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# Design, synthesis, and structural aspects of chalcogen-substituted pyridine dicarboxamide donors and their reactions

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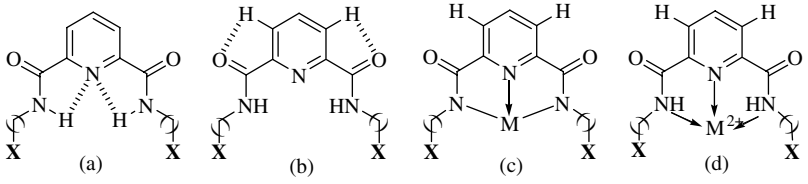
Respectfully dedicated in honor of Professor Bal Krishan Puri on the occasion of his superannuation and 62nd birthday

**Abstract**—The design and synthesis of a new family of potentially pentadentate $N_3Se_2$ or $N_3Te_2$ type donors bearing a 2,6-disubstituted pyridine dicarboxamide moiety as the central fragment [–NH–C(=O)–pyridine–C(=O)–NH–] functionalized with chalcogen as additional donors in the appended arms of the pyridine ring through the alkyl spacers and their potential applications and reactivity toward $d^8$ and $d^{10}$ metal ions have been demonstrated.


The design, synthesis, and study of organic host molecules that can accommodate cationic, neutral, or anionic guests is a thriving field of research[1–5] with increasing emphasis on the use of a combination of dynamic coordination chemistry and hydrogen bonding to allow more efficient syntheses of host molecules through self-assembly.[6,7] Intimately, organic carboxamides have proved to be spectacular ligands in self-assembly processes through hydrogen bonding and have also shown relevance to biological systems.[8]

It has been established that the protonated forms of these species prefer the *syn–syn* conformation because of electrostatic interactions between the amide (NH) protons and the pyridine nitrogen. The presence of '*exo*' amide carbonyl oxygen (C=O) atoms that can act as hydrogen bond acceptors, present two favorable N–H···N and C–H···O electrostatic interactions (Chart 1a and b).[9] Consequently, the known patterns of hydrogen bonding of the amide functionality make the systems useful building blocks for supramolecular architectures. For example, oligoamides have been designed such that can fold to give single or double helices as well as other supramolecular assemblies.[8] In addition, amide-linked catenanes, rotaxanes, and knots have been prepared by template synthesis.[10] Cyclic peptides

**Chart 1.**




X = heteroatom donors; such as N, P, O, or S; ( ) = alkyl or aryl spacers

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can self-assemble to give interesting supramolecular structures, most notably nanotubes via amide–amide hydrogen bonding.[8,9] Pyridinedicarboxamides have also proved to be excellent tridentate ligands in coordination chemistry after deprotonation of the amide nitrogens (Chart 1c).[11] In this manner, complexation does not induce a conformational change of the ligand (Chart 1c and d). Additionally, incorporation of heteroatom(s) in such systems through appended arms has meanwhile had a further dramatic influence on the reactive properties of these systems.[12] For example, polydentate amide-containing ligands have been instrumental in uncovering structure–activity relationships in bleomycin models and in determining the details of iron–bleomycin redox chemistry.[13] On the other hand, exploiting the unique coordination properties of these donors provides opportunities for the design of selective sensors and extractants with high affinity and selectivity for specific ions and has been another ongoing goal of researchers in this area.[14] Due to the above reasons and our continued efforts to understand the role of chalcogens (in particular, selenium and tellurium) in multifunctional frameworks, we report herein chalcogen-substituted pyridine dicarboxamide systems, potentially pentadentate ($N_3Se_2$) in nature, with the motivation that judicially positioned chalcogen atoms in a multifunctional core may substantially reduce the flexibility of the appended arms and ensure the possibility that the designed molecular species would retain their solid-state structures in solution.[15] Moreover, the presence of chalcogens in such frameworks in addition to carboxamide units may provide new opportunities for their study and, in principle, might provide different coordination possibilities, thus new structural motifs may also be expected.[16] In view of the above facts, we disclose our preliminary results on potentially pentadentate donors bearing $N_3Se_2$ type donors and their reactivity toward $d^8$ and $d^{10}$ metal ions. Molecular species **1**–**7**, possessing 2,6-disubstituted central pyridine frameworks [O=C–N(H)–(diamide)linkage] and appended arms bearing selenium or tellurium as additional donors, were prepared by the reaction of 2,6-pyridinedicarbonyl dichloride and arylselenoethylamine in acetonitrile at room temperature Scheme 1. Formation of both mono- and disubstituted derivatives was observed.

