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Metal Complexes with Unsymmetrical Tetradentate Schiff Bases

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A simple method for the synthesis of 1-amino-3-aza-4-methylhept-4-ene-6-one is presented. The dominant tautomeric form of the compound in $CDCl_3$ *has been established. Using this compound eight (five new) unsymmetrical tetradentate Schiff bases and their nickel(II), palladium(II) and copper(II) complexes have been prepared and characterized by various physical techniques. Data for the complexes indicate that they are all of square-planar geometry. High resolution* ^1H *nmr studies, including lanthanide shift reagents on nickel and palladium chelates, allowed us to assign almost all proton resonances. Data for nickel(II) and palladium(II) chelates with 1-(2'-hydroxyphenyl)-1-phenyl-2,5-diaza-6-methylnona-1,6-diene-8-one are consistent with the ketoenamine structure of both the acetylacetone and hydroxybenzophenone portions of the molecules. Good resolved nitrogen hyperfine splitting was observed in the esr spectrum of the copper complex with the aforementioned ligand.*

Introduction

In the course of our study on metal complexes with unsymmetrical Schiff bases of the type presented in Fig. 4, we searched for a convenient method for the synthesis of free ligands. We considered earlier [1, 2] the stepwise synthesis via intermediates formed by condensation of acetylacetone at only one end of ethylenediamine. There are few papers reporting the preparation of monocondensation products of several diamines with salicylaldehyde [3–5] and β-diketones [6, 7]. In most cases products were isolated as metal complexes or acidic salts and their preparation was usually troublesome. Very recently Costes *et al.* [8, 9] published a method of preparation of 1-amino-3-aza-4-methylhept-4-ene-6-one by allowing a 1:1 mixture of acetylacetone and ethylenediamine in chloroform solution to stand for 10 hours. Our FD mass spectral studies have shown that the reaction leads to the product of monocondensation in high yield when the molar ratio of ethylenediamine to acetylacetone is equal to 3:1. This observation, as well as the ease of separation of the monocondensed product from the reaction mixture by distillation under reduced pressure, allowed us to work out a simple and relatively fast method of preparation of 1-amino-3-aza-4-methylhept-4-ene-6-one HL^1, which due to its high reactivity turned out to be an excellent intermediate in the synthesis of unsymmetrical Schiff bases. This paper deals with preparation and characterization of HL^1, several new unsymmetrical Schiff bases and their copper(II), nickel(II) and palladium(II) complexes. Data for several related compounds not reported earlier are also included in Tables.

Experimental

Reagents

Metal acetates were obtained from E. Merck and were used without further purification. Ethylenediamine (Fluka) was dried over potassium hydroxide and distilled. Acetylacetone (Koch-Light) was dried over anhydrous sodium sulphate and distilled. 5-Methoxy-2-hydroxybenzaldehyde (Aldrich) was distilled *in vacuo.* 5-Methyl-2-hydroxybenzaldehyde, 5-bromo-2-hydroxybenzaldehyde, 5-nitro-2-hydroxybenzaldehyde and 2-hydroxy-1-naphthaldehyde were prepared by the literature methods [10–13]. Physical properties of all compounds were in accordance with the published data.

Preparation of 1-Amino-3-aza-4-methylhept-4-ene-6-one HL^1

Freshly distilled acetylacetone (25.5 ml; 0.25 mol) was added very slowly to the vigorously stirred and cooled solution of ethylenediamine (50 ml; 0.75 mol) in anhydrous ethanol (150 ml). The temperature of the reaction mixture was maintained below 20 °C. After addition was complete the mixture was stirred for 15 minutes. The resulting solution was evaporated *in vacuo* to remove the solvent and the excess of amine. The oily residue was distilled under reduced

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TABLE I. Analytical Data for the Ligands and for the Complexes.

