Inorganica Chimica Acta, 42 (1980) 197–202
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Unsymmetrical Schiff Base Complexes of Nickel(II) and Palladium(II)

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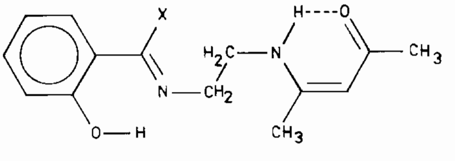
Received March 12, 1980

The unsymmetrical Schiff bases salicylaldehydeacetylacetoneethylenediimine (Hsal)(Hacac)en, o-hydroxyacetophenoneacetylacetoneethylenediimine-(Hhap)(Hacac)en, o-hydroxybenzophenoneacetylacetoneethylenediimine(Hhbp)(Hacac)en, and their nickel(II) and palladium(II) complexes have been synthesized and studied by different techniques. Mass, pmr and double pmr spectra suggest that the free Schiff bases comprise two different hybridized nitrogen atoms. Diamagnetism and spectral data of Ni(II) and Pd(II) chelates are consistent with their square-planar stereochemistry. Pmr spectra indicate that a conjugation between aromatic rings in Ni(hbp)(acac)en and Pb(hbp)(acac)en favours the keto-amine form of the aromatic part of complexes rather than the normal Schiff base struture. Pmr spectrum of Ni(sal)(acac)en studied over the –70 °C, +30 °C range suggests a high flexibility of the five-membered chelate ring.*

Introduction

Complexes of low symmetry are very important in biological systems as well as in industrial catalysis. They are interesting also from the theoretical point of view. Recently Kuska *et al.* [1] obtained several copper complexes with unsymmetrical Schiff bases by reacting a copper(II) salt with a mixture of the condensation products of acetylacetone, ethylenediamine and salicylaldehyde or its derivatives. Separation of unsymmetrical from symmetrical Schiff base complexes followed by crystallization. The interesting properties of unsymmetrical Schiff base complexes encouraged us to study the similar systems. This paper reports on syntheses and properties of the following unsymmetrical Schiff bases



(I) X=H, CH_3, C_6H_5

and their Ni(II) and Pd(II) chelates.

Experimental

Materials

Salicylaldehydeacetylacetoneethylenediimino-copper(II) Cu(sal)(acac)en, has been prepared according to the method described by Kuska *et al.* [1].

Salicylaldehydeacetylacetoneethylenediimine (Hsal)(Hacac)en

A sample of salicylaldehydeacetylacetoneethylenediimino-copper(II) Cu(sal)(acac)en (15.35 g, 0.05 mol) was dissolved in chloroform (500 cm^3) and stirred vigorously with a saturated aqueous solution (250 cm^3) of disodium ethylenediaminotetraacetate Na_2H_2Y at 40 °C. After 15 minutes of mixing the aqueous solution was replaced by a fresh portion of the Na_2H_2Y solution and the mixture stirred again. The process was repeated many times until the color of the chloroform layer changed from violet into a light green one. The chloroform solution was washed twice with water, dried over anhydrous magnesium sulphate and concentrated by evaporation of the solvent. The resulting oily residue was extracted several times with hot n-hexane. The collected extracts yielded upon standing 6.8 g of crystalline (Hsal)(Hacac)-en in the form of yellow needles, m.p. 71.5 °C (yield 55%). *Anal.* Calcd. for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N. 11.37. Found: C, 68.17; H, 7.44; N, 11.41.

o-Hydroxyacetophenoneacetylacetoneethylenediimine, (Hhap)(Hacac)en

To a solution of 27.2 cm^3 (0.2 mol) of o-hydroxyacetophenone and 20.0 cm^3 (0.2 mol) of acetyl-

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*Throughout this paper the terminology of Schiff bases and their complexes is similar to that used in earlier reports [1, 2] acetone in 400 cm^3 benzene at 70 °C was added 13 2 cm^3 (0.2) mol of ethylenediamine The reaction mixture was then refluxed in a flask equipped with a Dean-Stark trap and a condenser The Dean-Stark trap allowed to measure the amount of water formed in the reaction After removing of 7 2 cm^3 (0.4 mol) of water the reaction mixture was allowed to cool whereupon the symmetrical Schiff base (Hhap)$_2$-en deposited After filtration the solution was concentrated to a small volume and the partially crystalline residue dissolved in acetone Upon concentration a crystalline compound separated which was twice recrystallized from the same solvent to yield 7 6 g of chromatographically pure (Hhap)(Hacac)en (R_f = 0 43), m p 133 5 °C, in form of yellow prisms (yield 15%) *Anal* Calcd for $C_{15}H_{20}N_2O_2$ C, 69 20, H, 7 74, N, 10 76 Found C, 69 32, H, 7 75, N, 10 70

