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## Carbon-Carbon Bond Forming and Breaking by a Metal-Assisted Redox Process in a Nickel(II)-Schiff Base Complex

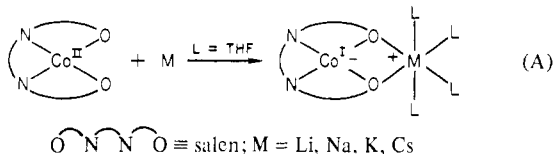
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Alkali metals (M = Li, Na) promote the reductive coupling of imino functional groups in [Ni(salophen)] (salophen = *N,N'*-*o*-phenylenebis(salicylidaminato) dianion). By such a reaction, two Ni(salophen) units are joined through a C-C bond to form a dimeric structure, [Ni(salophen)ML<sub>n</sub>]<sub>2</sub> (L = THF; M = Li, n = 2; M = Na, n = 3). No change in the oxidation state of the metal and in its coordination geometry was observed as a consequence of the reaction with alkali metals. In the final dimeric complex salophen acts as a bidentate ligand toward the alkali cation. The most relevant structural parameters concern the C-C bridging unit [1.64 (4) Å, M = Li; 1.58 (2) Å, M = Na] and the change occurring on the C=N imino functional unit of salophen [C-N<sub>av</sub> = 1.48 (3) Å; C=N<sub>av</sub> = 1.30 (3) Å]. An excess of alkali metals reacted with [Ni(salophen)] promoting its polymerization through a C-C bond formation involving all the C=N units present in the ligand. Mild oxidizing agents (MeI, O<sub>2</sub>, I<sub>2</sub>) removed two electrons from the dimeric compounds, promoting the C-C bond cleavage and restoring the original imino group. [Ni(salophen)] was recovered from all these reactions. The attack of the oxidizing agent does not occur at the ligand. Crystallographic details for [Ni(salophen)Li(THF)<sub>2</sub>]<sub>2</sub>·2THF: space group C2/c (monoclinic); a = 39.619 (5), b = 12.461 (2), c = 24.522 (4) Å; β = 91.28 (2)°; V = 12 103 Å<sup>3</sup>; Z = 8; final R factor 0.089 for 1509 observed reflections. Crystallographic details for [Ni(salophen)Na(THF)<sub>3</sub>]<sub>2</sub>·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>: space group P2<sub>1</sub>/c (monoclinic); a = 11.194 (2), b = 17.597 (3), c = 16.639 (3) Å; β = 90.59 (1)°; V = 3277 Å<sup>3</sup>; Z = 2; final R factor 0.060 for 1447 observed reflections.

### Introduction

Transition-metal complexes having polydentate unsaturated ligands can be reduced to become "electron reservoirs". The electronic enrichment of such compounds is possible because of π multiple metal-ligand interactions.<sup>1</sup> Electron-rich complexes of this type contain either a metal in a low oxidation state or the ligand in a reduced form.<sup>2</sup> Therefore the reactive site involved in electron-transfer processes may be either on the metal or on the ligand. M(salen)-type complexes (M = a transition metal; salen = *N,N'*-ethylenebis(salicylidaminato)) have been found to undergo reduction reactions.<sup>3</sup> Use of alkali metals as reducing agents led to the subsequent complexation of the alkali cation by the M(salen)-type complex acting as a bidentate ligand. Such a reaction produces for the case of [Co(salen)]

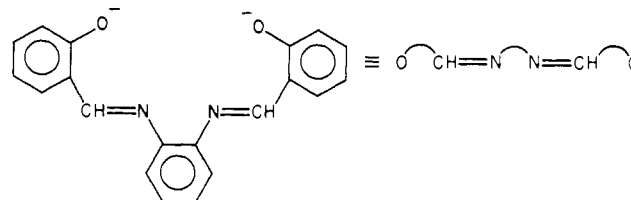


bimetallic cobalt(I)-alkali cation complexes, namely "bifunctional complexes", serving as acid-base sites for binding CO<sub>2</sub>.<sup>4</sup>

The present report concerns the extension of reaction A to the analogous nickel(II) complex [*N,N'*-*o*-phenylenebis(salicylidaminato)]nickel(II), [Ni(salophen)]. Alkali metals (Li, Na) promote the unprecedented reductive coupling of two [Ni(salophen)] units generating polynuclear nickel(II)-alkali ion complexes. The C-C bond formed between two [Ni(salophen)] units by the reaction with alkali metals is cleaved by mild oxidizing agents regenerating the original [Ni(salophen)] units. This result emphasizes how a metal can control C-C bond breaking and forming by a redox process<sup>5</sup> and how a C-C bond can be, as a matter of fact, an electron reservoir. The structure of one of the nickel(II)-alkali cation complexes here reported was recently communicated.<sup>6</sup>

### Experimental Section

Reactions were carried out under an atmosphere of purified nitrogen. Solvents were carefully purified and dried by standard methods. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. The magnetic measurements were carried out with a Faraday balance. Microanalytical determinations are unreliable due to the simultaneous presence of nickel and alkali cation. The content of THF for various compounds described depends on the crystallization rate and on the drying conditions. Gas volumetric absorption measurements were done by a published procedure.<sup>7</sup> The content of THF in the solid was determined by heating the solid at 150-160 °C and analyzing the resulting liquid by GLC. Abbreviations: THF = tetrahydrofuran, DMF = *N,N*-dimethylformamide, and salophen =



**Synthesis of [*N,N'*-*o*-Phenylenebis(salicylidaminato)]nickel(II), [Ni(salophen)] (I).** NiCl<sub>2</sub>·6H<sub>2</sub>O (38.2 g, 160.7 mmol) and CH<sub>3</sub>COONa·3H<sub>2</sub>O (14 g, 102.9 mmol) have been dissolved in 1000 mL of water. The aqueous solution was reacted with a suspension of salophenH<sub>2</sub> (60.0 g, 189.7 mmol) in 500 mL of EtOH. The reaction mixture was refluxed for 1 h. The resulting microcrystalline red solid was washed with H<sub>2</sub>O and Et<sub>2</sub>O, dried in vacuo, and recrystallized from DMF to give a deep red solid that was washed with THF and

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dried in vacuo at 130 °C for 1 h (41.2 g, 68.7%). Anal. Calcd for  $C_{20}H_{14}N_2O_2Ni$ : C, 64.39; H, 3.78; N, 7.51. Found: C, 64.10; H, 4.23; N, 7.32.

