Inorg. Chem. **1993**, *32*, 4131–4138

Comparative Study on the Coordination Chemistry of Cobalt(II), Nickel(II), and Copper(II) with Derivatives of Salen and Tetrahydrosalen: Metal-Catalyzed Oxidative Dehydrogenation of the C–N Bond in Coordinated Tetrahydrosalen

Arnd Böttcher,[1a] Horst Elias,*,[1a] Ernst-Gottfried Jäger,[1b] Helena Langfelderova,†,[1c] Milan Mazur,[1c] Lutz Müller,[1a] Helmut Paulus,[1d] Peter Pelikan,[1c] Manfred Rudolph,[1b] and Marian Valko[1c]

Anorganische Chemie III, Eduard-Zintl-Institut der Technischen Hochschule Darmstadt,
D-64289 Darmstadt, Federal Republic of Germany, Department of Inorganic Chemistry,
Slovak Technical University, 81237 Bratislava, Slovakian Federal Republic, and Chemische Fakultät,
Friedrich-Schiller-Universität Jena, D-07743 Jena, Federal Republic of Germany

Received February 4, 1993

The salen complexes ML (M^{II} = Cu, Ni, Co) and the corresponding tetrahydrosalen complexes $M[H_4]L$ (M^{II} = Cu, Ni) were prepared and characterized by their vis absorption and EPR spectra, by their magnetic moments, and by cyclic voltammetry in acetonitrile (L^{2-}, $[H_4]L$ = anions of the following: H_2L^1 = *N,N'*-bis(3-*tert*-butyl-5-methylsalicylidene)-2,3-diamino-2,3-dimethylbutane; $H_2[H_4]L^1$ = *N,N'*-bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)-2,3-diamino-2,3-dimethylbutane; H_2L^2 = *N,N'*-bis(3-*tert*-butyl-5-chlorosalicylidene)-2,3-diamino-2,3-dimethylbutane; $H_2[H_4]L^2$ = *N,N'*-bis(2-hydroxy-3-*tert*-butyl-5-chlorobenzyl)-2,3-diamino-2,3-dimethylbutane). Complexes CoL are low-spin d^7 systems (μ_{exp} = 2.31 (CoL^1) and 2.44 (CoL^2) μ_B), and complexes NiL and $Ni[H_4]L$ are weakly paramagnetic at ambient temperature, with μ_{exp} ranging from 0.39 to 0.53 μ_B. The copper complexes CuL and $Cu[H_4]L$ are magnetically normal (μ_{exp} = 1.69–1.75 μ_B). X-ray structure analysis of CoL^1 (=$C_{30}H_{42}N_2O_2Co$; orthorhombic, $C222_1$; a = 23.972(6), b = 10.106(3), c = 11.696(3) Å; Z = 4; R_w = 0.0283) confirms a slightly distorted planar geometry of the CoN_2O_2 coordination core. In acetone solution, complexes CoL form adducts with pyridine according to CoL + py $\rightleftharpoons$ CoL·py with K_1 = 0.15 M^{-1} (CoL^1) and 1.67 M^{-1} (CoL^2). The EPR spectra at 120 K of oxygenated frozen toluene solutions of complex CoL^2 confirm the reversible formation of $(Co^{III}L^2)^+\cdots O_2^-$. In acetonitrile the reduction M(II)/M(I) is reversible for ML (M = Cu, Ni, Co) and for $Ni[H_4]L$, whereas the oxidation M(II)/M(III) is reversible for CoL and $Ni[H_4]L$ only. In acetone solution at ambient temperature, complexes $Cu[H_4]L$ are stable, while complexes $Ni[H_4]L$ activate dioxygen and are slowly oxidatively dehydrogenated to form the half-salen complexes $Ni[H_2]L$ with one C–N and one C=N bond in the ligand. This process is considerably faster with H_2O_2 instead of O_2 and leads finally to NiL. In oxygenated organic solution, the complex formation between Co^{2+} ions and ligands $H_2[H_4]L$ is followed by oxidative dehydrogenation of both C–N bonds and the (salen)cobalt(II) complexes CoL are formed. The metal dependence (Co ≫ Ni ≫ Cu) and the mechanism of the process $M[H_4]L \rightarrow M[H_2]L \rightarrow ML$, as induced by dioxygen, is discussed.

Introduction

In contrast to the extensive literature on transition metal complexes with the tetradentate Schiff base ligand salen[2] and, in particular, on the dioxygen affinity of Co(salen) and its derivatives,[3] rather little is known about the corresponding tetrahydrosalen[2] complexes. Most of the earlier investigations were carried out with $H_2[H_4]$salen,[2] the hydrogenation product of nonsubstituted salen. The coordination chemistry of this ligand with nickel,[4,5] zinc,[4,5] cobalt,[5,6] molybdenum,[7,8] copper,[5,9] and iron[10] was studied, and mononuclear as well as dinuclear complexes (Fe,[10a] Cu,[11] Co[6]) were obtained. Floriani et al.[12] reported recently on a trinuclear cobalt complex, prepared by the reaction of a mixture of H_2salphen[2] and $H_2[H_4]$salphen[2] with cobalt. The effect of ligand modification on complex formation with copper was investigated with various derivatives of $H_2[H_4]$salen.[11,13]

---

† Deceased on January 5, 1993.

(1) (a) Institut für Anorganische Chemie, Technische Hochschule Darmstadt. (b) Friedrich-Schiller-Universität Jena. (c) Slovak Technical University. (d) Fachbereich Materialwissenschaft, Technische Hochschule Darmstadt.

(2) Abbreviations: salen = H_2salen = *N,N'*-disalicylidene-1,2-diaminoethane; tetrahydrosalen = $H_2[H_4]$salen = *N,N'*-bis(2-hydroxybenzyl)-1,2-diaminoethane; H_2salphen = *N,N'*-disalicylidene-1,2-diaminobenzene; $H_2[H_4]$salphen = *N,N'*-bis(2-hydroxybenzyl)-1,2-diaminobenzene; $H_2(Bu)_2$salen = *N,N'*-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminoethane; $H_2(Bu)_2[H_4]$salen = *N,N'*-bis(2-hydroxy-3,5-di-*tert*-butylbenzyl)-1,2-diaminoethane; $H_2(Bu,Me)[H_4]$salen = *N,N'*-bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)-1,2-diaminoethane; $H_2(Bu,Me)$salen = *N,N'*-bis(3-*tert*-butyl-5-methylsalicylidene)-1,2-diaminoethane; $H_2(Bu)$salen = *N,N'*-bis(3-*tert*-butylsalicylidene)-1,2-diaminoethane; $H_2(Bu)[H_4]$salen = *N,N'*-bis(2-hydroxy-3-*tert*-butylbenzyl)-1,2-diaminoethane; H_2-(Bu,Cl)salen = 1,2-diaminobis(3-*tert*-butyl-5-chlorosalicylidene)ethane; $H_2(Bu,Cl)[H_4]$salen = *N,N'*-bis(2-hydroxy-3-*tert*-butyl-5-chlorobenzyl)-1,2-diaminoethane; H_2L^1 = *N,N'*-bis(3-*tert*-butyl-5-methylsalicylidene)-2,3-diamino-2,3-dimethylbutane; $H_2[H_4]L^1$ = *N,N'*-bis(2-hydroxy-3-*tert*-butyl-5-methylbenzyl)-2,3-diamino-2,3-dimethylbutane; H_2L^2 = *N,N'*-bis(3-*tert*-butyl-5-chlorosalicylidene)-2,3-diamino-2,3-dimethylbutane; $H_2[H_4]L^2$ = *N,N'*-bis(2-hydroxy-3-*tert*-butyl-5-chlorobenzyl)-2,3-diamino-2,3-dimethylbutane.

(3) (a) Martell, A. E.; Sawyer, D. T. *Oxygen Complexes and Oxygen Activation by Transition Metals*; Plenum Press: New York, 1988. (b) Chen, D.; Martell, A. E. Inorg. Chem. **1987**, *26*, 1026. (c) Chen, D.; Martell, A. E.; Sun, Y. *Inorg. Chem.* **1989**, *28*, 2647.

(4) O'Connor, M. J.; West, B. O. *Aust. J. Chem.* **1967**, *20*, 2077.

(5) Gruenwedel, D. W. *Inorg. Chem.* **1968**, *7*, 495.

