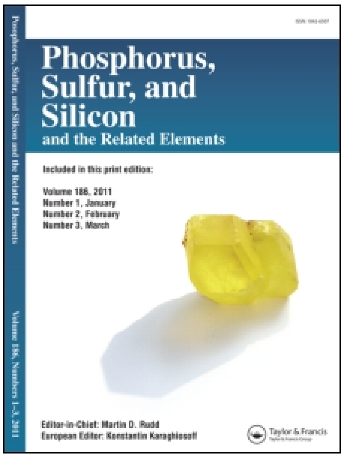

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# A NEW FAMILY OF CHALCOGEN BEARING MACROCYCLES: SYNTHESIS AND CHARACTERIZATION OF $N_4O_2E_2$ (E = Se,Te) TYPE COMPOUNDS

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*A new series of 24- and 28-membered macrocyclic systems associated with "hard" (N and O) and "soft" (Se or Te) donor atoms have been developed via template free (2 + 2) condensation reactions of bis(aminoalkyl)selenides/tellurides,* $\{NH_2(CH_2)_n\}_2E$ *(E = Se, Te; n = 2,3) with 2,6-diacetyl-4-methylphenol. A macroacycle,* $Se\{(CH_2)_2N{=}C(CH_3)C_6H_2(OH)(CH_3)C{=}O(CH_3)\}_2$*, has also been obtained. These compounds have been characterized by ESMS, IR, and* $^1H$*,* $^{13}C$*, and* $^{77}Se$ *NMR spectroscopy.*

*Keywords:* Hybrid ligands; macrocyclic compounds; $N_4O_2Se_2/N_4O_2Te_2$ donors; Schiff bases; template free ligand synthesis

## INTRODUCTION

The design and synthesis of cyclic Schiff bases have witnessed an explosive growth in research over the past four decades.[1–3] Interest in this field has been mainly due to their important role in many aspects of chemistry, the chemical industry, and medicine.[4] The macrocyclic ligands have the capability of binding metal ions and developing multimetallic systems useful as catalysts,[5–8] bioinorganic models[9–12]

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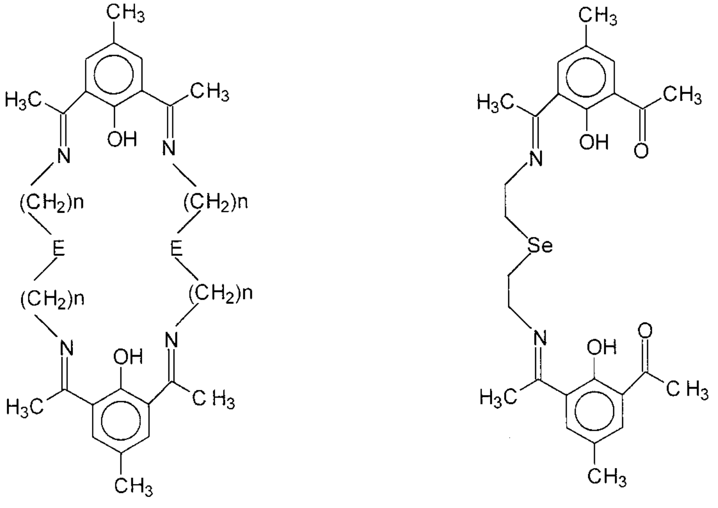
and spacers for crystal engineering.[13] Numerous macrocyclic ligands with a wide spectrum of electronic and structural features are being designed and synthesized to further explore their potential applications and optimize efficiency in their existing roles. Most of the work in the area of synthetic cyclic compounds has focused on "hard" donors such as nitrogen,[14–16] oxygen,[17–19] sulphur,[20] and phosphorus[21–23] atoms.

