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Synthesis of β-ketoenamine donors having O, N, Se/Te donor functionalities and their reaction chemistry with Pd(II) and Pt(II) metal ions

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Dedicated to Professor Sakae Uemura, on the occasion of his superannuation and 63rd birthday

Abstract—Monoanionic tridentate ligands **LH$_a$** and **LH$_b$** containing ONSe and ONTe donor sequences and their Pd^{2+} and Pt^{2+} derivatives were synthesized and characterized. The formation of a five- and a six-membered ring around the central metal atom and associative phenomena in solutions provide extra stability to the metal complexes.

In the last few decades various heavier organochalcogens (selenium and tellurium) bearing variable donor functionalities and their metal complexes have been studied extensively owing to their novel and unprecedented properties.[1] Recently, we became interested in designing hetero-functionalized chalcogen-bearing donors anticipating that these ligands might exhibit a partial lability leading to coordinatively unsaturated metal centers upon coordination. This is particularly a prerequisite for complexes that might have an application in catalysis. Transition metal complexes of heterofunctionalized tridentate donors with (C, N, O),[2] (C, N, S),[3] (P, N, O),[4] (P, O, N),[5] (O, P, N),[6] (N, O, P),[7] (P, N, C),[8] (P, N, S)[9] (O, N, S)[10] and (N, S, O)[11] donor sequences have received considerable attention over the past 15 years due to their improved catalytic properties and have continued to be an area of current research interest.

We considered that the synthesis of suitable ligands bearing (O, N, Se/Te) donor combinations would be an ideal choice for study as these ligands may exhibit new chemistry in terms of their heterofunctionalized nature. We also considered that the deprotonated form of the ligands might act as a tridentate ligand coordinating through O, N, Se/Te. Of the three heteroatoms, one would also expect Se/Te to be bonded the strongest to platinum group metals (soft acceptor), the oxygen to be the weakest bonded and nitrogen to be intermediate in its donor ability. Thus, the ligands might be induced to exhibit tridentate (O, N, Se/Te bonded), bidentate (N, Se/Te bonded) or unidentate (Se or Te bonded) bonding modes. If the ligand adopted a tridentate mode of binding then cleavage of the weak metal–oxygen (M–O) bond of the chelate ring might occur rapidly and reversibly, exhibiting interesting chemistry. Their behavior may involve organochalcogen hemilabile ligands, a phenomenon, which has seldom been addressed, despite the fact that organoselenium and tellurium based system have been used in asymmetric synthesis and asymmetric catalysis.[12]

The protonated forms of tridentate chelating ligands (O, N, Se/Te) are easily accessible by the addition of 1 equiv of $C_6H_5E(CH_2)_2NH_2$ (E = Se or Te) to 1 equiv of 2,4-pentanedione in refluxing methanol to give the desired ligands in high yields as low melting solids or brownish-yellow viscous materials of sufficient purity for further reactions.[13] In the ^1H NMR spectra of the ligands, an –N*H* signal was observed in the region of δ 10.84–10.96.

Further, the carbon NMR spectra (in $CDCl_3$) showed carbonyl signals between δ 194.89–193.61 indicating a

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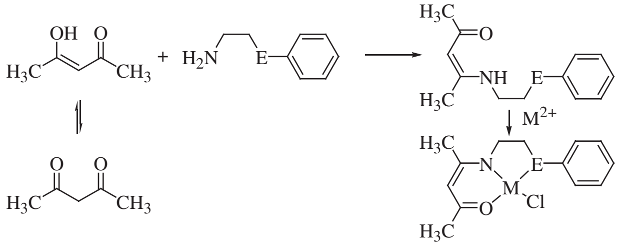
slight delocalization of the C–O bond and thus it can be concluded that the ligands exist practically solely in the ketoenamine form, at least in $\mathrm{CDCl_3}$ solution. Owing to the heterofunctionalized nature of the ligands, we first set out to establish their coordination chemistry by reacting them with platinum group metals, which should force the ligand to assume a square planar configuration.