H	Yield %	Color	M.P. °C	Anal. % Found (Calcd)		
				C	H	N
H_2L^5	85	yellow	64	69.49(69.20)	7.73(7.74)	10.35(10.76)
H_2L^6	82	yellow	78	65.05(65.20)	7.31(7.30)	10.02(10.14)
H_2L^7	79	yellow	97	51.26(51.71)	5.26(5.27)	8.81 (8.61)
H_2L^8	88	yellow	151[d]	57.66(57.72)	5.86(5.88)	14.14(14.42)
H_2L^9	82	yellow	143	72.95(72.95)	6.76(6.80)	9.46 (9.45)
NiL^5	86	red-brown	202	55.60(56.83)	5.97(5.97)	8.56 (8.84)
NiL^6	88	red-brown	188	53.85(54.10)	5.44(5.45)	8.44 (8.41)
NiL^7	82	brown	203	43.43(44.03)	3.99(3.96)	7.23 (7.34)
NiL^8	84	red-brown	282[d]	48.67(48.32)	4.36(4.34)	12.13(12.07)
NiL^9	96	red-brown	264	61.12(61.23)	5.13(5.14)	7.90 (7.93)
PdL^5	76	yellow	196[d]	48.89(49.40)	4.84(4.97)	7.77 (7.68)
PdL^6	82	orange	213[d]	46.86(47.32)	4.81(4.77)	7.34 (7.36)
PdL^7	85	yellow	246[d]	38.87(39.14)	3.50(3.52)	6.53 (6.52)
PdL^8	93	golden	326[d]	42.42(42.50)	3.82(3.82)	10.54(10.26)
PdL^9	82	orange	216[d]	53.99(53.95)	4.54(4.53)	7.26 (6.99)
CuL^4	84	purple	252	62.52(62.57)	5.20(5.25)	7.38 (7.30)
CuL^5	83	olive	188	56.61(55.98)	5.66(5.64)	8.54 (8.70)
CuL^6	89	olive	165	53.32(53.32)	5.37(5.36)	8.19 (8.29)
CuL^7	92	green	219	43.74(43.48)	3.88(3.91)	7.14 (7.24)
CuL^8	91	purple	256[d]	48.00(47.76)	4.28(4.29)	11.75(11.91)
CuL^9	94	purple	216	60.89(60.41)	5.12(5.07)	7.97 (7.83)

[d] With decomposition.

pressure to give HL^1 as a colorless, odorless, viscous liquid, B.P. 108–110 °C/2 mm Hg. Yields ranged from 46 to 61%, based on used acetylacetone.

Ligands

The solution of HL^1 (7.11 g; 0.05 mol) in chloroform (30 ml) and a warm solution of the appropriate aldehyde (0.05 mol) in chloroform (200 ml) were mixed together vigorously and then refluxed for 30 minutes. After the reflux the mixture was concentrated until a colored solid precipitated. It was recrystallized from methanol (in the case of H_2L^7, H_2L^9), acetone (H_2L^3, H_2L^4), n-hexane (H_2L^2), methanol–diisopropyl ether mixture (H_2L^5), chloroform–diisopropyl ether mixture (H_2L^6) and methanol–chloroform mixture (H_2L^8) to give the following products:

H_2L^2, 1-(2′-hydroxyphenyl)-2,5-diaza-6-methylnona-1,6-diene-8-one,

H_2L^3, 1-(2′-hydroxyphenyl)-2,5-diaza-1,6-dimethylnona-1,6-diene-8-one,

H_2L^4, 1-(2′-hydroxyphenyl)-1-phenyl-2,5-diaza-6-methylnona-1,6-diene-8-one,

H_2L^5, 1-(2′-hydroxy-5′-methylphenyl)-2,5-diaza-6-methylnona-1,6-diene-8-one,

H_2L^6, 1-(2′-hydroxy-5′-methoxyphenyl)-2,5-diaza-6-methylnona-1,6-diene-8-one,

H_2L^7, 1-(2′-hydroxy-5′-bromophenyl)-2,5-diaza-6-methylnona-1,6-diene-8-one,

H_2L^8, 1-(2′-hydroxy-5′-nitrophenyl)-2,5-diaza-6-methylnona-1,6-diene-8-one,

H_2L^9, 1-(2′-hydroxy-1′-naphthyl)-2,5-diaza-6-methylnona-1,6-diene-8-one.

Structural formulae of ligands are given in Fig. 4. The compounds H_2L^2, H_2L^3 and H_2L^4 were obtained by us earlier [14] by a different method; two have also been synthesized by Costes *et al.* [9]. Analytical data of newly prepared compounds are listed in Table I.

Complexes

Copper(II) and nickel(II) complexes with unsymmetrical Schiff bases H_2L^x (x = 2–9) of the general

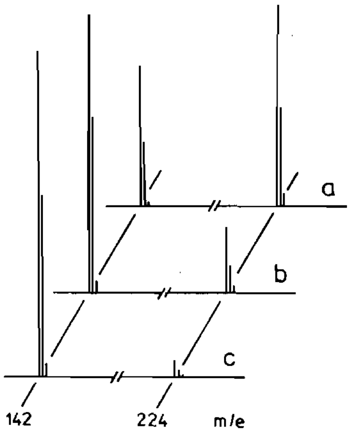

Fig. 1. FD mass spectra of condensation products of ethylenediamine and acetylacetone. Ethylenediamine and acetylacetone were mixed in anhydrous ethanol in the following ratios: a) 1:1, b) 2:1, c) 3:1.