The macrocyclic ligand systems having both "hard" and "soft" donor atoms are of greater importance because they can easily stabilize metal ions in their low oxidation states as well as high oxidation states. This gives rise to useful multimetallic systems and forces the metal ions to adopt an unusual coordination geometry resulting in unique chemical and structural features. In this context the ligand system incorporating N, O, and Se/Te donor atoms described in this communication, acquires significance. In fact, reports on selenium/tellurium bearing macrocyclic Schiff bases are scarce though some polyseleno[24–27] and telluroethers[28,29] are known. Recently Singh and coworkers[30,31] have reported a few 22-membered selenium and tellurium containing azamacrocycles. Herein, we demonstrate template free synthesis of the first 24- and 28-membered $N_4O_2E_2$ ($H_2L$) macrocycles along with a $N_2O_4Se$ ($H_2L_x$) macroacycle (Figure 1).



($H_2L$) ($H_2L_X$)

E = Se; n= 2 ($H_2L_A$), 3 ($H_2L'_A$)

E = Te; n = 2 ($H_2L_B$), 3($H_2L'_B$)

**FIGURE 1** Macrocyclic ($H_2L$) and Macroacyclic ($H_2L_2$) systems.

## RESULTS AND DISCUSSION

The 24-membered ($H_2L_A$ and $H_2L_B$) and 28-membered ($H_2L'_A$ and $H_2L'_B$) macrocyclic Schiff type ligands with O, N, and Se/Te donor sets are isolated via template free (2 + 2) condensation reactions of bis(aminoalkyl)selenides/tellurides with 2,6-diacetyl-4-methylphenol in methanol under dry conditions. During the synthesis of $H_2L_A$ a yellowish product ($H_2L_x$), being less soluble in methanol, precipitated out. This was identified by its ES mass [m/z, 517 ($H_2L_x.H^+$)], IR and $^1H$ NMR as a one side condensed product. However, in the other cases and following a similar methodology, no significant amount of such product was observed. The analytical (elemental analyses, ESMS, IR, NMR) data of the major products in all the cases are compatible with the presence of four Schiff base units. Although the number of associated methanol molecules varied with time under vacuum, all the initially prepared compounds irrespective of the number of C-linkers between N and E showed peaks corresponding to [$H_2L.6MeOH.H^+$]. The peak pattern of selenium and tellurium containing fragments could be easily reorganized due to their typical isotopic cluster and is indicative of two Se or Te atoms in the molecules of the compounds as illustrated by the ES mass spectrum of $H_2L_B$ (Figure 2). The calculated and observed isotopic patterns are in good agreement.

The IR spectra of $H_2L$ display a moderate intensity band in the region 1620–1615 $cm^{-1}$ attributable to $\nu$(C=N) indicating complete cyclization. Furthermore, the absence of a $\nu$(C=O) band around 1670 $cm^{-1}$ evidences the completion of the condensation reaction. It is noteworthy that the IR spectrum of the one side condensed product ($H_2L_x$) displays a greater intensity $\nu$(C=O) band at 1664 $cm^{-1}$ and a moderate intensity $\nu$(C=N) vibration at 1615 $cm^{-1}$. Thus, the IR technique is diagnostic for differentiating between noncyclic and cyclic products as exemplified in Figure 3.

The $^1H$ NMR spectra of these compounds are generally as expected but still have a couple of interesting features. The four methyl groups attached to azomethine carbon are not equivalent at least in all the cases. In $H_2L_A$ and $H_2L'_B$ they appear as two singlets of equal intensities. Realizing the coplanarity of 2,6-diacetyl-4-methylphenol substituted moiety it could be attributed to unequal intramolecular hydrogen bonding between the phenolic oxygen and the azomethine nitrogen. Although no resonances were seen for phenolic protons because of rapid exchange with the solvent, that of $H_2L_A$ in $CDCl_3$ did show a downfield shift of 4.4 ppm as compared with the corresponding phenol (13.13 ppm), suggesting strong hydrogen bonding between phenolic O and azomethine N. The $^{13}C$ NMR spectrum of $H_2L_A$ also supports the different

