

Novel unsymmetrical tetradentate Schiff base complexes of cobalt (II) and palladium (II) with N_2O_2 donor sets

Davar M. Boghaei* and Sajjad Mohebi

Department of Chemistry, Sharif University of Technology, P.O. BOX 11365 - 9516 Tehran, Iran

J. Chem. Research (S),
2001, 224–226
J. Chem. Research (M),
2001, 0660–0688

The novel unsymmetrical tetradentate Schiff base complexes of Co(II) and Pd(II) with the general formula $M(\text{Sal.Phen.Acac.})$ and $M(\text{Sal.Phen.Naph.})$, have been synthesised by template and non-template method.

Keywords: cobalt, palladium, nonsymmetrical N_2O_2 Schiff base complexes

Metal complexes of Schiff bases have contributed widely to the inorganic chemistry of chelate systems. Recently, particular attention has been paid to the complexes of tetradentate diamino bases such as N_2O_2 systems.^{2–4} It is noteworthy that the nonsymmetrical complexes lie between the symmetrical ones in many of their properties. Many of these transition metal complex derivatives of Schiff base have been prepared and investigated, with particular emphasis on the reactivity of metal ions in transmethylation reactions and the reversible absorption of molecular oxygen. In some chemical processes they are used as catalysts, and also as biological models in understanding the structure of biomolecules and biological process.⁵ In the course of our study of transition metal complexes with aromatic unsymmetrical quadridentate Schiff bases, we have looked for convenient methods for the synthesis of such compounds. In the present study complexes with general formula of $M(\text{Sal.Phen.Acac.})$, $M(\text{Sal.Phen.Naph.})$; ($M = \text{Co (II)}$, Pd (II)) were synthesised and characterised. In the previous paper we reported the synthesis of Cu (II) and Ni (II) complexes.⁶ Now we reported a modified method, described in the experimental section for the synthesis of a mono Schiff base (half-unit) by condensation of 2-hydroxy-1-naphthaldehyde or acetylacetone with *o*-phenylenediamine (HA^1 , HA^2). Unsymmetrical Schiff bases H_2A^3 and H_2A^4 were then obtained by the reaction of the half-units with salicylaldehyde. The corresponding Co (II) and Pd (II) complexes were then synthesised and characterised.

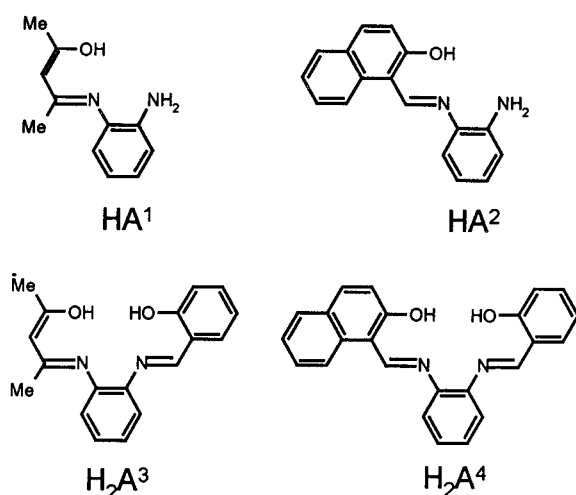


Fig. 1 Half-units HA^1 and HA^2 ; H_2A^3 and H_2A^4 ligands.

The reaction of salicylaldehyde with the precursors HA^1 and HA^2 were monitored by $^1\text{H NMR}$ spectrometry. Comparing $^1\text{H NMR}$ spectra, which are taken in the same condition, the chemical shift of NH_2 in HA^1 is less than for that of HA^2 . The result also shows that the reactivity toward salicylaldehyde generally follows the decrease in NH_2 proton acidity $\text{HA}^2 > \text{HA}^1$. This increase follows as the increase in electron-withdrawing properties of the aromatic ring, which decrease the electron-density at the site of electrophilic attack, thus inhibiting the condensation. The H_2A^3 , H_2A^4 ligands were isolated as yellow-orange solids and characterised by IR, $^1\text{H NMR}$, and elemental analysis C, H, N. The ligands were then used without further purification to prepare the metal complexes.

