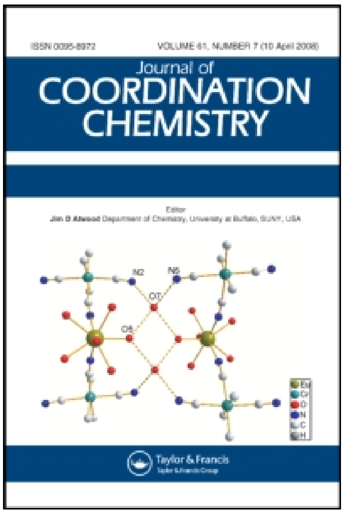

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Synthesis, characterization, catalytic and biological activity of some bimetallic selenocyanate Lewis acid derivatives of <i>N</i>, <i>N</i>'-<i>bis</i>(2-chlorobenzylidene)ethylenediamine

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Synthesis, characterization, catalytic and biological activity of some bimetallic selenocyanate Lewis acid derivatives of *N*, *N′*-*bis*(2-chlorobenzylidene)ethylenediamine

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Complexes of $MM'(SeCN)_4$, ($M = Co^{2+}$, Ni^{2+}; $M' = Cd^{2+}$, Zn^{2+}) with the Schiff base, *N*,*N′*-*bis*(2-chlorobenzylidene)ethylenediamine have been synthesized and characterized by elemental analysis, molar conductance, magnetic moment, FTIR, ^1H-NMR, $^{13}C\{^1H\}$-NMR and electronic spectroscopy. The catalytic activity of these complexes for hydrolysis of benzonitrile has been investigated. The complexes have also been investigated for antibacterial activity against *Escherichia Coli* and found to exhibit good growth inhibiton.

Keywords: Homobimetallic; Heterobimetallic Selenocyanate; Schiff base

1. Introduction

Thiocyanate and selenocyanate have generated considerable interest in bimetallic monomeric and polymeric systems due to their ambidentate nature [1]. Bimetallic complexes are of interest due to metal centers in close proximity for catalytic activity [2], or presence of two metal centers coupled with radionucleotide at one end and antibodies at the other by a bifunctional chelating agent in nuclear medicine [3]. Synthesis of $[ZnCd(SeCN)_4]_n$ and $[CdHg(SeCN)_4]_n$ as second order non-linear optical coordination polymers [4] and alpha-$(ET)_2TlHg(SeCN)_4$ as an anionic complex [5], have given impetus to bimetallic selenocyanate chemistry.

Aromatic Schiff bases and their metal complexes have been used as catalysts in polymerization reactions, oxidation of ascorbic acid and cystines and decomposition of hydrogen peroxide [6]. Some Schiff-base chelates are reported to show antifungal [7], antibacterial [8] and even anticancer activity [9].

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Therefore, it was of interest to examine reactions of the bimetallic Lewis acids, $MM'(SeCN)_4$, $(M = Co^{2+}, Ni^{2+}; M' = Zn^{2+}, Cd^{2+})$ and *N*,*N*′-*bis*(2-chlorobenzylidene)ethylenediamine, (2-Cl BENEN) in 1 : 1 and 1 : 2 molar ratios.

2. Experimental

The metal salts $Co(NO_3)_2 \cdot 6H_2O$; $Ni(NO_3)_2$; $Cd(NO_3)_2 \cdot 4H_2O$; $Zn(NO_3)_2 \cdot 6H_2O$ (all BDH) were used as received without further purification. Methanol and ethanol (both BDH) were dried and distilled as described by Vogel [10]. Potassium selenocyanate (Aldrich, UK) was used as received. Ethylenediamine and 2-chlorobenzaldehyde (both CDH) were used as received. FTIR spectra were recorded on a Schimadzu–8400 S FTIR spectrophotometer using KBr pellets in the range 4000–200 cm^{-1}. Electronic spectra were measured on a UV–VIS–NIR CARY-5000 spectrophotometer in acetonitrile/DMSO. ^1H-NMR spectra and $^{13}C\{^1H\}$-NMR spectra were recorded in DMSO-d_6 on a Bruker DRX-300. Molar conductances were measured in DMSO with an Elico CM-180 conductivity bridge using a dipping type of cell at 25°C. Guoy's balance was used for measurement of magnetic susceptibility. Cobalt mercury tetrathiocyanate was used as the standard. Diamagnetic correction was made using Pascal's constants.

