Metal Complexes with Unsymmetrical Tetradentate Ketoenamines Derived from β-Diketones or Ethoxymethylene-β-dicarbonyl Compounds and 1-Amino-4-methyl-3-azahept-4-ene-6-one

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New preparative possibilities of the monocondensation product of pentane-2,4-dione and 1,2-diaminoethane for the synthesis of unsymmetrical ligands and their deuterated derivatives are demonstrated. Using this compound several new unsymmetrical tetradentate ketoenamines, various 9, 10, 11 substituted 4-methyl-5,8-diazaundeca-3,9-diene-2,11-diones and their copper(II), nickel(II) and palladium(II) complexes were obtained. On the basis of the ^1H nmr studies the structure of ligands and complexes were established. An unexpected stereochemistry was observed for the product of the reaction of 1,1,1-trifluoro-4-phenylbutane-2,4-dione with the monocondensation product of pentane-2,4-dione and 1,2-diaminoethane. Spectroscopic data for the metal complexes are consistent with their planar structure. Utilizing the double resonance technique, deuteration of ligands, lanthanide and solvent shift reagents the assignment of almost all the ^1H nmr resonances of ligands and complexes was accomplished.

Introduction

A large number of symmetrical tetradentate Schiff bases and β-ketoenamines have been reported in the literature. Relatively little is known, however, of the related asymmetrical compounds which may be useful as models for metal binding sites in various metal-proteins. The preparation of asymmetrical compounds by mixing an aromatic carbonyl compound with a diketone and a diamine and separating out the symmetrical and asymmetrical products was efficient in only a few cases [1–3]. The application of the reaction between a diamine and a mixed chelate containing β-diketone and aromatic hydroxyaldehyde anions has been reported [4].

Routes in which the product of monocondensation of the diamine with one carbonyl compound is used for further condensation with a second carbonyl compound seem to be more general. Recently the product of monocondensation of pentane-2,4-dione and 1,2-diaminoethane 1-amino-4-methyl-3-azahept-4-ene-6-one HL^0 was isolated in two different ways [5, 6]. This compound condensed easily with salicylaldehyde and its derivatives to give asymmetrical tetradentate Schiff bases in excellent yields [6, 7]. We observed that the compound also reacts with a variety of β-diketones and 2-ethoxymethylene-1,3-diketones to give asymmetrical ketoenamines. This paper shows new possibilities of application of HL^0 and reports on new types of asymmetrical tetradentate ketoenamines and their copper(II), nickel(II) and palladium(II) complexes.

Experimental

General

Carbon, hydrogen and nitrogen contents were determined on a Carlo Erba Elemental Analyzer MOD 1106. Mass spectra were recorded on a Varian MAT 711 spectrometer at 70 eV. U.v. and visible absorption spectra were recorded on a Perkin Elmer UV VIS 402 spectrometer. I.r. spectra were obtained using a Specord 71 IR spectrometer. ^1H nmr spectra were obtained using a Tesla BS 487 80 MHz spectrometer. Lanthanide induced shifts were studied by use of tris(1,1,1,2,2,3,3-heptafluoro-7.7-dimethyloctane-4,6-dionato)europium(III) (Fluka) within the molar ratio of $Eu(fod)_3$ to complex of 0–0.1. Benzene-induced shifts were studied using benzene (BDH) for spectroscopy within the range of v/v% of benzene in $CDCl_3$ of 0–50%.

Reagents

Metal acetates were purchased from E. Merck and were used without further purification. 1,1,1-Trifluoropentane-2,4-dione (Fluka) was dried over anhydrous magnesium sulphate and distilled. 1-Phenylbutane-1,3-dione (Fluka) was recrystallized from petrol ether. 1,1,1-Trifluoro-4-phenylbutane-2,4-dione was prepared according to the general procedure described in [8] and distilled, b.p. 105–107 °C/15 mmHg. 1,1,1-Trifluoro-3,5,5,5-tetradeuteriopentane-2,4-dione and 4-phenyl-1,1,1,3-tetradeuteriobutane-2,4-dione were obtained by the