(6) Mäcke, H.; Fallab, S. *Chimia* **1972**, *26*, 422.

(7) Mitchell, P. C. H.; Parker, D. A. *J. Chem. Soc., Dalton Trans.* **1972**, 1828.

(8) (a) Subramanian, P.; Spence, J. T.; Ortega, R.; Enemark, J. H. *Inorg. Chem.* **1984**, *23*, 2546. (b) Hinshaw, C. J.; Peng, G.; Singh, R.; Spence, J. T.; Enemark, J. H.; Bruck, J. M.; Kristofzski, J.; Merbs, S. L.; Ortega, R. B.; Wexler, P. A. *Inorg. Chem.* **1989**, *28*, 4483.

(9) Amundsen, A. R.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1977**, *99*, 6730.

(10) (a) Borer, L.; Thalken, L.; Ceccarelli, C.; Glick, M.; Hua Zhang, J.; Reiff, W. M. *Inorg. Chem.* **1983**, *22*, 1719. (b) Borer, L.; Thalken, L.; Hua Zhang, J.; Reiff, W. M. *Inorg. Chem.* **1983**, *22*, 3174.

(11) Patel, K. V.; Bhattacharya, P. K. *Ind. J. Chem.* **1984**, *23A*, 527.

(12) Solari, E.; Floriani, C.; Cunningham, D.; Higgins, T.; McArdle, P. *J. Chem. Soc., Dalton Trans.* **1991**, 3139.

(13) (a) Csaszar, J. *Acta Phys. Chem.* **1984**, *30*, 61. (b) Csaszar, J. *Acta Chim. Hung.* **1991**, *128*, 255.

0020-1669/93/1332-4131$04.00/0

Complexes of Cu(II), Co(II), Ni(II), V(IV) (=VO^{2+}), Mn(III), and Pd(II) with $H_2(Bu)_2$salen[2] and $H_2(Bu)_2[H_4]$salen[2] were prepared and EPR-studied by Kasumov et al.[14]

Comparing the ligand properties of salen and tetrahydrosalen, one expects increased N-basicity and greater flexibility as a consequence of C=N bond hydrogenation. Tetrahydrosalen should thus coordinate more easily in a folded fashion, which is found to be the case. Borer et al.[10a] prepared the dinuclear complex $[Fe([H_4]salen)(OH)]_2 \cdot 2H_2O \cdot 2py$, in which the two iron(III) units are bridged by two hydroxyl ions and capped by the folded anion $[H_4]salen^{2-}$. We reported recently[15] on the dinuclear complex $[Fe\{(Bu,Me)[H_4]salen\}(OMe)]_2$,[2] which is another example of this folded mode of coordination.

In mononuclear complexes, such as Ni($[H_4]$salen) and Zn($[H_4]$salen), the ligand $H_2[H_4]$salen was suggested[4] to be coordinated in its planar, unfolded form. We recently reported the first X-ray structure analysis of a mononuclear Ni(II) tetrahydrosalen complex.[16] The nickel in the cherry-red, practically diamagnetic complex Ni{(Bu)$[H_4]$salen}[2] is indeed coordinated to the tetradentate ligand in planar fashion, with the NiN_2O_2 plane being slightly distorted.

The most remarkable property of the three planar Ni(II) complexes Ni{(Bu,X^5)$[H_4]$salen} (X^5 = H, Me, Cl) is their interaction with dioxygen.[16] In organic solution, the complexes are subject to oxidative dehydrogenation, in the sense that in the presence of dioxygen, *one* of the two C–N bonds is dehydrogenated to form a C=N imine bond. Further dehydrogenation of this half-salen species to the salen complex with *two* C=N bonds is not observed under the given experimental conditions.

The O_2-activating properties of complexes Ni{(X^3)$[H_4]$salen}, where X^3 = *tert*-butyl, led to preparation and study of Ni(II), Co(II), and Cu(II) complexes with the ligands H_2L^1, H_2L^2, $H_2[H_4]L^1$, and $H_2[H_4]L^2$ (see Chart I). The permethylated ethylene bridge in those complexes was deliberately chosen in order to increase, in addition to the effects of the *tert*-butyl groups, steric crowding around the metal center and thus hinder M–O–M and/or M–O–O–M bridging. The present work contributes to the more general aspects of reaction 1, with the metal M and the pattern of substitution on the ligand being the variables. The relevance of reaction 1 for the understanding of the role of metal ions in biological systems and for catalysis is obvious.

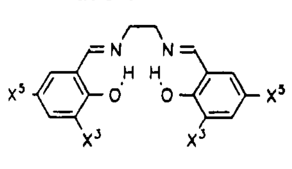
$$[M([H_4]salen)] \underset{-2H}{\overset{O_2}{\rightarrow}} [M([H_2]salen)] \underset{-2H}{\overset{O_2}{\rightarrow}} [M(salen)] \qquad (1)$$

Experimental Section

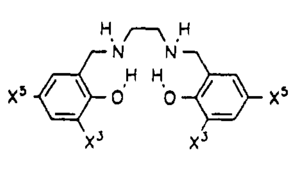
The following chemicals (reagent grade) were used without further purification: $Ni(AcO)_2 \cdot 4H_2O$ (Merck); $Co(AcO)_2 \cdot 4H_2O$ (Merck); $Cu(AcO)_2 \cdot H_2O$ (Merck); $Na[BH_3(CN)]$ (Fluka); 2-*tert*-butylphenol (Fluka); 2-*tert*-butyl-4-methylphenol (Aldrich); 2-nitropropane (Aldrich). The solvent acetone (reagent grade, Merck) was used without further purification. DMF (*N,N*-dimethylformamide; BASF) was purified by fractional distillation.

3-*tert*-Butylsalicylaldehyde was prepared[17] from 2-*tert*-butylphenol and chlorinated[18] to obtain 3-*tert*-butyl-5-chlorosalicylaldehyde (characterized by its ^{1}H-NMR, ^{13}C-NMR, and mass spectra). 3-*tert*-Butyl-5-methylsalicylaldehyde was prepared from 2-*tert*-butyl-4-methylphenol.[19] To obtain the dihydrochloride of 2,3-diamino-2,3-dimethylbutane, 2-nitropropane was converted[20,21] into 2,3-dinitro-2,3-dimethylbutane, which was reduced to the diamine with Sn/HCl.[21,22]

Chart I. Structural Formulas of the Ligands and Abbreviations[2]

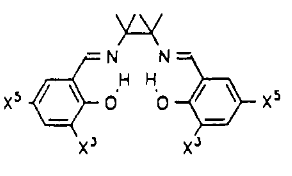


$H_2(X^3,X^5)$salen

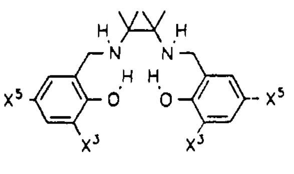


$H_2(X^3,X^5)[H_4]$salen

Ligands studied in the present work:



H_2L



$H_2[H_4]L$

ligand	X^3	X^5
H_2L^1	t-Bu	Me
$H_2[H_4]L^1$	t-Bu	Me
H_2L^2	t-Bu	Cl
$H_2[H_4]L^2$	t-Bu	Cl

Schiff Bases H_2L^1 and H_2L^2.[2] A solution of 0.05 mol of the dihydrochloride of 2,3-diamino-2,3-dimethylbutane and 0.1 mol of solid KOH in 50 mL of ethanol was added slowly to a stirred solution of 0.1 mol of the corresponding salicylaldehyde in 120 mL of ethanol at 60 °C. After 30 min of refluxing a yellow solid precipitated, which was separated by filtration and washed with cold methanol (yield about 70%), mp 186 °C (H_2L^1) and 173 °C (H_2L^2). IR (KBr) of H_2L^1 and H_2L^2: 1620 cm^{-1} (ν(C=N)).

