

Soluble Ni^{II} alkoxides based on dimethylaminoisopropoxide ligands: molecular structure of [Li(PrⁱOH)Ni(η²-OR)₂Cl]₂ and of *cis*-NiCl₂(ROH)₂ (R = CHMeCH₂NMe₂)

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Abstract—Various routes to Ni^{II} aminoalkoxides have been investigated. A nickel isopropoxide derivative **1** was prepared by anodic dissolution of the metal in the presence of LiCl as electrolyte. Alcoholysis reactions of **1** with 1-dimethylamino-2-propanol afforded the homoleptic nickel(II) aminoalkoxide **2** together with a Ni–Li species **3**. **2** was also obtained by metathesis reactions between sodium alkoxide and the nickel hexamine complex whereas the reaction between the latter and the aminoalcohol led to an halide solvate, *cis*-NiCl₂(η²-ROH)₂, **4**. The various compounds were characterized by elemental analysis, FT-IR and UV–vis spectroscopies as well as by X-ray diffraction for **3** and **4**. **3** corresponds to [Li(PrⁱOH)Ni(η²-OCHMeCH₂NMe₂)Cl]₂ and the overall structure can be seen as two [Ni(η²-OCHMeCH₂NMe₂)Cl][−] moieties assembled by Li(PrⁱOH)⁺. The lithium atom is 4-coordinate due to its interaction with the oxygen atoms of the aminoalkoxide ligands. Nickel is 5-coordinate with a distorted tetragonal pyramidal stereochemistry, one nitrogen being in the apical position. The metal displays a distorted octahedral surrounding for the NiCl₂ adduct **4**. The bond distances vary in the order Ni—OR < Ni—N ≈ Ni—O(H)R < Ni—Cl for **3** and **4**. The various compounds (except **1**) are soluble in organic media. © 1997 Elsevier Science Ltd

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Simple or complex perovskites based on late transition metals such as cobalt or nickel have interesting properties as resonators for microwaves, multilayer capacitors, ferroelectrics and catalysts [1]. Chemical routes to such materials are hampered by the lack of solubility and/or stability of molecular oxide precursors for these transition metals [2]. Indeed, classical metal alkoxides [M(OR)_n]_m (M = Co, Ni; R = Me, Et, Prⁱ, Bu^t, ...) are insoluble and thus remain poorly

characterized [3]. Insoluble homo or heteroleptic ethanolamine derivatives Ni(OR)(OC₂H₄NH₂) (R = Me, Prⁱ) have also been reported [4]. Acetylacetonates and various salts have been used as alternative sources of metal oxides [1]. β-diketonatoalkoxides [Ni₄(OMe)₄(β-dik)₄(MeOH)₄] (β-dikH = acetylacetonate, dibenzoylmethane) have been reported [5]. (η³-allyl) Ni(OR) derivatives have been used as catalysts for the dimerisation of olefins [6]. The poor solubility and/or stability of late transition metal alkoxides, the difficult access to trimethylsilylamide derivatives for Ni^{II} and Co^{II} has led to the development of less usual synthetic routes such as for instance insertion reactions in nickel σ-alkyl bonds [7]. Soluble mixed-metal Ni^{II} alkoxides

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such as $\text{Ni}[\text{Al}(\text{OPr}^i)_4]_2$, $\text{Ni}[\text{Nb}(\text{OPr}^i)_6]_2$ [3] and more recently $[\text{Ni}_2\text{Sb}_4(\text{OEt})_{16}]$, $[\text{Ni}_5\text{Sb}_3\text{O}_2(\text{OEt})_{15}(\text{EtOH})_4]$ and some of their hydrolysis products have also been described [8]. The non-*oxo* derivatives have been obtained by metathesis reactions as a means to overcome the insolubility (and inertness) of the classical nickel alkoxides.