It was also possible to prepare those mentioned complexes by *in situ* reactions (Template method). In our previous work, we used this unique method to synthesise the nickel unsymmetrical Schiff bases complexes.⁶ However, in this work, the yield of the non-template reactions were more than those of the template methods. MA^x complexes ($x = 1, 2$) were obtained by template reaction and attempts to obtain the free ligands were unsuccessful. The elemental analysis and physical properties of the ligands and their complexes are listed in Table 1.

IR spectral data of the compounds show that, several IR absorption bands in the $1450\text{--}1650\text{ cm}^{-1}$ region can be attributed to the $\text{C}=\text{O}$, $\text{C}=\text{N}$, $\text{C}=\text{C}$ stretching vibrations of the coordinate ligand molecule.¹⁰ The infrared spectra of the "half units" (HA^1 , HA^2) show bands at 3338 and 3275 cm^{-1} . These bands are assigned to the primary amine stretching. An intense sharp band at 1615 cm^{-1} in the spectrum of H_2A^3 and a broad intense band at 1623 cm^{-1} in the H_2A^3 are assigned to azomethine vibrations. The lack of a band due to the free OH stretching vibration in the spectra of HA^1 , HA^2 , H_2A^3 and H_2A^4 is consistent with the finding of Kovacic that "intermolecular hydrogen bonding results in the formation of a stable six-membered ring for the condensation product of salicylaldehyde and aniline".^{5b} The infrared spectra of the complexes have no bands between 3100 and 4000 cm^{-1} , indicating the absence of enamine protons and water.¹ The absorption

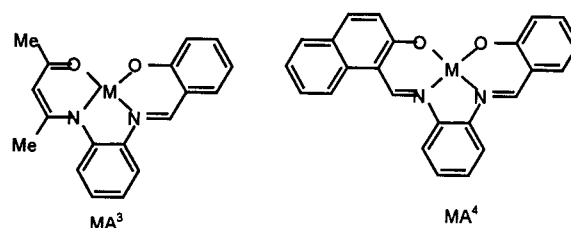


Fig. 2 The unsymmetrical Schiff base complexes MA^3 , MA^4 ; $M = \text{Co(II)}$ or Pd(II) .

* To receive any correspondence. E-mail dboghaei@sina.sharif.ac.ir

Table 1 Analytical data of the ligands and their complexes

NO.	Compound formula	M.P./°C (dec.)	Colour	Yield ^a /%	Found (calcd.)/%		
					C	H	N
1	HA ¹	viscose liquid	Yellow	50–80		ND	
2	H ₁₄ C ₁₁ N ₂ O ₁	162	Yellow	55–60		ND	
	HA ²						
3	H ₁₄ C ₁₇ N ₂ O	185	Yellow	85–90	73.21	7.51	9.56
	H ₂ A ³						
4	H ₂ C ₁₈ N ₂ O ₂ H ₁₆	182.4	Orange	75–80	(73.47)	(7.23)	(9.52)
	H ₂ A ⁴						
5	H ₂ C ₂₄ N ₂ O ₂ H ₁₆	(237)	Yellow	45–50	(78.26)	(5.43)	(7.61)
	Pd A ^{3a}						
6	PdC ₁₈ N ₂ O ₂ H ₁₆	(230)	Light green	35–40	54.02	(4.04)	(7.03)
	Pd A ^{4b}						
7	PdC ₂₄ N ₂ O ₂ H ₁₆	(270)	Brown	85	(61.23)	(3.43)	(5.95)
	CoA ^{3c}						
8	CoC ₁₈ N ₂ O ₂ H ₁₆	(240)	Brown	80–85	61.36	4.48	7.69
	CoA ^{4d}						
	CoC ₂₄ N ₂ O ₂ H ₁₆				(68.09)	(3.81)	(6.62)

a, b, c, d were synthesised by both method (a,b) but yields were reported on bases of method a. ^a%Pd = 26.25 (26.71); ^b%Pd = 22.30 (22.62); ^c%Co = 16.30 (16.79); ^d%Co = 13.35 (12.93); ^ethe yield range is due to different methods used. ND : Not determined.

