



## Simultaneous coordination of a ketone by two cadmium(II) ions and conversion to its *gem*-diolate(−1) form

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### ABSTRACT

Reaction of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and di-2-pyridyl ketone  $[(\text{py})_2\text{CO}]$  in dry MeCN led to complex  $[\text{Cd}_2(\text{NO}_3)_4\{(\text{py})_2\text{CO}\}_2]$  (**1**) in which the ketonic grouping of each organic ligand bridges the two  $\text{Cd}^{\text{II}}$  atoms. Complex **1** is extremely reactive towards nucleophiles; it reacts with  $\text{H}_2\text{O}$  giving the cubane cluster  $[\text{Cd}_4(\text{NO}_3)_4\{(\text{py})_2\text{C}(\text{OH})(\text{O})_4\}]$  (**2**) possessing the 3.3011 (Harris notation) *gem*-diolate(−1) form of the ligand. Upon excitation at 380 nm, solid **1** displays blue green photoluminescence at room temperature.

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The carbonyl group of ketones and aldehydes is one of the most important functional groups in organic chemistry. Its intrinsically high reactivity can be enhanced by electrophilic activation with Lewis acids [1,2]. The two principal modes of ligation of ketones to metals in organometallic and coordination chemistry are the  $\eta^2$ - $\pi$ -bonded and the  $\eta^1$ - $\sigma$ -bonded modes **I** and **II** (Scheme 1), respectively [3]. Simultaneous coordination by two Lewis acids, i.e. double electrophilic activation (modes **III**, **IV** and **V**, Scheme 1), can lead to even greater increases in reactivity toward nucleophilic addition and to useful stereochemical effects [4]. Examples of these bridging coordination modes are uncommon, and the  $\mu$ -di- $\sigma$  mode **V** has been extremely rare [1,3,4]. We have now structurally characterized a ketonic grouping exhibiting type **V** coordination to two  $\text{Cd}^{\text{II}}$  atoms and have also demonstrated its conversion to the *gem*-diolate(−1) form which is able to bridge three metal ions.

To favor bridging of the ketonic grouping, we have decided to use ligands L incorporating two nearby donor sites X, see Scheme 2, capable of forming chelating rings with the involvement of the

carbonyl oxygen. The latter can interact with one metal atom at a time, or it can interact symmetrically or unsymmetrically with both at once. A suitable framework for juxtaposing a ketone and two metal ions is provided by di-2-pyridyl ketone,  $(\text{py})_2\text{CO}$  (Scheme 2), a currently very popular ligand in several interdisciplinary fields [1] such as single-molecule magnetism [5], single-chain magnetism [6], photoluminescent molecular materials [7], bioinorganic chemistry [8], molecular encoding at the nanoscale [9] and organic chemistry of metal complexes [10]. This preliminary communication can be considered as a continuation of our interest in the coordination chemistry of  $(\text{py})_2\text{CO}$ -based ligands [5a,7b,8,10c,11,12] and in several areas of cadmium(II) chemistry [13].

The reaction of  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{py})_2\text{CO}$  in a 1:1 molar ratio in dry MeCN at room temperature led to a colorless solution, from which slowly grew crystals of  $[\text{Cd}_2(\text{NO}_3)_4\{(\text{py})_2\text{CO}\}_2]$  (**1**) upon layering with  $\text{Et}_2\text{O}$  [14].

