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An Eight-Coordinate Mononuclear Double Helical Complex

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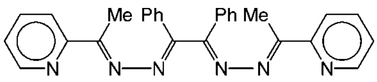
From the reaction of $Cd(CH_3COO)_2{\cdot}2H_2O$ with the 1:2 condensate (L) of benzil dihydrazone and 2-acetylpyridine, $[CdL(CH_3COO)(H_2O)]PF_6{\cdot}3H_2O$ (**1**) is isolated by adding NH_4PF_6. L reacts with $Cd(ClO_4)_2{\cdot}xH_2O$ to yield $[CdL_2](ClO_4)_2{\cdot}0.5H_2O$ (**2**). The yellowish complexes **1** and **2** are characterized by NMR and single-crystal X-ray diffraction. **1** is found to be a seven-coordinate single helical complex having a $Cd^{II}N_4O_3$ core and homoleptic **2** an eight-coordinate double helical complex with a $Cd^{II}N_8$ core.

Introduction

Many naturally occurring molecules are helical.[1] But synthetic helical organic molecules like [*n*]helicenes[2] are rare. These are achieved only through designed synthesis.[3,4] Non-helical organic molecules containing suitable hetero donor atoms can give rise to helical topology when they bind to many metal ions because of the coordination properties of the metal ions.[1,5,6] This has been an important area of research in metallo-organic chemistry in recent times. Metallo-organic helices, commonly, can be single, double, or triple. A single helical complex may contain a single metal ion or multiple metal ions. But for multiple helical complexes, it seems that at least two metal ions in combination with an at least tetradentate ligand are necessary. So far, only one example of a mononuclear triple helical complex is known where the metal ion is nine-coordinate La^{III} and the helicand is tridentate.[7] To date there is no example of a mononuclear double helical inorganic complex. Herein we report such a complex. The metal ion in our case is Cd^{II} and the ligand is a tetradentate N donor.

Results and Discussion

The ligand L we used is helical. It is a 1:2 condensate of benzil dihydrazone and 2-acetylpyridine.[8] In the area of inorganic helices, others have been using non-helical ligands. But for quite some time, we have been engaged in generating helical topologies by using ligands which are themselves helical.[9,10] The helical twist in L is brought about by the N=C(Ph)–C(Ph)=N torsion angle which is 85.9(5)° in the solid state.[11]



ligand L

Reaction of $Cd(CH_3COO)_2{\cdot}2H_2O$ with L in an equimolar ratio in methanol at room temperature and subsequent addition of a stoichiometric amount of NH_4PF_6 gives $[CdL(CH_3COO)(H_2O)]PF_6{\cdot}3H_2O$ (**1**) in 65% yield. From the reaction of $Cd(ClO_4)_2{\cdot}xH_2O$ and L in an equimolar ratio in methanol at room temperature, $[CdL_2](ClO_4)_2{\cdot}0.5H_2O$ (**2**) is isolated in 20% yield. The yield of **2** increased to 60% when the Cd/L ratio was 1:2. Both complexes **1** and **2** have a faint yellow colour.

The X-ray crystal structures of **1** and **2** have been determined. The structure of the cation of **1** is shown in Figure 1 together with the atomic numbering scheme. The metal atom is bonded to four nitrogen atoms of the tetradentate ligand L, two oxygen atoms of an acetate group at 2.354(9), 2.396(10) Å and a water molecule at 2.342(7) Å. The bond lengths to the four nitrogen atoms of L are 2.390(7) Å to N(11), 2.411(7) Å to N(18), 2.428(6) Å to N(23), and 2.405(7) Å to N(30), thus the distances to the pyridine nitrogen atoms are slightly shorter. The conformation of the ligand is described by the N=C(Ph)–C(Ph)=N torsion angle which is 75.4(1)°. The geometry of the coordination sphere can be described as a capped trigonal prism with the water molecule O(100) capping the face of N(11), N(23), N(30), and O(52) but this is severely distorted by the small bite of the acetate group. The Cd atom in **1** is seven-coordinate; but in the homoleptic complex **2**, its coordination sphere expands to

