

THE STEREOCHEMISTRY OF FOUR- AND FIVE-COORDINATE SCHIFF BASE COMPLEXES OF COBALT(II) AND NICKEL(II)

By

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The stereochemistry of chelate complexes of Co(II) and Ni(II) with Schiff bases derived from salicylaldehyde and various amines, both in the solid state and in solution, has been discussed on the basis of magnetic, dielectric and spectral properties.

Metal complexes of Schiff bases are of considerable interest in inorganic chemistry. It is well known that the coordination numbers and the configurations of transition metal complexes depend upon the ligands. Some excellent articles [1—8] have been published recently on this field; in several previous papers [9—20] we have discussed the properties of Ni(II) chelates of aromatic Schiff bases.

The present review discusses the stereochemistry of four- and five-coordinate Co(II) and Ni(II) chelates both as solids and in solution.

General remarks

The cobalt(II) and nickel(II) ions have $3d^7$ [$S=3/2$] and $3d^8$ [$S=1$] valence electron configurations. From Table I it can be seen that the magnetic properties of chelates of these ions are completely different [4,21—23], and the following general conclusions are drawn:

a) the square-planar Ni(II) complexes are diamagnetic; the Co(II) complexes are low-spin types with medium orbital contributions;

b) the magnetic moments of six-coordinate Ni(II) complexes lie in the range 2.9—3.3 B.M., while the corresponding Co(II) complexes show a high orbital contribution (the experimental values lie in the range 4.8—5.5 B.M.);

c) the tetrahedral Co(II) and Ni(II) complexes are paramagnetic, with a medium and a high orbital contribution, respectively; the total moments of the latter are concentration and temperature-dependent.

The stereochemistries of solid complexes have been well determined on the basis of the magnetic properties. The solid complexes give in solution or in the molten state a concentration and temperature-dependent equilibrium of various configurational isomers.

The various geometries of these chelates are also easily distinguishable on the

Table I
Magnetic properties of Co(II) and Ni(II) compounds of various geometries

	Co(II)	Ni(II)
$\Sigma 3d$	7	8
Ground state	4F	3F
$\mu_{s.o.}$ (B.M.)*	3.88	2.83
$[4S(S+1) + L(L+1)]^{1/2}$	5.2	4.46
μ_{eff} (exper.)	1.9—5.5	0—4.3
μ_{eff} (square-planar)	1.9—2.4	0
μ_{eff} (tetrahedral)	4.3—4.8	3.3—4.1
μ_{eff} (octahedral)	4.8—5.5	2.9—3.3
$-\lambda$ (cm^{-1})	180	315

* spin-only values

basis of their crystal field spectra. The diamagnetic square-planar Ni(II) chelates have only one medium intensity band and a shoulder, at around 20—22 kK; the tetrahedral and octahedral molecules show three well-defined bands with totally different energies and intensities [e.g. 1]. For Co(II) chelates with whatever geometries, term splitting must be taken into account [e.g. 4], the spectral properties of the individual forms being completely different.

The configurations of these complexes may change on dissolution in pyridine, depending on the ligand field and the steric hindrance of the substituents. When there is no steric hindrance, the molecules bind two pyridine molecules to form six-coordinate complexes. When the steric hindrance is considerable, the molecules retain their configurations even in pyridine, or binding with one pyridine molecule results in five-coordination. These facts are reflected clearly in the magnetic and spectral properties.

In non-coordinating solvents, different structural equilibria systems can be formed [1, 4, 24, 25]. The fundamental equilibria for four-coordinate Ni(II) and Co(II) complexes are the following:

- planar ($S=0$) ↔ tetrahedral ($S=1$), and
planar ($S=1/2$) ↔ tetrahedral ($S=3/2$).

It must be noted that there are several other equilibria, involving species with an effective coordination number exceeding four.

From investigations of such equilibria, the following conclusions are drawn [25]:

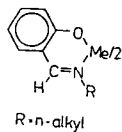
- a) ligands which stabilize a measurable amount of tetrahedral Ni(II) produce ~100% tetrahedral Co(II);
- b) ligands which stabilize a measurable amount of planar Co(II) produce ~100% square-planar Ni(II);
- c) the stability (enthalpy) difference between tetrahedral and planar Ni(II) is greater than that in the case of Co(II) (minimal ligand structural differences).

The dipole moment values too provide very useful information regarding stereochemical problems [e.g. 26]. A detailed discussion of the above characteristics is given below.

Discussion

Bis[N-n-alkylsalicylaldiminato]M(II) complexes.

The Co(II) and Ni(II) complexes (Structure 1) formed with the same ligands display very different properties

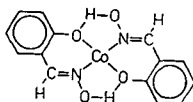


Structure 1

The values of the magnetic moments of the Co(II) complexes, ranging between 4.4 and 4.6 B.M. [27—29], are those predicted for a tetrahedral structure [30]. The Co(II) chelates are monomeric in benzene solution [29]. The tetrahedral structure is supported by the high dipole moments values (see Table II) and the spectra [31]. The reflectance spectra are very similar in shape to the spectra of the benzene solutions, so it is concluded that they maintain their structure in solution. The bands at around 8 and 16 kK can be assigned to the ${}^4T_1(F) \leftarrow {}^4A_2(F)$ and ${}^4T_1(P) \leftarrow {}^4A_2(F)$ transitions (Fig. 1, curves 2,3; Fig. 1/2,3).

The magnetic moments of the complexes in pyridine solution are higher (4.9—5.4 B.M.); this suggests that in solution the complexes coordinate two molecules of pyridine to become six-coordinate and octahedral [32]. The characteristic bands of the adducts can be found at around 10 and 18 kK (Fig. 1/4) (${}^4T_{2g}(F) \leftarrow {}^4T_{1g}(F)$ and ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}(F)$ transitions).

