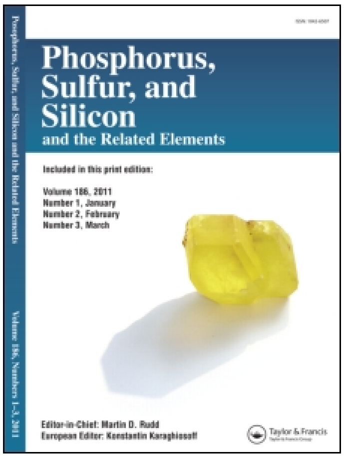

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Organoselenium/Tellurium-Bearing Macroacyclic and Cyclic Ligand Systems and Their Complexation Reactions

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Organoselenium/Tellurium-Bearing Macroacyclic and Cyclic Ligand Systems and Their Complexation Reactions

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A series of phenol-substituted acyclic Schiff bases, 2,6-$\{RE(CH_2)_nN{=}C(CH_3)\}_2$*-*$C_6H_2(4\text{-}CH_3)(OH)$*, (*$E = Te$*:* $R = C_6H_5$*,* $n = 2$*(**L_a**), 3(**L_b**);* $R = C_6H_4\text{-}4\text{-}OCH_3$*,* $n = 2$*(**L_c**), 3(**L_d**);* $E = Se$*:* $R = C_6H_5$*,* $n = 2$*(**L_e**), 3(**L_f**)), of the type* E_2N_2O *have been synthesized by condensation of 2,6-diacetyl-4-methylphenol with arylchalcogenoalkylamines. This ligand framework is useful for designing molecular complexes with a variety of coordination modes depending upon the nature of the central metal atom. The reactivity of the tellurium-bearing macroacyclics ligands towards Zn(II), Cd(II), and Hg(II) has been examined. The ligands **L_a**–**L_d** with Zn(II) and Cd(II), and only **L_a** and **L_b** with Hg(II) form complexes of composition* M_2X_4L*, (*$X = Cl$ *or Br), whereas **L_c** and **L_d** with Hg(II) give products of composition* $HgBr_2L$*. The modes of ligand interaction with Zn(II) and Cd(II) are different than that with Hg(II).*

Following a multistep reaction involving abstraction of bridged Br atoms and subsequent addition of more ligand, the mercury complex, Hg_2Br_4L *has been used for developing metallocyclic system of the type* $[Hg_2Br_2L_2]^{2+}$*. The latter has been found to encapsulate Zn(II) and Cd(II) to give multimetallic systems.*

Keywords Group 12 metal complexes; macroacyclic and cyclic systems; multimetallic systems; organochalcogens; Schiff bases

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INTRODUCTION

The coordination chemistry of organochalcogen ligands containing *hard* donor atoms (such as N and O) along with *soft* selenium/tellurium is interesting as such ligand framework can provide insight into competitive coordination behavior between the *hard* and *soft* donors towards a metal center[1,2] and also stabilize low as well as high oxidation states of a metal atom. Such molecular systems may be important in transition metal catalyzed asymmetric synthesis[3,4] and as single source precursors in MOCVD processes.[5–7] Recently Khandelwal et al. have reported some pyridine based acyclic[8,9] and phenol based cyclic[10] Schiff bases. In fact, a number of polydentate ligands bearing N_3N_2, N_3O_2, N_3S_2 and NS_2P_2 are well documented and among them, a few of the systems have shown promising catalytic, biological, environmental, and material properties.[11–14] The present communication deals with the synthesis and reactivity of phenol substituted acyclic Schiff bases and their metal-induced cyclization. The interest in synthesizing such ligand systems stems from their capability to form binuclear metal complexes in which two metal centers are forced to stay close to each other by their molecular topology.

EXPERIMENTAL

Solvents were purified by standard procedures[15] and were freshly distilled prior to use. All reactions were carried out under a dinitrogen or an argon atmosphere. Arylchalcogenoalkylamines[16] and 2,6-diacetyl-4-methylphenol[17] were prepared following the literature methods. Mercury(ll) bromide (Acros), cadmium(ll) chloride (Fluka), and zinc(ll) bromide (Acros) were used as received.

Physical Measurements

Melting points were recorded in capillary tubes and are uncorrected. Elemental analyses were performed with a Carlo-Erba model-DP 200 instrument. The molar conductance in 10^{-3} mol dm^{-3} MeOH solution was measured using a Global DCM 900 digital conductivity meter. The electrospray ion mass spectra (ESIMS) were recorded on a MICROMASS QUATTRO II triple-quadrupole mass spectrometer using acetonitrile/methanol solution. The solution was introduced into the ESI source through a syringe pump at the rate of 5 μ/min. The ESI capillary was set at 3.5 kV and the cone voltage was 40 V. The spectral print outs are the average of 6–8 scans. The IR spectra in the range of

4000–400 cm^{-1} were recorded as CsI pellets on a Nicolet Megna 750 FT-IR spectrophotometer. The far IR spectra in the range 500–30 cm^{-1} were recorded in polyethylene in a Perkin-Elmer 1700 XFT–IR spectrophotometer. The ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$ at 300 and 75.45 MHz, respectively, on a Brucker 300 MHz machine and chemical shifts are relative to $SiMe_4$. The $^{77}Se\{^{1}H\}$ and $^{125}Te\{^{1}H\}$ NMR spectra were recorded on a Brucker AMX-400 FT NMR spectrometer at 76 and 126 MHz using Ph_2Se_2 and Ph_2Te_2 as external references, respectively.

Synthesis of 2,6-Di(arylchalcogenoalkyliminoacetyl)-4-methylphenol: $[2,6\text{-}\{RE\text{-}(CH_2)_nN = C(CH_3)\}_2C_6H_2\ (4\text{-}CH_3)(OH)]$, (E = Te, R = C_6H_5; n = 2 (L_a), n = 3 (L_b); R = C_6H_4-4-OCH_3, n = 2 (L_c), n = 3 (L_d); E = Se, R = C_6H_5; n = 2 (L_e), n = 3 (L_f)

A solution of 2,6-diacetyl-4-methylphenol (2 mmol in 15 cm^3 methanol) was added dropwise to a solution of arylchalcogenoalkylamine (4 mmol in 10 cm^3 methanol) and heated under reflux at 60°C in the presence of molecular sieves (4 A°) under an argon atmosphere for about 10 h. After cooling the solution and filtering off any solid, the clear solution was concentrated under reduced pressure to give an oily liquid. It was thoroughly washed with hexane and dried under vacuum.

