



## SELENIUM BEARING 24- AND 28-MEMBERED MACROCYCLIC SCHIFF BASES: SYNTHESSES AND ELECTROCHEMICAL BEHAVIOR

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### ABSTRACT

In this communication we illustrate an effortless, convenient and less hazardous route for the synthesis of phenol based 24- and 28-membered macrocyclic Schiff bases,  $[\text{Se}_2\{(\text{CH}_2)_n\text{N}=\text{C}(\text{PhC}_6\text{H}_2(\text{OH})(4\text{-CH}_3)\text{PhC}=\text{N}(\text{CH}_2)_n\}_2]$  (where  $n=2, \text{L}_a\text{H}_2$ ;  $n=3, \text{L}_b\text{H}_2$ ) of  $\text{Se}_2\text{N}_4\text{O}_2$  type have been developed by end-off [2+2] dipodal condensation of 2,6-dibenzoyl-4-methylphenol with the appropriate bis(aminoethyl/ propyl)selenide. The Schiff-bases ( $\text{L}_a\text{H}_2$  and  $\text{L}_b\text{H}_2$ ) have been well characterized by mass spectrometry, IR, electronic,  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{77}\text{Se}\{^1\text{H}\}$  NMR spectroscopy and cyclic voltammetry. Applications of most of such organoselenium compounds have, however, been restricted by difficulties in synthetic methodologies, purification and instabilities of their certain derivatives. To overcome these potential difficulties, sterically bulky substituents and chelating groups in close proximity to selenium have been used. These Schiff-base framework is highly interesting as they can provide insight into competitive coordination behaviour between “hard (N and O)” and “soft (Se)” donors towards the metal center and also stabilize low as well as high oxidation states of a metal atom.

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### INTRODUCTION

#### Experimental Procedure

The chemicals were of reagent grade. Solvents were purified by standard methods<sup>1</sup> and freshly distilled prior to use. The precursors, 2, 6-dibenzoyl-4-methylphenol<sup>2</sup> and bis(aminoethyl/ propyl) selenide<sup>3</sup> were synthesized by the reported methods.

The electrospray ion mass spectra (ESIMS) were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. Infrared spectra were recorded on a Nicolet Magna 750 FT-IR spectrophotometer with KBr pellets (400–4000  $\text{cm}^{-1}$ ). Electronic spectra in  $10^{-4}\text{mol L}^{-1}$   $\text{CH}_3\text{CN}$  were obtained using a Perkin Elmer Lambda 35 UV-Vis. spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX-400 FT NMR spectrophotometer in  $\text{CDCl}_3$ ; the chemical shifts were recorded relative to  $\text{SiMe}_4$ . The  $^{77}\text{Se}\{^1\text{H}\}$  NMR spectra were recorded on the same instrument using  $\text{Ph}_2\text{Se}_2$  as an external reference.

Cyclic voltammetric measurements were carried out with an Advanced Electrochemical System, PARSTAT 2253 instrument equipped with a three-electrode system.

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The micro-cell model KO264 consisted of platinum/ glassy carbon as a working electrode, Pt wire as auxiliary electrode and a non-aqueous  $\text{Ag}/\text{Ag}^+$  reference electrode with  $0.1 \text{ mol L}^{-1}$   $\text{AgNO}_3$  in acetonitrile as filling solution. Tetrabutylammonium perchlorate ( $0.1 \text{ mol L}^{-1}$  solution in  $\text{CH}_3\text{OH}$ ) was used as supporting electrolyte. Cyclic voltammograms with scan speeds of  $100\text{--}500 \text{ mVs}^{-1}$  were run in  $10^{-4}\text{mol L}^{-1}$   $\text{CH}_3\text{OH}$  under nitrogen.

#### Synthesis of macrocyclic Schiff bases $\text{L}_a\text{H}_2$ and $\text{L}_b\text{H}_2$

A solution of 2,6-dibenzoyl-4-methylphenol ((1.89 g, 5.98 mmol) in acetonitrile (200 mL) was added drop wise to a solution of appropriate bis(aminoethyl)selenide (1.0 g, 5.98 mmol)/ bis(aminopropyl)selenide (1.16 g, 5.98 mmol) in dry acetonitrile (600 mL) in a 1:1 molar ratio with stirring for 7-8 h. Progress of the reaction was monitored by thin layer chromatography (TLC). The reaction took 72 h for completion. The organic solvent was removed under reduce pressure and the viscous, oily product, thus obtained, was purified by column chromatography (silica gel, 60-120 mesh, second fraction) using a solvent mixture of hexane: ethyl acetate in 80:20 ratio. The characteristics of these compounds are given below.