2.1. *Preparation of 2-Cl BENEN*

Schiff-base ligand (2-Cl BENEN) was prepared by stirring ethylenediamine (0.66 mL, 0.01 mol) with 2-chlorobenzaldehyde (2.25 mL, 0.02 mol) in 1 : 2 molar ratio, for 3–4 h in water. A white precipitate was obtained which was washed with water, filtered and dried in vacuo. It was recrystallized from ethanol–water, 2 : 1, v/v, to obtain white shining crystals. Yield: 3.52 g (67.82%). M.p. = 75°C. Found: C, 62.86; H, 4.53; N, 9.11; $(M\tau = 305)$ calcd: C, 62.96; H, 4.62; N, 9.17. Selected infrared absorptions (KBr, cm^{-1}): $\nu(>CH{=}N)$, 1625(s); $\nu(CH_2{-}CH_2)$, 912(s), 842(s). ^1H-NMR spectra (δ value in ppm): $\delta(CH{=}N)$, 8.54(s, 2H); $\delta(Ar{-}H)$, 7.52–7.79(m, 8H); $\delta(CH_2\_CH_2)$, 2.85(s, 4H).

2.2. *Preparation of complexes*

Metal diselenocyanates (metal = Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}) were prepared following literature procedure [11] with solutions of $M(SeCN)_2$ and $M'(SeCN)_2$ mixed in 1 : 1 molar ratio and stirred for 1 h. To the solution or suspension of the mixture of diselenocyanates in ethanol, a solution of 2-Cl BENEN in the same solvent was added in 1 : 1 and 1 : 2 molar ratios and stirred for 12–15 h. A solid separated in each case and was filtered off, washed with ethanol, dried in vacuo and recrystallized from chloroform-acetone 1 : 2, (v/v).

A slightly different method was employed for preparation of the homobimetallic zinc complex [12]. To a solution of $Zn(SeCN)_2$ in ethanol, an ethanolic solution of Schiff base ligand (2-Cl BENEN) was added in 1 : 1 molar ratio and stirred for 2 h, and then 1 mole of ethanolic solution of $Zn(SeCN)_2$ was added and stirred for 8 h. A white solid formed which was filtered off, washed with ethanol, dried in vacuo and recrystallized from chloroform-acetone, 1 : 2 (v/v) mixture.

(a) 2-Cl BENEN CoCd(SeCN)$_4$ (1). Yield: 0.31 g (69.16). M.p. = 180°C (d). Found: C, 26.68; H, 1.55; N, 9.32; (Co + Cd), 18.98. $C_{20}H_{14}N_6Se_4CoCdCl_2$ ($M\tau = 896$) calcd: C, 26.79; H, 1.57; N, 9.37; (Co + Cd), 19.10. Λm at 25° ($\Omega^{-1}\,cm^2\,mol^{-1}$): 21.18 in DMSO. $\mu_{eff} = 4.26_{\mu B}$. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2140(sh); 2121(s); ν(>CH=N), 1600(s); ν(C–Se), 740 (m); δ(NCSe), 430(w); ν(M–N), 248(m); ν(M′Se), 212 (w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 856(221); 408(360); 291(630); 265(706).

(b) 2-Cl BENEN NiCd(SeCN)$_4$ (2). Yield: 0.22 g (49.09%). M.p. = 130°C (d). Found: C, 26.36; H, 1.52; N, 9.30; Ni, 6.45; Cd, 12.42. $C_{20}H_{14}N_6Se_4NiCdCl_2$ ($M\tau = 896$); calcd: C, 26.80; H, 1.57; N, 9.37; Ni, 6.54; Cd, 12.54. Λm 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 33.90 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2145(s); 2120(sh); ν(>CH=N), 1598(s); ν(C–Se), 748(m); δ(NCSe), 442(w); ν(M–N), 256(m); ν(M′-Se), 221(w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 418(306); 358(603); 291(802); 276(700). ^{1}H-NMR spectra (δ value in ppm): δ(CH=N), 9.06 (s, 2H); δ(A-H), 7.42–7.76 (m, 8H); $\delta(CH_2)$, 2.86 (s, 4H). $^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(CH=N), 178.06(s); δ(SeCN), 139.06(s), 137.25(s); δ(Ar–C), 125.02–132.62(m).