$\mathbf{L_a}$: Viscous orange oily liquid; yield 0.84 g (60%). MS (ESI) (m/z): 655 [$\mathbf{L_a}$.H^+]. UV/VIS (λ_{max}, nm) (εL mol^{-1} cm^{-1}) (MeOH): 401 (2200), 271 (10100). IR (cm^{-1}): 2820br [ν(OH)], 1615s [ν(C=N)], 1580s [ν(C=C)], 1252s [ν(C—O)], 1154s [ν(C—N)], 455m [ν(Te-C_{alkyl})], 175s [ν(Te-C_{aryl}]. ^{1}H NMR ($CDCl_3$, δ, ppm): 17.13 (s, 1H, OH), 7.78–7.21 (m, 12H, Ar, Ph), 3.91 (t, 4H, N-CH_2), 3.25 (t, 4H, Te-CH_2), 2.70 (s, 3H, Ar-CH_3), 2.29 (s, 3H, CH_3C=N), 2.26 (s, 3H, CH_3C=N); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ ppm): 177.99 (C^8 and C^6), 163.88 (C^1), 138.92 (C^2), 137.96 (C^4), 134.79 (C^3), 129.35 (C^{11}), 128.08 (C^{13}), 127.83 (C^{12}), 110.71 (C^{10}), 50.78 (N-CH_2), 31.89 (Te-CH_2), 20.48 (C^5), 14.90 (C^7 and C^9); $^{125}Te\{^{1}H\}$ NMR($CDCl_3$, δ, ppm): 474.

$\mathbf{L_b}$: Viscous orange oily liquid; yield 0.83 g (60%). MS (ESI) (m/z): 683 [$\mathbf{L_b}$.H^+]. UV/VIS (λ_{max}, nm) (εL mol^{-1} cm^{-1}) (MeOH): 410 (2800), 270 (10100). IR (cm^{-1}): 2856br [ν(OH)], 1615s [ν(C=N)], 1574s [ν(C=C)], 1252s [ν(C—O)], 1187m [ν(C—N)], 455m [ν(Te-C_{alkyl}], 175s [ν(Te-C_{aryl}]. ^{1}H NMR ($CDCl_3$, δ, ppm): 17.52 (s, 1H, OH), 7.43–7.06 (m, 12H, Ar, Ph), 3.62 (t, 4H, N-CH_2), 3.02 (t, 4H, Te-CH_2), 2.75 (s, 3H, Ar-CH_3), 2.27 (m, 10H, CH_3C=N and, mid-CH_2); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, δ, ppm): 172.50 (C^6 and C^8), 164.70 (C^1), 138.30 (C^2), 137.90 (C^4), 134.90 (C^3), 133.20 (C^{11}), 129.20 (C^{13}), 128.00 (C^{12}), 124.30 (C^{10}), 50.47 (N-CH_2), 32.33 (Mid-CH_2), 31.88 (Te-CH_2), 20.41 (C^5), 14.64 (C^9), 14.47 (C^7); ^{125}Te{^{1}H} NMR ($CDCl_3$, δ ppm): 470, 474.

L_c: Orange solid; m.p. 102°C; yield 1.34 g (67%). MS (ESI) (m/z): 713 [L_c.H^+]. IR (cm^{-1}): 2930 b[ν(OH)]. 1622s [ν(C=N)], 1570m [ν(C=C)], 1252s [ν(C—O)], 1158 [ν(C—N)], 453 [ν(Te=C_{alkyl})], 175 [ν(Te-C_{aryl}). ^{1}H NMR ($CDCl_3$, δ ppm): 17.30 (s, 1H, OH), 7.70–6.75 (m, 12H, Ar, Ph), 3.90 (t, 4H, N-CH_2), 3.75 (s, 6H, OCH_3), 3.08 (t, 4H, Te=CH_2), 2.70 (s, 3H, ArCH_3), 2.25 (s, 6H, CH_3C=N).

L_d: Dark orange viscous liquid; yield, 1.30 g (65%). MS (ESI) (m/z): 741 [L_d.H^+]. IR (cm^{-1}) 2921 b[ν(OH)], 1628s [ν(C=N)], 1565m [ν(C=C)], 1252m [ν(C—O)], 1165s [ν(C—N)], 456m [ν(Te-C_{alkyl})], 175 [ν(Te-C_{aryl})]. ^{1}H NMR ($CDCl_3$, δ ppm): 17.60 (s, 1H, OH), 7.69–7.70 (m, 12H, Ar, Ph), 3.80 (s, 6H, OCH_3), 3.67 (t, 4H, N-CH_2), 3.00 (t, 4H, Te-CH_2), 2.71 (s, 3H, ArCH_3), 2.26 (s, 10H, CH_3C=N and mid -CH_2).

L_e: Brown viscous liquid; yield 60%; MS (ESI) (m/z): 557 [L_e.H^+]. IR (cm^{-1}): 2845 b [ν(OH)], 1615s [ν(C=N)], 1583s [ν(C=C)], 1258s [δ OH], 1158s [ν(C—N)], 455m [ν(Se—C)]. ^{1}H NMR ($CDCl_3$, δ ppm): 17.15 (s, 1H, OH), 7.23–7.53 (m, 12H, Ar, Ph), 3.80 (t, 4H, N-CH_2), 3.23 (t, 4H, Se-CH_2), 2.71 (s, 3H, Ar-CH_3), 2.26 (s, 3H, CH_3C=N); ^{13}C{^{1}H} NMR ($CDCl_3$, δ ppm): 172.39 (C^8 and C^6), 163.62 (C^1), 134.63 (C^2), 132.71 (C^4), 131.69 (C^3), 129.20 (C^{11}), 129.05 (C^{13}), 127.35 (C^{12}), 124.80 (C^{10}), 59.40 (OCH_3), 50.26 (N-CH_2), 20.45 (C^5), 14.94 (C^7 and C^9), 14.74 (SeCH_2); ^{77}Se{^{1}H} NMR ($CDCl_3$, δ, ppm): 285.