**Reduction of [Ni(salophen)] Using Sodium Metal. Synthesis of Complex II (M = Na).** A THF (100 mL) suspension of [Ni(salophen)] (13.30 g, 35.65 mmol) was reacted with sodium sand (0.785 g, 34.15 mmol). The solution turned green, and the solid dissolved. A small amount of undissolved solid was filtered out after 4 h, and  $Et_2O$  (100 mL) was added. The solution gave on standing for 3 days a microcrystalline deep green solid (9.0 g). Anal. Calcd for [Ni(salophen)Na(THF) $_3$ ] $_2$ ,  $C_{64}H_{76}N_4O_{10}Ni_2Na_2$ : C, 62.76; H, 6.26; N, 4.57. Found: C, 61.90; H, 6.31; N, 5.02. After the solid (0.893 g) was allowed to decompose at 150–160 °C for 6 h, 0.258 g of THF were collected (28.9%; calcd 35.3%). If the reduction of [Ni(salophen)] is carried out in more dilute solution and in the presence of a small amount of dioxane, complex II (M = Na) is recovered as crystals suitable for the X-ray analysis containing dioxane: [Ni(salophen)-Na(THF) $_3$ ] $_2$ · $C_4H_8O_2$ . The ESR spectrum of the solid as well as of the solution does not show the presence of any paramagnetic species. The magnetic susceptibility is  $\chi_M^{cor} = 210 \times 10^{-6}$  cgsu at 297 K.

**Reduction of [Ni(salophen)] with Lithium Metal. Synthesis of Complex II (M = Li).** A THF suspension of complex I (10.0 g, 26.81 mmol) was reacted with lithium metal (0.25 g, 36.02 mmol) under argon atmosphere. Complex I dissolved, giving a green solution in 1 h. The final filtered solution gave on standing for 1 day deep green crystals of [Ni(salophen)Li(THF) $_2$ ] $_2$  (II) (M = Li), which were filtered off and dried in vacuo (8.70 g, 71.8%). Anal. Calcd for [Ni(salophen)Li(THF) $_2$ ] $_2$ ,  $C_{56}H_{60}N_4O_8Ni_2Li_2$ : C, 64.16; H, 5.77; N, 5.34. Found: C, 64.05; H, 6.56; N, 5.12. The ESR spectrum both in the solid state and in solution did not show the presence of any paramagnetic species.  $\chi_M^{cor} = 64 \times 10^{-6}$  cgsu at 297 K. The mother liquor with addition of  $Et_2O$  (100 mL) gave on standing crystals suitable for an X-ray analysis: [Ni(salophen)Li(THF) $_2$ ] $_2$ ·2THF.

**Reaction of Complex II (M = Na) with Dicyclohexano-18-crown-6.** A green THF solution (50 mL) of complex II (M = Na) (1.16 g, 0.95 mmol) was treated with dicyclohexano-18-crown-6 (DHCH) (0.60 g, 1.61 mmol). A green microcrystalline solid precipitated immediately (1.04 g). Anal. Calcd for [Ni(salophen)Na] $_2$ (DHCH),  $C_{60}H_{64}N_4O_{10}Ni_2Na_2$ : C, 61.85; H, 5.50; N, 4.82. Found: C, 60.90; H, 5.47; N, 4.47.  $\chi_M^{cor} = 213 \times 10^{-6}$  cgsu at 294.5 K.

**Reaction of Complexes II with Iodine.** [Ni(salophen)Na(THF) $_3$ ] $_2$  (1.22 g, 1.00 mmol) dissolved in THF (50 mL) was reacted with iodine (0.70 g, 2.76 mmol). The reaction gave in a few minutes a red crystalline solid (0.80 g). The solid was shown to be complex VI (M = Na) by comparison with an authentic sample (vide infra). Moreover complex VI (M = Na) recrystallized from DMF gave [Ni(salophen)]. The reaction of complex II (M = Li) with  $I_2$  carried out under very similar conditions gave as red crystalline solid VI (M = Li), identified by comparison with an authentic sample.

**Reaction of Complexes II with Methyl Iodide.** A THF (50 mL) solution of [Ni(salophen)Na(THF) $_3$ ] $_2$  (1.00 g, 0.82 mmol) was reacted with MeI (0.5 mL, 8.03 mmol). The solution turned red in a few minutes giving complex VI (M = Na) as a crystalline solid (0.45 g). The low yield is due to the solubility of complex VI in THF. No attempt was made to recover additional complex from solution. Moreover, methane was identified as a product of the reaction. The lithium analogue [complex II, (M = Li)] reacted much more slowly (3 weeks) with MeI to form complex VI (M = Li) and methane.

**Preparation of [Ni(salophen)MI(THF) $_n$ ], Complexes VI (M = Na, Li).** Complex I (2.0 g, 5.36 mmol) reacted with a THF (50 mL) solution of an excess of dry NaI (2.0 g, 13.3 mmol). The suspension was stirred for 1 day. The crystalline solid formed was filtered and dried in vacuo (0.8 g). Anal. Calcd for [Ni(salophen)NaI(THF) $_{0.5}$ ],  $C_{22}H_{18}N_2O_{2.5}NiNaI$ : C, 47.27; H, 3.24; N, 5.01; I, 22.70. Found: C, 46.30; H, 3.02; N, 4.87; I, 21.71. [Ni(salophen)NaI(THF) $_{0.5}$ ] recrystallized from DMF gave [Ni(salophen)]. The synthesis of complex VI (M = Li) was performed by the same route. Anal. Calcd for [Ni(salophen)LiI(THF) $_{0.5}$ ],  $C_{22}H_{18}N_2O_{2.5}LiNiI$ : C, 48.67; H, 3.34; N, 5.16; I, 23.37. Found: C, 48.56; H, 3.65; N, 5.32; I, 23.80.

**Reaction of Complexes II with  $O_2$ .** Complex II (M = Na) (1.11 g, 0.89 mmol) absorbed in THF at 19.0 °C 0.85 mmol of  $O_2$  in 2 h in a gas volumetric apparatus.<sup>7</sup> For five runs the value ranged from 0.95 to 0.98 mol of  $O_2$ /mol of II (M = Na). When a THF (50 mL) solution of complex II (M = Na) (0.966 g) was exposed to dry oxygen, the color changed rapidly from green to red. The solution was allowed to stand for 3 days, yielding a red solution (0.42 g), VII (M = Na).

**Table I.** Experimental Data for the X-ray Diffraction Studies on Crystalline [Ni(salophen)Li(THF) $_2$ ] $_2$ ·2THF and [Ni(salophen)Na(THF) $_3$ ] $_2$ · $C_4H_8O_2$

	$C_{64}H_{76}Li_2N_4Ni_2O_{10}$	$C_{68}H_{84}N_4Na_2Ni_2O_{12}$
(A) Crystal Parameters at Room Temperature (~21 °C)		
cryst syst	monoclinic	monoclinic
space group	$C2/c$ [ $C_{2h}^2$ -No. 15]	$P2_1/c$ [ $C_{2h}^2$ -No. 14]
<i>a</i> , Å	39.619 (5)	11.194 (2)
<i>b</i> , Å	12.461 (2)	17.597 (3)
<i>c</i> , Å	24.522 (4)	16.639 (3)
$\beta$ , deg	91.28 (1)	90.59 (1)
<i>V</i> , Å <sup>3</sup>	12103 (3)	3277 (1)
<i>Z</i> (formula units)	8	2
<i>d</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.31	1.33
mol wt	1192.6	1312.8
cryst dimens, mm	0.47 × 0.11 × 0.96	0.32 × 0.37 × 0.63
linear abs coeff, cm <sup>-1</sup>	12.27	13.30
(B) Measurement of Intensity Data		
diffractometer	Siemens AED	
radiation	nickel-filtered Cu K $\alpha$ ( $\lambda = 1.5418$ Å)	
scan type	$\theta$ - $2\theta$	
scan speed	3–12°/min	
scan width	[ $\theta_{Mo K\alpha} - 0.5^\circ$ ] – [ $\theta_{Mo K\alpha} + 0.5 + \Delta\theta$ ]; $\Delta\theta = \{(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda\} \tan \theta_{Mo K\alpha}$	
reflens measd	$\pm h, +k, l$	$\pm h, k, l$
$2\theta$ range, deg	6–110	6–120
std reflens <sup>a</sup>	531	411
unique total data	7606	4886
unique obsd data ( $I > 2\sigma$ )	1509	1447
no. of variables	309	246

<sup>a</sup> These were measured after every 50 reflections; no significant changes in intensity were observed.

