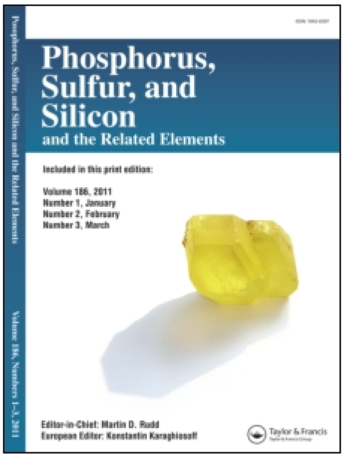

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NEW ACYCLIC CHALCOGEN BEARING LIGANDS AND THEIR COMPLEXATION REACTIONS

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Two (N_3Se_2) type acyclic Schiff-bases, $[\{PhSe(CH_2)_n N=C(CH_3)\}_2C_5H_3N]$ (n = 2,3), and their complexes with Cd(II) have been synthesized and characterized. The geometry around central cadmium has been assigned on the basis of physicochemical and spectral studies. Structure of the cadmium complex $[PhSe(CH_2)_3NC(CH_3)C_5H_5N.C(CH_3)NH]$ $.CdCl_2$ has been confirmed by single crystal X-ray diffraction method.

Keywords : (N_3Se_2) donors; synthesis; characterization; cadmium (II) complexes; single crystal X-ray.

INTRODUCTION

The coordination chemistry of hybrid (Se, N) donors is interesting for various reasons viz., (i) they can provide insight into the competitive coordination behaviour between the 'hard' and 'soft' donors towards the same metal centre[1,2], (ii) such molecular species may potentially be useful as single-source precursors in MOCVD processes[3-5], (iii) and such molecular systems may also be important in transition-metal catalyzed asymmetric synthesis[6,7]. In continuation to our previous work on hybrid ligands having 'hard' (N,O) and 'soft' (Te) donor atoms[8], we have initiated an investigation into the design, synthesis and characterization of chalcogen donors that could control the coordination sphere about the metal atom. The main impetus for the development of such ligand system is to synthesize monomeric metal complexes incorporating heavier chalcogens (Se and Te) with a view to use them for the generation of technologically advanced materials.

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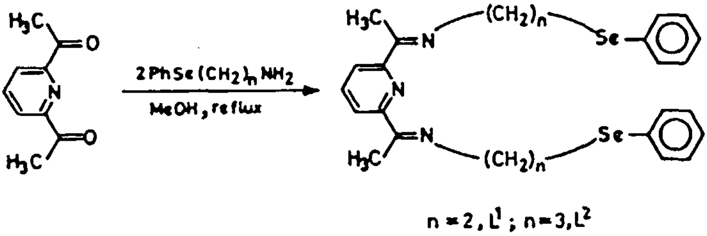
RESULTS AND DISCUSSION

The ligands are prepared by mixing methanolic solutions of 2,6-diacetylpyridine and aminoalkyl(phenyl)selenides (Scheme 1).



(SCHEME 1)

Structurally, these ligands are interesting because the two heteroatom donors create a variety of potential bonding modes. The reactivity of the newly synthesized organoselenium ligands towards cadmium(II)chloride has been approached by reacting the ligand (L_1 and L_2) with cadmium(II)chloride and by the reaction of 2, 6-diacetylpyridine, aminoalkyl(phenyl)selenide and cadmium(II)chloride in 1:2:1 molar ratio. A yellow powdery product having composition $[CdCl_2.L_1]$ (1) and $[CdCl_2.L_2]$ (2) precipitated out immediately and the two preparative methods yielded the products of same composition. These complexes show a reasonably good solubility in common organic solvents and are non-electrolytic in nature. They are also found to be monomeric by molecular measurements.

In the ^1H NMR spectrum (see experimental), the complex (1), appreciable shifts in N-CH_2 and Se-CH_2 protons with respect to free ligand (L_1) indicate that both the 'hard' (N) and 'soft' (Se) donors are involved in coordination. However, in the complex (2), the situation is different and, only pyridyl nitrogen with imine donors are involved in coordination with cadmium leaving the (Se) atom uncoordinated. This suggests a hepta - and penta-coordination around cadmium in complex (1) and (2) respectively. This can probably be attributed to geometric constraints imposed by the two relatively short ethylene bridges joining the selenium atom to the two azomethine nitrogens in (L_1) which is considerably removed by increase in chain lengths in (L_2).