Ligands $H_2[H_4]L^1$ and $H_2[H_4]L^2$.[2] A 0.028-mol amount of the corresponding Schiff base H_2B was dissolved/suspended in 75 mL of glacial acetic acid, and 0.06 mol of $Na[BH_3(CN)]$ was added portionwise under stirring at ambient temperature. The solution slowly lost its yellow color. After 2 h of stirring solid NaOH was added to establish pH ≈ 7 in the solution, which was extracted twice with CH_2Cl_2 to separate the hydrogenated ligand. The organic phase was shaken once with a dilute aqueous solution of Na_2CO_3, dried with solid Na_2SO_4, and concentrated to precipitate the colorless ligand $H_2[H_4]L$. The product was recrystallized from ethanol (yield about 55%), mp 234 °C ($H_2[H_4]L^1$) and 223 °C ($H_2[H_4]L^2$). IR (KBr) of H_2L^1 and H_2L^2: 3320 cm^{-1} (ν(N–H)). ^{1}H NMR ($CDCl_3$): δ 5.7 (2H, s, NH) for $H_2[H_4]L^1$ and 5.3 (2H, s, NH) for $H_2[H_4]L^2$.

Complexes. Unless stated otherwise, the Co(II), Ni(II), and Cu(II) complexes ML and $M[H_4]L$ were prepared according to the following procedure.

A stirred solution/suspension of 0.002 mol of H_2L or $H_2[H_4]L$ in 10 mL of ethanol was heated to boiling, and a solution of 0.002 mol of the metal acetate in 25 mL of ethanol was added dropwise, which led to an immediate color change and to complete dissolution of the ligand. After addition of 2 mL of 2 M NaOH the solution was stirred and refluxed for 0.5 h, whereupon the complex began to precipitate. After cooling, the product was separated by filtration and recrystallized from $CHCl_3$/petroleum ether or methanol. Complexes $Ni[H_4]L$ were prepared under a nitrogen atmosphere.

Anal. Calcd for CuL^1: C, 68.48; H, 8.05; N, 5.32; Cu, 12.07. Found: C, 68.72; H, 8.06; N, 5.63; Cu, 12.13. Calcd for $Cu[H_4]L^1$: C, 67.52, H, 8.74; N, 5.28; Cu, 11.98. Found: C, 67.41; H, 8.77; N, 5.19; Cu, 11.79. Calcd for NiL^1: C, 69.1; H, 8.06; N, 5.37. Found: C, 69.06; H, 7.98; N, 5.29. Calcd for $Ni[H_4]L^1$: C, 68.32; H, 9.17; N, 5.31; Ni,

---

(14) Kasumov, V. T.; Medzhidov, A. A.; Golubeva, I. A.; Vishnyakova, T. I.; Shubina, D. V.; Rzaev, R. Z. *Coord. Khim.* **1991**, *17*, 1698.

(15) Baran, P.; Böttcher, A.; Elias, H.; Haase, W.; Hüber, M.; Fuess, H.; Paulus, H. *Z. Naturforsch.* **1992**, *47b*, 1681.

(16) Böttcher, A.; Elias, H.; Müller, L.; Paulus, H. *Angew. Chem.* **1992**, *104*, 635; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 623.

(17) Duff, J. C. *J. Chem. Soc.* **1941**, 547.

(18) Biltz, H.; Stepf, K. *Ber. Dtsch. Chem. Ges.* **1904**, *36*, 4022.

(19) Ligget, R. W.; Diehl, H. *Proc. Iowa Acad.* **1945**, *52*, 191.

(20) Seigle, L. W.; Hass, H. B. *J. Org. Chem.* **1940**, *5*, 101.

(21) Sayre, R. *J. Am. Chem. Soc.* **1955**, *77*, 6690.

(22) Bewad, J. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 1232.

11.12. Found: C, 68.29; H, 9.20; N, 5.19; Ni, 10.97. Calcd for CoL^1: C, 69.08; H, 8.12; N, 5.37; Co, 11.29. Found: C, 69.05; H, 8.13; N, 5.5; Co, 11.18. Calcd for CuL^2: C, 59.26; H, 6.35; N, 4.94; Cu, 11.20. Found: C, 58.99; H, 6.29; N, 4.82; Cu, 11.14. Calcd for $Cu[H_4]L^2$: C, 58.89; H, 7.06; N, 4.91; Cu, 11.16. Found: C, 58.68; H, 6.98; N, 4.71; Cu, 11.22. Calcd for NiL^2: C, 59.76; H, 6.42; N, 4.98; Ni, 10.43. Found: C, 59.79; H, 6.50; N, 4.98; Ni, 10.29. Calcd for $Ni[H_4]L^2$: C, 59.42; H, 7.10; N, 4.95; Ni, 10.37. Found: C, 59.47; H, 7.07; N, 4.93; Ni, 10.43. Calcd for CoL^2: C, 59.79; H, 6.44; N, 4.94. Found: C, 59.86; H, 6.46; N, 4.83.

Instrumentation. UV/vis spectra: diode array spectrophotometer (Hewlett-Packard, type 8451) and double-beam spectrophotometer (Varian, type DMS 300). ^1H- and ^{13}C-NMR spectra: NMR spectrometer (Bruker, type AC 300). IR spectra: IR spectrometer (Beckman, type Acculab 2). Magnetic susceptibility: Faraday-type magnetic balance,[23] equipped with a Cahn D-200 electrobalance. EPR spectra: EPR spectrometer (Bruker, type SRC-200 D), operating at X-band, with variable-temperature unit.

Cyclic Voltammetry. The measurements were carried out in O_2-stripped (Ar) acetonitrile (0.1 M $[Et_4N](ClO_4)$) at 293 K with [complex] $\approx 10^{-3}$ M. The data was obtained with the aid of a home-built, computer-based apparatus by using the three-electrode technique. A hanging Hg drop electrode and a glassy-C electrode served as working electrodes for measuring the cathodic and anodic processes, respectively. The reference electrode was a Ag/AgCl electrode in acetonitrile (0.25 M $[(n\text{-}Bu)_4N](ClO_4)$), and a large Pt wire served as counter electrode. The resistance of the electrolyte between the working electrode and the tip of the reference electrode was compensated for by means of a positive feedback loop connecting the output of the current follower to the input of the adder potentiostat. Before the start of the experiment, the uncompensated resistance was determined by measuring the impedance spectrum of the blank electrolyte with a nine-frequency "pink-noise" signal. The scan rate was 20 V/s for reduction at the Hg electrode and 0.2 V/s for oxidation at the glassy-C electrode.

EPR Measurements. Solutions of the complexes in toluene (10 mg/10 mL) were filled into cylindrical EPR tubes and then purged with Ar or O_2 at ambient temperature for several minutes before they were cooled to 100–200 K. The reversibility of the reactions of the complexes with O_2 was checked by warming up the oxygenated frozen solutions, purging with Ar, and repeating the low-temperature measurement. The solid polycrystalline samples were measured at 100–293 K.

The spectra were evaluated by computer simulation with a program[24] optimizing the spin Hamiltonian parameters.

Spectrophotometric Titration. The addition of pyridine to CoL according to (2) was followed spectrophotometrically in acetone. The

$$\text{CoL} + \text{py} \overset{K}{\rightleftharpoons} \text{CoL·py} \qquad (2)$$

$$A = (A_0 + A_\infty K[\text{py}])/(1 + K[\text{py}]) \qquad (3)$$

A/[py] data for a given wavelength were computer-fitted to eq 3 to obtain K. The symbols A_0 and A_∞ refer to the absorbance A of the species CoL and CoL·py, respectively, at a concentration of $[\text{Co}]_{\text{tot}}$.

Determination of Oxygen Uptake. The apparatus used for the volumetric determination of the amount of O_2 taken up by solutions of cobalt(II) acetate and the ligand $H_2[H_4]L^1$ in DMF is described elsewhere.[25]

X-ray Structure Determination. Crystals of CoL^1 were grown from $CHCl_3$/petroleum ether as short prisms. The crystal chosen for X-ray measurements had the dimensions 0.25 × 0.28 × 0.5 mm. Intensities were measured on a four-circle diffractometer (Stoe-Stadi-4) using graphite-monochromatized Mo Kα radiation (λ = 0.710 69 Å; scan $2\theta:\omega$ = 1:1). Cell constants were determined by the least-squares method from the 2θ angles of 48 reflections (T = 294 K) on the same instrument. LP and background corrections and a numerical absorption correction (SHELX 76) were applied.

The structure was solved by direct methods with SHELXS-86 and refined by least-squares to the R values given in Table II. Hydrogen atoms were positioned geometrically (C–H distance = 1.08 Å) and not refined. An empirical extinction correction was applied. All crystallographic calculations were performed with the programs SHELX-76 and SHELXS-86 on an IBM 3081 K computer at the Technische Hochschule Darmstadt. Scattering factors f_0, f', and f'' for C, H, N, and O are stored in SHELX-76.[26] The final positional parameters are given in Table III.