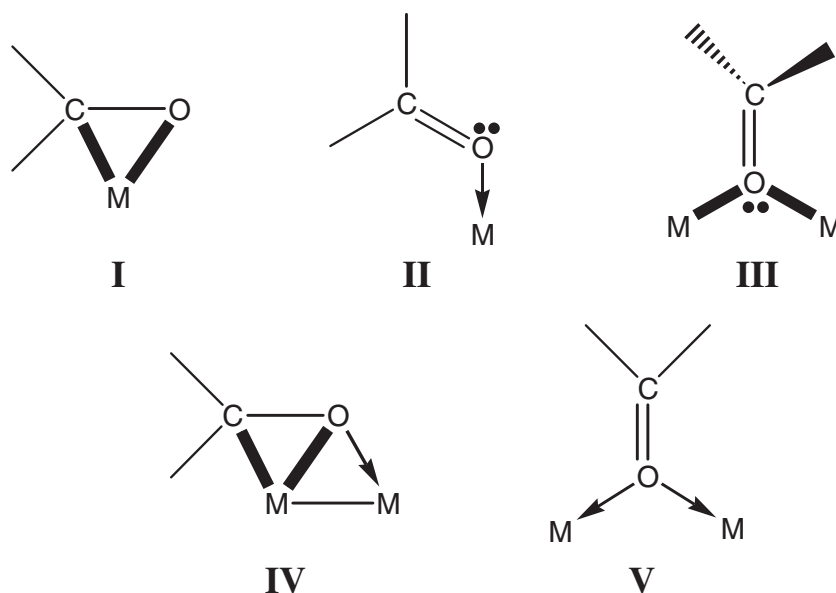
Complex **1** crystallizes in the tetragonal space group I41/acd [15]. Its structure consists of dinuclear  $[\text{Cd}_2(\text{NO}_3)_4\{(\text{py})_2\text{CO}\}_2]$  molecules (Fig. 1). There are two crystallographically imposed, orthogonal 2-fold axes which meet at the center of the  $\text{CdO1Cd'O1'}$  rhomb; one passes through the metal centers and the other through C6 and O1. The two  $\text{Cd}^{\text{II}}$  atoms are doubly bridged by the ketonic oxygen atoms (O1, O1') of the 2.211 (Harris notation [16])  $(\text{py})_2\text{CO}$  ligands (Scheme 3), while two bidentate chelating nitrate groups and two pyridyl nitrogen atoms from different ligands complete octa coordination at each metal center. The C6–O1 bond length of 1.217(4) Å is typical for a double

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**Scheme 1.** The modes of coordination of ketones to metals.

carbon–oxygen bond and indicates the ketonic character of the ligand. The Cd...Cd' distance is 4.134(2) Å. The angle between the two pyridyl rings of each (py)<sub>2</sub>CO ligand is 38.2°; the angle between the pyridyl ring and the carbonyl plane (defined by O1, C6 and the two carbon atoms that are bonded to C6) is 20.9°. The torsion angle Cd-N1-C5-C6 in the almost planar 5-membered chelate ring is 6.2°. The coordination polyhedron of the eight donor atoms about Cd is best described as a triangular dodecahedron (Fig. 2) [17].

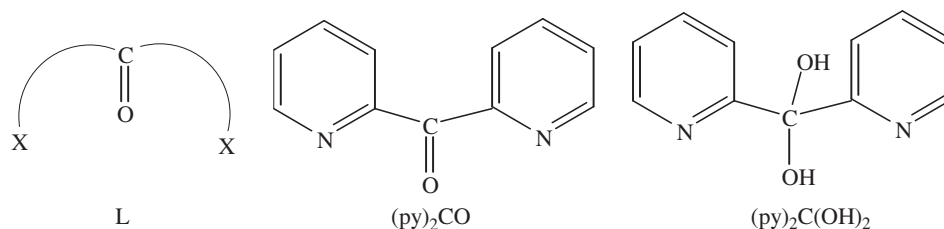
Compound **1** is extremely reactive towards several nucleophiles [18]. When a slurry of **1** in MeCN was treated with a little H<sub>2</sub>O, the resulting colorless solution gave crystals of [Cd<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>{(py)<sub>2</sub>C(OH)(O)}<sub>4</sub>] (**2**) upon layering with Et<sub>2</sub>O in 25% yield; (py)<sub>2</sub>C(OH)(O)<sup>−</sup> is the monoanion of the *gem*-diol form of di-2-pyridyl ketone. This complex can be also prepared by the reaction of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and (py)<sub>2</sub>CO in MeCN/H<sub>2</sub>O in the presence [19] or absence of a base.

