Assembling Processes in a System Comprising Four Constituents: Two Metal Ions (Na, Ni) and Two Anionic Ligands (Perchlorato and 3-(2-Methoxyethoxy)salicylaldiminato(1−))

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Introduction

It has been shown that the nickel(II) complexes of 3-methoxysalicylaldimine and related compounds with polyether side arms are able to bind alkali-metal cations.[1−7] To date, two types of dimetallic (Ni, Na) complexes have been structurally characterized (Figure 1). A paramagnetic species (L^1_2-NiNaX)$_2$·H$_2$O (X stands for the picrate ion) has been obtained from the Schiff base L^{1}H. That dimer displays an unexpected cage structure with two side arms used to bind Na, an other to bind Ni, and a fourth free-standing functionality.[3,6] On the contrary, in the diamagnetic monomeric complex L$^2_2$NiNaClO$_4$·H$_2$O the Na atom is actually incorporated into an O$_4$ pseudocavity.[8] In order to improve the crown ether character of the latter compound we have substituted the imine L^{3}H for L^{2}H (Figure 1). Indeed, due to the presence of two oxygen atoms within each side arm, we expected the formation of an (L$^3_2$NiNaClO$_4$) entity with an external binding site comprising six oxygen atoms.

Experimental Section

Elemental analyses were carried out by the Service de Microanalyse du Laboratoire de Chimie de Coordination, Toulouse, France (C, H, N). Electronic spectra were obtained with a Cary 2300 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC200 spectrometer. Chemical shifts are given in ppm *versus* TMS (^{1}H and ^{13}C) using CDCl$_3$, CD$_3$COCD$_3$, or d_6-dmso as solvents.

Caution. The dinuclear complex reported here was isolated as the perchlorate salt. We have worked with these complexes in a number of organic solvents without any incident, and as solids, the complexes seem to be reasonably stable to shock and heat. In spite of these observations, the unpredictable behavior of perchlorate salts[9] necessitates extreme care in their handling.

Materials. All starting materials were purchased from Aldrich and were used without further purification. (2-Methoxyethoxy)-*p*-toluenesulfonate[10] and 2-hydroxy-3-(2-methoxyethoxy)salicylaldehyde[3] were prepared according to published procedures.

(1) van Staveren, C. J.; van Eerden, J.; van Veggel, F. C. J. M.; Harkema, S.; Reinhoudt, D. N. *J. Am. Chem. Soc.* **1988**, *110*, 4994.
(2) Lindsey, J. S. *New. J. Chem.* **1991**, *15*, 153.
(3) Schall, O. F.; Robinson, K.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1993**, *115*, 5962.
(4) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
(5) Schepartz, A.; McDevitt, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 5976.
(6) Schall, O. F.; Robinson, K.; Atwood, J. L.; Gokel, G. W. *J. Am. Chem. Soc.* **1991**, *113*, 7434.
(7) Jones, M. W.; Gupta, N.; Schepartz, A.; Thorp, H. H. *Inorg. Chem.* **1992**, *31*, 1308.
(8) Costes, J. P. ; Dahan, F. ; Laurent, J. P. *Inorg. Chem.* **1994**, *33*, 2738.
(9) Everett, K.; Graf, F. A., Jr. In *CRC Handback of Laboratory Safety*, 2nd ed.; Steere, N. V., Ed.; Chemical Rubber Co.: Cleveland, OH, 1971.
(10) Ouchi, M.; Inoue, Y.; Kanzaki, T.; Hakushi, T. *J. Org. Chem.* **1984**, *49*, 1408.
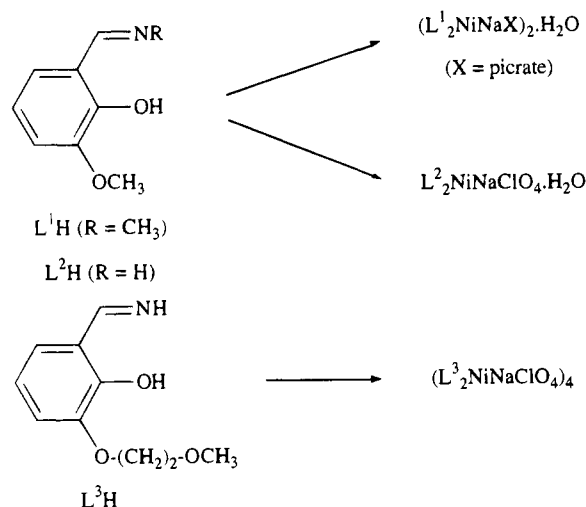
Figure 1. Schematic representation of the ligands mentioned in the text and formulas of the resulting complexes.