Table I. Visible Absorption [λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})] of the Complexes ML and $M[H_4]L$ in Acetone[a]

Co	Ni	Cu
	Complexes ML^1	
420 (14 600), 490 sh; 420 (12 700),[b] 490 sh[b]	420 (6500), 450 sh, 560 (160)	380 (14 000), 570 (600)
	Complexes $M[H_4]L^1$	
	366 (2740), 514 (1400)	410 (2200), 584 (1200)
	Complexes ML^2	
416 (1400), 500 sh	420 (6900), 450 sh, 555 (130)	380 (11 400), 570 (560)
	Complexes $M[H_4]L^2$	
	360 (2400), 510 (1050)	416 (1800), 580 (1040)

[a] [complex] = 10^{-4} M; d = 1 cm. [b] In DMF.

Table II. Crystallographic Data for Complex CoL^1 = Co{(Bu,Me)saltmen}

$C_{30}H_{42}N_2O_2Co$	$Z = 4$
fw = 521.61	T = 21.0 °C
space group: $C222_1$ (No. 20)	λ = 0.710 69 Å
a = 23.972(6) Å	ρ(calcd) = 1.22 g cm^{-3}
b = 10.106(3) Å	μ = 6.29 cm^{-1}
c = 11.696(3) Å	$R(F_o)$[a] = 0.0283 (0.0436)[b]
V = 2833.7 ± 2.3 Å^3	$R_w(F_o)$[c] = 0.0273 (0.0426)[b]

[a] $R(F_o) = \sum|F_o - F_c|/\sum F_o$. [b] Values in brackets: inverse structure. [c] $R_w(F_o) = \sum w^{1/2}|F_o - F_c|/\sum w^{1/2}|F_o|$.

Table III. Atomic Parameters (×10^4) for CoL^1 = Co{(Bu,Me)saltmen} (Excluding H)

atom	x/a	y/b	z/c	U_{eq}, Å^2 [a]
Co	5492(0.2)	5000(0)	5000(0)	295(2)
O(1)	6054(1)	6146(2)	5454(1)	330(9)
C(1)	6017(1)	7359(3)	5857(2)	321(13)
C(2)	6516(1)	8084(3)	6146(2)	344(14)
C(3)	6456(1)	9361(3)	6539(2)	412(15)
C(4)	5941(1)	10004(4)	6667(2)	443(14)
C(5)	5474(1)	9312(3)	6403(2)	416(15)
C(6)	5499(1)	7989(3)	6024(2)	359(13)
C(7)	4983(1)	7310(2)	5862(2)	355(14)
C(8)	7095(1)	7431(3)	6010(2)	366(15)
C(9)	7564(1)	8364(3)	6412(3)	509(18)
C(10)	7134(1)	6174(3)	6734(3)	480(18)
C(11)	7198(1)	7109(3)	4748(2)	493(18)
C(12)	5913(1)	11422(3)	7086(3)	626(21)
N(1)	4924(1)	6111(2)	5497(2)	320(12)
C(13)	4354(1)	5476(3)	5523(2)	347(14)
C(14)	4315(1)	4704(3)	6654(2)	478(18)
C(15)	3878(1)	6477(3)	5469(3)	479(17)

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

Results and Discussion

Preparation of the Complexes. The Schiff base ligands H_2L^1 and H_2L^2 react with the corresponding metal acetates in ethanol with immediate color change, to form the crystalline complexes ML^1 and ML^2 (M = Co, Ni, Cu) in good yield (>80%). The color ranges from red (Co) and orange (Ni) to black-green (Cu). Of interest is that the cobalt(II) complexes CoL^1 and CoL^2 are air-stable and not oxidized to the corresponding cobalt(III) species.

The nickel (cherry-red) and copper (black-green) tetrahydrosalen complexes $M[H_4]L^1$ and $M[H_4]L^2$ were prepared analogously. The reaction of cobalt acetate with $H_2[H_4]L^1$ and $H_2[H_4]L^2$ in ethanol, however, was remarkably different. There was no immediate color change, and extended refluxing was necessary to obtain the red products, which were surprisingly found to be CoL^1 and CoL^2, respectively, instead of the expected

---

(23) Gehring, S.; Fleischhauer, P.; Paulus, H.; Haase, W. *Inorg. Chem.* **1993**, *32*, 54.

(24) Liska, M.; Pelikan, P.; Valko, M. To be published.

(25) Vancova, V.; Ondrejkovikova, I.; Ondrejovic, G. *Chem. Pap.* **1984**, *38*, 363.

(26) Data for Co was taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974, Vol. IV.

tetrahydrosalen complexes. When the reaction of cobalt acetate with $H_2[H_4]L^1$ and $H_2[H_4]L^2$ was repeated strictly under nitrogen, formation of the complexes $Co[H_4]L$ obviously occured[27] without being accompanied by a substantial color change. Admission of oxygen (air) initiated a strong color change, leading to the Schiff base Co(II) complexes CoL^1 and CoL^2. This oxidative dehydrogenation of the coordinated tetrahydrosalen ligands was investigated further (see below).

Visible Absorption, Stability in Solution, and Magnetic Properties of the Complexes. The characteristics of the vis spectra of the complexes in acetone solution are compiled in Table I.

The Schiff base complexes CoL and NiL are characterized by a rather intense CT band at about 420 nm and a weaker d–d band (shoulder) at about 500 nm (Co) and 450 nm (Ni). For CuL^1 and CuL^2 the CT band is blue-shifted (380 nm) and the d–d band is red-shifted (570 nm). The effect of substituent X^5 (=Me in ML^1 and Cl in ML^2) on the absorption properties is very minor.

Compared to the corresponding Schiff base complexes, the tetrahydrosalen nickel complexes $Ni[H_4]L^1$ and $Ni[H_4]L^2$ have a weaker and considerably blue-shifted CT band and a red-shifted d–d band. For $Cu[H_4]L^1$ and $Cu[H_4]L^2$ similar changes are found, the CT bands being slightly red-shifted, however.

In acetone, DMF, or alcohols, all of the Schiff base complexes ML^1 and ML^2 (M = Co, Ni, Cu) are stable for weeks (an exceptional behavior is only observed for the cobalt complexes, CoL^1 and CoL^2, dissolved in tetrachloromethane).[28] The behavior of organic solutions of the tetrahydrosalen complexes, $M[H_4]L^1$ and $M[H_4]L^2$ (M = Co, Ni, Cu), is however not consistent. Solutions of $Cu[H_4]L$ in a variety of organic solvents are totally stable under aerobic conditions, whereas in the case of cobalt, as discussed above, the initially formed tetrahydrosalen complexes $Co[H_4]L$ readily react with dioxygen to form the corresponding Schiff base complexes CoL. In comparison to cobalt and copper, the nickel complexes $Ni[H_4]L$ are of intermediate stability. In the presence of oxygen (air), the red solutions of these complexes in acetone slowly become yellow upon standing for several days. The spectral changes associated with this slow process strongly point to the formation of the half-salen species $Ni[H_2]L$, with one of the two C–N bonds being oxidatively dehydrogenated. This behavior is analogous to that of the complex Ni{(Bu,Me)-$[H_4]$salen},[2] which, in aerated acetone solution, activates dioxygen and is converted to Ni{(Bu,Me)$[H_2]$salen}[2] with a half-life of several hours at 298 K.[16]

Regarding the metal effect, the reactivity of the tetrahydrosalen complexes $M[H_4]L$ toward O_2 is thus given by the sequence Cu $\ll$ Ni $\ll$ Co. The reaction of $Ni[H_4]L^1$ with O_2 at 298 K has a half-life of about 7 days in acetone and proceeds much more slowly in DMF. In addition to this solvent effect there is also a rate effect of substituents X^5 with $Ni[H_4]L^2$ being less reactive than $Ni[H_4]L^1$. Both solvent and substituent effects are in line with earlier results[16] obtained for the complexes Ni{(Bu,X^5)-$[H_4]$salen}.[29]

The copper complexes, CuL^1 and CuL^2, as well as $Cu[H_4]L^1$ and $Cu[H_4]L^2$, are magnetically normal (see Table IV). The data for μ_{exp} range from 1.69 to 1.75 μ_B and are thus close to the value of 1.73 μ_B expected for these $3d^9$ systems. Therefore, there is obviously no coupling in the solid state.