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eight to accommodate two ligands. The structure of the cation of **2** is shown in Figure 2 together with the atomic numbering scheme. The geometry is a distorted dodecahedron in which the pyridine nitrogen atoms N(11), N(30), N(41), N(60) form one plane (r.m.s. deviation 0.01 Å) and the acyclic nitrogen atoms N(18), N(23), N(48), N(53) (r.m.s. deviation 0.30 Å) the other plane, the two planes intersecting at 85.8°. In this structure there is a much greater variation in Cd–N bond lengths, no doubt because of steric crowding in the metal coordination sphere. For one of the ligands, distances are Cd(1)–N(11) 2.422(4), Cd(1)–N(18) 2.504(4), Cd(1)–N(223) 2.495(4), and Cd(1)–N(30) 2.414(4) Å showing a regular pattern in which the bonds to the acyclic nitrogen atoms are longer than the bonds to the pyridine nitrogen atoms. However, the distances to the other ligand are more irregular with Cd(1)–N(41) 2.506(4), Cd(1)–N(48) 2.596(4), Cd(1)–N(53) 2.513(4), and Cd(1)–N(60) 2.460(4) Å. The conformations of the ligands are the same as that found in **1**; the N=C(Ph)–C(Ph)=N torsion angle in the two independent ligand moieties are 73.6 and 77.7 °, respectively. Complexes **1** and **2** contain seven-membered chelate ring(s).

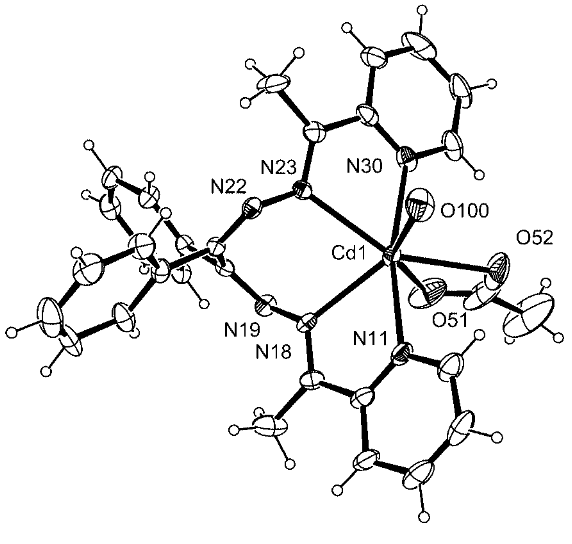

Figure 1. The structure of the cation in **1** with ellipsoids at 25% probability. The hydrogen atoms on the water molecule were not located. Selected bond lengths [Å] and angles [°]: Cd1–O100 2.342(7), Cd1–O51 2.354(9), Cd1–N11 2.390(7), Cd1–O52 2.396(10), Cd1–N30 2.405(7), Cd1–N18 2.411(7), Cd1–N23 2.428(6); O100–Cd1–O51 144.9(4), O100–Cd1–N11 88.4(3), O51–Cd1–N11 93.2(3), O100–Cd1–O52 90.7(5), O51–Cd1–O52 54.9(5), N11–Cd1–O52 83.6(3), O100–Cd1–N30 85.2(3), O51–Cd1–N30 85.3(3), N11–Cd1–N30 166.5(3), O52–Cd1–N30 84.6(3), O100–Cd1–N18 126.9(3), O51–Cd1–N18 85.0(4), N11–Cd1–N18 66.5(2), O52–Cd1–N18 128.7(4), N30–Cd1–N18 126.6(2), O100–Cd1–N23 81.6(3), O51–Cd1–N23 125.0(4), N11–Cd1–N23 123.0(2), O52–Cd1–N23 151.7(3), N30–Cd1–N23 67.8(3), N18–Cd1–N23 75.8(2).

