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Synthesis, characterization and molecular structures of homo- and heterometallic nickel(II) aminoalkoxides $Ni(\eta^2\text{-}OR^N)_2$ and $Ni(Ni_{0.25}Cu_{0.75})_2(\mu_3\text{-}OH)(\mu\text{-}OAc)(\eta^1\text{-}OAc)_2(\mu,\eta^2\text{-}OR^N)_2(\eta^2\text{-}R^NOH)$ ($R^N = CHMeCH_2NMe_2$)

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Abstract

Soluble Ni(II) alkoxides, namely the dimethylaminoisopropoxide clathrate with toluene, $Ni(\eta^2\text{-}OR^N)_2{\cdot}C_7H_8$ (**I**) and the solvent free crystalline $Ni(OR^N)_2$ ($R^N = CHMeCH_2NMe_2$) species (**II**), obtained by sublimation of **I** in vacuo, were characterized by X-ray diffraction. The reaction between $Ni(OR^N)_2$ and copper carboxylates such as propionate and copper acetate hydrate in hydrocarbons afforded $[CuNi_2(O_2CEt)_3(OR^N)_3(R^NOH)]$ (**III**) and $[Ni(Ni_{0.25}Cu_{0.75})_2(\mu_3\text{-}OH)(\mu\text{-}OAc)(\eta^1\text{-}OAc)_2(\mu,\eta^2\text{-}OR^N)_2(\eta^2\text{-}R^NOH)]$ (**IV**), respectively. The structures of **I** and **II** are based on square planar molecules of the *trans* isomer. The structure of **IV** corresponds to triangular aggregates with a $M_3(\mu_3\text{-}OH)$ central core. The remarkable feature is the presence of three types of coordination sphere, one metal is coordinated octahedrally and corresponds to nickel and the other two have square pyramidal and square planar coordinations, respectively, and an electronic density corresponding to Cu (75%) and Ni (25%). The monodentate behavior of the two acetato ligands is stabilized by intramolecular hydrogen bonding involving the hydroxyl functionalities of the μ_3-hydroxo (2.776(9) Å) and the solvated aminoalcohol ligand (2.573(6) Å). Magnetic data in the 20–300 K temperature range for **III** and **IV** account for three uncoupled metal centers at high temperature whereas ferromagnetic exchange interactions are likely below 20 K. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Nickel; Copper; Functional alkoxides; Carboxylates; Sol–gel; Heteronuclear; X-ray structures

1. Introduction

Multicomponent oxides such as perovskites or spinels based on transition metals like iron, manganese, nickel or cobalt display a number of attractive properties [1,2]. Rare earth nickelates, $LnNiO_3$, are attractive as electrode materials but low temperature routes are desirable in view of their poor stability [3]. Ferroelectrics, catalysts [4], optical or magnetic materials are some of their other technological applications. While metal alkoxides are the usual oxide precursors for early-transition metals [5], such derivatives have been less studied for late-transition metals due to the low solubility and/or stability of classical alkoxide ligands [6]. Alkoxides with donor sites or aryloxides are required generally for overcoming these drawbacks [7].

Aminoalcohols generally show higher solubility than alkoxyalcohols as shown by copper(II) complexes [8]. Soluble Ni(II) alkoxides remain scarce, the few examples being based on aryloxides [9] or on 2-dimethylaminoisopropoxide. The latter could be prepared by different synthetic routes but its structural characterization was hampered by stability problems of the single crystals [10]. We report herein the molecular structures of two forms of $Ni(\eta^2\text{-}OCHMeCH_2NMe_2)_2$, the toluene clathrate **I** and the solvent free species **II**, as well as the

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investigation of the reactions of **II** with copper carboxylates in non-polar media. Heterometallic Cu–Ni species **III** and **IV** of 1:2 and 1:1 stoichiometry, respectively, were obtained and the molecular structure of the latter reported.

