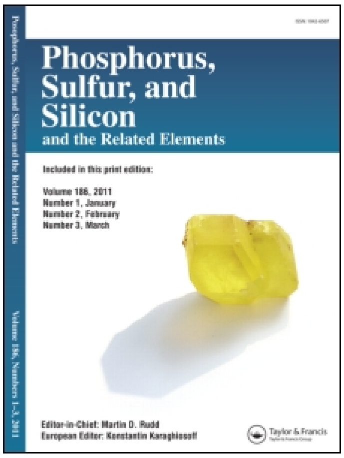

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Design, Synthesis and Structural Aspects of $NH_2(CH_2)_nE(CH_2)_nNH_2$ (n=2 or 3; E=Se or Te) N_2Se or N_2Te Donors and its Complexes with Group 12 Metals

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Design, Synthesis and Structural Aspects of $NH_2(CH_2)_nE(CH_2)_nNH_2$ (n = 2 or 3; E = Se or Te) N_2Se or N_2Te Donors and its Complexes with Group 12 Metals

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Reaction of group 12 metal chlorides with dialkylchalcogeno diamine $[\{NH_2(CH_2)_nE(CH_2)_nNH_2\}$ (n = 2 or 3 and E=Se and Te)] afforded the complexes $[M_2\{NH_2(CH_2)_nE(CH_2)_nNH_2\}_2Cl_4]$ (M = Zn, Cd and Hg) and with CdI_2 $[Cd\{NH_2(CH_2)_nE(CH_2)_nNH_2\}_2]$ $[CdI_4]$. Complexes were characterized by elemental analyses, IR, ^1H, ^{13}C NMR, FAB mass and by single crystal X-ray structure determinations. In all the complexes, the ligand acts as a neutral tridentate (N, Se, N or N, Te, N) donor. Thermal analyses for the complexes were also performed by thermogravimetry.

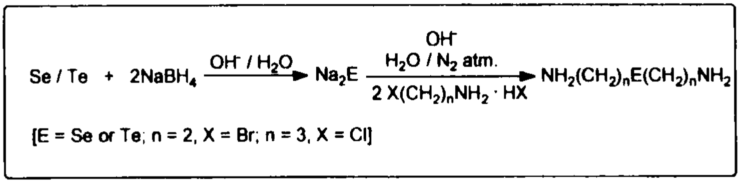
Keywords: (N, Se, N) and (N, Te, N) donors; Zn(II); Cd(II) & Hg(II) complexes; Octahedral; X-ray structure; TG analysis

INTRODUCTION

Organochalcogen donors having a mixed donor set of chalcogen (S, Se and Te) and nitrogen heteroatoms differ in their metal binding properties from their purely chalcogen or nitrogen counterparts.[1-2] Recently, we described the synthesis of a pyridine based potentially pentadentate acyclic ligand 2,6-bis(phenylselenoethylimino)pyridine [$PhSe(CH_2)_2N{=}CH\text{-})_2C_5H_3N$],($N_3Se_2$) and bis(phenyltelluroethyl-imino) pyridine [$PhTe(CH_2)_2N{=}CH\text{-})_2C_5H_3N$], ($N_3Te_2$) incorporating nitrogen and selenium/tellurium donor atoms and their interactions with Zn(II), Cd(II) and Hg(II) acceptors. In these complexes we found that only the nitrogen heteroatoms serve as donors.[2] Presumbly, the differences lie in the topology of the designed acyclic ligands and relative orientation and connectivity of the appended arm bearing chalcogen. We feel that the incorporation of two counterparts (2,6-pyridinedicarboxaldehyde or 2,6-diacetylpyridine and phenylchalcogenoalkyl amines) into a single structure may generate both limited conformational rigidity and flexibility in the donor unit and thus holds great promises for structural diversity and geometrical control, such as, size, shape and symmetry. In fact, incorporation of heavier chalcogens (covalent radius, Se 1.17Å; Te 1.37Å) (N 0.73Å; S 1.03Å) should result in a change in the size, shape and orientation of the donor sites of the ligand and hence allow for some interesting coordination behavior.[3-4] There has also been considerable recent interest in the synthesis of such mixed donors and their metal complexes as they would seem potentially useful precursors for metal-organic chemical vapor deposition (MOCVD) processes for the generation of technologically advanced materials.[5-7] We are specifically interested in the design and synthesis of new organochalcogen donors that could serve as 'extended-reach structures' in the presence of suitable metal ions. We are now extending our exploratory work to potentially tridentate (N,Se,N) and (N,Te,N) donors and their coordination behavior towards group 12 metals.