Table 2 Important IR absorption bands (cm⁻¹) of the ligands and their complexes^a

Compound	ν (O–H)	ν (N–H)	ν (C=N)	ν (C–O)
HA ¹	3400(br)	3338	1607	1276
HA ²	34100(br)	3275	1623	1284
H ₂ A ³	3438(br)	–	1615	1276
H ₂ A ⁴	3400(br)	–	1623	1284
Pd A ³	–	–	1615	1276
Pd A ⁴	–	–	1607	1350
CoA ³	–	–	1607	1330
CoA ⁴	–	–	1607	1361

^a Nujol mull and KBr pellets; br= broad band.

values of the C=N vibrations at about 1607–1615 cm⁻¹ for the complexes are lower by about 8–15 cm⁻¹ for the free ligands. A comparison between the IR spectra of H₂A^x (x=3,4) and those complexes also showed that the (C–O) band at 1276 cm⁻¹ is shifted to higher frequency by about 31–37 cm⁻¹ in the spectrum of the complexes which indicate the formation of a C–O–M bond.¹¹ In the IR spectra of MA⁴, the N–H stretching band is absent which indicates the loss of this proton in the complex. IR studies thus indicate that these ligands behave as tetradentate ligands.

In the ¹H NMR spectra of the ligands HA¹, HA², H₂A³, H₂A⁴ and some of their complexes, the signals at δ 3.0 and δ 3.2 in the spectra of HA¹ and HA² is assigned to the NH₂ group, based on the absence of this signal in the spectra of H₂A³ and H₂A⁴. Two series of peaks are present for the acidic protons of the unsymmetrical Schiff bases H₂A³ (OH, NH), presumably due to tautomeric forms,¹¹ and H₂A⁴ (OH, OH).

The ¹H NMR spectra of the PdA³ complex in CDCl₃ solution has a peak at δ 8.25, and the PdA⁴ complex has peaks at δ 8.4 and 9.2 which are assigned to the hydrogen of the azomethine moiety of salicylaldehyde and 2-hydroxy-napthaldehyde, respectively. From these data, it can be concluded that the ligands are tetradentate and their palladium complexes are diamagnetic and low spin, which indicates a square-planar or distorted square-planar structure. The ¹H NMR of the cobalt complexes are due to paramagnetism, broad.

In the mass spectra of the ligands, the molecular ion is significantly more abundant than other fragment ions. The proposed fragmentations accord with the proposed structure of the ligands.

For the Pd(II) complexes, d–d transition appears below 470 nm, which is a characteristic of square-planar or distorted square-planar.^{1,8} The electronic absorption spectra of the Co(II) complexes consist of weak d–d transition in the visible region as a shoulder on intense, broad UV band. These posi-

Table 3 ¹H NMR (400 MHz) chemical shift (δ ppm) of the ligands and their palladium complexes

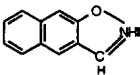
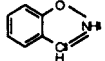

Compound	NH ₂	O–H	CH=N	CH ₃	Aromatic protons
HA ^{1a}	3.0 (br)	–	8.65	1.4	6.5–7.5 (m)
HA ²	3.2 (br)	15.1	9.5	2.1	6.7–8.2 (m)
H ₂ A ⁴	–	13 (br)	8.65 (s)	1.8 (s)	6.5–7.5 (m)
Pd A ³	–	15.3 (d)	8.7 (s)	2.1 (s)	6.5–7.5 (m)
Pd A ⁴	–	12.7 (3)	9.45 (s)	–	6.7–8.3 (m)
Pd A ³	–	–	8.25 (s)	1.5 (s)	6.5–7.8 (m)
Pd A ⁴	–	–	8.4 (s)	2.1 (s)	7.3–8.2 (m)
			9.2 (d)		

s = singlet, d = doublet, m = multiplet, ^a δ H C=N (HA¹) = 8.65 (s), ^b δ H azomethine (H₂A³) = 5.2 (s).