However, the disubstituted derivatives were the major products and were obtained as light yellow viscous liquids after chromatographic separation.[17] These compounds were found to be soluble in common organic solvents such as dichloromethane, chloroform, methanol, and acetonitrile. The structures of these species were established on the basis of physicochemical studies such as IR, $^1$H NMR, $^{13}$C NMR, and mass spectrometry. Molecular species based on the pyridine dicarboxamide unit can assume various conformations as observed previously, but if intramolecular hydrogen bonding is assumed to be operational then only two arrangements of the dicarboxamide-based compounds in the present study can be considered to occur in solution state (Fig. 1).

The probability of a *syn–anti* conformation across the aryl-CO bond (ii) is low on the basis of the $^1$H NMR spectrum of the compound, because if this had been the case there should be two signals for the amide protons but only one signal for the amide protons is

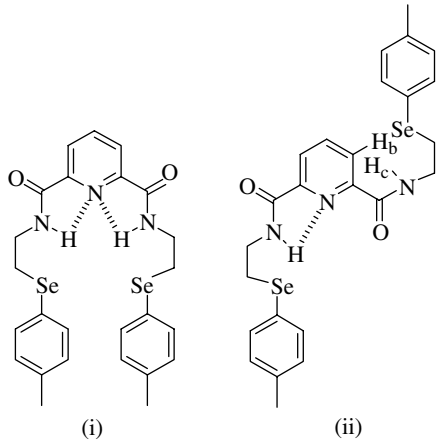
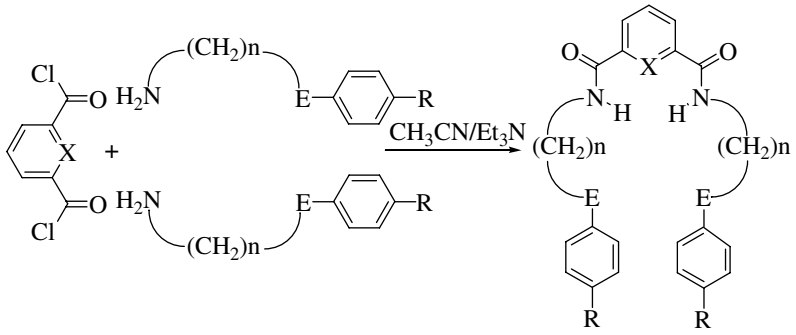



**Figure 1.** Two energetically different conformations (i) and (ii) of **1**.




R = $CH_3$; X = N; n = 2; E = Se **1** ( 58%); R = $CH_3$; X = N; n = 3; E = Se **2** ( 52%);
R = H; X = N; n = 2; E = Se **3** ( 51%); R = H; X = N; n = 3; E = Se **4** ( 53%);
R = H; X = H; n = 2; E = Se **5** ( 59%); R = H; X = H; n = 2; E = Se **6** ( 53%);
R = H; X = N; n = 3; E = Te **7** ( 53%).