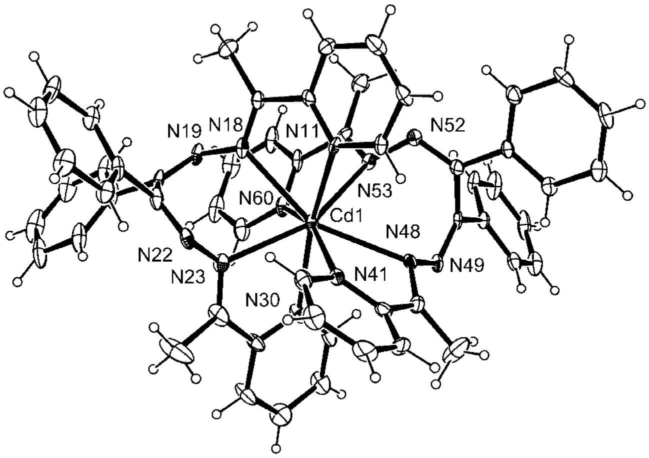

Figure 2. The structure of the cation in **2** with ellipsoids at 25% probability. Selected bond lengths [Å] and angles [°]: Cd1–N11 2.422(4), Cd1–N18 2.504(4), Cd1–N23 2.495(4), Cd1–N30 2.414(4), Cd1–N41 2.506(4), Cd1–N48 2.596(4), Cd1–N53 2.513(4), Cd1–N60 2.460(4); N30–Cd1–N11 160.2(1), N30–Cd1–N60 79.1(1), N11–Cd1–N60 120.7(1), N30–Cd1–N23 66.9(1), N11–Cd1–N23 108.8(1), N60–Cd1–N23 93.7(1), N30–Cd1–N18 127.2(1), N11–Cd1–N18 64.7(1), N60–Cd1–N18 73.1(1), N23–Cd1–N18 71.1(1), N30–Cd1–N41 80.3(1), N11–Cd1–N41 79.9(1), N60–Cd1–N41 159.4(1), N23–Cd1–N41 77.0(1), N18–Cd1–N41 119.6(1), N30–Cd1–N53 118.9(1), N11–Cd1–N53 73.9(1), N60–Cd1–N53 64.7(1), N23–Cd1–N53 153.9(1), N18–Cd1–N53 88.0(1), N41–Cd1–N53 128.1(1), N30–Cd1–N48 78.5(1), N11–Cd1–N48 92.4(1), N60–Cd1–N48 112.5(1), N23–Cd1–N48 131.5(1), N18–Cd1–N48 153.9(1), N41–Cd1–N48 64.1(1), N53–Cd1–N48 73.0(1).

The topologies of the complexes **1** and **2** are helical which can be discerned better from their space-filling models shown in Figure 3. Complex **1** is a mononuclear single helix. Many examples of such mononuclear single helices are known,[5,6] but very few with Cd.[12,13] Complex **2** is a mononuclear double helical complex which is unprecedented in its coordination chemistry. Though similar experimental conditions were used for obtaining complexes **1** and **2**, their compositions are different. We believe this difference is due to the difference in the coordinating ability of the anions. Since acetate is much more coordinating in nature than perchlorate, the presence of acetate gives rise to a heteroleptic complex such as **1**. At present we are engaged in studying the effect of the anion on the nature of the product of our synthetic method. Starting with $Cd(NO_3)_2{\cdot}4H_2O$, it seems that we obtain a single helical complex of composition $CdL(NO_3)_2{\cdot}H_2O$.

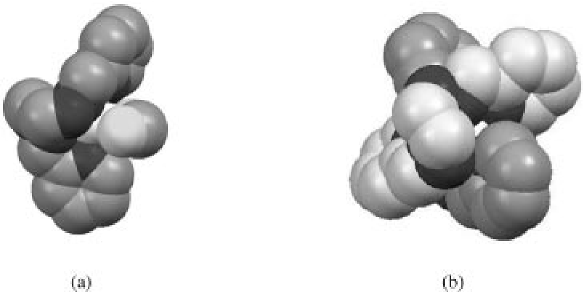

Figure 3. Space-filling models of the cations in **1** (a) and **2** (b) showing the helical nature of the complexes. The methyl and phenyl groups, and H atoms are removed for clarity. Code: (a) C, dark grey; N, black; O, light grey; Cd, white; (b) in one of the ligand strands C is dark grey and in the other light grey, the others are the same as in (a).

Since compounds **1** and **2** are helical, enantiomers are expected. Complex **1** crystallises in the non-centrosymmetric space group *Cc* and twinned refinement gave no evidence for a twin being present, so the structure can be considered as non-racemic in the individual single crystals. On the other hand, complex **2** crystallises in the centrosymmetric space group *Pbca* and therefore represents a racemic mixture in the solid state.

Bidentate ligands cannot afford a mononuclear helix. However, they can form at least dinuclear helicates by bridging two metal ions.[14] From the example of the La^{III} compound of Renaud et al.,[7] it is clear that, to generate a mononuclear helical metal complex, the minimum denticity of the helicand (ligand) has to be three. Now, with some imagination it can be realized that with a six-coordinate metal ion, which can give rise to an octahedral geometry, a tridentate ligand will never yield a mononuclear double helix. This is the reason why so far a mononuclear double helical complex has never been found with a six-coordinate metal ion. So the next choice is a tetradentate ligand with an eight-coordinate metal ion. Both the conditions are fulfilled in complex **2**.

Experimental Section

General: L was synthesised as reported earlier.[8] Microanalyses were performed with a Perkin–Elmer 2400II elemental analyser. FT-IR spectra (KBr) were recorded with a Shimadzu FTIR-8400S spectrometer, UV/Vis spectra in CH_2Cl_2 with a Shimadzu UV-160A spectrophotometer and 300 MHz NMR spectra in CD_2Cl_2 (reference: TMS) with a Bruker DPX300 spectrometer.