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

| Compound	Yield %	M.P.[a] °C	Anal. % Found (Calcd)		
			C	H	N
H_2L^1	51	147	51.99(51.80)	5.98(6.16)	9.44(10.07)
H_2L^2	62	98	71.48(71.30)	7.85(7.74)	9.81 (9.78)
H_2L^4	64	131	61.89(61.88)	8.02(7.99)	11.05(11.10)
H_2L^5	79	131	68.68(68.77)	7.06(7.05)	8.88 (8.91)
H_2L^6	74	91	60.05(59.56)	7.97(7.85)	9.97 (9.92)
CuL^1	67	207	40.27(42.42)	3.59(4.45)	7.82 (8.24)
CuL^2	90	141	59.18(58.69)	5.75(5.79)	7.92 (8.05)
CuL^4	74	161	49.94(49.75)	5.87(5.78)	8.78 (8.93)
CuL^5	94	218	57.70(57.51)	5.41(5.36)	7.65 (7.45)
CuL^6	95	140	50.21(48.90)	5.98(5.86)	8.00 (8.15)
NiL^1	26	209	43.15(43.03)	4.53(4.51)	8.40 (8.36)
NiL^2	91	184	60.10(59.52)	5.88(5.88)	8.10 (8.17)
NiL^3		215	51.80(51.43)	4.45(4.32)	6.99 (7.06)
NiL^4	49	183	50.42(50.53)	5.85(5.87)	8.98 (9.07)
NiL^5	84	201	58.41(58.26)	5.49(5.43)	7.61 (7.55)
NiL^6	81	140	49.84(49.60)	6.24(5.95)	8.37 (8.26)
PdL^1	25	205d	37.23(37.67)	3.47(3.95)	7.33 (7.32)
PdL^2	76	205d	52.12(52.25)	5.16(5.16)	7.07 (7.17)
PdL^4	93	195d	43.69(43.77)	5.10(5.09)	7.73 (7.86)
PdL^5	80	199d	51.40(51.63)	5.04(4.81)	6.98 (6.69)
PdL^6	85	171	43.73(43.48)	5.23(5.21)	7.29 (7.24)

[a]d = with decomposition.
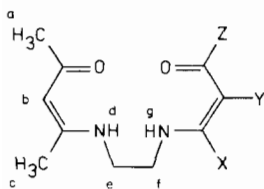
Fig. 1. Schematic representation of ligands: X = CH_3, Y = H, Z = CF_3 1,1,1-trifluoro-4,9-dimethyl-5,8-diazadodeca-3,9-diene-2,11-dione H_2L^1; X = CH_3, Y = H, Z = C_6H_5 1-phenyl-3,8-dimethyl-4,7-diazaundeca-2,8-diene-1,10-dione H_2L^2; X = C_6H_5, Y = H, Z = CF_3 1,1,1-trifluoro-4-phenyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dione H_2L^3; X = H, Y = $COCH_3$, Z = CH_3 3-acetyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dione H_2L^4; X = H, Y = COC_6H_5, Z = CH_3 3-benzoyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dione H_2L^5; X = H, Y = $COOC_2H_5$, Z = CH_3 3-ethoxycarbonyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dione H_2L^6.

general method described for the deuteration of pentane-2,4-dione [9]. 3-Ethoxymethylenepentane-2,4-dione, 2-ethoxymethylene-1-phenylbutane-1,3-dione and ethyl 2-ethoxymethylene-3-oxobutanoate were obtained by literature methods [10, 11]. The preparation of 1-amino-4-methyl-3-azahept-4-ene-6-one HL^0 was described in [6].

Ligands

The solution of HL^0 (7.11 g, 0.05 mol) in chloroform (30 ml) was added dropwise to the warm solution of appropriate β-diketone or freshly prepared ethoxymethylene-β-dicarbonyl compound (0.05 mol) in chloroform (300 ml). The mixture was refluxed for 30 minutes (H_2L^1, H_2L^{4-6}) or 2 hours ($H_2L^{2,3}$) then concentrated under reduced pressure until a white solid precipitated. The crude ligand was recrystallized from methanol–diisopropyl ether mixture (H_2L^1, H_2L^{4-6}) or chloroform–diisopropyl ether mixture (H_2L^2) and dried *in vacuo* at room temperature.