Planar four-coordinate nickel(II) ($3d^8$) complexes should be diamagnetic, as found, for example, for Ni(salen) with $\mu_{exp} = 0$ μ_B. The magnetic moments at ambient temperature of the four nickel complexes of the present study are close to zero, ranging from 0.39 μ_B for $Ni[H_4]L^1$ to 0.54 μ_B for NiL^2. These values point to planarity and correspond to $\mu_{exp} = 0.35$ μ_B found for the complex Ni{(Bu,Me)$[H_4]$salen, the planarity of which was proven by X-ray structure analysis.[16]

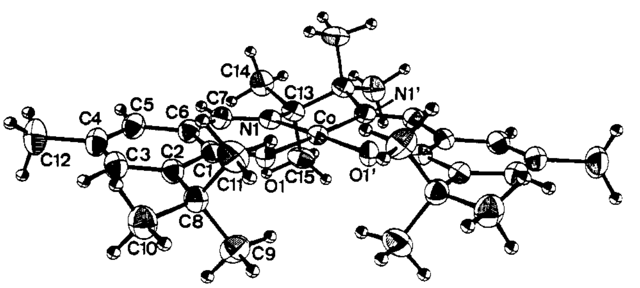


Figure 1. View of the coordination geometry in the complex CoL^1.

To our knowledge, all of the square-planar cobalt(II) complexes described in the literature so far are low-spin. Their magnetic moments, expected to be close to the spin only value of 1.73 μ_B, are however higher and lie in the range 2.2–2.7 μ_B.[34] Complexes CoL^1 and CoL^2 are accordingly found to have magnetic moments of 2.31 μ_B and 2.44 μ_B, respectively, which classifies them to be planar low-spin d^7 systems. The temperature dependence of the magnetic susceptibility of CoL^1 and of the nickel complexes discussed above are at present under study.

Structure of the Complex CoL^1. When the cobalt coordinates to the ONNO type ligand H_2L^1, the resulting complex is asymmetric. There are two possibilities for the arrangement of the tetramethylated ethylene bridge, which are related to each other like right and left hands. The solution of the complex should contain equal amounts of both enantiomers. The complex crystallizes in the orthorhombic space group $C222_1$ with four formula units per unit cell. It follows from the acentric space group that a given crystal contains only molecules of one "handedness". The crystal chosen for the X-ray study could be refined to $R_w = 0.0283$ for the one enantiomer, whereas data refinement for the other enantiomer led to $R_w = 0.0426$ only (see Table II).

Figures 1 and 2 give a view of the coordination geometry and of the arrangement of the molecules in the unit cell, respectively. The cobalt coordinates the tetradentate ONNO ligand, $(L^1)^{2-}$, in a planar fashion and there is a 2-fold axis along [100] passing through the cobalt and the C–C bond of the ethylene bridge. The molecule consists therefore of two identical halves. It is important to note that the four methyl groups of the ethylene bridge and the six methyl groups of the two *tert*-butyl substituents in 3-position of the salicylaldehyde moieties produce extensive steric crowding around the metal (see Figure 1). The cobalt atoms of neighboring complex units are separated by 5.72 Å. The arrangement of the methyl groups on the ethylene bridge is such that two are in axial and two in equatorial positions.

---

(27) Spectrophotometric monitoring revealed the fast formation of a strong absorption band at 310 nm and of a weak and broad absorption band around 500 nm.

(28) At room temperature these solutions lose their red-orange color within minutes and become green. The CT band at 420 nm disappears, and a very broad absorption at about 800 nm builds up. The details of this reaction, which is obviously photosensitive and leads most probably to cobalt(III) species, are at present under study. The participation of CCl_4 follows from the finding that even in acetone, containing 1 M CCl_4, the color change from red to green occurs within 1 h. It is worthwhile to mention that the corresponding Schiff base complexes of copper and nickel are stable in CCl_4 and that solutions of CoL^1 and CoL^2 in dichloromethane and chloroform are also stable.

(29) It was pointed out by a reviewer that, in a broader sense, the oxidative dehydrogenation observed for complexes $M[H_4]L$ can be related to the more general area of ligand oxidation processes occuring in metal complexes. As studied and discussed, for example, by Collins et al.,[30] high-valent transition metal complexes undergo intramolecular ligand oxidation and metal reduction processes whenever there are H substituents at the saturated carbon atoms α to the donor nitrogen and β to the metal. This condition is indeed fulfilled in Co(II) polyamine complexes, as studied by Martell et al.,[31] and in complexes $M[H_4]L$ of the present work. The difference is however that the O_2-induced, metal-centered dehydrogenation $M[H_4]L \rightarrow M[H_2]L \rightarrow ML$ leaves M = Co, Ni in the divalent oxidation state. The role of M is thus restricted to O_2-activation.

(30) See for example: Collins, T. J.; Kostka, K. L.; Uffelman, E. S.; Weinberger, T. L. *Inorg. Chem.* **1991**, *30*, 4204.

(31) See pp 95–102 in ref 3a.

(32) Gall, R. S.; Rogers, J. F.; Schaefer, W. P.; Christoph, G. G. *Inorg. Chem.* **1976**, *98*, 5135.

(33) Brückner, S.; Calligaris, M.; Nardin, G.; Randaccio, L. *Acta Crystallogr. B* **1969**, *25*, 1671.

(34) Boudreaux, E. A.; Mulay, L. N. *Theory and Applications of Molecular Paramagnetism*; Wiley: New York, 1976; pp 220–223.

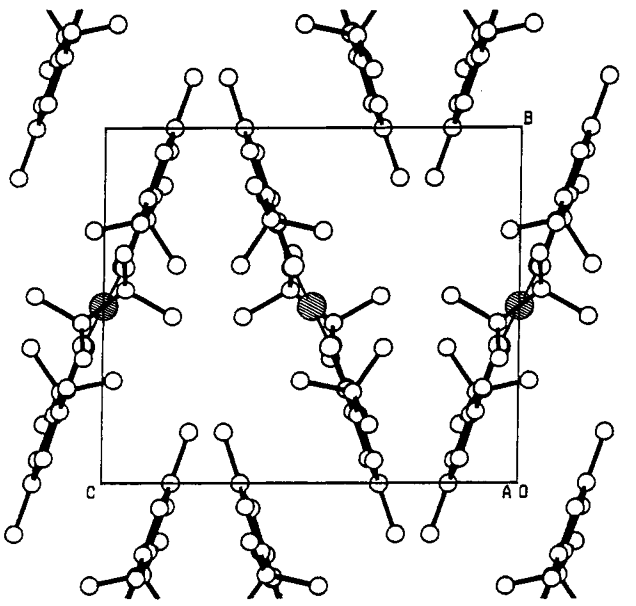


Figure 2. Projection of half of the unit cell ($0.25 < x < 0.75$) of the complex CoL^1 along [100].

The planar arrangement of the Co(ONNO) core is slightly distorted, which follows from the O–Co–O, O–Co–N, and N–Co–N angles not being 90 and 180°, respectively (see Table IV). It follows from Figure 2 that the Co(ONNO) core and the two phenyl rings are almost coplanar.

The structural details of the complex CoL^1 are very close to those of the complex CoL with $X^5 = H$ instead of $X^5 = Me$, as in CoL^1. For this complex, Schaefer et al.[32] also reported a planar structure, and the Co–O and Co–N distances found for CoL^1 (1.852 and 1.860 Å, respectively; see Table IV) agree with those obtained for CoL with $X^5 = H$ within the limits of error. The Co···Co separation is 5.64 Å, as compared to 5.72 Å in CoL^1. This large separation demonstrates the above mentioned shielding effect of the methyl and *tert*-butyl groups when compared to the Co–Co distance of about 2.85 Å in the oxygen-inactive Co(salen) dimer.[33]

Adduct Formation with Pyridine. The metal center in complexes ML and $M[H_4]L$ is only of weak Lewis acidity. Spectrophotometric titration of CoL^1 and CoL^2 with pyridine in acetone leads to spectral changes which fit satisfactorily the relationship (3), describing monoadduct formation according to eq 2. The values obtained for equilibrium constant K (Table VI) are small, 0.15 M^{-1} and 1.67 M^{-1}, respectively. They reflect the electronic effects of substituents X^5 whereby the electron-withdrawing chloro substituent, compared to the methyl group, increases K by a factor of about 10.