(c) 2-Cl BENEN NiZn(SeCN)$_4$ (3). Yield: 0.30 g (70.61%). M.p. = 170°C (d). Found: C, 28.12; H, 1.58; N, 9.75; Ni, 6.83; Zn, 7.62. $C_{20}H_{14}N_6Se_4NiZnCl_2$ ($M\tau = 849$) calcd: C, 28.27; H, 1.65; N, 9.88; Ni, 6.90; Zn, 7.75. (Λm at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 25.45 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2167(m), 2076(s); ν(>CH=N), 1585(sh), ν(C–Se), 752(m), 650(w); 700(w); δ(NCSe), 432(w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in DMSO: 408(322); 291(622); 265(706). ^{1}H-NMR spectra (δ value in ppm): δ(CH=N), 9.02 (s, 2H), δ(Ar–H), 7.38–7.72(m, 8H); $\delta(CH_2)$, 2.76 (s, 4H).$^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(CH=N), 179.12(s). δ(SeCN), 139.06(s), 135.42(s); δ(Ar–C), 124.10–133.60(m).

(d) 2-Cl BENEN CoZn(SeCN)$_4$ (4). Yield: 0.20 g (47.06%). M.p. = 160°C. Found: C, 28.18; H, 1.52; N, 9.72; Co, 6.82; Zn, 7.63. $C_{20}H_{14}N_6Se_4CoZnCl_2$ ($M\tau = 849$) calcd: C, 28.26; H, 1.65; N, 9.88; Co, 6.93; Zn, 7.75; Λm at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 16.90 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2174(s); 2114(s); ν(>CH=N), 1600(s); ν(C–Se), 760(m); δ(NCSe), 480(w), 440(w); ν(M–N), 252(s); ν(M′-Se), 220(w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in DMSO: 415 (380); 293(708); 256(800). $\mu_{eff} = 4.22_{\mu B}$.

(e) 2-Cl BENEN ZnCd(SeCN)$_4$ (5). Yield: 0.311 g (68.84%). M.p. = 200°C (d). Found: C, 26.42; H, 1.43; N, 9.18; Cd, 12.32; Zn, 7.19. $C_{20}H_{14}N_6Se_4ZnCdCl_2$ ($M\tau = 903$); calcd: C, 26.58; H, 1.56; N, 9.30; Cd, 12.44; Zn, 7.29. Λm at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 18.63 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2119(s); ν(>CH=N), 1597(m); ν(C–Se), 720(sh); 670(sh); 617(w); δ(NCSe), 450(w); 430(w), ν(M–N), 248(s); ν(M′-Se), 210(w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}cm^{-1}$)) in DMSO: 298(688); 268(760). ^{1}H-NMR spectra (δ value in ppm): δ(CH=N), 8.92(s, 2H); δ(Ar–H), 7.49–7.86(m, 8H); $\delta(CH_2)$, 2.68 (s, 4H). $^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(CH=N), 179.53(s). δ(SeCN), 138.64(s), 138.08(s); δ(Ar–C), 127.78–134.85(m).

(f) (2-Cl BENEN)$_2$ CoCd(SeCN)$_4$ (6). Yield: 0.36 g (59.91%). M.p. = 205°C (d). Found: C, 35.82; H, 2.28; N, 9.30; (Co + Cd), 14.01. $C_{36}H_{28}N_8Se_4CoCdCl_4$ ($M\tau = 1201$), calcd: C, 35.98; H, 2.34; N, 9.32; (Co + Cd), 14.25. m at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 81.62 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2155(s), 2108(s);

ν(>CH=N), 1598(s); ν(C–Se), 760(m); δ(NCSe), 435(m); ν(M–N), 246(s); ν(M′–Se), 225(w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 856(180); 428(408); 300(708); 260(802). $\mu_{eff} = 4.16_{\mu B}$.