**Scheme 1.**

actually observed for this species. Furthermore, if conformation (ii) was present in solution then a 'through–space' interaction of the amide proton ($H_c$) with the *meta* proton ($H_b$) of the pyridine ring can be expected. Thus, the molecules in the present study exclusively exist in the *syn–syn* conformation (i) in solution at least. Molecules bearing architectures of the *type* (i) have shown wide applications in diverse areas of chemistry. For example, in molecular recognition as receptors or as ligands for solvent extraction which in addition to their unique coordination chemistry have been the prime targets of studies.[12,18] The receptor abilities of the molecular species, in particular, the reactions of **1** with $ZnCl_2$, $Zn(ClO_4)_2$, $CdCl_2$, $Cd(ClO_4)_2$, and $HgCl_2$ were examined. Since the donor moiety contains both '*hard*' 'N' and '*soft*' 'Se' atoms, it seemed unnatural to us to accept that the donors had no affinity with $d^{10}$ metal ions ($Zn^{2+}$, $Cd^{2+}$, and $Hg^{2+}$). It has been observed by Borovik et al. that in polydentate systems the relative position of the heteroatom and their interactions with metal ions largely depends on the stereochemical preference of the metal ion and not on the geometric requirements of the ligand.[19] Thus, in order to check the effect of the size and influence of the metal ion on the geometry of the resulting complex, the behavior of **1** was also examined with smaller $d^8$ metal(II) ions. Further, the molecular species **1** showed no affinity for Ni and Pt ions even under basic conditions where deprotonation of the donor is also expected. Even in the cases of $Ni^{2+}$ or $Ag^{1+}$ ions no complexation was observed even after several days of reaction at room temperature. $^1H$ NMR titrations of **1** with $Zn^{2+}$, $Cd^{2+}$, and $Ag^{+}$ were also carried out in order to understand the nature and extent of possible interactions taking place in solution state. The NMR data were processed using the Win EQ NMR program and were found to fit well with a 1:1 (M:L) model for $Zn^{2+}$ and $Cd^{2+}$ species and with a 2:1 (M:L) model for $Ag^{+}$ species. However, when **1** was treated with $Pd^{2+}$ under normal reaction conditions at ambient temperature, a bright orange precipitate was produced.[20] The interaction of species **1** with $Pd^{2+}$ ions, and the exclusion of $Zn^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Ni^{2+}$, and even $Ag^{1+}$ ions is intriguing. Even if the size matters and the ligand is excluding the larger $Cd^{2+}$ and $Hg^{2+}$ ions and the smaller $Zn^{2+}$ ion then it should allow complexation with either the $Ni^{2+}$ or $Ag^{1+}$ ions that approximate to $Pd^{2+}$ in their ionic radii and also have affinity for selenium. The ES-MS spectrum for the palladium complex did not reveal the molecular ion peak for this complex but revealed the presence of a signal at *m*/*z* 666, which corresponded to the Pd:L moiety. Definitive elucidation of the coordination behavior of donor **1** toward palladium and the final structure of the complex were established by single crystal X-ray diffraction studies.[21] The crystal structure for the palladium complex[22] of **1** is shown in Figure 2.

The complex adopted a '*chair-like*' conformation thereby separating the planes of the $N_3$ and $Se_2$ donor sets considerably. The $N_3$ donor set behaves as the back-rest of the chair while the $Se_2$ donor set is placed on the armrest of the so called '*chair-like*' conformation. The '*chair-like*' conformation is further stabilized by strong intramolecular hydrogen bonding between one of the chlorine atoms attached to palladium and the amide protons, which further conclusively explains the downfield shift of the amide protons observed in the $^1H$ NMR spectrum of the complex.[20] Molecular modeling[23] revealed that the similar specific orientation might also be present in solution for the ligand **1**, which hence can be held responsible for the different behavior of the ligand toward $d^8$ and $d^{10}$ metal ions.