Metal alkoxides can be stabilized by alkanolamines and soluble derivatives have been reported for copper(II) [9, 10]. We report herein the results of our investigations for access to soluble nickel(II) alkoxides based on dimethylaminoisopropanoxide ($\text{R} = \text{CHMeCH}_2\text{NMe}_2$). The obtaining of the mixed-metal species $[\text{Li}(\text{Pr}^i\text{OH})\text{Ni}(\eta^2\text{-OR})_2\text{Cl}]_2$, **3** by alcohol exchange from the insoluble nickel isopropanoxide derivative **1** isolated by anodic dissolution of nickel in isopropanol and in the presence of lithium chloride as electrolyte, accounts for the easy formation of 'ate' derivatives. The homometallic alkoxide $[\text{Ni}(\text{OR})_2]_m$, **2** was better obtained by metathesis reactions applied to $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ whereas the reaction between the hexamine and aminoisopropanol afforded the $\text{NiCl}_2(\text{ROH})_2$ adduct **4**. The various compounds were characterized by elemental analyses, FT-IR and UV-vis spectroscopies and by X-ray diffraction for **3** and **4**.

EXPERIMENTAL

All manipulations were performed under dry nitrogen using standard Schlenk tubes and vacuum line techniques with solvents purified by standard methods. 1-Dimethylamino-2-propanol was dried over 3 Å molecular sieves. Electrochemical syntheses were achieved using a cell without separation of the anode and cathode spaces equipped with a reflux condenser, an anode of nickel and a platinum cathode [11]. IR spectra were run on a IR-FTS 45 spectrometer and were obtained as Nujol mulls. UV-vis spectra were obtained on an Unicam 5 Spectrometer. Analytical data were obtained from the Centre de Microanalyses du CNRS.

Electrochemical synthesis of $[\text{Ni}(\text{OPr}^i)_2]_2$, **1**

Anodic dissolution of nickel in Pr^iOH and in the presence of LiCl as electrolyte gives a dark violet precipitate. It was washed with anhydrous Pr^iOH several times until no reaction was observed in the filtrate with AgNO_3 and dried. Analytical data showed, however that it contains significant amounts of LiCl . Anal. Found: C, 37.1; N, 7.3; Cl, 4.1; Li, 0.7; Ni, 30.3. Calc. for $\text{C}_6\text{H}_{14}\text{O}_2\text{Ni}$: C, 40.7; H, 7.9; Ni, 33.3%. The composition is thus approximately $\text{Ni}(\text{OPr}^i)_2$, 0.2 LiCl .

Synthesis of $[\text{Li}(\text{Pr}^i\text{OH})\text{Ni}(\eta^2\text{-OR})_2\text{Cl}]_2$, **3** and $[\text{Ni}(\text{OR})_2]_2$, **2** ($\text{R} = \text{CHMeCH}_2\text{NMe}_2$)

0.88 g of $\text{Me}_2\text{NCH}_2\text{CHMeOH}$ in 10 cm^3 of toluene and 2 cm^3 of isopropanol were added to 0.76 g of **1**.

The reaction mixture was refluxed for 1 h and evaporated to dryness. The crude product was composed of two types of crystals: green-brown needles (**2**) and bright green polyhedra (**3**), the latter being the minor species. **2** and **3** were separated by their solubility properties: **2** was highly soluble in toluene and isopropanol, while **3** was soluble in Pr^iOH but insoluble in toluene.

2 can be converted into **3** by refluxing (0.75 g) for 30 min with a solution of LiCl (0.18 g) in 15 cm^3 of toluene/ Pr^iOH (1:1) and 0.87 g of aminoalcohol. Evaporation to dryness gave **3** in quantitative yield. Anal. Calcd for $\text{C}_{13}\text{H}_{32}\text{O}_3\text{N}_2\text{ClLiNi}$ (**3**): C, 42.7; H, 8.8; N, 7.7; Cl, 9.7; Li, 1.9. Found: C, 42.5; H, 8.9; N, 7.6; Cl, 9.8; Li, 1.8%. IR (cm^{-1}): 3328m [$\nu(\text{OH})$]; 521m, 501m, 428m, 410m, 378m, 300sh, 274s [$\nu(\text{M}-\text{OR})$, $\nu(\text{M}-\text{N})$].

