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Role of ligand conformation in the structural diversity of divalent complexes containing phosphinic amide ligand

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ABSTRACT

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Keywords: Zinc Cobalt Phosphinic amide 1-D coordination polymer Reactions of the phosphinic amide ligand *N*-(4-methyl-2-pyrimidinyl)-P,P-diphenyl-phosphinic amide, **L**, with the corresponding metal salts afforded the complexes $[Zn(L)Cl_2]_{\infty}$, **1**, and $Co_3(L)_4Br_6$, **2**, which have been structurally characterized by X-ray crystallography. The molecules of the free **L** ligands are interlinked through N–H—N and C–H—O hydrogen bonds to form a linear chain, whereas complex **1** shows the 1D helical chain structure, which is the first coordination polymer containing phosphinic amide ligands, and **2** is a linear Co(II) trimer with a rare mixed T_d – O_h – T_d geometry. While the free **L** ligand adopts the *aligned* conformation, those in **1** and **2** adopts the *cis* and both the *cis* and *trans* conformations, respectively.

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The bis(2-pyridyl)amine (Hdpa) ligand and its anion (dpa⁻) has been subjected to many investigations of their coordination abilities to metal centers. Three types of conformations were found for these ligands (Fig. 1, top). In the bidentate mode of coordination, the two pyridyl nitrogen atoms are arranged in a *cis* conformation, which was found in the crystal structure of a copper(II) complex [1], while the *trans* conformation was found in the crystal structure of the free Hdpa ligand [2]. The dpa⁻ ligands in the linear trinuclear complexes were found to possess the *aligned* conformations [3], in which the three nitrogen atoms are arranged in a near linear array for coordination to the metals. Dimolybdenum complexes of Hdpa and dpa⁻ligands which show the three conformations have also been reported [4].

To investigate the coordination chemistry of the phosphinic amide ligand, we have synthesized *N*-(4-methyl-2-pyrimidinyl)-P,P-diphenyl-phosphinic amide (**L**) and reacted with metal salts. We found that the **L** ligand can adopt various ligand conformations similar to the Hdpa and dpa⁻ligands. Based on the relative orientations of the pyrimidyl nitrogen atom adjacent to the methyl group, the amide nitrogen atom and the amide oxygen atom, the ligand **L** can also possibly show three conformations in the solid state (Fig. 1, bottom). We report herein the crystal structures of the free **L** ligand, the 1D helical chain $[Zn(L)Cl_2]_{\infty}$, **1**, and the linear trinuclear complex Co₃(**L**)₄Br₆, **2**, in which the three ligand conformations can be observed.

The reactions of **L** with ZnCl_2 and CoBr_2 in MeOH/THF afforded the 1D helical chain complex $[\text{Zn}(\text{L1})\text{Cl}_2]_{\infty}$, **1**, and the discrete linear trinuclear complex $\text{Co}_3(\text{L1})_4\text{Br}_6$, **2**, respectively [5]. The IR spectra for **1** and **2** show bands at 1129 and 1125 cm⁻¹, respectively, assignable

to the P O stretching vibrations. These energies are smaller than that of the free ligand (1235 cm⁻¹), indicating the coordination of the oxygen atoms to the metal centers (see Fig. S1 in the supplementary materials). The solid state emission spectra of **1** and **2** show emissions at 397 and 399 nm, respectively, upon excitations at 245 nm, which are similar to those of the free **L** (397 nm) ligand (see Table S1 and Fig. S2 in the supplementary materials). Since the identity of the metal center and the structural type hardly changes the emission wavelength, these emission bands may be tentatively assigned as intraligand (IL) $\pi \rightarrow \pi^*$ transitions.

The crystals of **L** conform to the space group P_{21}/c with four molecules in each unit cell. Fig. 2(a) depicts the molecular structure for **L** [7]. The molecules are held together by a series of the donor–acceptor–donor–acceptor (DADA) quadruple hydrogen bonds and the donor–acceptor (DA) double hydrogen bonds (Fig. 2b) to form 1D linear chains. The centrosymmetric DADA:ADAD self-complementary interaction involves two N–H–N [H–N=2.084 (3) Å; \angle N–H–N=173.2 (2)°] and two C–H–O [H–O=2.657 (3) Å; \angle C–H–O=138.1 (2)°] hydrogen bonds, while the centrosymmetric DA:AD interaction involves two C–H–O [H–O=2.551 (2) Å; \angle C–H–O=138.1 (2)°] hydrogen bonds. The free ligand adopts the *aligned* conformation, presumably due to the constraints from the N–H–M and C–H–O hydrogen bonds.