L_f: Brown viscous liquid; yield 62%; IR (cm^{-1}): 2810b [ν(OH)], 1616s [ν(C=N)], 1579s [ν(C=C)], 1253s [δ OH], 1163s [δ(C—N)], 469m [ν(Se—C)]. ^{1}H NMR ($CDCl_3$, δ ppm): 17.50 (s, 1H, OH), 7.52–7.45 (m, 12H, Ar, Ph), 3.71 (t, 4H, N-CH_2), 3.05 (t, 4H, Se-CH_2), 2.71 (s, 3H, Ar-CH_3), 2.33 (s, 3H, CH_3C=N), 2.23 (s, 3H, CH_3CN–CH_2P), 2.18 (m, 4H, mid-CH_2); ^{13}C{^{1}H} NMR ($CDCl_3$, δ ppm): 172.53 (C^6 and C^8), 164.59 (C^1), 136.86 (C^2), 134.93 (C^4), 132.66 (C^3), 129.63 (C^{11}), 129.13 (C^{12}), 128.19 (C^{13}), 124.41 (C^{10}), 59.60 (OCH_3), 47.96 (NCH_2), 29.66 [mid CH_2], 25.13 (C^5), 20.43 (C^7 and C^9), 14.66 (Se-CH_2); ^{77}Se{^{1}H} NMR ($CDCl_3$, δ, ppm): 286.

Synthesis of Zn(II) Complexes with L_a, L_b, L_c and L_d ligands

To a methanolic solution of 2.6-di(aryltelluroalkyliminoacetyl)-4-methylphenol (0.36 g, 0.55 mmol), a solution of $ZnBr_2$ (0.247 g, 1.10 mmol in 15 cm^3 methanol) was added dropwise under an argon atmosphere. The reaction mixture was stirred for 11 h at 55°C and the reaction progress was monitored by TLC. On completion of the reaction a dark brown solution was obtained. It was concentrated under vacuum, and recrystallized with acetone-diethylether (60:40).

$Zn_2Br_4L_a$ (1)

Dark brown solid; m.p., 124°C; yield, 84%; Anal. Found: C, 29.29; H, 2.69; N, 2.72; Te, 22.84; Br, 28.80; Calc. for $C_{27}H_{30}N_2Te_2Br_4Zn_2O$: C, 29.34; H, 2.71; N, 2.71; Te, 23.13; Br, 28.94%. MS (ESI) (m/z): 1105 [**1H**$^+$]. IR (cm^{-1}): 3352 [ν(O—H)], 1577 [ν(C=N)], 1378 [δ (O—H)], 1230 [ν (C—O)], 1200 [ν(C=N)], 456 [ν(Te-C)], 206 [ν (Zn-Br)], 174 [ν(Te-C$_{aryl}$)], 136 [ν(μZn-Br)].

$Zn_2Br_4L_b$ (2)

Dark brown solid; m.p., 122°C; yield, 83%; Anal. Found: C, 31.01; H, 2.90; N, 2.71; Te, 22.44; Br, 28.27; Calc. for $C_{29}H_{34}N_2Te_2Br_4Zn_2O$: C, 30.74; H, 3.00; N, 2.65; Te, 22.44; Br, 28.27%. MS (ESI) (m/z): 1133 [**2H**$^+$]. IR (cm^{-1}): 3359 [ν(O—H)], 1578[ν(C=N)], 1386 [δ(O—H)], 1231 [ν(C—O)], 1199 [ν(C—N)], 456 [ν(Te-C)], 203 [ν(Zn-Br)], 170 [ν(Te-C$_{aryl}$)], 138 [ν(μZn-Br)].

$Zn_2Br_4L_c$ (3)

Dark brown hygroscopic solid; m.p., 118°C; yield, 81%; Anal. Found: C, 29.85; H, 2.91; N, 2.53; Te, 21.95; Br, 27.51; Calc. for $C_{29}H_{34}N_2Te_2Br_4Zn_2O_3$: C, 29.89; H, 2.92; N, 2.57; Te, 21.83; Br, 27.49%. MS (ESI) (m/z): 1163 [**3H**$^+$]. IR (cm^{-1}): 2928 [ν(O—H)], 1577 [ν(C=N)], 1378 [δ(O—H)], 1230 [ν(C—O)], 1199 [ν(C—N)], 456 [ν(Te-C$_{alkyl}$)], 208 [ν(Zn-Br)], 170 [ν(Te-C$_{aryl}$)], 144 [ν(μZn-Br)].

$Zn_2Br_4L_d$ (4)

Dark brown hygroscopic solid; m.p., 121°C; yield, 83%; Anal. Found: C, 31.14; H, 3.15; N, 2.44; Te, 21.19; Br, 26.79; Calc. for $C_{31}H_{38}N_2Te_2Br_4Zn_2O_3$: C, 31.20; H, 3.18; N, 2.50, Te, 21.32; Br, 26.84%. MS (ESI) (m/z): 1191 [**4H**$^+$]. IR (cm^{-1}): 2928 [ν(O—H)], 1577 [ν(C=N)], 1378 [δ(O—H)], 1230 [ν(C—O)], 1200 [ν(C—N)], 456 [ν(Te-C$_{alkyl}$)], 203 [ν(Zn-Br)], 179 [ν(Te-C$_{aryl}$)], 144 [ν(μZn-Br)].

Synthesis of Cd(II) Complexes with L_a, L_b, L_c and L_d Ligands

A suspension of $CdCl_2$ (0.336 9, 1.839 mmol) in 20 cm^3 ethanol was slowly added to solution of 2,6-di(aryltelluroalkyliminoacetyl)-4-methylphenol (0.6 g, 0.91 mmol) in 50 cm^3 acetone under an inert atmosphere. The reaction mixture was stirred for 13 h at 55°C and the reaction progress was monitored by TLC. On completion of the reaction, a dark yellow solution was obtained. It was concentrated under vacuum and recrystallized with acetone-diethylether (60:40).