Bis(2-hydroxy-3-(2-methoxyethoxy)salicylaldiminato(1−))nickel-(II), L$^3_2$Ni. To 2-hydroxy-3-(2-methoxyethoxy)salicylaldehyde (1 g, 5.1×10^{-3} mol) in ethanol (20 mL) was first added nickel acetate Ni(OAc)$_2$·4H$_2$O (0.64 g, 2.5×10^{-3} mol). The pH of the stirred and heated solution was made basic by addition of concentrated ammonia (pH $\approx$ 8). The precipitate which formed was cooled, filtered out, washed with ethanol and diethyl oxide, and dried (0.53 g, 47% yield).

^{1}H NMR (200 MHz, 20°C, CDCl$_3$): δ 3.45 (s, 6H, CH$_3$), 3.73 (t, *J* = 4.3 Hz, 4H, C*H*$_2$O CH$_3$), 4.05 (t, *J* = 4.3 Hz, 4H, C*H*$_2$OAr), 6.44 (t, *J* = 7.7 Hz, 2H, ArCH), 6.83 (d , *J* = 7.7 Hz, 2H, ArCH), 6.87 (d, *J* = 7.7 Hz, 2H, ArCH), 7.62 (d, *J* = 11.7 Hz, 2H, HC=N), 7.90 (d, *J* = 11.7 Hz, 2H, NH). ^{13}C{^{1}H} NMR (50.32 MHz, 20 °C, CDCl$_3$): 59.1 (s, CH$_3$), 69.0 (s, CH$_2$), 71.6 (s, CH$_2$), 114.1 (s, ArCH), 118.8 (s, ArCH), 121.2 (s, ArC), 126.1 (s, ArCH), 149.8 (s, ArC), 155.0 (s, ArC), 163.5 (s, HC=N). dd transition (dmso): 555 nm. Anal. Calcd for C$_{20}$H$_{24}$N$_2$NiO$_6$: C, 53.7; H, 5.4; N, 6.3. Found: C, 53.2; H, 5.4; N, 6.2.

L$^3_2$NiNaClO$_4$. L$^3_2$Ni (0.15 g, 3.3×10^{-4} mol) was partly dissolved in ethanol (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 ethanol and diethyl oxide and dried (0.14 g, 74% yield). Crystals suitable for X-ray analysis were obtained by slow evaporation of a THF solution containing equimolar amounts of L$^3_2$Ni and NaClO$_4$.

