZ SOUIZI[b]

[a]*Département de Chimie, Faculté des Sciences et Techniques, Université Sidi Mohamed Ben Abdellah, Saiss-Fes, Maroc;* [b]*Laboratoire de Chimie Organique et d'Agrochimie, Université Ibn Tofail, Faculté des Sciences, Kénitra, Maroc;* [c]*Laboratoire de Chimie Inorganique, Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse, France;* [d]*Laboratoire de Chimie et Physico-chimie Organique (ESA CNRS 5068), Université P. Sabatier, 118 route de Narbonne, 31062 Toulouse, France;* [e]*Département de Chimie, Université de Montréal, C.P. 6128, Succ. Centre-ville, Montréal, Québec H3C 3J7 Canada*

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The first Ni(II) compounds with aminophenol ligands were synthesized by reaction of 2-diethylaminomethylphenol and 2-diethylaminomethyl-4-methylphenol (N ~ OH) with dehydrated $NiCl_2$ in ethanol. They were characterized as *trans*-square planar $Ni(N\sim O)_2$ complexes by NMR and IR spectroscopies, mass spectrometry, elemental analysis and X-ray structure determination. When the ligand was reacted with $Eu(NO_3)_3$, the new dimeric complex $[Eu(NO_3)_3(HN\sim O)_2]_2$ was isolated. Elemental analysis, IR, magnetic moment and X-ray diffraction indicated that in this case formally neutral aminophenol ligands, in their zwitterionic form, are attached to the metal center through the phenolato oxygen and act either as bridging or as terminal groups. Their protonated amino substituents are involved in strong N—H---O

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*Corresponding author. Fax: 05 61 55 61 18, e-mail: dartigue@iris.ups-tlse.fr

hydrogen bridging. The metal shows nine-coordination, the coordination sphere of each europium being completed by three NO_3 groups.

Keywords: Nickel; Europium; Aminophenol; Synthesis; X-ray diffraction

INTRODUCTION

As a continuation of our work on the complexing properties of chelating aminophenol and phosphinophenol ligands, we have examined the reaction of the bidentate ligands 2-diethylaminomethylphenol and 2-diethylaminomethyl-4-methylphenol ($N\sim OH$) on NiX_2 ($X = Cl$, SO_4, NO_3) and on europium(III) nitrate. Our interest in this field originates from the high coordinative ability of such ligands for main group, transition and lanthanide metal centers and their ability to generate species that could be used as precursors for applications in medicinal chemistry [1, 2].

We have previously shown that 2-(dialkylaminomethyl)phenols ($N\sim OH$) bind to first row metals such as Cu(II) and Zn(II) [3, 4], as chelates *via* the deprotonated phenolate oxygen and nitrogen atoms but the complexes obtained had different stoichiometries. For Cu(II), a *trans* square-planar $Cu(N\sim O)_2$ compound precipitated. In contrast, $ZnCl_2$ gave a clean reaction only in the presence of Et_3N, yielding the $(HNEt_3)[ZnCl_2(N\sim O)]$ salt containing a tetrahedral zincate anion. With Ni(II), to our knowledge, no complexes have been reported so far, although a number of ($N\sim OH$) Schiff-base compounds are known [5], and a *trans* square-planar complex $Ni(N\sim O)_2$ has been described with the enolate of 2-piperidineacetophenone $[N(C_5H_{10})CH{=}C(Ph)O]^-$ [6]. This may be due to the basic character of the aminophenol, which likely enhances the formation of hydroxo-bridged polynuclear $[Ni(OH)_n]_{2-n}$ species in basic media [7–9], thus preventing complexation.

When NEt_3 is used to deprotonate the aminophenol, the $(HNEt_3)^+$ cation generated does not usually participate in complex formation as would the Li^+, Na^+ or other small counter cations [10]. Indeed, the aminophenol may behave as a ligand in the presence of hard metals like Li^+, Na^+, lanthanide ions or metals in their highest oxidation state. The trinuclear Ln_2Na complexes $[ClLn(N\sim O)_3Ln(N\sim O)_3Na]$, (where $Ln = Lu$ and Y) obtained by reaction of the sodium salt on Ln(III) chloride [11], is one example in which Ln and Na compete for the oxygen donor of the chelating ligand. However, no lanthanide complex with an $N\sim OH$ ligand has been reported yet. Interestingly, $N\sim OH$ reacted with the Re(V) complex $ReOCl_3(PPh_3)_2$, to give the zwitterionic $ReOCl_3(O\sim NH)PPh_3$ complex containing a monodentate O-bonded phenoxo ligand and an intramolecular N—H---Cl hydrogen bond [12].