Thin layer chromatography of a product precipitated in the case of H_2L^3 (E. Merck silica gel aluminium sheets, acetone:petrol ether 2:3 v/v as the eluting solvent) showed that the solid is the mixture of H_2L^3 and 4,9-dimethyl-5,8-diazadodeca-3,9-diene-2,11-dione H_2L^7. A small sample of comparatively pure H_2L^3 sufficient for nmr was isolated by means of semi-preparative thin layer chromatography on 20 × 20 cm silica gel glass plates (E. Merck) with 2:3 v/v acetone–petrol ether mixture as an eluent. Partially deuterated ligands d-H_2L^1 and d-H_2L^2 were prepared similarly by use of deuterated β-diketones as starting materials. Struc-

TABLE II. ^{1}H nmr Data for the Ligands in CDCl$_3$ Solution with Hexamethyldisiloxane HMDS as Internal Reference.

Compound	Chemical shift δ, ppm												
	Methyl				Methine			Methylene			Aromatic	Enamine	
	a^h	c^h	X	Y	b	X	Y	e,f^i	Y	Z		d	g
H$_2$L^1	1.77s	1.90s	1.955s^k		4.87s	5.22s^k		3.40m				10.77br	11.05br
H$_2$L^2	1.77s	1.85s	1.90s^k		4.82s	5.55s^k		3.32m			7.10–7.35m 7.52–7.75m	10.72br	11.30br
H$_2$L^3	1.72s	1.90s			4.90s		5.30s	3.30m			7.02–7.30m	10.60br	11.00br
H$_2$L^4	1.71s	1.84s		2.06s	4.86s	7.57db^l		3.39m		2.32s		10.79br	
H$_2$L^5	1.71s	1.88s			4.89s	n		3.28m		2.31s		10.71br	10.90br
H$_2$L^6	1.75s	1.85s		1.16t	4.85s	7.78db^l		3.36m	4.02q	2.31s	7.09–7.48m	10.72br	10.95br

^{h}These assignments may be interchangeable. ^{i}Chemical shift of the baricenter of symmetrical multiplet. ^{k}The signal disappears or reduces its intensity in the spectrum of deuterated derivative. ^{l}J$_{Xg}$ = 13 Hz. ^{n}Signal obscured by overlapping aromatic bands. Key: s singlet, db doublet, t triplet, q quartet, m multiplet, br broadened band. Meaning of a, b, c, d, e, f, g, X, Y and Z as in Fig. 1.

tural formulae of ligands and their names are given in Fig. 1; analytical data are listed in Table I.

Complexes

Copper(II) and nickel(II) complexes ML^x (M = Cu, Ni, x = 1, 2, 4–6) were prepared by addition of the stoichiometric amount of the appropriate ligand dissolved in methanol to the hot methanolic solution of metal acetate and refluxing the mixture for 30 minutes. NiL^3 was prepared similarly by the reaction of crude ligand mixture H$_2$L^3/H$_2$L^7 with nickel acetate tetrahydrate. On cooling (and if necessary, evaporating) purple copper and red-brown nickel complexes precipitated. They were filtered off, recrystallized and dried *in vacuo* at 100 °C. Preparation of yellow palladium(II) complexes PdL^x (x = 1, 2, 4–6) followed a similar procedure except that acetone was used instead of methanol.

For recrystallization of the complexes the following solvents were used: methanol (NiL^1, NiL^3, PdL^6), methanol–diisopropyl ether mixture (CuL^1, CuL^4, CuL^6, NiL^4, NiL^6, PdL^4), methanol–acetonitrile mixture (CuL^2, CuL^5, NiL^2, NiL^5, PdL^5) and chloroform–diisopropyl ether mixture (PdL^1, PdL^2). The crude complexes ML^1 (M = Cu, Ni, Pd) partially underwent disproportionation on recrystallization, forming scarcely-soluble complexes with the symmetrical ligand 1,1,1,12,12,12-hexafluoro-4,9-dimethyl-5,8-diazadodeca-3,9-diene-2,11-dione H$_2$L^8. Deuterated complexes d-NiL^2 and d-PdL^2 were prepared as NiL^2 and PdL^2, by use of deuterated ligand d-H$_2$L^2. Table I lists analytical data for the complexes.