^{1}H NMR (200 MHz, 20 °C, CD$_3$COCD$_3$) δ 3.44 (s, 6H, CH$_3$), 3.74 (t, *J* = 4.3 Hz, 4H, C*H*$_2$O CH$_3$), 4.20 (t, *J* = 4.3 Hz, 4H, C*H*$_2$OAr), 6.63 (t, *J* = 7.8 Hz, 2H, ArCH), 7.07 (d, *J* = 7.8 Hz, 2H, ArCH), 7.13 (dd, *J* = 7.8, 1.4 Hz, 2H, ArCH), 8.05 (d, *J* = 11.6 Hz, 2H, HC=N), 8.57 (d, *J* = 11.6 Hz, 2H, NH). ^{13}C{^{1}H} NMR (50.32 MHz, 20 °C, CD$_3$COCD$_3$): 58.4 (s, CH$_3$), 69.1 (s, CH$_2$), 70.2 (s, CH$_2$), 115.2 (s, ArCH), 118.3 (s, ArCH), 119.7 (s, ArC), 126.5 (s, ArCH), 148.6 (s, ArC), 156.1 (s, ArC), 167.8 (s, HC=N). dd transition (dmso): 535 nm. Mass spectrum (FAB, 3-nitrobenzyl alcohol matrix): *m/z* = 469 (100), [C$_{20}$H$_{24}$N$_2$NaNiO$_6$]$^+$, 1037 (0.6), [C$_{40}$H$_{48}$N$_4$Na$_2$Ni$_2$O$_{16}$Cl]$^+$. Anal. Calcd for C$_{20}$H$_{24}$ClNaN$_2$NiO$_{10}$: C, 42.1; H, 4.2; N, 4.9. Found: C, 41.7; H, 4.3; N, 4.8.

X-ray Structure Determination. Data Collection and Processing. Crystal data are gathered in Table 1. Diffraction measurements were made on an Enraf-Nonius CAD4 diffractometer. The unit-cell parameters were obtained from a least-squares fit of 25 reflections (with θ between 12.0 and 18.6°). Data were collected with the $\omega-2\theta$ scan technique (scan width, (0.80 + 0.35 tan θ)°; $2\theta_{max} = 50°$, $+h,+k,\pm l$) and a variable scan rate with a maximum scan time of 60 s/reflection. Lorentz and polarization corrections and empirical absorption corrections[11] from ψ scans ($T_{min-max} = 0.856-0.999$) were applied using the

(11) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A21*, 351.
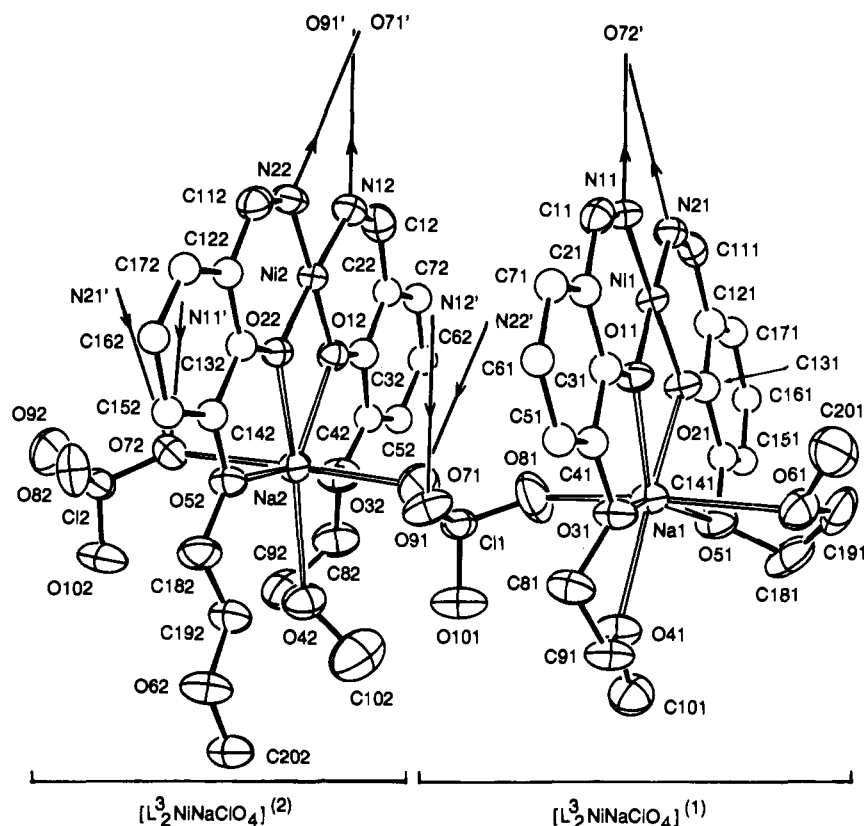
Figure 2. Ortep plot for $L^3_2NiNaClO_4$. Symmetry operation: (') $1 - x$, $1 - y$, $1 - z$. Hydrogen bonds are schematized by fine arrows.