It can be recrystallized from DMF to give [Ni(salophen)]. Conventional methods (reactions with KI,  $KMnO_4$ , etc.) have been found inappropriate for identifying peroxide species in this compound, since they did not reveal the presence of peroxides even in a mixture of  $Na_2O_2$  and Ni(salophen). Reaction of  $O_2$  with the lithium derivative, II (M = Li), (1.29 g, 1.23 mmol) in THF (50 mL) was carried out under similar conditions. The solution reacted significantly slower giving [Ni(salophen)] (0.6 g). The apparent difference with the sodium derivative depends on the fact that the supposed adducts [Ni(salophen)] $_2$ M $_2$ O $_2$ L $_n$  are probably very labile decomposing in the presence of a coordinating solvent. In a gas volumetric experiment II (M = Li) (0.93 g, 0.89 mmol) absorbed at 19 °C in THF 0.87 mmol of  $O_2$ . The value for five different experiments ranged from 0.94 to 0.98 mol of  $O_2$ /mol of II (M = Li).

**Preparation of the Polymeric Complex V.** A THF (50 mL) suspension of complex I (3.50 g, 9.38 mmol) was reacted with sodium sand (0.44 g, 19.1 mmol) and stirred for 24 h. Complex I and sodium were completely consumed affording a yellow jelly-like material. By exposure to oxygen this material became immediately green, slowly giving a red maroon solid. The suspension was allowed to stir for 2 days more and then evaporated to dryness. The recrystallization of the residue from DMF gave [Ni(salophen)] (1.60 g).

**X-ray Crystallography.** The crystals selected for study were mounted in glass capillaries and sealed under nitrogen. Extensive preliminary investigations employing rotation and Weissenberg photographs showed the crystals of the two complexes to be monoclinic with systematic absences consistent with the space groups  $C2/c$  or  $Cc$  for complex II (M = Li) and with the space group  $P2_1/c$  for complex II (M = Na). Crystal data and details of the parameters associated with data collection are given in Table I. Lattice constants came from a least-squares refinement of the  $2\theta$  values for 20 reflections having  $2\theta > 60^\circ$ .

Data were collected at room temperature on a single-crystal automated Siemens AED diffractometer. The pulse height discriminator was set to accept 90% of the Cu K $\alpha$  peak. For intensities and background, the profile measurement technique was used.<sup>8</sup> The

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**Table II.** Fractional Atomic Coordinates ( $\times 10^4$ ) with Estimated Standard Deviations in Parentheses for Complex II ( $M = \text{Li}$ )

atom	$x/a$	$y/b$	$z/c$	atom	$x/a$	$y/b$	$z/c$
Ni	1640 (1)	3128 (4)	3333 (2)	C10A	2373 (4)	1194 (14)	3460 (7)
NiA	1245 (1)	-709 (4)	3668 (2)	C11A	2431 (4)	762 (14)	3978 (7)
O1	1489 (4)	3393 (13)	2613 (6)	C12A	2179 (4)	167 (14)	4228 (7)
O2	1997 (4)	3992 (14)	3127 (6)	C13A	1870 (4)	3 (14)	3960 (7)
O1A	893 (4)	-877 (14)	3148 (6)	C14A	1581 (6)	-850 (22)	4691 (11)
O2A	973 (4)	-1582 (14)	4102 (6)	C15A	1303 (4)	-1470 (13)	4917 (8)
N1	1283 (4)	2269 (15)	3502 (8)	C16A	1342 (4)	-1704 (13)	5471 (8)
N2	1788 (5)	2924 (16)	4046 (8)	C17A	1089 (4)	-2252 (13)	5742 (8)
N1A	1496 (5)	150 (17)	3245 (8)	C18A	796 (4)	-2566 (13)	5458 (8)
N2A	1588 (5)	-582 (18)	4181 (8)	C19A	757 (4)	-2332 (13)	4904 (8)
Li	1828 (13)	4197 (46)	2397 (19)	C20A	1010 (4)	-1784 (13)	4633 (8)
LiA	610 (16)	-1721 (53)	3601 (24)	O3	2120 (5)	3543 (17)	1857 (8)
C1	1159 (3)	3268 (16)	2450 (7)	C21	1983 (10)	3070 (36)	1369 (17)
C2	1030 (3)	3979 (16)	2057 (7)	C22	2275 (11)	2672 (32)	1032 (15)
C3	696 (3)	3881 (16)	1871 (7)	C23	2578 (8)	2537 (26)	1434 (13)
C4	491 (3)	3073 (16)	2076 (7)	C24	2467 (10)	3127 (33)	1929 (15)
C5	620 (3)	2363 (16)	2468 (7)	O4	1761 (5)	5707 (17)	2215 (8)
C6	954 (3)	2460 (16)	2655 (7)	C31	1703 (10)	6401 (36)	2687 (16)
C7	1080 (6)	1674 (21)	3088 (9)	C32	1620 (11)	7458 (37)	2434 (19)
C8	1270 (5)	1984 (14)	4048 (5)	C33	1564 (12)	7260 (40)	1861 (21)
C9	1019 (5)	1374 (14)	4290 (5)	C34	1701 (8)	6196 (31)	1650 (14)
C10	1032 (5)	1185 (14)	4851 (5)	O5	211 (5)	-851 (18)	3724 (9)
C11	1296 (5)	1606 (14)	5170 (5)	C41	109 (10)	-484 (36)	4259 (15)
C12	1547 (5)	2216 (14)	4928 (5)	C42	-65 (11)	523 (42)	4220 (18)
C13	1534 (5)	2405 (14)	4367 (5)	C43	-42 (10)	892 (36)	3674 (19)
C14	2072 (8)	3216 (24)	4288 (11)	C44	95 (9)	19 (33)	3316 (13)
C15	2330 (4)	3765 (14)	3954 (8)	O6	503 (8)	-3145 (24)	3414 (10)
C16	2637 (4)	3891 (14)	4235 (8)	C51	190 (16)	-3652 (55)	3219 (22)
C17	2909 (4)	4372 (14)	3978 (8)	C52	307 (12)	-4821 (42)	3267 (16)
C18	2873 (4)	4727 (14)	3440 (8)	C53	665 (15)	-5048 (49)	3430 (20)
C19	2565 (4)	4602 (14)	3160 (8)	C54	796 (15)	-3967 (54)	3344 (20)
C20	2294 (4)	4121 (14)	3417 (8)	O7	3077 (7)	351 (21)	-68 (10)
C1A	925 (5)	-695 (16)	2598 (5)	C61	3425 (10)	113 (28)	-139 (13)
C2A	740 (5)	-1330 (16)	2230 (5)	C62	3569 (8)	459 (27)	459 (13)
C3A	764 (5)	-1153 (16)	1671 (5)	C63	3292 (8)	1023 (26)	758 (12)
C4A	973 (5)	-341 (16)	1480 (5)	C64	2991 (9)	1184 (30)	332 (14)
C5A	1158 (5)	294 (16)	1848 (5)	C71	4773 (18)	1779 (59)	4608 (37)
C6A	1134 (5)	116 (16)	2407 (5)	C72	4754 (19)	1634 (64)	5130 (32)
C7A	1334 (6)	811 (23)	2798 (10)	C73	4433 (16)	930 (46)	5071 (24)
C8A	1811 (4)	435 (14)	3441 (7)	C74	4298 (17)	819 (53)	4510 (32)
C9A	2063 (4)	1030 (14)	3191 (7)	C75	4564 (20)	1359 (61)	4215 (28)