Nevertheless, the reactivity which is dependent upon numerous factors such as the nature of the metal (coordination numbers and stereochemical preferences), the structure of the ligand, the existence of noncovalent interactions, etc., needs to be addressed in a given system before one can arrive at a conclusion about their structures, reactivity, and applications. These reactions are yet to be optimized in order to achieve the long-term goal of proving the role of selenium and its value in precursors for supramolecular species as well as its application in ion-exchange extraction methodology for rapid screening of potential extractants, and as receptors and sensors for toxic metals. This optimization, along with

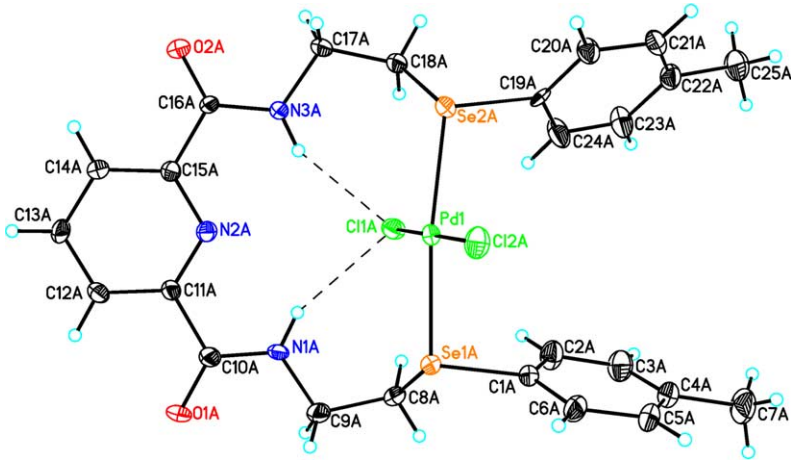



**Figure 2.** ORTEP diagram of the palladium complex of **1**.

the preparation and study of complexes with different metal ions are under progress and are the focus of our ongoing studies. We are also planning extensive structural and spectroscopic studies with **1** and analogous chelates to define the role of selenium in such systems.