Platinum complexes were prepared by the treatment of $\mathrm{K_2PtCl_4}$ with the corresponding ligands in an acetone–water (1:1, v/v) mixture at room temperature.[14] To our surprise, the reaction conditions for both the ligands $\mathbf{LH_a}$ and $\mathbf{LH_b}$ were found to be sufficient to deprotonate the ligands and produce the complexes $[\mathrm{Pt}(\mathbf{L_a})\mathrm{Cl}]$ **2a** and $[\mathrm{Pt}(\mathbf{L_b})\mathrm{Cl}]$ **2b** as pale yellow crystalline materials in quantitative yields. Under identical reaction conditions, ligands $\mathbf{LH_a}$ and $\mathbf{LH_b}$ reacted with $\mathrm{K_2PdCl_4}$ to give a mixture of products where hydrolysis of the parent ligands was also observed. However, the syntheses of comparable Pd(II) complexes were accomplished by reacting the ligands $\mathbf{LH_a}$ and $\mathbf{LH_b}$ with $\mathrm{Pd(C_6H_5CN)_2Cl_2}$ in methanol in a 1:1 molar ratio and again it was observed that deprotonation occurred without a base, suggesting the existence of the ligand in the β-ketoenamine form in solution. Microanalysis and spectral data confirmed the proposed stoichiometry and geometry (Scheme 1). The complexes once isolated are not sensitive to oxygen or moisture, and the reactions can be carried out in air with no change in efficiencies or yields. FAB mass spectra of the various complexes showed the expected molecular ion peaks. The monomer–dimer association observed in molecular weight determinations in solution was also observed by low-ionization FAB mass spectrometry (LI-MS) and peaks corresponding to dimers were detected.



Ligand $\mathbf{LH_a}$: E = Se; Ligand $\mathbf{LH_b}$: E = Te
(E = Se) Complex **1a** (M = Pd): **2a** (M =Pt)
(E = Te) Complex **2a** (M = Pd): **2b** (M =Pt)

Scheme 1.

Single crystal X-ray diffraction studies[15] of the complex $[\mathrm{Pt}(\mathbf{L_b})\mathrm{Cl}]$ **2b** revealed that the molecule $[\mathrm{PhTe(CH_2)_2N{-}C(CH_3)CHC(CH_3)(O)PtCl}]$ crystallizes in a monoclinic, $P2_1/n$ space group with four molecules per unit cell. The ligand coordinates to the central platinum ion through all its donor sites resulting in the formation of five and six-membered rings around platinum, which is tetra coordinated to Te, N, O and Cl. The rigid chelate rings force platinum to adopt a slightly distorted square-planar geometry with the four bond angles in the range of 87.6–94.2°. The N–Pt–Cl and Te–Pt–O bond angles are 174.3(3)° and 172.3(3)°, respectively, which suggests that these bonds have been displaced from the mean plane of platinum by 5.7° and 7.7°, respectively. The C(9)–C(10) and C(10)–C(11) bond distances of 1.40 and 1.36 Å, respectively, are much shorter than normal C–C single bonds [1.51 Å], the C(9)–N bond distance of 1.34 Å is longer than a normal imine C=N double bond [1.28 Å] but much shorter than a C–N single bond [1.47 Å]. Furthermore, the C(11)–O bond length of 1.256(16) Å is longer than a carbonyl bond but much shorter than a normal C–O single bond [1.34 Å]. These data clearly indicate delocalization of the six-membered β-ketoenamine unit of the ligand. The Pt–Te bond distance [2.504(2) Å] appears to be the shortest Pt–Te bond known so far.[16] A perspective view of the molecular structure is given in Figure 1.

The molecules crystallize as dimeric units held together by Pt···Te (3.584 Å) intermolecular contacts. The shortest Pt···Pt (4.016 Å) and Te···Te (4.702 Å) distances are clearly larger than the sum of their van der Waals radii, which suggest that there is no direct bonding between