2. Experimental

All experiments were done routinely under nitrogen using Schlenk tubes and vacuum line techniques. Compound **I** was prepared as reported in Ref. [10]. Compound **II** was obtained by the sublimation of **I** at 93–95°C under 10^{-2} mmHg. $Cu_2(OAc)_4(H_2O)_2$ was purchased from Merck. $Cu(O_2CEt)_2$ was obtained from $Cu_2(CO_3)(OH)_2$ by dissolution in a propionic anhydride–propionic acid (1:1) mixture, refluxing for 6 h and subsequent removal of volatiles in vacuo at 60°C. IR spectra were registered as Nujol mulls with a Perkin–Elmer IR-1700 spectrometer. UV spectra were recorded using a U-2001 spectrophotometer. Mass spectra (electron beam ionization, direct probe introduction) were recorded using a JEOL JMS-SX/SX-102A spectrometer. The metal ratio in **III** and **IV** was determined by energy dispersive analysis (EDS) (Arrhenius Laboratory, Stockholm University, Sweden) on a JEOL-820 scanning electron microscope, supplied with Link AN-10000. Analytical data for **I**–**IV** were obtained from Mikrokemi AB, Uppsala, Sweden, and the Laboratory of Organic Microanalysis of Moscow State University, Russia.

2.1. $CuNi_2(O_2CEt)_3(OR^N)_3(R^NOH)$ (III)

Dissolution of $Cu(O_2CEt)_2$ (0.273 g, 1.3 mmol) in a solution of $Ni(OR^N)_2$ (0.340 g, 1.3 mmol) in 15 ml of toluene gave a turquoise solution. The latter was evaporated and the residue redissolved in THF (2 ml) and MeOH (0.5 ml) and left overnight at −30°C. A light blue crystalline solid was collected by filtration (yield ≈40% with respect to copper propionate). *Anal.* Found: C, 41.25; H, 7.50; N, 6.50. Calc. for $C_{29}H_{56}N_4O_{10}CuNi_2$: C, 42.99; H, 7.96; N, 6.92%. IR (cm^{-1}): 3400 (m br), $\nu(OH)$ 3240 (sh), 1712 (m), 1592 (s br), 1541 (m), $\nu(CO_2)$, 1297 (m), 1282 (w), 1262 (w), 1223 (w), 1134 (m), 1090 (s), 1050 (m), 1026 (m), 1014 (m), 942 (s), 881 (m), 869 (m), 841 (m), 810 (m br), 610 (m), ν(M–O) 531 (m). UV–Vis: λ (nm) (ε, $M^{-1} cm^{-1}$) (toluene): 686 (900). MS; m/z (I%): 733 (1) (P), 689 (1), 631 (1.5), (P − Me), 600 (3), 570 (2), 529 (2), 422 (2), 393 (3), 368 (6), 364 (4), 272 (27), 262 (55), 223 (26), 199 (54), 159 (18), 58 (100).

2.2. $Ni(Ni_{0.25}Cu_{0.75})_2(\mu_3\text{-}OH)(\mu\text{-}OAc)(\eta^1\text{-}OAc)_2(\mu,\eta^2\text{-}OR^N)_2(\eta^2\text{-}R^NOH)$ (IV)

Solid $Cu_2(OAc)_4(H_2O)_2$ (0.412 g, 1.0 mmol) was added to $Ni(OR^N)_2$ (1.092 g, 4.2 mmol) in 30 ml of a toluene–MeOH (5:1) solution giving a dark blue medium which became transparent in an hour, after the precipitation of a gray blue compound containing only nickel. The filtrate was evaporated to dryness and the green blue residue was redissolved on heating in 10 ml of THF and 5 ml of hexane. Turquoise crystals of **IV** (70% yield with respect to copper acetate) were obtained at 0°C overnight. The identity of the bulk with the formula established by single-crystal X-ray study was proved by microanalysis and by indexing the X-ray powder patterns. *Anal.* Found: C, 36.65; H, 6.90; N, 6.0. Calc. for $C_{21}H_{47}N_3O_{10}Ni_{1.5}Cu_{1.5}$: C, 36.81; H, 6.90; N, 6.13%. IR (cm^{-1}): $\nu(OH)$ 3400 (m br), 1716 (m), 1603 (s), 1567 (s), $\nu(CO_2)$ 1549 (sh), 1286 (w), 1255 (w), 1230 (w), 1135 (s), 1090 (s), 1072 (m), 1047 (w), 1025 (m), 1017 (s), 951 (s), 941 (m), 662 (s), 613 (m), 537 (m), ν(M–O) 500 (m). UV–Vis: λ (nm) (ε, $M^{-1} cm^{-1}$) (toluene): 675 (600). MS; m/z (I%): 685 (1), 680 (1), 640 (2), 635 (2), 583 (1), 578 (1), 572 (2), 570 (1.5), 568 (1), 563 (3), 560 (3), 557 (4), 555 (3.5), 544 (1.5), 539 (1), 512 (3), 501 (4), 453 (2), 394 (3), 379 (5), 336 (7), 286 (3), 267 (3), 262 (18), 244 (16), 223 (10), 218 (9), 185 (20), 159 (22), 100 (8), 58 (100).