$Cd_2Cl_4L_a$ (5)

Brown-yellow solid; m.p., 138°C; yield, 86%; Anal. Found: C, 31.30; H, 2.61; N, 2.79; Te, 24.85; Cl, 13.87; Calc. for $C_{27}H_{30}N_2Te_2Cl_4Cd_2O$: C, 31.76; H, 2.94; N, 2.74; Te, 24.90; Cl, 13.92%. MS (ESI) (m/z): 1021 [**5H**$^+$]. IR (cm^{-1}): 2921 [δ(O—H)], 1584 [ν(C=N)], 1219 [ν(C—O)], 1150 [ν(C—N)], 456 [μ(Te-C$_{alkyl}$)], 208 [ν(Cd-Cl)], 177 [ν(Te-C$_{aryl}$)], 155 [ν(μCd-Cl)].

$Cd_2Cl_4L_b$ (6)

Brown-yellow solid; m.p., 142°C; yield, 88%; Anal. Found: C, 33.17; H, 3.30; N, 2.82; Te, 24.19; Cl, 13.42; Calc. for $C_{29}H_{34}N_2Te_2Cl_4Cd_2O$:C, 33.20; H, 3.24; N, 2.86; Te, 24.23; Cl, 13.56%. MS (ESI) (m/z): 1049 [**6H**$^+$]. IR (cm^{-1}): 2922 [ν(O—H)], 1589 [ν(C=N)], 1376 [δ(O—H)], 1222 [ν(C—O)], 1161 [ν(C—N)], 456 [(Te-C$_{alkyl}$)], 209 [ν (Cd-Cl)], 182 [ν(Te-C$_{aryl}$)], 159 [ν(μCd-Cl)].

$Cd_2Cl_4L_c$ (7)

Dark brown solid; m.p., 128°C; yield, 84%; Anal. Found: C, 32.12; H, 3.20; N, 2.68; Te, 23.51; Cl, 13.15; Calc. for $C_{29}H_{34}N_2Te_2Cl_4Cd_2O_3$: C, 32.22; H, 3.14; N, 2.77; Te, 23.51; Cl, 13.14%. MS (ESI) (m/z): 1079 [**7H**$^+$]. IR (cm^{-1}): 2922 [ν(O—H)], 1589 [ν(C=N)], 1385 [δ(O—H)], 1222 [ν(C—O)], 1123 [ν(C—N)], 456 [(Te-C$_{alkyl}$)], 201 [ν(Cd-Cl)], 169 [ν(Te-C$_{aryl}$)], 160 [ν(μCd-Cl)].

$Cd_2Cl_4L_d$ (8)

Dark brown solid; m.p., 133°C; yield1 85%; Anal. Found: C, 33.59; H, 3.24; N, 2.68; Te, 22.12; Cl, 12.84; Calc. for $C_{31}H_{38}N_2Te_2Cl_4Cd_2O_3$: C, 33.57; H, 3.42; N, 2.70; Te, 22.93; Cl, 12.82%. MS (ESI) (m/z): 1107 [**8H**$^+$]. IR (cm^{-1}): 2922 [ν(O—H)], 1585 [ν(C=N)], 1375 [δ(O—H)], 1220 [ν(C—O)], 1164 [ν(C—N)], 456 [ν(Te-C$_{alkyl}$)], .206 [ν(Cd-Cl)], 174 [ν(Te-C$_{aryl}$)], 160 [ν(μCd-Cl)].

Synthesis of Hg(II) Complexes with L_a and L_b Ligands

A solution of $HgBr_2$ (0.397, 1.10 mmol) in 10 cm^3 methanol was added dropwise under an argon atmosphere at room temperature to a stirred methanolic solution of 2,6-di(phenyltelluroalkyliminoacetyl)-4-methylphenol (0.36 g, 0.55 mmol). A small amount of yellow precipitate appeared almost immediately. More quantity of the product was obtained by concentrating the filtrate under vacuum. It was washed with diethylether and recrystallized with acetone-diethyl ether (60:40).

$Hg_2Br_4L_a$ (9)

Dark yellow solid; m.p., 185°C; yield, 88%; Anal. Found: C, 23.51; H, 2.20; N, 2.16; Te, 18.49; Br, 23.29; Calc. for $C_{27}H_{30}N_2Te_2Br_4Hg_2O$: C, 23.58; H, 2.78; N, 2.18; Te, 18.49; Br, 23.29%. MS (ESI) (m/z): 1376 [**9H**$^+$]. IR (cm^{-1}): 2924 [ν(O—H)], 1619 [ν(C=N)], 1383 [δ(O—H)], 1260 [ν(C—O)], 1163 [ν(C—N)], 415 [ν(Te-C$_{\text{alkyl}}$)], 201 [ν(Hg-Cl)], 160 [ν(μHg-Cl)], 174 [ν(Te-C$_{\text{aryl}}$)].

$Hg_2Br_4L_b$ (10)

Dark yellow solid; m.p., 192°C; yield, 89%; Anal. Found: C, 24.74; H, 2.28; N, 1.97; Te, 18.09; Br, 22.79; Calc. for $C_{29}H_{34}N_2Te_2Br_4Hg_2O$: C, 24.85; H, 2.42; N, 2.20; Te, 18.14; Br, 22.85%. MS (ESI) (m/z): 1404 [**10H**$^+$]. IR (cm^{-1}): 2922 [ν(O—H)], 1622 [ν(C=N)], 1312 [δ(O—H)], 1260 [ν(C—O)], 1157 [ν(C—N)], 417 [ν(Te-C$_{\text{alkyl}}$)], 252 [ν(Hg-Br)], 184 [ν(μHg-Br)], 141 [ν(Te-C$_{\text{aryl}}$)].

Synthesis of Hg(II) Complexes with L_c and L_d Ligands

Procedure as mentioned above in case of the synthesis of Cd(II) complexes was followed by the using 2,6-di(4-methoxyphenyltelluroethyliminoacetyl)-4-methylphenol and $HgBr_2$ in 1:2 molar ratio.