It is interesting that $\text{Co}[\text{HSAL-NH}]_2$ and $\text{Co}[\text{HSAL-N-OH}]_2$ are low-spin, with magnetic moments of 2.25 and 2.6 B.M. [28], respectively. The spectra of both compounds are characteristic of four-coordinate square-planar Co(II) complexes. If we assume a trans-planar structure, strong hydrogen bonds of N-H-O and O-H-O types (Structure 2), respectively, may be possible [33].



Structure 2

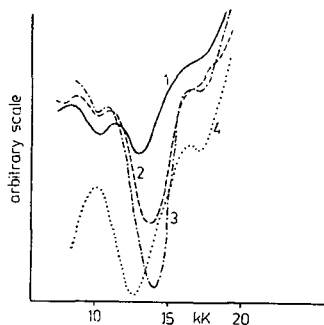


Fig. 1. Solution spectra of some Co(II) chelates. 1: $\text{Co}[\text{HSAL-N-CH}_3]_2$ in chloroform; 2: $\text{Co}[\text{HSAL-N-}i\text{-C}_4\text{H}_9]_2$ in ethanol; 3: $\text{Co}[\text{HSAL-N-}t\text{-C}_4\text{H}_9]_2$ in benzene; 4: $\text{Co}[\text{HSAL-N-}i\text{-C}_4\text{H}_9]_2$ in pyridine

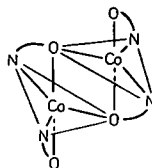
It was earlier supposed that $\text{Co}[\text{HSAL-N-CH}_3]_2$ was square-planar [34]; however, in the light of the magnetic (4.62 B.M. [27]) and spectral investigations (see Fig. 1/1)

Table II
Magnetic moments of some Co(II) complexes of various structures

Co(HSAL-N-alkyl) ₂ a)			Co(HSAL-N-R-N-HSAL) b)			Co(HSAL-NXphenyl) ₂ c)					
alkyl =	B.M. Solid	Conf.	μ(D)	R =	B.M. Solid	Conf.	X =	B.M. Solid	Conf.	B.M. In benzene	B.M. In pyridine
-CH ₃	4.62 ⁽²⁷⁾	P		-(CH ₂) ₂ ⁻	2.28	S	-H	4.46 ⁽²⁰⁾	T	4.50 ^{9a}	4.97 ⁽⁸³⁾
-C ₂ H ₅	4.28	T	4.67 ^a	-(CH ₂) ₃ ⁻	4.56 ⁽⁷¹⁾	T	-3-CH ₃	4.42 ⁽⁸³⁾	T	4.46 ^{9a}	4.86 ⁽⁸³⁾
- <i>n</i> -C ₃ H ₇	4.35	T	4.69 ^b	-(CH ₂) ₄ ⁻	4.36 ⁽⁷¹⁾	T	-4-CH ₃	4.36 ⁽⁸⁸⁾	T	4.32 ^{9a}	4.84 ⁽⁸³⁾
- <i>i</i> -C ₃ H ₇	4.38	T	4.62 ^b	-(CH ₂) ₅ ⁻	4.41 ⁽⁷¹⁾	T	-2-OCH ₃	4.48 ⁽⁸³⁾	T	insol.	4.54 ⁽⁸³⁾
- <i>n</i> -C ₄ H ₁₀	4.47 ⁽²⁰⁾	T	4.62 ^b	-(CH ₂) ₆ ⁻	4.33 ⁽⁷¹⁾	T	-3-OCH ₃	4.42	T	4.38	4.72
- <i>i</i> -C ₄ H ₁₀	4.40	T	4.63 ^b	-(CH ₂) ₇ ⁻	4.65 ⁽⁷⁰⁾	T	-4-OCH ₃	4.34 ⁽⁸³⁾	T	4.33 ^{9a}	4.84 ⁽⁸³⁾
- <i>n</i> -C ₅ H ₁₁	4.52	T	5.05 ^b	-(CH ₂) ₈ ⁻	4.65 ⁽⁷⁰⁾	T	-4-Cl	4.53 ⁽⁸⁸⁾	T	4.22 ^{9a}	4.91 ⁽⁸³⁾
-H	4.42 ⁽²⁰⁾	T	4.62 ^a				-4-Br	4.34 ⁽⁸³⁾	T	4.56 ^{9a}	4.74 ⁽⁸³⁾
-OH	2.25	S					-4-F	4.45	T	4.50	4.90
	2.6 ⁽²⁸⁾	S									

T: tetrahedral; S: square-planar; P: five-coordinated; a: M. Ciampolini, F. Maggio, F. P. Cavasino: Inorg. Chem., **3**, 1188 (1964); b: L. Sacconi, M. Ciampolini, F. Maggio, F. P. Cavasino: J. Inorg. Nucl. Chem., **19**, 73 (1961).

this is not correct. X-ray measurements on single-crystals have shown that the complex is isostructural with the Zn(II) complex [35], so it has a five-coordinate (Structure 3) high-spin structure [36]. Its reflectance spectrum shows bands at 5.60, 11.40, 15.20



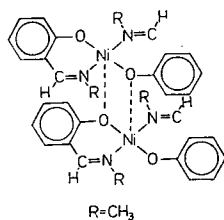
Structure 3

and 19.60 kK. In benzene solution the bands lie at 7.80, 11.80 and 12.50 kK, indicating the presence of tetrahedral forms. The strong concentration and temperature-dependences of the spectrum lead to the conclusion that in non-coordinating solvents equilibrium occurs between the tetrahedral monomeric and the five-coordinate dimeric forms [27]. In pyridine the spectrum of the N-CH₃ derivative shows bands at 10.30 and 17.80 kK, which indicate an octahedral adduct with two molecules of pyridine.