2.3. Crystallography of I, II and IV

Crystals of **I** and of **II** were chosen from the mother liquor and from the sublimate, respectively, and mounted into Lindeman capillaries. Data collection was carried out with a SMART CCD Bruker diffractometer. The rotation photographs taken with different exposure times showed that the crystals of **I** melted and recrystallized under the X-ray beam giving polycrystals. Therefore a large ($1.20 \times 0.80 \times 0.80$ mm^3) single crystal was chosen for **I** and the data were collected with rather short exposure time (1 s per frame). The unit cell parameters and orientation matrix were determined after the data collection using 1556 and 1493 reflections with $I \geq 6\sigma(I)$ for **I** and **II**, respectively. The data collection for the air-stable crystals of **IV** was carried out using a Siemens P3/PC diffractometer. The unit cell parameters were determined using 48 randomly chosen intense reflections. Basic crystallographic information is shown in Table 1.

The structures were solved by direct methods using SHELXTL-NT programs [11]. The positions of all non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. The hydrogen atoms were included in the final refinement in calculated positions with temperature factors $U_{iso} = 1.5U_{eq}(C_i)$, where C_i is the carbon atom to which the corresponding hydrogen atom is bonded. Absorption corrections for **I** and **II** were applied using SADABS. No absorption correction was made for **IV**. The disorder in the occupation of metal atom positions in **IV** could not be resolved by free variation of occupation factors in view of the very close electron density of Cu and Ni [and thus the ability to diffract X-rays]. Therefore a comparison of different models proposed on the basis of metal analysis was carried out (Table 2), the best agreement with the experimental data was obtained for a distribution of Cu and Ni (0.75Cu + 0.25Ni) between the positions M(1) and M(2).

2.4. Magnetic susceptibility measurements

The ac magnetic susceptibility on polycrystalline samples of **III** and **IV** were measured (500 Hz and 500 A m^{-1}) in the temperature range 11–320 K using a Lake Shore Inc. AC Susceptometer, Model 7130, equipped with a helium cryostat. Corrections for diamagnetic contributions were made using Pascal's constants [12].

3. Results and discussion

3.1. Molecular structures of Ni(II) aminoalkoxides

Nickel(II) alkoxides based on the 1,2-dimethylamino-2-propoxide ligand ($OR^N = OHCHMeCH_2NMe_2$) were prepared either by metathesis between $NiCl_2$ or $[Ni(NH_3)_6]Cl_2$ and the sodium aminoalkoxide [10]. The compounds were highly soluble in toluene and isopropanol. Mass spectrometry data displayed only monomeric fragments whereas the UV–Vis spectrum in toluene was comparable to that of [*cis*-$NiCl_2(\eta^2\text{-}OR^N)_2$]. Previous attempts to get solid state structural data were precluded by the lack of stability of the single crystals.

Compound **I** isolated from toluene solution turned out to be a clathrate with toluene, with one solvent molecule per molecule of complex. The latter is a monomeric *trans* isomer with four-coordinated nickel atoms (Fig. 1, Table 3). The sum of the angles at nickel is 359.98(13)° showing it to be almost ideally square planar. The Ni–O (1.829(3) Å) and Ni–N (1.931(3) Å) distances lie in the range usually observed for tetra-co-