$HgBr_2L_c$ (11)

Greenish yellow solid; m.p., 162°C; yield, 87%; Anal. Found: C, 32.38; H, 3.20; N, 2.54; Te, 23.66; Br, 14.89; Calc. for $C_{29}H_{34}N_2Te_2Br_2HgO_3$: C, 32.40; H, 3.16; N, 2.79; Te, 23.66; Br, 14.89%. MS (ESI) (m/z): 1074 [**11H**$^+$]. IR (cm^{-1}): 2928 [ν(O—H)], 1618 [ν(C=N)], 1363 [δ(O—H)], 1260 [ν(C—O)], 1162 [ν(C—N)], 414 [ν(Te-C$_{\text{alkyl}}$)], 258 [ν(Hg-Br)], 144 [ν(Te-C$_{\text{aryl}}$)].

$HgBr_2L_d$ (12)

Greenish yellow solid; m.p., 166°C; yield, 88%; Anal. Found: C, 33.69; H, 3.50; N, 2.53; Te, 23.08; Br, 14.49; Calc. for $C_{31}H_{38}N_2Te_2Br_2HgO_3$: C, 33.75; H, 3.44; N, 2.72; Te, 23.10; Br, 14.53%. MS (ESI) (m/z): 1102 [**12H**$^+$]. IR (cm^{-1}): 2923 [ν(O—H)], 1622 [ν(C=N)], 1380 [δ(O—H)], 1264

[ν(C—O)], 1150 [ν(C—N)], 410 [ν(Te-C_{alkyl})], 254 [ν (Hg-Br)], 144 [ν (Te-C_{aryl})].

Cyclization of Acyclic Complex Hg_2Br_4L

Addition of methanolic silver nitrate solution to a $\mathbf{Hg_2Br_4L}$ (where $\mathbf{L} = \mathbf{L_a}$ or $\mathbf{L_b}$) solution in acetone in 2:1 molar ratio results in an immediate precipitation of AgBr. After filtering off the precipitate, the ligand solution in acetone was added to the clear solution in 1:1 molar ratio and the mixture was refluxed for 24 h under an argon atmosphere. The reaction progress was checked by TLC, using acetone-diethylether (60:40). On completion of the reaction, dark brown solution was obtained. It was concentrated under vacuum and recrystallized with acetone/diethylether (60:40).

$[Hg_2Br_2(L_a)_2](NO_3)_2$ (13)

Dark brown solid; m.p., 255°C; yield, 71.5%; Anal found: C, 30.01; H, 2.41; N, 3.93; Te, 24.81; Br, 7.70; Calc. for $C_{54}H_{60}N_6Te_4Br_2Hg_2O_{10}$: C, 31.48; H, 2.91; N, 4.08; Te, 24.90; Br, 7.78%. MS (ESI) (m/z): 1029 [$\mathbf{13H^+/2}$]. IR (cm^{-1}): 2922 [ν(O—H)], 1757, 1521, 823, 702 [ν(NO_3)], 1607 [ν(C=N)], 1379 [δ(O—H)], 1250 [ν(C—O)], 1046 [ν(C—N)], 415 [ν(Te-C_{alkyl}], 257 [ν(Hg-Br)], 144 [ν(Te-C_{aryl})].

$[Hg_2Br_2(L_b)_2](NO_3)_2$ (14)

Dark brown solid; m.p., 235°C; yield, 72%; Anal found: C, 32.81; H, 3.15; N, 3.74; Te, 24.19; Br, 7.50 Calc. for $C_{58}H_{68}N_6Te_4Br_2Hg_2O_{10}$; C, 32.90 H, 3.20; N, 3.97; Te, 24.24; Br, 7.59%. MS (ESI) (m/z): 1057 [$\mathbf{14\ H^+/2}$]. IR (cm^{-1}): 2923 [ν(O—H)], 1757, 1525, 822, 704 [ν(NO_3)], 1605 [ν(C=N)], 1379 [δ(O—H)], 1250 [ν(C—O)], 1141 [ν (C—N)], 415 [ν (Te-C_{alkyl})], 255 [ν(Hg-Br)], 144 [ν(Te-C_{aryl})].

Reactions of $ZnBr_2$ and $CdCl_2$ with Cyclized System

A suspension of $CdCl_2$ in acetone or a solution of $ZnBr_2$ in methanol was added slowly to a solution of the compound **13** or **14** in acetone in 2:1 molar ratio and refluxed for 25–30 h under an argon atmosphere. The reaction progress was checked by TLC, using acetone-methanol (50:50). On completion of the reaction, a brown solution was obtained. It was concentrated under vacuum and recrystallized with acetone-diethyl ether (60:40).

$[Hg_2Cd_2Br_2Cl_4(L_a)_2](NO_3)_2$(15)

Brown yellow solid; m.p., 268°C; yield, 84%; Anal found: C, 26.31; H, 2.31; N, 3.39; Te, 20.80; Br, 5.9; Cl, 5.73; Calc. for $C_{54}H_{60}N_6Te_4Br_2Cl_4Hg_2Cd_2O_{10}$: C, 26.73; H, 2.47; N, 3.46; Te, 21.13; Br, 6.60; Cl, 5.78%. MS (ESI) (m/z): 1212 [**15H$^+$/2**]. IR (cm^{-1}): 2922 [ν(O—H)], 1761, 1521, 824, 702 [ν(NO3)], 1595 [ν(C=N)], 1383. [δ(O—H)], 1246 [ν (C—O)], 1036 [ν(C—N)], 417 [ν(Te-C$_{alkyl}$)], 261 [ν(Hg—Br)], 206 [ν(Cd-Cl)], 139 [ν(Te-C$_{aryl}$)].