Results and Discussion

Characterization of Ligands

H$_2$L^1 (X = CH$_3$, Y = H, Z = CF$_3$ in Fig. 1) had been obtained and partially characterized earlier [12]. Its formation by the general method described in this earlier paper proceeded in high yield. Our mass spectral, TLC and ^{1}H nmr studies have shown that H$_2$L^1 undergoes disproportionation in polar solvents to give symmetrical products 4,9-dimethyl-5,8-diazadodeca-3,9-diene-2,11-dione H$_2$L^7 and 1,1,1,12,12,12-hexafluoro-4,9-dimethyl-5,8-diazadodeca-3,9-diene-2,11-dione H$_2$L^8. H$_2$L^2 (X = CH$_3$, Y = H, Z = C$_6$H$_5$) formed also readily in high yield while H$_2$L^3 the product of condensation of 1,1,1-trifluoro-4-phenylbutane-2,4-dione and HL^0 could be isolated by chromatographic methods in poor yield. The formation of H$_2$L^3 seems to be hindered by an unfavorable electron density distribution in the 1,1,1-trifluoro-4-phenylbutane-2,4-dione molecule due to the negative mesomeric effect of the phenyl ring and the electron-withdrawing properties of the trifluoromethyl group strongly favor-

TABLE III. Electron Impact Monoisotopic Mass Spectra[a] of the Ligands.

H_2L^1	H_2L^2	H_2L^4	H_2L^5	H_2L^6	Assignment
278(5)	268(3)	252(52)	314(11)	282(11)	$H_2L^{+\cdot}$
235(1)	243(2)	209(7)	271(5)	239(1)	$[H_2L - CH_3CO^\cdot]^+$
179(15)	187(76)	153(12)	215(17)	183(8)	$[ZC(O)C(Y)C(X)NH-CH=CH_2]^{+\cdot}$
166(24)	174(100)	140(5)	202(6)	170(1)	$[ZC(O)C(Y)C(X)NH=CH_2]^+$
	160(6)		188(3)	156(7)	$[ZC(O)C(Y)C(X)NH]^+$
125(31)	125(60)	125(63)	125(19)	125(18)	$[CH_3C(O)CHC(CH_3)NH-CH=CH_2]^{+\cdot}$
112(100)	112(57)	112(100)	112(100)	112(100)	$[CH_3C(O)CHC(CH_3)NH=CH_2]^+$
98(32)	98(44)	98(24)	98(24)	98(20)	$[CH_3C(O)CHC(CH_3)NH]^+$
97(16)	105(54)				$[ZCO]^+$
43(32)	43(34)	43(21)	43(13)	43(18)	$[CH_3CO]^+$

[a]m/e values for the most abundant isotopes. Relative abundance of ions in parentheses. Meaning of X, Y and Z is the same as in Fig. 1.
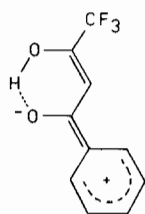

Fig. 2. One of the possible mesomeric structures of 1,1,1-trifluoro-4-phenylbutane-2,4-dione.

ing the enolization of the neighboring carbonyl group (Fig. 2).

HL^0 reacted readily with 2-ethoxymethylene-1,3-dicarbonyl compounds derived from pentane-2,4-dione, 1-phenylbutane-1,3-dione and ethyl 3-oxobutanoate to give H_2L^4 (X = H, Y = CH_3CO, Z = CH_3), H_2L^5 (X = H, Y = C_6H_5CO, Z = CH_3) and H_2L^6 (X = H, Y = $COOC_2H_5$, Z = CH_3) respectively. The ligands formed in high yield, due to easy aminolysis of the C−O bond of the ethoxymethylene group.

The infrared spectra of ligands exhibit a broad band of NH groups in the 3150−3400 cm^{-1} region, consistent with the ketoenamine structure of the ligands. ^{1}H nmr data of ligands are listed in Table II.