Complex **2** crystallizes in the tetragonal space group I41/acd [20]. Its structure consists of tetranuclear [Cd<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>{(py)<sub>2</sub>C(OH)(O)}<sub>4</sub>] molecules (Fig. 3). The molecule of **2** lies on a rotoinversion four-fold axis ( $\bar{4}$ ) and the asymmetric unit contains a quarter of the cluster molecule. The tetranuclear molecule has a cubane {Cd<sub>4</sub>(μ<sub>3</sub>-OR)<sub>4</sub>}<sup>4+</sup> core with Cd<sup>II</sup> and μ<sub>3</sub>-O<sup>−</sup> atoms occupying alternative vertices. In addition to three μ<sub>3</sub>-O<sup>−</sup> atoms, each Cd<sup>II</sup> center is coordinated to two N-donor atoms that belong to two different (py)<sub>2</sub>C(OH)(O)<sup>−</sup> ligands and to two O atoms that belong to a bidentate chelating nitrate group. Thus, the coordination sphere is Cd<sup>II</sup>O<sub>5</sub>N<sub>2</sub>. The Cd<sup>II</sup>...Cd<sup>II</sup> distances are 3.587(1) and 3.605(2) Å. One O atom of each (py)<sub>2</sub>C(OH)(O)<sup>−</sup> ligand remains protonated and unbound to the metals; the resultant monoanion functions as a 3.3011 ligand (Scheme 3). The Cd–O (alkoxide-type) bonds are of three types; one bond is short to a distance of 2.263(5) Å, one bond is relatively long to a distance of

2.396(5) Å, while the third bond is of intermediate strength [2.328(5) Å]. The cube deviates from the ideal geometry. The internal cube angles at the metal vertices (RO–Cd–OR) average 77.8°, whereas the corresponding angles at the alkoxide corners (Cd–OR–Cd) are considerably larger averaging 101.0°. The sp<sup>3</sup> hybridized O1 atom would have three angles at 109.5°, and this is achieved by compressing the four oxygens along the body diagonals of the cube (tetrahedral distortion), increasing the angles at oxygen (from the ideal value of 90°), but concurrently decreasing the angles at the metal below 90°. The coordination polyhedron of the seven donor atoms about Cd is best described as a capped octahedron (Fig. 4) [17], with the nitrate oxygen atom O5 as the capping atom. Four symmetry related hydrogen bonds form within the cubane, with the hydroxyl O atom of the (py)<sub>2</sub>C(OH)(O)<sup>−</sup> ligand (O2) as the donor and the coordinated nitrate atom O3 as the acceptor (O2...O3 = 2.853 Å).

Complex **2** is the third structurally characterized cadmium(II) compound containing the monoanion (py)<sub>2</sub>C(OH)(O)<sup>−</sup> as ligand [7a,21]; complexes [Cd<sub>2</sub>Br<sub>4</sub>(py)<sub>2</sub>C(OH)<sub>2</sub>] [22a] and [Cd<sub>4</sub>(NCS)<sub>4</sub>(py)<sub>2</sub>C(OMe)(O)<sub>4</sub>] [22b], possessing the neutral *gem*-diol and the deprotonated hemiketal forms of di-2-pyridyl ketone, respectively, have also been structurally characterized. Compound **1** is the first structurally characterized cadmium(II) complex with the ketone form of di-2-pyridyl ketone as ligand and joins a very small family of metal complexes with the μ-di-σ coordination mode **V** of (py)<sub>2</sub>CO [23].

Complex **2** has no emission in the visible region. Complex **1** exhibits photoluminescent behavior (Fig. 5). Upon maximum excitation at 380 nm, a solid sample of the dinuclear compound displays blue-green photoluminescence at room temperature consisting of five clearly distinguished peaks and shoulders at 408, 425, 467, 481 and 518 nm. Since Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and (py)<sub>2</sub>CO [7a] are non-luminescent,



**Scheme 2.** The ligands discussed in the text; note that the *gem*-diol form (py)<sub>2</sub>C(OH)<sub>2</sub> and its anions [(py)<sub>2</sub>C(OH)(O)<sup>−</sup>, (py)<sub>2</sub>CO<sub>2</sub><sup>2−</sup>] do not exist as free species, but they exist only in the presence of metal ions. X is a donor atom.

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