$[Hg_2Cd_2Br_2Cl_4(L_b)_2]$ $(NO_3)_2$ (16)

Dark brown solid; m.p., 286°C; yield, 86%; Anal found: C, 27.91; H, 2.51; N, 3.32; Te, 2.68; Br, 6.47; Cl, 5.63; Calc. for $C_{58}H_{68}N_6Te_4Br_2C_{14}Hg_2Cd_2O_{10}$; C, 28.06; H, 2.74; N, 3.38; Te, 20.70; Br, 6.46; Cl, 5.66%. MS (ESI) (m/z): 1240 [**16H$^+$/2**]. IR (cm^{-1}): 2928 [ν(O—H)], 1761, 1515, 825, 702 [ν(NO_3)], 1577 [ν(C=N)], 1382 [δ(O—H)], 1248 [ν(C—O)], 1037 [ν(C—N)], 415 [ν(Te-C$_{alkyl}$)], 252 [ν(Hg-Br)], 208 [ν(Cd-Cl)], 144 [ν(Te-C$_{aryl}$)].

$[Hg_2Zn_2Br_6(L_a)_2](NO_3)_2$ (17)

Dark brown solid; m.p., 242°C; yield, 81%; Anal found: C, 25.61; H, 2.43; N, 3.34; Te, 20.39; Br, 19.09; Calc. for $C_{54}H_{60}N_6Te_4Br_6Hg_2Zn_2O_{10}$: C, 25.83; H, 2.39; N, 3.35; Te, 20.44; Br, 19.15%. MS (ESI) (m/z): 1254 [**17H$^+$/2**]. IR (cm^{-1}): 2927 [ν(O—H)], 1757, 1513, 824, 701 [ν(NO3)], 1578 [ν(C=N)], 1381 [δ(O—H)], 1248 [ν(C—O)], 1039 [ν(C—N)], 415 [ν(Te-C$_{alkyl}$)], 257 [ν(Hg-Br)], 206 [ν(Zn-Br)], 144 [ν (Te-C$_{aryl}$)].

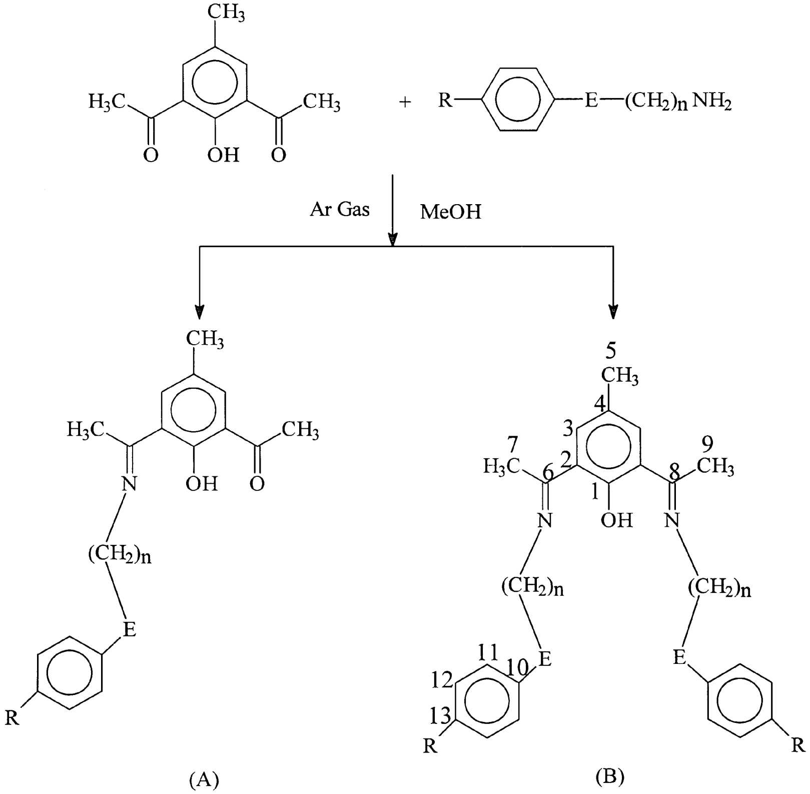
$[Hg_2Zn_2Br_6(L_b)_2]$ $(NO_3)_2$ (18)

Dark brown solid; m.p., 263°C; yield, 83%; Anal found: C, 26.90; H, 2.51; N, 3.25; Te, 19.87; Br, 18.70; Calc. for $C_{58}H_{58}N_6Te_4Br_6Hg_2Zn_2O_{10}$; C, 27.14; H, 2.65; N, 3.27; Te, 19.99; Br, 18.73%. MS (ESI) (m/z): 1282 [**18H$^+$/2**]. IR (cm^{-1}): 2928 [ν(O—H)], 1760, 1513, 825, 701 [ν(NO_3)], 1577 [ν(C=N)], 1381 [δ(O—H)], 1252 [ν(C—O)], 1039 [ν(C—N)], 421 [ν(Te-C$_{alkyl}$)], 257 [ν(Hg-Br)], 209 [ν(Zn-Br)], 142 [ν(Te-C$_{aryl}$)].

RESULTS AND DISCUSSION

Synthesis and Properties of Ligands

The reactions of phenyltelluroethylamine with 2,6-diacetyl-4-methylphenol in methanol alone invariably resulted in a mixture of one side condensed (A) (open-chain end-off unsymmetrical of ENO_2 type) and both side condensed (B) (open-chain end-off symmetrical of E_2N_2O type) compounds (as shown in Scheme 1); the former being less soluble in the solvent system separated out first. However, following the experimental conditions, the symmetrical macroacyclic moisture sensitive compounds (**L_a-L_f**) were obtained in pure form.



E=Te; R=H; n=2 (L_a), E=Te; R=H; n=3 (L_b)
E=Te; R=OCH_3; n=2 (L_c), E=Te; R=OCH_3; n=3 (L_d
E=Se; R=H; n=2 (L_e), E=Se; R=H; n=3 (L_f)

SCHEME 1

Mass Spectra

The ESIMS show molecular-ion peaks along with typical isotopic patterns for tellurium/selenium containing peaks. The spectrum of **L_a** as a representative one is shown in Figure 1.

