Inorg. Chem. **1994**, *33*, 2738–2742

A Monomeric, Self-Assembling, Alkali-Metal Binding Nickel Complex: Reappraisal of the Original Model from Solid-State and Solution Studies

Jean-Pierre Costes,* Françoise Dahan, and Jean-Pierre Laurent

Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne,
31077 Toulouse Cedex, France

Received March 23, 1994[⊗]

The nickel(II) complex of 3-methoxysalicylaldimine, L^2_2Ni, reacts with lithium, sodium, and potassium salts to afford dimetallic complexes L^2_2NiNaY and L^2_2NiLiY ($Y = ClO_4$) and L^2_2NiKI. Structural analysis performed both in the solid state (X-ray diffraction) and in solution (UV–vis, ^1H, ^{13}C, and ^{23}Na NMR spectroscopy, magnetic measurements) points to an almost perfect similitude with the simple model of self-assembling ionophore, initially suggested. The two steps of the process are structurally characterized. $L^2_2Ni{\cdot}2H_2O$ (**1**) crystallizes in the monoclinic space group $P2_1/n$ (No. 14) with two formula weights in a cell having the dimensions $a = 11.084(1)$ Å, $b = 4.8503(8)$ Å, $c = 15.519(1)$ Å, and $\beta = 97.85(1)°$. The dimetallic complex $L^2_2NiNaClO_4{\cdot}H_2O$ (**2**) crystallizes in the orthorhombic space group *Pbca* (No. 61) with eight formula weights in a cell having the dimensions $a = 11.232(1)$ Å, $b = 15.530(1)$ Å, and $c = 22.698(2)$ Å. In the first complex two imine molecules assemble themselves around a nickel ion to form the monometallic complex L^2_2Ni with a *trans*-NiN_2O_2 chromophore. Upon addition of lithium, sodium, or potassium cations, the chromophore adopts a *cis* configuration with the formation of an outer O_4 site able to bind an alkali-metal cation. Evaluation of the stability constants shows that the monometallic species L^2_2Ni displays a substantial selectivity for sodium ions.

Introduction

The assembly of enzyme complexes to form binding sites which do not preexist in the subunits is an important mechanism of molecular recognition in biological systems.[1] Until recently the possibility of fitting together two discrete molecules to obtain a new binding unit was restricted to high molecular weight systems. No longer ago than 4 years, it was reported[2] that this phenomenon could be modeled using small molecules. Indeed exerimental evidence shows that nickel(II) complexes of *N*-methyl-3-methoxysalicylaldimine and related compounds with polyether side arms (L^1_2Ni in Figure 1) are able to bind alkali-metal cations. The binding was tentatively attributed to the formation of a pseudo-crown cavity according to Figure 1, but recent structural studies[3] performed on a "sodium bound" species highlighted an unexpected cage structure comprising four salicylaldimine molecules, one water molecule, two anions, and two nickel and two sodium ions in accordance with the overall formula $(L^1_2NiNaY)_2{\cdot}H_2O$ (Y standing for the picrate ion). In keeping with the octahedral coordination of both nickel(II) ions, the complex is paramagnetic. A precise solution structure is still open to debate.[4,5] In our opinion a major difficulty in elucidating the solution structure arises from the paramagnetism of the sample which may be related either to an intrinsic octahedral coordination of the nickel ion as it is the case in the solid or to other origins if the solid-state structure in not preserved in solution.

Indeed it is well-known that salicyladimines may react with nickel(II) ions to form diamagnetic square-planar complexes of the L_2Ni type.[6,7] In solution these complexes may acquire a certain degree of paramagnetism via square-planar (diamagnetic)–tetrahedral (paramagnetic) equilibria,[8] axial coordination of solvent molecules, or self-association.[9] In an attempt to rule out this difficulty we have planned to use as starting material a complex with low steric constraints L^2_2Ni with L^2 representing the deprotonated form of 3-methoxysalicylaldiamine (Figure 1). Reacting this complex with alkali metal cations in acetone has allowed the isolation of the well-defined species $L^2_2NiNaClO_4$ and $L^2_2NiLiClO_4$, which, as anticipated, are diamagnetic both in the solid state and in solution. The related $L^2_2NiKClO_4$ cannot be obtained owing to the insolubility of the starting salt ($KClO_4$). Nevertheless, we succeeded in preparing L^2_2NiKI. For comparison, we have included in the present paper some characteristics of the related complexes L^3Ni and $L^3NiNaClO_4$,[10] which are forced to adopt a *cis* configuration with a performed external site of complexation O_4.

Results and Discussion

The direct condensation of *o*-vanillin with ammonia fails to yield the expected Schiff base L^2H, but the related monometallic complexes L^2_2M (M = Ni, Cu)[11] are easily prepared by the two-step procedure outlined in Figure 2. The same procedure can be used in the case of L^3M, but it is also possible to prepare the free Schiff base L^3H_2, which is then reacted with a nickel(II) (or copper(II)) salt. Reaction of these monometallic complexes with sodium (or lithium) perchlorate is performed in acetone to afford the dimetallic complexes which precipitate from the reaction mixture as orange powders. Due to the insolubility of $KClO_4$ in acetone, the related potassium complex was obtained in the L^2_2NiKI form.