Other syntheses of **2**

0.22 g of sodium (9.56 mmol) were added to a mixture of 1 cm^3 of $\text{HOCHMeCH}_2\text{NMe}_2$ and 10 cm^3 of toluene and heated to 80°C for 2 h until all sodium was dissolved. 1.03 g of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ (REAKHIM, pure, 4.81 mmol) were added to the light yellowish solution obtained. The mixture was refluxed for 2 h. The solution turned greenish brown, NaCl was formed and was separated by decantation. The volume of solution was reduced approximately twice and left overnight at -15°C. Greenish-brown needle-shaped crystals were separated by filtration, washed with 2 cm^3 of hexane and dried to yield 1.09 g of $[\text{Ni}(\text{OR})_2]$ (86%). Calcd for $\text{C}_{10}\text{H}_{24}\text{O}_2\text{N}_2\text{Ni}$: C, 45.7; H, 9.2; N, 10.6. Found: C, 45.3; H, 9.1; N, 10.8%. IR (cm^{-1}): 661vs, 551s, 521m, 501m, 427m, 415w, 374m, [$\nu(\text{Ni}-\text{O})$, $\nu(\text{Ni}-\text{N})$]. MS (200°C, 70 eV, m/z^+ (%): $[\text{Ni}(\text{OR})_2]$ (P) (100); $[\text{Ni}(\text{OR})(\text{OC}_3\text{H}_6)]$ (P-NMe₂) (14); $[\text{Ni}(\text{OC}_3\text{H}_6)_2]$ (P-2NMe₂) (14); $[\text{Ni}(\text{OC}_3\text{H}_6\text{N})]$ (P-ROH) (84); ROH (100).

2 was also obtained by metathesis of NiCl_2 with $\text{NaOCHMeCH}_2\text{NMe}_2$ (1:2 stoichiometry) in THF. **2** is soluble in hexane.

Synthesis of $\text{NiCl}_2(\text{ROH})_2$, **4** ($\text{R} = \text{CHMeCH}_2\text{NMe}_2$)

1.89 g (8.15 mmoles) of $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ were refluxed for 3 h with 8 cm^3 (64.9 mmoles) of $\text{OHCHMeCH}_2\text{NMe}_2$, 5 cm^3 of isopropanol and 20 cm^3 of toluene. The violet precipitate dissolved slowly with formation of a bright green solution and of a white-greenish precipitate containing NH_4Cl (XRD evidence). The solution was evaporated leaving a viscous green oil which was layered with 15 cm^3 of hexane. Yellow green crystals of **4**, suitable for X-ray analysis, sparingly soluble in toluene, more soluble in alcohols (EtOH , Pr^iOH) formed at room temperature. A microcrystalline powder was obtained by refluxing of the oily crude product in hexane (1.9 g, 72%). Anal.: Found: C, 36.6; H, 7.9; N, 7.4; Cl, 18.8; Ni, 18.0%.

Calcd for C₁₀H₂₆N₂O₂Cl₂Ni C, 35.9; H, 7.2; N, 8.4; Cl, 21.3; Ni, 17.7%. IR (cm⁻¹): 3260br (νOH), 605s, 520m, 493m, 475sh, 450w. [ν(Ni—Cl), ν(Ni—O)].

Structure determination of 3 and 4

The selected crystals of 3 and 4 were mounted into capillaries on Enraf–Nonius CAD-4 and Philips PW 1100 automatic diffractometers, respectively. The unit cell parameters and basic information about data collection and structure refinement are given in Table 1. Lattice parameters and orientation matrices were obtained from least-squares refinement of the setting angles of 25 well-centred reflections [$11 < \theta < 11.5^\circ$ for 3 and $13 < \theta < 13.5^\circ$ for 4]. The intensities of three standard reflections monitored every hour showed no decay. Corrections for Lorentz and polarization effects were applied.