Assignment of resonances was based on spectra of partially-deuterated derivatives, double resonance experiments, and comparisons of spectra of the free ligands and their complexes. Irradiation of ligands H_2L^{1-6} with resonance frequencies of both enamine protons (d and g in Fig. 1) alters the shape of the ethylene bridge multiplet (protons e and f in Fig. 1). This indicates vicinal coupling between enamine and ethylene bridge protons, strongly supporting the hypothesis of the bis(ketoenamine) structure of ligands. Vicinal coupling of enamine proton g to the methine proton X in H_2L^4 and H_2L^6 results

in a splitting of the methine signal which in both compounds appears as doublet (the resonance of proton X in H_2L^5 is obscured by overlapping aromatic bands). This splitting disappears on irradiation of H_2L^4 and H_2L^6, with the resonance frequency of the enamine signal occurring at lower field, thus giving the immediate assignment of protons g and X. Spacing between lines of the aforementioned doublet equal to 13 Hz is comparable with the trans coupling constants in N-monosubstituted formamides (J = 11.6−13.6 Hz [13]), suggesting that methine proton X and enamine proton g are in a trans position as shown in Fig. 1. ^{1}H nmr spectra of partially deuterated ligands d-H_2L^1 and d-H_2L^2 comprising deuterated X and Y substituents were helpful in differentiating between the two methine resonances of protons in b and Y positions and between the resonance of the methyl group X and the singlets of protons a and c. Main peaks in mass spectra of ligands are listed in Table III.

The molecular peaks are of moderate abundance, the most abundant peaks arising from fragmentation within the ethylene bridge moiety. The m/e values are interpreted as fragments of the molecular ion of the structure presented in Fig. 1. Thus mass spectral data support the proposed structure of the ligands.

Characterization of the Complexes

Complexes of the fomrula ML^x (M = Cu, Ni, Pd, x = 1, 2, 4−6) and NiL^3 were obtained from preformed ligands and metal(II) acetates. After one recrystallization the complexes were analytically pure. Similarly to H_2L^1, complexes ML^1 (M = Cu, Ni, Pd) underwent rapid disproportionation in solution to ML^7 and ML^8 enhanced by the presence of a metal ion. Fortunately a distinct difference in solubility of complexation products allowed us

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

Compound	λ_{max}, nm ($\log \epsilon_{max}$)
CuL[1]	255(4.12), 273sh(3.96), 300(4.15), 554(2.13)
CuL[2]	233(4.39), 277(4.07), 317(4.32), 351(3.99), 544(2.36)
CuL[4]	227(4.05), 270(4.40), 303(4.25), 540(2.45)
CuL[5]	229(4.31), 288(4.32), 304(4.34), 542(2.49)
CuL[6]	246(4.42), 301(4.28), 540(2.43)
NiL[1]	233(4.41), 263(4.05), 348(3.61), 422sh(2.74), 568(1.84)
NiL[2]	233(4.52), 241(4.52), 265(4.19), 297(4.11), 371(3.70), 397(3.62), 432sh(3.35), 560(2.08)
NiL[3]	235(4.44), 344(3.72), 356sh(3.66), 432sh(2.86), 566(1.88)
NiL[4]	242(4.43), 285(4.30), 344(3.69), 358(3.70), 534(1.96)
NiL[5]	236(4.56), 300(4.10), 340(3.91), 350sh(3.87), 538(1.94)
NiL[6]	240(4.52), 268(4.45), 345(3.69), 357(3.70), 536(1.94)
PdL[1]	240sh(3.93), 307(3.68), 339(3.81)
PdL[2]	232sh(4.29), 290(3.99), 350(3.93)
PdL[4]	235(4.08), 270(4.31), 335(3.90)
PdL[5]	235(4.32), 296(4.13), 325sh(4.02)
PdL[6]	254(4.36), 336(3.91)

[a]10^{-3} M solutions in acetonitrile; sh denotes shoulder.

to isolate ML^1 complexes with no difficulty, though the yield was reduced considerably.

The infrared spectra of the complexes have no bands between 3100–4000 cm^{-1}, indicating the absence of enamine protons and water.

