The Separation of Copper(II) Nickel(II) and Palladium(II) Complexes of New Tetradentate Schiff Bases Using Normal Phase HPLC

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Summary: The copper and nickel complexes of tetradentate ligands bis(salicylaldehyde) phenylpropylenediimine (H_2SA_2PP) and bis-(o-hydroxylacetophenone)phenylpropylenediimine (H_2HA_2PP) and copper(II), nickel(II) and palladium(II) complexes of bis (benzoylacetone) phenylethylenediimine (H_2BA_2PE) and bis(o-hydroxyacetophenone) phenylethylenediimine (H_2HA_2PE) have been prepared and their structure is elucidated using IR, UV, ^1H NMR and mass spectroscopic techniques. The metal complexes are less sensitive for spectrophotometric determination of metal ions, but show high value of molar absorptivities in UV regions, which enabled to use UV-detector with HPLC system for separation of copper and nickel, and copper, nickel palladium complexes at ng levels. The separation is achieved on 250x4mm column packed with Licrosorb Si 100, 5μ using isocratic elution with mixture of chloroform-n-hexane. Detection was achieved within 290-310 nm using UV detector, linear calibration range were found in the ng levels and detection limits at sub ng levels of metal ions.

Introduction

The reactions of tetradentate ketoamine schiff bases towards copper(II), nickel(II), palladium(II) and vanadium(IV) oxide have produced valuable separations of certain metal ions using Gas Chromatography (GC) [1-6] and High Performance Liquid Chromatography (HPLC) [7-9]. HPLC which is not limited by thermal stability and volatility of the complexes have proved suitable for the separation and quantitative determination of metal ions as metal complexes, particularly for less volatile metal complexes. Thus in the present work metal complexes of four new ligands bis (salicylaldehyde)phenylpropylenediimine(H_2SA_2PP), bis(o-hydroxyacetophenone)phenylpropylenediimine (H_2HA_2PP),bis(benzoylacetone) phenylethylenediimine (H_2BA_2PE) and bis-(o-hydroxyaceto phenone)phenylethylenediimine (H_2HA_2PE) have been prepared to explore the potentials of these reagents for simultaneous quantitative separation of copper, nickel and palladium as their metal complexes.

Experimental

Preparation of Reagents:

Bis (salicyladehyde)phenylpropylenediimine (H_2SA_2PP), Bis(o-hydroxyacetophenone) phenyl propylenediimine(H_2HA_2PP),Bis-(benzoylacetone) phenylethylenediimine(H_2BA_2PE) and Bis (o-hydroxyacetophenone)phenylethylenediimine (H_2HA_2PE):

1-phenyl-1,2-diaminopropane hydrochloride or 1-phenyl-1,2-diaminoethane hydrochloride (0.01M) dissolved in water was neutralized with ammonia and diamine was extracted with chloroform. The dried extract of 1-phenyl-1,2-diaminopropane over anhydrous sodium sulphate was added to the ethanolic solution of salicylaldehyde (0.02M) and o-hydroxyacetophenone (0.02M). The dried extract of 1-phenyl-1,2-diaminoethane was added to benzoylacetone (0.02M) or o-hydroxyacetophenone (0.02M). The mixture was refluxed each time for 30 min and was concentrated. The solid to gummy mass so obtained was dissolved in n-hexane or mixture of n-hexane :ethanol (1:1). The compounds gradually precipitated and were recrystallised from ethanol and benzene.

Mass spectrum of the reagent H_2SA_2PP indicates m/z (rel. intensity %) M^+ 358 (7) 341(0.7), 281(0.5), 237(10), 210(100), 148(90), 77(20), H_2HA_2PP indicates M^+ at m/z (rel. intensity %) 386 M^+, (5.4), 251(23.6), 226(50), 225(70), 162(12), 161(100), 120(18), 91(38), H_2BA_2PE m/z (rel. intensity %) M^+ 424 (0.45), 312(1.5), 251(37.7), 250(100), 174(52.6), 146(8.7), 105(82), 77(30.7),

H_2HA_2PE m/z (rel. intensity %) 372 M^+ (13), 236(22), 237(71.3), 225(57), 224(100), 208(20), 148(26), 135(12), 132(10), 120(38), 83(13).