The results, described here, are in agreement with the reactivity of the N$\sim$OH ligand. We have found an experimental procedure that allowed synthesis of the first Ni(II) complexes with aminophenol, which were shown by an X-ray structure determination to consist of square-planar Ni(II) species containing *trans*-O,O-coordinated diaminophenolate units. When reacted with $Eu(NO_3)_3$, N$\sim$OH behaves as a substituted phenolate group, giving a new zwitterionic, dimeric Eu(III) complex, stabilized by hydrogen bonds, which was characterized by X-ray diffraction.

EXPERIMENTAL

2-(Diethylaminomethyl)phenol (N1$\sim$OH) and 2-(diethylaminomethyl)-4-methylphenol (N2$\sim$OH) were synthesized by the standard literature method [13]. Commercial $NiCl_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (Aldrich) were used as received. Dehydration of the nickel salts was achieved by refluxing in dimethoxypropane. $Eu(NO_3)_3 \cdot 5H_2O$ was dehydrated by heating the solid *in vacuo* for 1 h. Ethanol was freshly distilled over 3 Å molecular sieves before use. All syntheses were run under a nitrogen atmosphere.

Infrared spectra ($4000-200\,cm^{-1}$) were recorded as KBr pellets on a Bruker Vector 22 spectrophotometer. ^1H NMR spectra were recorded in CD_2Cl_2 at RT on Bruker AC 80 and WM 250 spectrometers. The residual solvent signal for CD_2Cl_2 at 5.3 ppm was used as an internal standard and the chemical shifts (δ) are reported in ppm with respect to Me_4Si. Desorption Chemical Ionization mass spectra using NH_3 (DCI/NH_3) were recorded on a NERMAG R 1010 spectrometer. The magnetic moments were determined in the solid state at room temperature by the Faraday method, using a Cahn microbalance coupled with a Drusch electromagnet. $HgCo(NCS)_4$ was used as standard ($Xg = 16.44\ 10^{-6}$ cgs emu). The experimental values were corrected for the diamagnetism of the ligands [14]. Microanalyses were carried out at the Service de Microanalyse du CNRS, Lyon, for Ni and Eu, and at the Laboratoire de Chimie de Coordination du CNRS, Toulouse, for C, H and N.

Syntheses

Bis[2-(diethylaminomethyl)phenolato]nickel(II), Ni(N1$\sim$O)$_2$ (1)

To a stirred solution of N1$\sim$OH (1.07 g; 6.0 mmol) and NEt_3 (0.61 g; 6.0 mmol) in ethanol (10 mL) was slowly added a solution of $NiCl_2$ (0.38 g;

3.0 mmol) in ethanol (5 mL). The dark red solution was stirred for 30 min at RT. The red precipitate was filtered off, washed with cold alcohol and ether, and dried *in vacuo*. Yield: 90%. The same complexes were obtained starting from anhydrous Ni(SO$_4$) and Ni(NO$_3$)$_2$. Anal. Calcd. for $C_{22}H_{32}N_2O_2Ni$ (%): C, 63.64; H, 7.77; N, 6.76; Ni, 14.14. Found: C, 63.68; H, 7.87; N, 6.71; Ni, 13.93. Mass spectrum (*m*/*z*, DCI/NH$_3$): 415 [M+H]]$^+$. ^{1}H NMR (CD$_2$Cl$_2$, 250.13 MHz, ppm): 2.02 (*t*, 12H, N(CH$_2$—C*H*$_3$)$_2$); 2.30 (*m*, 4H, N(C*Ha*Hb—CH$_3$)$_2$; 2.94 (*s*, 4H, Ph—C*H*$_2$—N); 3.14 (*m*, 4H, N(CHa*Hb*—CH$_3$)$_2$; 6.42–7.12 (*m*, 8H, Ph). IR (KBr): 1285 cm^{-1}, ν(C—ONi).

Bis[2-(diethylaminomethyl)-4-methylphenolato]nickel(II), Ni(N2 ~ O)$_2$ (2)

The red complex was prepared like **1** by reacting 0.39 g (3.0 mmol) of NiCl$_2$ in ethanol (5 mL) with a mixture of 1.16 g (6.0 mmol) of N2 ~ OH and 0.60 g (6 mmol) of NEt$_3$ in EtOH (20 mL). Yield: 90%. Anal. Calcd. for $C_{24}H_{36}N_2O_2Ni$ (%): C, 65.03; H, 8.20; N, 6.33; Ni, 13.24. Found: C, 65.27; H, 8.27; N, 6.32; Ni, 13.29. Mass spectrum (*m*/*z*, DCI/NH$_3$): 443 [M+H]$^+$. ^{1}H NMR (CD$_2$Cl$_2$, 80.13 MHz, ppm): 2.01 (*t*, 12H, N(CH$_2$—C*H*$_3$)$_2$); 2.16 (*s*, 6H, C*H*$_3$—Ph); 2.34 (*m*, 4H, N(C*Ha*Hb—CH$_3$)$_2$; 2.94 (*s*, 4H, Ph—C*H*$_2$—N); 3.19 (*m*, 4H, N(CHa*Hb*—CH$_3$)$_2$; 6.25–7.06 (*m*, 6H, Ph). IR (KBr): ν(C—ONi), 1282 cm^{-1}.