(g) (2-Cl BENEN)$_2$ NiCd(SeCN)$_4$ (7). Yield: 0.49 g (81.66%). M.p. = 150°C (d). Found: C, 35.85; H, 2.21; N, 9.25; Ni, 4.46; Cd, 9.00. $C_{36}H_{28}N_8Se_4NiCdCl_4$ ($M\tau = 1201$), calcd: C, 35.99; H, 2.34; N, 9.32; Ni, 4.88; Cd, 9.35. Λm at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 70.00 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2106(s); ν(>CH=N), 1590(s); ν(C–Se), 760(m), 707(sh), 630(w); δ(NCSe), 480(w) 430(w); ν(M–N), 252(s); ν(M′–Se), 223(w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$) in acetonitrile: 866(161); 645(282); 306(582). ^{1}H-NMR spectra (δ value in ppm): δ(CH=N), 9.08(s, 4H); δ(Ar–H), 7.25−7.92(m, 16H); δ(CH$_2$), 2.75(s, 8H). $^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(CH=N), 178.62(s); δ(SeCN), 136.42(s); δ(Ar–C), 124.12–132.62(m).

(h) (2-Cl BENEN)$_2$ NiZn(SeCN)$_4$ (8). Yield: 0.51 g (88.35%). M.p. = 195°C. Found: C, 37.32; H, 2.35; N, 9.62; Ni, 4.95; Zn, 5.42. $C_{36}H_{28}N_8Se_4NiZnCl_4$ ($M\tau = 1154$), calcd: C, 37.45; H, 2.44; N, 9.70; Ni, 5.08; Zn, 5.66. Λm at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 140.00 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2095(s); ν(>CH=N), 1595(s); ν(C–Se), 768(m),700(sh), δ(NCSe), 435(w); ν(M–N), 252(s); ν(M′-Se), 220(w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in DMSO: 825(105); 460(320); 291(506); 276(680); 259(900). ^{1}H-NMR spectra (δ value in ppm): δ(CH=N), 9.12(s, 4H); δ(Ar–H), 7.18–7.86(m, 16H); δ(CH$_2$), 2.80(s, 8H). $^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(CH=N), 182.42(s), δ(SeCN), 139.80(s); δ(Ar–C), 122.62–132.42(m).

(i) (2-Cl BENEN)$_2$ CoZn(SeCN)$_4$ (9). Yield: 0.33 g (57.16%). M.p. = 185°C (d). Found: C, 37.42; H, 2.36; N, 9.62; Co, 4.98; Zn, 5.42. $C_{36}H_{28}N_8Se_4CoZnCl_4$ ($M\tau = 1154$); calcd: C, 37.44; H, 2.44; N, 9.70; Co, 5.10; Zn, 5.66. Λm at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$); 128.37 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2102(s); ν(>CH=N), 1592(s); ν(C–Se), 760(m), 735(m); δ(NCSe), 432(w); ν(M–N), 242(s), ν(M′-Se), 216(w). Electronic spectra ($_{max}$, nm (ε in $M^{-1}\,cm^{-1}$)) in DMSO: 850(280); 428(360); 295(680); 256(703). $\mu_{eff} = 4.18_{\mu B}$.

(j) (2-Cl BENEN)$_2$ ZnCd(SeCN)$_4$ (10). Yield: 0.35 g (57.94%). M.p. = 225°C (d). Found: C, 35.62; H, 2.28; N, 9.15; Zn, 5.25; Cd, 9.20; $C_{36}H_{28}N_8Se_4ZnCdCl_4$ ($M\tau = 1208$), calcd: C, 35.79; H, 2.33; N, 9.27; Zn, 5.41; Cd, 9.30; Λm at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$); 105.07 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2110(s); ν(>CH=N), 1598(s); ν(C–Se), 730(m); δ(NCSe), 425(w); ν(M–N), 432(s); ν(M′-Se), 215(w). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 295(645); 252(780). ^{1}H-NMR spectra (δ value in ppm): δ(CH=N), 9.26(s, 4H); δ(Ar–H), 7.02–7.76(m, 16H); δ(CH$_2$), 2.85(s, 8H). $^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(CH=N), 180.40(s); δ(SeCN), 138.42(s); δ(Ar–C), 122.40–133.40(m).