Table 1
Crystallographic data for compounds **I**, **II** and **IV**

	I	**II**	**IV**
Chemical formula	$C_{17}H_{32}N_2O_2Ni$	$C_{10}H_{24}N_2O_2Ni$	$C_{21}H_{47}N_3O_{10}Ni_{1.5}Cu_{1.5}$
Formula weight	355.16	263.02	684.99
Temperature (K)	295(2)	295(2)	295(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2$	$P2_1/c$	$P2_1/n$
Unit cell dimensions			
a (Å)	14.969(4)	5.6041(16)	11.923(5)
b (Å)	8.935(4)	10.361(3)	16.716(6)
c (Å)	8.531(3)	11.559(3)	15.600(6)
α (°)	90	90	90
β (°)	121.877(14)	93.237(5)	102.32(3)
γ (°)	90	90	90
V (Å^3)	968.9(6)	670.0(3)	3037.7(19)
Z	2	2	4
Absorption coefficient μ (mm^{-1})	1.009	1.434	2.012
Independent reflections	1614 [$R_{int} = 0.0383$]	1493 [$R_{int} = 0.0468$]	7923 [$R_{int} = 0.0445$]
Observed reflections	1529 [$I > 2\sigma(I)$]	1493 [$I > 2\sigma(I)$]	3950 [$I > 4\sigma(I)$]
R_1	0.0457	0.0503	0.0662
wR_2	0.1117	0.1132	0.1018

Table 2
Different refinement models for **IV**

	Position M(1)	Position M(2)	R_1 for 3950 reflections with $I > 4\sigma(I)$	wR_2 for all 7885 reflections	Goodness-of-fit
1	Cu	Cu	0.0693	0.1464	1.077
2	0.5Cu+0.5Ni	Cu	0.06920	0.1462	1.074
3	Cu	0.5Cu+0.5Ni	0.0690	0.1461	1.073
4	Cu	Ni	0.0697	0.1475	1.083
5	0.75Cu+0.25Ni	0.75Cu+0.25Ni	0.0662	0.1018	1.054

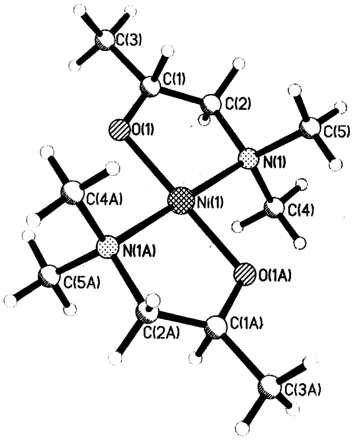

Fig. 1. Molecular structure of **I** showing the atom-numbering scheme.

Table 3
Bond lengths (Å) and bond angles (°) for **I** and **II**

Compound **I**	
Bond lengths	
Ni(1)–O(1)	1.829(3)
Ni(1)–O(1′)	1.829(3)
Ni(1)–N(1)	1.931(3)
Ni(1)–N(1′)	1.931(3)
Bond angles	
O(1)–Ni(1)–O(1′)	175.6(10)
O(1)–Ni(1)–N(1)	87.98(13)
O(1′)–Ni(1)–N(1)	92.00(12)
O(1)–Ni(1)–N(1′)	92.00(12)
O(1′)–Ni(1)–N(1′)	87.98(13)
N(1)–Ni(1)–N(1′)	179.6(8)
C(5)–O(1)–Ni(1)	112.9(3)
Compound **II**	
Bond lengths	
Ni(1)–O(1)	1.829(3)
Ni(1)–O(1′)	1.829(3)
Ni(1)–N(1′)	1.938(3)
Ni(1)–N(1)	1.938(3)
Bond angles	
O(1)–Ni(1)–O(1′)	180.0(2)
O(1)–Ni(1)–N(1′)	91.72(13)
O(1′)–Ni(1)–N(1′)	88.28(13)
O(1)–Ni(1)–N(1)	88.28(13)
O(1′)–Ni(1)–N(1)	91.72(13)
N(1′)–Ni(1)–N(1)	180.0(2)
C(1)–O(1)–Ni(1)	112.1(3)

Symmetry transformations used to generate equivalent atoms: $-x$, $-y$, $-z$.

ordinated nickel. They are shorter than the corresponding distances in [Li(^{i}PrOH)Ni(OR^N)$_2$Cl] (Ni–O, 1.937(5) and 2.017(5), and Ni–N, 2.109(7) and 2.151(8) Å) and in Ni(OR^N)$_2$Cl$_2$ (Ni–O, 2.147(8) and 2.171(7), and Ni–N, 2.142(9) and 2.148(9) Å), where the nickel atoms are penta- and hexa-coordinated, respectively [10]. It is to be noticed that the N(1)–Ni(1)–N(1′) angle in **I** (179.8(6)°) is closer to 180° than the O(1)–Ni(1)–O(1′) angle (175.6(10)°), which can serve as an indication of a slightly more covalent character of Ni–N bonding in comparison with Ni–O, which is very common for nickel [13]. The bite angles of the aminoalkoxide ligand have values of 87.98(13) and 92.00(12)°. These values are larger than those found for NiCl$_2$(η^2-OHCHMeCH$_2$NMe$_2$)$_2$ where nickel is six-coordinated. The toluene molecules are disordered with two orientations of the CH$_3$ groups [C(14) and C(14A)], they are located among the layers of planar Ni(OR)$_2$ molecules (Fig. 2). This fact explains the easy recrystallization of **I** under X-rays that made the determination of its structure difficult.

