

# A Novel Synthetic Approach to Asymmetric Salen, Dihydrosalen, and Tetrahydrosalen Ligands: Structures and O<sub>2</sub>-Activating Properties of their Nickel(II) and Cobalt(II) Complexes

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*Dedicated to Prof. Dr. Helmut Werner on the occasion of his 60th birthday*

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Activation of Dioxygen, Asymmetric Salen, Dihydrosalen, Tetrahydrosalen, Crystal Structure

A synthetic procedure is described for the preparation of the tetradentate N<sub>2</sub>O<sub>2</sub> ligands H<sub>2</sub>[H<sub>4</sub>]L<sup>1</sup> = 6-(2-hydroxyphenyl)-2,5-diaza-3,3-dimethyl-1-(2-hydroxy-3-*t*-butyl-5-methylphenyl)heptane, H<sub>2</sub>[H<sub>2</sub>]L<sup>1</sup> = 6-(2-hydroxyphenyl)-2,5-diaza-3,3-dimethyl-1-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-1-heptene, and H<sub>2</sub>L<sup>1</sup> = 6-(2-hydroxyphenyl)-2,5-diaza-3,3-dimethyl-1-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-1,5-heptadiene, which are asymmetric derivatives of the ligands tetrahydrosalen, dihydrosalen, and salen. Complexes Ni[H<sub>4</sub>]L<sup>1</sup>, Ni[H<sub>2</sub>]L<sup>1</sup>, NiL<sup>1</sup>, CoL<sup>1</sup>, Ni[H<sub>4</sub>]L<sup>2</sup> ([H<sub>4</sub>]L<sup>2</sup>)<sup>2-</sup> = anion of H<sub>2</sub>[H<sub>4</sub>]L<sup>2</sup> = N,N'-bis(2-hydroxy-3-*t*-butyl-5-methylbenzyl)-*trans*-(S,S)-1,2-diaminocyclohexane), and NiL<sup>2</sup> were prepared, characterized (VIS and IR absorption, magnetic moment) and subjected to spectrophotometric titration with pyridine, to determine the equilibrium constants for adduct formation. Single crystal X-ray structure analyses were carried out for Ni[H<sub>2</sub>]L<sup>1</sup> (monoclinic, P2<sub>1</sub>/n; *a* = 8.926(4), *b* = 29.324(7), *c* = 8.411(4) Å; β = 95.3(1)°; *Z* = 4), CoL<sup>1</sup> (monoclinic, C2/c; *a* = 25.389(2), *b* = 18.139(2), *c* = 10.179(1) Å; β = 112.227(6); *Z* = 8), and Ni[H<sub>4</sub>]L<sup>2</sup>·acetone (tetragonal, P4<sub>1</sub>2<sub>1</sub>2; *a* = 13.928(3), *c* = 33.698(5) Å; *Z* = 8). In all of the three complexes, the N<sub>2</sub>O<sub>2</sub>-metal coordination core is square-planar. The skeleton of the tetradentate ligand is more or less twisted. The planar cobalt(II) complex CoL<sup>1</sup> is a low spin d<sup>7</sup> system with μ<sub>exp</sub> = 2.02 BM at 298 K, whereas the planar complexes NiL<sup>1</sup>, Ni[H<sub>2</sub>]L<sup>1</sup>, and Ni[H<sub>4</sub>]L<sup>2</sup> are diamagnetic (μ<sub>exp</sub> = 0.28–0.64 BM). The blue solvate Ni[H<sub>4</sub>]L<sup>1</sup>·3EtOH·H<sub>2</sub>O is paramagnetic (μ<sub>exp</sub> = 3.04 BM), which points to octahedral coordination. In aerated acetone solution, the tetrahydrosalen-type complex Ni[H<sub>4</sub>]L<sup>1</sup> activates dioxygen and one C–N bond is oxidatively dehydrogenated. The VIS spectrum of the dihydrosalen-type complex formed is virtually identical with that of the aldimine complex Ni[H<sub>2</sub>]L<sup>1</sup>. In the presence of dioxygen, Co[H<sub>4</sub>]L<sup>1</sup> and Co[H<sub>2</sub>]L<sup>1</sup> are readily oxidized to CoL<sup>1</sup> in acetone solution.

# Abbreviations: salen, H<sub>2</sub>salen = N,N'-disalicylidene-1,2-diaminoethane; tetrahydrosalen, H<sub>2</sub>[H<sub>4</sub>]salen = N,N'-bis(2-hydroxybenzyl)-1,2-diaminoethane; dihydrosalen, H<sub>2</sub>[H<sub>2</sub>]salen = N-(2-hydroxybenzyl)-N'-salicylidene-1,2-diaminoethane; H<sub>2</sub>(Bu.X<sup>5</sup>)[H<sub>4</sub>]salen, N,N'-bis(2-hydroxy-3-*t*-butyl-5-X-benzyl)-1,2-diaminoethane; H<sub>2</sub>[H<sub>2</sub>]L<sup>1</sup>, 6-(2-hydroxyphenyl)-2,5-diaza-3,3-dimethyl-1-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-1-heptene-6; H<sub>2</sub>[H<sub>4</sub>]L<sup>1</sup>, 6-(2-hydroxyphenyl)-2,5-diaza-3,3-dimethyl-1-(2-hydroxy-3-*t*-butyl-5-

methylphenyl)heptane; H<sub>2</sub>L<sup>1</sup>, 6-(2-hydroxyphenyl)-2,5-diaza-3,3-dimethyl-1-(2-hydroxy-3-*t*-butyl-5-methylphenyl)-1,5-heptadiene; H<sub>2</sub>[H<sub>4</sub>]L<sup>2</sup>, N,N'-bis(2-hydroxy-3-*t*-butyl-5-methylbenzyl)-*trans*-(S,S)-1,2-diaminocyclohexane; H<sub>2</sub>L<sup>2</sup>, N,N'-bis(3-*t*-butyl-5-methylsalicylidene)-*trans*-(S,S)-1,2-diaminocyclohexane.

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## Introduction

In contrast to the rich literature on transition metal complexes with the tetradentate Schiff base ligand salen<sup>#</sup> and, in particular, on the dioxygen affinity of Co(salen) and its derivatives [1], rather little is known about the corresponding tetrahydro-salen<sup>#</sup> complexes [2]. Our recent systematic work on the coordination chemistry of the ligand tetrahydro-salen revealed that complexes with most surprising and remarkable properties can be obtained, when the ligand carries a specific set of substituents. The nickel(II) complexes Ni{(Bu,X<sup>5</sup>)[H<sub>4</sub>]salen}<sup>#</sup> (X<sup>5</sup> = H, Me, Cl), for example, interact with dioxygen in organic solvents and are oxidatively dehydrogenated [3]. The corresponding copper(II) complexes are stable towards O<sub>2</sub>, but in the case of cobalt(II) the interaction with dioxygen is even more pronounced [4].

The interesting results obtained with complexes based on specifically substituted tetrahydro-salen ligands led us to study the effect of ligand asymmetry. The tetrahydro-salen ligand H<sub>2</sub>(X)[H<sub>4</sub>]salen is symmetric in the sense that the two N-bound

benzyl moieties are identical. This is not so in the case of H<sub>2</sub>(X)(Y)[H<sub>4</sub>]salen, where the different substituents X and Y introduce asymmetry. The synthesis of asymmetric salen and tetrahydro-salen ligands is by no means trivial. In the present study a simple and efficient synthetic route has been developed, leading to the highly asymmetric dihydro-salen ligand H<sub>2</sub>[H<sub>2</sub>]L<sup>1</sup> and the corresponding tetrahydro-salen ligand H<sub>2</sub>[H<sub>4</sub>]L<sup>1#</sup> (see Chart I). The latter ligand reacts with nickel acetate to form the complex Ni[H<sub>4</sub>]L<sup>1</sup>, which, in aereated organic solvents, is subject to oxidative dehydrogenation and formation of a “half-salen” complex. In the presence of dioxygen, the “half-salen” ligand H<sub>2</sub>[H<sub>2</sub>]L<sup>1</sup> reacts with cobalt acetate to form the “salen” complex CoL<sup>1#</sup> (see Chart I).