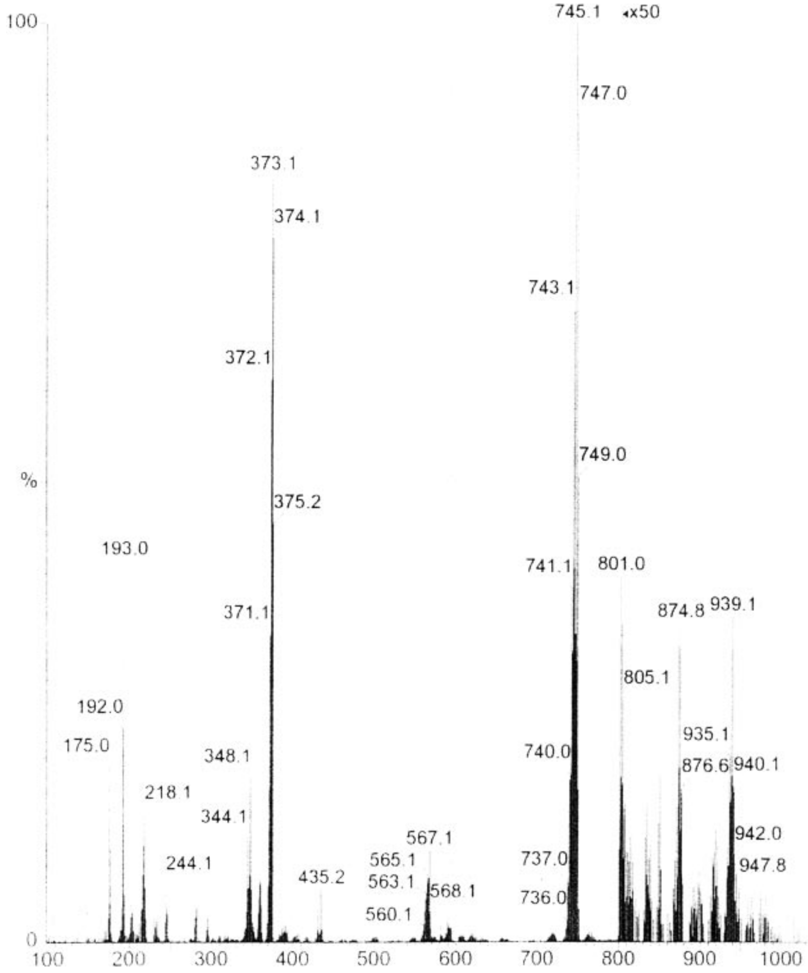


**FIGURE 1** ES mass spectrum of $H_2L_B$.

environment around methine C. Further, the methyl protons of $ArCH_3$ as compared with those attached to methine carbon are relatively more shielded in $H_2L'_A$ and $H_2L'_B$ and deshielded in $H_2L_A$ and $H_2L_B$. This probably arises out of different orientations of the Schiff base units in space;[32,33] $C_3$ linkers affording a bent conformation whereas $C_2$ linkers yield a more planar arrangement. The $^{77}$Se NMR spectrum of $H_2L_A$ exhibits only one signal whereas that of $H_2L'_A$ shows two signals. This further supports the above view.

Despite the lower stability of these macrocycles, their coordination chemistry is under investigation and will be described in due course.