Table 1. Crystallographic Data for $L^3_2NiNaClO_4$

chem formula =	space group =
$C_{20}H_{24}N_2O_{10}NaClNi$	$P2_1/n$ (No. 14)
$a = 17.447(2)$ Å	$T = 293$ K
$b = 13.876(1)$ Å	$\lambda = 0.710\,73$ Å
$c = 19.966(2)$ Å	$\varrho_{calc} = 1.566$ g cm^{-3}
$\beta = 91.16(1)°$	$\mu = 0.99$ mm^{-1}
$V = 4832.7(9)$ Å^3	$R^a = 0.034$
$Z = 8$	$R_w^b = 0.033$
fw = 569.56	

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

MolEN package,[12] and the data were reduced to $|F_o|$ values. Three reflections measured every 2 h showed no significant intensity variations. Of the 8777 reflections which were collected 8490 were unique ($R_{int} = 0.021$).

Structure Solution and Refinement. The structure was solved by direct methods[13] and refined by full-matrix least-squares.[14] The non-hydrogen atoms were refined anisotropically, except those of phenyl rings which were refined isotropically. The hydrogen atoms were included in calculated positions, riding on the atom to which they are bonded, with isotropic thermal parameters kept fixed. The final refinement cycle was based on 4699 observed reflections ($F_o^2 > 3\sigma$-(F_o^2)) and 266 variable parameters and converged to $R = 0.034$ and $R_w = 0.033$ with unit weights, goodness of fit $= 1.114$ (largest shift-to-error ratio $= 0.002$). The maximum and minimum peaks on the final Fourier difference map corresponded to 0.38 and -0.32 e Å^{-3}, respectively. Neutral atom scattering factors, including anomalous dispersion effects, were taken from the standard compilation.[15] All calculations were performed on a MicroVax 3400 computer. Significant atomic coordinates are given in Table 2.

(12) Fair, C. K. *MolEN. Structure Solution Procedures*; Enraf-Nonius: Delft, Holland, 1990.
(13) Sheldrick, G. M. *SHELXS-86. Program for Crystal Structure Solution*; University of Göttingen: Göttingen, FRG, 1986.
(14) Sheldrick, G. M. *SHELX 76. Program for Crystal Structure Determination*; University of Cambridge: Cambridge, U.K., 1976.
(15) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

Table 2. Significant Atomic Coordinates and Equivalent Isotropic Displacement Coefficients (Å$^2 \times 100$) for $L^3_2NiNaClO_4$