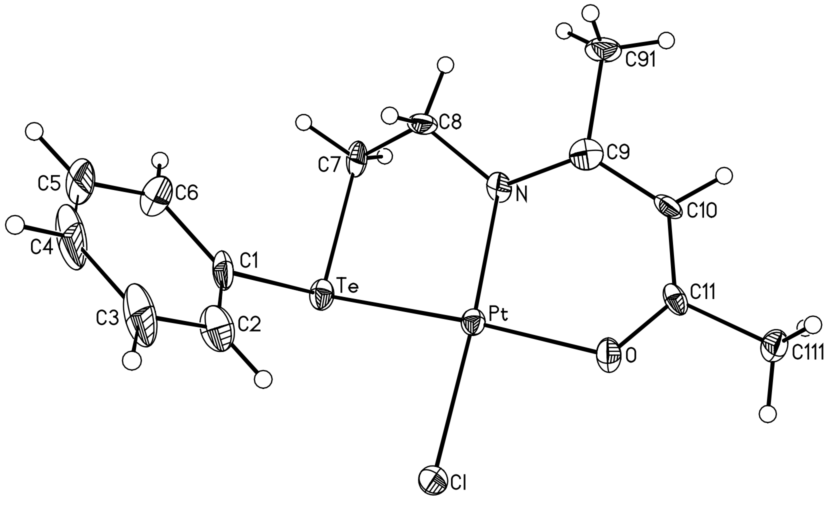


Figure 1. ORTEP diagram of $[\mathrm{PhTe(CH_2)_2N{-}C(CH_3)CHC(CH_3)(O)PtCl}]$.

the two platinum atoms or tellurium atoms. Attempted reaction of the metal complexes with molecular iodine or with methyl iodide failed under various conditions. The formation of two strong chelate rings around the metal center and delocalized (N,O) coordination of the β-ketoenamine unit provides extra stability to the resulting metal complexes. Thus, the M–O coordination between the '*hard*' oxygen donor of the ligand framework and the '*soft*' metal center was found to be strong enough and hence no '*hemilability*' was displayed.