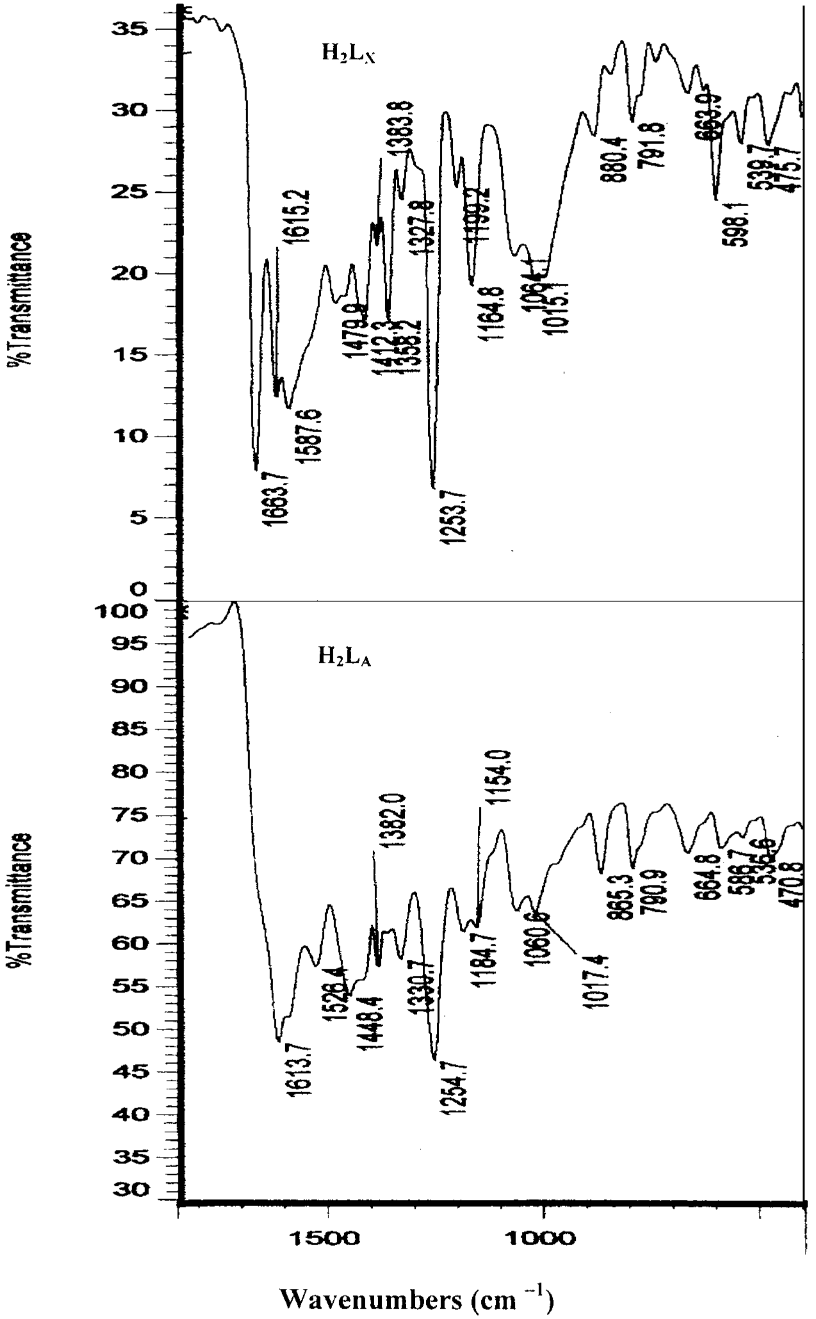


**FIGURE 2** IR spectrum of $H_2L_x$ and $H_2L_A$.

## EXPERIMENTAL

Bis(aminoalkyl)tellurides were prepared as described previously.[34] The corresponding selenides were also prepared following a similar procedure. Bis(aminoethyl)selenide: $^1$H NMR ($CD_3OD$): δ 2.85 (t, 4H, $NCH_2$), 2.67 (t, 4H, $SeCH_2$); $^{13}C\{^1H\}$ NMR ($CD_3OD$): δ 42.66 ($NCH_2$), 27.35 ($SeCH_2$). IR (CsI, $cm^{-1}$): 3285 ν(N—H), 1589 δ(N—H), 1198 ν(C—N). Bis-(aminopropyl)selenide: $^1$H NMR ($CDCl_3$): δ 2.79 (t, 4H, $NCH_2$), 2.61 (t, 4H, $SeCH_2$), 1.81 (m, 4H, mid-$CH_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$), δ 42.06 ($NCH_2$), 34.18 ($SeCH_2$), 21.12 (mid-$CH_2$). IR (CsI, $cm^{-1}$): 3280 ν(N—H), 1595 δ(N—H), 1192 ν(C—N). 2,6-Diacetyl-4-methylphenol was either obtained commercially or prepared according to literature.[35] The reactions were carried out in an inert dry atmosphere and monitored by TLC using prepared plates. Melting points are uncorrected.