Computations were performed using the PC version of CRYSTALS [12]. Scattering factors and corrections for anomalous dispersion were taken from ref. [13]. The structures were solved using direct methods [SHELXS] [14] and standard Fourier techniques. All non-hydrogen atoms were refined anisotropically for 4. For 3, hydrogen atoms were located on a difference Fourier map and put into the refine-

ment in fixed positions with an overall isotropic thermal parameter. Only hydroxyl H atoms [linked to O(1) and O(11)] were located on a difference Fourier map, other hydrogen atoms were calculated. All hydrogen atoms were included in the refinement as fixed contributors.

Atomic coordinates, non-essential bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

Synthesis and characterization

Various routes to soluble Ni^{II} oxide precursors have been investigated. The anodic dissolution of nickel in usual alcohols (methanol, isopropanol) has been reported as an easy route to halide free alkoxides [15]. It proceeded smoothly in the presence of lithium chloride as an electrolyte with the formation of a dark violet precipitate, 1. The reaction between 1 and functional alcohols, 2-methoxyethanol or 1-dimethylamino-2-propanol occurs at room temperature. The isopropoxide derivative is thus more reactive than the methoxide one for which the alcohol interchange reac-

Table 1. Crystal data for [Li(Pr'OH)Ni(μ-OR)₂Cl]₂, 3 and *cis*-NiCl₂(ROH)₂, 4 (R = CHMeCH₂NMe₂)

Formula	(C ₁₃ H ₃₂ O ₃ N ₂ CLiNi) ₂	NiCl ₂ (C ₅ H ₁₃ ON) ₂
<i>F</i> _w	727	335.9
<i>a</i> (Å)	9.398(3)	12.601(7)
<i>b</i> (Å)	22.324(22)	11.028(5)
<i>c</i> (Å)	9.692(4)	12.548(6)
β (°)	106.62(3)	113.91(4)
<i>V</i> (Å ³)	1954(15)	1594(6)
<i>Z</i>	2	4
Crystal system	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /a
Linear absorption coefficient μ (cm ⁻¹)	11.4	15.5
Density ρ (g cm ⁻³)	1.21	1.40
Diffractometer	CAD4—Enraf-Nonius	PHILLIPS PW 1100
Radiation	MoKα (λ = 0.71069 Å)	MoKα (λ = 0.71069 Å)
Scan type	ω/2θ	ω/2θ
Scan range (°)	0.8 + 0.345tgθ	1.20 + 0.345tgθ
θ Limits (°)	1–25	2–25
Temperature of measurement	Room temperature	Room temperature
Octants collected	–11, 10; 0, 26; 0, 11	h: –14, 13; k: 0, 13; 11: 0, 14
Nb of data collected	3760	3057
Nb of unique data collected	3433	2758
Nb of unique data used (<i>F</i> _o) ² > 3σ(<i>F</i> _o) ²	1375	1009
<i>R</i> (int)	3.94	0.052
<i>R</i> = Σ <i>F</i> _o – <i>F</i> _c /Σ <i>F</i> _o	0.0481	0.046
<i>R</i> _w = Σw(<i>F</i> _o – <i>F</i> _c) ² /Σw <i>F</i> _o ²	0.0508 w = 1.0	0.052 w = 1.0
Absorption correction	DIFABS (min = 0.71, max = 1.48)	DIFABS (min = 0.81, max = 1.14)
Extinction parameter (× 10 ⁻⁶)	38	no
Goodness of fit	2.5	1.02
Nb of variables	192	155
Δρ min (e/Å ³)	–0.39	–0.34
Δρ max (e/Å ³)	0.35	0.37