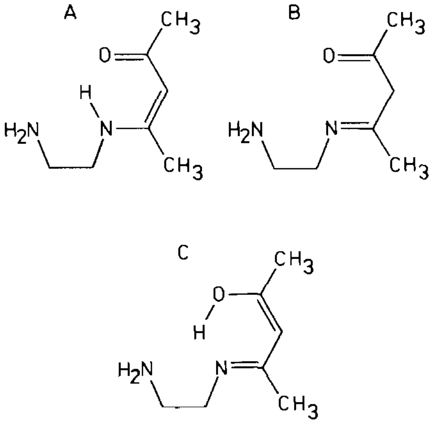

Fig. 2. Tautomeric forms of the monocondensation product of acetylacetone and ethylenediamine.

formula ML^x (M = Cu, Ni) were prepared by slow addition of the stoichiometric amount of the appropriate ligand dissolved in methanol to the hot methanol solution of metal acetate, with constant stirring. On cooling and if necessary evaporating, a colored solid precipitated. It was filtered off, washed with the cold solvent, recrystallized and dried under vacuum at 80 °C. Preparation of palladium(II) complexes followed a similar procedure to that described above, except that acetone was used instead of methanol.

For recrystallization of the complexes the following solvents were used: acetonitrile (CuL^7, CuL^8, NiL^8, PdL^8), chloroform (PdL^6, PdL^7), methanol (NiL^5, NiL^6, NiL^7), acetonitrile–methanol mixture (CuL^9, NiL^9), chloroform–diisopropyl ether mixture (PdL^5, PdL^9) and methanol–diisopropyl ether mixture (CuL^4, CuL^5, CuL^6).

Table I lists analytical data for the complexes. Their structural formulae are given in Fig. 6.

Apparatus and Measurements

Mass spectra were recorded on a Varian MAT 711 spectrometer. ^1H nmr spectra were run on Bruker WM 360, Bruker WM 250 and Tesla BS 487 80 MHz spectrometers. ^{13}C nmr spectra were obtained using a Bruker WM 250 spectrometer. Esr spectra were run on a X-band spectrometer produced by Polish Academy of Sciences. Electronic spectra of ligands and chelates were recorded on a Perkin Elmer UV VIS 402 spectrometer using silica cells. Elemental analysis data were obtained using a Carlo Erba Elemental Analyser MOD 1106.

Results and Discussion

Characterization of Intermediate and Ligands

Some years ago Martell *et al.* [15] reported that the reaction between acetylacetone and ethylenediamine yielded the 2:1 condensation product even if equimolar amounts of both reactants were used. On the other hand Costes *et al.* [8] reported that the 1:1 condensation product formed in an equimolar mixture of both reactants. Our studies on this reaction by mass spectrometry showed that the reaction mixture comprises both condensation products, and at the molar ratio of amine to diketone equal to 3:1 the 1:1 condensation product HL^1 became the main product of the reaction (Fig. 1).

HL^1 was isolated from the reaction mixture as a viscous, colorless and odorless liquid. HL^1 is moderately unstable. Stored at the temperature of 25 °C for a few days it deposited crystals of the 2:1 condensation product and free ethylenediamine. However it could be stored for a week at −15 °C with no apparent traces of decomposition. HL^1 can exist in various tautomeric forms (Fig. 2).

^1H nmr spectrum of HL^1 (Table II) comprises the signals of two methyl, two methylene, vinyl and primary amino groups, and moreover a broadened singlet at 10.8 ppm whose relative intensity corresponds to one proton.

Double irradiation experiments showed that this proton is coupled with one of the methylene groups, because irradiation with the resonance frequency of the proton removed the additional splitting which was observed in the multiplet of the methylene group resonating at lower field (Fig. 3).

These results allowed to assign the 10.8 ppm resonance to the proton of the secondary amino group which is present only in the tautomeric form A (Fig. 2). Thus the ^1H nmr data suggest that A is the dominant form in $CDCl_3$ solution of HL^1.

As we reported earlier [1, 2] HL^1 reacts readily with aldehydes and ketones to give corresponding Schiff bases in high yield. Due to the ease of preparation and high reactivity HL^1 may be considered as

TABLE II. ^{1}H nmr (80 MHz) Data for the Intermediate HL^1 and the Ligands in $CDCl_3$ Solutions with Hexamethyldisiloxane, HMDSO, as Internal Reference.