structure amplitudes were obtained after the usual Lorentz and polarization reduction,<sup>9</sup> and the absolute scale was established by Wilson's method.<sup>10</sup> No correction for absorption was applied.

The function minimized during the full-matrix least-squares refinement and  $\sum w|\Delta F|^2$ . The weighting scheme used was  $w = k/[\sigma^2(F_o) + |g|(F_o^2)]$ ;  $k$  is redetermined after each structure factor calculation and refined by fitting  $(|F_o| - |F_c|)^2$  to  $[\sigma^2(F_o) + |g|(F_o^2)]/k$ . The value for  $g$  was that giving the smallest variation of the mean value of  $w(|F_o| - |F_c|)^2$  as a function of the magnitude of  $F_o$ . Neutral-atom scattering factors for Ni, Na, Li,<sup>11</sup> O, N, C,<sup>12</sup> and H<sup>13</sup> were used, and the real ( $\Delta f'$ ) and imaginary ( $\Delta f''$ ) corrections<sup>11</sup> for anomalous dispersion were included in all structure factor calculations. Residual  $R$  and weighted residual  $R_w$  indices were defined as  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ . The "goodness of fit" parameter was determined by the equation  $[\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$  where NO is the number of observed reflections and NV is the number of variables refined. In each structure, phenyl rings were treated as rigid groups and constrained with C-C = 1.395 Å and C-C-C = 120° with carbon temperature factors individually varied isotropically. For each structure, refinement was continued until shifts in all parameters were less than 1 esd in the

respective parameter. Further details of refinement of the individual structures are given below. Final fractional atomic coordinates are given in Tables II and III and SI (supplementary material), and the temperature factors appear in Tables SII and SIII (supplementary material).<sup>14</sup>

**Structure Solution and Refinement for Complex II ( $M = \text{Li}$ ).**  $E$ -statistics calculated as a function of  $\sin \theta$  favor the centric case,  $\{|E^2 - 1|\}$  being equal to 0.93 ( $\sim 0.97$  and  $\sim 0.74$  are the theoretical values accepted for centrosymmetric and noncentrosymmetric structures, respectively). The space group  $C2/c$  was then assumed and was confirmed by the successful solution and refinement of the structure. The structure was solved by the heavy-atom method starting from a three-dimensional Patterson map that gave the approximate coordinates for the two independent nickel atoms. The remaining non-hydrogen atoms of the complex molecule were located from successive  $\Delta F$  maps. Refinement was by full-matrix least-squares refinement down to the final  $R$  and  $R_w$  values of 0.089 and 0.093, respectively, by using the 1509 reflections having  $I > 2\sigma(I)$ . During the refinement only the nickel atoms and the nitrogen and oxygen atoms of salophen were allowed to vary anisotropically. Attempts to locate hydrogen atoms were unsuccessful. The asymmetric unit contains two molecules of THF of solvation. Peaks that were interpreted as representing these molecules were discernible only after the refinement had progressed for some time. Thermal motion in one of them was so high that it was not possible to distinguish which atom was the oxygen, perhaps due to rotational disorder within this group. Final temperature factors for these atoms, all of them considered as carbons, ranged from 18 to 21 Å<sup>2</sup>.

The ratio NO:NV (number of observations:number of variables) is 1509:309  $\approx$  5:1 and accounts for the low accuracy of this analysis. In the final stage of refinement, the values for  $k$  and  $g$  were 0.5792

(9) Data reduction, structure solution, and refinement were carried out on a Cyber 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale, using: "SHELX-76 System of Crystallographic Computer Programs"; Sheldrick, G. University of Cambridge; Cambridge, England, 1976. Calculations were performed with the financial support of the University of Parma.

(10) Wilson, A. J. C. *Nature (London)* **1942**, *150*, 151-2.

(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

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(14) See paragraph at end of paper regarding supplementary material.

Table III. Fractional Atomic Coordinates ( $\times 10^4$ ) with Estimated Standard Deviations in Parentheses for Complex II ( $M = Na$ )

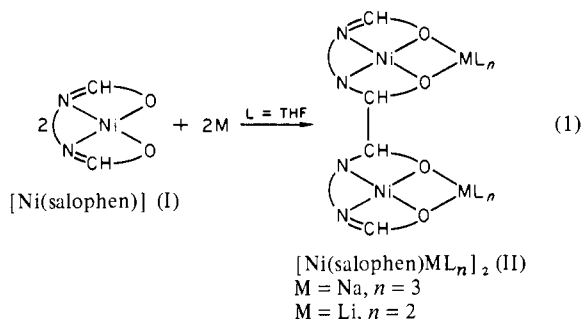
atom	$x/a$	$y/b$	$z/c$	atom	$x/a$	$y/b$	$z/c$
Ni	3336 (2)	588 (1)	1410 (1)	C2	6685 (6)	152 (1)	2116 (4)
Na	4700 (4)	2056 (3)	2110 (3)	C3	7599 (6)	-86 (4)	2161 (4)
O1	4924 (6)	893 (4)	1525 (4)	C4	7606 (6)	-699 (4)	1630 (4)
O2	3027 (6)	1317 (4)	2184 (4)	C5	6701 (6)	-774 (4)	1053 (4)
O3	6108 (11)	3042 (8)	2159 (7)	C6	5787 (6)	-236 (4)	1008 (4)
O4	3588 (11)	2825 (9)	1154 (9)	C7	4859 (9)	-284 (6)	354 (6)
O5	5110 (11)	1835 (8)	3465 (7)	C8	2707 (7)	-568 (4)	426 (4)
N1	3671 (7)	-164 (5)	676 (5)	C9	2713 (7)	-1189 (4)	-94 (4)
N2	1754 (7)	296 (5)	1288 (5)	C10	1649 (7)	-1567 (4)	-277 (4)
C31	6141 (22)	3804 (17)	2332 (16)	C11	579 (7)	-1324 (4)	61 (4)
C32	7200 (34)	4138 (14)	1972 (15)	C12	574 (7)	-703 (4)	582 (4)
C33	7879 (23)	3515 (23)	1935 (20)	C13	1638 (7)	-324 (4)	764 (4)
C34	7159 (27)	2884 (14)	1969 (16)	C14	851 (10)	605 (7)	1626 (6)
C41	3122 (27)	3508 (14)	1407 (12)	C15	903 (6)	1212 (5)	2201 (5)
C42	1895 (29)	3464 (18)	1220 (14)	C16	-179 (6)	1461 (5)	2515 (5)
C43	1760 (32)	2886 (17)	675 (21)	C17	-188 (6)	2015 (5)	3115 (5)
C44	2847 (40)	2496 (12)	564 (15)	C18	886 (6)	2320 (5)	3401 (5)
C51	4830 (15)	1136 (15)	3782 (11)	C19	1968 (6)	2071 (5)	3086 (5)
C52	5661 (33)	928 (14)	4418 (19)	C20	1977 (6)	1517 (5)	2487 (5)
C53	6214 (27)	1657 (28)	4578 (19)	C1S	490 (31)	217 (16)	4294 (15)
C54	5785 (24)	2214 (14)	4042 (15)	O1S	-575 (29)	479 (13)	4711 (16)
C1	5779 (6)	377 (4)	1539 (4)	C3S	-1322 (29)	110 (24)	5176 (25)