Titration of the copper and nickel complexes ML^1, ML^2, $M[H_4]L^1$, and $M[H_4]L^2$ with pyridine produces only very minor spectral changes, too small for the evaluation of reliable K data on the basis of eq 3. One can conclude therefore that $K(Cu)$, $K(Ni) \ll 1$.

The very limited Lewis acidity of complexes ML and $M[H_4]L$ is obviously due to the steric and electronic effects of the methyl groups on the ethylene bridge. This follows from the comparison of complex $Ni[H_4]L^1$ ($K \ll 1$) with complex Ni{(Bu,Me)-$[H_4]$salen}^{2}, as studied earlier.[16] The latter complex, which differs only by the absence of the four methyl groups on the ethylene bridge, adds even two molecules of pyridine (see Table VI).

Electrochemical Behavior of the Complexes. The redox potentials of the complexes ML and $M[H_4]L$ are summarized in Table VII. All of the Schiff base complexes ML give a reversible one-electron reduction $M(II) \rightarrow M(I)$. The electron-withdrawing effect of the chloro substituent is reflected by the more positive potentials found for $X^5 = Cl$ compared to $X^5 = Me$.[35] The potentials of the complexes NiL are more negative than those of the corresponding copper (and cobalt) complexes, as is found for many Schiff base complexes.[37] Inspite of the relatively high scan rate of 20 V/s, peak separations of about 60 mV were observed, which is close to the theoretical value of 57 mV for infinitely fast charge-transfer processes.

Table IV. Selected Distances (Å) and Bond Angles (deg) for CoL^1 = Co{(Bu,Me)saltmen}

Distances			
Co–O(1)	1.852(2)	C(5)–C(6)	1.410(3)
Co–N(1)	1.860(2)	C(6)–C(7)	1.429(3)
O(1)–C(1)	1.316(3)	N(1)–C(7)	1.293(3)
C(1)–C(6)	1.407(3)	N(1)–C(13)	1.510(3)
C(1)–C(2)	1.444(3)	C(13)–C(13)′	1.556(5)
C(2)–C(3)	1.378(4)	C(13)–C(14)	1.539(3)
C(3)–C(4)	1.403(3)	C(13)–C(15)	1.526(3)
C(4)–C(5)	1.355(4)	C(2)–C(8)	1.545(3)
Angles			
O(1)–Co–O(1)′	86.94(1)	Co–N(1)–C(7)	126.15(1)
O(1)–Co–N(1)	93.78(1)	Co–N(1)–C(13)	114.43(1)
O(1)–Co–N(1)′	178.02(1)	C(7)–N(1)–C(13)	119.32(1)
N(1)–Co–N(1)′	85.68(1)	N(1)–C(13)–N(1)′	104.29(1)
Co–O(1)–C(1)	129.48(2)	N(1)–C(13)–C(14)	106.66(2)
O(1)–C(1)–C(6)	122.04(2)	C(13)′–C(13)–C(14)	111.24(1)
C(2)–C(1)–C(6)	117.95(2)	N(1)–C(13)–C(15)	113.24(1)
C(1)–C(6)–C(7)	121.90(2)	C(14)–C(13)–C(15)	109.06(1)
C(6)–C(7)–N(1)	125.99(2)		

The rate of charge transfer is significantly smaller for the tetrahydrosalen type complexes $M[H_4]L$. Surprisingly, the characteristics of the charge-transfer processes change in the case of the nickel complexes $Ni[H_4]L$. They undergo a fast reversible oxidation and an irreversible reduction, whereas the opposite behavior is found for the corresponding Schiff base complexes NiL. On the other hand, the copper complexes $Cu[H_4]L$ are reversibly reduced but irreversibly oxidized. It is interesting to note that for $Ni[H_4]L^1$, which reacts faster with O_2 than $Ni[H_4]L^2$, the formal potential for oxidation is less anodic than for $Ni[H_4]L^2$.

The increase in reduction potential observed upon going from CuL to $Cu[H_4]L$ (300 and 240 mV for L^1 and L^2, respectively) is somewhat unexpected, since the more basic hydrogenated ligand should induce a higher electron density on the metal. The observed stabilization of the Cu(I) state in the complexes $Cu[H_4]L$ could possibly be due to the hydrogenated ligands being more able to allow tetrahedral coordination around the d^{10} center of Cu(I). The effect of substituent X^5 on the potential of complexes $Cu[H_4]L^1$ is the same as for complexes CuL.

Reaction of Cobalt(II) with $H_2[H_4]L$ and Dioxygen. As described above, in the presence of O_2 the tetrahydrosalen ligands $H_2[H_4]L^1$ and $H_2[H_4]L^2$ react with cobalt(II) acetate to finally form the Co(II) salen complexes CoL^1 and CoL^2. Neither the oxidative dehydrogenation of the two C–N bonds nor the nonoccurence of Co(II) oxidation in the resulting salen complexes are necessarily expected.[38]

The preparative studies described above were carried out in ethanol. Dioxygen uptake measurements in this solvent were

---

(35) The effects of a wide range of substituents X^3 and X^5 on the potential of the Co(II)/Co(III) redox couple of Co(salen) complexes was studied by Speiser et al.[36] A detailed comparison of their results with the present data is hampered by the fact that the strongly coordinating solvent DMF was used instead of acetonitrile and that the complexes Co(saltmen) of the present study carry additionally four methyl groups on the ethylene bridge.

(36) Nishinaga, A.; Tajima, K.; Speiser, B.; Eichhorn, E.; Rieker, A.; Ohya-Nishiguchi, H.; Ishizu, K. *Chem. Lett.* **1991**, 1403.

(37) (a) Jäger, E.-G.; Häussler, E.; Rudolph, M.; Schneider, A. *Z. Anorg. Allg. Chem.* **1985**, *525*, 67. (b) Jäger, E.-G.; Rudolph, M.; Müller, R. *Z. Chem.* **1978**, *18*, 229. (c) Jäger, E.-G.; Schlenvoigt, G.; Kirchhof, B.; Rudolph, M.; Müller, R. *Z. Anorg. Allg. Chem.* **1982**, *485*, 173.

(38) In aerated solution, most of the known Co^{II}(salen) complexes are oxidized to Co(III) species. The complex CoL[32] with $X^5 = H$ instead of $X^5 =$ Me and Cl appears to be another example of an air-stable Co^{II}(salen) complex, where steric crowding around the cobalt prevents oxidation.

Table V. Magnetic Moments[a]

	complex									
	CoL^1	CoL^2	NiL^1	$Ni[H_4]L^1$	NiL^2	$Ni[H_4]L^2$	CuL^1	$Cu[H_4]L^1$	CuL^2	$Cu[H_4]L^2$
μ_{exp}, μ_B	2.31	2.44	0.43	0.39	0.54	0.41	1.69	1.75	1.71	1.72

[a] At ambient temperature.

Table VI. Equilibrium Constants for Adduct Formation of CoL^1 and CoL^2 with Pyridine According to (2) in Acetone at 298 K

complex	K, M^{-1} [a]	complex	K, M^{-1} [a]
CoL^1	0.15 ± 0.01	Ni(Bu,Me)[H_4]salen[2]	0.37,[b] 15.8[b,c]
CoL^2	1.67 ± 0.03		

[a] Calculated by computer-fitting of the A/[py] data to eq 3. [b] Data from ref 16. [c] Equilibrium constant K_2 for NiL·py + py $\rightleftharpoons$ NiL·2py.