Attempts to grow single crystals (1) have not yet been successful. However, crystal (complex 3) suitable for X-ray analysis were grown from $CHCl_3$-CH_3OH(9:1) solution of (2). The X-ray diffraction study revealed unusual constitutions of the complex and confirmed the existence of one unaltered -$(CH_2)_3$ SePh arm and the cleavage of the other. Fig. 1 and 2 shows the molecular structure and packing of molecules in the crystals for the complex (3).

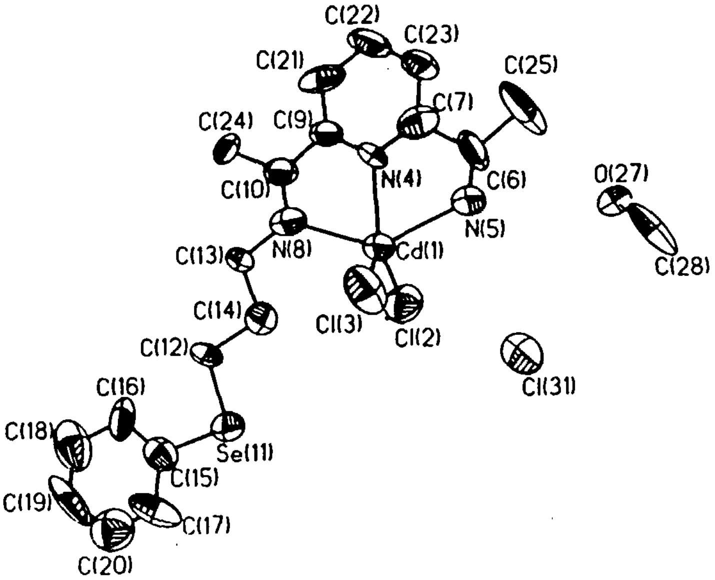
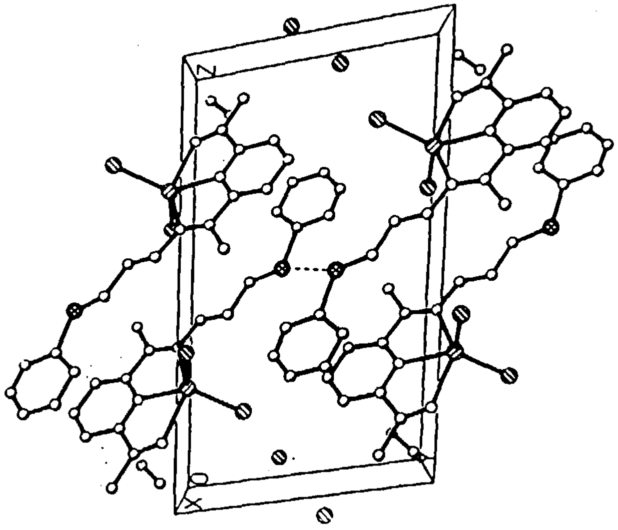


FIG. 1 Molecular structure of cadmium complex (3)

Selected Bond Lengths and Angles : distance (A°) Cd(1)-Cl(1) 2.425 (8), Cd(1)-Cl(3) 2.438 (5), Cd(1)-N(4) 2.24 (2), Cd(1)-N(5) 2.40 (2), Cd(1)-N(8) 2.40 (2), Se(11)-C(12) 1.90 (2), Se(11)-C(15) 1.91 (2), N(5)-C(6) 1.25 (3), N(8)-C(10) 1.25 (3) ; angle (°), N(5)-Cd(1)-N(8) 138.1 (6), N(4)-Cd(1)-N(8) 69.0 (5), N(4)-Cd(1)-N(5) 69.1 (6), Cl(3)-Cd(1)-N(8) 101.3 (4), Cl(3)-Cd(1)-N(5) 98.8 (5), Cl(3)-Cd(11)-N(4) 121.7 (4), Cl(2)-Cd(1)-N(5) 99.4 (5), Cl(2)-Cd(1)-N(4) 119.2 (4), Cl(2)-Cd(1)-Cl(3) 119.0 (2).



The X-ray crystal structure of (3) reveals that the molecule adopts a highly distorted trigonal-bipyramidal geometry around cadmium. Due to the geometrical constraints imposed by the designed ligand, as we believe, the nitrogen donor sets (N,N,N) occupying one equatorial and two axial positions, force the two chlorine atoms to fill the remaining equatorial positions. The crystal also reveals the intermolecular Se...Se contacts (3.82 A°) (-X, -Y, -Z+1) and are quite longer[9,10]. One non-coordinating CH_3OH solvent molecule, probably stabilizing the crystal lattice, is found to be associated with each complex molecule during refinement.