tion with 2-methoxyethanol requires a long reflux. The alcoholysis reaction with the aminoalcohol occurs readily and afforded two compounds **2** and **3**, separated by their solubility properties in toluene. **2** was analyzed as $\text{Ni}(\text{OCHMeCH}_2\text{NMe}_2)_2$ whereas **3** corresponds to a mixed metal Ni–Li species (*vide infra*). The unexpected obtaining of **3** indicates retention of lithium chloride in **1**. The synthesis of **3** could be optimized and its formation is quantitative if the preceding alcoholysis reaction is carried out in the presence of lithium chloride. $\text{Ni}(\text{OCHMeCH}_2\text{NMe}_2)_2$ can be obtained by metathesis reaction between nickel chloride or $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ and sodium aminoalkoxide (1 : 2 stoichiometry) but no crystals suitable for X-ray analysis could be grown. $\text{NiCl}_2(\text{ROH})_2$ ($\text{R} = \text{CHMeCH}_2\text{NMe}_2$) **4** was isolated by reaction between nickel hexamine dichloride and 1-dimethylamino-2-propanol.

The various compounds were characterized by microanalysis, infra-red and UV–visible spectroscopy. The formation of an alcohol solvate **3** is evidenced by the presence of a $\nu(\text{OH})$ stretching absorption band at 3328 cm^{-1} in the FT-IR. Several absorption bands below 600 cm^{-1} are indicative of the presence of Ni–OR bonds. Mass spectrometry showed that **2** is monomeric in the vapour phase. The UV–visible spectra for the various compounds are given in Fig. 1. Compound **3** is characterized by two well defined absorptions at 490 and 640 nm. **4** displays *d–d* absorption bands at 415, 690 nm and a shoulder at 800 nm as expected for 6-coordinate nickel(II) [3,16]. **2** exhibits a spectrum having a pattern comparable to that of **3** but with bands located at 480 and 580 nm. UV–vis spectra of **2** suggest 5-coordinate nickel and thus dinuclear species in solution.

Molecular structures of $[\text{Li}(\text{Pr}^i\text{OH})\text{Ni}(\text{OR})_2\text{Cl}]_2$ and $\text{NiCl}_2(\text{ROH})_2$ ($\text{R} = \text{CHMeCH}_2\text{NMe}_2$)

The nature of compound **3** was established by single crystal X-ray diffraction. The structure is built up by

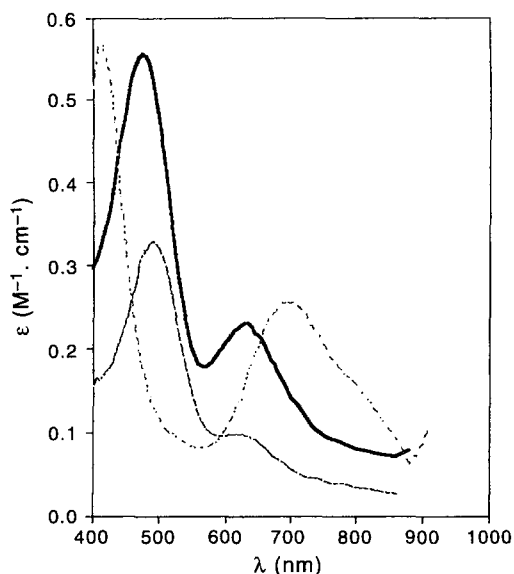


Fig. 1. Molecular structure of $[\text{Li}(\text{Pr}^i\text{OH})\text{Ni}(\eta^2\text{-OCHMeCH}_2\text{NMe}_2)\text{Cl}]_2$ showing the atom numbering scheme ellipsoids at 30% probability.

