

Nickel(II) Complexes of New Asymmetrical, Tetradentate (N_2O_2) Schiff Bases Derived from N-(2-Hydroxyethyl)ethylenediamine

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Abstract

Five new nickel(II) complexes are described. They are obtained from Schiff bases resulting from the condensation of N-(2-hydroxyethyl)ethylenediamine with 2,4-pentanedione, 3-(ethoxymethylene)-2,4-pentanedione, 1-benzoylacetone, salicylaldehyde, and 2-hydroxyacetophenone, respectively. Chemical analyses, conductivity measurements, and infrared data support a dimeric structure involving a single O–H–O bridge.

Introduction

It is well known that the reactivity (affinity towards dioxygen, redox behaviour, etc.) of the metal centre in macrocyclic or acyclic Schiff base complexes is very sensitive to the structure of the equatorial ligands and, especially, to the inductive effect of the substituents and the extent of electronic π -delocalization [1–6]. Recently, in an attempt to investigate the mechanism of methyl transfer between cobalt(III) and tin(IV), we observed that in model complexes of the $CH_3Co(Chel)B^*$ type, the behaviour of the Co–C bond is very dependent upon such effects [7–9]. For instance, a homolytic or heterolytic cleavage of this bond is observed when Chel = BAE or TIM, respectively, while Salen and DMG induce the formation of dinuclear Co–Sn species. In continuation of these studies, we deal with complexes of Schiff base ligands including simultaneously unsaturated and saturated moieties. They are expected to limit the π -delocalization in the equatorial plane and modulate the metal charge and its reactivity. Compounds of this

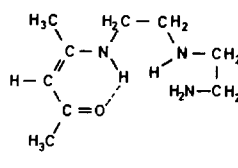
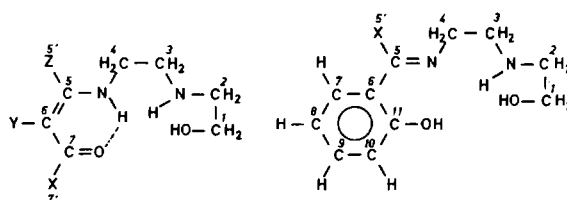


Fig. 1. An example of unsymmetrical (N_3O) Schiff Base [10].



- IIa:** X = CH_3 , Y = H, Z = CH_3
IIb: X = CH_3 , Y = ${}^6C(O)CH_3$, Z = CH_3
IIc: X = C_6H_5 , Y = H, Z = CH_3
IIc': X = CH_3 , Y = H, Z = C_6H_5
IIIa: X = H
IIIb: X = CH_3

Fig. 2. Ligands with their abbreviations (this work).

type with a N_3O donor set have been reported by Cummings [10] (Fig. 1). In this paper, we present the first examples involving a N_2O_2 donor set around a nickel(II) centre (Fig. 2).

Experimental

Preparation

The preparation of the ligands **IIa**, **IIc**, **IIIa** and **IIIb** was carried out in a Dean and Stark apparatus. Stoichiometric amounts of N-(2-hydroxyethyl)ethylenediamine and diketo precursor (2,4-pentanedione, 1-benzoylacetone, salicylaldehyde or 2-hydroxyacetophenone) were dissolved in benzene. The mixture was kept boiling till the required quantity of water

*Chel may be BAE, TIM, Salen, DMG; BAE = N,N'-ethylenbis(acetylacetonato), TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraenato, Salen = N,N'-ethylenbis(salicylideneiminato), DMG = bis(dimethylglyoximate).

was collected. The solvent was then removed under reduced pressure to give the desired ligands in the form of microcrystalline powders or viscous liquids. The ligands **IIb** was obtained by refluxing equimolar quantities of N-(2-hydroxyethyl)ethylenediamine and 3-(ethoxymethylene)-2,4-pentanedione prepared according to literature processes [11] in absolute ethanol for 2 h. The resulting solution was concentrated and the yellow material collected by filtration.