Synthesis of [CdL(CH_3COO)(H_2O)]PF_6·$3H_2O$ (1): Cd(CH_3COO)$_2$·$2H_2O$ (0.13 g, 0.5 mmol), dissolved in methanol (5 mL), was added to a methanolic (20 mL) solution of the ligand L (0.22 g, 0.5 mmol), synthesised by a procedure previously published.[8] After stirring the resulting light-yellow solution for 30 min, a methanolic solution (5 mL) of NH_4PF_6 (0.84 g, 0.5 mmol) was added and the mixture left for the solvent to evaporate. When the volume was ca. 5 mL, the deposited yellow crystals were filtered off and found to be suitable for X-ray diffraction. Yield: 0.27 g (65%). $C_{30}H_{35}CdF_6N_6O_6P$ (833.01): calcd. C 43.23, H 4.24, N 10.09; found C 43.33, H 4.12, N 10.19. FTIR (KBr): $\tilde{\nu}$ = 839 (vs) [$\nu(PF_6)$] cm^{-1}. UV/Vis: λ_{max} (ε_{max}) = 219 ($6.2\cdot10^4$), 265 ($2.5\cdot10^4$), 310 ($2.8\cdot10^4$ $M^{-1}cm^{-1}$) nm. ^1H NMR: δ = 2.03 (s, methyl of acetate), 2.51 (s, methyl of L), 7.11–8.01 (aromatic protons) ppm.

Synthesis of [CdL_2](ClO_4)$_2$·$0.5H_2O$ (2): Cd(ClO_4)$_2$·xH_2O (0.15 g, 0.5 mmol), dissolved in methanol (5 mL), was added to a methanolic (35 mL) solution of L (0.44 g, 1 mmol) and the mixture stirred for 2 h (a white crystalline compound started appearing within 15 min). Then the precipitate was filtered, washed with petroleum ether (5 mL) and dried in air. Yield: 0.36 g (60%). Single crystals were grown by direct diffusion of *n*-hexane into a moderately concentrated solution of the complex in dichloromethane. $C_{56}H_{49}CdCl_2N_{12}O_{8.5}$ (1208.36): calcd. C 55.29, H 4.08, N 13.52; found C 55.41, H 4.12, N 13.78. FTIR (KBr): $\tilde{\nu}$ = 1089 (vs), 623 (s) [$\nu(ClO_4)$] cm^{-1}. UV/Vis: λ_{max} (ε_{max}) = 265 ($8.6\cdot10^4$), 305 ($8.8\cdot10^4$ $M^{-1}cm^{-1}$) nm. ^1H NMR: δ = 2.52 (s, methyl protons), 7.12–8.03 (aromatic protons) ppm.

X-ray Crystallography: Crystal Data for **1**: $C_{30}H_{35}CdF_6N_6O_6P$, M = 833.01, monoclinic, space group *Cc*, Z = 4, a = 19.74(2), b = 11.304(14), c = 17.277(19) Å, β = 100.59(1)°, V = 3790(8) Å^3, $d_{calcd.}$ = 1.460 $g\,cm^{-3}$. Crystal data for **2**: $C_{56}H_{48}$ Cd Cl_2 N_{12} $O_{8.50}$, M = 1208.36, orthorhombic, space group *Pbca*, Z = 8, a = 16.2318(7), b = 21.0442(10), c = 32.2236(14) Å, V = 11007(1) Å^3, $d_{calcd.}$ = 1.458 $g\,cm^{-3}$. Data for **1** were collected with a Marresearch Image Plate system at 293 K using Mo-K_α radiation. The crystal was positioned at 70 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data reduction was carried out using the XDS program[15] to give 5256 independent reflections. Data for **2** were collected with an Oxford Instruments X-Calibur CCD system at 150 K using Mo-K_α radiation. The crystal was positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data reduction was carried out using the Crysalis program[16] to give 16192 independent reflections. Both structures were solved using Shelxs97.[17] The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they are attached. Absorption corrections were carried out using the DIFABS program[18] for **1** and the ABSPACK program[19] for **2**. The structures were refined on F^2 using Shelxl97 to give $R1$ = 0.0525, $wR2$ = 0.1382 (for **1**) and $R1$ = 0.0964, $wR2$ = 0.1239 (for **2**) using 4786 (for **1**) and 9503 (for **2**) reflections with $I > 2\sigma(I)$. CCDC-611911 (for **1**) and -611912 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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