Bis{μ-[2-(diethylammoniomethyl)-4-methylphenolato]} bis[2-(diethylammoniomethyl)-4-methylphenolatotrinitratoeuropium (III)], [Eu(NO$_3$)$_3$(HN2 ~ O)$_2$]$_2$ (3)

To a stirred solution of N2 ~ OH (0.77 g; 4.0 mmol) in ethanol (10 mL) was slowly added Eu(NO$_3$)$_3$ (0.68 g, 2.0 mmol) dissolved in ethanol (10 mL) at RT. The yellow solution was stirred for 2 h at 20°C. Removing the solvent *in vacuo* gave a residue that was extracted with CH$_2$Cl$_2$. Concentration of this solution and drying *in vacuo* gave a yellow product. Yield: 90%. Anal. Calcd. for $C_{24}H_{38}N_5O_{11}Eu$ (%): C, 39.79; H, 5.29; N, 9.67; Eu, 20.97. Found: C, 40.2; H, 5.11; N, 9.90; Eu, 20.97. IR (KBr): 1268 cm^{-1}, ν(C—OEu). μ_{eff}, 3.72 B.M. (solid). Recrystallization of the solid from CH$_2$Cl$_2$/ether at 20°C gave yellow single crystals suitable for X-ray work.

X-ray Diffraction Studies

In both cases, the crystal was mounted on a glass fiber and transferred to an Enraf-Nonius CAD-4 diffractometer. The reduced cell was determined from rotation photographs [15]. The space group was uniquely determined from the Laue symmetry and systematic absences checked in the final data set. Intensities were corrected for absorption (NRCVAX package [16], Gaussian integration based on crystal faces), and averaged. Crystal data and conditions for data collection are summarized in Table I.

TABLE I Crystal data

Compound	1	3
Chemical formula	$C_{22}H_{32}N_2NiO_2$	$[C_{24}H_{38}N_5O_{11}Eu]_2 \cdot 2\,CH_2Cl_2$
Formula weight, M_r	415.20	1619.0
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a(Å)	8.157(2)	11.991(2)
b(Å)	9.753(2)	15.470(2)
c(Å)	13.310(3)	18.135(2)
α(°)	90	90
β(°)	96.35(2)	102.94(2)
γ(°)	90	90
Volume, V(Å^3)	1052.4(4)	3279(1)
Z	4	2
D_{calc} (g cm^{-3})	1.310	1.640
μ(mm^{-1})	1.44	2.14
Radiation	CuKα	MoKα
Wavelength, λ (Å)	1.54056	0.71073
Temperature (K)	293(2)	170(2)
Transmission range		
$T_{max} - T_{min}$	0.70, 0.79	0.34, 0.64
No. of reflections measured	7413	5319
No. of independent reflections	1986	5136
No. of observed reflections	1765	3676
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.027	0.022
θ_{max}(°)	70.0	24.0
Ranges of h, k, l	$-9 \leq h \leq 9$ $-11 \leq k \leq 11$ $-16 \leq l \leq 16$	$-13 \leq h \leq 13$ $0 \leq k \leq 17$ $0 \leq 1 \leq 20$
Final R indices, $I > 2\alpha(I)$[a]	$R1 = 0.032$ $wR1 = 0.040$	$R1 = 0.0256$ $wR2 = 0.0463$
R indices, all data[a]	$R1 = 0.035$ $wR2 = 0.041$	$R1 = 0.0442$ $wR2 = 0.0486$
Goodness-of-fit S[a]	1.34 (on$\vert F \vert$)	0.937 (on F^2)

[a] $R1 = \Sigma(\|F_o| - |F_c\|/\Sigma(|F_o|)$, $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $wR1 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma(w|F_o|)^2)]^{1/2}$, S (on F^2) $= [\Sigma[w(F_o^2 - F_c^2)^2]/(\text{No. reflns} - \text{No. params})]^{1/2}$, S (on $|F|$) $= [\Sigma w(|F_o| - |F_c|)^2/(\text{No. reflns} - \text{No. params})]^{1/2}$.

Structure Resolution for Ni(N1 ~ O)$_2$ (1)

Suitable crystals were obtained by recrystallization from a toluene/ether mixture at −4°C. Structure resolution and refinement were done with NRCVAX. The Ni atom was found by direct methods and the remaining non-hydrogen atoms from ΔF syntheses. Refinement was done on $|F|$ by full-matrix least squares. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were initially introduced at idealized positions and refined isotropically in the last cycles. Refinement converged normally to $R = 0.032$. The highest residuals in the final ΔF map were $+0.24$ and -0.30 e/Å^3, whereas the general background was below ± 0.18 e/Å^3.