and 0.012948, respectively. The goodness of fit was 0.67.

**Structure Solution and Refinement for Complex II ( $M = Na$ ).** The 1447 reflections with  $I > 2\sigma(I)$  were used in the solution and refinement. The structure was solved by the heavy-atom method and refined to final  $R$  and  $R_w$  values of 0.060 and 0.063, respectively. During the refinement, the appearance in difference density maps of three peaks in the vicinity of an inversion center indicated the presence of solvent of crystallization. This could be interpreted as one molecule of dioxane having its gravity center on the symmetry center. Final isotropic temperature factors for these atoms ranged from 18 to 27  $\text{\AA}^2$  indicating a high thermal motion in this group. All the hydrogen atoms were located from successive difference Fourier syntheses and introduced as fixed contributors with isotropic temperature factors fixed at 6.3  $\text{\AA}^2$ . During the refinement all atoms of the complex molecule except the carbon atoms of salophen were allowed to vary anisotropically. The NO:NV ratio is 1447:246  $\approx$  6:1. The values for  $k$  and  $g$  were 0.6515 and 0.001496, respectively. The goodness of fit was 1.05.

## Results and Discussion

A tetrahydrofuran (THF) suspension of [ $N,N'$ -*o*-phenylenebis(salicylideneamino)]nickel(II), [Ni(salophen)], reacted with an alkali metal forming a green solution from which complexes II were isolated:



The isolation of complexes II as deep green crystals were achieved by addition of ether to the THF solutions. Complexes II are diamagnetic both in solution and in the solid state. They do not show any peculiar spectroscopic feature for the sure identification of their structure, which was ascertained by an X-ray analysis. Their structure would allow discussion of their genesis and reactivity. They present quite similar features but for some interesting aspects.

In both compounds two Ni(salophen) units are linked in dimers by a  $C_{sp^3}-C_{sp^3}$  bond (C7-C7A) between the imine carbon atoms of the original salophen molecules. In II ( $M = Na$ ) the middle point of the C-C bond lies on a crystallo-

graphic symmetry center, so the dimer is centrosymmetric; in II ( $M = Li$ ) there is a local  $C_2$  pseudosymmetry and the geometry of the two [Ni(salophen)] units is practically the same. The formation of the dimers does not modify the coordination of nickel, but markedly influences the conformation of the organic ligand. As a consequence of the tetrahedral character of C7 and C7A, the chelation rings involving them are folded with respect to the O1...C7 line by 29 (2) $^\circ$  (mean value) in II ( $M = Li$ ) and 41.1 (8) $^\circ$  in II ( $M = Na$ ), the rest of each [Ni(salophen)] unit remaining almost planar. The conformation of these rings is midway, neither boat nor twist in the lithium derivative while it is boat in the sodium derivative as indicated by asymmetry parameters: [ $M = Li$ ]  $\Delta C_s(O1) = 19 (2)^\circ$ ,  $\Delta C_s(C1-C6) = 23 (2)^\circ$ ,  $\Delta C_2(Ni) = 26 (1)^\circ$ ,  $\Delta C_2(C1-O1) = 18 (2)^\circ$ ; [ $M = Na$ ]  $\Delta C_s(O1) = 3.9 (4)^\circ$ ,  $\Delta C_s(C1-C6) = 5.3 (9)^\circ$ .<sup>15</sup> In both complexes coordination around nickel is nearly planar with small tetrahedral displacements that are significant only for the sodium derivative. Accordingly, no paramagnetism (expected for a geometry approaching a tetrahedral coordination) is observed.

Although the hydrogen atoms could not be directly located, bond distances and angles around C7 and C7A clearly indicate an  $sp^3$  hybridization state for these atoms, which are chiral. Their configuration is different in the two compounds, being  $R,R$  (or  $S,S$ ) for both carbons in II ( $M = Li$ ) and  $R,S$  (or  $S,R$ ) in II ( $M = Na$ ). As a consequence there is a significant difference in the mutual orientation of the two [Ni(salophen)] units, as can be seen from the Newman projections along the C7-C7A bonds (Figures 1 and 2) and from the values of the torsion angles (Table V). In II ( $M = Li$ ) the H atoms at C7 and C7A have an almost trans configuration, which is imposed by crystallographic requirements in II ( $M = Na$ ).

Bond distances and angles within the [Ni(salophen)] moiety of each dimer are very close and fall in the range found for [M(salen)M']-type complexes,<sup>3,16</sup> except for the C-N units involved in the dimerization process (Table IV). N1-C7 and

(15) Duax, W. L.; Weeks, C. M.; Rohrer, D. C. *Top. Stereochem.* **1976**, *9*, 271-383.

(16) Complexation of alkali cations by Schiff base complexes gives rise to complexes that have been structurally identified: Floriani, C.; Calderazzo, F.; Randaccio, L. *J. Chem. Soc., Chem. Commun.* **1973**, 384-5. Bresciani-Pahor, N.; Calligaris, M.; Delise, P.; Nardin, G.; Randaccio, L.; Zotti, E.; Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 2310-6. Armstrong, L. G.; Lip, H. C.; Lindoy, L. F.; McPartlin, M.; Tasker, P. A. *Ibid.* **1977**, 1771-4. Pasquali, M.; Marchetti, F.; Floriani, C.; Cesari, M. *Inorg. Chem.* **1980**, *19*, 1198-202.

