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Synthesis, Characterization of Some Diorganyl Dichalcogenides as Ligands in Coordination Chemistry

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ABSTRACT

The synthesis of some novel organochalcogenides compounds having coordination bond with cadmium and mercury. The complexes of mercury and cadmium are readily formed by its reaction with sterically less demanding dichalcogenides. However, complexes of cadmium/mercury with ligands containing selenium and sulfur are polymeric in nature as indicated by their not solubility in any of the solvents. The synthesized compounds have been characterized analytically with the help of various spectroscopic techniques viz., IR, CHN, TGA and ED-XRF.

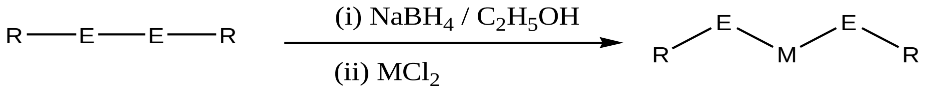
Keywords: Sulfur, Selenium, Cadmium, Intermolecular coordination, metal chalcogenolates.

INTRODUCTION

Metal-organic frameworks have attracted much interest because of their exploitable properties for potential applications such as storage, ion exchange, catalysis, magnetism, chemical vapor deposition and electrical conductivity [1-5]. As an important research field in both coordination chemistry and organic chemistry, *in situ* metal/ligand reactions have been extensively investigated for many decades for the discovery of new organic reactions and elucidations of reaction mechanisms, as well as the generation of novel coordination compounds, especially for those that are inaccessible in direct preparation from the ligands[6,7]. Pyridyl chalcogenolates are ideally suited for preparing stable, volatile chalcogenolate compounds in varying oxidation states.

These ligands are interesting because of the presence of two heteroatom donors that offer different binding modes. Pyridylthiolate complexes have been carefully studied in this regard [8-10]. On the other hand, pyridylselenolate and tellurolate complexes which are expected to be structurally more diverse than their sulphur analogs are yet to be explored. Recently, the pyridylselenolate ligand have been shown to be useful in the synthesis of volatile compounds of cadmium and mercury that decompose at elevated temperatures to give CdSe and HgSe, respectively [11-14]. In this unit, an attempt has been made to explore the coordination chemistry of 5-bromo-2[2-(5-bromopyridine-2-yl) disulfanyl] pyridine, bis(diphenylmethyl) diselenide, bis[4-chlorophenyl(phenyl)methyl] diselenide, bis(4-dichloro diphenymethyl) diselenide and 3,3'-dipyridyl diselenide.

A survey of the literature reveals that the transition metal compounds containing chalcogen atoms have attracted much attention in recent years, owing to their importance in fundamental research as well as in technological fields. The presence of chalcogen atoms appear to be decisive in cluster aggregation and condensation reactions [15]. The complexes of zinc and cadmium are readily formed by its reaction with sterically less demanding ligands[16], which crystallizes into non-molecular lattices. However, complexes of mercury with ligands containing selenium $(HgSePh)_2$ are polymeric[17] in nature as indicated by their low solubility in non co-ordinating solvents, but are readily solublized by the addition of donor ligands such as phosphines[18] In order to explore further the studies, it was planned to prepare complexes of cadmium and mercury with a variety of selenolate including 3-pyridyl selenolate ions.



E = S, Se
M = Cd, Hg

R= $3\text{-}C_5H_4N$; $5\text{-Br-}2\text{-}C_5H_3$; $(C_6H_5)_2CH$; $4\text{-}ClC_6H_4(C_6H_5)CH$; $(4\text{-}Cl.C_6H_4)_2CH$

Reaction Scheme

MATERIALS AND METHODS

To a solution of appropriate dipheyl/dipyridyl dichalcogenide (0.30 mmol) in 20 mL ethanol was added 0.23gm (0.62 mmol) of sodium borohydride in parts with continuous stirring to generate corresponding selenoate ion, 0.52 mmol of $CdCl_2/HgCl_2$ was added to the freshly prepared selenoate ion. The reaction mixture was stirred 2 h to obtain an insoluble yellow precipitate. The compound thus obtained was then filtered under nitrogen. The compounds obtained **1**, **2**, **6** and **7** are white powder whereas compounds **3** to **5** are dark red in color. All these compounds are insoluble in various organic and inorganic solvent like dichloromethane, chloroform, THF, pyridine and acetonitrile. It shows that these compounds are polymeric in nature. These are high melting solids and decomposed above 200 °C.