o-Hydroxybenzophenoneacetylacetoneethylenediimine, (Hhbp)(Hacac)en

To a boiling solution of 7 92 g (0 04 mol) of o-hydroxybenzophenone and 4 0 cm^3 (0 04 mol) of acetylacetone in methanol, was added 2 7 cm^3 (0 04 mol) of ethylenediamine and the mixture refluxed for 3 hours When cooled yellow crystals appeared The crystals were washed with methanol, dried and identified as (Hhbp)$_2$en (R_f = 0 72) The filtrate was concentrated to give a residue which was extracted repeatedly with 200 cm^3 portions of a hot benzene–n-hexane (1 5) mixture until no more material was being extracted The combined extracts yielded solid material which was recrystallized from the acetone, 1 11 g (9% yield) of yellow crystals of (Hhbp)(Hacac)en, m p 118 °C were obtained *Anal* Calcd for $C_{20}H_{22}N_2O_2$ C, 74 51, H, 6 88, N, 8 69 Found C, 74 40, H, 6 96, N, 8 79

Salicylaldehydeacetylacetoneethylenediiminonickel(II), Ni(sal)(acac)en

To the solution of 0 49 g (0 002 mol) of (Hsal)(Hacac)en in acetone (200 cm^3) was added 0 352 g (0 002 mol) of nickel(II) acetate tetrahydrate After approximately 3 hours of mixing at the room temperature the mixture became homogeneous Evaporation of the solvent yielded a solid residue which was recrystallized twice from benzene, 0 45 g of Ni(sal)(acac)en in form of light brown flakes which melt at 239 °C were obtained (yield 75%) *Anal* Calcd for $NiC_{14}H_{16}N_2O_2$ Ni, 19 37, C, 55 50, H, 5 32, N, 9 24 Found Ni, 19 32, C, 55 51, H, 5 37, N, 9 16

o-Hydroxyacetophenoneacetylacetoneethylenediimino-nickel(II)

Ni(hap)(acac)en was prepared by mixing methanol solutions of both nickel(II) acetate tetrahydrate (5 mmol in 40 cm^3) and the (Hhap)(Hacac)en (5 mmol in 85 cm^3) for 3 hours at room temperature The concentrated solution deposited crystals upon cooling which were filtered off and recrystallized from methanol to give 1 15 g of Ni(hap)(acac)en, m p 240 °C in the form of light brown needles with a metallic glance (yield 72%) *Anal* Calcd for $NiC_{15}H_{18}N_2O_2$ C, 56 83, H, 5 72, N, 8 84 Found C, 57 04, H, 5 63, N, 8 76

o-Hydroxybenzophenoneacetylacetoneethylenediimino-nickel(II)

Ni(hbp)(acac)en was prepared in a manner similar to that of Ni(hap)(acac)en The concentrated solutions separated a solid material which was recrystallized from the methanol–chloroform mixture (1 1) to give Ni(hpb)(acac)en, m p 275 °C in the form of dark brown crystals (yield 75%) *Anal* Calcd for $NiC_{20}H_{20}N_2O_2$ C, 63 37, H, 5 32, N, 7 39 Found C, 63 57, H, 5 35, N, 7 53

Salicylaldehydeacetylacetoneethylenediimino-palladium(II), Pd(sal)(acac)en

To the solution of 0 229 (0 001 mol) of palladium(II) acetate in acetone (100 cm^3), was added the Schiff base (Hsal)(Hacac)en 0 246 g (0 001 mol) dissolved in the same solvent (50 cm^3) After 4 hours of mixing the orange solution was concentrated in a rotary evaporator and the residue recrystallized twice from benzene, 0 19 g of orange crystals of Pd(sal)(acac)en were obtained (yield 53%) Upon heating the complex begins to decompose above 240 °C *Anal* Calcd for $PdC_{14}H_{16}N_2O_2$ C, 47 95, H, 4 60, N, 7 99 Found C, 47 87, H, 4 82, N, 7 86

o-Hydroxyacetophenoneacetylacetoneethylenediimino-palladium(II)