Structure Resolution for [Eu(NO$_3$)$_3$(HN2 ~ O)$_2$]$_2$

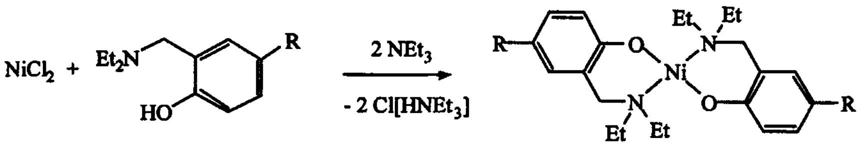
Single crystals were obtained by recrystallization from a CH_2Cl_2-ether mixture. The Eu atom was found by the direct methods of SHELXS-86 [17]. The remaining non-hydrogen atoms, including those of a CH_2Cl_2 solvent molecule, were located from successive ΔF syntheses calculated with SHELXL-93 [18]. Refinement was done on F^2 with SHELXL-93. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced at idealized positions and allowed to ride on the supporting atom, with C—H distances of 0.95 (ring), 0.86 (N—H) or 0.98 Å (others), and isotropic thermal parameters U_H set to 1.2 U_C (ring) or 1.5 $U_{C,N}$ (others). Refinement proceeded normally down to $R = 0.026$. The highest residuals in the final ΔF map were $+1.09$ and -0.85 e/Å^3 (near the CH_2Cl_2 molecule), whereas the general background was below ± 0.3 e/Å^3.

RESULTS AND DISCUSSION

Nickel Complexes

The addition of 1 equiv of anhydrous $NiCl_2$ to an ethanol solution containing 2 equiv of N ~ OH and 2 equiv of NEt_3 under an oxygen-free atmosphere resulted instantly in the quantitative formation of a dark-red precipitate of Ni(N ~ O)$_2$ (Scheme 1). This experimental procedure is essential since changes in the solvent or in the order of reactant addition generate the precipitation of an insoluble green solid.

The microanalyses are consistent with the proposed formula. The DCI/NH_3 mass spectra of **1** and **2** exhibit major peaks for the $[M+H]^+$ fragments at *m*/*z* values of 415 and 443, respectively. Coordination *via*, the



R = H (1)
R = Me (2)

SCHEME 1

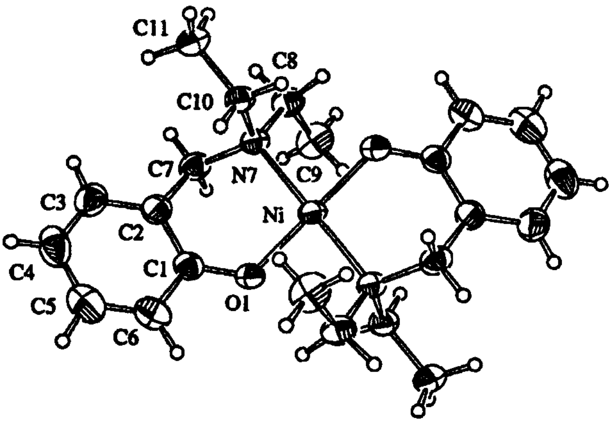


FIGURE 1 ORTEP drawing of the $Ni(N1 \sim O)_2$ (1). The Ni atom lies on a crystallographic inversion center. Ellipsoids correspond to 35% probability. Hydrogens are shown as spheres of arbitrary size.

phenolato oxygen is evidenced in the solid-state IR spectra by the shift of the ν(C—ONi) vibration to $\sim 1284\,cm^{-1}$ from the free ligand ν(C—OH) values of $\sim 1258\,cm^{-1}$. The two complexes are diamagnetic in the solid state, in agreement with square-planar coordination.

The crystal structure of 1 was determined by X-ray diffraction. The unit cell contains *trans* square-planar $Ni(N1 \sim O)_2$ molecules (Fig. 1) lying on crystallographic inversion centers. Selected bond lengths and angles are listed in Table II.

The metal is surrounded by a slightly distorted square plane created by two symmetry-equivalent 2-(diethylaminomethyl)phenolato ligands forming chelate rings *via* the phenolate oxygen and the amino nitrogen atom. The *trans* bond angles are exactly 180° and the NiN_2O_2 core is rigorously planar by symmetry. The main distortion results from the bite of the ligand, which makes the intra-ring N—Ni—O angle (93.17(6)°) slightly greater than 90°

TABLE II Selected interatomic distances (Å) and bond angles (deg) in $Ni(N1 \sim O)_2$ (1)

Distances			
Ni—O1	1.8520(12)	Ni—N7	1.9924(14)
O1—C1	1.338(2)		
Angles			
O1—Ni—O1[a]	180.0	O(1)—Ni—N7	93.17(6)
O1—Ni—N7[a]	86.83(6)	N7—Ni—N7[a]	180.0
Ni—O1—C1	119.5(1)	Ni—N7—C7	112.7(1)
Ni—N7—C101	111.4(1)	Ni—N7—C102	104.8(1)
C7—N7—C101	108.4(1)	C7—N7—C102	110.1(1)
C101—N7—C102	109.3(1)		

[a] $-x, -y, -z$.