centrosymmetric $[\text{Li}(\text{Pr}^i\text{OH})\text{Ni}(\text{OR})_2\text{Cl}]_2$ ($\text{R} = \text{CHMeCH}_2\text{NMe}_2$) dimeric molecules (Fig. 1). Selected bond lengths and angles are given in Table 2. Nickel atoms are pentacoordinated with a distorted tetragonal pyramidal surrounding it formed by two oxygen atoms, two nitrogens and one chlorine, one of the nitrogens, N(1) being in the apical position. The $\text{Ni}(\text{OR})_2\text{Cl}$ 'ate' moieties have several coordination sites and they are assembled *via* lithium atoms which interact with three oxygen atoms of the chelating alkoxide ligand. The lithium atom is apparently too small to span all donor sites of the functional alkoxide ligands and an additional isopropanol molecule is required to ensure tetracoordination of the alkali metal. The non-bonding Ni–Li distance is 2.869(15) Å. The Ni–O bond distances, Ni–O(1) and Ni–O(2), 2.017(5) and 1.937(5) Å, respectively, are

Table 2. Selected bond lengths (Å) and angles (°) for $\{[\text{NiC}_{10}\text{H}_{23}\text{N}_2\text{O}_2\text{Cl}](\text{C}_3\text{H}_7\text{O})\text{Li}\}_2$

Ni(1)—Cl(1)	2.381(3)	Ni(1)—O(1)	2.017(5)
Ni(1)—O(2)	1.937(5)	Ni(1)—N(1)	2.109(7)
Ni(1)—N(2)	2.151(8)		
Li(1)—O(1)	2.03(1)	Li(1)—O(1')	1.99(1)
Li(1)—O(2)	1.89(2)	Li(1)—O(11)	1.89(2)
Cl(1)—Ni(1)—O(1)	95.9(2)	Cl(1)—Ni(1)—O(2)	154.6(2)
O(1)—Ni(1)—O(2)	85.5(2)	Cl(1)—Ni(1)—N(1)	98.0(2)
O(1)—Ni(1)—N(1)	85.1(3)	O(2)—Ni(1)—N(1)	107.4(3)
Cl(1)—Ni(1)—N(2)	90.8(2)	O(1)—Ni(1)—N(2)	163.1(3)
O(2)—Ni(1)—N(2)	81.9(3)	N(1)—Ni(1)—N(2)	109.3(3)
O(1)—Li(1)—O(1')	97.1(6)	O(1)—Li(1)—O(2)	86.2(6)
O(1')—Li(1)—O(2)	132.2(8)	O(1)—Li(1)—O(11)	126.4(8)
O(1')—Li(1)—O(11)	98.9(7)	O(2)—Li(1)—O(11)	117.2(7)