(k) 2-Cl BENEN Zn$_2$(SeCN)$_4$ (11). Yield: 0.37 g (63.73%). M.p. = 140°C (d). Found: C, 28.01; H, 1.51; N, 9.72; Zn, 15.12. $C_{20}H_{14}N_6Se_4ZnZnCl_2$ ($M\tau = 855$); calcd: C, 28.06; H, 1.64; N, 9.81; Zn, 15.28. Λm at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 19.45 in DMSO. Selected infrared absorptions (KBr, cm^{-1}): ν(CN), 2130(s), 2095(s); ν(>CH=N), 1595 (s), ν(M–Se), 212(w). ^{1}H-NMR spectra (δ value in ppm): δ(CH=N), 9.25(s, 2H); δ(Ar–H), 7.28–7.84 (m, 8H); δ(CH$_2$), 2.84(s, 4H). $^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(CH=N), 181.02(s). δ(SeCN), 139.62(s); δ(Ar–C), 123.60–132.52(m).

3. Results and discussion

The stoichiometry of the complexes agrees with elemental analyses. The conductance of **1**, **2**, **3**, **4**, **5** and **11** in DMSO are low (16–33 mho $cm^2 mol^{-1}$) indicating non-electrolytic nature [16], but conductance of **6**, **7**, **8**, **9** and **10** are high (70–140 mho $cm^2 mol^{-1}$) indicating electrolytic nature [12].

3.1. *IR spectra*

The FTIR spectra of **1**–**11** exhibit one or two sharp bands in the –CN stretching region, between 2170–2110 cm^{-1} clearly indicating the presence of bridged selenocyanate unit. Similarly the presence of one or two characteristic ν(CN) bands between 2074–2106 cm^{-1} is indicative of the presence of Se bonded SeCN. The presence of bands in ν(C–Se)/δ(NCSe), ν(M–N) region for all 1 : 1 complexes indicates the presence of N-bonded terminal NCSe [13].

A strong band at 1625 cm^{-1} in Schiff bases is characteristic of azomethine (>CH=N) group. In all complexes this band is shifted to lower frequency ($\sim$30 cm^{-1}) indicating coordination of the Schiff base through azomethine nitrogens [14–15].

Infrared spectra of 1 : 2 complexes, **6**–**10**, show only two peaks in –CN stretching region in the range 2080–2110 cm^{-1} indicating the presence of only Se-bonded terminal SeCN groups. Other bands like δ(NCSe), ν(C–Se), ν(M′–Se) and ν(M–N) are also present at their own position and evident of cationic–anionic structure for these complexes [1].

In **11**, the homobimetallic complex, ν(M–Se) bands appeared at 212 cm^{-1}. The presence of two peaks at 2130 cm^{-1} and 2095 cm^{-1} for ν(CN) is indicative of bridging as well as terminal SeCN [16].

3.2. *Electronic spectra and magnetic moments*

Magnetic moments of all the complexes containing cobalt viz. **1**, **4**, **6** and **9** are between 4.18–4.26 BM. The electronic spectra of these complexes show four bands. The band at about 850 nm was assigned to the transition, $^4A_2(F) \rightarrow {}^4T_1(\nu_2)$ and the band at 425 nm was assigned to $^4A_2(F) \rightarrow {}^4T_1(P)$ (ν_3). Two bands at 290 nm and 250 nm with high extinction coefficient may be assigned to MLCT transitions [17].

All complexes containing nickel, **2**, **3**, **7** and **8** are diamagnetic. The electronic spectra show four bands. The band at 410 nm was assigned to $^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2) and 300 nm assigned to $^1A_{1g} \rightarrow {}^1B_{3g}$ (ν_3) transitions. The band at 260 nm with high extinction coefficient is assigned to MLCT [17].

Complexes containing cadmium and zinc or only zinc show only charge transfer bands in electronic spectra.

