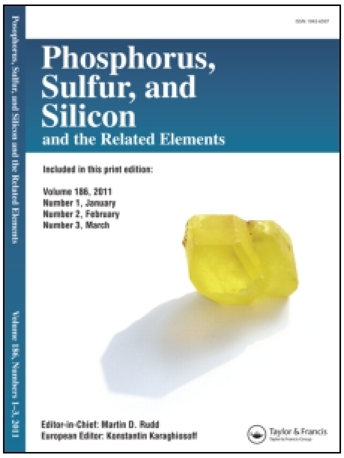

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Design, Synthesis and Structural Aspects of Acyclic N_3E_2 (E=Se or Te) Type Donors and its Complexes with Group 12 Metals

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Design, Synthesis and Structural Aspects of Acyclic N_3E_2 (E = Se or Te) Type Donors and its Complexes with Group 12 Metals

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(N_3E_2) type acyclic Schiff-base [$PhE(CH_2)_2N{=}CH\text{-})_2C_5H_3N$] and its complexes with Zn, Cd and Hg have been synthesized and characterized. The geometry around the central metal atom has been assigned on the basis of physiochemical and spectral studies. The structure of the complexes [$PhSe(CH_2)_2N{=}CH\text{-})_2C_5H_3N$].$CdCl_2$ has been confirmed by single crystal X-ray crystallography.

Keywords: Pentadentate acyclic ligands; N_3Se_2/ N_3Te_2donors; synthesis; characterization; Cadmium complexes; single crystal X-ray

INTRODUCTION

Synthesis and characterization of pyridine based polydentate ligands bearing N_3N_2, N_3O_2, N_3S_2, N_3P_2 and NS_2P_2 donors are well documented and among them few of the systems have shown promising catalytic, biological, environmental and material properties[1-5]. In recent years such systems revealed renewed attraction due to the recognition of metal ions in supramolecular chemistry[5-9]. In our ongoing research programme[10], we paid attention to the design and synthesis of new molecular (N_3E_2) systems having both 'hard' and 'soft' donors in the ligand framework. The design factors used in developing new donors are shown in Fig. 1.

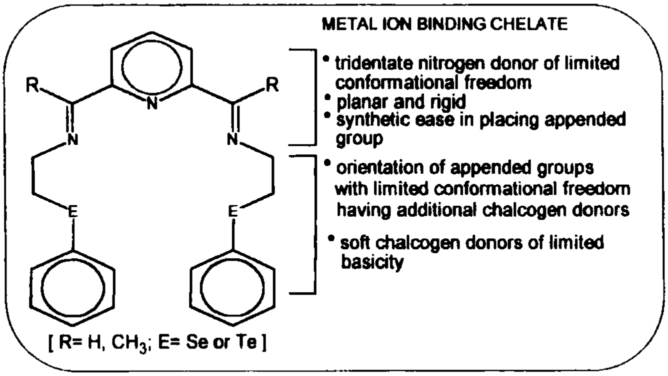


FIGURE 1

The availability of both kind of donor sites in the ligand framework would make it practical to design molecular complexes with a variety of coordination modes depending upon the specific metal and the reaction conditions used. The present study deals with the synthesis of potentially pentadentate acyclic ligand 2,6-bis(phenylselenoethylimino)pyridine [$PhSe(CH_2)_2N{=}CH\text{-})_2C_5H_3N$] (**L**) , ($N_3Se_2$) and bis(phenyltelluroethyl imino)pyridine [$PhTe(CH_2)_2N{=}CH\text{-})_2C_5H_3N$] (**L'**) ,($N_3Te_2$) incorporating nitrogen and selenium or tellurium donor atoms and their interactions with Zn(II) ,Cd(II) and Hg(II) acceptors.

RESULTS AND DISCUSSION

The design factors used in developing new ligands are shown in figure 1. The presence of both 'hard' and 'soft' donor sites in the ligand framework would make it practical to design molecular complexes with a variety of coordination modes, depending on the nature of the central metal atom (refer to Figure 2).