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## References and notes

1. (a) Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; VCH: New York, 2000; (b) Bondy, C. R.; Gale, P. A.; Loeb, S. J. *J. Supramol. Chem.* **2002**, *2*, 93–96; (c) Albrecht, M. *Chem. Rev.* **2001**, *101*, 3457–3498; (d) Piguet, C.; Bernardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005–2062; (e) Barbour, L. J.; Orr, G. W.; Atwood, J. L. *Nature* **1998**, *393*, 671–673.
2. (a) Beer, P. D.; Szemes, F.; Balzani, V.; Salà, C. M.; Drew, M. G. B.; Dent, S. W.; Maestri, M. *J. Am. Chem. Soc.* **1997**, *119*, 11864–11875; (b) Sun, S.-S.; Lees, A. J. *Chem. Commun.* **2000**, 1687–1688; (c) Sun, S.-S.; Lees, A. J.; Zavalij, P. Y. *Inorg. Chem.* **2003**, *42*, 3445–3453.
3. (a) Kavallieratos, K.; Hwang, S.; Crabtree, R. H. *Inorg. Chem.* **1999**, *38*, 5184–5186; (b) Kondo, M.; Okubo, T.; Asami, A.; Noro, S.-I.; Yoshitomi, T.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Seki, K. *Angew. Chem., Int. Ed.* **1999**, *38*, 140–143; (c) Liu, Y.; Chen, Y.; Li, B.; Wada, T.; Inoue, Y. *Chem. Eur. J.* **2001**, *7*, 2528–2535; (d) Liu, Y.; Song, Y.; Wang, H.; Zhang, H.-Y.; Wada, T.; Inoue, Y. *J. Org. Chem.* **2003**, *68*, 3687–3690; (e) Camiolo, S.; Gale, P. A.; Hursthouse, M. B.; Light, M. E. *Org. Biomol. Chem.* **2003**, *1*, 741–744.
4. (a) Chang, S.-K.; Engen, D. V.; Fan, E.; Hamilton, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 7640–7645; (b) Kumar, S.; Hundal, M. S.; Kaur, N.; Singh, R.; Singh, H.; Hundal, G.; Ripoll, M. M.; Aparicio, J. S. *J. Org. Chem.* **1996**, *61*, 7819–7825; (c) Velasco, T.; Lecollinet, G.; Ryan, T.; Davis, A. P. *Org. Biomol. Chem.* **2004**, *2*, 645–647.
5. (a) Camiolo, S.; Gale, P. A.; Sessler, J. L. In *Encyclopedia of Supramolecular Chemistry*; Atwood, J. L., Steed, J. W., Eds.; Marcel Dekker: NY, 2004; (b) *Fundamentals and Applications of Anion Separations*; Moyer, B. A., Singh, R. P., Eds.; Kluwer, Academic/Plenum: NY, 2004.
6. (a) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097; (b) Qin, Z.; Jennings, M. C.; Puddephatt, R. J. *Chem. Commun.* **2002**, 345–346, **2001**; 2676–2677; (c) Qin, Z.; Jennings, M. C.; Puddephatt, R. J. *Chem. Commun.* **2002**, 354–355; (d) Qin, Z.; Jennings, M. C.; Puddephatt, R. J. *Inorg. Chem.* **2003**, *42*, 1956–1965; (e) Qin, Z.; Jennings, M. C.; Puddephatt, R. J. *Chem. Eur. J.* **2002**, *8*, 735–738.
7. (a) Redmore, S. M.; Rickard, C. E. F.; Webb, S. J.; Wright, J. *Inorg. Chem.* **1997**, *36*, 4743–4748; (b) Vance, A. L.; Alcock, N. W.; Busch, D. H.; Heppert, J. A. *Inorg. Chem.* **1997**, *36*, 5132–5134; (c) Vance, A. L.; Alcock, N. W.; Heppert, J. A.; Busch, D. H. *Inorg. Chem.* **1998**, *37*, 6912–6920; (d) Hausmann, J.; Jameson, G. B.; Brooker, S. *Chem. Commun.* **2003**, 2992–2993; (e) Hausmann, J.; Brooker, S. *Chem. Commun.* **2004**, 1530–1531; (f) Alcock, N. W.; Clarkson, G.; Glover, P. B.; Lawrance, G. A.; Moore, P.; Napitupulu, M. *Dalton Trans.* **2005**, 518–527.