Compound	Chemical shifts, ppm							
	a	b	c	d	e	f	g	h
HL^1	1.81s 1.84s	2.72t 3.19q	4.84s			10.76br		1.50s^{i}
H_2L^5	1.75s 1.82s	3.32–3.75m	4.76s	8.16s	6.68db^{k}, 6.98db^{l} 6.91s^{n}	10.82br	12.56s	2.18s^{j}
H_2L^6	1.75s 1.86s	3.36–3.76m	4.82s	8.16s	6.60–6.88m	10.81br	12.38s	3.62s^{j}
H_2L^7	1.72s 1.82s	3.28–3.71m	4.80s	8.10s	6.69db^{k} 7.16–7.38m^{l,n}	10.79br	12.88s	
H_2L^8	1.81s 1.89s	3.45–3.90m	4.89s	8.36s	6.90db^{k}, 8.11db^{l} 8.16s^{n}	10.85br	14.04s	
H_2L^9	1.71s 1.85s	3.29–3.71m	4.78s	8.71s	6.86db^{k} 7.00–7.91m^{h}	10.90br	14.38s	

Signals from the protons of the following groups: a, two methyl; b, two methylene; c, vinyl; d, azomethine; e, aromatic; f, enamine; g, hydroxy (phenolic); h, other; i, primary amino; j, methyl of the X substitutent; k, aromatic 3′; 1, aromatic 4′; n, aromatic 6′.

Key: s, singlet; db, doublet; t, triplet; q, quartet; m, multiplet; br, broadened.

TABLE III. Electron Impact (70 eV) Monoisotopic Mass Spectra[a] of the Ligands.

H_2L^5	H_2L^6	H_2L^7	H_2L^8	H_2L^9	Assignment
260(45)	276(57)	324(15)	291(14)	296(42)	$H_2L^{+\cdot}$
245(3)	261(3)	309(3)	276(3)	281(1)	$(H_2L-CH_3)^+$
243(3)	259(11)	307(2)	274(8)	279(1)	$(H_2L-OH)^+$
217(30)	233(68)	281(16)	248(22)	253(14)	$(H_2L-CH_3CO)^+$
161(23)	177(33)	225(10)	192(2)	197(35)	$C_6H_2XY(OH)CH{=}N{-}CH{=}CH_2^{+\cdot}$
148(32)	164(19)	212(12)	179(5)	184(72)	$C_6H_2XY(OH)CH{=}N{=}CH_2^+$
136(46)	152(28)	200(6)	167(1)	172(13)	$C_6H_2XY(OH)CH{=}NH_2^+$
125(18)	125(11)	125(23)	125(25)	125(7)	$C_5H_7(O)NH{-}CH{=}CH_2^{+\cdot}$
112(100)	112(100)	112(100)	112(100)	112(100)	$C_5H_7(O)NH{=}CH_2^+$

[a] m/e values for the most abundant isotopes. Relative abundance of ions in parentheses.

an excellent intermediate for the synthesis of unsymmetrical Schiff bases comprising acetylacetone and ethylenediamine moieties. Using this compound we obtained eight (five new) Schiff bases of the structure presented on Fig. 4.

Table II lists ^{1}H nmr resonances of free ligands and assignments: ^{1}H nmr data in addition to mass spectral data are given in Table III and are consistent with the structural formulation given in Fig. 4 where the acetylacetone part of the ligand is in ketoenamine and the aromatic part in the salicylaldimine form. Particularly informative seems to be the loss of 43 mass units from the molecular ion in mass spectra (Table III) which is believed to correspond to the loss of the acetyl group and the presence of one NH signal in the ^{1}H nmr spectra (Table II). The molecular ion is not the base peak in mass spectra of ligands. The most abundant fragment ions are formed by cleavage of the C–C bond of the $N-CH_2-CH_2-N$ moiety.

Characterization of Complexes

Nickel(II) complexes of the type NiL^x ($x = 2–9$) are red-brown diamagnetic crystalline solids which are soluble in most organic solvents. The uv–vis spectrum of each compound (Table IV) shows a low-energy band in the 540–554 nm region, which is assigned to the $^1A_1-^1B_1$ transition [16] and is typical of square-planar nickel(II) complexes, and more

TABLE IV. Electronic Spectra for the Metal Complexes.[a]