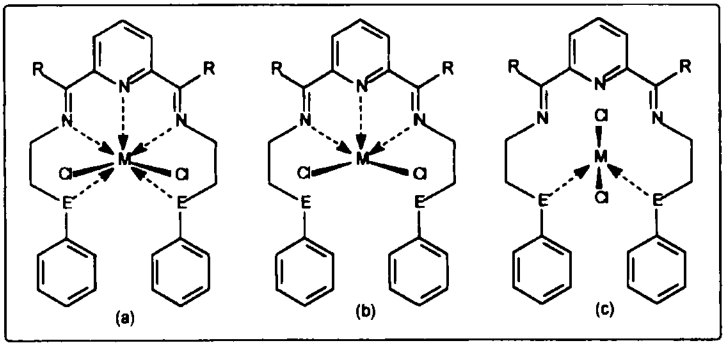
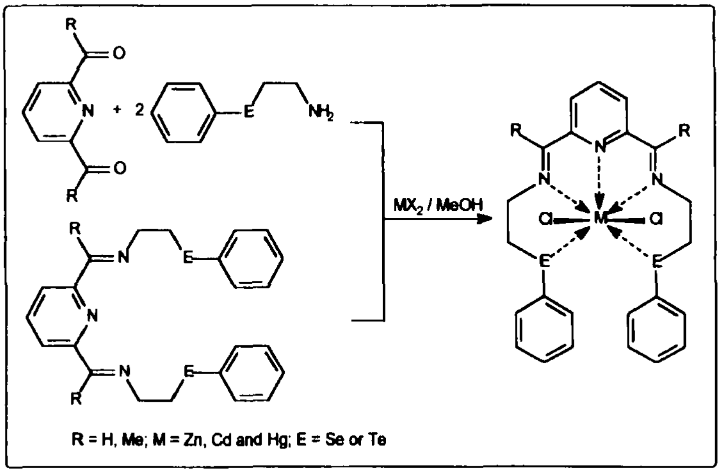


FIGURE 2

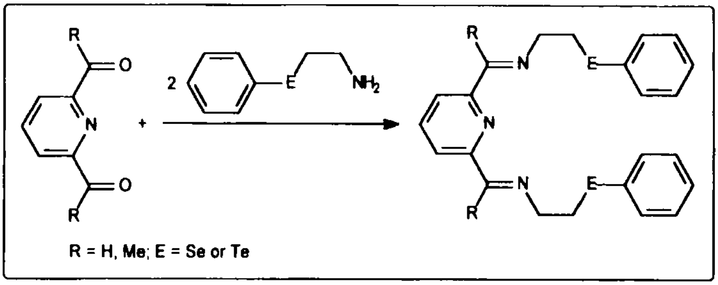
The ligand was prepared by gently heating methanol solutions of 2,6-pyridinedicarboxaldehyde and phenylselenoethylamine (refer to Scheme 1).



SCHEME 1

The reactivity of the ligand system towards d^{10} metal ions was studied by reacting the ligands with MCl_2 (M = Zn, Cd, Hg) in a 1:1 molar ratio (refer to Scheme 2). The complexes were prepared by reacting MCl_2 and the ligands and also by the template reaction of 2,6-pyridine dicarboxaldehyde, aminoalkyl(phenyl)selenide or telluride and MCl_2 in a 1:2:1 molar ratio. The metal complexes obtained by both methods presented the same composition $[MCl_2 . L]$.

The ligand and their complexes were characterized by physicochemical methods. The complexes have fair to moderate solubility in common organic solvents except hexane and petroleum ether and exhibits non-electrolytic behavior in both polar and non-polar solvents.



SCHEME 2

In solution they are monomeric in nature. In the FAB mass spectra for all the complexes, the parent molecular ion peaks were not observed. Loss of one chloride atom always occurred from the parent ion and the resulting peak corresponds to $[M(L)Cl]^+$ or $[M(L')Cl]^+$ ions. The IR spectra of these complexes do not show any appreciable shift in most characteristic ν(C=N) frequencies with respect to the free ligands. However, in the ^1H NMR spectra the magnitude of the chemical shifts of $-N-CH_2$ and $-SeCH_2$ protons of the complexes with respect to the free ligands reveals that all the donor sites of the ligands are participating in the coordination. Whatsoever, this does not permit us to state on the coordination number of the metal ions. The conclusions regarding geometry were confirmed by X-ray crystallography. Crystals suitable for single crystal X-ray were grown for $[CdCl_2 . L]$ from a CH_3OH-$CHCl_3$ solution of the complex. The complex $[CdCl_2.L]$, crystallizes in the monoclinic space-group $P2_1/c$, with $a = 8.7120(180)$Å, $b = 33.4770(10)$Å, $c = 9.7990(10)$Å, $\alpha = \gamma = 90^0$, $\beta = 115.47(10)^0$, and $z=4$. The coordination sphere approximates a trigonal bipyramidal with the nitrogen donor sets N_3 (N, N, N) of the ligand occupying one equatorial and two axial positions. The minimum Cd-Se distance was found to be 4.87Å and indicates that the appended arm bearing two (Se) donor set remain uncoordinated in the complex. The molecule seems to be roughly linear and the appended arms bearing selenium are almost perpendicular to the pyridine ring (Figure 3). In the light of this structure and the NMR data it can be stated that all of the complexes of Zn(II), Cd(II) and Hg(II) adopt very similar structures in which the metal atoms are penta-coordinated with coordination of each being completed by three nitrogens of the acyclic ligand and two chloride ions.