Solid-State Structural Study of $L^2_2Ni{\cdot}2H_2O$ (1) and $L^2_2NiNaClO{\cdot}_4H_2O$ (2). ORTEP plots of both structures are shown in Figures 3 and 4. Relevant distances and angles are given in Tables 4 and 5. $L^2_2Ni{\cdot}2H_2O$ (Figure 3) displays a simple

---

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1994.

(1) (a) Hammes, G. G. In *Enzyme Catalysts and Regulation*; Academic Press: New York, 1982; Chapter 8. (b) Huang, C. Y.; Rhee, S. G.; Chock, P. B. *Am. Rev. Biochem.* **1982**, *51*, 935.

(2) Schepartz, A.; McDevitt, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 5976.

(3) Schall, O. F.; Robinson, K.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1991**, *113*, 7434.

(4) Jones, M. W.; Gupta, N.; Schepartz, A.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1308.

(5) Schall, O. F.; Robinson, K.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5962.

(6) Holm, R. H.; Everett, G. W., Jr.; Chakravorty, A. *Prog. Inorg. Chem.* **1966**, *7*, 83.

(7) Holm, R. H.; O'Connor, M. J. *Prog. Inorg. Chem.* **1971**, *14*, 241.

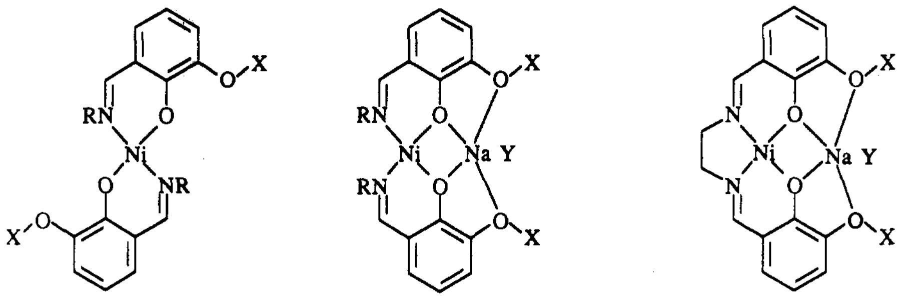
(8) Holm, R. H.; Chakravorty, A.; Dudek, G. O. *J. Am. Chem. Soc.* **1963**, *85*, 821.

(9) Holm, R. H. *J. Am. Chem. Soc.* **1961**, *83*, 4683.

(10) Costes, J.-P.; Laurent, J.-P. Unpublished results.

(11) Pfeiffer, P.; Bucholz, E.; Bauer, O. *J. Prakt. Chem.* **1931**, *129*, 163.

0020-1669/94/1333-2738$04.50/0



L_2Ni **L_2NiNaY** **LNiNaY**

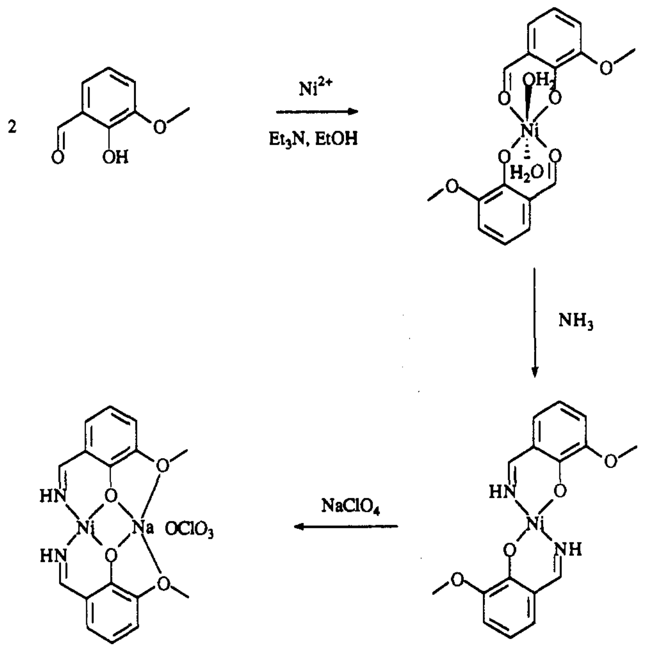
$L = L^1$ ($R = CH_3$, $X = CH_3$ or $CH_2CH_2OCH_3$)[a]

$L = L^2$ ($R = H$, $X = CH_3$, $Y = ClO_4$)[b, c]

$L = L^3$ ($X = CH_3$, $Y = ClO_4$)[b, c]

a) Ref. 2, b) this work, c) solvent molecules not included.

Figure 1. Schematic representation of the different complexes used in this study.