In a typical preparation of the complexes, a solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (5×10^{-3} mol) in 10 ml of methanol was added dropwise to a hot solution of the ligand (5×10^{-3} mol) and of the deprotonating agent, $\text{N}(\text{C}_2\text{H}_5)_3$ or NaOCH_3 (5×10^{-3} mol). A yellow–orange precipitate readily formed. It was filtered off and washed with cold methanol and diethylether, and dried *in vacuo* for several hours.

Physical Measurements

Microanalyses were performed by the Service Central de Microanalyse du CNRS (Lyon). Proton and ^{13}C NMR spectra of the ligands were run on a Bruker WH90 instrument using TMS (^1H spectra) and CDCl_3 (^{13}C spectra) as internal reference. All chemical shifts (^1H and ^{13}C) are given in ppm vs. TMS using CDCl_3 as solvent. IR spectra were recorded on a Perkin Elmer model 984 spectrometer with KBr disks or with KBr pellets. Visible and UV spectra were measured on 3×10^{-3} M methanolic solutions or as Nujol mulls on a Cary 2300 instrument. Magnetic susceptibility measurements were performed using the Faraday method. Conductivity measurements were obtained from 5×10^{-3} M methanolic solutions.

Results and Discussion

Characterization of the Ligands

The ligands are readily obtained by condensing N-(2-hydroxyethyl)ethylenediamine with 2,4-pentanedione (**IIa**), 3-(ethoxymethylene)-2,4-pentanedione (**IIb**), 1-benzoylacetone (**IIc**), salicylaldehyde (**IIIa**) and 2-hydroxyacetophenone (**IIIb**), respectively. (**IIb**) and (**IIIa,b**) are yellow crystalline products while (**IIa,c**) are isolated as yellow oils. These compounds are first identified by chemical analysis. The data collected in Table I are consistent with the expected formulation. This is further supported by the NMR (^1H and ^{13}C) results reported in Tables II and III. The assignments are made based on literature data [6, 12].

In the case of benzoylacetone, two isomeric forms (**IIc** and **IIc'**) would be obtained [13]. Actually, the ^1H NMR spectrum of a crude sample shows signals at 2.0 and 2.2 ppm, *i.e.* in the range of methyl proton resonances. However, the (**IIc**) isomer is strongly favoured [12, 14] and we can observe that the relative intensity of these signals is 15/1. Consequently, the assignment of the related ^{13}C spectra is difficult.

The IR spectra of the five ligands show the typical pattern of Schiff bases with broad bands at *ca.* 3300 cm^{-1} attributed to the O–H and N–H stretching modes and strong overlapping absorptions at *ca.* 1630 , 1580 and 1550 cm^{-1} , related to the 'double-bond' stretching modes [15, 16].

Characterization of the Nickel(II) Complexes

The complexes are prepared by reaction of nickel perchlorate with the required ligands in the presence of a deprotonating agent. Triethylamine is used in all instances leading to the precipitation of a

TABLE I. Analytical Data.

	Found (Calcd.) %				
	C	H	N	Cl	Ni
Ligands					
IIa	59.1(58.0)	10.1(9.7)	15.5(15.0)		
IIb	56.4(56.1)	8.7(8.5)	13.3(13.1)		
IIc	68.0(67.7)	8.4(8.1)	11.1(11.3)		
IIIa	63.2(63.4)	7.6(7.7)	13.3(13.5)		
IIIb	64.6(64.8)	8.1(8.2)	12.3(12.6)		
Ni(II) complexes					
IIa	37.2(36.9)	5.8(5.7)	9.4(9.6)	5.8(6.1)	19.7(20.0)
IIb	36.9(37.4)	5.2(5.2)	8.2(8.7)	5.7(5.5)	18.0(18.3)
IIc	47.2(47.3)	5.0(5.2)	7.8(7.9)	5.1(5.0)	16.0(16.5)
IIIa	40.5(41.9)	4.1(4.6)	8.3(8.9)	5.7(5.6)	19.0(18.6)
IIIb	43.7(43.8)	5.1(5.1)	8.5(8.5)	5.4(5.4)	18.9(18.7)