The structure of $[Zn(L)Cl_2]_{\infty}$, **1**, was solved in the space group $P3_2$ with three molecules in the unit cell. Fig. 3(a) depicts a drawing showing the environment about the Zn(II) center which is coordinated by one nitrogen atom of pyrimidyl group, one oxygen atom of the phosphinic amide group and two Cl atoms to form a distorted tetrahedral geometry. The Zn(II) metal centers are bridged by the L ligands to form the 1D helical chain(Fig. 3b and c). The Zn–Zn distance separated by the bridging L ligand is 6.595 (1) Å and the length of the repeating unit of the helical chain involving four zinc

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Fig. 1. The three possible conformations for 2,2'-dipyridylamine (top) and L (bottom).

atoms and three **L** ligands is 12.480 (2) Å along the 3₁ screw axis. The **L** ligands adopt the *cis* conformation which is required to form the 1D helical chain. The 1D chains are also interlinked through C–H—Cl hydrogen bonds [H—Cl=2.926 (2) Å, \angle C–H—Cl=133.0 (5)°] (see Fig. S3 in the supplementary materials). To our best knowledge complex **1** is the first coordination polymeric complex containing phosphinic amide ligand.

The structure of $Co_3(L)_4Br_6$, **2** was solved in the space groups $P_{2_1/n}$ with two molecules in the unit cell, and Fig. 4(a) depicts the molecular structure showing the arrangements about the Co(II) metal centers. The central Co(1) atom which is located at a crystallographic inversion center is chelated by two L ligands and coordinated by two *trans* oxygen atoms from two bridging L ligands to form a

distorted octahedral geometry, while the two terminal Co(II) atoms adopts the tetrahedral coordination environment, resulting in a linear trimeric cobalt(II) complex with a mixed T_d – O_h – T_d geometry. The Co(1)—Co(2) distance separated by the bridging **L** ligand is 7.319 (1) Å and the angle of Co(2)–Co(1)–Co(2A) is 180.0°. Two types of the ligand conformation are found for the **L** ligands. While the two **L** ligands that chelate the central Co(II) atoms adopt the *cis* conformation, those that bridge the Co(II) atoms adopt the *trans* conformation. Fig. 4(b) and (c) shows the intermolecular C–H— π interactions [H— π =2.866 (1) Å, \angle C–H— π =164.74 (24)°] and C–H—Br hydrogen bonds [H—Br=2.984 (1) and 3.023 (1) Å, \angle C–H—Br=163.19 (21) and 135.34 (23)°], respectively, among the trimeric molecules in the solid state. The T_d – O_h – T_d geometry in **2** is in marked contrast to those



Fig. 2. (a) A drawing showing the molecular structure of L. Selected bond distances (Å) and angles (°): P-O = 1.474(3), P-N(3) = 1.664(3), P-C(6) = 1.793(4), P-C(12) = 1.801(3), O-P-N(3) = 106.8(2), O-P-C(6) = 112.0(2), N(3)-P-C(6) = 108.6(2), O-P-C(12) = 112.6(2), N(3)-P-C(12) = 109.0(2), C(6)-P-C(12) = 107.6(2). (b) A drawing showing the hydrogen-bonded linear chain of L.



Fig. 3. (a) Coordination environment about the Zn(II) center of 1. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zn–O(A) = 1.958(4), Zn–N(1) = 2.077(5), Zn–Cl(1) = 2.202(2), Zn–Cl(2) = 2.226(2), O(A)–Zn–N(1) = 103.5(2), O(A)–Zn–Cl(1) = 113.2(1), N(1)–Zn–Cl(1) = 108.8(2), O(A)–Zn–Cl(2) = 104.4(1), N(1)–Zn–Cl(2) = 107.6(2), Cl(2)–Zn–Cl(1) = 118.3(1). Symmetry transformations used to generate equivalent atoms: (A) -x + y + 1, -x + 2, z + 1/3. (b) A view of the helical structure looking down the *a*axis. (c) A view of the helical structure looking down the *c*axis.

reported for cobalt complexes with the trimeric unit which adopt the $O_h-T_d-O_h$ or O_h-O_h geometry [3,11]. Noticeably, the complex $Co_3(OH)_2(pa)_2(ina)_2$ [pa = 3-(1 *H*-benzimidazol-2-yl)propanoic carboxylate, ina = isonicotinate] consists of the linear Co(II) trimeric units with the mixed $T_d-O_h-T_d$ geometry, which are linked by the single-carboxylate-aromatic amine ligands to form 2D layers [11]. Complex **2** is thus the first discrete linear trinuclear Co(II) complex containing phosphinic amide ligand, where the metal centers adopt the mixed $T_d-O_h-T_d$ geometry.