8. (a) Berl, V.; Huc, I.; Khoury, R. G.; Krische, M. J.; Lehn, J.-M. *Nature* **2000**, *407*, 720–723; (b) Berl, V.; Huc, I.; Khoury, R. G.; Lehn, J.-M. *Chem. Eur. J.* **2001**, *7*, 2810–2820; (c) Berl, V.; Huc, I.; Khoury, R. G.; Lehn, J.-M. *Chem. Eur. J.* **2001**, *7*, 2798–2809; (d) Huc, I.; Maurizot, V.; Gornitzka, H.; Léger, J.-M. *Chem. Commun.* **2002**, 578–579; (e) Maurizot, V.; Linti, G.; Huc, I. *Chem. Commun.* **2004**, 924–925; (f) Acocella, A.; Venturini, A.; Zerbetto, F. *J. Am. Chem. Soc.* **2004**, *126*, 2362–2367; (g) Jiang, H.; Maurizot, M.; Huc, I. *Tetrahedron* **2004**, *60*, 10029–10038; (h) Dolain, C.; Zhan, C.; Léger, J.-M.; Daniels, L.; Huc, I. *J. Am. Chem. Soc.* **2005**, *127*, 2400–2401.
9. Odriozola, I.; Kyritsakas, N.; Lehn, J.-M. *Chem. Commun.* **2004**, 62–63.
10. (a) Jeong, K.-S.; Cho, Y. L.; Song, J. U.; Chang, H.-Y.; Choi, M.-G. *J. Am. Chem. Soc.* **1998**, *120*, 10982–10983; (b) Jeong, K.-S.; Choi, J.-S.; Chang, S.-Y.; Chang, H.-Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 1692–1695; (c) Collinson, S.; Alcock, N. W.; Raghunathan, A.; Kahol, P. K.; Busch, D. H. *Inorg. Chem.* **2000**, *39*, 757–764; (d) Noveron, J. C.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **2001**, *123*, 3247–3259; (e) Burkill, H. A.; Vilar, R.; White, A. J. P.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **2002**, 837–839; (f) Preston, A. J.; Fraenkel, G.; Chow, A.; Gallucci, J. C.; Parquette, J. R. *J. Org. Chem.* **2003**, *68*, 22–26; (g) Harrop, T. C.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **2004**, *126*, 14714–14715; (h) Patra, A. K.; Rose, M. J.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **2004**, *126*, 4780–4781; (i) Jeong, K.-S.; Park, E.-J. *J. Org. Chem.* **2004**, *69*, 2618–2621; (j) Arunkumar, E.; Forbes, C. C.; Noll, B. C.; Smith, B. D. *J. Am. Chem. Soc.* **2005**, *127*, 3288–3289; (k) Fuller, A.-M. L.; Leigh, D. A.; Lusby, P. J.; Slawin, A. M. Z.; Walker, D. B. *J. Am. Chem. Soc.* **2005**, *127*, 12612–12619.
11. (a) Patra, A. K.; Ray, M.; Mukherjee, R. *J. Chem. Soc., Dalton Trans.* **1999**, 2461–2466; (b) Dutta, S. K.; Beckmann, U.; Bill, E.; Weyhermüller, T.; Wieghardt, K. *Inorg. Chem.* **2000**, *39*, 3355–3364; (c) Zhang, J. Y.; Liu, Q.; Duan, C.; Shao, Y.; Ding, J.; Miao, Z.; You, X. Z.; Guo, Z. J. *J. Chem. Soc., Dalton Trans.* **2002**, 591–597; (d) Jain, S. L.; Bhattacharyya, P.; Milton, H. L.; Slawin, A. M. Z.; Crayston, J. A.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **2004**, 862–871.
12. (a) Hu, Z.-Q.; Chen, C.-F. *Tetrahedron Lett.* **2004**, *45*, 3957–3960; (b) Hu, Z.-Q.; Chen, C.-F. *Chem. Commun.* **2005**, 2445–2447; (c) Yang, D.; Li, X.; Fan, Y.-F.; Zhang, D.-W. *J. Am. Chem. Soc.* **2005**, *127*, 7996–7997; (d) Kavallieratos, K.; Rosenberg, J. M.; Chen, W.-Z.; Ren, T. *J. Am. Chem. Soc.* **2005**, *127*, 6514–6515.
13. (a) Chavez, F. A.; Rowland, J. M.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **1998**, *120*, 9015–9027; (b) Rowland, J. M.; Thornton, M. L.; Olmstead, M.