Preparation of Metal Complexes:

Bis (salicylaldehyde) phenylpropylenediimine nickel(II) (SA2PPNi): *Bis (salicylaldehyde) phenyl propylenediimine copper(II)* (SA2PPCu): *Bis (O-hydroxyacetophenone) phenylpropylenediimine nickel(II)* (HA_2PPNi): *Bis (o-hydroxyacetophenone) pheneylenediimine copper(II) (HA$_2$PECu): Bis (benzoylacetone) phenylethylenediimine nickel(II)* (BA2PENi): *Bis (benzoylacetone) phenylethylenediimine copper(II)* (BA2PECu): *Bis (o-hydroxyacetophenone) phenylethylenediimine nickel(II)* (HA2PENi) *and Bis (o-hydroxy- acetophenone) phenylethylenediimine copper(II)* (HA2PECu):

Equimolar solution of copper acetate or nickel acetate in methanol was slowly added to the solution of the reagents H_2SA_2PP, H_2HA_2PP, H_2BA_2PE or H_2HA_2PE in ethanol, and the mixture was refluxed for 1 hr. The solutions were concentrated and cooled. The precipitate obtained was filtered and recrystallised from ethanol. The results of elemental analysis are summarized in Table-1.

Bis (benzoylacetone) phenylethylenediimine palladium(II) (BA_2PEPd) *and Bis (o-hydroxyacetophenone) phenylethylenediimine palladium(II)* (HA_2PEPd):

Palladium chloride (200 mg) was heated with 2-3 ml of benzonitrile and the clear solution of palladium benzonitrile complex formed was diluted with benzene (5 ml). The solution was added to an equimolar amount of H_2BA_2PE or H_2HA_2PE in benzene and the mixture was refluxed for 12 hrs and filtered while hot. Most of the solvent was distilled out and the residue was dissolved in n-hexane. The precipitate obtained was recrystallised (BA_2PEPd) from n-hexane and HA_2PEPd from ethanol.

Table 1: Elemental micro-analysis of the reagents and their metal complexes

Compound	Mol.Formula	M.P°C	C	H	N	C	H	N
H_2SA_2PP	$C_{23}H_{22}N_2O_2$	155	77.09	6.14	7.28	77.02	6.13	7.85
SA_2PPNi	$C_{23}H_{20}N_2O_2Ni$	335	66.66	4.83	6.76	65.87	4.83	7.01
SA_2PPCu	$C_{23}H_{20}N_2O_2Cu$	328	65.87	4.77	6.68	65.07	3.51	6.81
H_2HA_2PP	$C_{25}H_{26}N_2O_2$	120	77.72	6.73	8.29	77.73	6.84	7.33
HA_2PPNi	$C_{25}H_{24}N_2O_2Ni$	338	67.87	5.42	6.33	67.34	4.95	6.53
HA_2PPCu	$C_{25}H_{24}N_2O_2Cu$	330	67.11	5.38	6.26	67.83	5.48	6.51
H_2BA_2PE	$C_{28}H_{28}N_2O_2$	145	79.24	6.60	6.60	78.34	6.56	6.44
BA_2PENi	$C_{28}H_{26}N_2O_2Ni$	239	69.89	5.40	5.82	69.88	4.81	5.87
BA_2PECu	$C_{28}H_{26}N_2O_2Cu$	230	69.20	5.35	5.76	68.92	5.00	5.55
BA_2PEPd	$C_{28}H_{26}N_2O_2Pd$	258	63.58	4.92	5.29	63.45	4.41	5.55
H_2HA_2PE	$C_{24}H_{24}N_2O_2$	160	77.41	6.45	7.52	77.39	7.04	7.73
HA_2PENi	$C_{24}H_{22}N_2O_2Ni$	250	67.25	5.15	6.53	66.68	5.21	6.44
HA_2PECu	$C_{24}H_{22}N_2O_2Cu$	250	66.42	5.07	6.45	65.62	5.72	6.55
HA_2PEPd	$C_{24}H_{22}N_2O_2Pd$	-	60.45	4.61	5.87	58.89	4.41	5.62