Compound **I** is volatile. Its sublimation at 93–95°C (0.01 mmHg) yielded brownish green crystals of **II**, the volatiles being essentially toluene and the parent alcohol (^{1}H NMR). The presence of the latter indicates that sublimation proceeds with some decomposition. Partial resublimation of **II** was achieved at 85°C/10^{-2} mmHg. Thus, compound **II** appears more volatile but less stable than the copper(II) analog Cu(OR^N)$_2$ [8]. Its molecular structure is essentially the same as that of **I** with similar metric parameters (Table 3). The absence of toluene molecules in the lattice leads to both N(1)–Ni(1)–N(1′) and O(1)–Ni(1)–O(1′) angles having values of 180°.

3.2. Reactions between *II* and copper(II) carboxylates

Heteroleptic alkoxides of late transition metals such as Cu and Ni attracted attention during the last decades due to their unusual magnetic properties namely ferromagnetism in [Ni(acac)(OMe)(MeOH)]$_4$ [14,15] and diamagnetism in [Cu$_4${(O$_2$CMe)(2-C$_5$H$_4$N)$_2$}$_4$-(OMe)$_2$]$^{2+}$ for instance [16]. Ni–Cu species of various nuclearity have been reported, most of them being di- or trinuclear [16b] but larger aggregates such as M$_6$Cu$_2$(μ$_3$-OH)$_4$(mhp)$_2$(OCPh)$_{10}$(Hmhp)$_4$(H$_2$O)$_2$ with Hmhp = 6-methyl-2-pyridone and M = Ni have also been obtained [17]. Reactions between metal alkoxides and carboxylates have afforded a number of heterometallic aggregates of unusual structural features [18]. We used this strategy to access Ni–Cu species.

The interaction of Ni(OR^N)$_2$ with anhydrous copper propionate in 1:1 ratio afforded a crystalline product **III** containing Cu and Ni in 1:2 ratio according to EDS analysis (Cu, 37.1(7); Ni, 62.9(7)). Its composition was supported further by analytical and mass spectral data. The latter displayed the ions originating from the fragmentation of **III**, e.g. with m/z 733 [CuNi$_2$(O$_2$CEt)$_2$-(OR^N)$_4$]$^+$, 689 ([CuNi$_2$(O$_2$CEt)$_3$(OR^N)$_3$Me]$^+$), 631 [CuNi$_2$(O$_2$CEt)$_2$(OR^N)$_3$]$^+$ and 500 [CuNi$_2$(O$_2$CEt)$_3$-(OR^N)]$^+$ along with some minor fragments characteristic of homometallic species.

The reaction between Ni(OR^N)$_2$ and copper(II) acetate hydrate in 2:1 ratio lead to the precipitation of 1