$L^2{}_2NiNaClO_4$ $L^2{}_2Ni$

Figure 2. Reaction scheme retained for the preparation of the complexes.

structure, similar to those previously reported[7] and which deserves very few comments. The two ligands coordinate the nickel ion in a *trans* configuration. The chromophore NiN_2O_2 adopts a symmetry imposed perfectly planar geometry. We note the presence of two water molecules. They are involved in an interesting pattern of hydrogen bonds: Ow···O(2), Ow···Owi, and Ow···N′, which, on the one hand, stabilize the *trans* configuration around each nickel ion and, on the other hand, connect indirectly different $L^2{}_2Ni$ units. However there is no evidence from intermolecular contacts for direct association between formula units and the nickel ion is undoubtedly four-coordinated.

Surprisingly the structure of the dimetallic complex $L^2{}_2NiNaClO_4 \cdot H_2O$ (Figure 4) is also simple and identical to the "model" originally proposed.[2] We are faced with a monomeric species devoid of any short contact able to support a direct association between $L^2{}_2NiNaY$ units. The NiN_2O_2 chromophore adopts a *cis* configuration so that the two ligands are now organized around the nickel ion to create an external binding site via four oxygen atoms from the side arms and the phenolate groups. The sodium cation affixes itself to this site and achieves its environment with two oxygen atoms coming from a water molecule and the perchlorate anion. Its coordination polyhedron is the rather unusual pentagonal pyramid which is probably imposed by the rigidity of the $L^2{}_2Ni$ backbone.

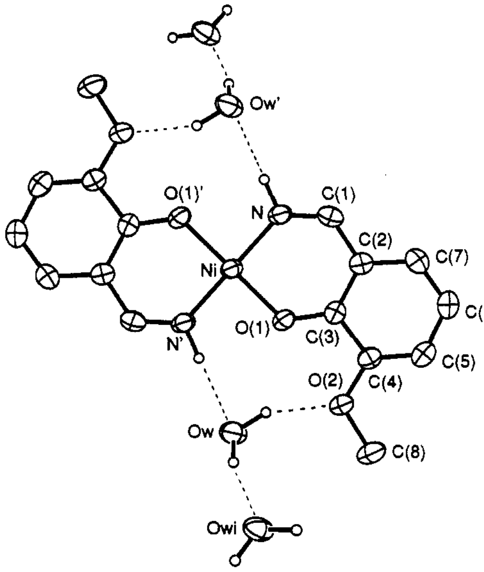


Figure 3. Ortep plot of $L^2{}_2Ni \cdot 2H_2O$ with the numbering scheme. Only hydrogen atoms involved in hydrogen bonds (dotted lines) are presented, the other ones being omitted for clarity. Symmetry operations: (′) $1 - x, 2 - y, 1 - z$; (i) $^1/_2 - x, -^1/_2 + y, ^1/_2 - z$.

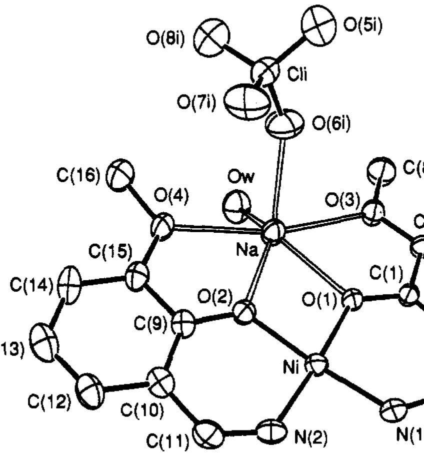


Figure 4. Ortep plot for $L^2{}_2NiNaClO_4 \cdot H_2O$ with the numbering scheme. Hydrogen atoms are omitted for clarity. Symmetry operation: (i) $^1/_2 + x, y, ^1/_2 - z$.

The Na–O separations [from 2.345(3) to 2.497(3) Å] are in the usual range.[12-15] However it may be noted that the phenolato

Table 1. Crystallographic Data for $L^2{}_2Ni \cdot 2H_2O$ (**1**) and $L^2{}_2NiNaClO_4 \cdot H_2O$ (**2**)

	1	**2**
formula	$C_{16}H_{20}N_2O_6Ni$	$C_{16}H_{18}N_2O_9NaClNi$
mol wt	395.0	499.5
color and habit	orange-red needle	dark-red block
cryst size, mm	0.50 × 0.15 × 0.05	0.50 × 0.45 × 0.35
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	*Pbca* (No. 61)
a, Å	11.084(1)	11.232(1)
b, Å	4.8503(8)	15.530(1)
c, Å	15.519(1)	22.698(2)
β, deg	97.85(1)	
V, Å^3	826.5(2)	3959.3(6)
Z	2	8
F(000)	412	2048
D_{calcd}, g cm^{-3}	1.587	1.676
λ, Å	0.710 73 (Mo)	0.710 73 (Mo)
μ(Mo Kα), cm^{-1}	12.1	11.9
T_{min}–T_{max}	0.923–0.998	0.933–0.999
data collct *T*, K	293	293
2θ range, deg	3–52	3–50
scan mode	ω-2θ	ω-2θ
scan width, deg	$0.80 + 0.35 \tan \theta$	$0.80 + 0.35 \tan \theta$
no. of measd data	1686	3476
no. of unique data	1611 ($R_{av} = 0.023$)	3476
no. of obsd data, NO, with $F_o > 4\sigma(F_o)$	873	2352
no. of refined params, NV	121	277
final $\Delta\rho$, e Å^{-3}	0.21	0.24
final $(\Delta/\sigma)_{max}$	0.009	0.020
R^a	0.027	0.032
$R_w{}^b$	0.030	0.033
gof^c	0.85	1.38