Procedure for the synthesis of ccoordination complexes of diorganyl dichalcogenides using $CdCl_2$ and $HgCl_2$: To a solution of appropriate diorganyl chalcogenide 1.0g in 20 ml ethanol was added 0.23g (0.62 mmol) of sodium borohydride in parts with continuous stirring followed by the addition of 0.52 mmol of $CdCl_2/HgCl_2$ under nitrogen atmosphere. The reaction mixture was stirred for 9-10 hrs, insoluble yellow precipitate was obtained. The compound thus obtained was then filtered under nitrogen.

[3,3'-dipyridyldiselenide]cadmium, $[3\text{-}C_5H_4NSe]_2Cd$ (1) : Yield: 90%, white solid, m.pt. 230°C (decom.); IR (ν_{max}/cm^{-1}, KBr): 3379.7, 3165.1, 1640.1, 1460.6, 1376.3, 1299.5, 1150.2, 1081.3, 1031.5, 966.5, 840.1, 786.8, 721.8, 637.3.; Anal. calcd. for $C_{10}H_8N_2Se_2Cd$: C, 26.47; H, 2.33; N, 5.41, Found: C, 26.35; H, 2.20; N, 5.39.

[5-bromo-2[2-(5-bromopyridine-2-yl)disulfanyl]pyridine]cadmium,$[(5\text{-Br-}2\text{-}C_5H_3N)S]_2Cd$ (2): Yield: 92%, white solid, m.pt. 210°C (decom.); IR ($\nu_{max}cm^{-1}$, KBr), 3380.0, 3151.2, 1642.3, 1461.7, 1376.4, 1214.7, 1141.0, 1100.46, 1004.6, 823.9, 722.2; Anal. Calc. for $C_{10}H_6Br_2N_2S_2Cd$: C, 24.48; H, 1.22; N, 5.71; S, 13.40, Found: C, 24.86; H, 1.13; N, 5.65; S, 13.06.

[Bis(diphenylmethyl) diselenide]cadmium, $[(C_6H_5)_2CHSe]_2Cd$ (3): Yield: 85%, red solid, m.p. 220°C (decom.); IR (ν_{max}/cm^{-1}, KBr): 3350.5, 3151.2, 2923.8, 1660.8, 1458.1, 1376.4, 1152.0, 1074.6, 1026.7, 842.3, 790.7, 722.0; Anal. Calcd. for $C_{26}H_{22}Se_2Cd$: C, 51.63; H, 3.66, Found: C, 51.58; H, 3.60.

[Bis{4-chlorophenyl(phenyl)methyl}diselenide]cadmium,[4-Cl$C_6H_4(C_6H_5)$CHSe]$_2$Cd (4) : Yield: 86%, red solid, m.p. 220°C (decom.); IR (ν_{max}/cm^{-1}, KBr): 3398.6, 3168.2, 2922.3, 1654.5, 1459.7, 1376.4, 1154.3, 1086.8, 1011.4, 967.7, 888.3, 844.6, 721.9, 558.8; Anal. Calcd. for $C_{26}H_{20}Cl_2Se_2Cd$: C, 41.96; H, 2.88, Found: C, 41.88; H, 2.79.

[Bis(4-chlorodiphenyl)methyl diselenide)]cadmium, [(4-Cl.C_6H_4)$_2$CHSe]$_2$Cd (5): Yield: 90%, red solid, m. p. 200°C (decomp.); IR (ν_{max}/cm^{-1}, KBr): 3424.3, 2954.6, 2872.3, 2147.6, 1638.7, 1458.0, 1373.2, 1089.4, 1008.2, 790.7; Anal. Calcd. for $C_{26}H_{18}Cl_4Se_2Cd$: C, 41.82; H, 2.49, Found: C, 41.78; H, 2.32.