RESULTS AND DISCUSSION

N,N-bis(2-aminoalkyl)chlcogenides can easily be prepared by the reduction of elemental selenium or tellurium in aqueous or aqueous ethanol to Na_2E (E = Se or Te) and its further reaction with aminoalkyl halides [$NH_2(CH_2)_nX.HX$] (X =Cl or Br) (Scheme 1).



$$Se/Te + 2NaBH_4 \xrightarrow{OH^- / H_2O} Na_2E \xrightarrow[2\,X(CH_2)_nNH_2 \cdot HX]{OH^- \; H_2O / N_2\ atm.} NH_2(CH_2)_nE(CH_2)_nNH_2$$

[E = Se or Te; n = 2, X = Br; n = 3, X = Cl]

SCHEME 1

Both N,N-bis(2-aminoalkyl)selenide and -telluride are viscous liquids, soluble in common organic solvents and are stable in their pure form. These ligands can be stored in the dark at room temperature. The reaction of N,N-bis(2-aminoethyl)selenide and -telluride with Zn(II), Cd(II) and Hg(II) chlorides in anhydrous methanol in 1:1 ratio readily affords the binuclear species which were isolated as air-stable white solids. The complexes are generally insoluble in common organic solvents except in N,N-dimethylformamide and dimethylsulfoxide. Molar conductance of these complexes in (DMF) or (DMSO) solution proved their non-electrolytic nature. The position of the symmetric and asymmetric stretching vibrations of coordinated primary amine functions may sense variations in metal coordination number. All complexes exhibit two strong absorptions in the 3310-3200cm^{-1} region. These absorptions were assigned to $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ stretching vibrations of the -CH_2NH_2 groups. In the Cd(II) complex, the $\nu_s(NH_2)$ and $\nu_{as}(NH_2)$ vibrations are observed at higher frequencies than those of the Zn(II) and Hg(II) species. Here, the different N-H stretching frequencies may be a result of different coordination numbers (the higher the coordination number, the longer the M-NH_2 bond, and the stronger the N-H bond). A decrease in the frequencies of the N-H stretching vibrations were observed as Cd(II) > Zn(II) > Hg(II) and may be suggestive for higher coordination number around Cd(II). The low solubility of these complexes in NMR observing solvents did not allow us to provide a definitive proof for the coordination around the central metal ion. However, ^{1}H NMR spectra of Zn(II) and Cd(II) complexes and its free ligand $[NH_2(CH_2)_2Te(CH_2)_2NH_2]$ (in dmso-d^6) were obtained. The ^{1}H NMR data for Cd(II) complex revealed that both -CH_2NH_2 (-0.17 ppm) and -$TeCH_2$- (-0.11 ppm) protons have appreciable shifts in their position with respect to the free ligand, indicating that all (**N**, **Te**, **N**) donor sites of the tridentate ligand are involved in the coordination. In the Zn(II) complex, these shifts in -CH_2NH_2 (-0.10 ppm) and -$TeCH_2$- (-0.02 ppm) indicates uncoordinated tellurium atom. Single crystal structure of Cd(II) with ligand $[NH_2(CH_2)_2Te(CH_2)_2NH_2]$ crystallizes out as $[Cd_2\{NH_2(CH_2)_2Te(CH_2)_2NH_2\}Cl_4]$ (monoclinic, space group p2_1/n). The ligand $[NH_2(CH_2)_2Te(CH_2)_2NH_2]$ act as a neutral tridentate (**N**, **Te**, **N**) donor and the geometry around the metal ion is typical distorted octahedral. The ligand atoms around the metal are arranged in such a way that Te occupies the position *trans* to the chlorine. In fact, two bridging chlorines and the ligand's N and Te donors are at equatorial positions, while one terminal chlorine and one nitrogen of the tridentate ligand are at the apical positions (Fig 1).