TABLE III Torsion angles (deg) in the chelate rings of $Ni(N1 \sim O)_2$ (1)

Ni—O1—C1—C2	54.0(1)	C2—C7—N7—Ni	54.7(1)
O1—C1—C2—C7	1.7(1)	C7—N7—Ni—O1	−7.8(1)
C1—C2—C7—N7	−59.0(1)	N7—Ni—O1—C1	−45.0(1)

and reduces the inter-ring angle to 86.83(6)°. The Ni—O and Ni—N bond lengths of 1.852(1) Å and 1.992(1) Å, respectively, compare well with those of known square-planar Ni(II) complexes [5, 19]. The related copper complex shows a similar *trans* square-planar structure, with greater bond lengths (by 0.05 Å for Cu—O and 0.10 Å for Cu—N), in agreement with the greater ionic radius of Cu^{2+}, and smaller O—Cu—N bite angle (92.42(10)°). The six-membered metallacycle is not planar, but adopts an approximate boat conformation. The pattern of torsion angles around the ring for an idealized boat conformer would be 60°/0°/−60°/60°/0°/−60°. The set of values in Table III (54°/2°/−59°/55°/−8°/−45°) reveals deviations similar to those found in other complexes [3, 4], due to the disparity in bond lengths around the ring and the presence of both sp^2 (aromatic ring) and sp^3 (side arm) hybridized atoms.

The ligand shows no unexpected structural features. The C—O distance of 1.338(2) Å, close to those found in the Zn(II) and Cu(II) compounds, is significantly shorter than the C—OH distance (1.356(2) Å) noted when the phenol group is not deprotonated [32]. The mean value of the C—N—C angles (109.3°) is typical of a coordinated —CH_2NR_2 side-arm [3, 4, 32].

Complexes **1** and **2** retain their *trans* square-planar structure and diamagnetism in solution as evidenced from their electronic and ^{1}H NMR spectra. The UV-visible spectra for both complexes show three low-intensity bands at 370 nm ($\varepsilon = 540\,M^{-1}cm^{-1}$), 526 nm (*sh*, $\varepsilon = 97\,M^{-1}cm^{-1}$) and 610 nm (*sh*, $\varepsilon = 90\,M^{-1}cm^{-1}$), assigned to the lowest-energy spin-allowed ligand-field absorptions expected for d^8 square-planar coordination [20].

The ^{1}H NMR spectra of **1** and **2**, taken in CD_2Cl_2 at RT immediately after dissolution, show singlets at 2.94 ppm for the methylene group adjacent to the phenyl ring. Although the two methylene protons are not equivalent in the solid-state structure since the six-membered ring is puckered, only one singlet is observed because fast exchange between the two mirror-related conformers averages these two protons. The multiplets in the range 6.2–7.2 ppm are due to the phenyl protons and the singlet at 2.16 ppm for **2** corresponds to the ring methyl group. Non-rigidity of the metallacycle also makes the two ethyl substituents of the amino group equivalent. The methyl protons appear as a *pseudo*-triplet at ~2.01 ppm, significantly shifted downfield with respect to the free ligands (~1.11 ppm). The two ethyl CH_2 protons are not equivalent and appear as well separated signals, as commonly observed for aminophenol chelates. The doublet of quartets at ~2.32 ppm is assigned to one of these protons (Ha), which is shifted upfield from the free ligand value (~2.60 ppm) and coupled with the geminal proton Hb and the adjacent methyl protons. The second doublet of quartets at ~3.17 ppm, which resonates downfield from the free ligand, corresponds to the Hb proton similarly coupled with Ha and the methyl group.