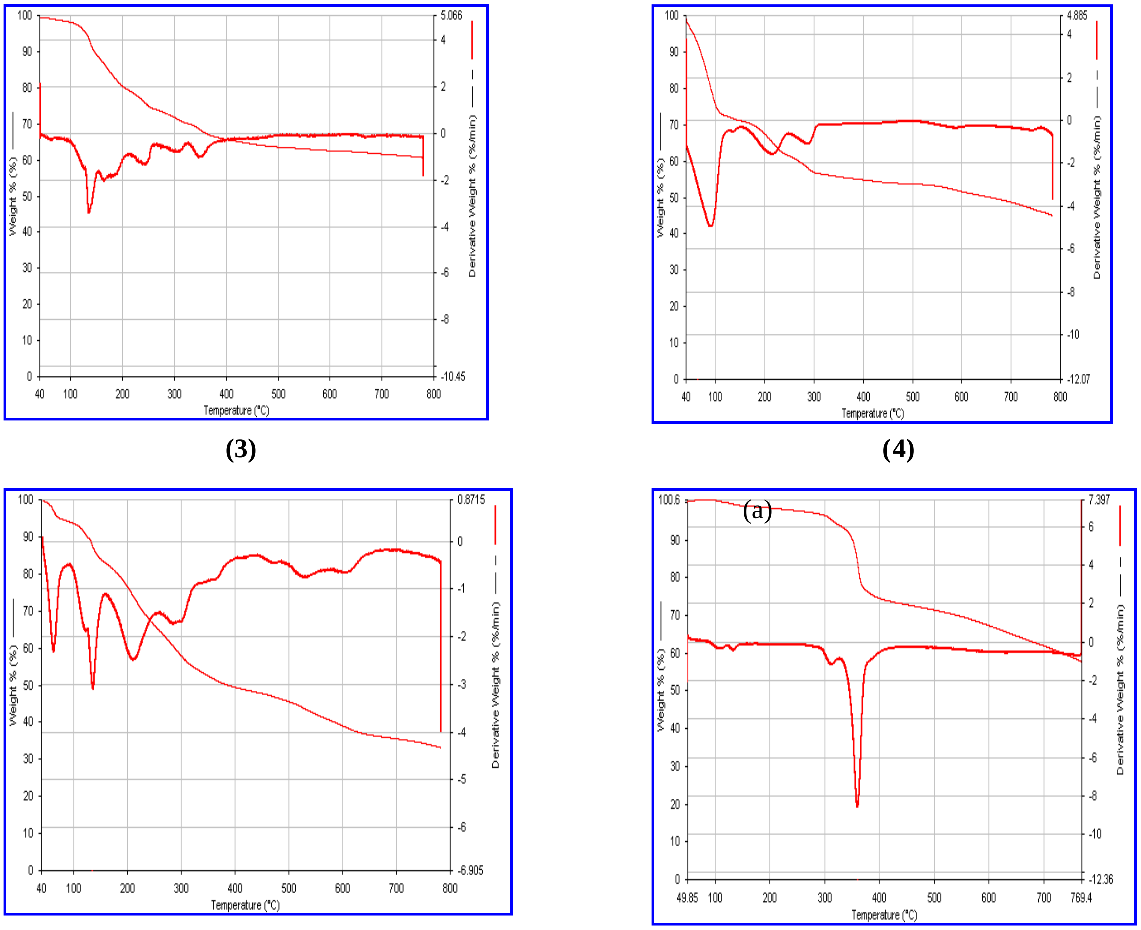
[3,3'-Dipyridyldiselenide]mercury, [3-C_5H_4NSe]$_2$Hg (6): Yield: 94%, white solid, m.p.210°C (decom.); IR (ν_{max}/cm^{-1}, KBr): 2922.0, 1662.5, 1567.2, 1459.1, 1376.3, 1146.4, 1109.4, 1070.9, 820.8, 722.0, 689.8, 614.3, 467.6; Anal. Calcd. for $C_{10}H_8Br_2N_2Se_2Hg$: C, 23.34; H, 1.57; N, 5.44, Found: C, 23.29; H, 1.51; N, 5.32.

[5-bromo-2[2-(5-bromopyridine-2-yl)disulfanyl]pyridine]Hg,[(5-Br-2-C_5H_3N)S]$_2$Hg (7) : Yield: 97%, white solid, m. p. 180°C (decomp.); IR (ν_{max}/cm^{-1}, KBr): 3350.9, 3168.2, 2923.9, 1458.5, 1376.5, 1301.2, 1150.3, 1078.9, 935.9, 787.0, 721.9, 558.8, 455.5 ; Anal. calcd. for $C_{10}H_6Br_2N_2S_2Hg$: C, 20.75; H, 1.05, N; 4.84, Found: C, 20.03; H, 1.03; N, 4.78.

RESULTS AND DISCUSSION

Infrared Spectral Studies: Infrared data of various 3-pyridyl-, C-5 bromo substituted pyridine-, monochloro-, dichloro- and diarylphenylmethyl-, complexes of cadmium and mercury (**1-7**) with sulfur and selenium were recorded as KBr pellets in the region 4000-400 cm^{-1}. The bands in the region 3060-2800 cm^{-1} are assigned to the C-H stretching vibrations of the aryl and alkyl groups. Bands in the region of 1650-1450 cm^{-1} have been assigned to C=C stretching frequencies of the aromatic rings. The band in the range 470-477 cm^{-1} in the mercury compound is assigned to ν_{Hg-E}. The infrared data of these compounds (**1-7**) and the bands obtained are in agreement with values reported in literature [19].