Pd(hap)(acac)en was prepared in a manner similar to that described for Pd(sal)(acac)en The crude product has been recrystallized from acetone to give yellow needles of Pd(hap)(acac)en (yield 70%) The compound begins to decompose above 240 °C *Anal* Calcd for $PdC_{15}H_{18}N_2O_2$ C, 49 40, H, 4 97, N, 7 68 Found C, 49 77, H, 4 91, N, 7 65

o-Hydroxybenzophenoneacetylacetoneethylenediimino-palladium(II)

Pd(hbp)(acac)en was synthesized in a manner similar to that of Pd(sal)(acac)en The crude product was recrystallized from the chloroform–acetone mixture (1 1) to yield Pd(hbp)(acac)en in the form of light orange needles (yield 72%) The compound decomposes above 240 °C *Anal* Calcd for $PdC_{20}H_{20}N_2O_2$ C, 56 28, H 4 72, N, 6 56 Found C, 56 44, H, 4 78, N, 6 61

TABLE I. Electronic Spectra of Unsymmetrical Schiff Bases and Their Nickel(II) and Palladium(II) Complexes in Methanol.

Compound	Absorption^a
(Hsal)(Hacac)en	254(4.02), 310(4.34), 405(2.60)
(Hhap)(Hacac)en	254(3.96), 311(4.33), 389(3.35)
(Hhbp)(Hacac)en	259(4.07), 313(4.36), 404(2.98)
Ni(sal)(acac)en	242(4.70), 330(3.90), 360(sh, 3.75) 420(sh, 3.40), 555(2.07)
Ni(hap)(acac)en	243(4.64), 321(3.82), 361 (sh, 3.68) 402(3.39), 557(2.07)
Ni(hbp)(acac)en	239(4.60), 335(3.86), 414(3.35) 450(sh, 3.20), 555(1.97)
Pd(sal)(acac)en	230(4.40), 258(sh, 4.20), 340(3.80), 400(sh, 3.40)
Pd(hap)(acac)en	236(4.51), 269(sh, 4.07), 340(3.82) 400(sh, 3.40)
Pd(hbp)(acac)en	336(3.87), 395(3.51)

^{a}The values given are in nm; the numbers in parentheses are log ϵ values; sh, shoulder.

Apparatus and Measurements

Mass spectra were recorded on Varian MAT 711 spectrometer. The proton magnetic resonance spectra were run on Tesla BS 487 80 MHz and Varian 220 MHz spectrometers.

U.v. and visible absorption spectra of ligands and chelates were recorded on a Perkin Elmer UV VIS 402 and a Cary 17 spectrophotometer at room temperature using silica cells.

Thermal stabilities of chelates were studied on a Paulik–Paulik type OD 103 Derivatograph.

In the thin layer chromatography were utilized: silica gel G Merck, the mixture 50% acetone–50% hexane as a chromatographic solvent, and ferric chloride as a reagent for ligands containing the free phenolic hydroxyl group. All reported R_f data were obtained by using the above chromatographic system.

Results and Discussion

Thin layer chromatography studies have shown that condensation of acetylacetone and salicylaldehyde or o-hydroxyacetophenone or o-hydroxybenzophenone with ethylenediamine in boiling benzene or methanol yields a mixture of two symmetrical and one unsymmetrical Schiff bases. Separation of the unsymmetrical products occurred either by fractional crystallization of condensation products or of their copper(II) complexes with subsequent elimination of the copper ion in the following reaction:

$$\mathrm{Cu(sal)(acac)en} + \mathrm{H_2Y^{2-}} = \\ = \mathrm{CuY^{2-}} + \mathrm{(Hsal)(Hacac)en}$$

The unsymmetrical Schiff bases (Hsal)(Hacac)en, (Hhap)(Hacac)en, and (Hhbp)(Hacac)en are beautiful crystalline compounds soluble in most organic solvents. In water they are unstable towards hydrolysis particularly in acidic and basic solutions. Their nickel(II) and palladium(II) complexes are colored diamagnetic solids and are of moderate solubility in most solvents. Thermogravimetric studies showed that the nickel(II) chelates are more thermally stable than those of palladium(II).

Electronic Spectra

Absorption spectra of the free Schiff bases dissolved in methanol are characterized by three intensive bands. The low energy band shows X-subsitutuent and solvent dependence. The nickel complexes show two or three uv bands and moreover two or three visible absorption bands due to d–d transitions. No absorption bands were observed at about 1000 nm or higher wavelengths where the octahedral or tetrahedral nickel(II) complexes are expected to absorb. Diamagnetism and the spectrophotometric properties are consistent with a square-planar structure of nickel chelates.