Elemental analysis was performed with a Carlo Erba Strum DP200 analyser. ESMS were recorded on a Micromass Quattro II triple quadrupole mass spectrometer setting the ESI capillary at 3.5 kV and the cone voltage was 40 V : m/z values are given for $^1$H, $^{12}$C, $^{80}$Se and $^{128}$Te. $^1$H and $^{13}C\{^1H\}$ NMR spectra were obtained on a Jeol 400 MHz instrument at 399 MHz and 100 MHz, respectively, with $Me_4Si$ as internal standard. $^{77}Se\{^1H\}$NMR spectra were recorded on a Bruker AMX-400 FT-NMR spectrometer at 76 MHz using $(CH_3)_2Se$ as an external reference. IR spectra were recorded as KBr or CsI pellets on a Nicolet Magna 750 FT-IR spectrophotometer.

## SYTHESIS OF LIGANDS ($H_2L$)

A methanolic solution (30 $cm^3$) of 2,6-diacetyl-4-methylphenol (2.0 mmol) was added dropwise to a solution of bis(aminoalkyl)selenide or telluride (2.0 mmol) containing molecular sieves (4 Å) in methanol (20 $cm^3$) over a period of 30 min. A yellow product precipitated out almost immediately. The reaction mixture was warmed around 60°C for 8 h, cooled at room temperature, and filtered under an argon atmosphere. The yellow product ($H_2L_x$) was thoroughly washed with methanol and dried in vacuo. The clear filtrate was concentrated under reduced pressure to obtain an orange red oily product. It was washed with cold methanol and scratched with diethylether to obtain an orange red solid ($H_2L_A$).

The other compounds were also obtained in a similar fashion by mixing 2,6-diacetyl-4-methylphenol with the appropriate bis(aminoalkyl)chalcogenide. However, no significant amount of precipitate appeared on mixing the two reactants. Further, stirring the reaction mixture for a longer time without refluxing usually gave a better yield.

**$H_2L_x$:** Color, yellow; yield, 0.69 g, 36.8%; m.p., 80°C. Anal. Found: C, 59.19; H, 5.80; N, 4.68; Calc. For $C_{26}H_{32}N_2O_4Se$: C, 60.58; H, 6.20; N, 5.40%. ESMS (*m/z*): 517 (100%, $H_2L_x.H^+$). IR(CsI, $cm^{-1}$): 3427 $\nu$(O—H), 1664 $\nu$(C=O), 1615 $\nu$(C=N), 1254 $\nu$(C—O), 1165 $\nu$(C—N), 476 $\nu(Se—C_{alkyl})$. $^1H$ NMR ($CDCl_3$): $\delta$ 7.67, 7.66; 7.43, 7.42 (d, 4H, Ar), 3.89 (t, 4H, $NCH_2$), 3.04 (t, 4H, $SeCH_2$), 2.69 (s, 6H, $ArCH_3$), 2.35 (s, 6H, O=C—$CH_3$), 2.26 (s, 6H, N=C—$CH_3$).

**$H_2L_A$.6MeOH:** Color, reddish orange; yield, 0.80 g, 32%; m.p., 70°C. Anal. Found: C, 51.82; H, 7.10; N, 6.24; Calc. For $C_{36}H_{64}N_4O_8Se_2$: C, 51.43; H, 7.62; N, 6.66% ESMS (*m/z*): 841 (90%, $H_2L_A.6MeOH.H^+$), 649 (20%, $H_2L_A.H^+$). IR (CsI $cm^{-1}$): 3453 $\nu$(O—H), 1618 $\nu$(C=N), 1257 $\nu$(C—O), 1162 $\nu$(C—N), 471 $\nu(Se—C_{alkyl})$. $^1H$ NMR ($CDCl_3$) : $\delta$ 17.08 (s, 2H, ArOH), 7.66, 7.65; 7.43, 7.42 (d, 4H, Ar) 3.89 (t, 8H, $NCH_2$); 3.04 (t, 8H, $SeCH_2$), 2.69 (s, 6H, $ArCH_3$) 2.35 (s, 6H, N=C—$CH_3$), 2.26 (s, 6H, N=C—$CH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 15.09 ($SeCH_2$), 20.46 (N=C—$CH_3$), 24.62 (N=C—$CH_3$), 31.83 ($ArCH_3$), 49.90 (N—$CH_2$), 49.65 ($CH_3OH$), 125.07 ($ArC_4$), 134.64 ($ArC_3$), 163.39 ($ArC_2$), 172.56 ($ArC_1$), 184.44 (>C=N), 200.19 (>C=N). $^{77}Se\{^1H\}$NMR ($CDCl_3$): 145.