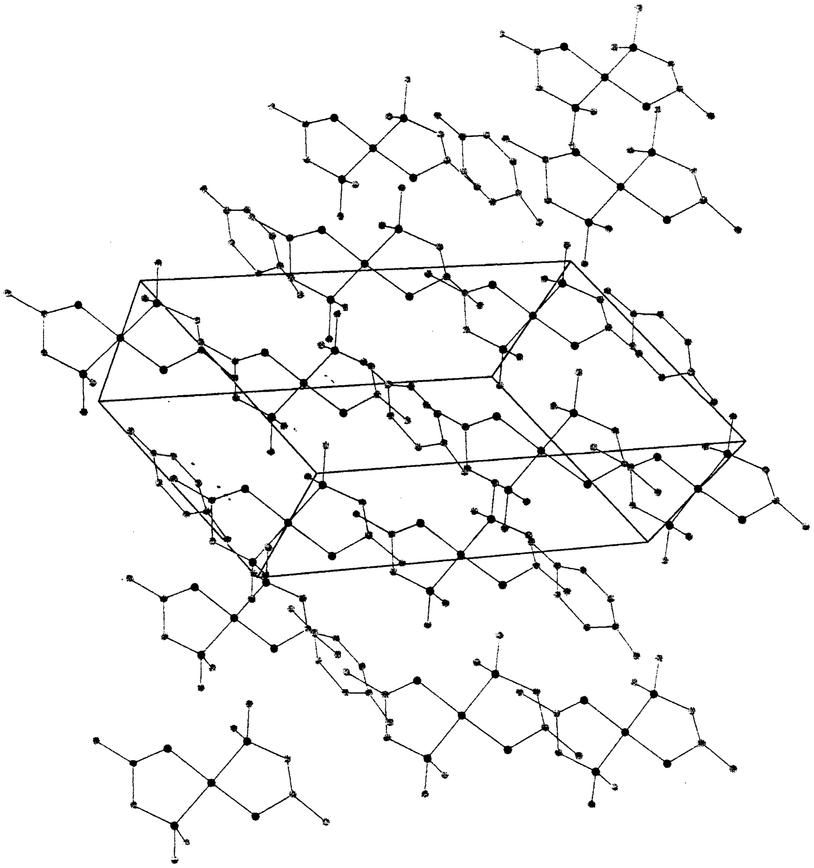

Fig. 2. Packing showing the toluene molecules among **I**.

equiv. of nickel (presumably as $Ni(OH)_2$) whereas the isolated crystalline product **IV** contained Cu and Ni in a 1:1 ratio (Cu 53.2(7) and Ni 46.8(7) for EDS analyses). The FT-IR spectra of compounds **III** and **IV** displayed absorption bands characteristic of $\nu(CO_2)$ vibrations in the 1700–1500 cm^{-1} region as well as bands around 3400 cm^{-1} indicating the presence of hydroxyl functionalities.

The X-ray single-crystal study of **IV** showed a triangular framework uncommon for mixed-metal species displaying a 1:1 stoichiometry (Fig. 3, Table 4). The first of the three different positions appeared to be occupied only by Ni atoms, while the other two turned out to be occupied by Cu (75%) and by Ni (25%), respectively (this gave the best result on both discrepancy factors and goodness-of-fit, Table 2). It can be explained chemically by the coexistence in the solid state of molecules of different compositions, namely $[CuNi_2(OH)(OAc)_3(OR^N)_2(R^NOH)]$ and $[Cu_2Ni(OH)(OAc)_3(OR^N)_2(R^NOH)]$, giving an overall 1:1 stoichiometry between the metals. The isotopic fragmentation patterns for both species (parent ions P^+, $[P-HNMe_2]^+$, $[P-R^NOH]^+$, $[P-R^NOH-Me]^+$, $[P-R^NOH-Me-NMe_2]^+$) were observed in the mass spectra along with those of homometallic species suggesting that some gas phase chemistry occurs [19]. For **III**, the intensity of most of the fragments observed is quite low. The salient structural feature is that each metal has a different coordination geometry: octahedral with no Jahn–Teller distortion for nickel, tetragonal pyramidal or square planar for M(1) and M(2), respectively. The square planar coordination geometry of the M(2) center is distorted slightly, this is in good agreement with the magnetic properties observed (Section

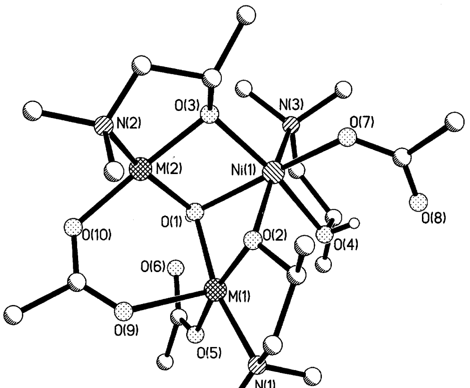

Fig. 3. Molecular structure of **IV** showing the atom-numbering scheme. Dotted lines indicate hydrogen bonding.