Table IV. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses for Complexes II

	M = Li	"A"-labeled dimer	M = Na <sup>a</sup>		M = Li	"A"-labeled dimer	M = Na <sup>a</sup>
Ni-O1	1.88 (2)	1.88 (2)	1.865 (7)	Ni-O2	1.86 (2)	1.88 (2)	1.853 (7)
Ni-N1	1.83 (2)	1.81 (2)	1.842 (9)	Ni-N2	1.85 (2)	1.84 (2)	1.853 (8)
O1-C1	1.37 (2)	1.38 (2)	1.32 (1)	O2-C20	1.37 (2)	1.33 (2)	1.33 (1)
C6-C7	1.52 (3)	1.50 (3)	1.50 (1)	C15-C14	1.49 (3)	1.46 (3)	1.43 (1)
N1-C7	1.48 (3)	1.50 (3)	1.45 (1)	N2-C14	1.31 (3)	1.30 (3)	1.28 (1)
N1-C8	1.39 (2)	1.37 (3)	1.35 (1)	N2-C13	1.44 (3)	1.45 (3)	1.40 (1)
C7-C7A		1.64 (4)	1.58 (2)				
O1-Ni-O2	82.6 (7)	83.9 (7)	85.1 (3)	Ni-O1-M	99 (2)	95.9 (2)	101.3 (3)
O1-Ni-N1	94.8 (8)	94.9 (8)	94.3 (3)	Ni-O1-C1	122 (1)	124 (1)	119.6 (5)
N1-Ni-N2	86.3 (9)	86.2 (9)	85.9 (4)	M-O1-C1	135 (2)	137 (2)	133.9 (5)
N2-N1-O2	96.3 (8)	95.0 (8)	94.8 (3)	Ni-O2-M	95 (2)	97 (2)	101.4 (3)
O1-Ni-N2	177.8 (9)	178.5 (9)	179.3 (4)	Ni-O2-C20	125 (1)	128 (1)	128.2 (6)
N1-Ni-O2	177.3 (8)	178.4 (9)	177.5 (4)	M-O2-C20	138 (2)	133 (2)	126.7 (6)
O1-C1-C6	122 (1)	121 (1)	122.1 (6)	O2-C20-C15	121 (2)	120 (2)	122.0 (7)
O1-C1-C2	118 (1)	119 (1)	118.0 (7)	O2-C20-C19	119 (2)	120 (2)	117.9 (6)
C1-C6-C7	122 (1)	121 (1)	119.6 (7)	C20-C15-C14	128 (2)	126 (2)	122.9 (8)
C5-C6-C7	118 (1)	119 (2)	120.2 (7)	C16-C15-C14	112 (2)	114 (2)	117.0 (8)
C6-C7-N1	109 (2)	111 (2)	110.7 (8)	C15-C14-N2	118 (2)	122 (2)	125.5 (9)
C6-C7-C7A	108 (2)	109 (2)	111.3 (8)				
N1-C7-C7A	107 (2)	107 (2)	111.9 (8)	Ni-N2-C14	130 (2)	127 (2)	126.2 (8)
Ni-N1-C7	123 (1)	121 (2)	122.8 (7)	Ni-N2-C13	111 (1)	111 (1)	111.5 (6)
Ni-N1-C8	115 (1)	118 (2)	114.5 (6)	C13-N2-C14	119 (2)	122 (2)	122.3 (9)
C7-N1-C8	120 (2)	119 (2)	122.7 (7)	N2-C13-C8	113 (1)	115 (2)	114.5 (7)
N1-C8-C13	114 (1)	111 (2)	113.5 (7)	N2-C13-C12	127 (1)	125 (2)	125.5 (7)
N1-C8-C9	126 (1)	129 (2)	126.4 (8)				

<sup>a</sup> For complex II (M = Na) "A" represents an atom related by the symmetry operation  $1 - x, \bar{y}, \bar{z}$ .

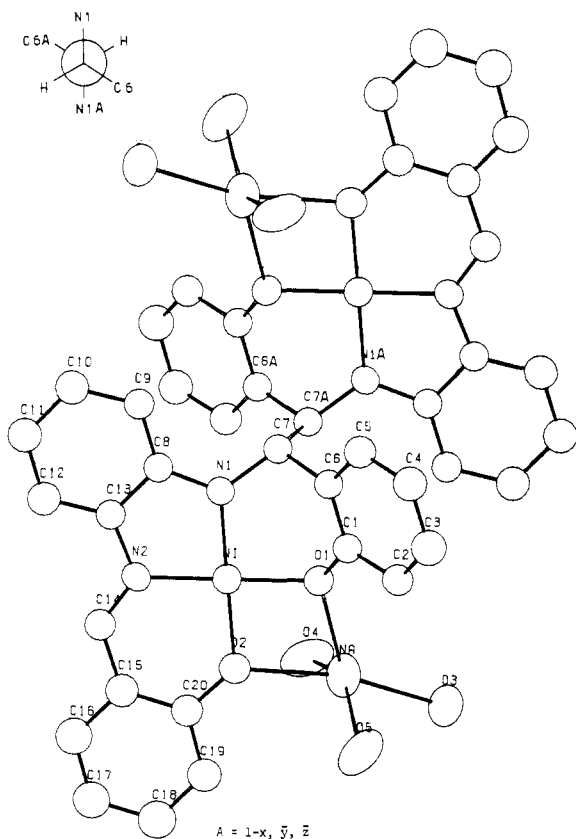


Figure 1. ORTEP drawing of complex II (M = Na). The Newman projection along the C7-C7A bond is shown at the top.

N1A-C7A in complex II (M = Li) [1.48 (3), 1.50 (3) Å] and N1-C7 in complex II (M = Na) [1.45 (1) Å] have values corresponding to a C-N single bond. These values are, as expected, longer than the C=N bond distances found for C14-N2 and C14A-N2A [for complex II (M = Li) 1.31 (3), 1.30 (3) Å; for complex II (M = Na) 1.28 (1) Å]. The C-C bond linking the two [Ni(salophen)] units is rather long [1.64

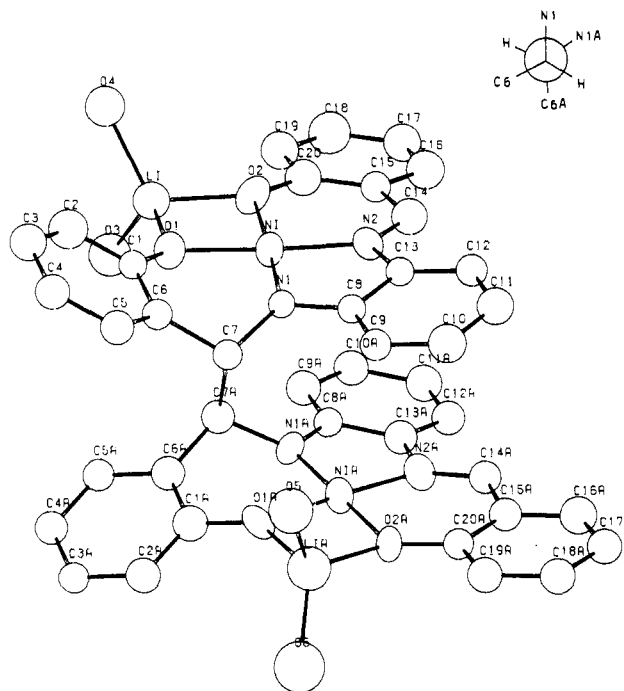


Figure 2. ORTEP drawing of complex II (M = Li). The Newman projection along the C7-C7A bond is shown at the top.