TABLE IIa. ^1H NMR Shifts for the Ligands.^a

	H ₁ , H ₂ ^{b,c}	H ₃ , H ₄	H ₅	H _{5'}	H ₆	H _{(6)γ'}	H _(7')	N-H...O
IIa	3.7(m)	3.0(m)		1.9(s)	5.0(s)		2.0(s)	11.2(m)
IIb	3.5(m)	2.8(m)	7.9(d)			2.5(s)	2.3(s)	11.0(m)
IIc	3.6(m)	2.8(m)		2.0(s)	5.7(s)			11.6(m)
IIIa	3.6(m)	2.9(m)	8.3(s)	2.4(s)				
IIIb	3.9(m)	3.1(m)						

^aTMS as internal reference (in CDCl₃); m = multiplet, d = doublet, s = singlet. ^bDue to the complexity of the ethylenic region, no assignments have been made for these protons. ^cO-H and N-H (diethylene bridge) signals overlap with methylene ^1H multiplets. The numbering scheme is indicated in Fig. 1.

TABLE IIb. ^{13}C Chemical Shifts (ppm) for the Ligands.

	C ₁	C ₂	C ₃	C ₄	C ₅	C _{5'}	C ₆	C _{6'}	C ₇	C _{7'}	C ₈	C ₉	C ₁₀	C ₁₁
IIa	59.5	50.6	48.9	48.0	164.1	20.3	94.5		193.7	27.7				
IIb	61.3	51.1	50.3	50.3	152.1		111.8	200.6	194.2	27.5				
IIIa	61.0	51.1	49.6	49.6	166.3		161.2		132.5		118.9	131.5	117.2	161.2
IIIb	61.0	51.3	49.3	49.3	172.8		119.7		133.0		119.4	133.0	117.0	162.0

TABLE III. Relevant IR Data^a for Ni(II) Complexes.

IIa	IIb	IIc	IIIa	IIIb	
3450(b,w)	3400(b,w)	3450(b,w)	3420(b,w)	3400	OH stretching
3210(m)	3210(m)	3210(m)	3210(m)	3200(m)	N-H ^b stretching
2020(b,w)	2020(bw)	2020(b,w)	2020(b,w)	2015(b,w)	H-O-H (bridge)
	1640(m)				C=O stretching
1582(s)	1600(s)	1595(m)	1630(s)	1590(s)	C=C (aromatic) stretching
1513(s)		1560(m)	1600(s)	1580(s)	
		1510(s)			
		1490(s)	1530(s)	1530(s)	
		1460(s)	1470(s)	1465(m)	C=C stretching
1430(s)		1430(s)	1450(s)	1430(s)	
1100(s)	1100(s)	1100(s)	1100(s)	1100(s)	C=N stretching
620(m)	620(m)	620(m)	620(m)	620(m)	CH ₃ and CH ₂ deformation
					ClO ₄ ⁻ asymmetric stretching
					ClO ₄ ⁻ asymmetric bending

^as = strong, m = medium, w = weak, b = broad. ^bPrimary amine in the diethylene bridge, not deprotonated in complexes.

yellow–orange powder, except in the case of complex (IIIa) whose precipitation is only induced by NaOCH₃.

The complexes were first characterized by chemical analysis. The data quoted in Table I show that the ratios nickel/ligand and nickel/perchlorate are 1 and 2, respectively. This suggests a dimeric formulation (NiL)₂ClO₄ which implies that the two ligands L would be responsible for an overall 3-charge. This point will be considered later.

The complexes are insoluble in common organic solvents but soluble (more or less) in potentially coordinating solvents such as methanol, DMSO and

DMF. This prevents the use of cryoscopic or osmometric methods for molecular weight determinations. Attempts to use mass spectra were unsuccessful because of decomposition. Conductivity measurements show the presence of 1:1 electrolytes in methanol solutions (Λ_M in the range 80–120 mhos cm² mol⁻¹).