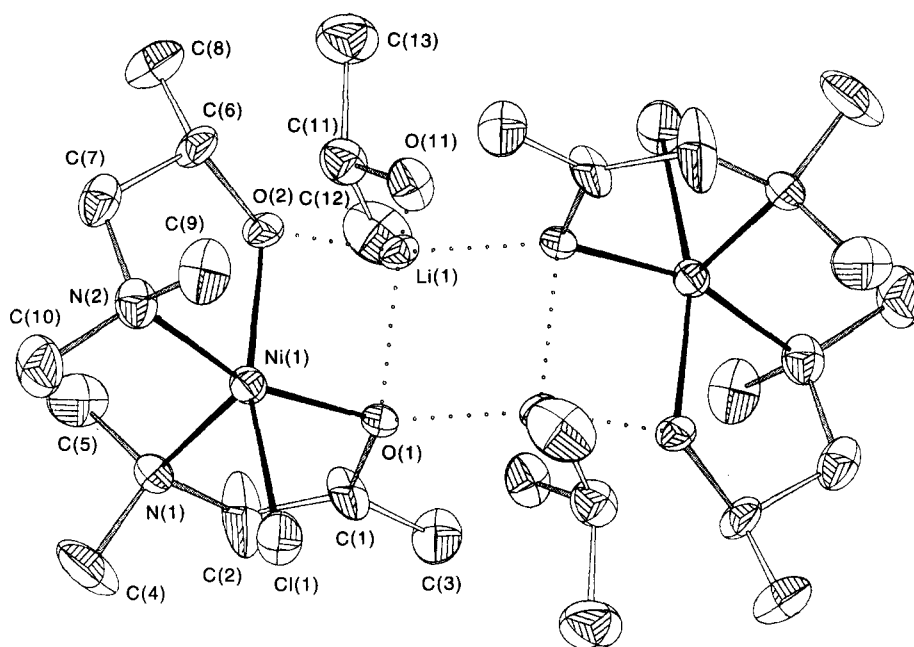


Fig. 2. Molecular structure of *cis*-NiCl₂(η²-OHCHMeCH₂NMe₂)₂ showing the atom numbering scheme.

significantly different, this can probably be related to the difference of the ligand in *trans* position since both oxygens interact with two lithium atoms. Although the molecule can be described as [Ni(OR)₂Cl]⁻ fragments assembled by [Li(PrⁱOH)]⁺, the dissection into ions is purely formal since the compound is molecular with an hydrocarbon periphery resulting in its solubility in organic media. The Li—O bond distances range from 1.89(2) to 2.03(1) Å and are thus in agreement with the values observed for instance for [LiZr₂(OPrⁱ)₉(PrⁱOH)] [17] or LiOR species [18]. The lithium atoms display a distorted tetrahedral stereochemistry [\angle OLiO varying from 86.2(6) to 132.2(8)[°]]. The smallest angle corresponds to O(2)—Li—O(1). The O(1)⋯O(11) distance of 2.952(8) Å is too long for efficient hydrogen bonding. The sharp band observed in the FT-IR for the ν(OH) stretching frequency is in agreement with the observations in the solid state [19].

The structure of **4** corresponds to *cis*-NiCl₂(η²-OHCHMeCH₂NMe₂)₂ (Fig. 2). Selected bond lengths and angles are given in Table 3. The bidentate coordination mode of the aminoalcohol [20] ensures hexacoordination of the central metal with a distorted octahedral surrounding. Several geometrical isomers, namely three *cis*-isomers and two *trans* isomers, are possible for MX₂ adducts involving unsymmetrical bidentate LL' ligands. The isomer observed for **4** in the solid state corresponds to the *cis*-isomer in which the oxygen atoms are *trans* to the chloride ligands whereas the nitrogen atoms are *trans* to each other and *cis* to the chlorides. Predictions of the relative stabilities of MX₂(LL')₂ type isomers (having a 'normalized' bite < 1.3 for LL') are in favour of the isomer in which the shortest metal–bidentate ligand bonds are *trans* to each other and *cis* to the unidentate ligands [21]. The Ni—N bond distances are the shortest one within compound **4** and the isomer observed

Table 3. Selected bond lengths (Å) and angles (°) for *cis*-NiCl₂(OHCHMeCH₂NMe₂)₂

Ni(1)—Cl(1)	2.441(3)	Ni(1)—Cl(2)	2.415(3)
Ni(1)—O(1)	2.171(7)	Ni(1)—O(2)	2.147(8)
Ni(1)—N(1)	2.148(9)	Ni(1)—N(2)	2.142(9)
Cl(1)—Ni(1)—Cl(2)	98.7(1)	Cl(1)—Ni(1)—O(1)	170.7(2)
Cl(2)—Ni(1)—O(1)	85.9(2)	Cl(1)—Ni(1)—O(2)	91.0(2)
Cl(2)—Ni(1)—O(2)	166.7(2)	O(1)—Ni(1)—O(2)	85.9(3)
Cl(1)—Ni(1)—N(1)	91.3(3)	Cl(2)—Ni(1)—N(1)	97.6(3)
O(1)—Ni(1)—N(1)	80.1(3)	O(2)—Ni(1)—N(1)	91.1(3)
Cl(1)—Ni(1)—N(2)	91.2(3)	Cl(2)—Ni(1)—N(2)	92.2(3)
O(1)—Ni(1)—N(2)	96.7(3)	O(2)—Ni(1)—N(2)	78.5(3)
N(1)—Ni(1)—N(2)	169.4(4)	Ni(1)—O(1)—C(1)	111.1(7)