$[\text{Se}_2\{(\text{CH}_2)_2\text{N}=\text{C}(\text{PhC}_6\text{H}_2(\text{OH})(4\text{-CH}_3)\text{PhC}=\text{N}(\text{CH}_2)_2\}_2]$ ;  $\text{L}_a\text{H}_2$   
Colour and state: Yellow viscous liquid, Yield (%): 40.  
ESIMS:  $m/z$  897 [ $\text{L}_a\text{H}^+$ ]. IR (KBr disc,  $\text{cm}^{-1}$ , selected):  $\nu(\text{O-H})$

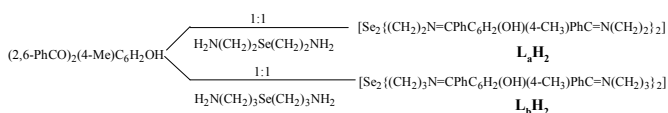
3448,  $\nu(\text{C}=\text{N})$  1612,  $\nu(\text{C}-\text{O})$  1253. UV-Vis. [ $\lambda_{\text{max}}$  (nm) ( $\text{CH}_3\text{CN}$ ): 399 ( $\text{PhO}^- \rightarrow \text{Ph}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 15.80 (s, 2H, OH), 6.82-8.01 (m, 24H, Ar-H), 3.53 (t, 8H, N- $\text{CH}_2$ ), 2.67 (t, 8H, Se- $\text{CH}_2$ ), 2.14 (s, 6H, Ar $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 196.2 (C=N), 51.6 (N- $\text{CH}_2$ ), 29.1 (Ar $\text{CH}_3$ ), 14.1 (Se- $\text{CH}_2$ ).  $^{77}\text{Se}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 153.

$\text{Se}_2\{(\text{CH}_2)_3\text{N}=\text{CPhC}_6\text{H}_2(\text{OH})(4\text{-CH}_3)\text{PhC}=\text{N}(\text{CH}_2)_3\}_2$ ;  $\text{L}_b\text{H}_2$   
 Colour and state: Yellow viscous liquid. Yield (%): 42. ESIMS: 951 [ $\text{L}_b\text{H}^+$ ]. IR (KBr disc,  $\text{cm}^{-1}$ ):  $\nu(\text{O}-\text{H})$  3471,  $\nu(\text{C}=\text{N})$  1614,  $\nu(\text{C}-\text{O})$  1255. UV-Vis. [ $\lambda_{\text{max}}$  (nm) ( $\text{CH}_3\text{CN}$ ): 396 ( $\text{PhO}^- \rightarrow \text{Ph}$ ).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 16.30 (s, 2H, OH), 7.20-7.90 (m, 24H, Ar-H), 3.39 (t, 8H, N- $\text{CH}_2$ ), 2.53 (t, 8H, Se- $\text{CH}_2$ ), 2.22 (s, 6H, Ar $\text{CH}_3$ ), 2.04 (q, 8H, - $\text{CH}_2$  between N- $\text{CH}_2$  and Se- $\text{CH}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 196.4 (C=N), 50.8 (N- $\text{CH}_2$ ), 31.0 (Ar $\text{CH}_3$ ), 14.3 (Se- $\text{CH}_2$ ).  $^{77}\text{Se}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $\delta$  ppm): 162.

## RESULTS AND DISCUSSION

### Schiff-base syntheses and characterization

The template free synthesis of [2+2] type of heteroatom octadentate ( $\text{Se}_2\text{N}_4\text{O}_2$ ) macrocylic Schiff base ligands  $\text{L}_a\text{H}_2$  (24-membered) and  $\text{L}_b\text{H}_2$  (28-membered) has been carried out and isolated (Scheme 1). The ligands have been purified by column chromatography on silica gel (60-120 mesh), using a solvent mixture of hexane: ethyl acetate in 80:20 ratio, respectively.



Scheme 1. Preparation of ligands

The analytical (ESIMS, IR, NMR, UV-Vis.) data of major products in both the cases are compatible with the presence of four Schiff base units. The ESI mass spectra of the Schiff-bases show the molecular ion peak ( $m/z$  897,  $\text{L}_a\text{H}_2$ ;  $m/z$  951,  $\text{L}_b\text{H}_2$ ). The peak pattern of selenium containing fragments could be easily recognized due to their typical isotopic cluster and is indicative of two Se atoms in the molecules. The calculated and observed isotopic patterns are in good agreement.

The IR spectra of both Schiff-bases ( $\text{L}_a\text{H}_2$  and  $\text{L}_b\text{H}_2$ ) show no N-H stretching frequency, suggesting that all the four nitrogens are tertiary (Fig 1). The bands at  $1612\text{ cm}^{-1}$  in  $\text{L}_a\text{H}_2$  and  $1614\text{ cm}^{-1}$  in  $\text{L}_b\text{H}_2$  are attributable to  $\nu(\text{C}=\text{N})$ . A broad band appearing around  $3449\text{ cm}^{-1}$  in  $\text{L}_a\text{H}_2$  and  $3471\text{ cm}^{-1}$  in  $\text{L}_b\text{H}_2$  due to  $\nu(\text{O}-\text{H})$  strongly suggests the presence of intramolecular hydrogen bonding between the phenolic hydrogen and azomethine nitrogen.