**$H_2L'_A$.6MeOH:** Color, orange; yield, 2.80 g, 62%; m.p., 55°C. Anal. Found: C, 53.53; H, 8.09; N, 6.65; Calc. For $C_{40}H_{72}N_4O_8Se_2$: C, 53.57; H, 8.05, N, 6.25%. ESMS (*m/z*): 897 (36%, $H_2L'_A.6MeOH.H^+$), 705 (48%, $H_2L'_A.H^+$). IR (KBr, $cm^{-1}$): 3412 $\nu$(O—H), 1617 $\nu$(C=N), 1254 $\nu$(C—O), 1169 $\nu$(C—N), 473 $\nu(Se—C_{alkyl})$. $^1H$ NMR ($CD_3OD$): $\delta$ 7.61 (m, 4H, Ar), 3.78 (t, 8H, $NCH_2$), 2.79 (t, 8H, $SeCH_2$), 2.61 (m, 8H, mid-$CH_2$), 2.24 (s, 12H, N=C—$CH_3$); 2.15 (s, 6H, $ArCH_3$). $^{77}Se\{^1H\}$NMR ($CDCl_3$): 151, 148.

**$H_2L_B$.10MeOH:** Color, reddish orange; yield, 1.32. g, 73%; m.p., 130°C; Anal. Found: C, 44.85; H, 7.59; N, 5.52; Calc. For $C_{40}H_{80}N_4O_{12}Te_2$: C 45.11; H, 7.52; N, 5.26% ESMS (*m/z*): 939 (35.6%, $H_2L_B.6MeOH.H^+$); 875 (35.6%, $H_2L_B.4MeOH.H^+$), 801 (40.6%, $H_2L_B.3H_2O.H^+$), 745 (100%, $H_2L_B.H^+$), 373 (83%, $H_2L_B.2H^{2+}$). IR (KBr, $cm^{-1}$): 3422 $\nu$(O—H), 1620 $\nu$(C=N), 1261 $\nu$(C—O), 1159 $\nu$(C—N), 424 $\nu(Te—C_{alkyl})$. $^1H$ NMR ($CD_3OD$): $\delta$ 7.98 (m, 4H, Ar), 4.11 (t, 8H, $NCH_2$), 3.16 (t, 8H, $TeCH_2$), 2.66 (s, 6H, $ArCH_3$), 2.38 (s, 12H, N=C—$CH_3$).

**$H_2L'_B$.10MeOH:** Color, yellow; yield, 1.14 g, 65%; m.p., 70°C. Anal. Found: C, 47.16; H, 7.83; N, 5.06%; Calc. For $C_{44}H_{88}N_4O_{12}Te_2$: C, 47.14; H, 7.85; N 5.00%. ESMS (*m/z*,): 993 (47%, $H_2L'_B.6MeOH.H^+$), 897 (8%, $H_2L'_B.3MeOH.H^+$), 819 (32%, $H_2L'_B.6H_2O.H^+$), 801 (53%, $H_2L'_B.H^+$), 401 (36.7%, $H_2L'_B.2H^+$). IR (KBr, $cm^{-1}$): 3411 $\nu$(O—H), 2920 $\nu$(C—H), 1615 $\nu$(C=N), 1254 $\nu$(C—O); 1153 $\nu$(C—N), 423 $\nu(Te—C_{alkyl})$.

$^1$H NMR($CD_3OD$): $\delta$ 7.88, 7.60 (m, 4H, Ar), 3.73 (t, 8H, $NCH_2$), 2.86 (t, 8H, $TeCH_2$), 2.61 (m, 8H, mid-$CH_2$), 2.34 (s, 6H, N=C—$CH_3$), 2.24 (s, 6H, C—$CH_3$), 2.15 (s, 6H, $ArCH_3$).

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