Thermo gravimetric analysis (TGA): In order to study the decomposition profile and the potential utility of the compounds (**3-5**) as single source precursor of cadmium selenide, CdSe the thermogravimetric analysis was carried out under nitrogen atmosphere on STA 6000 thermogravimetric analyzer (Perkin-Elmer). All these compounds showed multi-step degradation process. The initial weight loss is due to the removal of water molecule adsorbed on these compounds as there is a continuous weight loss upto 100°C. The maximum adsorption of water was noticed in case of [4-Cl$C_6H_4(C_6H_5)$CHSe]$_2$Cd which correspond to 25% of the total weight of the compound taken. The onset temperature is almost same in all these compounds and they decomposed before reaching their melting points. From this data, it can be concluded that all these compounds are equally stable. The compounds [$(C_6H_5)_2$CHSe]$_2$Cd and [4-Cl$C_6H_4(C_6H_5)$CHSe]$_2$Cd started decomposing as soon as the temperature reaches 100°C and goes on till 300°C. The thermogram after 300°C is almost parallel to the base line indicating the formation of a stable polymeric species. This property of compounds [$(C_6H_5)_2$CHSe]$_2$Cd and [4-Cl$C_6H_4(C_6H_5)$CHSe]$_2$Cd render them incapable to act as single source precursor for CdSe. However, the compound [(4-Cl.C_6H_4)$_2$CHSe]$_2$Cd decompose fully to CdSe at 650°C. This may be due to the intermolecular non-bonded interaction between the chlorine and the selenium atom. The results are inline with the literature findings that attachment of the substituents on the alkyl/aryl group suppresses the formation of polymeric material[20]. The order of polymer formation is found to be in the order [$(C_6H_5)_2$CHSe]$_2$ Cd = [4-Cl$C_6H_4(C_6H_5)$ CHSe]$_2$Cd > [(4-Cl.C_6H_4)$_2$CHSe]$_2$Cd. Thermo gravimetric analysis of the compound [(5-Br-2-C_5H_3N)S]$_2$Cd shows a single degradation step and the decomposed product include the polymeric cadmium sulfide. Compared to compounds **[**$(C_6H_5)_2$CHSe]$_2$Cd, [(4-Cl.C_6H_4)$_2$CHSe]$_2$ Cd, the onset temperature in compound [(5-Br-2-C_5H_3N)S]$_2$Cd is as high as 320^{o}C indicating that the sulfur containing compounds are thermally more stable than their selenium analogues. This is expected as the C-S bond is stronger than the C-Se bond. The fig 1 depicts the thermograms.



(3) **(4)**

(5) **(7)**

(4

Figure 1. Thermograms of (3) $[(C_6H_5)_2CHSe]_2Cd$, (4) $[4\text{-}ClC_6H_4(C_6H_5)CHSe]_2Cd$, (5) $[(4,4'\text{-}ClC_6H_4)_2CHSe]_2Cd$, (7) $[(5\text{-}Br\text{-}2\text{-}C_5H_3N)S]_2Cd$

ED-XRF Studies for Elemental Analysis: The x-ray and γ-ray photon can interact with target molecules by number of competing processes. The interaction can be either with the atom, as in photoelectric effect, or with one electron in the atom, as in Compton effect, or with the atomic nucleus as in the pair production. The characteristic x-ray are generated as a result of photoelectric interaction while scattering processes provide background contribution which interfere with the analysis of characteristic x-rays. The energy of the characteristic x-ray peak is used to identify the elements present in the target sample and its intensity is used for the qualitative analysis. The net count rate under the scattered or fluorescent peak is given by equation.