Table VII. Voltammetric Data[a,b] for the Complexes ML and $M[H_4]L$ in Acetonitrile at 293 K

		ML		$M[H_4]L$	
L	M	I/II	II/III	I/II	II/III
L^1	Cu	−1145	irr	−845[c]	irr
	Ni	−1535	irr	irr	+850
	Co	−1145	+685[d]		
L^2	Cu	−1015[d]	irr	−775[e]	irr
	Ni	−1350	irr	irr	+1035[f]
	Co	−960	+720[d]		

[a] In mV. [b] Unless stated otherwise, the peak separation was 60 ± 2 mV. [c] v = 5 V/s, $E_p{}^c - E_p{}^a$ = 130 mV. [d] $E_p{}^c - E_p{}^a$ = 75 mV. [e] $E_p{}^c - E_p{}^a$ = 100 mV. [f] $E_p{}^c - E_p{}^a$ = 90 mV.

hampered by the fact that the solubility of $H_2[H_4]L^1$ and $H_2[H_4]L^2$ in ethanol is rather limited. To have a homogeneous system the oxygen uptake was therefore studied in DMF. Figure 3 shows that, in the 1:1 reaction of Co^{2+} ions with $H_2[H_4]L^1$, 1 equiv of O_2 is taken up ($[O_2]/[Co]$ = 0.97). This result suggests that reaction 4 describes adequately the overall process. The

$$Co(AcO)_2 + H_2[H_4]L + O_2 \rightarrow CoL + 2AcOH + 2H_2O \quad (4)$$

oxidative dehydrogenation of the two C–N bonds will occur stepwise, $Co[H_4]L \rightarrow Co[H_2]L \rightarrow CoL$, with H_2O_2 possibly being an intermediate.[39] The possibility of reaction 5 being operative

$$Co(AcO)_2 + H_2[H_4]L + 2O_2 \rightarrow CoL + 2AcOH + 2H_2O_2 \quad (5)$$

has to be excluded on experimental grounds, since (i) the observed ratio $[O_2]/[Co]$ is close to unity and (ii) the product H_2O_2 attacks the product CoL.[40] The absorption spectra shown in Figure 4 prove that the product of the 1:1:1 reaction of Co^{2+}, $H_2[H_4]L^1$, and O_2 in DMF is indeed CoL.[1] The behavior of the system $Co^{2+}/H_2[H_4]L^2/O_2$/DMF is analogous to that with $H_2[H_4]L^1$.

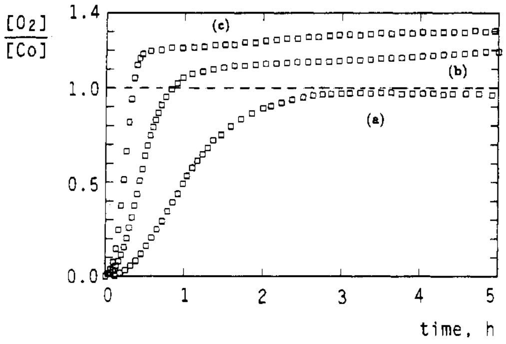


Figure 3. Time dependence of the uptake of dioxygen by a 1:1 mixture of cobalt(II) acetate and the ligand $H_2[H_4]L^1$ in DMF at 298 K ($[Co^{2+}]$ = $[H_2[H_4]L^1]$ = 5.1 × 10^{-4} M; curve a, [py] = 0; curve b, [py] = $[Co^{2+}]$; curve c, [py] = $10[Co^{2+}]$).

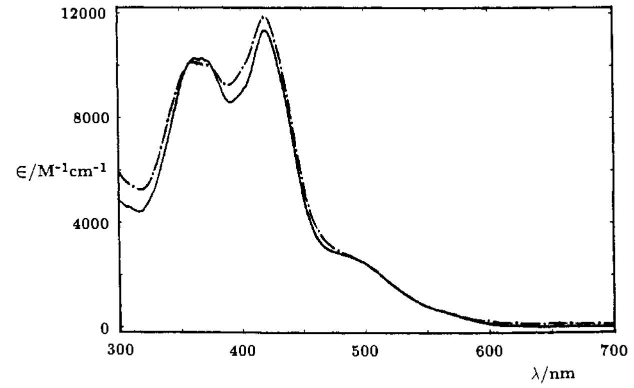


Figure 4. Vis absorption spectrum of the complex CoL^1 (solid line) and of the product of the 1:1 reaction of Co^{2+} with $H_2[H_4]L^1$ in oxygenated DMF at 298 K after 8 h (–··–).

The shape of the curve obtained for the time dependence of O_2 uptake (see lower curve in Figure 3) indicates that, from the mechanistic point of view, the reaction between Co^{2+}, $H_2[H_4]L^1$, and O_2 is not a simple one. The retarded start of the reaction points to autocatalysis and could well be due to the intermediate formation and participation of H_2O_2.[41] The addition of increasing amounts of pyridine enhances the rate of O_2 uptake considerably but raises the final ratio $[O_2]/[Co]$ to values >1.0 (see curves b and c in Figure 3), which would indicate additional Co(III) formation.

The rate of the reaction of $Ni[H_4]L$ with O_2 in DMF is extremely low ($t_{1/2} \approx$ 7 days of 298 K) making O_2 uptake studies with these nickel complexes not feasible. Spectrophotometric monitoring of $Ni[H_4]L^1$ reacting with H_2O_2 in acetone for 25 h at 298 K under pseudo-first-order conditions clearly reveals a two-step process according to (6), with k_1 = (8.0 ± 0.5) × 10^{-5} s^{-1} and k_1/k_2 = 13 under the given experimental conditions.[42] The observed spectral changes correspond to the formation of $Ni[H_2]L^1$ in the initial fast step and to the formation of NiL^1 in

$$Ni[H_4]L \underset{k_1}{\overset{H_2O_2}{\rightarrow}} Ni[H_2]L \underset{k_2}{\overset{H_2O_2}{\rightarrow}} NiL \quad (6)$$

---

(39) Evidence for this comes from the finding that the rate of CoL^1 formation from Co^{2+} and $H_2[H_4]L^1$ in aerated DMF is considerably increased by the addition of H_2O_2.

(40) When H_2O_2 is added ($[H_2O_2]:[CoL^1]$ = 2:1), the solution of CoL^1, prepared from cobalt(II) and H_2L^1, loses its red-orange color within a few hours and becomes yellow-greenish, most probably due to the formation of Co(III) species.

(41) This interpretation is supported by the fact that, in the presence of additional H_2O_2, the induction period, found for the reaction of Co^{2+} with $H_2[H_4]L^1$ (see Figure 3), is no longer observed.

(42) Except for the very first stage of the reaction, the absorbance/time data obtained for the reaction of $Ni[H_4]L^1$ (2 × 10^{-4} M) with H_2O_2 (2 × 10^{-3} M) in aerated acetone at 293 K could be well fitted to the sum of two exponentials, $A = a_1 \exp(-k_1t) + a_2 \exp(-k_2t) + A_\infty$, with k_1 = (8.0 ± 0.5) × 10^{-5} s^{-1} and k_2 = (6.0 ± 2.0) × 10^{-6} s^{-1} (averaged for the wavelength range 360-600 nm). At $[H_2O_2]_0$ = 100[complex]$_0$, both k_1 and k_2 were greater by a factor of about 10 and A_∞(420 nm) = 1.39 corresponded reasonably well to the value calculated for NiL^1 (A_∞(calc) = ϵcd = 6500 × 2 × 10^{-4} × 1 = 1.30; see Table I for $\epsilon(NiL^1)$ at 420 nm). These results imply two consecutive second-order reactions, which is in agreement with reaction 7. It is important to note that, under the given experimental conditions, H_2O_2 does not react with the free ligand $H_2[H_4]L^1$ to form $H_2[H_2]L^1$ and H_2L^1.

Table VIII. EPR Data[a] for Complexes ML and M[H_4]L

			frozen toluene solution,[b] saturated with									
	solid state[b]		Ar				O_2					
complex	$g_\perp$	$g_\parallel$	$g_\perp$	$g_\parallel$	$\lvert A_\perp \rvert$	$\lvert A_\parallel \rvert$	g_1	g_2	g_3	$\lvert A_1 \rvert$	$\lvert A_2 \rvert$	$\lvert A_3 \rvert$
CuL^1	2.033	2.095	2.044	2.187	25.5	209.5						
Cu[H_4]L^1	2.037	2.062	2.040	2.206	38.8	197.6						
CuL^2	2.035	2.098	2.043	2.196	21.9	212.5						
Cu[H_4]L^2	2.028	2.062	2.051	2.202	19.8	204.2						
CoL^1	1.713	1.925	1.700	1.978	14.0	83.7	2.080	2.000	1.958	26.9	30.9	29.6
CoL^2	1.819	3.325	1.860	3.584	*c*		2.079	2.012	1.981	24.2	18.9	11.8

[a] Hyperfine splitting constant *A* in G. [b] At 120 K. [c] Nonresolved hyperfine structure.