Table 2: ^{1}H NMR spectra of the reagents and their nickel and palladium complexes in δ PPM in $CDCl_3$ with possible assignments

Compound	-CH_3 group	bridge-CH_2	bridge -CH	= CH	H C=H	NH/OH	C-H aromatic
H_2SA_2PP	1.2054(d)	-	3.8321(m)	-	8.288(s)	11.56(b)	6.808(m)
	6.45Hz		4.3976(d) 7.56Hz	-	8.321(s)		6.921(m) 7.1574(m) 7.249(m) 7.3139(m) 7.391(m)
SA_2PPNi	1.6246(d)	-	3.4426(q) 4.0462(d)	-	7.9182(s) 7.9426(s)	-	6.5153(m) 7.069(m) 7.335(m)
H_2HA_2PP	1.3943(d) 6.3Hz 1.9998(s) 2.3465(s)	- 7.62Hz	4.3853(m) 4.837(d)	-	-	16.08(s) 16.261(s)	6.7288(m) 6.8114(m) 6.9869(m) 7.232(m) 7.282(m) 7.530(m)
HA_2PPNi	1.763(d)	-	3.898(q)	-	-		6.471(m) 7.658(m) 7.132(m) 7.302(m) 7.420(m)
	2.1355(s) 2.3545(s)		4.3227(s)				
H_2BA_2PE	1.941(s) 2.005(s)	3.7131(m)	4.83(m)	5.652(s) 5.74(s)	-	11.695(t) 12.207(d)	7.35(m) 7.85(m)
BA_2PENi	1.818(s) 1.897(s)	3.1(d) 3.36(q)	4.34(d)	5.608(s) 5.706(s)	-	-	7.38(m) 7.80(m) 8.15(m)
BA_2PENi	1.932(s) 1.9956(s)	3.58(d) 4.03(q)	4.75(d)	5.5307(s) 5.6273(s)	-	-	7.28(m) 7.34(m) 7.73(m) 7.90(m)
H_2HA_2PE	2.279(s) 2.362(s)	4.118(m)	5.265(m)	-	-	16.0(b)	6.981(m) 7.4(m)
HA_2PENi	2.1375(s) 2.2188(s)	3.510(d) 3.9313(q)	4.7033(d)	-	-	-	6.4905(m) 7.13(m) 7.354(m) 8.234(d)
HA_2PEPd	2.2573(s) 2.2817(s)	3.99(d) 4.339(d)	5.1217(d)	-	-	-	7.20(m) 7.25(m) 7.35(m) 7.46(m) 7.72(m)

1-phenyl-1,2-diaminopropane hydrochloride and 1-phenyl-1,2-diaminoethane hydrochloride were prepared by the reduction of phenylmethylglyoxime and phenylglyoxime respectively with sodium metal using a general procedure [10]. Elemental micro-analysis was carried out by elemental Micro-Analysis Ltd., U.K. I.R. spectra were recorded in KBr on Hitachi 260-30 in range of 4000-250 cm^{-1} and in nujol on Unicam SP 1025 in range of 3800-625 cm^{-1}. Mass spectra and ^1H NMR on Bruker AM 300 NMR spectrometer in $CDCl_3$ were recorded at HEJ Institute of Chemistry, University of Karachi and ^1H NMR on Jeol FX 100 were recorded at PINSTECH, Islamabad. All the spectrophotometric measurements in the range of 800-190nm were carried out on Hitachi 2000 spectrophotometer. Hitachi 655A Liquid Chromatograph equipped with variable wavelength UV monitor Hitachi 655-22, Rheodyne sample injector 7125 and Hitachi recorder 561 was used. Stainless steel colum 250x4mm was packed with Licrosrb Si 100, 5μ (Merck) using balanced density technique.