M.; Mascharak, P. K. *Inorg. Chem.* **2001**, *40*, 1069–1073; (c) Patra, A. K.; Rose, M. J.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **2004**, *126*, 4780–4781.

14. (a) Moriuchi, T.; Yoshida, K.; Hirao, T. *Org. Lett.* **2003**, *5*, 4285–4288; (b) Sessler, J. L.; Katayev, E.; Pantos, G. D.; Ustynyuk, Yu. A. *Chem. Commun.* **2004**, 1276–1277; (c) Sessler, J. L.; Katayev, E.; Pantos, G. D.; Scherbakov, P.; Reshetova, M. D.; Khrustalev, V. N.; Lynch, V. M.; Ustynyuk, Y. A. *J. Am. Chem. Soc.* **2005**, *127*, 11442–11446.
15. (a) Milton, M. D.; Singh, J. D.; Butcher, R. J. *Tetrahedron Lett.* **2004**, *45*, 6745–6747; (b) Milton, M. D.; Kumar, N.; Sokhi, S. S.; Singh, S.; Maheshwari, M.; Singh, J. D.; Asnani, M.; Butcher, R. J. *Tetrahedron Lett.* **2004**, *45*, 8941–8944.
16. Unpublished results from our laboratory. (a) Milton, M. D. Ph.D. Dissertation, Indian Institute of Technology Delhi, India, 2001; (b) Kumar, N. Ph.D. Dissertation, Indian Institute of Technology Delhi, India, 2005.
17. A general procedure was followed for the preparation of **1**–**7**. To a mixture of 2,6-pyridine dicarbonyl dichloride or isophthaloyl chloride (2.0 mmol) and triethylamine (4.0 mmol) in $CH_3CN$ (25 mL) was added a solution of the respective arylchalcogenoalkyl amine (4.0 mmol) (in $CH_3CN$, 20 mL) dropwise at room temperature. The contents were stirred for 2 h and the progress of the reaction was monitored by thin layer chromatography (silica-coated plates). The solution was then evaporated to dryness under reduced pressure and diluted with chloroform. The organic layer was washed with water, brine, and dried over anhydrous $Na_2SO_4$ and evaporated to dryness under reduced pressure to yield a dark brown viscous liquid. The viscous liquid was then subjected to chromatographic separation using silica as the stationary phase and chloroform/methanol (95:5) mixture as the eluent to yield **1**–**7** as light yellow viscous liquids.
*Characterization data for* **1**: Yellow viscous liquid (yield, 58%). IR (KBr pellets): $\nu$ ($cm^{-1}$) = 3332 (m, amide N–H stretching vibration), 2929.2 (w, aliphatic C–H stretch), 2360 (w), 1669 (m, C=O stretching vibration amide I band), 1527 (m, N–H bending vibration amide II band), 1490 (w), 1443 (w), 1218 (m), 1097 (w), 771 (s), 671 (w), 487 (w). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 8.31$ (2H, d, $J = 7.8$ Hz, pyH), 8.17 (2H, br t, –CONH–), 8.02 (1H, t, $J = 7.8$ Hz, pyH), 7.43 (4H, d, $J = 8.0$ Hz, ArH), 7.01 (4H, d, $J = 7.9$ Hz, ArH), 3.75 (4H, q, $J = 6.3$ Hz, $–CH_2–$NH–), 3.12 (4H, t, $J = 6.5$ Hz, $–CH_2–$Se–), 2.26 (6H, s, $–CH_3$). $^1$H NMR (300 MHz, $CD_3CN$): $\delta = 8.47$ (2H, br t, –CONH–), 8.18 (2H, d, $J = 7.8$ Hz, pyH), 8.05 (1H, t, $J = 7.7$ Hz, pyH), 7.45 (4H, d, $J = 8.0$ Hz, ArH), 7.04 (4H, d, $J = 8.1$ Hz, ArH), 3.72 (4H, q, $J = 6.2$ Hz, $–CH_2–$NH–), 3.14 (4H, t, $J = 6.3$ Hz, $–CH_2–$Se–), 2.23 (6H, s, $–CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 163.2$ (–*C*ONH–), 148.6 (py*C*), 139.0 (py*C*), 136.9 (Ar*C*), 132.6 (Ar*C*), 129.8 (Ar*C*), 125.6 (Ar*C*), 124.2 (py*C*), 39.9 ($–CH_2–$NH–), 26.3 ($–CH_2–$Se–), 20.0 ($–CH_3$). $^{13}$C NMR (75 MHz, $CD_3CN$): $\delta = 163.2$ (–*C*ONH–), 148.6 (py*C*), 139.0 (py*C*), 136.9 (Ar*C*), 132.6 (Ar*C*), 129.8 (Ar*C*), 125.6 (Ar*C*), 124.2 (py*C*), 39.9 ($–CH_2–$NH–), 26.3 ($–CH_2–$Se–), 20.0 ($–CH_3$). MS (ES) $m/z$ 560 ($M^+$, 60%).