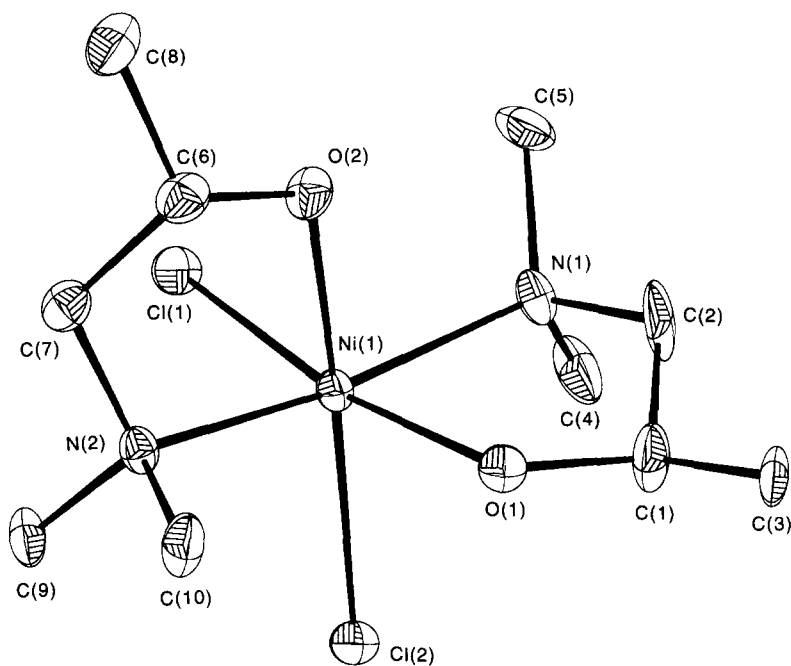


Fig. 3. UV-vis spectra of **2** (—) in toluene and of **3** (—) and **4** (---) in isopropanol.

corresponds thus to the one expected to be the most stable. The bite angles of the aminoalcohol ligand spread over the range $78.5(3)$ to $85.1(3)^\circ$, the highest value being observed for the ligand acting as O-donor [via O(1)] toward two lithium atoms for **3**, the smallest ones are observed for the hexacoordinated metal and thus correspond to **4**. The Ni—Cl bond distances are comparable for the two compounds although they are slightly longer for 6-coordinated nickel [$2.381(3)$ Å for **3** with respect to $2.428(3)$ Å av. for **4**]. The Ni—N bond lengths are comparable as well with values of $2.152(8)$ Å for **3** and of $2.145(9)$ Å av. for **4**. The bond distances vary in the order Ni—OR < Ni—N \approx Ni—O(H)R < Ni—Cl, their values are in agreement with the data reported in the literature [22].

CONCLUSIONS

A number of compounds in which the alkali metal reagent is retained within the metal-coordination sphere, especially for lanthanides giving salts or 'ate' compounds, have been reported [23]. Although retention of lithium has been observed during the electrosynthesis of molybdenum oxoalkoxides [24], the isolation of the heterometallic Li—Ni chloroalkoxide **3** was unanticipated in view of the small amount of electrolyte used. Our results show how easy it can be to incorporate small ligands such as Li^+ or Cl^- in heterometallic alkoxides [25]. They also suggest some explanation for the difficulty to obtain pure—namely chlorine and alkali free metal alkoxides—for late transition metals such as copper when metathesis reactions are used as a synthetic route. Indeed, **3** can be obtained quite easily by reacting **2** with LiCl in the presence of

isopropanol and 1-dimethylamino-2-propanol. These observations emphasize the importance of an appropriate choice of the electrolyte for the obtaining of pure transition metal alkoxides, especially for the late metals, by electrosynthesis.

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