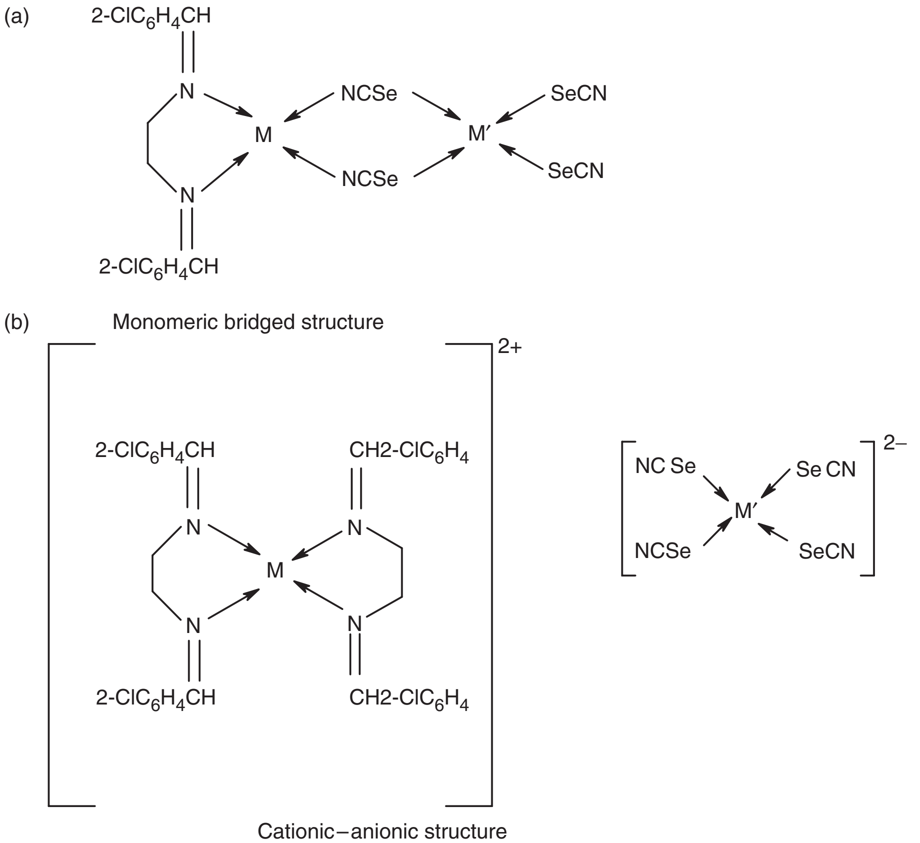
3.3. *NMR Spectra*

All the diamagnetic complexes viz. **2**, **3**, **5**, **7**, **8**, **10** and **11** were characterized by ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra and exhibit a multiplet between δ 7.02–7.92 ppm for aromatic protons. A singlet at δ 8.54ppm in the ligand is shifted downfield between δ 8.92–9.26 ppm in the complexes, probably due to lone pair donation from azomethine (>CH=N) nitrogen to the metal. A singlet observed at about δ 2.60ppm was assigned to CH_2.

$^{13}C\{^1H\}$-NMR spectra show a multiplet between δ 122.40–133.42 ppm, easily assignable for aromatic carbons. A signal at δ 170.00 ppm for (>CH=N) group in ligand shifted downfield to δ 180.00 ppm in the complexes, indicating coordination of azomethine nitrogen to the metal. Two signals were observed between δ 135.42–139.80 ppm, in all 1 : 1 complexes, assigned for SeCN carbon present in two environments; only one signal was observed in all 1 : 2 complexes.

On the basis of IR, electronic ^1H-NMR and $^{13}C\{^1H\}$-NMR spectra, we suggest monomeric bridged structure [figure 1(a)] for all the diamagnetic 1 : 1 complexes, where SeCN forms a bridge between the metals and the Schiff base ligand is linked with comparatively harder metals like Co(II) and Ni(II) through the azomethine nitrogen (figure 1). However, cationic–anionic structure [figure 1(b)] is proposed for all the diamagnetic 1 : 2 complexes, where only terminal SeCN is present and the Schiff base is linked with comparatively harder metal.

In the dizinc complex we suggest a structure in which only Se is bridging and the Schiff base is linked with one Zn (figure 2).



Monomeric bridged structure

Cationic–anionic structure
Where M= Co(II), Ni(II),Zn(II)
M′= Zn(II), Cd(II)

Figure 1. (a) Monomeric bridged structure; (b) Cationic–anionic structure.