18. (a) Hamuro, Y.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 10587–10593; (b) Kavallieratos, K.; Rosenberg, J. M.; Chen, W.-Z.; Ren, T. *J. Am. Chem. Soc.* **2005**, *127*, 6514–6515; (c) Yang, D.; Li, X.; Fan, Y.-F.; Zhang, D.-W. *J. Am. Chem. Soc.* **2005**, *127*, 7996–7997.
19. (a) Kawamoto, T.; Hammes, B. S.; Haggerty, B.; Yap, G. P. A.; Rheingold, A. L.; Borovik, A. S. *J. Am. Chem. Soc.* **1996**, *118*, 285–286; (b) Kawamoto, T.; Hammes, B. S.; Ostrander, R.; Rheingold, A. L.; Borovik, A. S. *Inorg. Chem.* **1998**, *37*, 3424–3427.
20. *Synthesis of the palladium complex*: To an acetonitrile solution of compound **1** (1 mmol), solid $PdCl_2(CH_3CN)_2$ (1 mmol) was added in small amounts at room temperature under a nitrogen atmosphere. A bright yellow precipitate was obtained immediately after the addition was complete. The solid precipitate was filtered and dried under vacuum. Yield: 94%. IR (KBr pellets): $\nu$ ($cm^{-1}$) = 3315 (s), 3010 (w), 2920 (w), 2360 (w), 1667 (s), 1589 (w) 1517 (s), 1440 (w), 1410 (w), 1356 (w), 1264 (m), 1233 (w), 1184 (m), 1118 (w), 1012 (m), 848 (m), 802 (m), 758 (m), 645 (m), 616 (m), 486 (m). $^1$H NMR (300 MHz, $CDCl_3$): $\delta = 8.97$ (2H, br, –CONH–), 8.43 (2H, d, $J = 7.7$ Hz, pyH), 8.07 (1H, *t*, $J = 7.8$ Hz, pyH), 7.74 (4H, d, $J = 7.5$ Hz, ArH), 7.15 (4H, d, $J = 7.7$ Hz, ArH), 4.65 (2H, m, aliphatic H), 4.26 (2H, m, aliphatic H), 3.78 (2H, m, aliphatic H), 2.78 (2H, m, aliphatic H), 2.36 (6H, s, $–CH_3$). $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta = 164.3$ (–*C*ONH–), 148.5 (py*C*), 140.6 (Ar*C*), 138.7 (py*C*), 133.0 (Ar*C*), 130.5 (Ar*C*), 125.4 (py*C*), 116.3 (Ar*C*), 38.4 ($–CH_2–$NH–), 31.3 ($–CH_2–$Se–), 21.3 (Ar*C*). MS (ES-MS) $m/z$ 666 ($M^+ - 2Cl$, 12%).
21. *Crystallographic data for the Pd(II) complex*: $C_{25}H_{25}Cl_2N_3O_2PdSe_2$, $M = 734.70$ g $mol^{-1}$, monoclinic, space group $P2(1)/c$, $a = 26.266(5)$, $b = 10.6442(19)$, $c = 31.721(6)$ Å, $V = 8409(3)$ Å$^3$, $Z = 12$, 19907 reflections collected, 19,907 independent reflections. Final $R1 = 0.0824$ and $wR2 = 0.2175$ (all data). The unit cell is composed of three crystallographically independent molecules exhibiting similar conformations. The amidate and pyridine nitrogens are in a sterically more prohibitive chelating role and adopt a chair-like conformation. This configuration allows both the selenium atoms of the ligand to coordinate with palladium providing a distorted square planar arrangement around palladium.
22. Crystallographic data for the Pd(II) complex have been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 246349. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (+44 1223 336408; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).
23. The energy minimized structure for compound **1** represents the chair-like conformation having $N_3$ donors and $Se_2$ donors in two different planes.