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# An acetylacetonate or a pyrazole? Both! 3-(3,5-dimethyl-pyrazol-4-yl)pentane-2,4-dione as a ditopic ligand<sup>†</sup>

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#### Abstract

The alternative coordination sites of 3-(3,5-dimethyl-pyrazol-4-yl)pentane-2,4-dione (H<sub>2</sub>acacPz) differ with respect to Pearson hardness. The softer, heterocyclic moiety was used as N donor towards Zn(II) and Ag(I); it yielded a tetrahedral, neutral Zn complex in the former and a monocationic, linear bis(ligand) Ag complex in the latter case. After deprotonation with silverbenzoate, the pyrazolyl ring may act as a monoanionic  $N,N^2$ -bridge between neighbouring cations in a hexanuclear Ag aggregate; in addition to ligand-supported Ag···Ag distances of *ca.* 3.2 Å, these aggregates feature ligand-unsupported argentophilic interactions of *ca.* 2.9 Å. With stronger bases and in the presence of oxophilic Mg cations, the harder hydroxyketone part of the H<sub>2</sub>acacPz ligand may be deprotonated to a chelating acetylacetonate. The resulting bis(ligand) Mg complex has been used as starting compound for a bimetallic derivative: the ditopic ligand allows to coordinate cadmium acetate to its dangling N donor site, thus, bridging

<sup>&</sup>lt;sup>†</sup>Supporting Information available

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divalent Mg and Cd in a bimetallic three-dimensional coordination network of **pts** topology.

# Introduction

Ligands with two or more coordination sites allow for assembling cations to coordination polymers. The wide range of cations and the plethora of potential linkers have given rise to considerable scientific efforts and to almost countless publications documenting syntheses, structures and applications of such compounds. Ditopic ligands with two distinctly different coordination sites allow to combine different metal centers and thus add an additional degree of freedom to these complex solids. Substituted acetylacetonates have often been used in this context; we here focus on derivatives with a potential N donor substituent in 3 position. Scheme 1 compiles three of these ditopic acetylacetones: for HacacCN, an efficient synthesis was introduced by Silvernail  $et \ al.$ <sup>1</sup> This ligand acts as a (substituted) acetylacetonate towards many different cations but successive N coordination is limited to Ag or Cu.<sup>2–8</sup> A different coordination behaviour was observed for the pyridyl derivative HacacPy. It was first applied as linker in a discrete supramolecular structure.<sup>9</sup> Complexes in which this ligand acts as O<sup>10</sup> or N<sup>11</sup> donor and extended bimetallic structures in which it links different cations<sup>10–15</sup> have been described. Quite obviously, HacacPy is a significantly better N donor than HacacCN. In addition to cation coordination, the pyridyl N has been used as nucleophilic group in halogen bonds.<sup>16</sup> We now wish to report our results concerning the pyrazolyl-substituted ditopic ligand 3-(3,5-dimethyl-pyrazol-4-yl)pentane-2,4-dione,  $H_2$ acacPz. A beryllium complex of this compound was published by Boldog *et al.*<sup>17</sup> Similar to the aforementioned alternatives, H<sub>2</sub>acacPz offers O and N donor sites of different Pearson hardness;<sup>18</sup> in addition, both the pyrazolyl and the acetylacetone moiety may be deprotonated, and the question about preferred O or N coordination has not yet been answered. Moving from single site coordination to ditopic topology,  $H_2acacPz$  should rank





Scheme 1: Three N-donor substituted acetylacetonates with different  $M \cdots M$  distances.

in-between the shorter acacCN<sup>-</sup> and the longer acacPy<sup>-</sup> linker: The former is associated with metal··· metal distances of *ca*. 8 Å, the latter of *ca*. 9.7 Å, whereas for the yet unexplored HacacPz<sup>-</sup> bridge *ca*. 9 Å, were expected based on simple geometry considerations. We here communicate the synthesis and characterization of *N* coordinated, *N*,*N*' bridging, *O* coordinated and *O*,*N*' bimetallic complexes. Scheme 2 compiles the compounds synthesized and structurally characterized in the context of this work.

# **Results and discussion**

We start our survey of the coordination modes of  $H_2acacPz$  by using the ligand as an N donor without deprotonation. With ZnCl<sub>2</sub>, the neutral mononuclear complex [ZnCl<sub>2</sub>(H<sub>2</sub>acacPz)<sub>2</sub>], **1** is obtained. The metal cation is located on a twofold crystallographic axis and adopts an almost undistorted tetrahedral coordination. This reaction product is depicted in Fig. 1. The N coordinated H<sub>2</sub>acacPz molecules subtend an interligand angle of 106.4° and unambiguously correspond to the enol tautomer, with significantly different C-C and C-O bond distances in acetylacetone moiety as shown in Scheme 3.

This enol geometry derived from the diffraction experiment matches the IR spectrum of **1**, and we anticipate that the same pattern is encountered in the spectra of **2**, **3** and that of



Scheme 2: Synthesis and composition of the coordination compounds 1-4 and the bimetallic polymeric solid 5.

the uncoordinated ligand H<sub>2</sub>acacPz itself: No IR absorptions in the region of 1720 cm<sup>-1</sup> were observed; they would be expected for a diketone, *e.g.* for unsubstituted acetylacetone.<sup>19</sup> **1** shows a Raman band at 290 cm<sup>-1</sup>; a resonance in the same range had been assigned to the Zn-N vibration in the tetrahedral complex  $[ZnCl_2(Pyridine)_2]$ .<sup>19</sup> Intermolecular N-H···Cl contacts in **1** are rather long and bifurcated (Fig. 1).