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum(w|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] gof = $[\sum(w(|F_o| - |F_c|^2)/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ with $w = 1$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2 × 100) for **1**

	x	*y*	*z*	$U_{eq}{}^a$
Ni	$^1/_2$	1	$^1/_2$	2.89(3)
O(1)	0.5336(2)	0.7343(6)	0.4206(2)	3.4(2)
N	0.6499(3)	0.9637(8)	0.5669(2)	3.4(2)
C(1)	0.7369(4)	0.8018(9)	0.5561(2)	3.5(2)
C(2)	0.7355(3)	0.6054(8)	0.4875(2)	3.1(2)
C(3)	0.6322(3)	0.5859(8)	0.4234(2)	3.1(2)
C(4)	0.6394(4)	0.3877(9)	0.3561(2)	3.3(2)
C(5)	0.7389(4)	0.2271(9)	0.3541(3)	3.9(2)
C(6)	0.8398(4)	0.2489(9)	0.4184(3)	4.1(2)
C(7)	0.8364(3)	0.4361(8)	0.4833(3)	3.8(3)
O(2)	0.5367(3)	0.3821(6)	0.2944(2)	4.3(2)
C(8)	0.5296(4)	0.1742(9)	0.2292(3)	5.0(3)
Ow	0.3077(3)	0.6408(6)	0.2783(2)	4.6(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å^2 × 100) for **2**

	x	*y*	*z*	$U_{eq}{}^a$
Ni	0.58119(4)	0.29236(3)	0.26239(2)	3.07(2)
Na	0.6756(1)	0.2290(1)	0.12793(7)	4.12(9)
O(1)	0.7025(2)	0.2267(2)	0.2307(1)	3.6(2)
C(1)	0.7847(3)	0.1830(2)	0.2575(2)	3.0(2)
C(2)	0.8002(3)	0.1825(2)	0.3200(2)	3.2(2)
C(3)	0.7210(4)	0.2280(3)	0.3573(2)	4.2(3)
N(1)	0.6283(3)	0.2713(2)	0.3392(1)	4.2(2)
C(4)	0.8971(4)	0.1368(3)	0.3448(2)	4.1(2)
C(5)	0.9750(4)	0.0909(3)	0.3102(2)	4.4(3)
C(6)	0.9574(4)	0.0890(3)	0.2496(2)	4.3(2)
C(7)	0.8656(4)	0.1329(3)	0.2238(2)	3.7(2)
O(3)	0.8403(3)	0.1350(2)	0.1644(1)	4.5(2)
C(8)	0.9081(4)	0.0767(3)	0.1273(2)	5.8(3)
O(2)	0.5490(2)	0.3163(2)	0.1843(1)	3.5(2)
C(9)	0.4619(4)	0.3614(2)	0.1622(2)	3.4(2)
C(10)	0.3743(4)	0.4047(2)	0.1957(2)	3.8(2)
C(11)	0.3767(4)	0.3974(3)	0.2587(2)	4.4(2)
N(2)	0.4533(3)	0.3568(2)	0.2888(2)	4.4(2)
C(12)	0.2836(4)	0.4526(3)	0.1675(2)	4.9(3)
C(13)	0.2779(4)	0.4590(3)	0.1081(2)	5.9(3)
C(14)	0.3637(4)	0.4169(3)	0.0743(2)	5.6(3)
C(15)	0.4546(4)	0.3674(3)	0.1001(2)	3.9(2)
O(4)	0.5407(3)	0.3231(2)	0.0706(1)	4.8(2)
C(16)	0.5462(5)	0.3351(3)	0.0080(2)	5.7(3)
Cl	0.3740(1)	0.37411(8)	0.44827(5)	4.97(6)
O(5)	0.4983(4)	0.3764(3)	0.4418(2)	9.3(3)
O(6)	0.3346(4)	0.2984(3)	0.4221(2)	9.3(3)
O(7)	0.3177(5)	0.4429(3)	0.4189(2)	11.6(4)
O(8)	0.3460(4)	0.3755(3)	0.5076(2)	11.0(4)
Ow	0.6428(3)	0.1226(2)	0.0550(2)	6.1(2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $L^2{}_2Ni \cdot 2H_2O$ (**1**)^a