Compound[b]	λ_{max}, nm (log ϵ)
NiL^5	238(4.59), 334(3.80), 360sh, 412(3.36), 430sh, 550(1.96)
NiL^6	239(4.70), 337(3.84), 356sh, 421(3.49), 442sh, 554(2.06)
NiL^7	242(4.71), 337(3.84), 356sh, 414(3.36), 433sh, 545(2.07)
NiL^8	245(4.52), 340(4.14), 354sh, 540sh
NiL^9	259(4.65), 311(4.04), 341(4.01), 418(3.48), 440sh, 542(2.20)
PdL^5	225(4.57), 257(4.33), 340(3.70), 418(3.54)
PdL^6	227(4.62), 263(4.30), 341(3.80), 436(3.61)
PdL^7	228(4.59), 256sh, 337(3.80), 415(3.58)
PdL^8	260(4.34), 378(4.30)
PdL^9	222(4.55), 251sh, 259(4.64), 308(4.18), 318(4.17), 335sh, 408(3.67), 429(3.69)
CuL^4	228(4.40), 275(4.13), 323(4.07), 381(3.59), 552(2.36)
CuL^5	230(4.54), 274(4.28), 324(4.16), 387(3.65), 554(2.50)
CuL^6	228(4.55), 273(4.23), 326(4.07), 404(3.68), 555(2.51)
CuL^7	231(4.63), 270(4.23), 323(4.12), 388(3.64). 555(2.50)
CuL^8	235(4.36), 259sh, 320(4.19), 369(4.23), 554(2.49)
CuL^9	226(4.51), 241(4.58), 246(4.60), 261(4.44), 271(4.43) 315(4.25), 322sh, 384(3.78), 398(3.84), 546(2.52)

[a] 10^{-3} *M* solutions in methanol (nickel complexes) or in acetonitrile (copper and palladium complexes). [b] Spectra for NiL^2, NiL^3, NiL^4, PdL^2, PdL^3, PdL^4, CuL^2 and CuL^3 were reported elsewhere [14, 22].

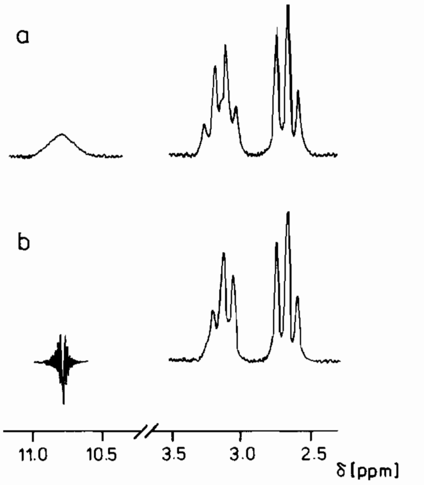

Fig. 3. Part of the 80 MHz ^1H nmr spectrum of 1-amino-3-aza-4-methylhept-4-ene-6-one HL^1 : a) unperturbed, b) during irradiation of HL^1 with the resonance frequency of the proton resonating at 10.8 ppm.

intense bands which are attributed to either a metal–ligand charge transfer band or to electronic transitions within the ligand. The ^1H nmr data for metal complexes are given in Table V.

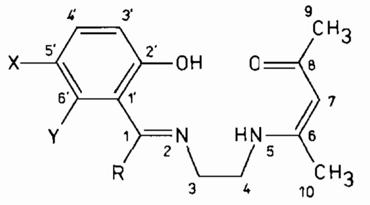

Fig 4. Ligands prepared from 1-amino-3-aza-4-methylhept-4-ene-6-one: H_2L^2 X = Y = R = H, H_2L^3 X = Y = H R = CH_3, H_2L^4 X = Y = H R = C_6H_5, H_2L^5 X = CH_3 Y = R = H, H_2L^6 X = OCH_3 Y = R = H, H_2L^7 X = Br Y = R = H, H_2L^8 X = NO_2 Y = R = H, H_2L^9 XY = –CH=CH–CH=CH– R = H.

An examination of the high resolution ^1H nmr spectra allows an unambiguous assignment of azomethine and vinyl protons. Methyl groups give rise to two singlets separated by *ca.* 0.1 ppm. For several years the assignment of methyl resonances in 4,9-dimethyl-5,8-diazadodeca-3,9-diene-2,11-dionatonickel(II), a compound related to the nickel chelates studied in this work, was a subject of controversy. McCarthy and Martell [17] made assignments based on the proposition that the methyls adjacent to the CO group are slightly less shielded than those near the

TABLE V. ^{1}H nmr (250 MHz) Data for the Nickel Complexes in $CDCl_3$ with TMS as an Internal Reference.