The variation of the NMR spectra with time in dichloromethane and benzene indicates that these nickel complexes are labile in solution. Figure 2

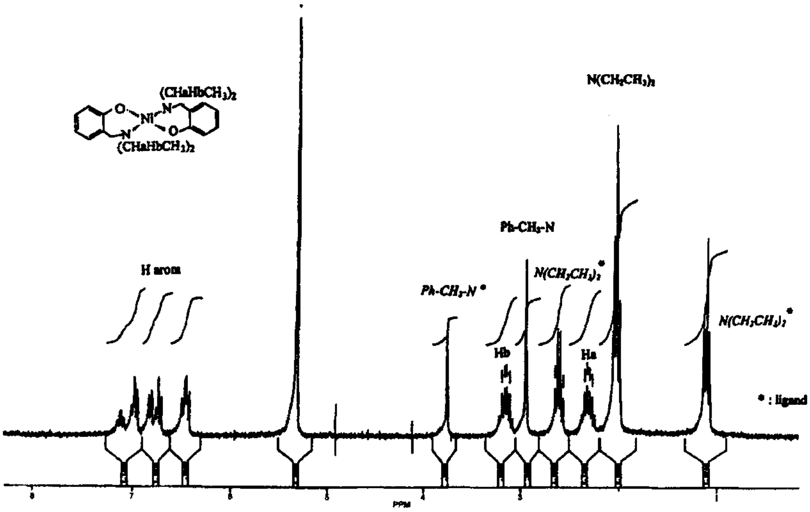


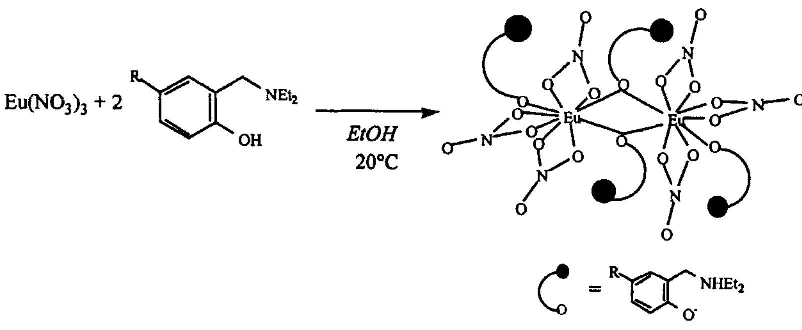
FIGURE 2 ^{1}H NMR spectrum (250 MHz) of Ni(N1 ~ O)$_2$ (**1**) at room temperature in CD_2Cl_2 30 minutes after dissolution.

shows the ^{1}H NMR spectrum of **1** taken 30 minutes after dissolution. Besides those of **1**, clean signals for the free ligand are present at 1.09 ppm for the methyl protons, at 2.60 for the ethyl methylene protons, and at 3.76 ppm for the methylene group bonded to the ring, whereas extra multiplets are detected between 6 and 7 ppm corresponding to the phenyl protons. After 1 h, these ligand signals have broadened and gained intensity, and after 24 h, only very broad resonances are present in this region, indicating the presence of paramagnetic species.

EUROPIUM COMPLEX

The addition of two equivalents of anhydrous $Eu(NO_3)_3$ (obtained by heating $Eu(NO_3)_3 \cdot 5H_2O$ at 100°C *in vacuo*) to an ethanol solution of N2$\sim$OH with or without NEt_3, under an oxygen-free atmosphere, afforded the dimeric complex $[Eu(NO_3)_3(HN2\sim O)_2]_2$ (**3**) as a yellow crystalline solid in nearly quantitative yield (Scheme 2). **3** is soluble in dichloromethane.

The microanalysis is consistent with the proposed formula. The IR spectrum shows signals at 1605, 1486 (aromatic ring stretch) and 1439 cm^{-1} due to the coordinated ligand. The strong ν(C—OEu) at 1268 cm^{-1} is slightly shifted to a higher wavenumber from the free ligand value (1259 cm^{-1}), indicating coordination *via* the phenolato oxygen. In the same energy range are expected the stretching bands of chelating bidentate NO_3^- anions [21], which are observed at 1493, 1320 and 1030 cm^{-1}. The presence of a quaternized nitrogen atom is deduced from the ν(N—H) stretch at 3176 cm^{-1} and by weak vibrations in the 2700–2900 cm^{-1} range [22]. The complex is paramagnetic as expected for a Eu(III) center with an [Xe]4f^6



3

SCHEME 2

configuration: its solid-state RT magnetic moment μ_{eff} is 3.72 B.M., in agreement with the values usually found for Eu(III) (3.86 B.M.) [23].

The crystal structure of 3 was determined by X-ray diffraction. An ORTEP drawing of the molecule is given in Figure 3 and a simplified diagram showing only the immediate environment of the metal is provided in Figure 4. Selected interatomic distances and bond angles are listed in Table IV.