Ni–N	1.843(3)	Ni–N′	1.843(3)
Ni–O(1)	1.855(3)	Ni–O(1)′	1.855(3)
N–Ni–O(1)	93.5(1)	N′–Ni–O(1)′	93.5(1)
N–Ni–O(1)′	86.5(1)	N′–Ni–O(1)	86.5(1)
N–Ni–N′	180.0	O(1)–Ni–O(1)′	180.0

[a] A prime denotes the symmetry operation $1 - x$, $2 - y$, $1 - z$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for $L^2{}_2NiNaClO_4 \cdot H_2O$ (**2**)^a

Ni–O(1)	1.848(3)	Ni–N(1)	1.851(3)
Ni–O(2)	1.845(3)	Ni–N(2)	1.850(4)
Na–O(1)	2.352(3)	Na–Ow	2.368(4)
Na–O(2)	2.345(3)	Na–O(6i)	2.375(4)
Na–O(3)	2.497(3)	Na–O(4)	2.475(3)
O(1)–Ni–O(2)	83.2(1)	O(2)–Ni–N(1)	174.6(1)
O(1)–Ni–N(1)	93.4(1)	O(2)–Ni–N(2)	92.9(1)
O(1)–Ni–N(2)	175.5(1)	N(1)–Ni–N(2)	90.8(1)
O(1)–Na–O(2)	62.93(9)	O(2)–Na–O(3)	127.3(1)
O(1)–Na–Ow	134.7(1)	O(2)–Na–O(4)	64.8(1)
O(1)–Na–O(6i)	112.6(1)	Ow–Na–O(6i)	95.7(1)
O(1)–Na–O(3)	64.34(9)	Ow–Na–O(3)	86.5(1)
O(1)–Na–O(4)	127.5(1)	Ow–Na–O(4)	87.1(1)
O(2)–Na–Ow	133.7(1)	O(3)–Na–O(6i)	82.3(1)
O(2)–Na–O(6i)	117.1(1)	O(3)–Na–O(4)	166.6(1)
O(4)–Na–O(6i)	86.6(1)		

[a] i denotes the symmetry operation $^1/_2 + x$, y, $^1/_2 - z$.

oxygen atoms approach the sodium ion more closely [2.345(3) and 2.352(3) Å] than the ethereal oxygen atoms [2.475(3) and 2.497(3) Å]. This likely results from the presence of a residual negative charge on the phenolato oxygen and the rigidity of the $L^2{}_2Ni$ unit.

The coordination around the nickel ion is approximately square-planar, the four donor atoms being coplanar with the metal within ±0.065 Å.

Magnetic measurements performed on microcrystalline samples show that $L^2{}_2Ni \cdot 2H_2O$ and $L^2{}_2NiNaClO_4 \cdot H_2O$ are devoid of any paramagnetism.

Solution Study. In any case, the UV–vis spectra do not show significant absorption beyond 1000 nm, clearly indicating square-planar geometry. The spectra of $L^2{}_2NiNaClO_4$, $L^3NiNaClO_4$, and L^3Ni are very similar with a d–d absorption at 542 ± 2 nm (ϵ from 70 to 100) and more intense bands near 400 and 340 nm. A slightly different pattern is observed for $L^2{}_2Ni$ which exhibits a d–d band at 560 nm ($\epsilon = 75$) and charge-transfer and intraligand absorptions at 408 and 330 nm, respectively. In addition a shoulder appears at 430 nm which is absent in the former spectra. From its low intensity this band may be a d–d transition in

---

(12) Poonia, N. S.; Bajaj, A. V. *Chem. Rev.* **1979**, *79*, 389.

(13) Moras, D.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 396.

(14) Moras, D.; Metz, B.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Chem.* **1973**, *B29*, 383.

(15) Gatto, V. J.; Gokel, G. W. *J. Am. Chem. Soc.* **1984**, *106*, 8240.

accordance with the attribution previously reported[16,17] for the nickel(II) salicylaldimine complex.

Very similar spectra characterize the lithium and potassium complexes. Finally, it appears that sodium (lithium or potassium) complexation, in its own right, does not affect significantly the spectral pattern while the change of configuration of the NiN_2O_2 chromophore is slightly but significantly perceptible.

Susceptibility measurements (Evan's method) show that all the complexes are diamagnetic in solution (acetone, dmso).

^1H and ^{13}C NMR spectroscopies characterize the main structural features (presence of the imino function, of the methoxy group, absence of the hydroxyl proton), but they hardly differentiate the dimetallic complexes from their monometallic precursors. The only significant differences are observed in the ^1H spectra.