Å in complex II (M = Li) and 1.58 Å in complex II (M = Na)]. Comparable C-C bond distances can be found in sterically hindered residues joined by a C-C bond (e.g. 1.612 (7) Å in an anthraline dimer).<sup>17</sup>

In both complexes the two oxygen atoms of each [Ni(salophen)] unit are chelating the alkali metal.<sup>3,16</sup> The tetrahedral coordination around lithium is achieved by the oxygens from two THF molecules. The departure from an ideal tetrahedron is indicated by the O-Li-O angles which range from 83 (2)

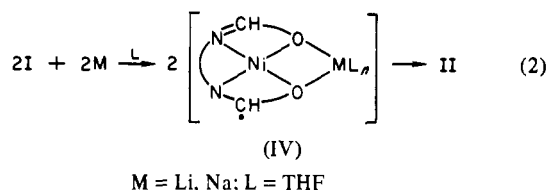
(17) Ahmed, F. R.; Neville, G. A. *Acta Crystallogr., Sect. B* 1982, B38, 2930-3.

Table V. Relevant Torsion Angles for Complexes II

	M = Li	"A"-labeled dimer	M = Na
Ni-O2-C20-C15	-13 (3)	-10 (3)	-4.3 (1.2)
O2-C20-C15-C14	0 (3)	4 (3)	7.0 (1.3)
C20-C15-C14-N2	8 (4)	-4 (4)	-2.9 (1.6)
C15-C14-N2-Ni	-3 (4)	10 (4)	-3.7 (1.6)
C15-C14-N2-C13	-179 (2)	-178 (2)	176.4 (9)
C14-N2-C13-C8	-170 (3)	-170 (2)	177.5 (9)
N2-C13-C8-N1	-8 (2)	-3 (2)	0.8 (1.0)
C13-C8-N1-Ni	0 (2)	-2 (2)	1.2 (9)
C13-C8-N1-C7	164 (2)	159 (2)	-175.2 (8)
C8-N1-C7-C6	144 (2)	144 (2)	-140.3 (8)
N1-C7-C6-C1	42 (3)	44 (3)	-49.1 (1.0)
C7-C6-C1-O1	2 (3)	1 (3)	5.2 (1.1)
C6-C1-O1-Ni	-36 (2)	-35 (3)	43.1 (9)
N1-C7-C7A-N1A	54 (2)		180.0 (7)
N1-C7-C7A-C6A	175 (2)		-55.5 (11)
C6-C7-C7A-C6A	-68 (2)		180.0 (7)
C6-C7-C7A-N1A	172 (2)		55.5 (11)

to 122 (2)°. There are no statistically significant differences in the Li-O distances [1.77 (6)–1.95 (6) Å]. The coordination around sodium is completed by the oxygen atoms from three THF molecules. It can be described as a severely distorted square pyramid whose apex is occupied by O1. The greatest distortions imply the angles O1-Na-O2 = 66.8 (3)°, O1-Na-O3 = 127.0 (4)°, O2-Na-O3 = 166.0 (4)°, and O4-Na-O5 = 145.5 (5)°, the others ranging from 86.4 (4) to 106.2 (4)°. There are significant differences among the Na-O distances, the shorter ones being those involving the oxygen atoms of salophen [Na-O1 = 2.281 (9), Na-O2 = 2.284 (8) Å]. In addition, Na-O4 = 2.423 (15) Å is significantly longer than Na-O3 and Na-O5 [2.345 (14) and 2.329 (13) Å], respectively. It can be concluded that the departure from the ideal coordination polyhedron is mainly due to the O...O bite of [Ni(salophen)].

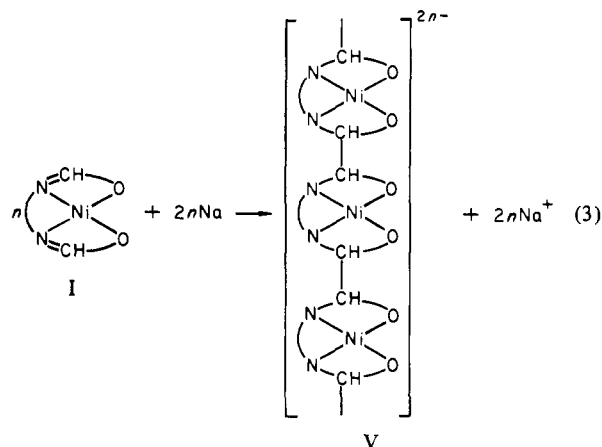
The genesis of complexes II can be viewed as derived from a free radical generated by alkali-metal reduction on the ligand:



Any possible equilibrium existing between IV and the final dimer II, must be, however, ruled out since complexes II are diamagnetic both in solution and in the solid state. Some precedents related to reaction 2 can be found. Oxidation of nickel(II) macrocyclic complexes can generate a free-radical site on the ligand leading to the dimerization.<sup>1a,5a,b</sup> Analogous reactions were communicated occurring via a C-C bond formation on oxovanadium(IV) complexes.<sup>5c</sup> Metal-free organic imino groups can themselves undergo coupling by the reduction with alkali metals.<sup>18</sup> It was expected, however, that in case of a Schiff base bonded to a metal the generation of a free-radical-type site can be stabilized by the metal-to-ligand system. This results is, however, not completely surprising since, in general, redox processes occurring on a cobalt chelate produce effective changes on the oxidation state of the metal, while in the case of nickel the ligand is the part preferably involved.<sup>2,19</sup> The utilization of bulky ligands for alkali cations,

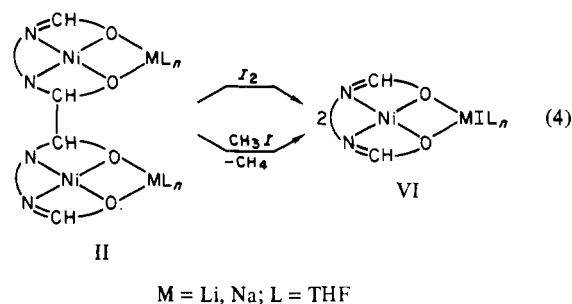
like crown ethers, in order to force a possible breaking of the C-C bond on behalf of a monomeric free-radical species (IV), was unsuccessful. Complex II (M = Na) reacted with dicyclohexano-18-crown-6 (DHCH) to give the diamagnetic complex  $\{[\text{Ni}(\text{salophen})\text{Na}]_2(\text{DHCH})\}_n$ . The structure of  $\{[\text{Ni}(\text{salophen})\text{Na}]_2(\text{DHCH})\}_n$  can be related to that of complex II (M = Na), where the THF molecules bonding Na<sup>+</sup> have been replaced by the oxygen atoms from the crown ether. Such a substitution occurred in the reaction of  $[\text{Co}(\text{salen})\text{Na}(\text{THF})]_n$  with DHCH.<sup>4</sup> On the basis of the structure of  $\{[\text{Co}(\text{salen})\text{Na}]_2(\text{DHCH})\}_n$  and of the retained C-C bond, a polymeric structure can be suggested for  $\{[\text{Ni}(\text{salophen})\text{Na}]_2(\text{DHCH})\}_n$  with DHCH filling the coordination sites of two sodium cations and bridging the dimeric units.