The N-*n*-alkyl (ethyl to *n*-decyl) derivatives of Ni(II) are all diamagnetic and trans-planar in the solid state; this structure is supported by X-ray [37, 38], dipole moment [37] and spectral [39, 40] investigations. In non-coordinating solvents at room temperature they are feebly paramagnetic and have a small dipole moment. In contrast to the former explanation [41–44], this behaviour may be interpreted by molecular association [39, 45]. The magnetic and dipole moments alternate as the chain increases in length, with maxima for odd numbers of

carbon atoms [37]. When R denotes *n*-alkyl, complexes of Ni[HSAL-N-R]₂ type dissolved in pyridine form sixcoordinated solvates, Ni[HSAL-N-R]₂.py₂.

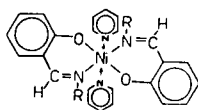
The first member of this series, Ni[HSAL-N-CH₃]₂, is an outstanding example of the anomalous Ni(II) complexes. It is diamagnetic, monomeric and essentially planar in the solid state, but it becomes partially paramagnetic in solution; in inert media magnetic moments in the range 1.7—2.4 B.M. have been reported [37, 38]. The magnetic moment and the near infrared absorption intensities show strong concentration and temperature-dependences [e.g. 40]. It may be concluded that the partial paramagnetism in inert solvents is predominantly, if not completely, a consequence of solute association. Above 456 K the solid complex is transformed into the buff-coloured γ -form [46], an insoluble polymer (Structure 4), $\mu_{\text{eff}} \sim 3.4$ B.M., the reflect-



Structure 4

tance spectrum of this compound indicating a distorted octahedral structure (Fig. 2/4) [10] obtained by means of bridging oxygen atoms.

The electronic spectra of these *N-n*-alkyl derivatives, measured in the solid state and in inert solvents, are practically identical (Fig. 2/1,2). In reflection the main band and a shoulder appear at 16.0—16.5 and 19.0—20.0 kK, respectively, which are assigned to the singlet-singlet transitions ${}^1B_{3g} \leftarrow {}^1A_g$ and ${}^1B_{1g} \leftarrow {}^1A_g$ [43, 47]. The paramagnetic bis-pyridine adducts (Structure 5) show two characteristic



Structure 5

bands (Fig. 2/3) at 10.0 and 18.0 kK, due to the ${}^3B_{1g}$, ${}^3B_{3g}$ and ${}^3B_{2g} \leftarrow {}^3B_{3g}$ transitions, respectively [e.g. 40]. It must be noted that the ring substituents have no influence on the structures and properties of these compounds.

The spectra of these diamagnetic square-planar chelates in chloroform undergo a profound change upon addition of pyridine or other nitrogen bases. With increasing base concentration the absorption curves

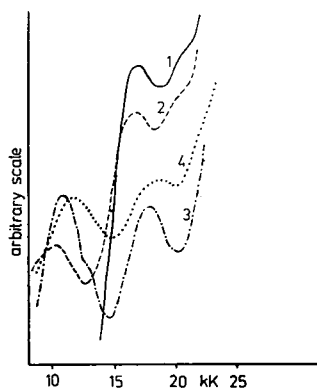


Fig. 2. Electronic spectra of Ni[HSAL-N-CH₃]₂. 1: reflectance spectrum; 2: in chloroform; 3: in pyridine; 4: reflectance spectrum of the paramagnetic isomer

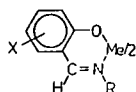
form a family of curves with an isobestic point, indicating the presence of only two species in solution, and two bands develop in the visible, characteristic of the octahedral bis-adducts. The log K values generally increase for ethyl- \rightarrow - n -amyl, but longer alkyl chains do not have any considerable influence upon the K values [10, 48—50]. This phenomenon may be interpreted by the inductive effects of the R groups [10, 48].

The dipole moments of the chelates measured in benzene are low ($0 < \mu(D) < 1$); a plot of $\mu(D)$ vs. $p\%$ ($p\% = 100 \cdot \mu_{\text{eff}}^2 / 3 \cdot 3^2$) gives to a good approximation a linear relationship.

The plot of $\log \eta$ (specific viscosity) vs. n (methyl \rightarrow dodecyl, $n = 1 - 12$) gives a straight line [12, 51].

Bis[N -branched-alkylsalicylaldiminato]M(II) complexes

From Table II it can be seen that $\text{Co}[\text{HSAL-}N\text{-}i\text{-C}_3\text{H}_7]_2$ and $\text{Co}[\text{HSAL-}N\text{-}s\text{-C}_4\text{H}_9]_2$ have paramagnetic moments of 4.38 and 4.40 B.M., respectively, these values being those predicted for a tetrahedral arrangement. This finding is also supported by the electronic spectra [32, 52]. The $N\text{-}t\text{-C}_4\text{H}_9$ derivative has a moment of 4.52 B.M.; it seems that, independently of the structure of the R group (Structure 6),



$R = n$ -alkyl and α, β -
and γ -branched alkyl

Structure 6

it always forms tetrahedral molecules. The bands in the spectra of these Co(II) chelates correspond to the ${}^4T_1(\text{F}) \leftarrow {}^4A_2(\text{F})$ and ${}^4T_1(\text{P}) \leftarrow {}^4A_2(\text{F})$ transitions. In pyridine the complexes coordinate two molecules of solvent to become six-coordinate and distorted octahedral. The bispyridine adducts are paramagnetic (> 5 B.M.); the characteristic bands correspond to the ${}^4T_{2g}(\text{F}) \leftarrow {}^4T_{1g}(\text{F})$ and ${}^4T_{1g}(\text{P}) \leftarrow {}^4T_{1g}(\text{F})$ transitions.

The complexes $\text{Co}[3\text{-OCH}_3\text{-SAL-NR}]_2$ in the solid state and in non-donor solvents are all tetrahedral and of highspin type. When R is n -alkyl or phenyl, the electronic spectra show that these Co(II) complexes assume an octahedral configuration in pyridine [53], whereas the $t\text{-C}_4\text{H}_9$ derivative retains its tetrahedral configuration in pyridine; this behaviour is considered to be due to the steric conditions stemming from the bulky $t\text{-C}_4\text{H}_9$ group.