The present contribution deals with the synthesis of the asymmetric tetrahydro-salen, dihydro-salen and salen ligands shown in Chart I and the properties of the corresponding Ni(II) and Co(II) complexes, especially with regard to their interaction with dioxygen. In addition, the results of the single crystal X-ray analyses of the complexes Ni[H<sub>2</sub>]L<sup>1</sup> and CoL<sup>1</sup> are presented. Information on the structure of the symmetric tetrahydro-salen nickel(II) complex Ni[H<sub>4</sub>]L<sup>2#</sup> (see Chart I) is included, which is of interest for stereochemical reasons.

## Experimental

Unless stated otherwise, the chemicals were commercial products of reagent grade quality.

### Preparation of the ligands

The preparation of H<sub>2</sub>L<sup>1</sup>, H<sub>2</sub>[H<sub>2</sub>]L<sup>1</sup>, and H<sub>2</sub>[H<sub>4</sub>]L<sup>1</sup> was based on the tridentate intermediates HL<sup>1</sup> = 2-(2-hydroxyphenyl)-3-aza-5-amino-5-methylhexene-2 and H[H<sub>2</sub>]L<sup>1</sup> = 2-(2-hydroxyphenyl)-3-aza-5-amino-5-methylhexane, respectively, which were prepared as follows. A solution of 0.136 mol of 2-hydroxyacetophenone in 50 ml of MeOH was added to a solution of 0.136 mol of 1,2-diamino-2-methylpropane in 10 ml of MeOH, and the mixture was refluxed for 30 min. Evaporation of the solvent *in vacuo* led to the mono-Schiff base HL<sup>1</sup> in the form of a yellow-brown oil (yield: >90%), which was characterized by <sup>1</sup>H NMR analysis. The reduction of HL<sup>1</sup> to H[H<sub>2</sub>]L<sup>1</sup> was carried out by adding 18.9 mmol of Na[BH<sub>4</sub>] in small portions to 12.6 mmol of yellow HL<sup>1</sup> dissolved in 50 ml of MeOH. The colourless solution was set to pH 1 with HCl, refluxed for 10 min, concentrated to

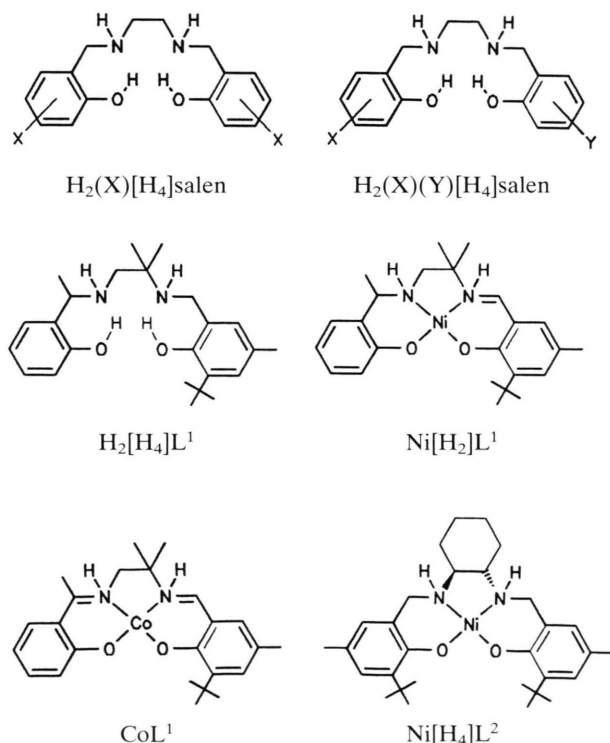


Chart I. Structural formulae of the ligands and complexes and abbreviations.

50–10 ml, set to pH 6–8 with 2 M NaOH, and extracted twice with  $\text{CH}_2\text{Cl}_2$ , which was dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent *in vacuo* led to slightly brownish, oily  $\text{H}[\text{H}_2]\text{L}^1$  (yield: 87%), which was characterized by  $^1\text{H}$  NMR analysis.

To obtain  $\text{H}_2\text{L}^1$ , a solution of 11.8 mmol of  $\text{HL}^1$  (see above) and 11.8 mmol of 3-*t*-butyl-5-methylsalicylaldehyde [4] in 30 ml of MeOH was refluxed for 30 min and evaporated to dryness. The brown, oily residue was dissolved in hot petroleum ether (b.p.: 40–80 °C). Standing of the yellow-brownish solution for 3–4 h at ambient temperature led to the formation of a brown oil, which was separated by decanting. Upon cooling of the solution, crystals of the yellow Schiff base  $\text{H}_2\text{L}^1$  formed (yield: 41%; m.p.: 121 °C).

$\text{H}_2[\text{H}_2]\text{L}^1$  was prepared by refluxing a solution of 10.9 mmol of  $\text{H}[\text{H}_2]\text{L}^1$  (see above) and 10.9 mmol of 3-*t*-butyl-5-methylsalicylaldehyde in 30 ml EtOH for 30 min. After partial evaporation of the solvent *in vacuo* and addition of petroleum ether the ligand began to crystallize slowly (yield: 77%; m.p.: 141–142 °C).

The reduction of  $\text{H}_2[\text{H}_2]\text{L}^1$  to colourless  $\text{H}_2[\text{H}_4]\text{L}^1$  was carried out as described above for the reduction of the Schiff base  $\text{HL}^1$  to  $\text{H}[\text{H}_2]\text{L}^1$  with  $\text{Na}[\text{BH}_4]$  (yield: 39%; m.p.: 121–122 °C).

The yellow ligand  $\text{H}_2\text{L}^2$  was prepared as follows: a solution of 0.0417 mol of 3-*t*-butyl-5-methylsalicylaldehyde [4] in 50 ml MeOH was added slowly to a solution of 0.0209 mol of *trans*-(S,S)-1,2-cyclohexane-diammoniumdi(+)D-hydrogen-tartrate [6] in 42 ml of 2 M NaOH. The yellow mixture was stirred and heated to about 65 °C for 15 min and then cooled in an ice bath. The solid product was filtered off, washed with cold water and recrystallized from hot EtOH to give yellow crystals (m.p.: 124 °C). The reduction of  $\text{H}_2\text{L}^2$  to  $\text{H}_2[\text{H}_4]\text{L}^2$  was carried out with  $\text{Na}[\text{BH}_4]$  in hot MeOH (60 °C), as described above for the reduction of  $\text{HL}^1$ . The colorless product was recrystallized from EtOH (m.p.: 145 °C).

The ligands  $\text{H}_2\text{L}^1$ ,  $\text{H}_2[\text{H}_2]\text{L}^1$ ,  $\text{H}_2[\text{H}_4]\text{L}^1$ ,  $\text{H}_2\text{L}^2$ , and  $\text{H}_2[\text{H}_4]\text{L}^2$  were characterized by  $^1\text{H}$  NMR, IR (N–H, C=N), and elemental analysis (C, H, N).

#### Preparation of the complexes

The complexes  $\text{NiL}^1$  (orange; m.p.: 261 °C),  $\text{Ni}[\text{H}_2]\text{L}^1$  (yellow-orange; m.p.: 239 °C),  $\text{Ni}[\text{H}_4]\text{L}^1$  (red; m.p.: 178 °C), and  $\text{CoL}^1$  (red; m.p.: 244 °C) were prepared by refluxing the solution of 1.3 mmol of the corresponding ligand and 1.3 mmol of nickel or cobalt acetate in 50 ml of MeOH for 30 min. After cooling the crystalline red products

were separated by filtration and recrystallized from MeOH or EtOH. The blue crystals obtained by recrystallization of  $\text{Ni}[\text{H}_4]\text{L}^1$  from EtOH became red upon heating *in vacuo*, which was accompanied by a loss in weight corresponding to  $3\text{EtOH} + 1\text{H}_2\text{O}$ .

$\text{Ni}[\text{H}_4]\text{L}^1$  and  $\text{CoL}^1$  were prepared under a nitrogen atmosphere to avoid oxidation to  $\text{Ni}[\text{H}_2]\text{L}^1$  and  $\text{Co(III)L}^1(\text{AcO})$ , respectively. An attempt to prepare  $\text{Co}[\text{H}_2]\text{L}^1$  (from  $\text{H}_2[\text{H}_2]\text{L}^1$  and cobalt acetate) under nitrogen failed. In agreement with analogous results reported recently [4], traces of  $\text{O}_2$  were sufficient to induce oxidative dehydrogenation of  $\text{Co}[\text{H}_2]\text{L}^1$  and formation of  $\text{CoL}^1$ .