Table 4 Mass spectra data of the unsymmetrical schiff base ligands H_2A^3

<i>m/z</i>	Assignments	Formula of fragment
294	H_2A^3 Ion molecule	$H_2C_{18}N_2O_2H_{16}$
299	$H_2A^3 - (CH_3)$	$H_2C_{17}N_2O_2H_{13}$
223	$H_2A^3 - (CH_3-C-CH=C-CH_3) - (H)$	$HC_{14}N_2OH_{10}$
210	$H_2A^3 - (CH_3-C-CH=C-CH_3) - (H)$	$HC_{13}N_2OH_9$
196	Hsal. Phen. NH_2	$HC_{13}NOH_9$
84	$CH_3-C-CH=C-CH_3$	C_5OH_7
60	$CH_3-C-CH=C-CH_2$	C_4OH_6
180	Hsal. Phen. $NH_2 \cdot O$	$HC_{13}NH_9$

Table 5 Mass spectra data of the unsymmetrical schiff base ligands H_2A^4

<i>m/z</i>	Assignments	Formula of fragment
366	H_2A^4 Ion molecule	$H_{18}C_{24}N_2O_2$
271	$H_2A^4 - C_6H_6O$	$H_{11}C_{18}N_2O$
259	$H_2A^4 - C_7H_6O$	$H_{11}C_{17}N_2O$
246	$H_2A^4 - C_7HNO$	$H_{12}C_{17}NO$
210	Hsal. Phen. 2H	$H_{10}C_{13}N_2O$
146	Hsal. Phen. $-(NH)$	$H_{10}C_{13}NO$
168		$H_6C_{11}NO$
120		H_6C_7NO
77		H_4C_6

tions are consistent with square-planer complexes of similar tetradentate Schiff base ligands with *o*-phenylenediamine as a diamine bridge.⁹ The lack of molar conductance of the complexes MA^x ($x = 3, 4$, $M = Pd, Co$, Fig.2), measured in DMSO and CH_2Cl_2 , indicate their non-electrolytic nature.

Experimental

Microanalyses were performed by the microanalytical laboratory, at the Research Institute of Petroleum of the Islamic Republic of Iran. FT-IR spectra were recorded using unicam Mattson 1000, visible spectra using a SHIMADZU, UV-2100, spectrophotometer. 1H NMR spectra were obtained on a Bruker FT-NMR AC- 80 (80 MHz) and 400 MHz spectrometers using TMS as internal standard and $CDCl_3$ as solvent. Mass spectra were obtained on the Varian, Quadrupole Mass Spectrometer Inco 550.

o-Phenylenediamine, acetylacetone, 2-hydroxy-1-naphtaldehyde, salicylaldehyde, palladium (II) acetate, cobalt (II) acetate tetrahydrate, (reagent grade, Merk) were used as supplied. Solvents (ethanol, ether, methanol and acetone) were dried and distilled before use by standard methods. Piperidine and DMSO were used without further purification.

Preparation of the ligands

Preparation of half-unit HA^1 : The precursor HA^1 was prepared according to the modified method described earlier.⁶ To a solution of *o*-phenylenediamine (30 mmol) in anhydrous ethanol (100 ml), a solution of distilled acetylacetone (30 mmol) in anhydrous ethanol (50 ml) was added. After the addition was complete the mixture was stirred for 30 min and then refluxed for 15 min. The resulting solution was evaporated in vacuum to remove the solvent. After extraction with anhydrous and cold ether, the resulting solid was recrystallised from ether. Yields ranged from 48–56%, based on the *o*-phenylenediamine half-units used.