EXPERIMENTAL

All solvents were dried and distilled before use. The reactions were carried out in an inert atmosphere. Elemental analysis were performed with a Perkin Elmer 240C analyser. ^1H NMR spectra were recorded on Bruker 300 MHz instrument with Me_4Si as internal standard and $CDCl_3$ as solvent. 2,6-diacetylpyridine (Fluka) was used as such. Aminoalkyl(phenyl)selenides were prepared according to our previous procedure[8]. Other physicochemical techniques used as described earlier . X-ray diffraction data were measured on an CAD4 Enraf-Nonius 4-circle automatic diffractometer [graphite-monochromatized, Mo kα (λ = 0.7093 A°) radiation] W-2θ scan mode. Crystal data for complex (3) : triclinic, space group P/1, a = 8.255 (2), b = 10.366 (2) C = 18.049 (3) A°, α = 77.44 (2)°, β = 81.07 (3)°, γ = 74.45 (2)°, V = 1444.6 (5) A°^{3}, Z = 2, D_c = 1.423 mg/m^3, μ (Mo - Kα) = 0.7093 A°. A total of 5455 reflection data were collected in the θ range 7-12° from a reddish rectangular crystal (1.1 x 0.2 x 0.6 mm). The structure was solved by direct method using SHELX - 76, SHELX - 86, SHELX - 93 programs[11]. Unfortunately, the refined structure contained few error and this was due, in part, to the chlorine contamination might be present in the data collection crystal[12]. However, this free chlorine is far off and cannot be fixed up during refinement of the structure.

Synthesis of ligand (L_1) and (L_2) : A solution of 2, 6-diacetylpyridine (2.0 mmol) in methanol (20 cm^3) was added dropwise to a solution of aminoalkyl(phenyl)selenide (4.0 mmol) in methanol (20 cm^3) and allowed to stir with reflux for 4 h. After cooling the mixture and evaporation of the solvent under reduced pressure gave a viscous yellow oil in 90% yield.
^1H NMR (300 MHz, $CDCl_3$) for (L_1): δ 8.04 (2H, d, J = 7.5 Hz, Py), 7.70 (1H, t, J = 7.8 Hz, py), 2.37 (6H, s, CH_3), 3.88 (4H, t, N-CH_2), 3.34 (4H, t, Se-CH_2) and 7.6-7.2 (10H, m, Ph-Se). For (L_2): (found : C, 58.61; H, 6.29. $C_{27}H_{31}N_3Se_2$ required C, 58.37; H, 5.58%). δ_H 8.08 (2H, d, J = 9Hz, Py), δ 7.71 (2H, t, J = 6Hz, Py), 2.38 (6H, s, CH_3), 3.62 (4H, t, N-CH_2), 3.12 (4H, t, Se-CH_2), 2.21(4H, m, -CH_2-) and 7.6-7.1 (10H, m, Ph-Se).

Reactions of L_1 and L_2 with $CdCl_2$: To a methanolic solution of L_1 (1.0 mmol), $CdCl_2$ (1.0 mmol) in methanol was added dropwise and stirred for 0.5h. The precipitated yellow product [$CdCl_2.L_1$] (**1**) was filtered off, washed with methanol and dried *in vacuo*. Yield, 0.65g, 91%, m.p. 165°C (Found : C, 42.08; H, 5.23; N, 6.21. $C_{25}H_{27}N_3Se_2CdCl_2$ requires C, 42.29; H, 3.80; N, 5.91%); δ_H for [$CdCl_2.L_1$], 8.01 (2H, d, 9Hz py), 8.24 (1H, t, 9Hz, py), 2.36 (6H, s, CH_3), 4.14 (4H, t, N-CH_2), 3.71 (4H, t, Se-CH_2) and 7.6-7.1 (10H, m, Ph-Se).

[$CdCl_2.L_2$] (**2**). Yield, 90%, m.p. 146°C (Found: C, 42.88; H, 4.02; N, 5.20.$C_{27}H_{31}N_3Se_2CdCl_2$ requires C, 43.87; H, 4.19; N, 5.68%). δ_H for [$CdCl_2.L_2$], 8.02 (2H, d, J = 9H$_z$, py), 8.26 (1H, t, 9Hz, py), 2.45 (6H, s, CH_3), 3.99 (4H, t, NCH_2), 3.05 (4H, t, Se-CH_2), 2.49 (4H, m, -CH_2-) and 7.6-7.1 (10H, m, Ph-Se).

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