$\text{Ni}[\text{H}_4]\text{L}^2$  and  $\text{NiL}^2$  were prepared as described previously [3, 4]. Recrystallization from acetone afforded the red adduct  $\text{Ni}[\text{H}_4]\text{L}^2 \cdot \text{acetone}$  (m.p.: 342 °C, dec.) and brown  $\text{NiL}^2$  (m.p.: 315 °C).

The complexes were additionally characterized by  $^1\text{H}$  NMR and IR analysis.

	Calcd Found	C C	H H	N % N %
$\text{NiL}^1$		65.94 65.93	6.92 6.80	6.41 6.38
$\text{Ni}[\text{H}_2]\text{L}^1$		65.63 65.38	7.34 7.29	6.38 6.24
$\text{Ni}[\text{H}_4]\text{L}^1 \cdot 3\text{EtOH} \cdot \text{H}_2\text{O}$		60.30 59.49*	9.11 8.20*	4.69 4.52
$\text{CoL}^1$		65.90 65.82	6.91 7.09	6.40 6.44
$\text{NiL}^2$		69.38 69.53	7.76 7.71	5.39 5.38
$\text{Ni}[\text{H}_4]\text{L}^2 \cdot \text{acetone}$		68.17 67.09*	8.67 8.61	4.82 5.04

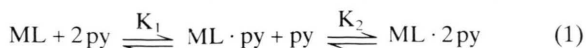
\* Data too low because of partial loss of crystal solvent upon analysis.

#### Instrumentation

UV/VIS spectra: diode array spectrophotometer (Hewlett-Packard, type 8451) and double beam spectrophotometer (Varian, type DMS 300).  $^1\text{H}$  NMR spectra: NMR spectrometer (Varian, type T-60). IR spectra: IR spectrometer (Beckman, type Acculab 2). Magnetic susceptibility: susceptibility balance, based on the Evans method (Johnson-Matthey).

#### Spectrophotometric titration

The stepwise addition of pyridine to the various complexes according to (1) ( $\text{M} = \text{Co}, \text{Ni}$ ) was followed spectrophotometrically



in acetone. The determination of  $K_1$  and  $K_2$  by computer fitting of the  $A/[\text{py}]$  data ( $A$  = absorbance for a given wavelength) is described elsewhere [4, 8].

#### X-ray structure determinations

The crystals for X-ray analysis were obtained by slow evaporation of the solvent ( $\text{Ni}[\text{H}_2]\text{L}^1$ : EtOH/petroleum ether (40–80 °C));  $\text{Ni}[\text{H}_4]\text{L}^2$ : acetone) or by cooling to –20 °C ( $\text{CoL}^1$  in  $\text{O}_2$ -stripped diethylether). Intensities were measured on a four-cycle diffractometer (Philips PW1100 (Darmstadt) or Enraf-Nonius CAD4 (Basel)) using

graphite-monochromatized  $\text{Mo-K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Cell constants were determined by least-squares methods from  $2\theta$  angles of 25 reflections ( $T = 289 \text{ K}$ ) on the same instruments. LP and background corrections were applied. Absorption correction has only been applied for  $\text{CoL}^1$ , using psi-scans. The structures of the nickel complexes were solved by direct methods using the program SHELXS-86 [9]. The refinements to the  $R$  values given in Table IV were carried out by using all  $F_o$  values (program SHELXL-93 [10]). Hydrogen atoms were positioned geometrically ( $\text{C-H}$  distance  $0.96 \text{ \AA}$ ) and not refined. The structure of  $\text{CoL}^1$  was solved and refined using the program

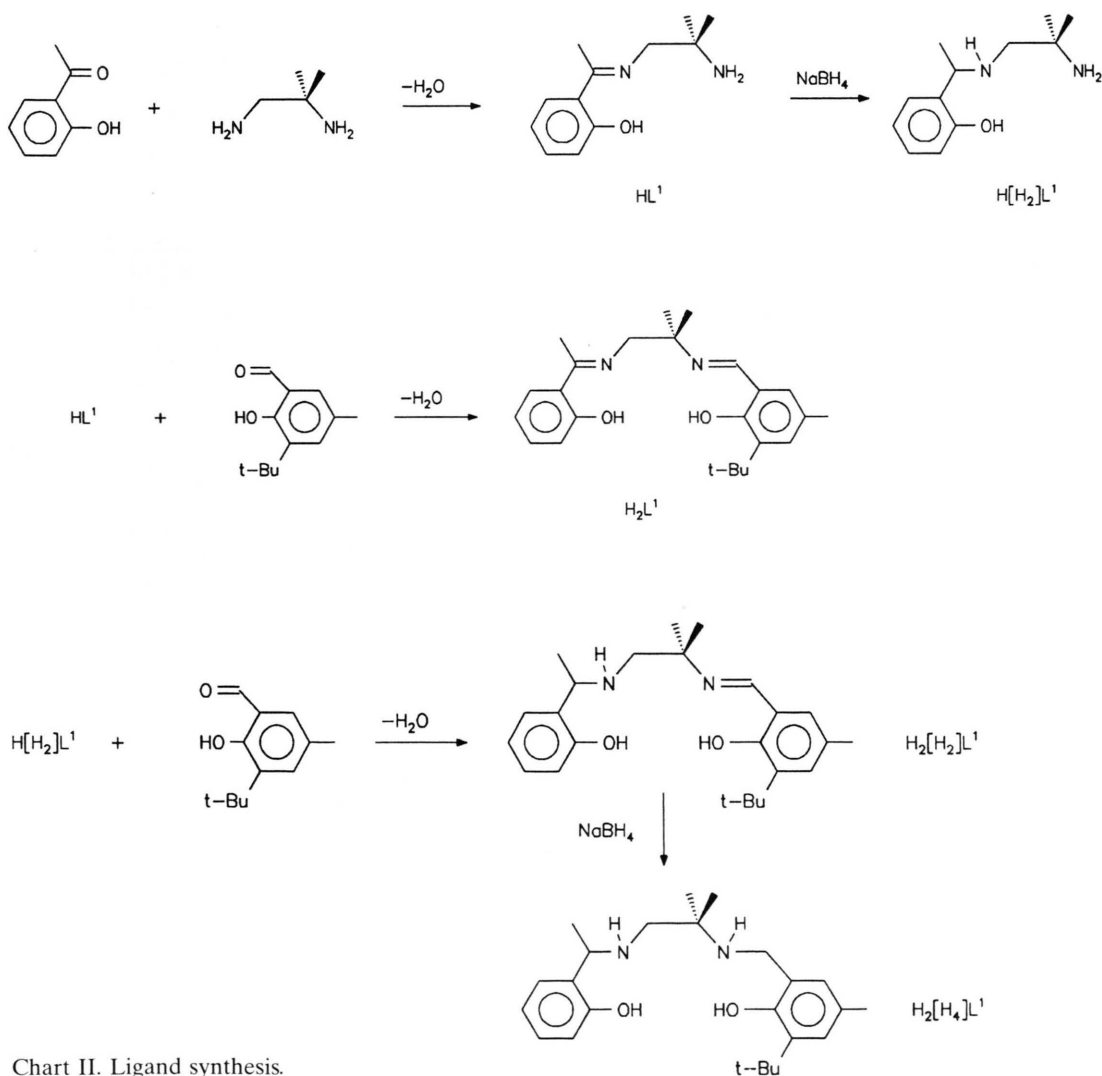


Chart II. Ligand synthesis.



CRYSTALS [11]. The final positional parameters and equivalent isotropic displacement parameters are presented in Tables V–VII. Lists of anisotropic thermal parameters and atomic parameters of the hydrogen atoms as well as structure factor tables have been deposited [12].

## Results

### Synthesis of the ligands

The synthetic procedure applied for the preparation of the various ligands is outlined in Chart II. It is based on the 1:1 reaction of the ketone 2-hydroxyacetophenone with the asymmetric diamine 1,2-diamino-2-methylpropane, leading to the mono-Schiff base  $\text{HL}^1$ . The  $^1\text{H}$  NMR spectrum confirms that, as expected, the ketone attacks the sterically less shielded amino group in the 1-position of the diamine. The 1:1 reaction of  $\text{HL}^1$  with the substituted salicylaldehyde leads to the di-Schiff base  $\text{H}_2\text{L}^1$ , albeit in relatively low yield.