Results and Discussion

The reagents and their metal complexes are readily prepared in good yield, following a simple synthetic routine. The IR of the ligands and their metal complexes follow a similar pattern as observed with related compounds [11,12], thus requiring little discussion. The mass spectra of the reagents H_2SA_2PP, H_2HA_2PP, H_2BA_2PE and H_2HA_2PE show molecular ion peaks at m/z 358, 386, 424 and 372 respectively, with relative intensity within the range 0.45-13%. This may indicate the ease of the fragmentation of the ligands particularly H_2BA_2PE, where lowest relative intensity of M^+ is observed. The main fragmentation pathway of all the ligands, with the base peaks at m/z 210, 161, 250 and 224 occurs with the breakage of C-C bond at bridge position.

^1HNMR of the reagents H_2SA_2PP and H_2HA_2PP (Table-2) show a doublet at $\delta1.20$ and 1.39 ppm respectively due to methyl groups at bridge position, but the corresponding signals in their nickel complexes shift to $\delta1.624$ and 1.673 ppm respectively. The reagent H_2HA_2PP also indicate two singlets at $\delta1.998$ and 2.3465 ppm due to methyl groups at azomethine groups, which changes to $\delta2.1355$ and 2.3545 ppm in nickel complex, due to fixed configuration in square planar configuration in nickel complexes. The reagent H_2SA_2PP shows a multiplet at $\delta3.832$ and a doublet at $\delta4.397$ ppm due to CH groups at bridge position. The multiplet due to the coupling with methyl group changes to quadruplet at $\delta3.4426$ and doublet into a singlet at $\delta4.0462$ ppm in nickel complex, due to the loss of intramolecular hydrogen bonded protons in complexation with metal ions. Similarly a multiplet at $\delta4.385$ ppm and a doublet at $\delta4.837$ ppm in H_2HA_2PP change into quadruplet at $\delta3.898$ ppm and a singlet at $\delta4.3227$ ppm in nickel complexes. A broad band at $\delta11.56$ ppm in H_2SA_2PP and two singlets at $\delta16.02$ and 16.26 ppm in H_2HA_2PP disappear in their nickel complexes as expected [11,12].

The reagents H_2BA_2PE and H_2HA_2PE contain a CH and CH_2 at the bridge position and each reagent shows two multiplets at $\delta3.713$, 4.83 and $\delta4.118$, 5.265 respectively, but two hydrogen of CH_2 group becomes chemical shift unequal in axial and equitorial hydrogen in nickel and palladium complexes, because of being adjacent to asymetric centre in a fixed configuration in metal complexes. The nickel and palladium complexes of H_2BA_2PE indicate a doublet and a quadruplet at $\delta4.34$ and 4.75 in nickel and palladium complexes respectively. Similarly nickel and palladium complexes of H_2HA_2PE also show a doublet and a quadruplet at $\delta3.51$, 3.93 respectively and $\delta3.99$, 4.339 for CH_2 groups, as well as a doublet at $\delta4.70$ and 5.121 ppm for -CH groups at bridge position respectively. The reagent H_2BA_2PE also show two peaks each corresponding to a proton at $\delta5.652$ and 5.74 due to =CH groups and these change to $\delta5.608$, 5.706 and to $\delta5.53$, 5.627 ppm in nickel and palladium complexes respectively.

The spectrophotometric studies of the reagents and their metal complexes were carried out in acetone and chloroform. The results of the spectrophotometric studies (Table-3) indicate the copper and nickel complexes absorb in the region within 535-565 nm with molar absorptivity within 140-370 $l.mole^{-1}$ cm^{-1} due to d-d transitions. The nickel and palladium complexes also show one to two charge transfer bands within 350-415 nm. The reagents are less sensitive for spectrophotometric purposes, but indicate high values of molar absorptivity in the range 10^4, and ideally useful for HPLC separation and quantitative determinations of metal ions, using UV detector.