Preparation of half-unit HA^2 : A solution of *o*-phenylenediamine (20 mmol) in anhydrous ethanol (150 ml), was added, dropwise and slowly, to a vigorously stirred and warm solution of 2-hydroxy-1-naphtaldehyde (20 mmol) in anhydrous ethanol (100 ml). After the addition was completed the mixture was stirred for 30 min and then refluxed for 30 min. The resulting solution was evaporated *in vacuo*

Table 6 Electronic spectral bands

HA^1	338 (br), 276 nm
HA^2	472, 450, 330, 273 nm
H_2A^3	336, 277 nm
H_2A^4	472, 450, 348, 323, 272 nm
$Pd A^3$	455, 378.5, 454.5 (sh), 336, 317, 271 nm
$Pd A^4$	468, 447 (sh), 334 (sh), 350.5, 322.5, 273.5 nm
CoA^3	600 (sh), 563, 524 (sh), 499, 388.5, 338, 296 nm
CoA^4	582 (sh), 450, 397, 318, 274 nm

to remove the solvent. The solid residue was filtered and washed with cold solvent. It was recrystallised from a mixed solvent (MeOH, EtOH, acetone; in ratio 1:1:1). After drying in a vacuum, HA^2 was obtained in 55% yield. (m.p. 62°C)

Preparation of H_2A^x : The solution of HA^x (10 mmol) in anhydrous ethanol and a solution of the salicylaldehyde (10 mmol) in anhydrous ethanol were mixed together and then refluxed. The product mixture was concentrated in vacuum until a colored solid precipitated. It was recrystallised from solvent to give yellow-orange crystals.

Preparation of complexes PdA^x, CoA^x

Method a: To a solution of $M(OAc)_2$ (1 mmol) in boiling solvent, a solution of the unsymmetrical Schiff bases H_2A^x ($x = 3, 4$), (1 mmol) in methanol was added followed a few drops of piperidine. The mixture was refluxed and evaporated yielding a viscous solution. Upon standing this deposited a few coloured crystals. The precipitate was filtered and washed with cool solvent and cool ether, then dried in an oven at 50°C.

Method b: To a solution of HA^x (1 mmol) ($x = 1, 2$) in solvent a methanolic solution of $M(OAc)_2$ (1 mmol), salicylaldehyde (1 mmol) in solvent was added. This mixture was refluxed and then was cooled and left to allow the precipitation of the complex. The precipitate was filtered and washed with solvent. The cobalt complexes were synthesised under argon atmosphere.

Received 4 November 2000; accepted 14 February 2001
Paper 00/592

References cited in this synopsis

- E. Kwiatkowski, M. Kwiatkowski, *Inorg. Chem. Acta*, 1984, **90**, 145–152.
- J.P. Costes, G. Cros, M.H. Darbieu, *Inorg. Chim. Acta*, 1982, **60**, 111, 114.
- D.F. Averill, R.F. Broman, *Inorg. Chem.*, 1978, **17**, 12, 3389.
- J.P. Costes, G. Cros, M.H. Darbieu, Y.P. Laurent, *Transition, Met. Chem.*, 1982, **7**, 219.
- (a) R. Atkins, G. Brfwer, *et al.*, *Inorg. Chem.* 1985, **24**, 2, 128; (b) J.E. Kovacic, *Spectrochim. Acta*, 1967, **23A**, 183.
- (a) M. Lashanizadegan and D.M. Boghaei, *Synth. React. Met. Org. Chem.*, 2000, **1**, 89; (b) D.M. Boghaei and M. Lashanizadegan, *Synth. React. Met.-Org. Chem.*, in press.
- (a) E. Kwiatkowski, M. Kwiatkowski, *Inorg. Chim. Acta*, 1980, **42**, 197; (b) H.P. Jensen, *Acta Chem. Scand.*, 1982, **A36**, 825.
- E. Kwiatkowski, M. Kwiatkowski, *Inorg. Chim. Acta*, 1986, **117**, 145.
- L.H. Vogt, JR., H.M. Faigenbaum and S.E. Wiberley, *Chem. Rev.*, 1963, **63**, 269–.
- M. Kwiatkowski and G. Bandoli, *J. Chem. Soc. Dalton Trans.*, **1992**, 379.
- E. Kwiatkowski, M. Kwiatkowski, *Inorg. Chim. Acta*, 1984, **82**, 101–9.