The intermediate  $\text{H}[\text{H}_2]\text{L}^1$ , as obtained by reduction of  $\text{HL}^1$ , is used to prepare the dihydrosalen ligand  $\text{H}_2[\text{H}_2]\text{L}^1$  and through further reduction, the tetrahydrosalen ligand  $\text{H}_2[\text{H}_4]\text{L}^1$ .

### Properties of the complexes

The VIS absorption of the complexes (see Table I) clearly reflects the degree of C=N bond hydrogenation of the ligands involved. In agreement with earlier results [3–5], the salen-type complexes  $\text{NiL}^1$ ,  $\text{NiL}^2$ , and  $\text{CoL}^1$  are characterized by a strong CT band ( $\epsilon = 7000\text{--}11,000 \text{ M}^{-1} \text{ cm}^{-1}$ ) at about 420 nm. The absorption of the tetrahydrosalen-type complexes  $\text{Ni}[\text{H}_4]\text{L}^1$  and  $\text{Ni}[\text{H}_4]\text{L}^2$  is less intense, with a d–d band at 510–520 nm and a considerably blue-shifted CT band at about 360 nm. As typically shown in Fig. 1, the absorption of the di-

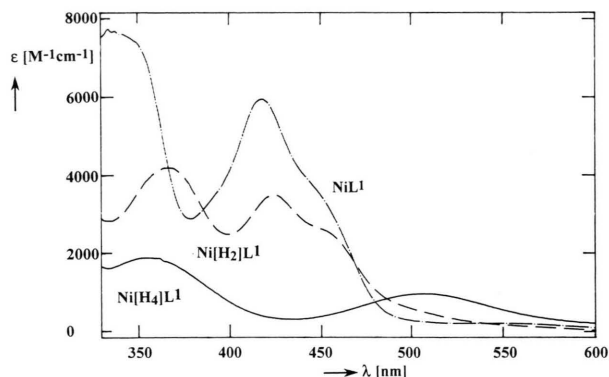


Fig. 1. Visible spectra of  $\text{Ni}[\text{H}_4]\text{L}^1$ ,  $\text{Ni}[\text{H}_2]\text{L}^1$ , and  $\text{NiL}^1$ .

hydrosalen-type complex  $\text{Ni}[\text{H}_2]\text{L}^1$  lies in between both types of absorption patterns. The stretching vibration of the C=N and N–H bonds at 1590–1615 and 3140–3320  $\text{cm}^{-1}$ , respectively, is observed or missing (see Table I), as expected from the steps of synthesis outlined in Chart II.

The Lewis acidity of the metal center in the various complexes is differing characteristically (see Table II). The salen-type and dihydrosalen-type nickel complexes do not add pyridine at all, whereas the tetrahydrosalen-type complexes  $\text{Ni}[\text{H}_4]\text{L}^1$  and  $\text{Ni}[\text{H}_4]\text{L}^2$  tend to become octahedral by stepwise addition of two molecules of pyridine. As found earlier [3–5], the five-coordinate species is less favored than the six-coordinate one, *i.e.*  $K_1 < K_2$ . In contrast to nickel, the cobalt center in  $\text{CoL}^1$  is a weak Lewis acid and adds one molecule of pyridine to become five-coordinate.

The magnetic moments listed in Table III are informative with regard to the coordination geometry of the nickel complexes.  $\text{NiL}^1$  is diamagnetic and the magnetic moments of  $\text{Ni}[\text{H}_2]\text{L}^1$  and  $\text{Ni}[\text{H}_4]\text{L}^2$

Complex	$\lambda_{\text{max}}$ [nm] ( $\epsilon_{\text{max}}$ [ $\text{M}^{-1} \text{ cm}^{-1}$ ])	$\tilde{\nu}$ [ $\text{cm}^{-1}$ ] C=N <sup>c</sup>	N–H <sup>c</sup>
$\text{NiL}^1$	418 (6690); 445 sh; 546 (217)	1600; 1615	–
$\text{Ni}[\text{H}_2]\text{L}^1$	368 (4860); 424 (4020); 445 sh	1605	3200
$\text{Ni}[\text{H}_4]\text{L}^1 \cdot 3 \text{ EtOH} \cdot \text{H}_2\text{O}$	356 (2100) <sup>c</sup> ; 510 (980) <sup>d</sup>	–	3280; 3320
$\text{CoL}^1$	356 (11200); 410 (12000); 475 sh	1590; 1605	–
$\text{Ni}[\text{H}_4]\text{L}^2 \cdot \text{acetone}$	364 (1890); 518 (970)	–	3140; 3175
$\text{NiL}^2$	424 (7830); 445 sh; 570 sh	1616	–

Table I. Visible absorption<sup>a</sup> of the complexes and selected IR data<sup>b</sup>.

<sup>a</sup> Solvent: acetone; <sup>b</sup> KBr matrix; <sup>c</sup> stretching vibrations; <sup>d</sup> solvent: methanol.

Table II. Equilibrium constants for adduct formation according to (1) in acetone (298 K).

Complex	$K_1, \text{M}^{-1}$	$K_2, \text{M}^{-1}$
$\text{NiL}^1$	n.o. <sup>a</sup>	n.o. <sup>a</sup>
$\text{Ni}[\text{H}_2]\text{L}^1$	n.o. <sup>a</sup>	n.o. <sup>a</sup>
$\text{Ni}[\text{H}_4]\text{L}^1$	$1.0 \pm 0.1$	$13.6 \pm 2.0$
$\text{CoL}^1$	$0.43 \pm 0.04^b$	—
$\text{Ni}[\text{H}_4]\text{L}^2$	$0.10 \pm 0.01$	$6.0 \pm 1.0$
$\text{NiL}^2$	n.o. <sup>a</sup>	n.o. <sup>a</sup>

<sup>a</sup> Addition of pyridine not observed; <sup>b</sup> measurements carried out under  $\text{N}_2$  atmosphere.

are small (0.28 and 0.64 BM, respectively), which points to square-planar coordination geometry in all of these complexes. The blue complex  $\text{Ni}[\text{H}_4]\text{L}^1 \cdot 3 \text{EtOH} \cdot \text{H}_2\text{O}$ , which loses ethanol and water upon heating *in vacuo*, has a magnetic moment of  $\mu_{\text{exp}} = 3.04$  BM, which points to octahedral coordination, as achieved by axial addition of water and/or ethanol. As discussed previously [4], the magnetic moment of  $\mu_{\text{exp}} = 2.02$  BM found for  $\text{CoL}^1$  is typical for a planar low spin  $d^7$  system.

#### Oxidative dehydrogenation of $\text{Ni}[\text{H}_4]\text{L}^1$

The tetrahydrosalen-type ligand in  $\text{Ni}[\text{H}_4]\text{L}^1$  is *asymmetric*, and its two C–N bonds are thus no longer equivalent. It was most interesting therefore to study the reaction of  $\text{Ni}[\text{H}_4]\text{L}^1$  with  $\text{O}_2$  in acetone

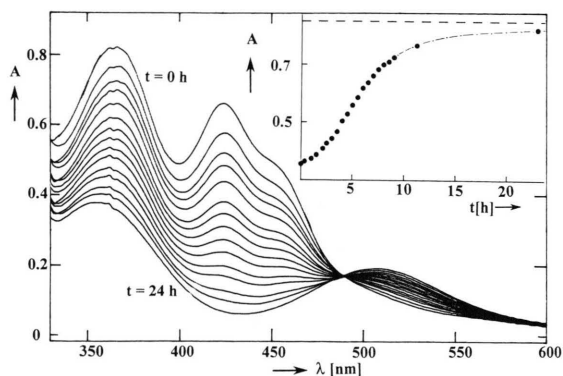


Fig. 2. Spectral changes for the reaction of  $\text{Ni}[\text{H}_4]\text{L}^1$  with dioxygen in acetone ( $[\text{complex}]_0 = 4 \times 10^{-4} \text{ M}$ ;  $d = 1 \text{ cm}$ ;  $T = 20^\circ \text{C}$ ) and change of the absorbance at 366 nm with time (the dashed line corresponds to the absorbance expected for  $\text{Ni}[\text{H}_2]\text{L}^1$ ).