From static susceptibility measurements it appears that solid samples of the five complexes under examination display a diamagnetic behaviour. However, ^1H NMR spectra related to solutions in CD₃OD show broad signals with paramagnetic shifts. These data are consistent with a square-planar geometry

of the N_2O_2 donor set around the nickel(II) and, in solution, axial bonding of solvent molecules. This interpretation is supported by electronic spectra. In the spectra of solid samples (nujol mulls) the lowest-energy band is located near $22,220\text{ cm}^{-1}$. It may be attributed to the ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition in square-planar complexes [17]. Two bands of much higher intensity are observed at $27,770\text{ cm}^{-1}$ and $33,330\text{ cm}^{-1}$. They are attributed to charge-transfer or intra-ligand transitions. Spectra related to solutions in methanol display two supplementary bands of low intensity at *ca.* $11,900\text{ cm}^{-1}$ ($\epsilon \sim 10$) and $13,330\text{ cm}^{-1}$ ($\epsilon \sim 5$), indicative of a change in nickel coordination from four to six.

The main infrared absorptions of the complexes are reported in Table III. Interestingly, comparing these data with those obtained for the related free ligands points to a large decrease of the intensity of the $\nu(O-H)$ at *ca.* 3300 cm^{-1} , an increase of the intensity of the $\nu(N-H)$ at *ca.* 3200 cm^{-1} , and the appearance of new absorptions at *ca.* 2010 , 1100 and 610 cm^{-1} . The bands at 1100 and 610 cm^{-1} are attributed to the ClO_4^- anion. The lack of any splitting would be consistent with non-coordination of this ion [18]. The absorption at 2010 cm^{-1} is not observed in the spectra of deuterated samples. This is a broad band, reminiscent of the band observed at 1775 cm^{-1} in the complex $Ni(DMG)_2$ which has been attributed to O-H-O bridges [19, 20].

Many nickel(II) complexes involving oximes or aminoalcohols as ligands are known to be associated through O-H-O bridges [21-24]. Recently, Bertrand [25, 26] reported the structure of complex A (Fig. 3) obtained by a template reaction of one mole of 2,4-pentanedione with two moles of ethanolamine in the presence of nickel(II) ions. By analogy, a structure involving two monomeric units joined by hydrogen bonding (B, Fig. 3) is suggested for the

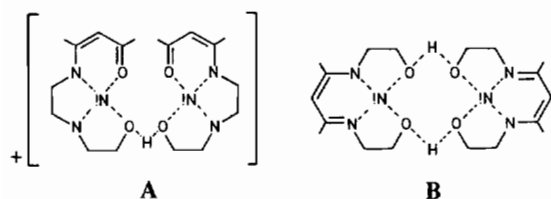


Fig. 3. A: Hydrogen-bonded dimer [25]; B: Possible schematic structure for the complexes.

complexes reported in the present work. This structure would be consistent with all the data obtained. The occurrence of one bridge is rather surprising but this type of bonding has been recently mentioned [24] in the case of a copper(II) complex formed from two monomeric units involving a non-deprotonated and a monodeprotonated amino alcohol respectively.

Formally, a similar description could be applied to our complexes which may be represented by $(L-H)(L-2H)Ni_2^+$, $(L-H)$ and $L-2H$ standing for the mono- and the dideprotonated forms of the ligands, respectively. We did not succeed in isolating the neutral monomeric species $(L-2H)Ni$. When a large excess of deprotonating agent is used in the synthesis, oily and untractable products are obtained. They have a somewhat variable composition. To obtain well-defined products, it is necessary to manage a limited deprotonation compatible with the formation of the $O\cdots H\cdots O$ bridge.

All attempts to obtain single crystals suitable for X-ray diffraction study have failed so far. However, using the relationship between the IR frequency characterizing the $O\cdots H\cdots O$ bridge to the $O\cdots O$ distance leads to an $O\cdots O$ separation of *ca.* 2.5 \AA , which compares well with the values previously reported in the literature, *i.e.* 2.3 \AA for the complex A [25] (Fig. 3) or 2.4 \AA for $Ni(DMG)_2$ [23].

Work is in progress to prepare the related copper compounds. It is expected that a study of their magnetic properties will confirm the dinuclear structure of these complexes.

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