An excess of the alkali metal promotes a polymerization of complex I by the process exemplified in reaction 3. Starting



from a THF suspension of I, reaction 3 afforded a polymeric material. The chemical characterization of V is practically prevented by its polymeric nature. Its chemical reactivity, however, is very close to that of complexes II. Oxidation reactions carried out on polymeric complex V by using O<sub>2</sub> regenerate complex I (vide infra). Reaction 3 is formally the reduction of the salophen ligand by two electrons.

Although complexes II are nickel derivatives, they are unexpectedly reactive with electron acceptor molecules. The results are strongly dependent on the nature of the substrate employed. We found that a THF solution of complexes II reacts with either iodine or methyl iodide as reported in reaction 4.

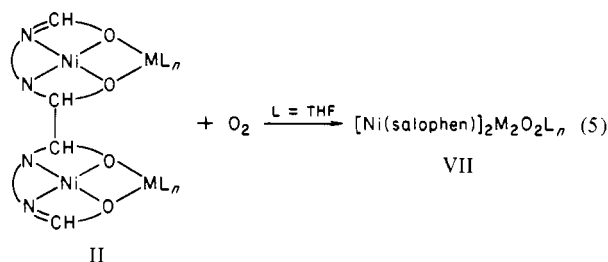


Complexes VI, which are labile adducts of [Ni(salophen)] and the corresponding alkali iodide, are easily decomposed into the two components by highly coordinating solvents like DMF. Sometimes such a decomposition occurs even in THF. Complexes VI have been synthesized by a direct reaction of [Ni(salophen)] with a THF solution of the corresponding alkali iodide. It is well-known that Msalen-type complexes act as bidentate ligands for alkali cations. Such complexes have been structurally identified with various salts.<sup>3,16</sup> For the case of methyl iodide complexes, VI forms along with methane coming from one-electron reduction of CH<sub>3</sub>I generating the methyl

(18) Smith, J. G.; Veach, C. D. *Can. J. Chem.* **1966**, *44*, 2497–502.

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free radical. Hydrogen abstraction from the solvent can explain the formation of methane. Complexes II are able to transfer two electrons to a substrate by a process that cleaves the C-C bond established between the two [Ni(salophen)] units and re-forms two imino groups. The property of II that deserves the main attention is their reducing ability associated with a C-C bond cleavage. Such a C-C bond acts, as a matter of fact, as an electron reservoir. This unique chemical behavior is emphasized by their reaction with O<sub>2</sub>. Complexes II absorb one molecule of O<sub>2</sub>/dimeric unit. The final material (VII) can be recrystallized from DMF giving [Ni(salophen)]. The expected presence of peroxides might be not confirmed by any conventional method (see Experimental Section). The reaction of II with dioxygen is reported in eq 5. Absorption of 1 mol



of O<sub>2</sub>/mol of dimer and, therefore, formation of peroxides are independent of the nature of the alkali cation. Formation of peroxides from the alkali metal itself is, on the contrary, highly dependent on the nature of the metal. The analytical identification of complexes VII is prevented by their lability being the cause of a partial decomposition into their components,

i.e., [Ni(salophen)] and alkali peroxides. This is a quite common evolution of such complexes in coordinating solvents and the reason why the treatment with DMF allowed us to break down adduct VII and to recover [Ni(salophen)]. In spite of the fact that reaction 1 does not produce Ni(I) complexes, reactivity of complexes II, however, is that expected for nickel(I) complexes having delocalized ligands. Results so far obtained seem to rule out any attack at the bridging C-C unit by the oxidizing agent. Although the C-C unit is a crucial site of the structure for the electron-transfer process, it does not become a reactive site. Reducing agents like complexes II having different metal centers and two electrons available seem to be rather promising for reducing CO<sub>2</sub> and CO<sub>2</sub>-like molecules.<sup>20</sup>

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**Registry No.** I, 36433-88-2; II (M = Li)·2THF, 87655-37-6; II (M = Li), 87655-36-5; II (M = Na)·C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, 87655-39-8; II (M = Na), 87655-38-7; VI (M = Li), 87681-04-7; VI (M = Na), 87655-40-1; {[Ni(salophen)Na]<sub>2</sub>(DHCH)}<sub>n</sub>, 87725-96-0; MeI, 74-88-4; Li, 7439-93-2; Na, 7440-23-5; O<sub>2</sub>, 7782-44-7; iodine, 7553-56-2; methane, 74-82-8.

**Supplementary Material Available:** Hydrogen coordinates for complex II (M = Na) (Table SI), thermal parameters (Tables SII and SIII), equations of least-squares planes (Table SIV), and listings of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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## Kinetic and Equilibrium Studies of Complex Formation of Nickel(II) with Carboxylate Ligands at High Pressure. 1. Nickel(II) Succinate and Nickel(II) Maleate

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Kinetic and equilibrium measurements were carried out for the complex-formation reaction of nickel(II) succinate and nickel(II) maleate in aqueous solution at pressures up to 1000 kg cm<sup>-2</sup>. From the pressure dependence of the stability constant and the rate constant, the reaction volume,  $\Delta V^\circ$ , and the activation volume,  $\Delta V_i^\ddagger$ , for the complex formation were estimated to be as follows:  $\Delta V^\circ = 11.1 \pm 0.9 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V_i^\ddagger = 14.1 \pm 0.8 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) succinate;  $\Delta V^\circ = 14.9 \pm 0.4 \text{ cm}^3 \text{ mol}^{-1}$  and  $\Delta V_i^\ddagger = 13.5 \pm 0.6 \text{ cm}^3 \text{ mol}^{-1}$  for nickel(II) maleate. When the volume change accompanied by the outer-sphere complex formation is taken into account, the activation volumes obtained were close to that found for the water-exchange reaction of the aquonickel(II) ion. This result is consistent with the interpretation that the rate-determining step is a water loss from the inner coordination shell of the nickel(II) ion, as postulated in the Eigen mechanism.

### Introduction

Kinetics of the complex-formation reaction of labile metal ions in aqueous solution have been extensively studied after the development of rapid-reaction techniques. The broad outline of the mechanism of these reactions is well understood in terms of the Eigen mechanism,<sup>1</sup> according to which the rate-determining step is the loss of a water molecule from the inner coordination shell of the metal after the formation of an external ion pair (or outer-sphere complex) between metal and ligand. However, some details still need to be elucidated concerning the details of the mechanism. For example, in the case of chelating ligands, the situation is more complicated due to the presence of a ring-closing step. For nickel(II)

monochelate complexes with malonate or substituted malonate anions, some discrepancies are seen in the literature concerning the assignment of the rate-determining step; some assign it to the first bond formation between the nickel(II) ion and the ligand,<sup>2,3</sup> and others to the chelate-ring closure.<sup>4</sup>

From measurements under variable pressure, one can obtain information about the volume change associated with the reaction under study.<sup>5</sup> Kinetic measurements at high pressure

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