$$N = I_0 G \frac{d\sigma}{d\Omega} m \, \varepsilon \, \beta$$

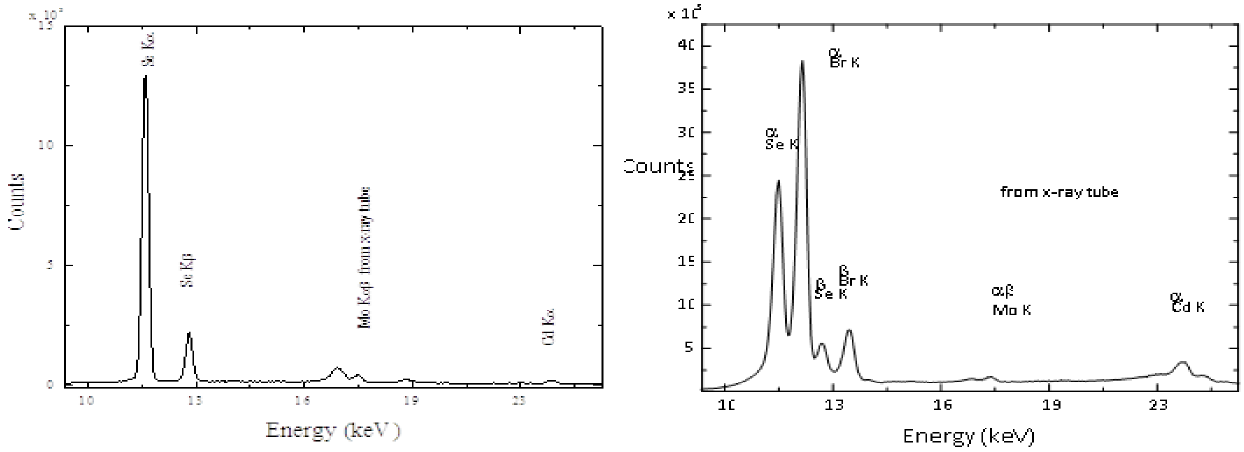
The differential scattering or x-ray fluorescent cross-section can be written as

$$N \propto m$$

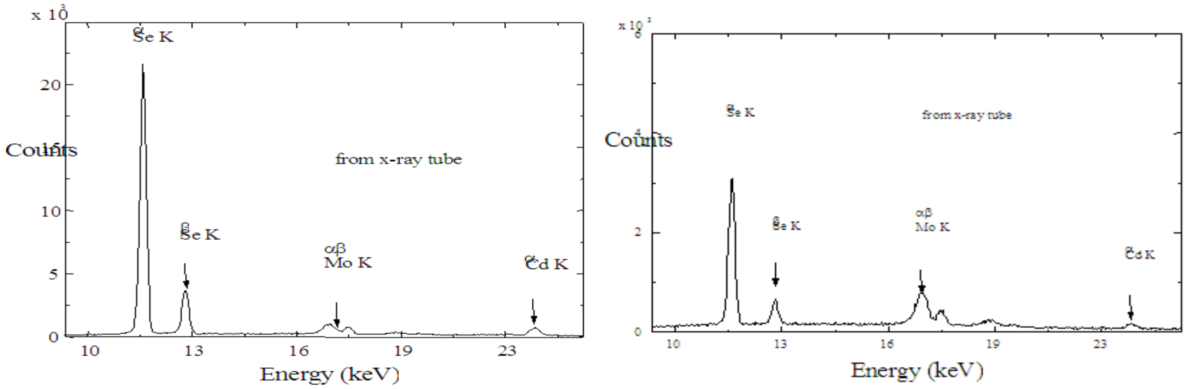
where I_o is the intensity of the incident photons on target visible to the detector, G is the geometrical factor related to the source-target and target detector solid angles, ε denotes the detector efficiency corresponding to energy of the observed photons, β is self absorption correction factor that accounts for the absorption of incident and emitted photons in the target and m is the mass in g $cm^{2\ -1}$ of the target element. It is clear from the above equation that for thin film of chemical compounds, I_o, G, ε and β factors are constant. Therefore, the peak area on the count rate of the characteristic x-rays is proportional to its constituents/mass.

Elemental analysis of the newly prepared compounds was carried out using 59.54 keV γ-rays from 241Am (300m(i)) radioisotopes for the excitation of the characteristic x-ray of the elements present in the compound. The typical spectra from the compounds *i.e.*, **1, 3, 4** and **5** with 59.54 keV photon energy are shown in figure 2 respectively. The count rate of metals (selenium, bromine and cadmium) and percentage composition with respect to each other metal obtained by using above equation comes out to be 44%, 100% and 6% for selenium, bromine and cadmium respectively in $[(5\text{-Br-}2\text{-}C_5H_3N)Se]_2Cd$. Whereas in compound $[(C_6H_5)_2CHSe]_2Cd$, the count rate are 100% and 5% for selenium and cadmium.

APPLICATIONS



(**1**) $[3\text{-}C_5H_4NSe]_2Cd$ (**3**) $[(C_6H_5)_2CHSe]_2Cd$



(**4**) $[4\text{-}ClC_6H_4(C_6H_5)CHSe]_2Cd$ (**5**) $[(4,4'\text{-}ClC_6H_4)_2CHSe]_2Cd$

Figure 2. X-ray Fluorescence Spectrum

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