Totally different behaviour can be observed for the Ni(II) complexes (Table III). The $N\text{-}i\text{-C}_3\text{H}_7$, $N\text{-}i\text{-C}_4\text{H}_9$, $N\text{-}s\text{-C}_4\text{H}_9$ and $N\text{-}t\text{-C}_4\text{H}_9$ derivatives are paramagnetic with moments of around 3.3 B.M. On the basis of these moments, their reflectance spectra and the dipole moments, a tetrahedral, but somewhat distorted structure must be assigned to the chelates [54]. The $N\text{-}i\text{-C}_5\text{H}_{11}$ compound (γ -branched) has similar properties to those of the $N\text{-}n$ -alkyl derivatives. The changes in the stereochemistry are determined primarily by the steric factors.

Table III
Magnetic and dipole moment data for some Ni[XSAL-N-alkyl]₂ type

No.	R =	X =	Solid		Solution		$\mu(D)^b$	p %
			B. M.	conf.	B. M.	conf.		
1	H	H	0	S	0.10 _a	S	—	—
2	CH ₃	H	0 ^[37]	S	1.92 _a ^[37]	S + A	0.88 ^[37]	34
3	C ₂ H ₅	H	0 ^[37]	S	0.91 _a ^[37]	S + A	0.63 ^[37]	8
4	<i>n</i> -C ₃ H ₇	H	0 ^[37]	S	1.25 _a ^[37]	S + A	0.73 ^[37]	14
5	<i>i</i> -C ₃ H ₇	H	3.28 ^d	T	2.14 _a ^[39]	T + S + A	2.51	42
6	<i>n</i> -C ₄ H ₉	H	0 ^[37]	S	0.89 _a ^[37]	S + A	0.66 ^[37]	7
7	<i>s</i> -C ₄ H ₉	H	3.36 ^[60]	T	1.98 _c	T + S + A	2.34 ^[45]	36
8	<i>t</i> -C ₄ H ₉	H	3.34	T	3.22 _c ^[39]	T + S + A	4.74 ^[45]	95
9	<i>n</i> -C ₅ H ₁₁	H	0 ^[37]	S	1.06 _a ^[37]	S + A	0.79 ^[37]	10
10	<i>i</i> -C ₅ H ₁₁	H	0	S	1.06 _a	T + S + A	—	10
11	<i>n</i> -C ₆ H ₁₃	H	0	S	1.29 _a	S + A	—	15
12	CH ₃	3-CH ₃	0 ^d	S	0 _a ^[40]	S	—	—
13	CH ₃	5-CH ₃	0 ^d	S	0.79 _a ^[40]	S + T	—	6
14	CH ₃	3- <i>i</i> -C ₃ H ₇	0 ^d	S	0 _a ^[40]	S	—	—
15	CH ₃	5- <i>i</i> -C ₃ H ₇	0 ^d	S	0.80 _a ^[40]	S + T	—	6
16	C ₂ H ₅	5- <i>i</i> -C ₃ H ₇	0 ^d	S	0.51 _a ^[40]	—	—	2

a: in CHCl₃; b: in benzene; c: in *o*-xylene; 0: octahedral; A: associates; d: R. H. Holm: Advances in the Chemistry of the Coord. Compounds, MacMillan Co., N. Y., 1961, p. 341.

The magnetic moments of these tetrahedral chelates are lower than those of [NiX₄] type complexes [23], this being due to the decrease of the orbital contributions [55, 56] caused by the delocalization of the unpaired electrons. The magnetic moments, the cryoscopic data and the electronic spectra [40] (see Fig. 3/1-4) measured in non-coordinating solvents suggest the following equilibria in solution:

square-planar ↔ tetrahedral ↔ associated forms.

Similarly to those of the [NiX₄] type complexes [57, 58], the spectra of the *i*-, *s*- and *t*-derivatives contain several bands between 6.0 and 20.0 kK, which are due to the spinallowed and spin-forbidden (¹T₂ ← ¹E ←) transitions.

The dependence on the steric effects of the R groups is exemplified by the fact that the N-*n*-C₄H₉ chelate is predominantly square-planar, both in the solid state and in non-coordinating solvents, while the bulky N-*t*-C₄H₉ derivative is tetrahedral. The geometries of the N-*s*-alkyl complexes are hardly dependent on the aldehydesubstituents; the percentage of paramagnetic forms increase in the order *n*-alkyl < *s*-alkyl < *t*-alkyl. The dipole moment values are in accordance with the above findings. The stabilities of the three species change with decreasing temperature in the sequence octahedral (associates) > square-planar > tetrahedral.

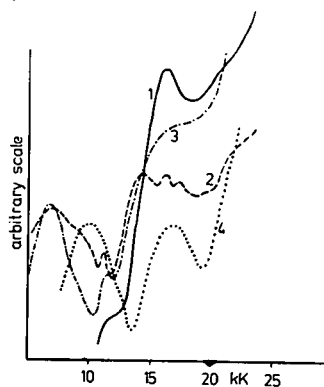
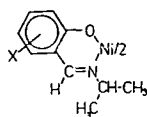


Fig. 3. Spectra of Ni(II) chelates. 1: reflectance curve of Ni[HSAL-N-*n*-C₃H₇]₂; 2: in the solid state; 3: in benzene; 4: in pyridine

CSÁSZÁR ET AL. [14] have studied the electronic spectra of $Ni[HSAL-N-n-C_3H_7]_2$ and $Ni[HSAL-N-i-C_3H_7]_2$ in N-bases as solvents, e.g. pyridine, picolines, lutidines. The solution spectra measured in 2,4- and 2,6-lutidines correspond to the reflectance spectra, while in 3- and 4-picolines and in 3,4- and 3,5-lutidines bands appear which can be assigned to the distorted octahedral forms of the bis-adducts. This behaviour can be interpreted by the steric effects of the substituents in the chelate molecules and in the N-bases, respectively. The spectra in N-substituted ethylenediamines similarly suggest a six-coordinate structure; the ligand field bands shift toward the lower energy region in the order