	Chemical shifts, ppm										
	a	b	c	d	e	f	g	h	i	j	
NiL^3	1.899s	1.807s	4.916s	3.134t	3.468t		6.914db	7.078t	6.747t	7.332db	2.274^k
NiL^4	1.943s	1.856s	4.973s	2.915m	3.005m		6.958db		6.296t	6.512db	7.276–7.032m^h ($H_{3''}$ and $H_{4''}$)^p 7.457–7.431m ($H_{2''}$)^p
NiL^5	1.933s	1.900s	4.961s	3.031t	3.355t	7.371s	6.861db	6.991db		6.829s	2.180s^k
NiL^6	1.935s	1.909s	4.967s	3.056t	3.361t	7.400s	6.502db	6.882db		6.893s	3.708s^k
NiL^7	1.940s	1.922s	4.991s	3.067t	3.372t	7.378s	6.848db	7.200db		7.165s	
NiL^8	1.967s a + b		5.053s	3.118t	3.442t	7.612s	6.909db	8.008db		8.210s	
NiL^9	1.962s	1.936s	4.997s	3.105t	3.488t	8.257s	7.122db	7.554db			7.775db($H_{1'''}$)^n 7.375t ($H_{2'''}$)^n 7.203t ($H_{3'''}$)^n 7.628db($H_{4'''}$)^n

Signals from the protons which occur in the following groups or parts of the molecule: a, methyl 9; b, methyl 10; c, vinyl 7; d, methylene 4; e, methylene 3; f, azomethine 1; g, aromatic 3′; h, aromatic 4′; i, aromatic 5′; j, aromatic 6′; k, substituent X or R; p, phenyl ring linked with the carbon 1 comprising the protons $H_{2''}$, $H_{3''}$ and $H_{4''}$ in ortho, meta and para positions respectively; n, naphthalene moiety with the protons: $H_{1'''}$ in peri position to $C_{1'}$, $H_{2'''}$ in amfi position to $C_{3'}$, $H_{3'''}$ in amfi position to $C_{2'}$ and $H_{4'''}$ in peri position to $C_{4'}$. Meaning of s, db, t and m is the same as in Table II.

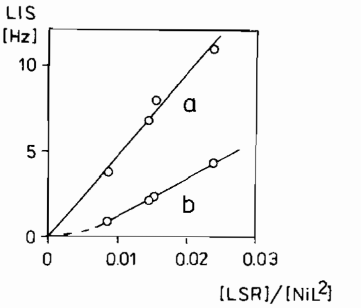

Fig. 5. Dependence of lanthanide induced shifts (LIS) on the molar ratio of $Eu(fod)_3$ to the nickel chelate NiL^2. The data correspond to the ^{1}H nmr signals of the methyl groups in 1-(2′-oxophenyl)-2,5-diaza-6-methyl-nona-1,6-diene-8-onatonickel(II) NiL^2. Solvent $CDCl_3$.

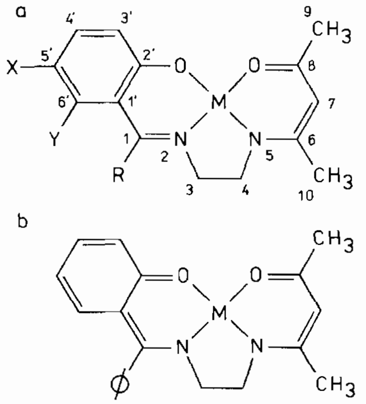

Fig. 6. Structural models of complexes: a) ML^x where x = 2, 3, 5–9; b) ML^4. M stands for Ni(II), Cu(II), Pd(II), ϕ is the phenyl ring.

CN group. Sakaguchi *et al.* [18] assigned the lower field signal to the methyl adjacent to the CN group on the basis of a shorter relaxation time of the methyl resonating at lower magnetic field. Some additional light on this problem might be shed by studies on the induced shift produced by lanthanide shift reagent (LSR). Upon addition of $Eu(fod)_3$ to the nickel chelates NiL^x (x = 2, 4–9) the lower field signal in the 1.8–2.0 ppm region experienced a larger induced downfield shift and larger broadening than did the higher field one. The effect of $Eu(fod)_3$ concentration on the magnitude of the induced shift of methyl resonances for NiL^2 is illustrated in Fig. 5.

Planar nickel(II) complexes with tetradentate N_2O_2 ligands are believed to coordinate to europium through both *cis* oxygen donors in $Eu(fod)_3$ adducts [19]. Assuming the same mode of coordination in our $Eu(fod)_3$ adducts we might expect a larger induced shift of the methyl group adjacent to CO because it is nearer to the LSR. The lower field

TABLE VI. ^{13}C nmr Data Obtained from ^{1}H Decoupled Spectra for the Nickel Complexes in $CDCl_3$ Solutions with TMS as a Reference.