In solution all the nickel chelates reported here are square planar, as indicated by the absence of any absorption above 650 nm in the optical spectra (Table IV). Furthermore the ^1H nmr spectra of the complexes in deuterated chloroform show no contact shifts. Data collected in Table IV reveal that the electronic absorption spectra of copper complexes dissolved in acetonitrile are very similar and possess characteristic d–d transition in the 540–554 nm region. The spectral pattern resembles that of the copper complex with the 2:1 condensation product of pentane-2,4-dione and 1,2-diaminoethane CuL^7 (d–d transition at 540.5 nm [14]), which has been confirmed by X-ray crystallography to be essentially square planar [15]. It is reasonable to assume that the copper complexes reported here are square planar. All the palladium complexes studied in this paper were diamagnetic. Data from the ^1H nmr spectra of nickel(II) and palladium(II) chelates are collected in Table V.

An inspection of Table V shows that complexation of ligand removes the two low-field enamine resonances from the spectrum and moreover results in collapsing of the methine X doublet into singlet in ML^4 and ML^6. Spectra of palladium and nickel complexes with the same ligands are similar, however signals of palladium complexes are located at lower field. Similarly to what we reported earlier [6], the largest shift is observed for protons in close proximity to the palladium ion, namely for ethylene bridge and methine X in $ML^{4,6}$ protons.

In order to assign ^1H nmr signals in the complexes we utilized partially deuterated ligands and shifts induced by an incremental addition of Eu(fod)$_3$ and by benzene. The magnitudes of induced shifts are presented in Table V as slopes of lines evaluated by the least squares method for the relations: Eu(fod)$_3$ induced shift *versus* the molar ratio of the europium compound to the metal complex and benzene induced shift *versus* the v/v% of benzene in the mixed benzene–CDCl$_3$ solvent.

Planar tetradentate metal chelates are believed to act towards europium ions either as bidentate ligands *via* two *cis* oxygen atoms or as non-coordinating compounds when the substituents neighbouring oxygen donors are either bulky or electron-withdrawing [16]. In each of the ML^1 and NiL^3 complexes there is one electron-withdrawing trifluoromethyl group, so we believe that these compounds act as monodentate ligands towards europium coordinating via the oxygen of the acetyl group. Complexes of the formula ML^{4-6} comprise an additional carbonyl group in the substituent Y. The oxygen atom of this group is uncoordinated and conjugated with a charge-delocalized chelate ring. Carbonyl groups

TABLE V. ^{1}H Nmr Data for the Nickel and Palladium Complexes in $CDCl_3$ with HMDS as an Internal Reference.*

Compound	Chemical Shift δ, ppm										
	Methyl					Methylene		Methine			Aromatic
	a	c	X	Y	Z	e,f[h]	Y	b	X	Y	
NiL^1	1.79s B1.2	1.82s B6.8	1.90s B9.7			2.97s B10.5		4.80s B2.7		5.22s B2.5	7.00–7.25m
NiL^2	1.81s L0.5 B0.0	1.79s L1.1 B6.1	1.90s[i] L1.6 B6.4			3.04s B8.6		4.85s B1.6		5.52s[i] B1.4	7.40–7.65m
NiL^3	1.80s B1.3	1.80s B6.6				2.82m B9.2		4.85s B2.7		5.30s B0.0	6.96–7.11m 7.16–7.32m
NiL^4	1.84s L0.9 B0.8	1.84s L0.9 B6.8		2.15s L13.5 B3.3	2.33s L10.1 B0.0	3.09m B10.1		4.88s L0.9	7.33s L9.9		
NiL^5	1.84s L1.7 B0.9	1.84s L0.5 B7.4			2.10s L7.9 B0.3	2.99m B11.1		4.90s L1.0	7.08s L9.9		7.25–7.55m L7.9[k]
NiL^6	1.84s L1.6 B0.3	1.84s L0.4 B7.8		1.20t L2.8 B2.8	2.30s L5.2 B0.9	3.05m B11.3	4.04q L10.2	4.85s L0.9	7.45s L7.7		
PdL^1	1.95s B0.3	1.93s B6.1	2.00s B8.5			3.45s B9.1		4.81s B2.8		5.28s B2.4	
PdL^2	1.98s L3.4 B0.3	1.86s L1.8 B5.8	1.99s[i] L2.5 B5.7			3.43s B7.9		4.79s B1.7		5.43s[i] B1.4	7.10–7.28m 7.58–7.75m
PdL^4	1.96s L1.3 B1.0	1.94s L1.1 B6.8		2.25s L12.7 B3.5	2.44s L10.2 B0.3	3.46m B9.6		4.70s L1.2	7.64s L10.0		
PdL^5	1.98s L1.6 B0.9	1.93s L0.6 B7.7			2.18s L6.2 B0.0	3.39m B10.8		4.81s L0.7	– L9.3		7.19–7.60m L6.9[k]
PdL^6	1.94s L1.9 B0.5	1.91s L0.5 B7.0		1.21t L3.7 B2.3	2.44s L6.6 B1.1	3.44m B10.2	4.13q L13.6	4.79s L0.7	7.80s L10.1		