in detail. Fig. 2 proves that, in the presence of dioxygen, there is a slow but continuous change in absorption, reflecting a color change from red to orange. The time dependence  $A_{366} = f(t)$  has an induction phase and is of sigmoidal shape, which is typically found for autocatalytic reactions. After about 6 h, the reaction appears to be half completed and the absorbance slowly approaches a limiting value. The spectrum obtained after 24 h is practically identical with that of authentic  $\text{Ni}[\text{H}_2]\text{L}^1$  (see Fig. 1). One learns therefore that the asymmetric tetrahydrosalen-type complex  $\text{Ni}[\text{H}_4]\text{L}^1$  is also subject to the oxidative dehydrogenation of one C–N bond. The spectral changes point to the formation of the aldimine  $\text{Ni}[\text{H}_2]\text{L}^1$ . As shown schematically in (2), ketimine formation has to be considered as well. Since the VIS spectrum of the ketimine is most probably not very different from that of the aldimine  $\text{Ni}[\text{H}_2]\text{L}^1$ , the question of aldimine *versus* ketimine formation cannot be answered conclusively at present.

#### Details of the crystal structures

The view of the coordination geometry of the complex  $\text{Ni}[\text{H}_2]\text{L}^1$  shown in Fig. 3 suggests that the  $\text{N}_2\text{O}_2$  set of donor atoms binds the nickel in a square-planar geometry. This is confirmed by the

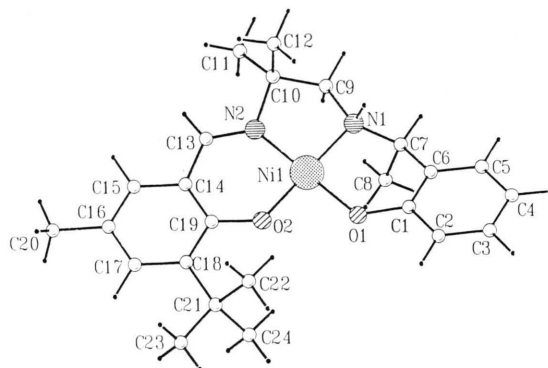
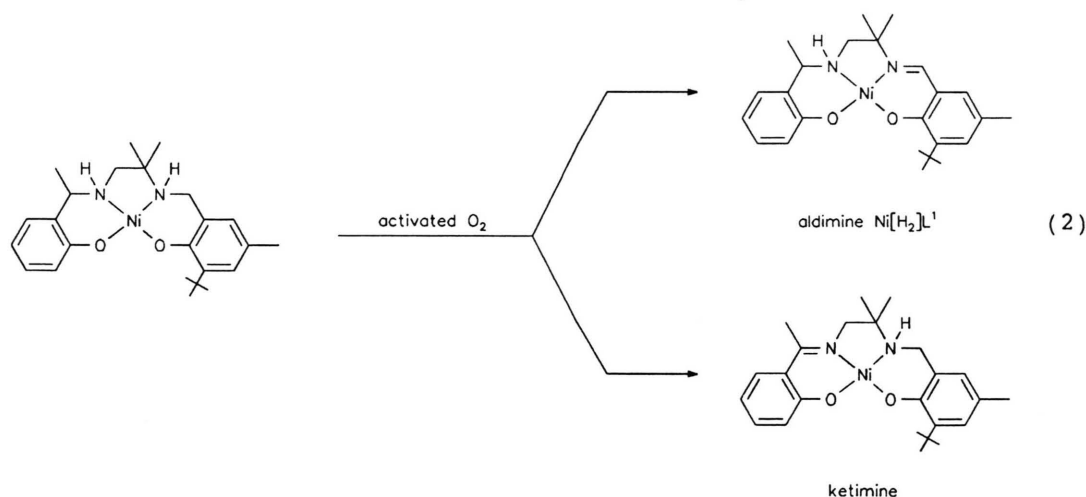


Fig. 3. View of the molecular structure of  $\text{Ni}[\text{H}_2]\text{L}^1$  (numbering of the atoms corresponds to Table V).

Complex	$\text{NiL}^1$	$\text{Ni}[\text{H}_2]\text{L}^1$	$\text{Ni}[\text{H}_4]\text{L}^1 \cdot 3 \text{EtOH} \cdot \text{H}_2\text{O}$	$\text{CoL}^1$	$\text{NiL}^1$	$\text{Ni}[\text{H}_4]\text{L}^2$
$\mu_{\text{exp}}$ , BM	0	0.28	3.04	2.02	0.48	0.64

Table III. Magnetic moments<sup>a</sup>.

<sup>a</sup> At ambient temperature.

Table IV. Crystal structure data for Ni[H<sub>2</sub>]L<sup>1</sup>, CoL<sup>1</sup>, and Ni[H<sub>4</sub>]L<sup>2</sup>.

	Ni[H <sub>2</sub> ]L <sup>1</sup>	CoL <sup>1</sup>	Ni[H <sub>4</sub> ]L <sup>2</sup>
Empirical formula	C <sub>24</sub> H <sub>32</sub> NiN <sub>2</sub> O <sub>2</sub>	C <sub>24</sub> H <sub>30</sub> CoN <sub>2</sub> O <sub>2</sub>	C <sub>30</sub> H <sub>44</sub> NiN <sub>2</sub> O <sub>2</sub> · C <sub>3</sub> H <sub>6</sub> O
Formula weight [g/mol]	431.16	437.45	581.47
Crystal system	monoclinic	monoclinic	tetragonal
Space group	P2 <sub>1</sub> /n; No. 14	C2/c; No. 15	P4 <sub>1</sub> 2 <sub>1</sub> 2; No. 92
Cell constants [Å; °]	<i>a</i> = 8.926(4) <i>b</i> = 29.324(7) <i>c</i> = 8.411(4) <i>β</i> = 95.3(1)	<i>a</i> = 25.389(2) <i>b</i> = 18.139(2) <i>c</i> = 10.179(1) <i>β</i> = 112.227(6)	<i>a</i> = 13.928(3) <i>c</i> = 33.698(5)
Formula units/unit cell	4	8	8
Volume of unit cell [Å <sup>3</sup> ]	2192(2)	4339.2(7)	6537(2)
<i>ρ</i> <sub>X-ray</sub> [g/cm <sup>3</sup> ]	1.306	1.339	1.025
Number of reflections collected	3269	7100	6350
Number of symmetry-independent reflections	2055	6570	5754
Reflections with <i>F</i> > 4σ( <i>F</i> )	1446	4073	3183
Number of parameters	235	193	320
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0928; 0.1773	<i>R</i> <sub>w</sub> = 0.039	0.1189; 0.2031
<i>R</i> 1, <i>wR</i> 2 ( <i>F</i> > 4σ( <i>F</i> ))	0.058; 0.1530	<i>R</i> <sub>w</sub> = 0.033	0.070; 0.1754
Weighting scheme	unit w.	Tukey and Prince; <i>w</i> = (weight) · [1 – (Δ <i>F</i> /6σ( <i>F</i> )) <sup>2</sup> ] <sup>2</sup> , using parameters: 8.75; –1.89; 7.57	unit w.
Absorption coefficient [cm <sup>–1</sup> ]	9.06	8.09	6.16
Crystal dimensions [mm]	plate: 0.12 × 0.5 × 0.05	block: 0.30 × 0.35 × 0.55	octahedron: 0.5 × 0.5 × 0.3

data listed in Table VIII. The four O–Ni–O, O–Ni–N, and N–Ni–N angles differ only slightly from 90°, and the two O–Ni–N angles are close to 180°. The two Ni–O distances are of the same length (1.857 and 1.843 Å, respectively), whereas the imine nitrogen N(2) is by 0.065 Å closer to the nickel than the amine nitrogen N(1). As expected,

the imine bond distance (N(2)–C(13); 1.315 Å) is clearly shorter than the amine bond distance (N(1)–C(7); 1.487 Å). The mean deviation from the least-squares plane P(1), formed by the four donor atoms and the nickel atom, is only ±0.013 Å. In contrast to the planar coordination core, however, the skeleton of the ligand is twisted. The phenyl ring