	x	y	z	$U_{eq}{}^a$
Ni(1)	0.78519(3)	0.43755(4)	0.51348(3)	3.76(3)
O(11)	0.7958(2)	0.3373(2)	0.4538(1)	4.4(2)
O(21)	0.8166(2)	0.5095(2)	0.4413(1)	4.5(2)
N(11)	0.7577(2)	0.3570(3)	0.5828(2)	4.6(2)
N(21)	0.7749(2)	0.5452(3)	0.5668(2)	4.5(2)
O(31)	0.8166(2)	0.2268(2)	0.3504(1)	5.5(2)
O(41)	0.8169(2)	0.3382(3)	0.2400(2)	7.2(3)
O(51)	0.8621(2)	0.5762(2)	0.3230(2)	6.3(2)
O(61)	0.9599(2)	0.4214(3)	0.3634(2)	7.6(3)
Ni(2)	0.41220(3)	0.53540(4)	0.46961(3)	4.26(3)
O(12)	0.4253(2)	0.6149(2)	0.3968(1)	4.6(2)
O(22)	0.4102(2)	0.4390(2)	0.4054(1)	4.4(2)
N(12)	0.4160(2)	0.6368(3)	0.5290(2)	5.8(3)
N(22)	0.3987(2)	0.4496(3)	0.5387(2)	5.6(3)
O(32)	0.4313(2)	0.6929(3)	0.2801(2)	7.1(2)
O(42)	0.4419(3)	0.5708(3)	0.1728(2)	8.7(3)
O(52)	0.4060(2)	0.3341(2)	0.2964(2)	5.3(2)
O(62)	0.4289(3)	0.2727(4)	0.1241(2)	10.4(3)
Na(1)	0.8176(1)	0.4069(1)	0.34957(8)	4.9(1)
Na(2)	0.4259(1)	0.5155(1)	0.30022(8)	5.1(1)
Cl(1)	0.62555(7)	0.43763(9)	0.28954(5)	5.08(7)
O(71)	0.5646(2)	0.4989(3)	0.3082(2)	9.2(3)
O(81)	0.6916(2)	0.4717(4)	0.3226(2)	12.3(4)
O(91)	0.6112(4)	0.3433(3)	0.3093(3)	13.8(5)
O(101)	0.6365(3)	0.4400(3)	0.2206(2)	8.9(3)
Cl(2)	0.22621(7)	0.4765(1)	0.25185(6)	5.45(7)
O(72)	0.2855(2)	0.5247(3)	0.2886(2)	7.4(3)
O(82)	0.2274(3)	0.3801(3)	0.2724(3)	14.3(5)
O(92)	0.1550(2)	0.5165(3)	0.2672(2)	9.6(3)
O(102)	0.2383(3)	0.4835(5)	0.1846(2)	13.8(4)

^{a} Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Results and Discussion

A procedure identical to that previously reported[8] for L^2_2-Ni·2H$_2$O allows the isolation of the monometallic precursor L^3_2-Ni which reacts with ClO$_4$Na to yield a dimetallic species which,