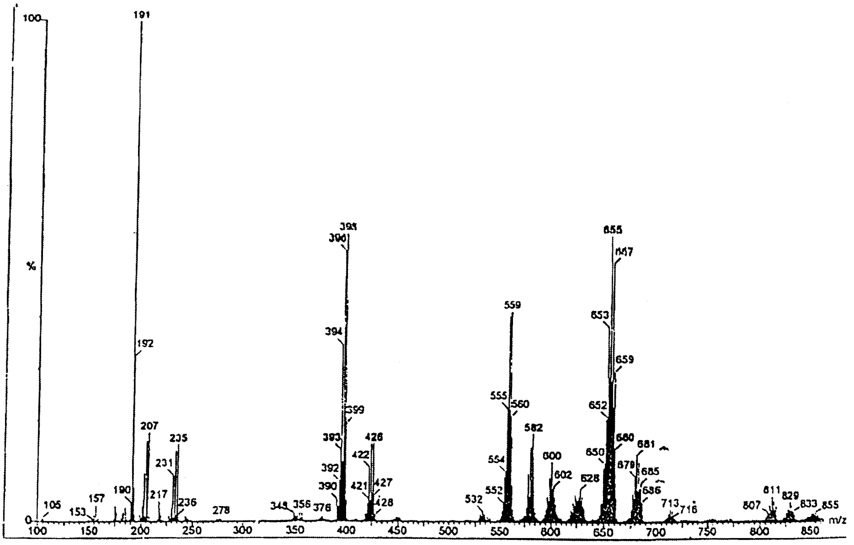


FIGURE 1 ESI Spectrum of 2,6-di(phenyltelluroethyl)iminoacetyl-4-methylphenol (**L**$_\mathbf{a}$).

IR and Electronic Spectra

The IR spectra of the compounds exhibited a strong band attributable to ν(C=N) around 1615 cm^{-1}. The absence of band in ν(C=O) region confirms the presence of only both side condensed products. It is noteworthy that the IR spectrum of the one side condensed product (ENO_2 type) displays a greater intensity ν(C=O) band at 1664 cm^{-1} and a moderate-intensity ν(C=N) vibration at 1615 cm^{-1}. Thus, the IR technique is diagonistic for differentiating between one-side and both-side condensed products. The appearance of a broad band around 2805 cm^{-1} due to ν(O—H) strongly suggests the presence of intramolecular hydrogen bonding.

Electronic spectra of all these ligands in methanol show a moderately intense band in the range 400–270 nm due to intraligand transitions.

NMR Spectra

The ^{1}H NMR spectra of **L**$_\mathbf{a}$-**L**$_\mathbf{f}$ in $CDCl_3$ were recorded immediately after dissolving them in NMR tubes since they seem to decompose with time. The methyl groups attached to the two iminoacetyl groups in **L**$_\mathbf{a}$ exhibit two singlets (except in **L**$_\mathbf{b}$ and **L**$_\mathbf{d}$ where they are merged with mid-CH_2 protons and **L**$_\mathbf{c}$ where it shows a singlet only) indicating their nonequivalence. This probably reflects the different electron density around the two iminoacetyl C-atoms arising out of unequal intramolecular hydrogen bonding between the phenolic oxygen and azomethane nitrogen. The hydrogen bonding results in significant deshielding of the hydroxyl proton in comparison with the 2,6-disubstituted phenol precursor. The other spectral features are as expected. The ^{13}C NMR spectra corroborate well with the ^{1}H NMR data and show one signal for both iminoacetyl carbon (except in $\mathbf{L_a}$) and methyl-carbon attached to iminoacetyl groups. The $^{125}Te\{^{1}H\}$ NMR spectrum of $\mathbf{L_a}$ exhibits one signal at δ474; however, that of $\mathbf{L_b}$ shows two resonances at 470 and 474 ppm relative to diphenyl ditelluride with ^{1}J (^{125}Te-^{13}C) 153 and 104 Hz, respectively. This observation probably suggests that the tellurium analogue with C_3 linker between N and Te is not fluxional on NMR time scale at room temperature. The $^{77}Se\{^{1}H\}$ NMR spectra of both $\mathbf{L_e}$ and $\mathbf{L_f}$ show only one signal. The proposed structure of the ligands is shown in Scheme 1 and three dimensional structure generated by Hyper chemistry programme of $\mathbf{L_b}$ is shown in Figure 2.

Structurally, this ligand framework is interesting as the presence of hetero (N, O, Te) 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.

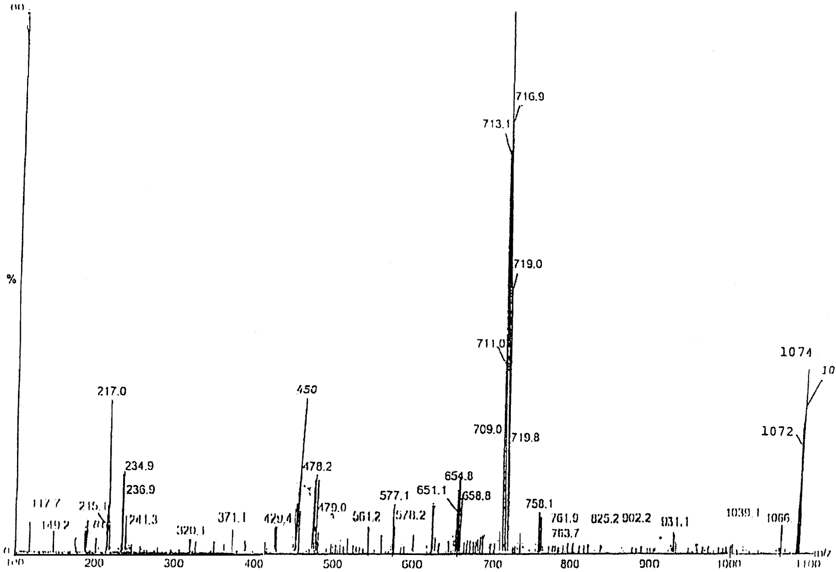


FIGURE 2 ESI spectrum of $HgBr_2\mathbf{L_c}$.

Synthesis and Properties of Complexes

The reactivity of the tellurium-bearing ligand systems towards Zn(II), Cd(II), and Hg(II) halides has been studied by reacting them in 1:2 molar ratios. The products obtained are found to have composition $M_2X_4\mathbf{L}$ except in the case of Hg(II) which with 2,6-bis(methoxyphenyltelluroalkyliminoacetyl)-4-methylphenol ($\mathbf{L_{c,d}}$) formed the product of composition $\mathbf{HgBr_2}$. $\mathbf{L_{c,d}}$. The metal complexes are soluble in acetone but only sparingly soluble in acetonitrile. The solubility of metal complexes with $\mathbf{L_{c,d}}$ is relatively more than with $\mathbf{L_{a,b}}$. They behave as nonelectrolytes in acetonitrile.