Table V. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Ni}[\text{H}_2]\text{L}^1$  ( $U_{\text{eq}}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Ni(1)	3972(1)	6606(1)	48(1)	34(1)
O(1)	4364(6)	6959(2)	1873(6)	42(2)
O(2)	5380(6)	6209(2)	1007(6)	34(1)
N(1)	2522(7)	7028(2)	−906(7)	35(2)
N(2)	3554(7)	6243(2)	−1734(7)	33(2)
C(1)	3713(5)	7358(1)	2208(5)	34(2)
C(2)	3844(6)	7496(2)	3796(4)	37(2)
C(3)	3209(6)	7905(2)	4224(4)	43(2)
C(4)	2442(6)	8177(2)	3065(6)	47(3)
C(5)	2311(5)	8039(2)	1477(5)	37(2)
C(6)	2947(4)	7630(1)	1049(4)	32(2)
C(7)	2917(9)	7517(3)	−653(10)	40(2)
C(8)	4481(7)	7620(2)	−1277(5)	49(3)
C(9)	2201(10)	6911(3)	−2644(9)	44(2)
C(10)	2209(9)	6391(3)	−2827(9)	40(2)
C(11)	2337(11)	6283(3)	−4601(10)	56(3)
C(12)	838(9)	6169(3)	−2208(12)	56(3)
C(13)	4262(6)	5869(2)	−2097(6)	34(2)
C(14)	5449(4)	5674(1)	−1068(4)	32(2)
C(15)	6068(5)	5282(1)	−1669(4)	38(2)
C(16)	7143(5)	5036(1)	−727(6)	36(2)
C(17)	7599(5)	5181(2)	816(5)	30(2)
C(18)	6980(5)	5572(2)	1416(4)	32(2)
C(19)	5904(5)	5819(1)	474(5)	31(2)
C(20)	7868(11)	4606(3)	−1399(11)	53(3)
C(21)	7450(9)	5725(3)	3149(9)	37(2)
C(22)	6079(10)	5792(3)	4096(11)	53(3)
C(23)	8474(12)	5378(3)	4056(12)	61(3)
C(24)	8311(10)	6175(3)	3103(11)	51(3)

of the salicylaldimine moiety (plane P(3)) is virtually co-planar with the  $\text{NiN}_2\text{O}_2$  unit (angle  $\text{P}(1) - \text{P}(3) = 6.8^\circ$ ), but the second phenyl ring (plane P(2), formed by  $\text{C}(1) - \text{C}(6)$ ), is significantly out of plane (angle  $\text{P}(1) - \text{P}(3) = 18.2^\circ$ ).

Compared to  $\text{Ni}[\text{H}_2]\text{L}^1$ , the view of the coordination geometry of the di-Schiff base complex  $\text{CoL}^1$  (see Fig. 4) suggests an overall planarity and also symmetry. The  $\text{CoN}_2\text{O}_2$  core (plane P(1)) and the phenyl ring adjacent to the  $\text{C}(7) = \text{N}(1)$  double bond are almost co-planar (angle  $\text{P}(1) - \text{P}(2) = 5.3^\circ$ ), whereas the second phenyl ring is bent off this plane (angle  $\text{P}(1) - \text{P}(3) = 16.5^\circ$ ). The two  $\text{Co} - \text{N}$  and  $\text{Co} - \text{O}$  bonds, as well as the two  $\text{C} = \text{N}$  bonds, are of comparable length (see Table VIII). It follows from the various angles  $\text{O} - \text{Co} - \text{O}$ ,  $\text{O} - \text{Co} - \text{N}$ , and  $\text{N} - \text{Co} - \text{N}$ , however, and from the deviations from the least-squares plane P(1) formed by the  $\text{CoN}_2\text{O}_2$  unit, that the coordination plane around the cobalt is slightly more distorted.

Table VI. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{CoL}^1$ .

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	$U_{\text{eq}}$
Co(1)	24867(1)	18998(1)	15649(2)	36.2(1)
O(1)	25851(5)	10060(7)	872(1)	48.5(6)
O(2)	32338(5)	18079(6)	2778(1)	42.9(6)
N(1)	17156(6)	19588(8)	382(2)	41.6(7)
N(2)	24126(6)	28281(8)	2246(2)	39.2(7)
C(1)	22065(8)	588(1)	−38(2)	44.9(9)
C(2)	24035(9)	−86(1)	−392(2)	54(1)
C(3)	2046(1)	−565(1)	−1357(3)	61(1)
C(4)	1474(1)	−402(1)	−2010(3)	66(1)
C(5)	1269(1)	237(1)	−1701(2)	58(1)
C(6)	16199(8)	762(1)	−718(2)	44.4(9)
C(7)	13945(7)	1468(1)	−502(2)	44.1(9)
C(8)	7785(9)	1644(2)	−1365(2)	61(1)
C(9)	14900(8)	2703(1)	436(2)	49(1)
C(10)	18075(7)	30584(9)	1861(2)	43.0(9)
C(11)	1614(1)	2741(1)	3001(3)	59(1)
C(12)	17107(9)	3890(1)	1715(3)	57(1)
C(13)	28228(8)	32482(9)	3022(2)	41.4(9)
C(14)	34123(7)	30411(9)	3629(2)	41.3(8)
C(15)	38141(9)	3584(1)	4358(2)	49(1)
C(16)	43804(9)	3413(1)	5007(2)	52(1)
C(17)	45413(8)	2673(1)	5007(2)	50(1)
C(18)	41711(7)	2110(1)	4323(2)	41.9(8)
C(19)	35878(7)	23087(9)	3542(2)	39.4(8)
C(20)	4823(1)	4004(2)	5649(3)	72(2)
C(21)	43599(7)	1304(1)	4367(2)	45.0(8)
C(22)	4260(1)	1015(1)	2871(2)	59(1)
C(23)	49953(9)	1215(1)	5258(3)	64(1)
C(24)	4030(1)	822(1)	5032(3)	59(1)

Knowing the structural essentials of the salen-type complex  $\text{CoL}^1$  (two  $\text{C} = \text{N}$  bonds) and of the dihydrosalen-type complex  $\text{Ni}[\text{H}_2]\text{L}^1$  (one  $\text{C} = \text{N}$  bond), the results obtained for the structure of the tetrahydrosalen-type complex  $\text{Ni}[\text{H}_4]\text{L}^2$  are of no surprise (see Fig. 5). The  $\text{NiN}_2\text{O}_2$  coordination

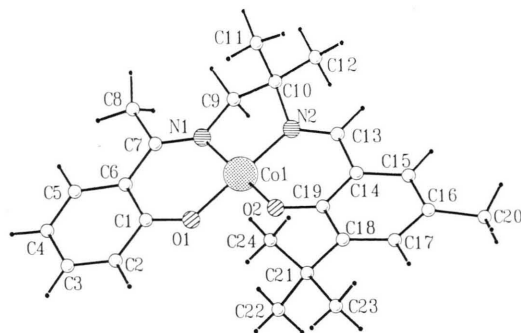


Fig. 4. View of the molecular structure of  $\text{CoL}^1$  (numbering of the atoms corresponds to Table VI).

Table VII. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for  $\text{Ni}[\text{H}_4]\text{L}^2$ .