*L denotes the slope value multiplied by 10^{-2} for the relation of lanthanide induced shift (Hz) *versus* the molar ratio of $Eu(fod)_3$ to metal complex for the particular signal. B denotes the slope value multiplied by (-10^{-1}) for the relation of benzene induced shift (Hz) *versus* the v/v% concentration of benzene in $CDCl_3$. [h]Chemical shift of the singlet or the baricenter of symmetrical multiplet. [i]Signal disappears or reduces its intensity in the spectrum of deuterated derivative. [k]Doublet of doublets of aromatic protons in *ortho* position. [j]Signal obscured by overlapping aromatic bands. Meaning of a, b, c, e, f, X, Y, Z, s, t, q and m is the same as in Table II.

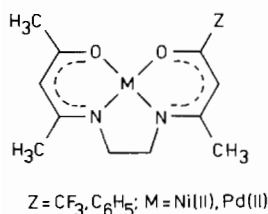Z = CF₃, C₆H₅; M = Ni(II), Pd(II)

Fig. 3. Structural formulae of complexes $ML^{1,2}$.

attached to charge-delocalized rings are unusually electron-rich, demonstrated recently [17] in studies on reactivity in chelate or macrocyclic systems. Therefore it seems reasonable to assume that ML^{4-6} complexes prefer to coordinate to europium through the oxygen of the Y side group.

Eu(fod)₃ induced shifts could be interpreted in terms of O-coordination of europium to the acetyl group in ML^1 and NiL^3 complexes and to the free carbonyl present in the side group Y of ML^{4-6} and in terms of a pseudocontact interaction between europium and hydrogen atoms. A pseudocontact mechanism predicts that the site of complexation would experience the largest shift and that induced shifts in axially symmetric complexes would be proportional to $(3\cos^2 - 1)/r^3$ [18]. This equation explains induced chemical shifts in ML^1, NiL^3 and ML^{4-6} but not in ML^2 complexes. The different mode of interaction of Eu(fod)₃ and ML^2 seems to arise from the unavailability of oxygen atoms to europium, owing to the steric effect of the phenyl group in the Z position.

To determine which resonance of the complex should be assigned to the methyl groups attached to the carbon atom bound with nitrogen, we utilized the observation that protons of substituents near the ethylene bridge and of the ethylene bridge itself in metal complexes with Schiff bases derived from 1,2-diaminoethane are shifted considerably upfield on addition of an aromatic solvent [19]. Upon addition of benzene to the CDCl₃ solution of $ML^{1,2}$ we observed an upfield shift of the two methyl and the ethylene bridge resonances. Two different possible stereochemistries for the condensation product of 1,1,1-trifluoropentane-2,4-dione and 1-phenylbutane-1,3-dione may arise because two carbonyl groups of each β-diketone are distinguishable and because condensation may occur at each of two carbonyl carbon atoms. The observed benzene-induced shifts suggest that two methyl groups in $ML^{1,2}$ complexes are in the vicinity of the ethylene bridge, so that in both cases the condensation occurred at the carbonyl carbon atom neighboring the methyl group (Fig. 3).