4. Antibacterial activity

Antibacterial activity of 2-Cl BENEN, **1**, **4**, **5** and **11** have been tested on *E. Coli*, MTCC 1304, a gram negative bacteria. Muller-Hinton Agar (MHA) plates were prepared and 50 µL suspension of *E. Coli*, MTCC 1304, was spread over it by spread plate technique [18] and then wells were made to fill with 50 µL solution of 0.2% of complexes and 2-Cl BENEN (dissolved in DMSO). One plate is used as a control in which only 50 µL DMSO is taken into well. The plates were incubated at 37 ± 1°C for 24–48 h in a refrigerated incubator shaker. No inhibition zone was observed around the well in the control and 2-Cl BENEN but **1**, **4**, **5** and **11** show inhibition zone formation around the well (table 1). *E. Coli* MTCC 1304, was grown over wells of control and 2-Cl BENEN but no growth was seen in the well for **1**, **4**, **5** and **11**, which show positive antibacterial activity probably due to enhanced lipophilicity of the complexes. These increased lipophilicity leads to breakdown of the permeability barriers of the cell and thus retards the normal cell processes [19–20].

5. Catalytic activity

Bimetallic selenocyanate complexes were found to have good catalytic properties in reactions such as decomposition of hydrogen peroxide [21].

Seven complexes were tested for catalytic activity in hydrolysis of benzonitriles to give benzamide. For this 1.5 mL of benzonitrile was added to 25 mL of hydrogen peroxide in a round bottom flask. The reaction mixture was stirred for five minutes and turned milky white. To this reaction mixture 0.5 mL of 10% sodium hydroxide solution was added, stirred for five minutes and refluxed until the oily suspension of benzonitrile was completely disappeared. Thereafter the reaction mixture was allowed to cool and white shining crystals of benzamide were obtained, filtered, washed with water and kept dry. Very little amount of benzamide was isolated from the mother liquor after vacuum evaporation.

When 96.6–99.8 µM of complexes were added to the above reaction mixture, it was found that for **4** and **9** vigorous reactions take place and time of completion was less than the control. The yield of benzamide also increased in each case. The results are summarized in table 2.

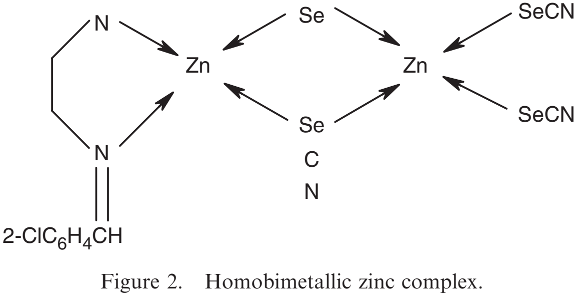


Figure 2. Homobimetallic zinc complex.

Table 1. Biological activity of the complexes.

Complexes	Sensitivity*	Inhibition area in mm
Schiff base, 2-Cl BENEN,	–	No Zone
Complex-**1** 2-Cl BENEN $CoCd(SeCN)_4$	+	27.5
Complex-**4** 2-Cl BENEN $CoZn(SeCN)_4$	+	32.5
Complex-**5** 2-Cl BENEN $ZnCd(SeCN)_4$	+	32.5
Complex-**11** 2-Cl BENEN $Zn_2(SeCN)_4$	+	30.2

*Inhibition zone of more than 8 mm was taken as positive (+).

Table 2. Catalytic activity of the complexes.

Complexes	Amount (in μ moles)	Yield of product (%)	*Turnover
Control	–	54	–
2-Cl BENEN $CoCd(SeCN)_4$	96.6	63	95
2-Cl BENEN $NiZn(SeCN)_4$	98	65	96
2-Cl BENEN $CoZn(SeCN)_4$	98	#66	98
2-Cl BENEN $ZnCd(SeCN)_4$	99.6	66	87
$(2\text{-Cl BENEN})_2$ $NiCd(SeCN)_4$	99.8	88	128
$(2\text{-Cl BENEN})_2$ $NiZn(SeCN)_4$	98.1	82	122
$(2\text{-Cl BENEN})_2$ $CoZn(SeCN)_4$	98.1	#86	128

*Moles of product per mole of catalyst.
#Vigorous reaction.

6. Conclusion

We have prepared eleven complexes by reaction of $[MM'(SeCN)_4]$ with 2-Cl BENEN in 1 : 1 and 1 : 2 molar ratio. The 1 : 1 complexes are monomeric bridged and 1 : 2 complexes are cationic–anionic probably due to steric requirements.

The Schiff base coupled with bimetallic Lewis acids have enhanced antibacterial effects on *E. coli*. These complexes are also catalytically active in hydrolysis of benzonitrile.

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