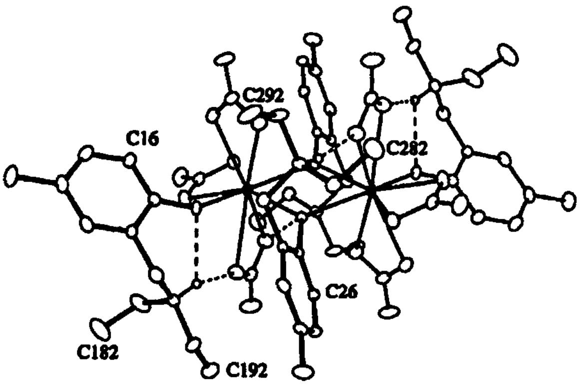


FIGURE 3 ORTEP drawing of $[\mathrm{Eu(NO_3)_3(HN2{\sim}O)_2}]_2$ (3). The dinuclear unit occupies a crystallographic inversion center lying halfway between the Eu atoms. The two aminophenol ligands in one of the asymmetric units are shown with full sticks. Dashed lines correspond to hydrogen bonds involving the protonated amino groups. Ellipsoids correspond to 35% probability and hydrogens (except those of the ammonium groups) are omitted for simplicity.

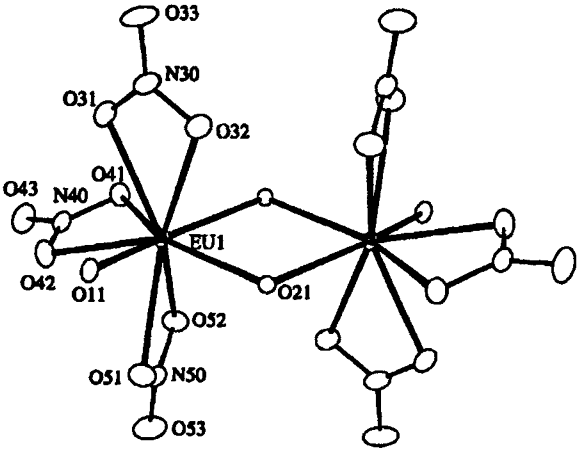


FIGURE 4 Central core of the dinuclear molecule of Figure 3, where the aminophenol ligands, except the phenolate oxygens, have been removed.

TABLE IV Interatomic distances (Å) and bond angles (deg) in $[\mathrm{Eu(NO_3)_3(HN2{\sim}O)_2}]_2 \cdot 2\mathrm{CH_2Cl_2}$ (3)

Environment of Europium			
Eu—O11	2.229(3)	Eu—O21	2.353(2)
Eu—O21[a]	2.430(2)	Eu—O31	2.492(3)
Eu—O32	2.534(3)	Eu—O41	2.567(3)
Eu—O42	2.506(3)	Eu—O51	2.595(3)
Eu—O52	2.521(3)		
O11—Eu—O21	89.13(9)	O11—Eu—O21[a]	156.27(9)
O21—Eu—O21[a]	71.58(9)	O31—Eu—O21[a]	95.43(9)
O32—Eu—O21[a]	80.07(9)	O41—Eu—O21[a]	75.13(8)
O42—Eu—O21[a]	124.60(9)	O51—Eu—O21[a]	114.62(9)
O52—Eu—O21[a]	76.56(9)	O11—Eu—O31	85.32(10)
O21—Eu—O31	127.54(10)	O11—Eu—O32	82.21(10)
O21—Eu—O32	76.91(9)	O31—Eu—O32	50.64(10)
O42—Eu—O32	125.03(10)	O52—Eu—O32	156.49(10)
O11—Eu—O41	126.37(9)	O21—Eu—O41	143.92(9)
O31—Eu—O41	68.73(10)	O42—Eu—O41	50.60(9)
O52—Eu—O41	65.55(10)	O32—Eu—O41	110.73(10)
O11—Eu—O42	78.73(10)	O21—Eu—O42	152.28(9)
O31—Eu—O42	76.65(10)	O11—Eu—O51	72.64(9)
O21—Eu—O51	77.31(9)	O31—Eu—O51	147.09(10)
O42—Eu—O51	75.31(10)	O52—Eu—O51	49.26(9)
O32—Eu—O51	143.96(9)	O41—Eu—O51	104.96(9)
O11—Eu—O52	119.36(10)	O21—Eu—O52	93.16(9)
O31—Eu—O52	134.13(10)	O42—Eu—O52	72.04(10)
C11—O11—Eu	146.7(2)	C21—O21—Eu	127.9(2)
C21[a]—O21[a]—Eu	121.5(2)	Eu—O21[a]—Eu	108.42(9)
Phenolate ligands			
O11—C11	1.338(5)	O21—C21	1.360(4)
O11—C11—C12	120.0(4)	O21—C21—C22	122.0(3)
O11—C11—C16	123.0(4)	O21—C21—C26	120.2(3)
C181—N17—C191	114.5(3)	C281—N27—C291	113.7(3)
C17—N17—C181	115.1(3)	C27—N27—C281	111.8(3)
C17—N17—C191	109.5(3)	C27—N27—C291	111.9(3)
C182—C181—N17	113.3(4)	C282—C281—N27	113.4(4)
C192—C191—N17	114.6(4)	C292—C291—N27	113.9(3)