The palladium(II) chelates are diamagnetic in the solid state and in solution. This indicates that they take planar four coordinated structure as well. The obtained electronic spectra do not reveal separate bands which could be assigned to d–d transitions. These are considered to be hidden by strong ligand and charge transfer bands in the uv region.

Pmr Spectra

Table II lists pmr resonances of free ligands and their complexes and assignments. It was shown earlier [2] that bis(acetylacetone)ethylenediimine (Hacac)$_2$en exists in solutions in appreciable amounts in the ketoenamine form. If we assume a ketoenamine structure for the acetylacetone moiety of Schiff bases studied in this work [as shown in (I)] we might expect a coupling between protons of the sec. amino group and the neighbouring methylene group of the ethylene bridge. Such coupling was observed in pyrrole [3] and N-methylformamide [4]. Consistent

TABLE II. Pmr Spectra of Unsymmetrical Schiff Bases and Their Nickel(II) and Palladium(II) Complexes.

Compound	a	b	c	e	f	g	h
(Hsal)(Hacac)en[i,n]	12.78 s	10.95 s	8.36 s	7.48–6.75 m	4.91 s	3.86–3.36 m	1.88 s 1.78 s
(Hhap)(Hacac)en[i,n]	15.43 s	10.78 s		7.44–6.47 m	4.80 s	3.60–3.43 m	2.12 s 1.81 s 1.75 s
(Hhbp)(Hacac)en[i,n]	14.83 s	10.75 s		7.54–6.55 m	4.80 s	3.34 s	1.82 s 1.71 s
Ni(sal)(acac)en[j,p]			7.405 s	7.18–7.04 m 6.737 d 6.479 t	4.954 s	3.346 t 3.046 t	1.862 s 1.842 s
Ni(sal)(acac)en[j,n]			7.402s	7.14–7.02 m 6.921 d 6.485 t	4.949 s	3.372 t 3.076 t	1.928 s 1.874 s
Ni(hap)(acac)en[i,n]				7.30–6.22 m	4.78 s	3.40 t 3.05 t	2.12 s 1.82 s 1.60 s
Ni(hbp)(acac)en[i,n]				7.38–5.99 m	4.79 s	2.82 t	1.80 s 1.71 s
Pd(sal)(acac)en[i,n]			7.41 s	7.22–6.26 m	4.75 s	3.59 t 3.35 t	1.89 s 1.80 s
Pd(hap)(acac)en[k,n]				7.32–6.25 m	4.68 s	3.36 t 3.59 t	2.05 s 1.85 s 1.65 s
Pd(hbp)(acac)en[i,n]				7.46–6.05 m	4.80 s	3.13 s	1.92 s 1.80 s

Chemical shifts for the [a]OH, [b]NH, [c]azomethine, [e]aromatic, [f]vinyl, [g]ethylene bridge, [h]methyl protons in ppm downfield from [i]hexamethyldisiloxane or from [j]TMS. [i]A 80 MHz spectrum. [j]A 220 MHz spectrum. [n]$CDCl_3$ solvent. [p]CD_2Cl_2 solvent. Key: s, singlet; d, doublet; t, triplet; m, multiplet.

with our expectations are the results of double resonance experiments. On irradiating the sample of (Hsal)(Hacac)en at the resonance frequency of the amino hydrogen, the multiplet of the CH_2–CH_2 protons becomes better resolved (Fig. 1). Irradiating at other resonance frequencies does not influence the spectrum. A slight concentration induced chemical shift was observed for the protons of the hydroxyl group of the aromatic part of the ligands indicating that this group may participate in the intermolecular hydrogen bonding. Complexation of (Hsal)(Hacac)en and (Hhap)(Hacac)en results in the disappearance of the OH and NH proton signals and a transformation of the multiplet of the ethylene bridge protons into two separate triplets.

Results of complexation of the (Hhbp)(Hacac)en are somewhat different. The bridge signals in Ni(hbp)(acac)en and Pd(hbp)(acac)en are shifted to more shielded positions and appear as one narrow 'triplet' or singlet respectively.