Table 4
Selected bond distances (Å) and bond angles (°) for **IV**

Bond lengths			
Ni(1)–O(2)	2.021(3)	M(1)–O(3)	1.933(3)
Ni(1)–O(3)	2.053(3)	M(1)–O(1)	1.953(3)
Ni(1)–O(7)	2.053(4)	M(1)–O(5)	1.957(4)
Ni(1)–O(1)	2.125(4)	M(1)–N(1)	2.039(4)
Ni(1)–O(4)	2.131(4)	M(1)–O(9)	2.304(4)
Ni(1)–N(3)	2.145(4)	M(2)–O(2)	1.924(3)
Ni(1)–M(1)	2.9098(15)	M(2)–O(10)	1.954(4)
Ni(1)–M(2)	2.9773(12)	M(2)–O(1)	1.961(4)
		M(2)–N(2)	2.050(5)
Bond angles			
O(2)–Ni(1)–O(3)	92.92(14)	O(1)–M(1)–N(1)	165.6(2)
O(2)–Ni(1)–O(7)	97.71(15)	O(5)–M(1)–N(1)	91.6(2)
O(3)–Ni(1)–O(7)	94.03(15)	O(3)–M(1)–O(9)	96.0(2)
O(2)–Ni(1)–O(1)	77.76(14)	O(1)–M(1)–O(9)	98.43(15)
O(3)–Ni(1)–O(1)	75.23(13)	O(5)–M(1)–O(9)	95.4(2)
O(7)–Ni(1)–O(1)	168.0(2)	O(2)–M(2)–O(10)	171.9(2)
O(2)–Ni(1)–O(4)	168.7(2)	O(2)–M(2)–O(1)	84.17(15)
O(3)–M(1)–O(1)	82.05(15)	O(10)–M(2)–O(1)	98.9(2)
O(3)–M(1)–O(5)	168.5(2)	O(2)–M(2)–N(2)	85.2(2)
O(1)–M(1)–O(5)	97.9(2)	O(10)–M(2)–N(2)	89.6(2)
O(3)–M(1)–N(1)	86.5(2)	O(1)–M(2)–N(2)	160.1(2)
M(1)–O(1)–M(2)	108.0(2)		
M(1)–O(1)–Ni(1)	90.94(14)		
M(2)–O(1)–Ni(1)	93.5(2)		
M(2)–O(2)–Ni(1)	97.96(15)		
M(1)–O(3)–Ni(1)	93.73(14)		

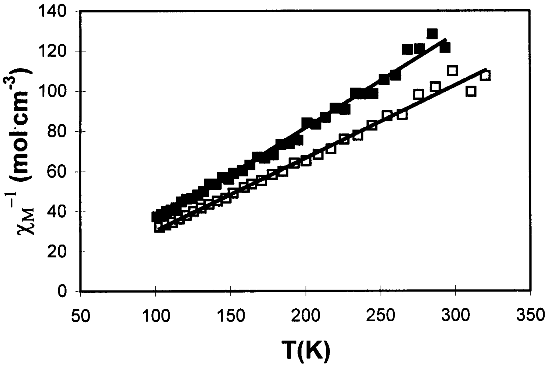

Fig. 4. Inverse molar susceptibility vs temperature for **III** (□) and **IV** (■).

3.3). The metal–oxygen and metal–nitrogen distances fall in the range usually observed for both Ni(II) and Cu(II) aminoalkoxides with the variation M–OR < MOAc < M-μ-OAc < M–N, the distances related to nickel being longer than those observed for copper. The Ni–OR and Ni–N distances are also longer than those observed for the mononuclear complexes **I** and **II** due to higher coordination numbers as well as the OR ligands having bridging functions. The presence of a M_3OH core is confirmed by the pseudotetrahedral oxygen environment, the detection of the hydrogen and by stoichiometry. While one acetate ligand bridges the M(1) and M(2) metallic centers, the other two act as terminal monodentate ligands. Indeed the Ni(1)–O(8) and M(1)–O(6) distances have values of 3.294(6) and 3.301(6) Å, respectively, and O(8) and O(6) are thus definitely out of the metal coordination sphere. This monodentate coordination behavior — quite scarce — [20] is stabilized actually by intramolecular hydrogen bonding with the hydroxide ligand (O(1)···O(6), 2.776(9) Å) and the hydrogen atom of the solvated alcohol molecule (O(4)···O(8), 2.573(6) Å) [21]. The metal–metal distances are rather short: Ni(1A)–Cu(1), 2.9098(15) and Ni(2A)–Cu(2), 2.9773(12) Å. They are shorter than those observed in $[\mathrm{Cu_3(\mu_3\text{-}OH)L_3A(H_2O)}_x]$ with L = 3-acetylamino-1,2,4-triazolate; A = $\mathrm{CF_3SO_3}$, $\mathrm{NO_3}$, $\mathrm{ClO_4}$ and $x = 0$, 2 [22]. The Ni···M distances are also shorter than those observed for the Ni(II) aminoalkoxide cluster $[\mathrm{Ni_7(\mu\text{-}NO_2)_8(\mu\text{-}OH)_2(\mu_3\text{-}OH)_2(OHR'^{N})_2(OR'^{N})_2]\cdot 7H_2O}$ with $\mathrm{OR'^{N}}$ = 1,3-diamino-propoxide = $\mathrm{OCH(CH_2NMe_2)_2}$ [23].