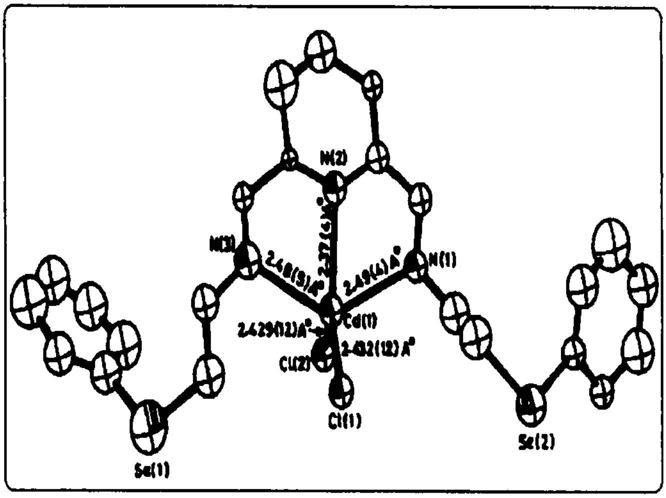


FIGURE 3

In conclusion, we have found an easily accessible (N_3E_2) ligand, which may be of use for encapsulating transition metals and uncoordinated selenium can be used for further coordination to construct multimetallic species. We are currently engage with the detailed study of these molecular systems to explore the possibility for the formation of extended reach structures.

EXPERIMENTAL

All the solvents were dried and distilled before use. The reactions were carried out in an inert atmosphere 2,6-pyridinedicarboxaldehyde (Aldrich) was used as such. Phenylselenoethylamines were prepared by the known literature procedures[10]. ^1H NMR spectra were recorded on a Brucker 300 MHz instrument with Me_4Si as internal standard and $CDCl_3$ as the solvent. Infrared spectra were recorded on a Nicolet proteg'e 460 spectrometer and are reported in cm^{-1}. X-ray diffraction data were measured on a CAD 4 Enraf-nonius 4-circle automatic diffractometer **[graphite monochromatised, Mo Kα(λ=0.7093A°) radiation]** W-2θ scan mode.

Synthesis of the Ligand

A solution of 2,6-pyridinedicarboxaldehyde (1mmol, 0.135g) in methanol (20mL) was added dropwise to a solution of phenylselenoethylamine (2mmol, 0.4g) in methanol (20mL) and the reaction mixture was allowed to stir with gentle heating (approx. 55°C) for 4h. Evaporation of the solvent under reduced pressure gave a white viscous liquid. Chromatographic separation resulted in the free ligand as a viscous mass in 85% yield. ^{1}H NMR (300MHz, $CDCl_3$): δ 8.38 (2H, s), δ 7.99 (1H, t), δ 7.92 (2H, d), δ 7.54 (4H, dd), δ 7.24 (6H, m), δ 4.01 (4H, t), δ 3.27 (4H, t).

Reaction of the Ligand with $CdCl_2$

To a methanolic solution of the ligand (1.0mmol), $CdCl_2$ (1.0mmol) in methanol was added dropwise and stirred for 0.5h. The precipitated white product was filtered off, washed with methanol and dried *in vaccuo.* Yield: 80%, Anal. Calcd. (%) For $C_{23}H_{23}N_3Se_2CdCl_2$: C, 40.44; H, 3.37; N, 6.15; Found: (%) C, 40.15; H, 3.21; N, 5.98. ^{1}H NMR (300MHz, $CDCl_3$): δ 8.3 (2H, t), δ 8.21 (2H, t), δ 7.80 (2H, d), δ 7.53 (4H, d), δ 7.20 (6H, m), δ 4.17 (4H, t), δ 3.55 (4H, t).

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