Structural studies on the bis(acetylacetone)ethylenediiminocopper(II), $Cu(acac)_2en$, showed [5] that the copper complex is approximately planar, except for the gauche configuration of the ethylene bridge. If the conformations of the five-membered chelate rings in M(sal)(acac)en and M(hap)(acac)en were similar to that of $Cu(acac)_2en$ the pmr spectra of Ni and Pd chelates would be more complex than observed due to the nonequivalence of the CH_2–CH_2 protons in their axial and equatorial positions with respect to the N–M–N plane. Buckingham and Stevens [6] predicted large deshielding effect for protons situated above the plane of square-planar d^8 systems. The spectra obtained in this work suggest that the both methylene groups are in different environments and that there is a rapid inversion of the five-membered chelate ring changing one puckered ring conformation into another so that average signals are observed. The ring inversion barrier seems to be relatively low since the pmr spectra are almost insensitive to variable temperature experiment ($CDCl_3$ solutions, temp. range –70 °C–+30 °C). The chemical nonequivalence of the bridge protons may be understood if we assume that in M(sal)(acac)en and M(hap)(acac)en the methylene groups are linked to different hybridized nitrogen atoms as shown in (II). The different both the electronic effects and magnetic anisotropies of the two nitrogen atoms may account for the different chemical shifts of protons of both CH_2 groups. Substituting of the phenyl group

TABLE III. Monoisotopic[a] Mass Spectra for Unsymmetrical Schiff Bases and Their Nickel(II) and Palladium(II) Complexes (70 eV).

(Hsal) (Hacac)en	(Hhap) (Hacac)en	(Hhbp) (Hacac)en	Ni (sal) (acac)en	Ni (hap) (acac)en	Ni (hbp) (acac)en	Pd (sal) (acac)en	Pd (hap) (acac)en	Pd (hbp) (acac)en	Interpretation
246(52)[b]	260(27)	322(36)	302(100)	316(100)	378(100)	350(79)	364(100)	426(39)	Mol. ion
203(34)	217(27)	279(20)	259(2)	273(3)	335(5)	307(2)	321(2)	383(2)	Mol. ion − 43
			191(5)	205(3)	267(24)	239(5)	253(9)	315(23)	$MOC_7H_4(X)NCH_2^+$
			169(99)	169(61)	169(37)	217(73)	217(51)	217(9)	$MOC_5H_7NCH_2^+$
147(16)	161(30)	223(18)							$HOC_7H_4(X)NCHCH_2^+$
134(38)	148(90)	210(100)							$HOC_7H_4(X)NCH_2^+$
			132(7)	146(7)	208(9)	132(79)	146(88)	208(100)	$OC_7H_4(X)NCH^+$
122(30)	136(100)	198(93)							$HOC_7H_4(X)NH_2^+$
			105(2)	119(2)	181(15)	105(3)	119(8)	181(16)	$OC_7H_4X^+$
125(38)	125(38)	125(20)							$OC_5H_7NHCHCH_2^+$
112(100)	112(85)	112(65)							$OC_5H_7NHCH_2^+$
						110(100)	110(78)	110(8)	$OC_5H_7NCH^+$
107(22)	107(71)	107(20)							$C_5H_6NCHCH_2^+$
			58(10)	58(5)	58(6)	106(6)	106(21)	106(3)	M^+

[a] The m/e values for the most abundant isotopes. [b] The numbers in parentheses are the relative abundances. Table lists only the most important peaks.

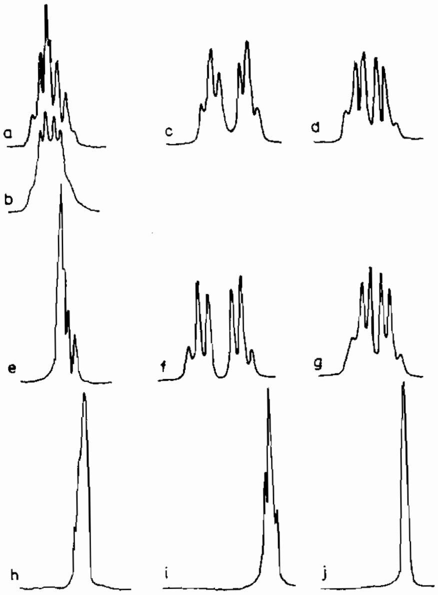
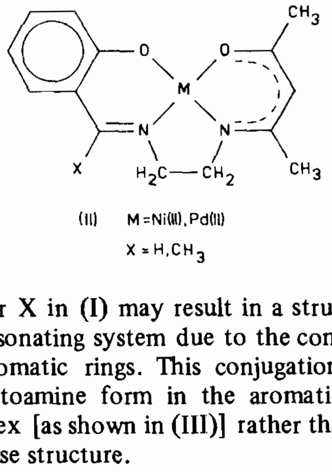
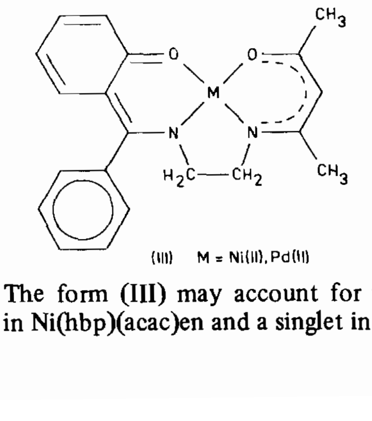