	Chemical shifts, ppm												
	a	b	c	d	e	f	g	h	i	j	k	l	
NiL^2	24.4	21.3	176.7	163.8	99.6	51.3	60.1	160.8	121.5	163.8	114.4	121.6	133.3, $131.6^{o,r}$
NiL^3	24.4	21.1	177.8	165.1	100.0	51.9	56.0	164.9	122.2	168.9	114.8	123.2	129.2^r, 132.5^o, 18.3^x
NiL^4	24.4	21.2	177.8	165.6	100.0	51.6	57.5	165.6	122.1	171.3	114.5	122.6	127.0, 129.3, 132.8, $136.4^{o,r,p}$
NiL^5	24.4	21.3	177.4	165.0	99.8	51.5	60.1	161.1	119.7	163.2	121.6	123.4	131.1^r, 135.3^o, 20.0^x
NiL^6	24.4	21.3	177.7	165.0	99.8	51.5	60.2	160.7	118.7	160.7		149.2	112.0, 122.8, $123.9^{k,o,r}$
NiL^7	24.3	21.3	177.4	165.2	99.9	51.4	60.3	160.4	121.7	164.1	123.7	105.6	133.4^r, 136.1^o
NiL^8	24.2	21.4	177.7	165.6	100.3	51.5	60.6	161.2	119.3	170.1	122.4		128.2^r, 129.9^o
NiL^9	24.5	21.2	177.2	166.1	99.8	51.7	60.7	165.1	110.7	155.6	118.6	126.6	124.6^o, 133.3^r, 122.1 127.2, 128.8, 133.6^n

Signals from the carbon atoms which occur in the following groups or parts of the molecule: a, methyl 9; b, methyl 10; c, carbonyl 8; d, enamine 6; e, vinyl 7; f, methylene 4; g, methylene 3; h, azomethine 1; i, aromatic 1′; j, aromatic 2′; k, aromatic 3′; l, aromatic 5′; o, aromatic 4′; r, aromatic 6′; p, phenyl linked with the carbon 1; n, naphthalene moiety.

TABLE VII. ^{1}H nmr (360 MHz) Data for the Palladium Complexes in $CDCl_3$ Solutions with TMS as an Internal Reference.

	Chemical shifts, ppm										
	a	b	c	d	e	f	g	h	i	j	
PdL^2	2.051s	1.970s	4.891s	3.483t	3.716t	7.558s	7.099db	7.286t	6.532t	7.121db	
PdL^3	2.066s	1.998s	4.922s	3.484t	3.748t		7.151db	7.225t	6.553t	7.486db	$2.475s^k$
PdL^4	2.092s	1.969s	4.941s	3.316s d + e					6.322t	6.678db	$7.150–7.226m^g$ $(H_{3}''–H_{4}'')^p$
PdL^5	2.061s	1.997s	4.916s	3.478t	3.724t	7.578s	7.034db	7.125db		6.911s	$2.209s^k$
PdL^6	2.062s	2.005s	4.922s	3.483t	3.738t	7.610s	7.073db	7.012db		6.585s	$3.730s^k$
PdL^7	2.053s	1.977s	4.908s	3.476t	3.740t	7.522s	6.976db	7.304db		7.216s	
PdL^8	2.104s	2.073s	5.013s	3.543t	3.831t	7.818s	7.076db	8.129db		8.277s	
PdL^9	2.089s	2.022s	4.947s	3.524t	3.867t	8.574s	7.293db	7.662db			7.213t $(H_{3}''')^n$ 7.418t $(H_{2}''')^n$ 7.644db$(H_{4}''')^n$ 7.837db$(H_{1}''')^n$

Signals from the hydrogen atoms which occur in the following groups or parts of the molecule: a, methyl 9; b, methyl 10; c, vinyl 7; d, methylene 4; e, methylene 3; f, azomethine 1; g, aromatic 3′; h, aromatic 4′; i, aromatic 5′; j, aromatic 6′; k, substituent X or R; p, phenyl ring linked with the carbon 1 comprising protons $H_{2}''–H_{4}''$ in ortho, meta and para positions respectively; n, naphthalene moiety with the protons $H_{1}'''–H_{4}'''$ located as described in Table V. Meaning of the symbols, s, db, t, m is the same as in Table II.

signal in NiL^2 and also in NiL^x ($x = 4$–9) is thus assigned to the methyl group in position 9 (Fig. 6).