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}$
Ni(1)	6144(1)	4146(1)	931(1)	85(1)
N(1)	6480(5)	5462(5)	875(2)	103(2)
N(2)	7314(4)	3843(5)	667(2)	95(2)
O(1)	5001(3)	4404(3)	1196(1)	91(1)
O(2)	5807(3)	2866(4)	970(2)	98(1)
C(1)	4731(3)	5253(3)	1358(1)	92(2)
C(2)	4115(3)	5245(4)	1682(1)	98(2)
C(3)	3786(3)	6105(5)	1842(1)	119(3)
C(4)	4073(4)	6973(4)	1676(2)	129(3)
C(5)	4689(4)	6981(3)	1352(2)	139(4)
C(6)	5019(3)	6122(3)	1193(1)	106(2)
C(7)	5685(4)	6083(5)	796(2)	132(3)
C(8)	7232(8)	5555(7)	568(2)	125(3)
C(9)	7907(6)	4749(8)	623(2)	114(3)
C(10)	7818(5)	3046(7)	837(2)	107(3)
C(11)	7281(2)	2122(3)	798(1)	83(2)
C(12)	7796(2)	1294(3)	710(1)	93(2)
C(13)	7326(3)	416(3)	683(1)	94(2)
C(14)	6340(3)	366(3)	744(1)	89(2)
C(15)	5825(2)	1194(3)	832(1)	81(2)
C(16)	6295(2)	2072(2)	859(1)	79(2)
C(17)	3751(3)	4293(4)	1888(1)	95(2)
C(18)	3110(4)	4462(4)	2227(1)	127(3)
C(19)	3141(5)	3756(6)	1557(2)	103(2)
C(20)	4598(5)	3663(6)	2009(2)	103(2)
C(21)	4712(4)	1158(6)	862(2)	92(2)
C(22)	4236(5)	1771(7)	546(3)	129(3)
C(23)	4392(6)	1472(7)	1275(3)	131(3)
C(24)	4335(6)	108(6)	812(3)	149(4)
C(25)	3747(9)	7944(7)	1844(4)	185(5)
C(26)	7867(6)	-489(7)	596(2)	126(3)
C(27)	7779(8)	6521(7)	569(3)	156(5)
C(28)	8553(14)	6487(10)	255(4)	223(10)
C(29)	9167(12)	5648(12)	273(4)	222(10)
C(30)	8649(7)	4684(8)	292(2)	147(4)
O(3)	3792(6)	6252(6)	104(2)	133(3)
C(31)	3228(11)	5867(8)	264(3)	146(4)
C(32)	3333(13)	4928(14)	437(6)	413(20)
C(33)	2233(16)	6224(15)	292(6)	415(24)

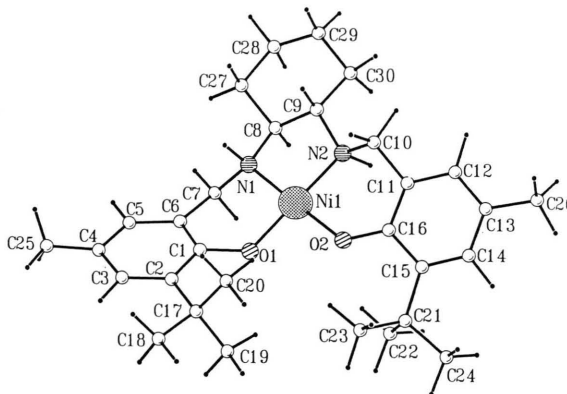
geometry is again nearly square-planar (see Table VIII). Due to the hydrogenation of both C=N bonds and the resulting flexibility, however, the skeleton of the ligand ( $[\text{H}_4]\text{L}^2$ )<sup>2-</sup> is strongly twisted, which puts both of the phenyl groups out of the coordination plane ( $\text{P}(1) - \text{P}(2) = 23.8^\circ$ ;  $\text{P}(1) - \text{P}(3) = 20.3^\circ$ ).

It is important to point out that in all of the three complexes the metal-metal distance between neighboring complex units is so large ( $\geq 3.9 \text{ \AA}$ ) that intermolecular interactions can be excluded. This is true also for the distance Ni-O(acetone) in the crystal of  $\text{Ni}[\text{H}_4]\text{L}^2 \cdot \text{acetone}$ .

Table VIII. Selected bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) characterizing the coordination sphere of the metal in  $\text{Ni}[\text{H}_2]\text{L}^1$ ,  $\text{CoL}^1$ , and  $\text{Ni}[\text{H}_4]\text{L}^2$ .

Complex	$\text{Ni}[\text{H}_2]\text{L}^1$	$\text{CoL}^1$	$\text{Ni}[\text{H}_4]\text{L}^2$
Distances			
M(1)–O(1)	1.857(5)	1.822(1)	1.859(5)
M(1)–N(1)	1.913(6)	1.874(1)	1.903(6)
M(1)–N(2)	1.848(6)	1.858(1)	1.904(6)
M(1)–O(2)	1.843(5)	1.838(1)	1.848(5)
d <sup>a</sup>	0.013(3)	0.036(3)	0.017(3)
N(1)–C(7)	1.487(10)	1.309(2)	1.429(8)
N(2)–C(13)	1.315(8)	1.291(2)	1.434(9) <sup>b</sup>
Angles			
O(1)–M(1)–N(1)	93.2(2)	93.74(6)	94.1(3)
N(1)–M(1)–N(2)	87.4(3)	87.67(6)	87.5(3)
N(2)–M(1)–O(2)	94.0(3)	93.20(6)	92.1(3)
O(1)–M(1)–O(2)	85.5(2)	85.50(5)	86.3(2)
O(1)–M(1)–N(2)	178.3(3)	177.37(6)	178.3(3)
N(1)–M(1)–O(2)	178.6(3)	177.18(6)	178.3(2)
P(1)–P(2) <sup>c</sup>	18.2(3)	5.3(5)	23.8(2)
P(1)–P(3) <sup>d</sup>	6.8(4)	16.5(6)	20.3(1) <sup>e</sup>

<sup>a</sup> d = RMS deviation ( $\text{\AA}$ ) from least-squares plane P(1), as formed by O(1), N(1), N(2), O(2), and M(1); <sup>b</sup> N(2)–C(10) instead of N(2)–C(13); <sup>c</sup> P(2) = plane of the phenyl ring formed by C(1)–C(6); <sup>d</sup> P(3) = plane of the phenyl ring formed by C(14)–C(19); <sup>e</sup> for  $\text{Ni}[\text{H}_4]\text{L}^2$ , plane P(3) is formed by C(11)–C(16).

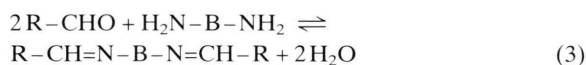
Fig. 5. View of the molecular structure of  $\text{Ni}[\text{H}_4]\text{L}^2$  (numbering of the atoms corresponds to Table VII).

## Discussion

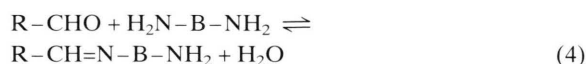
As reported recently [3–5], the nickel(II) and cobalt(II) complexes of specifically substituted tetrahydrosalen ligands are of broad interest because of their  $\text{O}_2$ -activating properties. The tetrahydrosalen complexes studied so far are all symmetric in the sense that the 2-hydroxybenzyl units

attached to the two nitrogen atoms of the bridging ethylenediamine are identical. The present study was undertaken in order to investigate the effect of asymmetry in the coordinated tetrahydrosalen ligands on the behavior of the corresponding nickel and cobalt complexes.

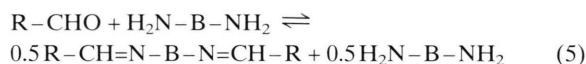
An easy synthetic route to tetrahydrosalen is the hydrogenation of salen. Following this route for the preparation of asymmetric tetrahydrosalen, one has first of all to prepare asymmetric salen as the precursor, which is not trivial. When a diamine  $\text{H}_2\text{N}-\text{B}-\text{NH}_2$  such as ethylenediamine ( $\text{B} = (\text{CH}_2)_2$ ) reacts with two or more equivalents of an aldehyde  $\text{R}-\text{CHO}$ , the di-Schiff base is formed



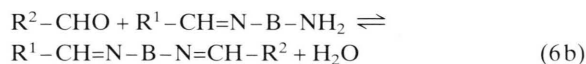
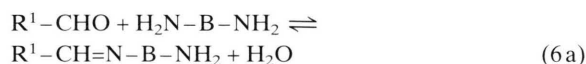
according to (3). The 1:1 reaction according to (4) does take



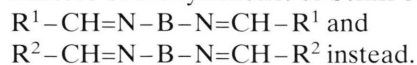
place only partially, and the formation of the di-Schiff base



according to equilibrium (5) appears to be favored. The simple synthetic concept to prepare an asymmetric salen according to the sequence (6a) and (6b) is thus not successful. One ends up with a