The formation of **III** and **IV** can be summarized by the following equations:

$$2\mathrm{Ni(OR^N)_2} + 2\mathrm{Cu(O_2CEt_3)_2} \rightarrow [\mathrm{CuNi_2(O_2CEt_3)_3(OR^N)_3(R^NOH)}] + \cdots \quad (1)$$

$$4\mathrm{Ni(OR^N)_2} + \mathrm{Cu_2(OAc)_4(H_2O)_2} \rightarrow [\mathrm{CuNi_2(OH)(OAc)_3(OR^N)_2(R^NOH)}] + [\mathrm{Cu_2Ni(OH)(OAc)_3(OR^N)_2(R^NOH)}] + \cdots \quad (2)$$

The structure of **IV** accounts for a redistribution reaction between the aminoalkoxide and the acetate ligands. The overall formula of **III** and **IV** differ essentially by the replacement of one aminoalkoxide ligand by a hydroxo ligand. This observation is in agreement with the higher hydrolytic susceptibility of an alkoxide ligand with respect to a carboxylate one. The structure of the nonhydroxo compound **III** for which no suitable crystals could be obtained is related probably to that of $[\mathrm{Ba_2Cu(\mu_3,\eta^2\text{-}OR^N)^2(\mu,\eta^2\text{-}thd)_2(thd)_2(^{i}PrOH)_2}]$ in which the linkage between the divalent metals is ensured by the aminoalkoxide ligand and bridging chelating tetramethylheptanedionate [24]. One can also notice the stability of a hydroxo versus an oxo triangular core for late-transition metals.

3.3. Magnetic susceptibility studies

Inverse molar susceptibility versus T plots (Fig. 4) give $C = 2.76$ emu K mol^{-1}, $\Theta = 6.00$ K and $C = 2.15$ emu K mol^{-1}, $\Theta = 11.7$ K for **III** and **IV**, respectively. The expected values of the Curie constants for completely uncoupled complexes are 2.375 and 2.062 emu K mol^{-1} for **III** and **IV**, respectively. These values were obtained assuming that $g = 2.00$ for both Cu(II) and Ni(II) although the actual values are probably higher [12]. However, this simple isotropic model shows at least a qualitative agreement with the results ob-

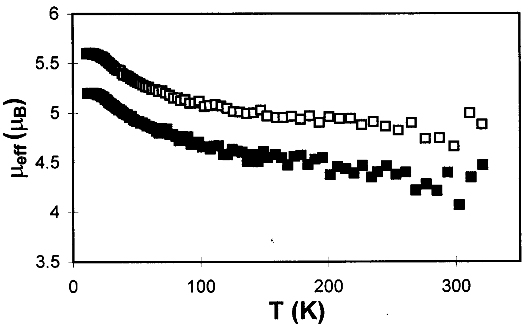

Fig. 5. Temperature dependence of the effective magnetic moment for **III** (□) and **IV** (■).

tained from the X-ray diffraction data. The temperature dependence of the effective magnetic moments (μ_{eff}) of **III** and **IV** is shown in Fig. 5. The data in the high temperature regions are consistent with the presence of three uncoupled metal centers for both the complexes. At temperatures below 20 K, the values of μ_{eff} are 5.6 and 5.2 BM for **III** and **IV**, respectively. The continuous increase of μ_{eff} with decreasing temperature may originate from ferromagnetic exchange interactions among the three metal centers. No attempts of modeling the exchange couplings within the trimeric clusters were made due to insufficient data in the low temperature region.

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 149421, 149420, 149422 for **I**, **II** and **IV**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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