Nitrate ligands					
N30—O31	1.279(5)	N30—O32	1.265(5)	N30—O33	1.212(5)
N40—O41	1.264(4)	N40—O42	1.276(4)	N40—O43	1.224(4)
N50—O51	1.261(4)	N50—O52	1.265(4)	N50—O53	1.217(4)
O33—N30—O32	122.7(4)	O33—N30—O31	121.9(4)	O32—N30—O31	115.4(3)
O43—N40—O41	121.5(4)	O43—N40—O42	121.2(3)	O41—N40—O42	117.2(3)
O53—N50—O51	122.6(4)	O53—N50—O52	122.3(4)	O51—N50—O52	115.2(3)

[a] $1-x, -y, 2-z$.

The unit cell contains a centrosymmetric dinuclear species in which two Eu(III) centers are bridged by two phenolato oxygens of aminophenol ligands in their zwitterionic form. Nine-coordination about each europium atom is completed by three bidentate NO_3^- anions and by a terminal zwitterionic aminophenol acting as a monodentate ligand *via* its phenolato oxygen.

Phenolato-bridged dimers are not common in europium chemistry and up to now, only two complexes with calixarene ligands have been described [24, 25]. The Eu-Eu separation of 3.880(1) Å is much greater than the sum of the Eu^{3+} ionic radii (2.24 Å) [26]. On the other hand, it is not uncommon for NO_3^- to stabilize lanthanide complexes by acting as bidentate oxygen donors. Several examples of such nitrate-Eu(III) complexes are known, in which the metal is nona- or decacoordinated, depending on the steric requirements of the ancillary ligand [27–31].

The phenolate bridge is asymmetric with Eu—O bond lengths of 2.353(2) and 2.430(2) Å. The terminal Eu—O bond is shorter (2.229(3) Å) as expected. The Eu—O—C angles are 121.5(2)° and 127.9(2)° for the bridging and 146.7(2)° for the terminal ligand. The observed combination of short M—O distances with large M—O—C angles has already been noted for early transition metal compounds in which oxygen-$p\pi$-to-metal-$d\pi$ interactions take place.

The three NO_3^- ions are bidentate with an approximate C_{2v} symmetry. The free N—O distances (mean 1.218 Å) are definitely shorter than those of coordinated N—O bonds (mean 1.269 Å). The Eu—O (nitrate) distances lie between 2.492(3) and 2.595(3) Å, significantly above those with the phenolate ligands, but in the range observed for the structurally characterized Eu-nitrato complexes. The three ligands are bonded in a slightly asymmetric fashion, the greatest disparity (Eu—O51 = 2.595(3), Eu—O52 = 2.521(3) Å) being found for the N50 ligand involved in hydrogen bonding.

The phenolato ligand shows no unexpected feature. The C—O distances of 1.338(5) Å (O11—C11, terminal) and 1.360(4) Å (O21—C21, bridging) are normal for terminal and bridging phenolato ligands, respectively. The mean values of the C—N—C angles in the protonated diethylaminomethyl group are 113.0° for terminal ligand and 112.5° for the bridging one. These values are typical of protonated ammonium pendent arms and agree with those observed for the nitrate salt of protonated 2-(diethylaminomethyl)-4-methylphenol and related molecules [32].

The compound is stabilized by hydrogen bonding. The ammonium group in the bridging aminophenol forms an almost linear N27—H---O52 bond (N27—O52 = 2.820(4) Å, N17—H—O52 = 166°) with a nitrate oxygen. The group in the terminal ligand is involved in a bifurcated interaction with another oxygen of the same nitrate and its own phenolate group: N17—O51 = 2.978(4) Å, N17—O11 = 2.870(4) Å, N17—H—O51 = 146°, N17—H—O11 = 124°.

In summary, the aminophenol ligands do not form chelate rings in the present compound, they behave simply as a sterically demanding phenolate ligand.

CONCLUSION

The aminophenols are readily deprotonated during the complexation with Ni(II) and they behave as chelating agents, giving mononuclear *trans*-$Ni(N{\sim}O)_2$ molecules. Such behavior was already observed for other first-row metal complexes. In contrast, the more electrophilic Eu^{3+} forms a dinuclear molecule, in which the aminophenols are bonded in their zwitterionic form and attached to the metal center through their phenolato oxygen, one acting as a bridging, the other as a terminal ligand. Their protonated amino substituent is involved in N—H---O hydrogen bonding providing extra stability to the complex. Few lanthanide complexes have been reported with aminophenolate ligands. Compounds such as **3** are of interest, since potentially bidentate ligands of this type could prevent the formation of insoluble polymeric species commonly observed with simple phenolates. Attempts to prepare Eu(III) species containing deprotonated ligands by adding NEt_3 have not been successful so far, only ill defined mixtures of products being obtained.

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