Table 3: Spectrophotometric data of the reagents and their metal complexes

Compound	Solvent	λ-max nm (ε- l.mole^{-1} cm^{-1})
H_2SA_2PP	Acetone	328(11300), 211(1250)
SA_2PPCu	Chloroform	652(364), 370(11600), 278(27000), 245(38200)
SA_2PPNi	Choroform	535(149), 417(7590), 350(8700), 325(8800), 258(59500)
H_2HA_2PP	Acetone	328(8530), 211(1680)
HA_2PPCu	Chloroform	545(364), 367(13300), 275(28100), 245(40900)
HA_2PPNi	Chloroform	552(175), 413(7800), 334(10100), 258(63900)
H_2BA_2PE	Acetone	338(63346)
BA_2PECu	Acetone	548(272), 345(3575), 211(3012)
BA_2PENi	Acetone	561(190), 408(9890), 330(14662)
BA_2PEPd	Acetone	381(12781), 295(15687), 252(24306)
H_2HA_2PE	Acetone	328(10600), 213(5000)
HA_2PECu	Acetone	555(322), 357(13900), 213(15400)
HA_2PENi	Acetone	545(165), 413(48221), 343(6699)
HA_2PEPd	Acetone	400(18468), 327(14298), 234(55603)

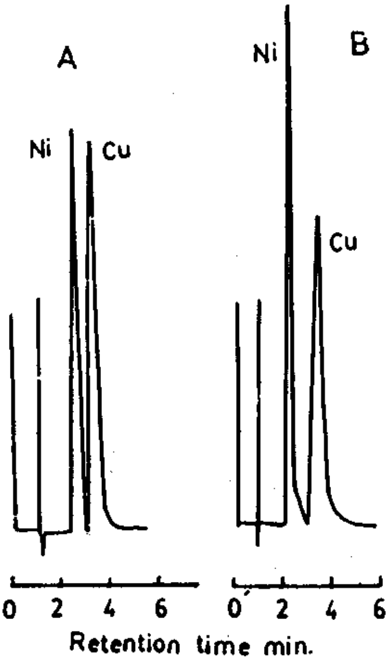

Fig. 1: HPLC separation of copper and nickel complexes of (A) H_2SA_2PP (B) H_2HA_2PP on column 250x4mm packed with licrosorb Si 100, 5μ, using UV detector at 298 nm. Eluent (A) chloroform: n-hexane (50:50), flow rate 2ml/min. (B) chloroform: n-hexane (57:43), flow rate 2.7 ml/min.

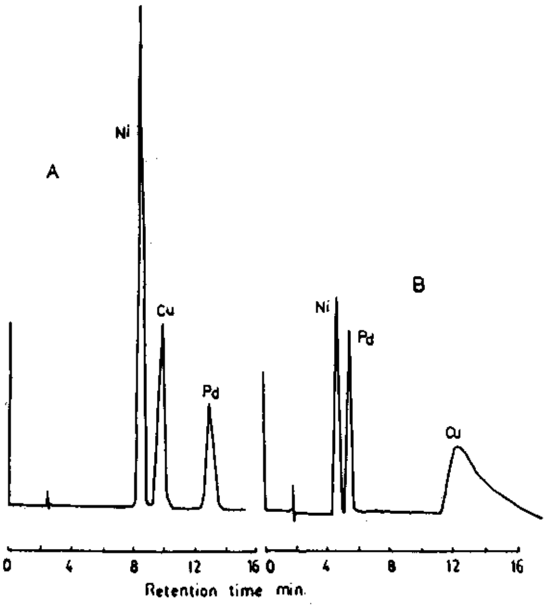

Fig. 2: HPLC separation of copper, nickel and palladium complexes of (A) H_2BA_2PE (B) H_2HA_2PE on column 250x4mm packed with licrosorb Si 100, 5μ, using UV detector at 290 nm. Eluent (A) 20% chloroform in n-hexane, flow rate 1 ml/min. (B) 80% chloroform in n-hexane, flow rate 1.5 ml/min.