Sodium or lithium binding to $L^2{}_2Ni$ and L^3Ni causes all the protons to be deshielded by *ca.* 0.10 ppm except the ethereal OCH_3 groups which suffer a deshielding of *ca.* 0.25 ppm. For the sodium complex, the width at half-height $\Delta\nu_{1/2}$ of the OCH_3 signal increases from 3 Hz in the monometallic species to 25 Hz in the dimetallic one. This effect is not attributable to paramagnetism, which is known to be absent from magnetic measurements. Furthermore the width of the other signals are not perturbed while their chemical shifts are marginaly modified. It is well-known[18] that in paramagnetic salicyladimine complexes, the proton on the axomethine carbon undergoes an important contact shift which obviously is not observed in the present case. Finally this effect may be attributed to quadrupolar relaxation. Indeed the nucleus ^{23}Na with a nuclear spin of $^3/_2$ has a large electric quadrupole moment which may interact with an electric field gradient to provide a very efficient mechanism of relaxation.[19-21] The effect of this mechanism is a prominent feature of the ^{23}Na RMN spectra. While the chemical shifts $\delta(^{23}Na)$ are little affected in going from ClO_4Na ($\delta^{23}Na$) = −6.0 ppm, acetone solution) to the dimetallic complexes ($\delta(^{23}Na)$ = −1.2 ± 0.4 ppm, acetone solution), an impressive broadening of the signal is observed: $\Delta\nu_{1/2}$ increases from 15 to 200 Hz. The large $\Delta\nu_{1/2}$ value, which characterizes the dimetallic complex, is consistent with a definite structure leading to important geometric and electronic disymmetries and electric field gradient at the ^{23}Na nucleus. Thus it is not unreasonable to think that, in solution, the dimetallic complex displays a structure very similar to that observed in the solid state.

According to the procedure described in the literature,[20,22,23] the quadrupolar broadening of the ^{23}Na resonance can be used to evaluate the formation constant K_{Na} which characterizes the equilibrium 1 and, by extension to system in which a second cation M^+ competes with Na^+ for binding, the constant K_M related to the equilibrium 2. From measurements performed in acetone

$$L^2{}_2Ni + Na^+ \rightleftharpoons L^2{}_2NiNa^+ \qquad (1)$$

$$L^2{}_2Ni + M^+ \rightleftharpoons L^2{}_2NiM^+ \qquad (2)$$

at 30 °C, we obtain

$$\log K_{Na} = 2.87 \pm 0.10 \qquad \log K_{Li} = 1.40 \pm 0.20 \qquad \log K_K = 1.60 \pm 0.30$$

It has been argued[3,5] that information about the nature of the species in solution can be provided by the cation binding profiles, charged species leading to the Coulombic order ($Li^+ > Na^+ > K^+$) and neutral crown ethers favoring K^+ over Na^+ and Li^+. According to this rationale, the $L^2{}_2NiMY$ complexes, in which there are direct interactions between phenoxide anions and M^+, are expected to comply with the Coulombic profile but they fail to do it. Tentatively, we suggest that the order actually observed results from a combination of charge effects, number of available donor (oxygen) atoms, solvation enthalpy and entropy of the cation, size relationship between the cation and the pseudo cavity, etc.[24-27] More examples are needed to appreciate the relative importance of these different factors, but, due to the rigidity of the $L^2{}_2Ni$ entity and the relatively small size of the external binding site, it may be anticipated that the "hole size" factor would play an important role.

Conclusion

A simple example of self-assembling, alkali-metal binding nickel(II) complex has been prepared, characterized, and studied. The complex $L^2{}_2Ni$ (L^2 standing for the deprotonated form of 3-methoxysalicyladimine) reacts with Li^+, Na^+, and K^+ to afford the dimetallic complexes $L^2{}_2NiNaY$, $L^2{}_2NiLiY$ ($Y = ClO_4$), and $L^2{}_2NiKI$, which, as anticipated, are diamagnetic. Structural analysis performed both in the solid state (X-ray diffraction) and in solution (UV–vis, ^1H, ^{13}C, and ^{13}Na spectroscopies, magnetic measurements) shows that the dimetallic complex is identical to the model originally suggested. The key points of the process are the assembly of two imine molecules around a nickel ion to form a *trans*-NiN_2O_2 chromophore and then, in the presence of Li^+, Na^+, or K^+ cations, the alteration of form *trans* to *cis* with the concomitant creation of an external O_4 binding site. It may be emphasized that the assembling process does not cause any dimerization and/or modification of the coordination sphere of the nickel(II) ions. Evaluation of the stability constants *via* the line width of the ^{23}Na NMR signal points to an unexpected binding profile: Na^+ is significantly favored over Li^+ and K^+.

Experimental Section

Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse, France (C, H, N) France and by the Service Central de Microanalyse du CNRS, Lyon, France (Ni, Li, Na, K). Electronic spectra were obtained with a Cary 2390 spectrometer. ^1H and ^{13}C NMR spectra were recorded with Bruker AC200 spectrometer, while ^{23}Na NMR spectra were obtained with Bruker WM250 spectrometer working at 303 K, with a relaxation delay of 1 s. Chemical shifts are given in ppm *versus* TMS (^1H and ^{13}C) or *versus* NaCl in D_2O (^{23}Na), using CD_3COCD_3 or d_6-dmso as solvents.

Magnetic susceptibility measurements of the complexes in solution were determined by NMR[28] using acetone as solvent and TMS as indicator.