In the case of N-*n*-alkyl derivatives the ring substituents X have a negligible effect on the stereochemistry. The structure assumed for these complexes (Structure 7)



Structure 7

is largely determined by the substituents X (Table IV). If $R=i-C_3H_7$, and $X=3-CH_3$, $3-Cl$, $5-CH_3$, $5-Cl$, $5-n-C_3H_7$, or $4,6-(CH_3)_2$, the solid complexes are diamagnetic and square-planar [1, 59, 60], while the derivatives with $X=5-C_2H_5$, $3-t-C_4H_9$, $4-CH_3$, $4,5-(CH_3)_2$, $3-C_2H_5$ or $3-i-C_3H_7$ are paramagnetic and tetrahedral. In non-coordinating solvents the paramagnetic moments decrease and equilibrium is observed between the tetrahedral and square-planar forms. An X substituent in the 4-, 5- and 6-

Table IV

Magnetic and dipole moment data for several $Ni[XSAL-n-i-C_3H_7]_2$ type complexes

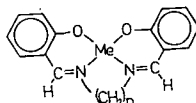
No.	X =	Solid		Solution		$\mu(D)^b$	p %
		B.M.	conf.	B.M.	conf.		
17	-3-Cl	0 ^[45]	S	2.06 _c	S+T	2.41 ^[45]	39
18	-5-Cl	0 ^[45]	S	2.17 _a ^[45]	S+T	3.19 ^[45]	43
19	-3-CH ₃	0 ^[60]	S	2.20 _a ^[60]	S+T	2.15	44
20	-4-CH ₃	3.29 ^d	T	2.36 _a ^d	S+T	2.30	51
21	-5-CH ₃	0 ^d	S	2.33 _a ^d	S+T	2.77	50
22	-4,5-(CH ₃) ₂	3.27 ^d	T	2.47 _a ^d	S+T	—	56
23	-4,6-(CH ₃) ₂	0 ^d	S	0.93 _a ^d	S+T	—	8
24	-3-C ₂ H ₅	3.30 ^[60]	T	2.48 _a ^[60]	S+T	2.54	56
25	-5-C ₂ H ₅	3.27 ^d	T	2.26 _a ^d	S+T	2.60	47
26	-5- <i>n</i> -C ₃ H ₇	0 ^d	S	2.19 _a ^d	S+T	2.30	44
27	-3- <i>i</i> -C ₃ H ₇	3.33 ^[60]	T	2.73 _a ^[60]	S+T	3.15	68
28	-3- <i>t</i> -C ₄ H ₉	3.30 ^[60]	T	3.16 _a ^[60]	S+T	4.91	92

a: in CHCl₃; b: in benzene; c: in toluene; d: R. H. Holm, A. Chakravorty, G. O. Dudek: J. Amer. Chem. Soc., 86,379 (1964).

positions does not have an important effect on the equilibrium, whereas the 3-X substituents cause serious steric hindrance. From Table III it can be seen that the p% values change in the sequence $\text{CH}_3\text{-C}_2\text{H}_5\text{-}i\text{-C}_3\text{H}_7\text{-}t\text{-C}_4\text{H}_9$. In pyridine, paramagnetic distorted octahedral bis-adducts are formed [8, 61].

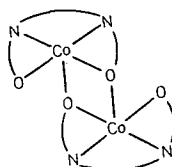
N,N' Polymethylenebis(salicylaldiminato)M(II) complexes

Both $\text{Co}[\text{HSALen}]$ (Table II) and $\text{Ni}[\text{HSALen}]$ are low-spin type complexes, with $\mu_{\text{eff}}=2.24$ B.M. [30, 62] and 0 B.M., respectively (Structure 8).



Structure 8

$\text{Co}[\text{HSALen}]$ was first reported by PFEIFFER ET AL. [63]. Structural investigations [64, 65] have shown that dimerization results from the interaction between the Co atoms and the phenolic oxygen atoms (Structure 9) of adjacent pairs of molecules.



Structure 9

In this manner the cobalt becomes five-coordinated in a distorted rectangular-based pyramid, with an intermolecular Co-O distance of 2.25 Å. The high affinity of $\text{Co}[\text{HSALen}]$ for molecular oxygen is well known [66—69]. No change in magnetism can be observed between the solid and the solution [70, 71]. The electronic spectrum has a structure characteristic of planar tetradentate type Co(II) complexes (Fig. 4/2); only one ligand field band of medium intensity appears in the near infrared range (about 9 kK, $\log \epsilon \sim 1.3$) [33, 72]. It is characteristic that the oscillator strength of this band is very small, indicating that this peak may be ascribed to a spin-forbidden d-d transition (${}^4A_{2g} \leftarrow {}^2B_{2g}$ or ${}^4E_g \leftarrow {}^2B_{2g}$) [73].

The magnetic and spectral properties show that a change in stereochemistry occurs when the di-imine bridge is lengthened from two to seven or more methylene

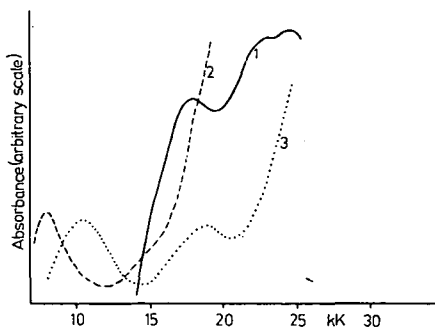


Fig. 4. Reflectance spectra of 1: $\text{Ni}[\text{HSALen}]$; 2: $\text{Co}[\text{HSALen}]$; 3: $\text{Ni}[\text{HSA}(\text{tmda})]$ (tmda = tetramethylenediamine)

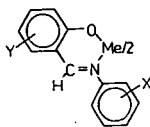
groups [70, 71, 74]. These polymethylene derivatives have paramagnetic moments of about 4.3–4.7 B.M., which are characteristic of tetrahedral compounds [70, 74] (see Table II). The complex bis(*N*-phenylsalicylaldiminato)Co(II) has been shown by spectral and other evidence to have pseudo-tetrahedral geometry [75] and the spectra of these polymethylene derivatives are similar to that of the phenyl compound and other bis-bidentate pseudo-tetrahedral Co(II) complexes [74]. The bands in the range 8–10 kK are best assigned as low-symmetry components of the second tetrahedral d^7 transition (${}^4T_1(F) \leftarrow {}^4A_2(F)$), while the band in the region 17–19 kK may be attributed to the ${}^4T_1(P) \leftarrow {}^4A_2(F)$ transition [74].