Table 4: Quantitative HPLC of metal complexes on column 250x4mm packed with licrosorb Si 100, 5μ

Compound	Solvent	Retention volume ml	Detection wavelength nm	Calibration range	detection Limit
SA_2PPNi	50% Chloroform 50% n-hexane	4.8	298	0.2-1.6μg of complex, corresponding to 28.5-228.0 ng of nickel	6ng of complex corresponding 0.85 ng nickel.
SA_2PPCu	-do-	6.4	298	0.2-1.6μg of complex, corresponding to 30-240 ng of copper	6 ng of copper, corresponding to 0.9 ng copper
HA_2PPNi	57% Chloroform 43% n-hexane	7.56	298	0.2-1.6μg of complex corresponding to 27-214 ng nickel	10 ng complex corresponding 2.8 ng nickel
HA_2PPCu	-do-	8.91	298	0.2-1.6μg of complex, corresponding to 28-225.5 ng of copper	20 ng of complex, corresponding to 2.8 ng of copper
BA_2PENi	20% Chloroform 80% n-hexane	8.35	290	0.4-2.8μg of the complex corresponding to 42-342 ng of nickel	96 pg of the nickel complex corresponding to 12 pg of Ni
BA_2PENi	-do-	10.00	290	0.4-1.4μg of the copper complex, corresponding to 52-183 ng of copper	128 pg of copper complex, corresponding 17 pg of copper
BA_2PEPd	-do-	13.00	290	0.2-1.4μg of the palladium complex, corresponding to 40-282ng of palladium	16 pg of the palladium complex, corresponding to 2 pg of palladium
HA_2PENi	80% Chloroform 20% n-hexane	6.9	290	0.2-1.6μg of the nickel complex corresponding to 27-219 ng of nickel	0.4 ng of nickel complex corresponding to 54 pg of nickel
HA_2PEPd	-do-	8.4	290	0.12-0.42μg of palladium complex, corresponding to 26-94 ng of palladium	0.5 ng of palladium complex, corresponding to 111 pg of palladium
HA_2PECu	-do-	25.0	290	0.2-1.2μg of copper complex corresponding to 29-175ng of copper	3.2ng of copper complex corresponding to 468 pg of copper

In order to investigate the possible separation between copper and nickel and copper, nickel and palladium complexes and their quantitative elution, adsorption HPLC was used with a column (250x4mm) packed with Licrosorb Si 100, 5μ. The complexes were eluted with binary mixture of chloroform-n-hexane. All the complexes were easily eluted giving a symmetrical single peak for each of the complex. However when the conditions of separation of copper and nickel complexes of H_2SA_2PP and H_2HA_2PP were optimized, complete separation between copper and nickel complexes was achieved with 50% and 57% chloroform in n-hexane respectivley using UV detector fixed at 298 nm, with the elution of nickel followed by copper (Fig. 1). Similarly when the conditions of separation for copper, nickel and palladium complexes of H_2BA_2PE and H_2HA_2PE were optimized, complete separation between copper, nickel and palladium was achieved using UV detector at 290 nm. The order of the elution for both the reagents was slightly different. For the reagents H_2BA_2PE, the order of elution was nickel followed by copper and palladium; but in the case of the metal complexes of H_2HA_2PE it was nickel, palladium, copper (Fig. 2). The order of elution was confirmed by using different ratios of chloroform and n-hexane as eluting solvents, and using a spiking technique where a small amount of a particular complex was added and the corresponding increase in peak height was noted.

In order to confirm the quantitative elution of the metal complexes at the conditions optimized for the separation of metal complexes, different amounts of metal complexes were injected and average peak height of atleast two injections were measured. Linear calibration curves were obtained for each of the complexes at the ng levels of metal ions and detection limits measured a tleast thrice, the background level were found to be at sub ng level of metal ions (Table-4).

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