Caution. The dinuclear complexes reported here were isolated as perchlorate salts. We worked with these complexes in a number of organic solvents without any incident, and as solids, they seem to be reasonably stable to shock and heat. In spite of these observations, the unpredictable behavior of perchlorate salts[29] necessitates *extreme care* in their handling.

Materials. All chemicals were reagent grade (Aldrich) and were used without further purification.

---

(16) Downing, R. S.; Urbach, F. L. *J. Am. Chem. Soc.* **1970**, *92*, 5861.

(17) Nishida, Y.; Kida, S. *Coord. Chem. Rev.* **1979**, *27*, 275.

(18) Holm, R. H.; Chakravorty, A.; Dudek, G. O. *J. Am. Chem. Soc.* **1964**, *86*, 379.

(19) Lazlo, P. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 254.

(20) Bouquant, J.; Delville, A.; Grandjean, J.; Lazzlo, P. *J. Am. Chem. Soc.* **1982**, *104*, 686.

(21) Lehn, J. M. *Struct. Bonding* **1973**, *16*, 1.

(22) Herwats, L.; Laszlo, P.; Gerrard, P. *Nouv. J. Chim.* **1977**, *1*, 173.

(23) Detellier, C.; Grandjean, J.; Laszlo, P. *J. Am. Chem. Soc.* **1976**, *98*, 3375.

(24) Takagi, P.; Ueno, K. *Top. Curr. Chem.* **1984**, *121*, 39.

(25) Michaux, G.; Reisse, J. *J. Am. Chem. Soc.* **1982**, *104*, 6895.

(26) Gokel, G. W.; Goli, D. M.; Minganti, C.; Echegoyen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786.

(27) *Cation Binding by Macrocycles*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker: New York, 1990.

(28) Evans, D. F. *Proc. Chem. Soc.* **1958**, 115.

(29) Everett, K.; Graf, F. A., Jr. In *CRC Handbook of Laboratory Safety*, 2nd ed.; Steere, N. V., Ed.; Chemical Rubber Co.: Cleveland, OH, 1971.

$L^2{}_2Ni\cdot 2H_2O$. 3-Methoxysalicyladehyde (1 g, 6.58 × 10^{-3} mol) and nickel acetate $Ni(OAc)_2\cdot 4H_2O$ (0.82 g, 3.29 × 10^{-3} mol) were mixed in ethanol (50 mL). The pH of the stirred and heated solution was made basic by addition of concentrated ammonia (pH ~ 8). The precipitate which formed was cooled, filtered out, washed with ethanol and diethyl oxide, and dried (85% yield). Dark red crystals suitable for X-ray analysis were obtained by slow evaporation of a saturated CH_2Cl_2 solution of this complex.

^1H NMR (200 MHz, 20 °C, d_6-dmso): δ 3.46 (s, 4H, H_2O), 3.78 (s, 6H, CH_3), 6.55 (t, J = 7.9 Hz, 2H, ArCH), 6.87 (dd, J = 7.9, 1.3 Hz, 2H, ArCH), 7.04 (dd, J = 7.9, 1.3 Hz, 2H, ArCH), 7.88 (d, J = 11.8 Hz, 2H, HC), 8.51 (d, J = 11.8 Hz, 2H, NH). $^{13}C\{^1H\}$ NMR (50.32 MHz, 20 °C, d_6-dmso) 55.68 (s, CH_3), 113.77 (s, ArCH), 114.31 (s, ArCH), 120.56 (s, ArC), 124.84 (s, ArCH), 150.85 (s, ArC), 153.97 (s, ArC), 164.75 (s, HC=N). UV–vis (acetone) [λ (ϵ)]: 560 (75), 430 (sh), 403 (3020), 330 (7200). Anal. Calcd for $C_{16}H_{18}N_2NiO_6$: C, 48.8; H, 4.6; N, 7.1; Ni, 15.0. Found: C, 49.3; H, 5.0; N, 7.1; Ni, 15.1.

$L^2{}_2NiNaClO_4\cdot H_2O$. $L^2{}_2Ni\cdot 2H_2O$ (0.22 g, 5.83 × 10^{-4} mol) was partly dissolved in acetone (20 mL). Addition of a slight excess of sodium perchlorate (0.1 g, 7 × 10^{-4} mol) to the stirred solution yielded the desired product which precipitated a few minutes later. The precipitate was filtered out, washed with cold acetone and diethyl oxide, and dried (68% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a THF solution containing equimolar amounts of $L^2{}_2Ni\cdot 2H_2O$ and $NaClO_4$.