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) in $L^3_2NiNaClO_4{}^a$

Ni(1)−N(11)	1.849(4)	Ni(2)−N(12)	1.840(4)
Ni(1)−N(21)	1.845(4)	Ni(2)−N(22)	1.841(4)
Ni(1)−O(11)	1.844(3)	Ni(2)−O(12)	1.843(3)
Ni(1)−O(21)	1.846(3)	Ni(2)−O(22)	1.853(3)
Na(1)−O(11)	2.333(3)	Na(2)−O(12)	2.371(3)
Na(1)−O(21)	2.320(3)	Na(2)−O(22)	2.375(3)
Na(1)−O(31)	2.499(4)	Na(2)−O(32)	2.496(4)
Na(1)−O(41)	2.386(4)	Na(2)−O(42)	2.676(4)
Na(1)−O(51)	2.534(4)	Na(2)−O(52)	2.541(4)
Na(1)−O(61)	2.499(4)	Na(2)−O(71)	2.432(4)
Na(1)−O(81)	2.427(4)	Na(2)−O(72)	2.460(4)
N(11)−Ni(1)−N(21)	91.6(2)	N(12)−Ni(2)−N(22)	90.9(2)
N(11)−Ni(1)−O(11)	93.3(1)	N(12)−Ni(2)−O(12)	92.7(2)
N(11)−Ni(1)−O(21)	175.4(1)	N(12)−Ni(2)−O(22)	176.2(2)
N(21)−Ni(1)−O(11)	175.0(1)	N(22)−Ni(2)−O(12)	176.4(2)
N(21)−Ni(1)−O(21)	92.7(1)	N(22)−Ni(2)−O(22)	92.9(2)
O(11)−Ni(1)−O(21)	82.5(1)	O(12)−Ni(2)−O(22)	83.6(1)
O(11)−Na(1)−O(21)	63.0(1)	O(12)−Na(2)−O(22)	62.5(1)
O(11)−Na(1)−O(31)	65.1(1)	O(12)−Na(2)−O(32)	63.8(1)
O(11)−Na(1)−O(41)	130.9(1)	O(12)−Na(2)−O(42)	127.5(1)
O(11)−Na(1)−O(51)	128.9(1)	O(12)−Na(2)−O(52)	126.7(1)
O(11)−Na(1)−O(61)	96.6(1)	O(12)−Na(2)−O(71)	91.3(1)
O(11)−Na(1)−O(81)	100.8(1)	O(12)−Na(2)−O(72)	91.5(1)
O(21)−Na(1)−O(31)	127.5(1)	O(22)−Na(2)−O(32)	126.1(1)
O(21)−Na(1)−O(41)	165.7(1)	O(22)−Na(2)−O(42)	170.0(1)
O(21)−Na(1)−O(51)	66.7(1)	O(22)−Na(2)−O(52)	64.2(1)
O(21)−Na(1)−O(61)	83.5(1)	O(22)−Na(2)−O(71)	91.9(1)
O(21)−Na(1)−O(81)	85.8(2)	O(22)−Na(2)−O(72)	88.5(1)
O(31)−Na(1)−O(41)	66.8(1)	O(32)−Na(2)−O(42)	63.9(1)
O(31)−Na(1)−O(51)	158.6(1)	O(32)−Na(2)−O(52)	167.8(1)
O(31)−Na(1)−O(61)	95.0(1)	O(32)−Na(2)−O(71)	93.6(1)
O(31)−Na(1)−O(81)	111.4(2)	O(32)−Na(2)−O(72)	88.5(1)
O(41)−Na(1)−O(51)	100.0(1)	O(42)−Na(2)−O(52)	105.8(1)
O(41)−Na(1)−O(61)	96.9(1)	O(42)−Na(2)−O(71)	88.1(1)
O(41)−Na(1)−O(81)	87.5(2)	O(42)−Na(2)−O(72)	91.0(1)
O(51)−Na(1)−O(61)	69.0(1)	O(52)−Na(2)−O(71)	92.5(1)
O(51)−Na(1)−O(81)	83.7(2)	O(52)−Na(2)−O(72)	85.0(1)
O(61)−Na(1)−O(81)	152.7(2)	O(71)−Na(2)−O(72)	177.0(2)
N(11)···O(72)′	3.153(5)	N(12)···O(91)′	3.283(7)
H(N11)···O(72)′	2.19	H(N12)···O(91)′	2.39
N(11)−H(N11)···O(72)′	170	N(12)−H(N12)···O(91)′	154
N(21)···O(72)′	3.242(5)	N(22)···O(71)′	3.193(5)
H(N21)···O(72)′	2.29	H(N22)···O(71)′	2.27
N(21)−H(N21)···O(72)′	169	N(22)−H(N22)···O(71)′	160

^{a} A prime represents is the symmetry operation $1 - x$, $1 - y$, $1 - z$.

on the basis of chemical analysis data, corresponds to the formula $(L^3_2NiNaClO_4)$. Inspection of the mass spectrum (FAB$^+$, 3-nitrobenzyl alcohol matrix) shows that the main peak occurs at $m/z = 469$ and consequently may be attributed to $[L^3_2NiNa]^+$. A signal of much lower intensity is observed at $m/z = 1037$ suggesting the presence of some amount of the related dimeric species $[(L^3_2Ni)_2ClO_4]^+$. In both cases, the correct ratios of the isotopes (C, Cl, Ni) are observed. The oligomeric nature of the species under study is clearly established by a structural determination. The structure is represented in Figure 2, while relevant bond lengths and angles are quoted in Table 3.