On the basis of these experimental results it is concluded that when three to seven bridging methylene groups are present, sufficient flexibility is introduced into the tetradentate ligands to allow them to adopt a pseudo-tetrahedral geometry about the Co(II). Substituents on the ethylene bridge cause no change in the stereochemistry [33]. It is interesting to note that the complex Co[3-OCH₃-SALen] is paramagnetic ($\mu_{\text{eff}} = 4.60$ B.M.) and its spectra suggests tetrahedral geometry [82].

Ni[HSALen], first reported by DUBSKÝ and SOKOL [76], exists as centrosymmetric dimers in the solid state, incorporating approximately planar Ni[HSALen] units; the Ni-Ni distance is 3.21 Å [77]. The diamagnetism [78] of this complex is typical for planar nickel compounds, and this magnetic property is also maintained in solutions of coordinating and non-coordinating solvents [79]. The spectra measured in the solid and in solution [20, 80] are quite similar (Fig. 4/1), the single band being assigned to the ${}^1B_1 \leftarrow {}^1A_1$ transition [43]; the other d-d bands are hidden by the intense $\pi^* \leftarrow \pi$ transitions. In pyridine the spectrum remains unchanged; no pyridine adduct is formed [20]. An increased solvating ability found on increasing the number of bridging methylene units in the ligand molecule is presumably due to a corresponding weakening of the ligand field [81]. The spectra and the magnetic moments of the polymethylene derivatives indicate distorted octahedral symmetry (Fig. 4/3). They form bis-pyridine adducts, the spectra of which show the octahedral bands; with increasing number of methylene groups these shift towards the lower energy region [20].

Bis[N-arylsalicylaldiminato]M(II) complexes

(Structure 10). According to X-ray investigations [75] Co[HSAL-N-C₆H₅]₂



Structure 10

has a pseudo-tetrahedral structure; its spectrum shows three bands, at 7.6, 10.7 and 19.23 kK [29], which can be assigned to the ${}^4T_2(F) \leftarrow {}^4A_2(F)$, ${}^4T_1(F) \leftarrow {}^4A_2(F)$ and ${}^4T_1(P) \leftarrow {}^4A_2(F)$ transitions.

All the Co[XSAL-N-YC₆H₄]₂ type complexes are paramagnetic (Table II), indicating a tetrahedral arrangement; this property does not change in solution. In pyridine the moments are between 4.8 and 5.2 B.M., so it may be concluded that bis-pyridine adducts with distorted octahedral structure are formed [29, 84]. Dissolu-

tion of $\text{Co}[\text{HSAL-N-2,6-(CH}_3)_2\text{C}_6\text{H}_3]_2$ in pyridine yields only a mono-pyridine adduct [6, 86] (see Fig. 5/1,2).

A significant difference is observed between the spectra of $\text{Co}[\text{HSAL-N-2-OCH}_3\text{C}_6\text{H}_4]_2$ and $\text{Co}[\text{HSAL-N-4-OCH}_3\text{C}_6\text{H}_4]_2$; that of the latter is typical of a tetrahedral complex. However, the spectrum of the 2-OCH₃ derivative is completely different from that of a tetrahedral Co(II) complex. It is most likely that the OCH₃ group at the 2-carbon position may be weakly bound to the Co(II) ion [84, 85]. In pyridine the weak bond is broken and a bis-adduct will be formed [8].

The structure of the Ni(II) complexes is dependent on the substituents both of the N-phenyl and of the aldehyde ring (Table V) [89].

The 2,4- 2,5- and 2,6-dimethyl and the 2-methyl complexes (Fig. 5/3) are diamagnetic solids and the first three are monomeric [39, 87] and completely diamagnetic in solution; the *o*-tolyl species is weakly paramagnetic in non-coordinating solvents. The 2-OCH₃ complex is paramagnetic, with a magnetic moment corresponding to two unpaired electrons. Detailed investigations clearly show that this complex is monomeric and octahedral in non-donor solvents [39, 87]. Examination of metal chelate scale models reveals that the effects of 2- and/or 2,6-substituents tend to constrain rotation of the aryl group about the N-C bond, thereby tending to keep the group

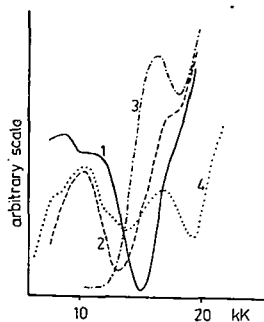


Fig. 5.: Electronic spectra of
1: $\text{Co}[\text{HSAL-N-2-CH}_3\text{C}_6\text{H}_4]_2$
in benzene;
2: $\text{Co}[\text{HSAL-N-2-CH}_3\text{C}_6\text{H}_4]_2$
in pyridine;
3: $\text{Ni}[\text{HSAL-N-2-CH}_3\text{C}_6\text{H}_4]_2$
in the solid state;
4: $\text{Ni}[\text{HSAL-N-3-CH}_3\text{C}_6\text{H}_4]_2$
in reflection

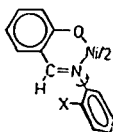
Table V

Magnetic and dipole moment data and stereochemistry of some $\text{Ni}[\text{YSAL-N-Xphenyl}]_2$ type complexes