^1H NMR (200 MHz, 20 °C, d_6-dmso): δ 3.45 (s, 2H, H_2O), 4.00 (s, 6H, CH_3), 6.63 (t, J = 8 Hz, 2H, ArCH), 6.96 (d, J = 8 Hz, 2H, ArCH), 7.08 (dd, J = 8, 1.3 Hz, 2H, ArCH), 8.03 (d, J = 11.3 Hz, 2H, CH), 8.65 (d, J = 11.3 Hz, 2H, NH). $^{13}C\{^1H\}$ NMR (50.32 MHz, 20 °C, d_6-dmso): 55.59 (s, CH_3), 113.45 (s, ArCH), 114.55 (s, ArCH), 119.92 (s, ArC), 124.49 (s, ArCH), 149.83 (s, ArC), 152.76 (s, ArC), 166.61 (s, HC=N). ^{23}Na NMR (66.16 MHz, 20 °C, CD_3COCD_3): δ –0.9 ppm ($\nu_{1/2}$ = 200 Hz). UV–vis (acetone) [λ (ϵ)]: 540 (72), 394 (3450), 338 (7050). Mass spectrum (FAB): m/z = 381, $[C_{16}H_{16}N_2NaNiO_4]^+$. Anal. Calcd for $C_{16}H_{18}ClNaNiO_9$: C, 38.4; H, 3.6; N, 5.6; Na, 4.6; Ni, 11.8. Found: C, 38.0; H, 3.5; N, 5.4; Na, 4.4; Ni, 11.6.

An identical preparation led to $L^2{}_2NiLiClO_4\cdot 2H_2O$. ^1H NMR (200 MHz, 20 °C, CD_3COCD_3): δ 3.03 (s, 4H, H_2O), 3.89 (s, 6H, CH_3), 6.74 (t, J = 8 Hz, 2H, ArCH), 7.00 (d, J = 8 Hz, 2H, ArCH), 7.10 (d, J = 8 Hz, 2H, ArCH), 8.08 (d, J = 11.6 Hz, 2H, CH), 8.22 (d, J = 11.6 Hz, 2H, NH). UV–vis acetone [λ (ϵ)]: 540 (75), 394 (3500), 338 (7070). Anal. Calcd for $C_{16}H_{20}ClLiN_2NiO_{10}$: C, 38.3; H, 4.0; Li, 1.4; N, 5.6; Ni, 11.8. Found: C, 38.5; H, 3.9; Li, 1.3; N, 5.9; Ni, 11.5.

$L^2{}_2NiKI\cdot H_2O$ was similarly prepared, using KI and acetone as solvent. ^1H NMR (200 MHz, 20 °C, CD_3COCD_3): δ 2.83 (s, 2H, H_2O), 3.83 (s, 6H, CH_3), 6.52 (t, J = 8 Hz, 2H, ArCH), 6.83 (d, J = 8 Hz, 2H, ArCH), 6.97 (d, J = 8 Hz, 2H, ArCH), 7.73 (d, J = 11.6 Hz, 2H, CH), 8.85 (d, J = 11.6 Hz, 2H, NH). UV–vis acetone [λ (ϵ)]: 540 (74), 400 (3480), 337 (7030). Anal. Calcd for $C_{16}H_{18}IKN_2NiO_5$: C, 35.3; H, 3.3; K, 7.2; N, 5.1; Ni, 10.9. Found: C, 35.2; H, 3.3; K, 7.0; N, 5.0; Ni, 10.5.

Single-Crystal X-ray Analysis. Suitable single crystals were obtained from CH_2Cl_2 and $L^2{}_2Ni\cdot 2H_2O$ (**1**) or THF and $L^2{}_2NiNaClO_4\cdot H_2O$ (**2**) upon slow evaporation. Crystals were glued on a glass fiber. The accurate unit cell parameters for each compound were obtained by means of least-squares fit of 25 centered reflections. The data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A summary of the crystallographic data and data collection and refinement parameters is given in Table 1. Three standard reflections were monitored every 2 h and showed no significant variation over the data collection. Data were reduced in the usual way with the MolEN package.[30] An empirical absorption correction[31] was applied on the basis of ψ scans. The structures of **1** and **2** were solved by direct methods[32] and refined by the full-matrix least-squares technique,[33] using anisotropic thermal parameters for non-hydrogen atoms. Hydrogen atoms were introduced in calculations with fixed isotropic displacement parameters, using a riding model, except those of water molecules, which were refined. Atomic scattering factors were taken from a standard source.[34] The fractional coordinates are given in Tables 2 (**1**) and 3 (**2**).

Supplementary Material Available: Hydrogen parameters (Tables S1.1 and S1.2) anisotropic thermal parameters (Tables S2.1 and S2.2), bond distances and angles (Tables S3.1 and S3.2), and least-squares plane equations (Tables S4.1 and S4.2) (11 pages). Ordering information is given on any current masthead page.

---

(30) Fair, C. K. MolEN. Structure Solution Procedures; Enraf-Nonius: Delft, Holland, 1990.

(31) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A21*, 351.

(32) Sheldrick, G. SHELXS-86. Program for Crystal Structure Solution, University of Gottingen, Gottingen, Federal Republic of Germany, 1986.

(33) Sheldrick, G. SHELX76. Program for Crystal Structure Determination, University of Cambridge, England, 1976.

(34) Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.