Mass Spectra

The ESI mass spectra of all the compounds exhibit molecular ion peak. The peak pattern of tellurium-containing fragments easily could be recognized due to its typical isotopic cluster and is indicative of two Te atoms in a molecule of the compounds. Besides the molecular ion peak, each spectrum clearly show peaks corresponding to $[\mathbf{L}.MX_2H^+]$, $[\mathbf{L}H^+]$ and $[RTeH^+]$ fragments as well. Substitution of methoxyphenyl group in place of phenyl with the tellurium in the ligand framework does not make any difference in the composition of Zn(II) and Cd(II) complexes, but it does for Hg(II). This is illustrated in the ESI spectrum of the compound 11 (Figure 2) and corroborate well with their chemical analyses. This suggests that the mode of bonding of the ligand with Hg(II) is different than with Zn(II) and Cd(II).

IR Spectra

The IR spectra of all the complexes show ν(OH) vibration almost at the same position as in the ligand suggesting noninvolvement of phenolic group in complexation with the metal ions. The ν(C=N) vibration exhibits a red shift of $\sim$30–40 cm^{-1} in Zn(II) and Cd(II) complexes, however, there is no shift in Hg(II) complexes. This fact strongly suggests the involvement of azomethine nitrogen in coordination with Zn and Cd but not with Hg. The ν(Te-C) vibrations do not show any shift in Zn(II) and Cd(II) complexes but they shift to lower wavenumbers in Hg(II) complexes indicating the coordination of Te with Hg only.

In all these complexes, except in $\mathbf{HgBr_2}$ $\mathbf{L_{c,d}}$ (where only one band appear in M-Br region), two bands appear in ν(M-X) region, one corresponding to terminal M—X bond and the other to the bridging one. The assignment is confirmed following the halogen exchange method by which the bridging M—X band disappears and the intensity of M—X terminal band is significantly reduced.

Thus, it could be inferred from the IR spectral study that the metal ions in **1–10** adopt a tetrahedral geometry in all the complexes. While each Zn(II) and Cd(II) atom is bonded with an azomethine N atom, the Hg(II) is linked with Te atom. Each metal species is surrounded by three halogen atoms, one is terminally bonded whereas the other two are bridging the two metal species. The complexes are molecular in nature as suggested by their conductance data.

The metal atom in complexes **11** and **12**, which have composition of $\mathbf{HgBr_2\ L_{c,d}}$, is also tetrahedral but is linked with both the Te atoms of the ligand molecule and with the two terminal bromine atoms.

It is interesting to note that while the ligand system $\mathbf{L_{a,b}}$ forms bimetallic complexes, that of $\mathbf{L_{c,d}}$ with Hg(II) forms only monometallic complexes. The presence of a methoxy group at the para position with respect to tellurium in the aromatic ring of the ligand system $\mathbf{L_{c,d}}$ results in the cyclization through a Hg atom which bonds with both the Te atoms of the ligand molecule. This observation suggests that the two Te atoms of the p-methoxyphenyltellurium moiety in the ligand system $\mathbf{L_{c,d}}$ are closer to each other as compared with the situation in $\mathbf{L_{a,b}}$ where only a phenyl group is attached with each Te atom. In other words, the increased electron density on Te atoms, due to the presence of electron donating methoxy group at the para position in $\mathbf{L_{c,d}}$, is presumably a factor which leads to a monometallic-cyclized system. This, of course, needs support from X-ray study which unfortunately is not available at the present stage.

The fact that the Zn(II) and Cd(II) presumably because of their small size as compared with Hg(II) still form bimetallic species with $\mathbf{L_{c,d}}$ further supports that these metal ions do not interact with the Te atoms of the ligand systems.

The NMR study has not proved to be very informative in these systems.

Cyclization of Acyclic Hg_2Br_4L System

Abstraction of bridged bromine atoms from Hg_2Br_4L by the addition of methanolic silver nitrate solution and subsequently the addition of more of appropriate ligand resulted in the formation of metallocyclic compounds of the type $\mathbf{[Hg_2Br_2L_2](NO_3)_22CH_3OH}$. They behave as 1:2 electrolytes in acetonitrile and their ESI mass spectra show peak corresponding to $\mathbf{\{[Hg_2Br_2L_2.2CH_3OH].(NO_3)_2\ 2H^+\}}$. The mass spectral data thus suggest strong ion pair association in them. Their IR spectra are very similar to those of the parent Hg(II) compound except that the band corresponding to the bridging Hg-Br-Hg is missing and those of free NO_3 ions are observed.

Reactions of Cyclic Systems with $CdCl_2$ and $ZnBr_2$

Considering that a number of functional sites are available in the cyclized system, their reactions with Zn(II) and Cd(II) have been attempted. They have led to the formation of complexes of composition $\mathbf{Hg_2Zn_2Br_6L_{a,b}(NO_3)_2{\cdot}2CH_3OH}$ (**17**,**18**) and $\mathbf{Hg_2Cd_2Br_2Cl_4L_{a,b}(NO_3)_2{\cdot}2CH_3OH}$ (**15**,**16**) which behave as 1:2 electrolytes in acetonitrile. However, ESI mass spectra suggest strong Ion-pair association in solution.

In all these complexes the ν(C=N) vibration shifts to low frequency side by 25–35 cm^{-1} as compared with the parent cyclic system suggesting strong interaction between the metal (Zn/Cd) species and the nitrogen atoms of the cyclic ligand system. The ν(O—H) remains unaltered. It can, therefore, be inferred that the two metal (Zn/Cd) atoms are inside the cavity and each one tetrahedrally is bonded with the two imino nitrogen atoms (leaving the hydroxyl group intact) and two halogen atoms.

Attempts to grow single crystals for X-ray study of these compounds are in progress.

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