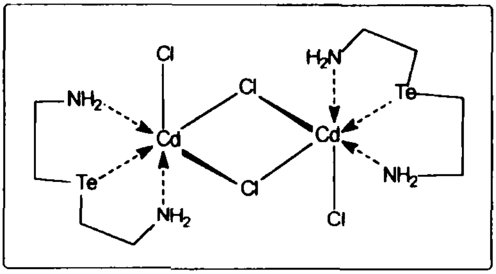


FIGURE 1

Under identical experimental conditions, the ligand $[NH_2(CH_2)_2Se(CH_2)_2NH_2]$ reacts with CdI_2 and crystallizes out as $[Cd\{NH_2(CH_2)_nE(CH_2)_nNH_2\}_2]$ $[CdI_4]$ (orthorhombic, space group $pna2_1$). Again the geometry around the central cadmium atom is typical distorted octahedral. Both the selenium atoms coordinated to cadmium are *trans* to the nitrogen of the tridentate ligand (fig. 2).

All the bond lengths and bond angles due to (Cd-N), (Cd-Cl), (Cd-Se) and (Cd-Te) and (Cd-I) are in the expected ranges as reported earlier.[8-11]

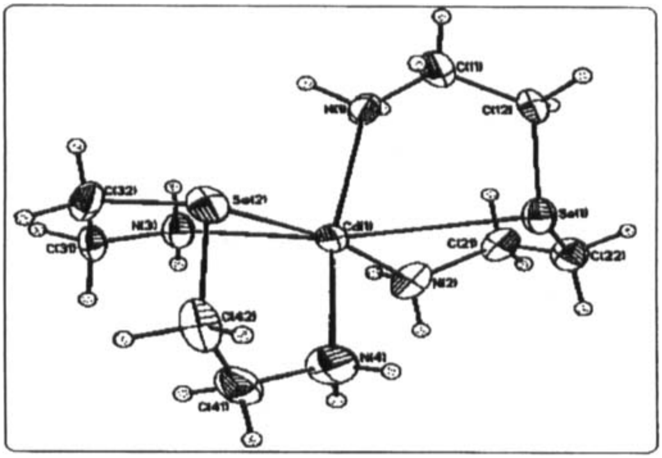


FIGURE 2

Thermogravimetry

TG analysis was performed by heating the complex at a rate of 20°C/min. The thermogram for $[Cd_2\{NH_2(CH_2)_nE(CH_2)_nNH_2\}_2Cl_4]$ is shown in Fig.3. The complex showed an initial weight loss of 13.93% and 13.17% corresponding to the loss of the organic components. The residual mass remained unchanged till 575°C and then a complete loss of the components was observed at higher temperature. The residual mass of this temperature range corresponds to the composition ratio Cd(1) : Se(2) : Cl(4).

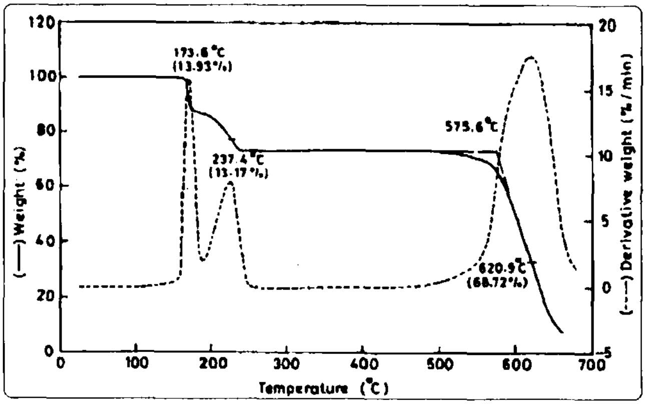


FIGURE 3

EXPERIMENTAL

The ligands N,N-bis(2-aminoalkyl)selenide and -telluride were prepared by the reduction of elemental Se or Te with $NaBH_4$ in H_2O or in aqueous ethanol under dry nitrogen atmosphere. The resulting chalcogenide ions formed were treated with chloroalkylamines/bromo alkylamines. The ligands N,N-bis(2-aminoalkyl) selenide and -telluride were extracted in chloroform and concentrated under vacuum. The ligands obtained were used as such without purification for further reaction. Complexes were obtained by mixing metal(II) chlorides or cadmium iodide in acetonitrile. The desired products precipitated out immediately. The complexes were analyzed by physicochemical techniques such as elemental analysis, IR, ^1H NMR and FAB mass spectra. Crystalline materials were obtained by dissolving the compound in DMF and layering with hexane or diethylether. Suitable crystals for X-ray were examined by single crystal X-ray.

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