No.	X =	Y =	Solid		Solution		$\mu(D)^b$	p %
			B. M.	conf.	B.M.	conf.		
29	H	H	0 ^[89]	S	2.93 _a ^[89]	S+A	2.68	79
30	2-CH ₃	H	0 ^[89]	S	1.00 _a	S+A	1.04	9
31	3-CH ₃	H	3.34 ^[89]	T	3.16 _a ^[89]	T+S+A	4.40	92
32	4-CH ₃	H	3.28 ^[89]	T	3.03 _a ^[89]	T+S+A	4.32	84
33	2-OCH ₃	H	3.25	T	2.22 _a	T+S+A	—	45
34	3-OCH ₃	H	3.24	T	3.11 _a	T+S+A	—	89
35	4-OCH ₃	H	3.28	T	3.02 _a	T+S+A	3.82	84
36	3-Cl	H	3.39 ^[89]	T	3.20 _a ^[89]	T+S+A	4.48	94
37	4-Cl	H	3.34 ^[89]	T	3.14 _a ^[89]	T+S+A	4.15	91
38	3,5-(CH ₃) ₂	H	3.33 ^[89]	T	3.28 _a ^[89]	T+S+A	4.52	99
39	3,4-(CH ₃) ₂	H	3.27 ^[89]	T	3.24 _a ^[89]	T+S+A	4.65	96
40	3,4,5-(CH ₃) ₃	H	3.18	T	2.64 _c	T+S+A	3.08	64
41	2,4-(CH ₃) ₂	H	0 ^[89]	S	0 ^[89]	S	—	—
42	2,5-(CH ₃) ₂	H	0 ^[89]	S	0 ^[89]	S	—	—
43	H	5-CH ₃	0	S	2.95 _a ^[89]	S+A	3.56	80
44	H	3- <i>i</i> -C ₃ H ₇	0 ^[89]	S	0.48 _a ^[89]	S+A	—	2

a: in CHCl₃; b: in benzene; c: in acetonitrile.

more nearly, but not exactly, normal to the rest of the molecule, which is taken as essentially planar (Structure 11).



Structure 11

The 3- and 4-X-phenyl complexes are paramagnetic, tetrahedral solids; in non-donor solvents the lowering of the moments and molecular association have been observed (Fig. 5/4). The magnetic moments and the intensity of the d-d bands are strongly concentration and temperature-dependent; in solution, equilibrium occurs between the square-planar, tetrahedral and associated species. In pyridine, bis-adducts form (with the exception of the 2,6-X₂ species) with normal paramagnetism and octahedral arrangement [8].

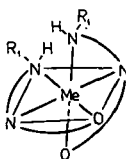
All diamagnetic complexes exhibit only one observable band in the visible (16—16.5 kK); the paramagnetic molecules show a band at around 11.0—13.0 kK, which is due to associates. With increasing temperature the intensity of this band decreases, while a new band corresponding to the tetrahedral form appears.

The Ni[XSAL-N-C₆H₅]₂ type complexes, independently of the aldehyde substituents, are diamagnetic and square-planar. In non-donor solvents they show a partial paramagnetism, dependent on the substituents, and a tetrahedral/square-planar equilibrium may be assumed [8, 88].

M[XSALen-N(R₁)(R₂)]₂ type complexes

Complexes of the general formula Co[XSALen-N(R₁)(R₂)]₂ are generally orange or red in colour and all the compounds are of high-spin type, the values of μ_{eff} ranging between 4.1 and 4.7 B.M.

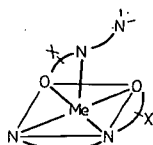
On the basis of the electronic spectra, three main types are exhibited. The spectrum of type I is characteristic of a distorted octahedral structure, showing two bands, at 9.3 and 11.5 kK (Fig. 6/1) [90]. The complexes of this type have high dipole moments (~6.9 D) and they must have a cis-octahedral structure (Structure 12).



Structure 12

The second type of complex has a spectrum characteristic of tetrahedral Co(II) complexes (~7.7, 11.2 and 18 kK) (Fig. 6/3) [29]; the dipole moments are about 3.5 D.

The spectrum of type III has three bands at 6.70, 11.40 and 16.80 kK; this spectrum is exhibited by the five-coordinated distorted square-pyramidal Co(II) complexes (Structure 13) (Fig. 6/2) [91].



Structure 13

In pyridine solution, all the Co(II) complexes, with the exception of the type I complexes, have a spectrum with two bands, at 10.0 and 17.0 kK, characteristic of octahedral bis-pyridine adducts [29].

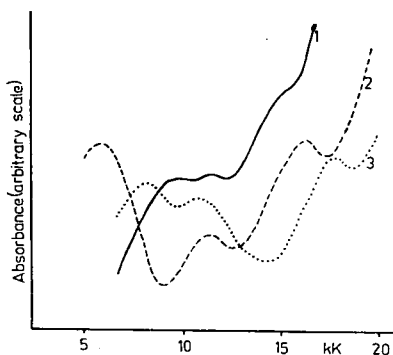


Fig. 6. Reflectance spectra of
1: $\text{Co}[\text{HSALEN-NHCH}_3]_2$;
2: $\text{Co}[5\text{-Cl-SALEN-N}(\text{C}_6\text{H}_5)_2]_2$;
3: $\text{Co}[\text{HSALEN-N}(\text{C}_6\text{H}_5)_2]_2$

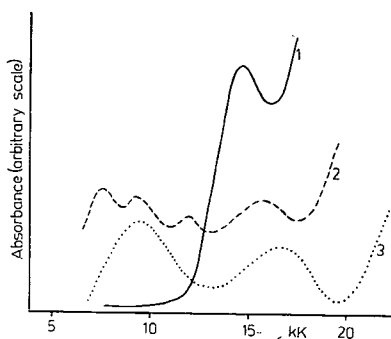


Fig. 7. Reflectance spectra of
1: $\text{Ni}[3\text{-CH}_3\text{-SALEN-N}(\text{C}_6\text{H}_5)_2]_2$;
2: $\text{Ni}[5\text{-Cl-SALEN-N}(\text{C}_6\text{H}_5)_2]_2$;
3: $\text{Ni}[\text{HSALEN-N}(\text{CH}_3)_2]_2$