Fig. 1. The ethylene bridge signals in the 80 MHz spectra of [a](Hsal)(Hacac)en, [b](Hsal)(Hacac)en after irradiating at the resonance frequency of the amino hydrogen in double resonance experiment, [c]Ni(sal)(acac)en, [d]Pd(sal)(acac)en, [e](Hhap)(Hacac)en, [f]Ni(hap)(acac)en, [g]Pd(hap)(acac)en, [h](Hhbp)(Hacac)en, [i]Ni(hbp)(acac)en, [j]Pd(hbp)(acac)en in $CDCl_3$.



(II) M = Ni(II), Pd(II)
X = H, CH_3

for X in (I) may result in a structural change in the resonating system due to the conjugation of the both aromatic rings. This conjugation would favour the ketoamine form in the aromatic part of the complex [as shown in (III)] rather than the normal Schiff base structure.

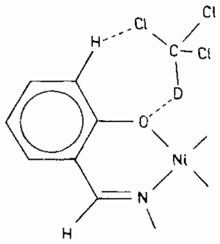


(III) M = Ni(II), Pd(II)

The form (III) may account for the narrow 'triplet' in Ni(hbp)(acac)en and a singlet in Pd(hbp)(acac)en.

Pmr resonances of the ethylene bridge protons are noticeably changed by a substitution of Pd for Ni in chelates, the radius of the former being about 10% larger than that of Ni. This could cause a lessening of the puckering of the ethylene bridge with consequent changes in the proton resonance.

Some resonance frequencies of chelates are slightly solvent dependent. A replacement of deuterated methylene chloride by deuterated chloroform results in a downfield shift in Ni(sal)(acac)en about 0.18 ppm of the 6.737 ppm doublet assigned to the aromatic proton attached in position 3, and a shift of methyl group resonances with changing their separation from 0.020 ppm in CD_2Cl_2 to 0.054 ppm in $CDCl_3$. It is likely that the former change is mainly due to the molecular interaction between $CDCl_3$ and Ni(sal)(acac)en with a formation of intermolecular hydrogen bonding involving an aromatic proton (IV)



(IV)

Mass Spectra

To receive additional information on the structure of ligands and complexes we studied their mass spectra. The results are summarized in Table III.

Molecular ions of ligands are of moderate abundance. Occurrence of m/e 43 and LH–43 ions may suggest a ketoenamine structure for ligands in which the terminal group is the acetyl group as shown in Formula I. The most abundant ions arise from the C–C and C–N fissions of the $N\text{–}CH_2CH_2\text{–}N$ moiety. Metal complexes gave mass spectra with strong molecular ion peaks. A major ion dissociation reaction involves fission of the $CH_2\text{–}CH_2$ carbon–carbon bond to give the following metal containing species ML_2–132–X and ML_2–111 where X is H, CH_3 and C_6H_5 respectively. It is interesting to note that the $(O)C_6H_4C(X)^+$ ion which would result from fissions of the M–O and C=N or C–N bonds in (II) and (III) is more abundant for the compound (III) (R.A. = 16%) in which X = C_6H_5 than for compounds (II) (R.A. below 3%) with X = H or CH_3. The higher relative abundance of this fragmentation in the former compound is consistent with the ketoamino structure for the M(hbp)(acac)en complexes [Formula (III)]. A conspicuous difference between the mass spectra of nickel and palladium chelates is that the spectra of the latter chelates contain many non-metal containing ions; the most abundant being 131 + X, 110 and 43. Lack of palladium in the most abundant ions (except of molecular ion) may be due to a relative ease of reduction of this metal to the zerovalent state in the fragmentation process.

Acknowledgement

We wish to thank mgr Maria Skonieczna for her experimental assistance at the earlier stage of the present work.

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