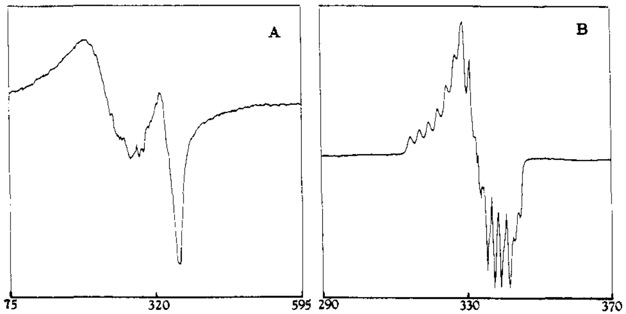


Figure 5. EPR spectra of the complex CoL^2 in frozen toluene solution at 120 K: A, toluene purged with Ar; B, toluene saturated with O_2.

the slow second step. Compared to O_2, the oxidant H_2O_2 is thus more reactive and dehydrogenates both C–N bonds in Ni[H_4]L.

EPR Spectra. In the solid state and in frozen toluene solution all of the copper(II) complexes exhibit axial spectra with *g* factors and hyperfine splitting constants *A*, summarized in Table VIII. The data for both *g* and *A* are indicative for a predominantly $d_{x^2-y^2}$ ground state with small mixing in of a d_{z^2} contribution.[43] The order $g_\parallel > g_\perp$ and $A_\parallel > A_\perp$ is found for all complexes studied. For X^5 = Cl the electron-withdrawing effect of the chloro substituent is reflected in a slightly lowered density of the unpaired electron on the copper, as indicated by a small decrease in the data for *A*. The small differences in the EPR data found for the salen complexes CuL and for the tetrahydrosalen complexes Cu[H_4]L are probably due to a slight tetrahedral distortion of the CuN_2O_2 plane in the complexes Cu[H_4]L. The EPR data do not provide any evidence for dioxygen interacting with CuL or Cu[H_4]L in the temperature range 100–293 K.

The solid-state spectra of the cobalt Schiff base complexes CoL^1 and CoL^2 exhibit axial symmetry and are typical of low-spin d^7 systems. Even at 100 K, the lines are very broad and the hyperfine splitting is therefore not resolved. In deaerated frozen toluene solution the spectra of CoL^1 and CoL^2 (see Figure 5A for CoL^2) are very similar and correspond to their solid-state powder spectra. The parameters obtained from the EPR spectra point to a d_{z^2} electronic ground state with small mixing in of a $d_{x^2-y^2}$ contribution. The hyperfine structure is badly resolved as a consequence of a strong exchange interaction between neighboring coordination polyhedra and very near energy levels of the involved electronic terms. This leads to a substantial contribution of excited states to the g tensor.

In the presence of dioxygen at 120 K, the frozen toluene solutions of CoL^1 and CoL^2 exhibit rhombic symmetry with well-resolved hyperfine structures in all three main directions of the g tensor (see Figure 5B for CoL^2). The shape of the spectra and the estimated *g* and *A* values indicate the interaction of the square-planar cobalt core with O_2 and suggest a nonlinear Co–O–O arrangement.[44] The interaction with O_2 is reversible and weak, as proven by purging with argon and reloading with O_2 and raising the temperature to 200 K.

The EPR data obtained for the nickel complexes NiL and Ni[H_4]L are not very informative due to the low level of paramagnetism. The solid-state spectrum of the weakly paramagnetic complex NiL^1 at 120 K gives a very broad and almost isotropic line (g_{iso} = 2.059), which is typical for nickel(II). In frozen toluene solution (saturated with Ar or O_2) this complex was practically EPR inactive, which is in line with its very weak paramagnetism.

The EPR spectrum of the tetrahydrosalen complex Ni[H_4]L^1 in the solid state (120 K) gave a pseudo-isotropic signal indicating a somewhat higher level of paramagnetism. A frozen toluene solution of Ni[H_4]L^2 (saturated with O_2) gave a well-defined singlet peak (g_{iso} = 2.123), suggesting a high level of paramagnetism and indicating a Ni···O_2 interaction.

It is well conceivable that the differing EPR activity of the various nickel complexes has to do with the differing extent of tetrahedral distortion of the planar NiN_2O_2 core in these complexes.[47]

Conclusions

Complex formation of Cu(II), Ni(II), and Co(II) with the colorless tetrahydrosalen ligands H_2[H_4]L^1 and H_2[H_4]L^2, obtained by hydrogenation of the two C=N bonds in the yellow salen ligands H_2L^1 and H_2L^2, is characteristically metal-dependent. For M = Cu, complexes M[H_4]L are well-characterized crystalline solids, which, in organic solution, are stable toward O_2, as well as H_2O_2. Complexes Ni[H_4]L, however, which can also be isolated as crystalline solids, are not stable in aerated organic solution. They are slowly oxidatively dehydrogenated through nickel-based O_2-activation, to form the corresponding half-salen complexes Ni[H_2]L. With H_2O_2 instead of O_2, the conversion Ni[H_4]L → Ni[H_2]L is considerably faster and followed by the formation of NiL.

In the absence of O_2, complex formation between Co^{2+} ions and the ligands H_2[H_4]L is fast and leads to complexes Co[H_4]L, which were not able to be isolated. In the presence of O_2, these complexes are oxidatively dehydrogenated and the Co(II) salen complexes CoL are formed according to (a). The cobalt(II) in CoL is not oxidized to cobalt(III), which is probably due to the extensive steric crowding around the metal. In oxygenated frozen toluene solution, however, there is convincing EPR evidence for the equilibrium $\mathrm{Co^{II}L} + \mathrm{O_2} \rightleftharpoons \mathrm{Co^{III}L^{+}\cdots O_2^{-}}$.

$$\mathrm{CoX_2 + H_2[H_4]L + O_2 \rightarrow CoL + 2HX + 2H_2O} \quad \text{(a)}$$

The process of stepwise oxidative dehydrogenation by dioxygen according to (b) is thus strongly metal-dependent, the order of "reactivity" being Co ≫ Ni ≫ Cu. The results suggest initial M···O_2 interaction and the intermediate formation and partic-

---

(43) Hathaway, B. H.; Billing, D. E. *Coord. Chem. Rev.* **1970**, *5*, 143.

(44) The nonlinear Co–O–O arrangement would be in agreement with the results of the low-temperature X-ray structure analysis of the O_2 adducts of the complexes CoL(base) (X^3 = t-Bu; X^5 = H),[32] CoL(base) (X^3 = F; X^5 = H),[45] and CoL(base) (X^3 = X^5 = H),[46] as carried out by Schaefer and co-workers.

(45) Avdeef, A.; Schaefer, W. P. *J. Am. Chem. Soc.* **1976**, *98*, 5153.

(46) Gall, R. S.; Schaefer, W. P. *Inorg. Chem.* **1976**, *15*, 2758.

(47) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance: Elementary Theory and Applications*; McGraw Hill: New York, 1972.

$$M[H_4]L \xrightarrow[-H_2O]{+O_2} M[H_2]L \xrightarrow[-H_2O]{+O_2} ML \qquad (b)$$

ipation of H_2O_2 in reaction b. It is to be expected that any divalent or trivalent transition metal M with a suitable potential M^{II}/M^{III} or M^{III}/M^{IV} will be able to effect sequence (b).

Acknowledgment. Sponsorship of this work by the Deutsche Forschungsgemeinschaft, Verband der Chemischen Industrie e.V., and Otto-Röhm-Stiftung is gratefully acknowledged. A.B. thanks the Studienstiftung des Deutschen Volkes and the Verband der Chemischen Industrie for a scholarship. The cooperation between Darmstadt and Bratislava was supported within the framework of the program "Scientific and Technological Cooperation", as established between the FRG and the CSFR (Project No. X 245.2). The authors appreciate the cooperation with Prof. Wolfgang Haase and Miss Martina Hüber (magnetic moments) and the help of Miss Elke Hilms with the synthesis of the ligands and complexes.

Supplementary Material Available: Tables SI–SIII, listing complex crystallographic data, calculated coordinates of hydrogens, thermal parameters, and interatomic distances not listed in Table IV (5 pages). Ordering information is given on any current masthead page.