A great number of $\text{Ni}[\text{XSALEN-N}(\text{R}_1)(\text{R}_2)]_2$ complexes are known. The complexes with $\text{X}=\text{R}_1=\text{H}$ and $\text{R}_2=n\text{-alkyl}$ are octahedral; they do not change in solution and form no pyridine adducts. If $\text{X}=\text{H}$ and $\text{R}_1=\text{R}_2=\text{C}_6\text{H}_5$, the complex is tetrahedral in the solid state and in solution, and in pyridine it forms bis-adducts. The complexes with $\text{R}_1=\text{R}_2=\text{C}_6\text{H}_5$ and $\text{X}=\text{H}$, 3-Cl or 5-Cl are paramagnetic, with μ_{eff} in the range 3.2–3.3 B.M. When $\text{X}=\text{H}$ the complex is octahedral. The 3-Cl and 5-Cl derivatives are five-coordinated distorted square-based pyramids.

In non-coordinating solvents the equilibria can be represented by the following scheme:

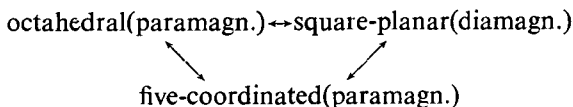


Table VI
Magnetic and dipole moment data of $Ni[XSAEn-N(R_1)(R_2)]_2$ complexes

No.	X =	R ₁ =	R ₂ =	Solid		Solution		$\mu(D)^b$	p %
				B. M.	conf.	B. M.	conf.		
45	H	H	CH ₃	3.13 ^[94]	0	3.16 _a	0	8.78 ^[94]	
46	H	H	C ₂ H ₅	3.10 ^[94]	0	3.14 _a	0		
47	H	H	<i>n</i> -C ₃ H ₇	3.13 ^[94]	0	3.15 _a	0	8.09 ^[94]	
48	H	H	<i>n</i> -C ₄ H ₉	3.12 ^[94]	0	3.15 _a	0		
49	H	H	CH ₂ -C ₆ H ₅	3.28 ^[94]	0	3.18 _a	0		
50	3-CH ₃	H	<i>n</i> -C ₃ H ₇	3.08 ^[94]	0	3.11 _a	0		
51	5-CH ₃	H	<i>n</i> -C ₃ H ₇	3.10 ^[94]	0	3.12 _a	0	8.31 ^[94]	
52	5-C ₂ H ₅	H	<i>n</i> -C ₃ H ₇	3.13 ^[94]	0	3.10 _a	0		
53	5-Cl	H	<i>n</i> -C ₃ H ₇	3.16 ^[94]	0	3.18 _a	0	10.05 ^[94]	
54	H	CH ₃	CH ₃	3.20 ^[95]	0	c)			
55	H	C ₂ H ₅	C ₂ H ₅	3.06 ^[95]	0	2.88 _a ^[95]	S+P		76
56	3-CH ₃	C ₂ H ₅	C ₂ H ₅	0 ^[95]	S	2.06 _a ^[95]	S+O+P		39
57	3-Cl	C ₂ H ₅	C ₂ H ₅	3.30 ^[95]	P	2.29 _a ^[95]	S+O+P		48
58	5-CH ₃	C ₂ H ₅	C ₂ H ₅	5 ^[95]	S	2.46 _a ^[95]	S+O+P		56
59	5-C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	0 ^[95]	S	2.53 _a ^[95]	S+O+P		59
60	5-Cl	C ₂ H ₅	C ₂ H ₅	3.30 ^[95]	P	3.15 _a ^[95]	S+O+P		91

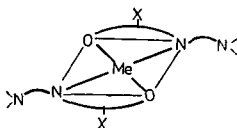
a: in CHCl₃, b: in benzene; c: insoluble.

In pyridine the compounds are transformed into octahedral adducts. Other examples may be found in the literature [92, 93].

The reflectance and absorption spectra of the compounds with $X=R_1=H$ show bands at 11.4–12.0 and 17.0–18.5 kK. These data and the high dipole moments (>8 D) (see Table VI) suggest a *cis*-octahedral structure [39, 90] and the complexes do not form pyridine adducts [94]. It may be concluded that the $R_2=$ *n*-alkyl or benzyl groups exert a strong electron-releasing influence and no determining steric hindrance [94].

The spectra of the compounds with $R_1=R_2=C_2H_5$ (see Fig. 7) are very complicated. In non-donor solvents the characteristic bands of the octahedral, tetrahedral and five-coordinated species can be observed [*e.g.* 95, 96]. *p*% is strongly dependent on the solvent; at high temperature the percentage of the planar form increases.

The compounds with $R_1=H$ and $R_2=$ *o*-Xphenyl are all diamagnetic and square-planar (Structure 14), regardless of the nature of the ring substituent X [94].



Structure 14

Their reflectance spectra are characteristic of square-planar complexes. When $R_1=H$ and $R_2=$ phenyl or *p*-Xphenyl, the complexes are octahedral or square-planar, depending on X.

Further detailed discussions are to be found in the literature [5,97–99].

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СТЕРЕОХИМИЯ КОМПЛЕКСОВ КОБАЛЬТА(II) И НИКЕЛЯ(II)
С КООРДИНАЦИОННЫХ ЧЛЕНОВ ЧЕТЫРЕ И ПЯТЬ С ШИФФОВЫМИ
ОСНОВАНИЯМИ

Й. Часар

На основании магнитных, диэлектрических и спектроскопических свойств хелатных комплексов Co(II) и Ni(II) с шиффовыми основаниями, полученными из салицилальдегида и различных аминов, обсуждена их структура как в твердом состоянии, так и в растворах.