In summary, we have successfully structurally characterized the phosphinic amide ligand **L** and two divalent metal complexes containing the **L** ligands. Complex **1** is the first coordination polymer containing the phosphinic amide ligand, and **2** is a discrete linear Co(II) trimer with a rare mixed T_d – O_h – T_d geometry. The **L** ligand exhibits three ligand formations similar to those reported for Hdpa and dpa⁻ligands. In the solid state, the molecules of the free **L** ligands are constrained by the N–H–N and C–H–O interactions, resulting in the *aligned* conformation, while those in **1** and **2** adopts the *cis* and both the *cis* and *trans*

conformations, respectively. The **L** ligand adopts the proper conformation that maximizes the intra- and intermolecular forces. This study shows that the phosphinic amide ligand **L** ligand may display a rich coordination chemistry which is under investigation.

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Appendix A. Supplementary material

Crystallographic data (CIF files) for the structures of L and 1–2 have been deposited with the Cambridge Crystallographic Data Centre,



Fig. 4. (a) A drawing showing the trimeric structure of **2**. The hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Co(1)–O(1) = 2.068(3), Co(1)–O(2) = 2.094(3), Co(1)–N(1) = 2.192(3), Co(2)–N(4) = 2.074(4), Co(2)–Br(3) = 2.373(1), Co(2)–Br(2) = 2.372(1), Co(2)–Br(1) = 2.410(1), O(1A)–Co(1)–O(1) = 180.0, O(1A)–Co(1)–O(2) = 91.8(1), O(1A)–Co(1)–O(1) = 0.82, (1), O(2)–Co(1)–O(2A) = 180.0, O(1A)–Co(1)–N(1) = 90.3(1), O(1)–Co(1)–N(1) = 89.7(1), O(2)–Co(1)–N(1) = 92.4(1), O(2A)–Co(1)–N(1A) = 87.6(1), O(2A)–Co(1)–N(1A) = 92.4(1), N(1)–Co(1)–N(1A) = 180.0, N(4)–Co(2)–Br(3) = 101.7(1), N(4)–Co(2)–Br(2) = 105.2(1), Br(3)–Co(2)–Br(2) = 118.4(0), N(4)–Co(2)–Br(1) = 109.3(1), Br(3)–Co(2)–Br(1) = 109.4(0), Br(2)–Co(2)–Br(1) = 111.9(0). Symmetry transformations used to generate equivalent atoms: (A) – x, – y + 1, – z + 1. (b) The trimeric molecules are linked through the intermolecular C–H– π interactions along the *a* axis. (c) A view showing the C–H–Br hydrogen bonds among the trimeric molecules, looking down the *a* axis.

CCDC 815928–815930. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or

www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j. inoche.2011.04.023.

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 [5] Preparation for 1: L (0.31 g, 1.0 mmol) [6] was placed in a flask containing MeOH/THF (30 mL; 1:1) and ZnCl₂ (0.14 g, 1.0 mmol) was added. The mixture
- [5] Preparation for 1: L (0.31 g, 1.0 mmol) [6] was placed in a flask containing MeOH/THF (30 mL; 1:1) and ZnCl₂ (0.14 g, 1.0 mmol) was added. The mixture was then stirred at room temperature for 24 h to afford a yellow solution with some white solid. The solution was filtered and then diethyl ether added to introduce precipitate. The precipitate was filtered and washed by diethyl ether (2×10 ml) and then dried under vacuum to give the white product. Colorless crystals were obtained by slow diffusion of diethyl ether into a methanol solution of the compound for several weeks. Yield: 0.25 g (56 % based on Zn). Anal. Calcd for C₁₇H₁₆Cl₂N₃OPZn (MW = 445.57): C, 45.82; H, 3.62; N, 9.43. Found: C, 45.75; H, 3.24; N, 9.56 %. IR (cm⁻¹): 3902(w), 3597 (m), 3191(br), 2365(m), 1962(m), 1612(s), 1433(m), 1326(m), 1258(s), 1129 (s), 1019(w), 905(w), 798(s), 757(m), 696(m), 544(w), 452(m), 440(s), 422 (w). Preparation for 2: Prepared as described for 1 except CoBr₂ (0.22 g, 1.0 mmol) was used. Yield: 0.58 g (71% based on Co). Anal. Calcd for C₆₈H₆₄Co₃Br₆N₁₂O₄P₄ (MW = 1925.48): C, 43.14; H, 3.41; N, 8.88. Found: C, 43.22; H, 3.41; N, 8.91 %. IR (cm⁻¹): 3382(b), 2995(b), 2742(w), 2366(w), 1970(m), 1828(m), 1665(s), 1530(m), 1477(w), 1430(m), 1328(m), 1257(m), 1125(s), 1017(s) 897(s), 760(w), 697(m), 623(w), 551(m), 502(m), 458(m).
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