Effects induced by LSR in NiL^3 are less informative. After addition of $Eu(fod)_3$ the lower field signal in the 1.8–2.0 ppm region broadens but undergoes a lesser induced shift than does the higher field one.

The bridging methylene groups 3 and 4 (Fig. 6) give rise to two triplets. An inspection of Table V shows that the lower field triplet is sensitive to structural changes in the aromatic part of the molecule and has been assigned to the methylene group situated nearer to the aromatic ring. Phenyl substitution on carbon 1 diminishes the difference in chemical shifts of both methylene groups so that two resolved triplets can be observed only in the high resolution spectrum (250 MHz or more). Small spacing of methylene signals in NiL^4 may accrue from long-range shielding effects produced by the phenyl group bound to carbon 1 and/or from equal hybridization of both nitrogen atoms leading to a ketoenamine structure in both aromatic and acetylacetone parts of the molecule, as shown in Fig. 6, tracing b. Consistent with the ketoenamine structure of the aromatic part is the chemical shift of the 6′ proton at 6.5 ppm which is characteristic for olefinic rather than for aromatic systems. The value of 6.5 ppm is readily obtained for the proton bound to carbon 3 in 2-methylenecyclohexa-3,5-dienone using additivity rules. The compound may serve as a model for the salicylaldehyde portion in NiL^4.

^{13}C nmr resonances of nickel complexes and their assignments are listed in Table VI.

The spectra of all the compounds are very similar, except for those resonances which are due to carbon atoms occurring in substituents X, Y and R. Four lines in the 160–178 ppm region may be attributed to carbon atoms linked to heteroatoms. The relatively high chemical shift, 171.3 ppm, in NiL^4 assigned to the carbon 2′ is consistent with the proposed ketoenamine structure of the cyclic part in this compound (Fig. 6, tracing b).

^1H nmr spectra of palladium chelates (Table VII) are very similar to the spectra of corresponding nickel chelates.

Resonances of bridging methylene protons are most sensitive to substitution of palladium for nickel. The baricenter of both triplets moves then by *ca.* 0.4 ppm and the spacing between them decreases. The downfield shift also involves other protons which are closest to palladium. This seems to indicate that the empty *d* orbitals of palladium are accepting electron density from adjacent atoms, leading to a more delocalized system and to deshielding of atoms which are in the vicinity of the metal. Ethylene bridge resonances in PdL^4 are so close that they give rise to a sharp singlet which is not resolved even in the 360 MHz spectrum.

TABLE VIII. g Values for the Copper Complexes.[a]

Compound	$g_\parallel$	$g_\perp$
CuL^5	2.154	2.054
CuL^6	2.145	2.054
CuL^7	2.148	2.054
CuL^8	2.180	2.045
CuL^9	b	2.052

[a] Measured for powdered samples at room temperature. [b] Not resolved.

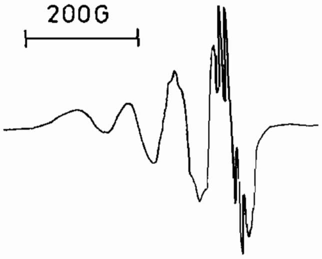

Fig. 7. Electron spin resonance spectrum of a $CHCl_3$ solution of 1-(2′-oxophenyl)-1-phenyl-2,5-diaza-6-methylnona-1,6-diene-8-onatocopper(II) (CuL^4) at room temperature.

Copper(II) complexes were obtained as green or purple crystalline solids. Dissolved in acetonitrile, however, they exhibit similar spectra in the visible part (Table IV). Maxima of low energy bands appear at *ca.* 550 nm and are close to those found for related copper complexes of approximately planar structure [20].

The esr spectra of polycrystalline copper complexes are typical of an axially symmetric system with $g_\parallel$ around 2.16 and $g_\perp$ appearing around 2.05 (Table VIII).

Kivelson and Neiman [21] suggested that $g_\parallel$ serves as a single parameter measuring the total covalency of the in plane coordinate σ and π bonding; the lower the $g_\parallel$ value the more covalent the coordinate bonding. According to this criterion the slightly higher value in $g_\parallel$ for CuL^8 may reflect a less covalent character of the in plane copper–ligand bonding in this compound as compared to other chelates. The esr spectrum of CuL^4 in $CHCl_3$ solution shows a clearly resolved superhyperfine structure due to the two nitrogen nuclei of the ligand (Fig. 7).

Copper complexes with Schiff bases unsubstituted at carbon 1 do not exhibit nitrogen superhyperfine splitting.

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