The most important and unexpected features of the structure originate in the contribution afforded by the perchlorate anions to the organization of the system. First, two independent monomeric subunits $(L^3_2NiNaClO_4)^{(n)}$ ($n = 1$ and 2) are bridged by one ClO_4 anion to form a dimeric entity while the second

ClO_4 anion acts as a terminal ligand. Then a network of hydrogen bonds (represented by arrows in Figure 2) from the imino NH groups to the oxygen atoms of the bridging and terminal ClO_4 anions links two symmetrically related dimers to yield a "dimer of dimers". Examples of bridging perchlorates have been previously reported,[16−18] but a striking particularity of the present structure consists in the fact that the perchlorates are simultaneously involved in bridges and in hydrogen bonds.

Within each of the monomeric species $(L^3_2NiNaClO_4)^{(n)}$ ($n = 1$ and 2), two deprotonated Schiff base ligands are assembled around the nickel ion so that the resulting chromophore NiN_2O_2 adopts a cis (or syn) configuration while a trans (or anti) configuration most likely exists in the monometallic precursor L^3_2Ni.[8] The syn configuration leads to the formation of an outer pseudo-crown unit comprising six potentially donor sites. Surprisingly, the way in which the oxygenated side arms are involved in Na binding differs in the two $(L^3_2NiNaClO_4)^{(n)}$ units. Indeed, in the $n = 1$ unit, Na is bonded to the six oxygen atoms of its related ligands $(L^3_2)^{(1)}$ and completes its environment with an oxygen coming from the bridging ClO_4. In the $n = 2$ unit, Na is surrounded by five oxygen atoms from its related ligands $(L^3_2)^{(2)}$ and two oxygen from the anions $(ClO_4)^{(1)}$ and $(ClO_4)^{(2)}$ which are bridging and terminal, respectively. The reason of this difference is not clear to us, but it may be recognized that it is necessary to and perhaps prescribed by the formation of the (Na)···ClO_4···(Na) bridge. A similar behavior has been observed for potassium complexes of N-substituted derivatives of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane and attributed to a high level of steric crowding.[19] This explanation is unlikely in the present case due to the fact that the two subunits $(L^3_2-NiNa)^{(n)}$ ($n = 1$ and 2) obviously have the same steric requirements. Furthermore the Na···O(ether) separations [from 2.386(4) to 2.676(4) Å] and the related O−Na−O angles (from 62.5(1) to 66.8(1)°] are not indicative of important steric strains. Indeed, the minimum strain energy for an oxygenated five-membered chelate ring has been reported to occur at a M···O separation of about 2.5 Å and a O−M−O angle of about 70°.[19−21]

Finally, it appears that the four constituents of the system are intimately involved in the assembling process to give a highly ordered solid state structure. The monometallic precursor L^3_2Ni likely reacts with ClO_4Na in its trans configuration[8] to yield a mixed-metal (Ni, Na) species which has an inner cis N_2O_2Ni chromophore and can accommodate the Na ion in the outer pseudocavity. Unexpectedly, the ClO_4 anions not only are integral parts of the structure but also participate in the organizing process. Indeed, formation of a dimeric entity is achieved by a bridging ClO_4 while hydrogen bonds from the imino groups to terminal and bridging ClO_4 link two dimers to yield a "dimer of dimers".

(16) Belin, C.; Chaabouni, M.; Pascal J. L.; Potier, J.; Roziere, J. *J. Chem. Soc., Chem. Commun.* **1980**, 105.
(17) Belin, C. H.; Chaabouni, M.; Pascal, J. L.; Potier, J. *Inorg. Chem.* **1982**, *21*, 3557.
(18) Foley, J.; Kennefick, D.; Phelan, D.; Tyagi, S.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1983**, 2333.
(19) Hancock, R. D.; Bhavan, R.; Wade, P. W.; Boeyens, J. C. A.; Dobson, S. M. *Inorg. Chem.* **1989**, *28*, 187.
(20) Hancock, R. D. In *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; Basel, 1992.
(21) Hay, B. P.; Rustad, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 6316.