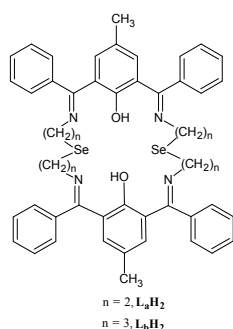


Figure 1 24- and 28-membered macrocyclic Schiff-base

Intramolecular hydrogen bonding is also confirmed by significant deshielding of the phenolic (OH) proton signal by the order of 3.6-4.1 ppm as compared to 2,6-dibenzoyl-4-methylphenol (appears at  $\delta$  12.2 ppm) in their  $^1\text{H}$  NMR spectra. The triplets due to N- $\text{CH}_2$  and Se- $\text{CH}_2$  protons in both Schiff-base molecules are appreciably shifted downfield as compared to the precursors bis(aminoethyl)selenide ( $\delta$  2.93 (t, 8H, N- $\text{CH}_2$ ), 2.61 (t, 8H, N- $\text{CH}_2$ )) and bis(aminopropyl)selenide ( $\delta$  2.81 (t, 8H, N- $\text{CH}_2$ ), 2.49 (t, 8H, N- $\text{CH}_2$ )). The appreciable deshielding in these proton signals along with the intensity ratios, as well as the disappearance of the - $\text{NH}_2$  signal [ $\delta$  = 1.63 ppm, {bis(aminoethyl)selenide};  $\delta$  = 1.45 ppm, {bis(aminopropyl)selenide}] suggest the condensation of benzoyl oxygen of 2,6-dibenzoyl-4-methylphenol with the - $\text{NH}_2$  groups of bis(aminoalkyl)selenide in a 1:1 molar ratio.  $^{13}\text{C}$  NMR spectra of both the ligands also support the environment around the carbon and the results of  $^1\text{H}$  NMR.  $^{77}\text{Se}$  NMR spectra exhibit only one resonating signal which indicates the purity of the molecules.

The electrochemical properties of these molecules were investigated by cyclic voltammograms (CV) in 0.1 M  $[\text{NBu}_4][\text{ClO}_4]$  in methanol solution with 100-500 mV/s scan rates. All CV data were collected under a nitrogen atmosphere and potentials are reported with reference to  $\text{Ag}/0.1\text{ M Ag}^+$ . The results are summarized in Tables 1. The cyclic voltammograms of the Schiff-bases  $\text{L}_a\text{H}_2$  and  $\text{L}_b\text{H}_2$  (Fig 2) exhibit an oxidation peak at  $E_{pa}$  0.330 V and 0.224 V, respectively. The oxidation of  $\text{L}_a\text{H}_2$  and  $\text{L}_b\text{H}_2$  is electrochemically irreversible in spite of the strong intramolecular O-H...N hydrogen bond involving the phenol O and the imine N atoms.

Table 1 CV data of 0.1 mM solutions of the Schiff-bases  $\text{L}_a\text{H}_2$  and  $\text{L}_b\text{H}_2$  in  $\text{CH}_3\text{OH}/0.1\text{ M NBu}_4\text{ClO}_4$  at a platinum electrode vs.  $\text{Ag}/0.1\text{ M AgNO}_3$  at different scan rates.

Ligand	Scan Rate	$E_{pa}$ (V)	$i_{pa}$ (mA)
$\text{L}_a\text{H}_2$	100	0.276	1.187
	200	0.296	2.246
	300	0.288	3.223
	400	0.288	4.114
	500	0.312	5.317
$\text{L}_b\text{H}_2$	100	0.248	0.640
	200	0.264	1.647
	300	0.272	2.583
	400	0.264	3.199
	500	0.272	3.696

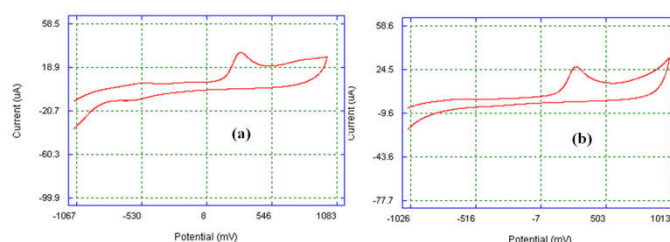


Figure 2 Cyclic voltammograms of 0.1 mM solutions of the Schiff-bases  $\text{L}_a\text{H}_2$ (a) and  $\text{L}_b\text{H}_2$ (b) in  $\text{CH}_3\text{OH}/0.1\text{ M NBu}_4\text{ClO}_4$  at platinum electrode vs  $\text{Ag}/0.1\text{ M AgNO}_3$  at 300 mV/s scan rate.

A number of acyclic and cyclic hybrid Schiff-bases with (O, N, Se/Te), ( $\text{N}_2\text{Se/Te}$ ), and ( $\text{N}_3\text{Se}_2/\text{Te}_2$ ) have been recently reported<sup>4-11</sup> and among them, a few of the systems have shown promising catalytic, biological, environmental and material properties<sup>12</sup>. In present communication, internal chelation has been extended to synthesize heterofunctionalized selenium-bearing Schiff-bases containing both ‘‘hard (N,O)’’ and ‘‘soft (Se)’’ donors. Structurally, this molecular framework is interesting as the presence of hetero (N, O, Se) donor sites

could make it practical to design molecular complexes with a variety of coordination modes, depending on the nature of the central metal atom.

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