Consistent with the suggested stereochemistry is the downfield Eu(fod)₃ induced shift of the third methyl resonance observed in ML^1, which according
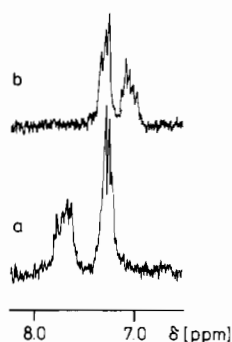

Fig. 4. ¹H nmr spectra of a) NiL^2 and b) NiL^3 in the aromatic protons region.

to the assumption of O-coordination of europium arises from methyl group bound to the carbonyl carbon atom. In order to distinguish the resonances of methyl groups X and c we prepared deuterated derivatives of NiL^2 and PdL^2 comprising the trideuteriomethyl group X (the preparation of deuterated ML^1 complexes failed due to rapid disproportionation of deuterated ligand $d-H_2L^1$ in the presence of metal ions). The disappearance of the lowest field methyl singlet from the spectra of ML^2 deuterated derivatives indicated that this signal should be assigned to the methyl group in position X.

The stereochemistry of $ML^{1,2}$ indicates that the carbonyl group near the trifluoromethyl or phenyl group is less reactive towards HL^0, thus the condensation occurs at the other carbonyl group. Although 1,1,1-trifluoro-4-phenylbutane-2,4-dione comprises both the less reactive groups we observed that it condenses with HL^0 to give the tetradentate ligand H_2L^3 which has been isolated in pure form and as the complex NiL^3. The question arises, which of the carbonyl groups underwent substitution. ¹H nmr spectra of NiL^2 and NiL^3, each comprising a phenyl group, differ considerably in the aromatic part (Fig. 4).

Two complex multiplets observed in the NiL^2 spectrum, one three-proton multiplet a little downfield from the chemical shift of benzene (δ = 7.23 ppm from HMDS) and the other strongly deshielded two-proton multiplet arising from *ortho* protons, are characteristic for monosubstituted benzene with a strongly deshielding group like a keto group [20]. In NiL^3 the aromatic pattern consists of a three-proton multiplet at the chemical shift of benzene and a two-proton one upfield from benzene, and is characteristic for a shielding group attached to the phenyl ring. The different substituent effect in NiL^2 and NiL^3 spectra suggests that unlike NiL^2 (Fig. 3) the phenyl group in NiL^3 is bound to the C—N group, as shown in Fig. 5. It is noteworthy to add that an incremental addition of benzene to NiL^3 in CDCl₃ solution results in an unequal
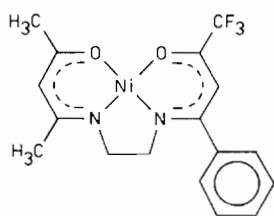
Fig. 5. Structural formula of NiL^3.

upfield shift of both methylene resonances of the ethylene bridge so the symmetrical multiplet observed at 2.82 ppm in CDCl$_3$ solution is gradually resolved to two well separated triplets at 1.80 and 2.12 ppm in pure benzene. Benzene also induces shifts of the methyl group c and methine group b resonances while the methine Y resonance remains unaffected. The observed asymmetry of benzene induced shifts may be explained by the steric effect of the phenyl group in position X interfering in the penetration of benzene molecules to this side of the ethylene bridge, which is closer to the bulky phenyl ring.

Interaction of Eu(fod)$_3$ with the free carbonyl group in ML$^{4-6}$ induces extensive downfield shifts of X, Y and Z resonances. On the other hand benzene induces upfield shifts of ethylene bridge and methyl c resonances. Combined results of those experiments immediately give the assignment of all signals. Benzene also induces an upfield shift of the additional methyl resonance in ML^4, though of different magnitude (Table V), which has been ascribed to the methyl group in the substituent Y on the basis of the carbonyl plane rule presented in [21]. The induced shift arises from the association between the benzene molecule and the free carbonyl group. Since in the case of ML^5 and ML^6 no induced shift of the other methyl resonances are observed, we concluded that these complexes assume the structure presented in Fig. 6, in which an oxygen atom of acetyl group is involved in coordination of metal ion whereas benzoyl and ethoxycarbonyl groups are the side substituents in Y position in the chelate ring.
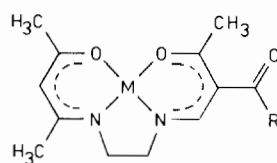
R = CH$_3$, C$_6$H$_5$, OC$_2$H$_5$; M = Ni(II), Pd(II)

Fig. 6. Structural formulae of complexes ML$^{4-6}$.

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