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References and notes

1. (a) Wirth, T. *Tetrahedron* **1999**, *55*, 1–28; (b) Wirth, T. *Angew. Chem., Int. Ed.* **2000**, *39*, 3740–3749; (c) Uemura, S. *Phosphorous, Sulfur, Silicon* **2001**, *171*, 13–30.
2. Basuli, F.; Peng, S.-M.; Bhattacharyya, S. *Inorg. Chem.* **2001**, *40*, 1126–1133.
3. Freisinger, E.; Willermann, M.; Lippert, B. *J. Organomet. Chem.* **2001**, *629*, 97–108.
4. (a) Bacchi, A.; Carcelli, M.; Costa, M.; Fochi, A.; Monici, C.; Pelagatti, P.; Pelizzi, C.; Pelizzi, G.; Roca, L. M. S. *J. Organomet. Chem.* **2000**, *593–594*, 180–191; (b) Pelagatti, P.; Bacchi, A.; Bobbio, C.; Carcelli, M.; Costa, M.; Pelizzi, C.; Vivorio, C. *Organometallics* **2000**, *19*, 5440–5446; (c) Correia, J. D. G.; Domingos, A.; Santos, I.; Alberto, R.; Ortner, K. *Inorg. Chem.* **2001**, *40*, 5147–5151; (d) Andrieu, J.; Steele, B. R.; Screttas, C. G.; Cardin, C. J.; Fornies, J. *Organometallics* **1998**, *17*, 839–845.
5. (a) Yabuta, M.; Nakamura, S.; Yamagata, T.; Tani, K. *Chem. Lett.* **1993**, 323–326; (b) Tani, K.; Yabuta, M.; Nakamura, S.; Yamagata, T. *J. Chem. Soc., Dalton Trans.* **1993**, 2781–2786; (c) Nagel, U.; Nadden, H. G. *Chem. Ber* **1997**, *130*, 385–391.
6. (a) Spiegel, G. U.; Stelzer, O. *Chem. Ber* **1990**, *123*, 989–997; (b) Yang, H.; Lugan, N.; Mathieu, R. *Organometallics* **1997**, *16*, 2089; (c) Green, M. J.; Cavell, K. J.; Edwards, P. G. *J. Chem. Soc., Dalton Trans.* **2000**, 853–858.
7. Hu, W.-Q.; Sun, X.-L.; Wang, C.; Gao, Y.; Tang, Y.; Shi, L.-P.; Xia, W.; Sun, J.; Dai, H.-L.; Li, X.-Q.; Yao, X.-L.; Wang, X.-R. *Organometallics* **2004**, *23*, 1684–1688.
8. Getty, A. D.; Goldberg, K. I. *Organometallics* **2001**, *20*, 2545–2551.
9. (a) Ankersmit, H. A.; Veldman, N.; Spek, A. L.; Vrieze, K.; Koten, G. V. *Inorg. Chim. Acta* **1996**, *252*, 339–354; (b) Pelagatti, P.; Bacchi, A.; Bobbio, C.; Carcelli, M.; Costa, M.; Fochi, A.; Pelizzi, C. *J. Chem. Soc., Dalton Trans.* **2002**, 1820–1825; (c) Correia, J. D. G.; Domingos, A.; Paulo, A.; Santos, I. *J. Chem. Soc., Dalton Trans.* **2000**, 2477–2482.
10. (a) Dutta, S. K.; Samanta, S.; Ghosh, D.; Butcher, R. J.; Chaudhury, M. *Inorg. Chem.* **2002**, *41*, 5555–5560; (b) Bhattacharyya, P.; Parr, J.; Slawin, A. M. Z. *J. Chem. Soc., Dalton Trans.* **1998**, 3609–3614; (c) Zhang, C.; Guzei, I. A.; Espenson, J. H. *Inorg. Chem.* **2001**, *40*, 2437–2438; (d) Chang, S.; Karambelkar, V. V.; di Targiani, R. C.; Goldberg, D. P. *Inorg. Chem.* **2001**, *40*, 194–195.
11. Kemp, G.; Roodt, A.; Purcell, W.; Koch, K. R. *J. Chem. Soc., Dalton Trans.* **1997**, 4481–4484.
12. (a) Nishibayashi, Y.; Singh, J. D.; Uemura, S. *Tetrahedron Lett.* **1994**, *35*, 3115–3118; (b) Nishibayashi, Y.; Singh, J. D.; Segawa, K.; Fukuzawa, S.-I.; Uemura, S. *Chem. Commun.* **1994**, 1375–1376; (c) Nishibayashi, Y.; Segawa, K.; Singh, J. D.; Fukuzawa, S.-I.; Ohe, K.; Uemura, S. *Organometallics* **1996**, *15*, 370–379; (d) Nishibayashi, Y.; Singh, J. D.; Fukuzawa, S.-I.; Uemura, S. *J. Org. Chem.* **1995**, *60*, 4114–4120.
13. A solution of phenylchalcogenoalkylamine (10 mmol) in methanol (10 mL) was added to a solution of 2,4-pentanedione (1.00 g, 10 mmol) in methanol (25 mL) and the mixture was refluxed for 3 h. Reaction extent was monitored by TLC. The solvent was evaporated under reduced pressure and the crude product was separated by column chromatography [silica gel/chloroform: hexane (9:1) mixture] to yield the pure ligands. Yield (80–85%).
14. A solution of ligand (**LH$_b$**) (0.30 mmol) in acetone (10 mL) was added dropwise to an aqueous solution of K_2PtCl_4 (0.12 g, 0.30 mmol). A yellow precipitate was obtained immediately. The reaction mixture was stirred for 2 h at room temperature and solid product was filtered off and dried under vacuum. Recrystallization from a mixture of chloroform–methanol (9:1) afforded orange-yellow crystals (0.14 g, 86%). Elemental analysis (%) calcd: C, 27.86; H, 2.88; N, 2.50; found: C 28.02, H 2.62, N 2.51. FAB-MS: *m*/*z* 562 for [M + H]. δ_H ($CDCl_3$) 8.07 (d, 2H, *J*(HH) 7 Hz, *o*-Ph), 7.44–7.33 (m, 3H, *m*- and *p*-Ph), 4.99 (s, 1H, –CH–), 4.99–4.91 and 3.57–3.48 (td and dt, 2H, *J*(HH) 4 and 12 Hz, N–CH_2), 2.62–2.53 and 2.27–2.22 (td and dt, 2H, *J*(HH) 4 and 12 Hz, Te–CH_2), 2.05 (s, 3H, $OCCH_3$), 1.98 (s, 3H, $NCCH_3$).
15. Crystallographic data for compound 2 have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 242587. 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).
16. Menon, S. C.; Panda, A.; Singh, H. B.; Butcher, R. J. *Chem. Commun.* **2000**, 143–144.