



Bis-Chelated Palladium (II) Complexes with Oxygen-Donor Chelating Ligands: Synthesis and Structural elucidation

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Abstract

Palladium(II) complexes with nine carboxy amide ligands viz. 4-(2-acetylhydrazino)-4-oxobut-2-enoic acid (AOBEH), 4-(2-acetylhydrazino)-4-oxobutanoic acid (AOBAH), 2-[(2-acetylhydrazino)carbonyl]benzoic acid (AHCBH), 4-[(2-cyanophenyl)amino]-4-oxobut-2-enoic acid (COBEH), 4-[(2-cyanophenyl)amino]-4-oxobutanoic acid (COBAH), 2-[[[(2-cyanophenyl)amino]carbonyl]benzoic acid (CACBH), 4-(1*H*-benzimidazol-2-ylamino)-4-oxobut-2-enoic acid (BOBEH), 4-(1*H*-benzimidazol-2-ylamino)-4-oxobutanoic acid (BOBAH) and 2-[(1*H*-benzimidazol-2-ylamino)carbonyl]benzoic acid (BYCBH) have been synthesized and characterized by elemental analysis, magnetic moments, molar conductivity, thermal studies, infrared, ¹H NMR and electronic spectral data.

Keywords: palladium (II) complexes, chelating amide ligands, synthesis, characterization

Introduction

The palladium (II) complexes of amide group containing ligands are of great interest because of their biological importance [1]. It has been attracted the attention of the chemists to synthesize the coordination compounds of transition metal ions with the ligands containing amide and to study the structure, anti-fungal, antibacterial and physiological activity of the ligands and their metal complexes [2-5]. In addition to the biological activity of the amide group containing ligands show diversified coordinating behavior in their metal complexes. According to the studies of Kroneck and co-workers [6] the diverse coordinating behavior of amide group in the complexes not only depends on the nature of the metal ion but also on the C-terminal and the N-terminal substituents of the amide (-CO-NH-) group. The involvement of carboxyl group in the chelation depends upon the second donor atom at the correct spacing for the formation of a stable chelate ring [7, 8]. Keeping the above facts in view, we have continued our research work on transition metal complexes with amide ligands [9-13] and we here with report the synthesis and characterization of nine Pd(II) complexes with carboxyamides. All these complexes were characterized by elemental analysis, magnetic moments, molar conductivity, thermal studies, infrared, ¹H NMR and electronic spectral data.

Materials and Methods

Experimental

All the chemicals used in the study were of AR grade. The ligands used in complexation were prepared by reported methods [9]. The solvents diethyl ether and methanol were distilled by standard procedures before use. The nine amide ligands, their complexes were synthesized and characterized by elemental analyses, IR, NMR and mass spectral data. The melting points of all the amide ligands and their metal complexes were obtained on a Buchi- 510 melting point apparatus. The percentages of carbon, hydrogen, nitrogen in metal complexes were determined using a Perkin-Elmer CHN analyzer at 240C. Gouy balance calibrated with Hg [Co(NCS)₄] was used for the determination of magnetic susceptibilities of complexes in solid state at room temperature. Conductance measurements were done on 10⁻³ M solution of compounds in dichloromethane at room temperature using Digisun Digital conductivity meter model DL-909. TG-DSC thermograms were recorded on Mettler-TA-2000C model. The IR spectra were recorded in KBr pellets on Perkin Elmer-283 spectrophotometer. The scanning rate was 6 min. in the range of 4000-200 cm⁻¹. UV-Visible spectra were recorded with Shimadzu UV-160A, a UV-Visible double beam spectrophotometer with matched quartz cells of path length 1 cm.

Synthesis of Pd(II) complexes

A general method was adopted in the preparation of the Pd(II) complexes of all nine amide ligands due to the similarity in the properties. A solution of PdCl₂ (0.354 g, 0.002 mole) in 0.1M HCl (30 ml) was added to a solution of the ligand (0.004 mole) in methanol (30 ml) with constant stirring and heating. The yellow colored precipitate formed was digested over a hot water bath for 2 hr. It was suction filtered, washed with methanol and dried in vacuum over anhydrous calcium chloride (yield 80-89%). The product was found to be TLC pure in 2:8 mixtures of chloroform and methanol tested in perpendicular direction.

Results and Discussion

All the Pd(II) complexes are crystalline yellow solids. The complexes are non-hygroscopic and stable up to 230°C. They are freely soluble in DMF and DMSO whereas moderately soluble in methanol.

Elemental analysis

The analytical and physical data of the Pd(II) complexes are presented in Table-1. It is clear from the table that the experimental values are in good agreement with the calculated values, supporting the molecular formulae proposed to the complexes.

Conductance measurements

The molar conductance values (Table-1) of all the complexes in DMF measured at 10⁻³ M concentration are in the range of 7-13 mho-mole⁻¹-cm² suggesting that they are non-electrolytes [14].