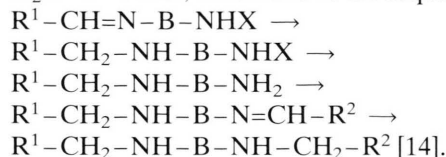


mixture of the symmetric di-Schiff bases



One can try, of course, to use the diamine in great excess and thus shift equilibrium (6a) to the right and avoid di-Schiff base formation according to (5). This approach has been tested [13], but the mono-Schiff base  $\text{R}^1-\text{CH}=\text{N}-\text{B}-\text{NH}_2$  could not be isolated, however, and was hydrogenated *in situ* to form  $\text{R}^1-\text{CH}_2-\text{NH}-\text{B}-\text{NH}_2$ . Compound  $\text{R}^1-\text{CH}_2-\text{HN}-\text{B}-\text{NH}_2$  is easily converted to asymmetric species  $\text{R}^1-\text{CH}_2-\text{HN}-\text{B}-\text{N}=\text{CH}-\text{R}^2$  and  $\text{R}^1-\text{CH}_2-\text{HN}-\text{B}-\text{NH}-\text{CH}_2-\text{R}^2$ , respective-

ly. Another approach to asymmetric tetrahydrosalen is the use of a partially protected diamine,  $\text{H}_2\text{N}-\text{B}-\text{NHX}$ , which allows the sequence



In the present study the principle of steric hindrance was applied (see Chart II). Compared to salicylaldehyde, 2-hydroxyacetophenone is a ketone and thus less reactive as compared to an aldehyde. Compared to ethylenediamine, asymmetric 1,2-diamino-2-methylpropane offers one ethylenediamine-like amino group (in 1-position), and one (in 2-position) which is much more shielded by two neighboring methyl groups. The 1:1 reaction of 2-hydroxyacetophenone with 1,2-diamino-2-methylpropane thus leads preferentially to the mono-Schiff base  $\text{HL}^1$  in good yield. As shown in Chart II, the availability of  $\text{HL}^1$  opens simple pathways to  $\text{H}_2\text{L}^1$ , as well as to  $\text{H}_2[\text{H}_2]\text{L}^1$  and  $\text{H}_2[\text{H}_4]\text{L}^2$ .

The reaction of  $\text{H}_2[\text{H}_2]\text{L}^1$  with nickel acetate affords  $\text{Ni}[\text{H}_2]\text{L}^1$ , which, to our knowledge, is the first structurally characterized "half-salen" or dihydrosalen-like complex. From a chemical point of view,  $\text{Ni}[\text{H}_2]\text{L}^1$  lies in between  $\text{NiL}^1$  and  $\text{Ni}[\text{H}_4]\text{L}^1$ . The latter tetrahydrosalen-type complex reacts slowly with dioxygen in acetone solution (see Fig. 2) to form the dihydrosalen-type complex  $\text{Ni}[\text{H}_2]\text{L}^1$ , which is stable towards  $\text{O}_2$ . It needs stronger oxidants such as  $\text{H}_2\text{O}_2$  to achieve further oxidation of  $\text{Ni}[\text{H}_2]\text{L}^1$  to  $\text{NiL}^1$ .

It follows from the X-ray structure analyses of  $\text{Ni}[\text{H}_2]\text{L}^1$ ,  $\text{CoL}^1$  (which can be taken as an analogue for  $\text{NiL}^1$ ),  $\text{Ni}\{(\text{Bu}_i\text{H})[\text{H}_4]\text{salen}\}^\#$  [3], and  $\text{Ni}[\text{H}_4]\text{L}^2$  that, with regard to structure and coordination geometry, in all of these complexes the set of  $\text{N}_2\text{O}_2$  donor atoms forms a square-planar coordination geometry, with  $\text{M}-\text{N}(\text{imine}) < \text{M}-\text{N}(\text{amine})$  by 0.05–0.06 Å. The characteristic differences in structure are obviously the consequence of an increase in ligand flexibility, following the order tetrahydrosalen > dihydrosalen > salen. In  $\text{Ni}\{(\text{Bu}_i\text{H})[\text{H}_4]\text{salen}\}$  and  $\text{Ni}[\text{H}_4]\text{L}^2$ , the skeleton of the ligand is twisted and the phenyl rings are far from being co-planar with the coordination plane. In  $\text{Ni}[\text{H}_2]\text{L}^1$  and in  $\text{CoL}^1$  one of the two phenyl rings is almost co-planar with the coordination core.



The second phenyl ring is either twisted ( $\text{Ni}[\text{H}_2]\text{L}^1$ ) or bent off ( $\text{CoL}^1$ ).

Another characteristic trend is observed for the Lewis acidity of the metal center, as quantified by the equilibrium constant for pyridine addition. In agreement with earlier results [3, 4] it is found that the nickel center in the tetrahydrosalen complexes is a relatively strong Lewis acid and tends to become octahedral. The nickel atoms in the corresponding dihydrosalen and salen complexes, however, do not exhibit Lewis acidity. One can conclude from these findings that the diimine salen-type ligands are shifting more electron density to the nickel atom, which keeps the metal from becoming six-coordinate. The low spin  $d^7$  cobalt center in  $\text{CoL}^1$  and similar cobalt complexes [3] interacts only weakly with pyridine to become five-coordinate.

Specifically substituted tetrahydrosalen nickel(II) complexes, most remarkably, are able to activate dioxygen [3–5]. There is a  $\text{Ni} \cdots \text{O}_2$  interaction, raising the reactivity of the “coordinated” oxygen molecule in such a way that it is able to attack the bound ligand, to dehydrogenate one of the C–N bonds and to form the corresponding “half-salen” or dihydrosalen complexes. The results obtained for the reaction of the asymmetric tetrahydrosalen-type complex  $\text{Ni}[\text{H}_4]\text{L}^1$  with dioxygen complement our previous findings for symmetric complexes in a twofold way. Firstly, they prove that the ligand asymmetry in  $\text{Ni}[\text{H}_4]\text{L}^1$  does not block the  $\text{O}_2$ -activating potential of the complex. Compared to the symmetric tetrahydrosalen complexes  $\text{Ni}\{(\text{Bu},\text{X})[\text{H}_4]\text{salen}\}^\#$  [3], the rate of reaction in acetone is approximately the same. Secondly, the  $\text{O}_2$ -induced oxidative dehydrogenation of  $\text{Ni}[\text{H}_4]\text{L}^1$  affords a dihydrosalen-type complex. The fact that only *one* C=N bond is formed, parallels the behavior of the corresponding symmetric complexes. The spectral changes observed support the interpretation that reaction (2) leads to the formation

of the aldimine  $\text{Ni}[\text{H}_2]\text{L}^1$ . The fact that  $\text{Co}[\text{H}_2]\text{L}^1$ , in the presence of  $\text{O}_2$ , is easily converted to  $\text{CoL}^1$  demonstrates, however, that ketimine formation is also possible. A detailed  $^1\text{H}$  NMR study of reaction (2) is therefore under way which should decide the question of aldimine *versus* ketimine formation unambiguously.

A consistent mechanistic interpretation of reaction (2) is not yet at hand. As reported recently [5], the  $\text{Ni}^{\text{II}}/\text{Ni}^{\text{III}}$  potential is obviously one important factor, but the Lewis acidity of the metal center might also be significant. The time dependence of the reaction is of sigmoidal shape (see Fig. 2), which points to autocatalysis. It follows from  $\text{O}_2$ -uptake studies that the conversion of 1 mol of  $\text{Ni}[\text{H}_4]\text{L}$  to  $\text{Ni}[\text{H}_2]\text{L}$  in acetone consumes 1 mol of  $\text{O}_2$  [15]. If water is the reaction product of the dehydrogenation of the C–N bond, the stoichiometry thus demands another O-consuming reaction, which might well be a solvent-assisted one. In conclusion, further experiments are necessary to set up a convincing mechanistic scheme. The present body of information indicates very strongly, however, that steric factors are highly significant. The tetrahydrosalen ligand has to carry *two* (as in  $\text{Ni}\{(\text{Bu},\text{X})[\text{H}_4]\text{salen}\}^\#$ ) or at least *one tert*-butyl group (as in  $\text{Ni}[\text{H}_4]\text{L}^1$ ) to be  $\text{O}_2$ -activating. Complexes such as  $\text{Ni}[\text{H}_4]\text{L}^2$ , which offer a specific stereochemistry, have therefore been chosen for this study. It is hoped that tetrahydrosalen complexes with ligands based on the enantiomers of *cis*- and *trans*-1,2-diaminocyclohexane will give further insight into the mechanistic details.

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