Thermal analysis

The thermal analysis data of Pd(II) complexes (Table-1) indicates that they are stable up to 230°C and hence exist in anhydrous state. The DSC curves show no endothermic peaks up to 230°C confirming the absence of lattice or coordinated water molecules in the complexes [15, 16]. The sharp decomposition corresponding to the loss of organic moiety in complexes can be seen in the DSC curves which contained one sharp exothermic peak falling in the range of 231-

328°C. The final product of decomposition of all the complexes above 750°C corresponds to metal oxide. Taking the loss of organic moiety as the decomposition temperature, the thermal stability of the palladium (II) complexes can be represented with respect to ligands as BYCBH > BOBAH > BOBEH > CACBH > COBAH > COBEH > AHCBH > AOBHAH > AOBHEH. Though it is difficult, every time, to explain the order of thermal stability in terms of the structure and the nature of the ligand this order can be explained, to some extent, on the basis of the steric factors such as bulkiness of the groups attached to the ligating groups, labile nature of ligand bonds and the number of chelate rings formed by each ligand [17, 18].

Table 1. Physical and analytical data of Pd(II) complexes

Complex Color	Decomp. Temp (°C)	Found (Calcd)%				Λ M
		C	H	N	M	
[Pd(AOBEH) ₂] Yellow	239	32.05 (32.12)	3.05 (3.15)	12.55 (12.49)	23.65 (23.71)	9.0
[Pd(AOBHAH) ₂] Yellow	246	31.75 (31.84)	3.98 (4.01)	12.40 (12.38)	23.40 (23.50)	12.0
[Pd(AHCBH) ₂] Yellow	244	43.65 (43.77)	3.25 (3.31)	10.25 (10.21)	19.30 (19.39)	11.0
[Pd(COBEH) ₂] Dark Yellow	247	49.20 (49.23)	2.65 (2.63)	10.40 (10.44)	19.75 (19.82)	8.0
[Pd(COBAH) ₂] Dark Yellow	258	48.80 (48.86)	3.15 (3.35)	10.25 (10.36)	19.60 (19.67)	13.0
[Pd(CACBH) ₂] Dark Yellow	254	56.60 (56.58)	2.78 (2.85)	8.75 (8.80)	16.65 (16.71)	13.0
[Pd(BOBEH) ₂] Light Yellow	231	46.55 (46.62)	2.80 (2.85)	14.85 (14.83)	18.65 (18.77)	7.0
[Pd(BOBAH) ₂] Light Yellow	236	46.30 (46.29)	3.50 (3.53)	14.80 (14.72)	18.70 (18.64)	11.0
[Pd(BYCBH) ₂] Light Yellow	237	54.10 (54.03)	2.99 (3.02)	12.65 (12.60)	15.98 (15.95)	10.5

Infrared spectra

The IR spectral data of nine Pd(II) complexes and respective ligands corresponding to important absorption bands are given in Table-2. The comparison of the absorption bands of the ligands and their complexes yielded the identification of the bonding sites of the ligands in the Pd(II) complexes. In the IR spectra the bands due to amide $\nu(\text{C}=\text{O})$ mode at 1660-1670 cm^{-1} for the free ligands are shifted to lower frequency 25-40 cm^{-1} while the amide $\nu(\text{C}-\text{N})$ shifted to higher frequency in all the complexes indicating the non-involvement of the amide nitrogen and involvement of the carbonyl oxygen of the amide group in coordination with the metal ion [12, 19]. The absorption bands around 1700 cm^{-1} and 1300 cm^{-1} in the free ligands attributed to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{OH})$ of the carboxyl group [20]. They are replaced by bands around 1550 cm^{-1} and 1380 cm^{-1} corresponding to $\nu(\text{COO})_{\text{asy}}$ and $\nu(\text{COO})_{\text{sym}}$ (i.e. asymmetric and symmetric stretching modes respectively) in all the nine complexes. The broad $\nu(\text{O}-\text{H})$ and $\delta(\text{O}-\text{H})$ bands of carboxylic group spreading near 3100 cm^{-1} and 900 cm^{-1} in the free ligands disappeared in all the complexes indicating the deprotonation and coordination of carboxyl group to the metal ion. Two new bands in the region of 350-420 cm^{-1} assignable $\nu(\text{Pd}-\text{O})$, which are absent in the free ligands, appeared in the spectra of all the complexes. This indicates the deprotonation and

involvement of carboxylic group in complexation [21, 22] and also confirms the coordination of amide group via carbonyl oxygen in all the complexes.

Table 2. Selected IR bands of Pd(II) complexes

Complexes	$\nu_{\text{N-H}}$	ν_{CO} (amide)	ν_{COO^-} (asym)	ν_{COO^-} (sym)	$\nu_{\text{C-N}}$	$\nu_{\text{M-O}}$
[Pd(AOBEH) ₂]	3300-3100	1620	1540	1380	1595	350
[Pd(AOBAH) ₂]	3400-3300	1625	1550	1375	1590	380
[Pd(AHCBH) ₂]	3450-3250	1630	1530	1370	1605	360
[Pd(COBEH) ₂]	3400-3200	1620	1560	1385	1585	370
[Pd(COBAH) ₂]	3350-3250	1635	1550	1380	1590	400
[Pd(CACBH) ₂]	3350-3280	1640	1540	1385	1580	420
[Pd(BOBEH) ₂]	3260	1625	1550	1370	1610	380
[Pd(BOBAH) ₂]	3380	1635	1500	1385	1600	395
[Pd(BYCBH) ₂]	3330-3310	1640	1540	1380	1595	360

PMR spectra

The PMR spectral data of all the ligands and their Pd(II) complexes are presented in Table-3. A comparison of the PMR spectra of the ligands and their complexes helped in identifying the coordination sites of the ligands in their complexes. The PMR spectra of all the nine palladium (II) complexes show the disappearance of the signal corresponding to carboxylic protons indicating the deprotonation of the carboxyl groups and the coordination of the carboxylate ions to the metal ion in the complexes [23]. Relatively small down field shift (0.05-0.20 δ) observed in the signal of amide proton of all the palladium (II) complexes compared to the ligands indicates the non-coordination of the amide nitrogen to the metal ion in the complexes [23]. No additional signal observed around 5.00 δ in the three palladium (II) complexes compared to the ligands indicates the absence of lattice or coordinated water in the complexes.

Table 3. ¹HNMR spectral data of Pd(II) complexes

Complexes	¹ HNMR bands	
	Amide proton(δ)	Aromatic protons(δ)
[Pd(AOBEH) ₂]	5.05-5.65(4H, s-br)	--
[Pd(AOBAH) ₂]	5.25-5.45(4H, s-br)	--
[Pd(AHCBH) ₂]	5.20-5.40(4H, s-br)	7.22-7.80(8H, m)
[Pd(COBEH) ₂]	6.50-6.90(2H, s-br)	7.10-7.60(8H, m)
[Pd(COBAH) ₂]	6.20-6.50(2H, s-br)	7.35-8.01(8H, m)
[Pd(CACBH) ₂]	6.50-6.80(2H, s-br)	7.05-8.06(16H, m)
[Pd(BOBEH) ₂]	5.70-5.90(4H, s-br)	7.10-7.80(8H, m)
[Pd(BOBAH) ₂]	5.65-5.85(4H, s-br)	7.25-7.84(8H, m)
[Pd(BYCBH) ₂]	5.70-6.00(4H, s-br)	7.05-8.09(16H, m)

Magnetic moments

All Pd(II) complexes were found to be diamagnetic as expected for square planar complexes. The diamagnetic nature of complexes was further confirmed by the sharp well defined signals in the PMR spectra.

Electronic spectra

The electronic spectra of the Pd(II) complexes were recorded in DMF. Theoretically three ligand field bands are expected for square planar Pd(II) complexes in the regions of 14500-16500, 18000-22000 and 24000-27000 cm^{-1} , but all these three are not observed in most of the complexes. The Pd(II) complexes prepared have been found to show a broad d-d transition band in the region of 21130-21760 cm^{-1} assignable to ${}^1B_{1g} \leftarrow {}^1A_{1g}$ transition typical for the square planar geometry [24, 25]. Further a relatively strong charge transfer band has been observed in the spectra of all the Pd(II) complexes in the range of 34750 - 36330 cm^{-1} . From the electronic spectral data and the diamagnetic behavior of the complexes square planar geometry has been proposed to all the Pd(II) complexes.

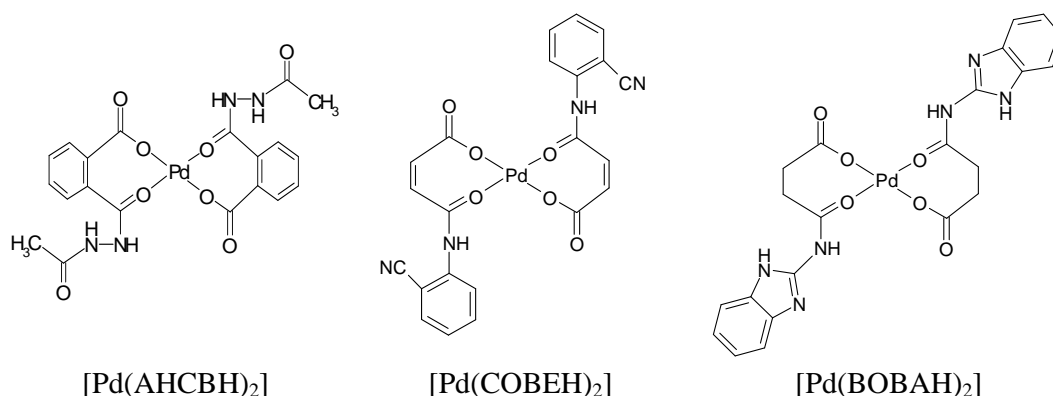


Figure 1. The representative structure of Pd(II) complexes

Conclusion

In the present investigations nine palladium (II) complexes with coordinated amides have been synthesized and characterized by elemental analysis, magnetic moments, molar conductivity measurements, thermal studies, infrared, ${}^1\text{H}$ NMR and electronic spectra. On the basis of the above data square planar structures are tentative proposed to all the palladium complexes.

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