Reaction of AgNO<sub>3</sub> with the neutral ligand H<sub>2</sub>acacPz leads to a cationic  $[Ag(H_2acacPz)_2]^+$ complex with nitrate as counter anion. This salt **2** crystallizes as a monohydrate in space group  $P\overline{1}$ . Cations and anions occupy alternating crystallographic centers of inversion along the *b* axis with shortest Ag···O (nitrate) distances of 2.894 Å (Fig. 2). The  $\overline{1}$  site symmetry imposes linear coordination for the metal center in the  $[Ag(H_2acacPz)_2]^+$  moiety and implies orientational disorder (see Experimental) for the nitrate anion and a closely associated water molecule. In **2**, hydrogen bonds link the ionic residues and the cocrystallized water molecule;



Figure 1: Coordination environment of Zn(II) and the bifurcate N-H····Cl contacts in 1. Ellipsoids are drawn at 50 % probability, only the H atoms at N2 are shown.  $d_{N2-H} = 0.881$ Å;  $d_{H\dots Cl1} = 2.792$  Å;  $d_{N2-H\dots Cl1} = 3.363$  Å;  $d_{H\dots Cl1B} = 2.536$  Å;  $d_{N2-H\dots ClB} = 3.244$  Å;  $\angle_{N2-H\dots Cl1} = 123.87^{\circ}$ ;  $\angle_{N2-H\dots Cl1B} = 137.86^{\circ}$ . Symmetry operations: A = 1-x, y, 1.5-z; B = 1-x, 2-y, 1-z.



Scheme 3: Enol geometry for  $H_2acacPz$  observed in the diffraction experiment on 1. A very similar pattern of comparable accuracy was encountered in crystals of **2**.

details have been compiled in the Supporting Information. The Ag-N vibration in the cation is associated with a band at  $240 \text{ cm}^{-1}$  in the Raman spectrum.<sup>20</sup>

In contrast to the alternative ditopic ligands shown in Scheme 1, H<sub>2</sub>acacPz may be deprotonated either at the N or the O donor site. In the presence of (soft) silver cations, benzoate is sufficiently basic to deprotonate the pyrazolyl moiety and the deprotonated anionic ligand HacacPz<sup>-</sup> N,N' bridges two Ag(I) cations; this coordination mode is observed in the closely related compounds **3a**, **3b** and **3c**. All three solids feature similar discrete [Ag<sub>6</sub>(HacacPz)<sub>6</sub>] molecules with crystallographic  $\overline{1}$  symmetry: **3a** contains one and the isomorphous com-



Figure 2: Arrangement of  $[Ag(H_2acacPz)_2]^+$  cations and nitrate anions along the *b* axis. Dashed lines indicate  $Ag \cdots O$  contacts of *ca*. 2.8 Å, hydrogen atoms and orientational disorder in the nitrate have been omitted.

pounds **3b** and **3c** two such independent residues. Therefore, five symmetrically independent hexanuclear  $[Ag_6(HacacPz)_6]$  aggregates have been characterized in total and are compared in the Supporting Information. In Fig. 3, we restrict our comparison to the  $Ag_6N_{12}$  cores in **3a** and **3b**. In all independent  $[Ag_6(HacacPz)_6]$  molecules, pairs of  $Ag_3$  triangles form; their  $Ag \cdots Ag$  edges (dashed lines) range between 3.3 and 3.5 Å, and are bridged by monoanionic HacacPz<sup>-</sup> ligands.

Aggregation of these triangles to a hexanuclear moiety is achieved via significantly shorter Ag-Ag contacts of *ca.* 2.9 Å. In view of the fact that these interactions occur directly and without any bridging ligand, even the term "cluster" might apply. Due to the concomitant presence of ligand supported and ligand unsupported contacts, we prefer the more general expression "aggregate". Table 1 compiles the Ag··· Ag distances in the five symmetrically independent aggregates in **3a**, **3b** and **3c**. Short Ag··· Ag contacts are generally referred to as "argentophilic", <sup>21–29</sup> and this type of interactions has recently been reviewed.<sup>30</sup> More specifically, pyrazolyl-bridged Ag triangles represent a rather well-established oligonuclear aggregate: In the CSD database, <sup>31,32</sup> coordinates for 43 well-ordered and error-free occurences of this fragment are available, with an average length for the pyrazolyl-bridged edges of 3.469

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Å. The second feature encountered in the case of our hexanuclear aggregates, namely short ligand-unsupported argentophilic interactions to neighbouring triangles, is less popular. Fujisawa and coworkers<sup>33</sup> have contributed five analogous structures and also compiled related examples from the literature. To the best of our knowledge, **3a** exhibits the shortest Ag-Ag distances between neighbouring  $[Ag_3(pyrazolyl)_3]$  moieties; slightly longer contacts between 2.9 and 3.0 Å have been reported in a few cases.<sup>34-36</sup>



Figure 3:  $Ag_6(HacacPz)_6$  cores in compound **3a** (left) and **3b** (middle and right). Symmetry operations: A = 1-x, 1-y, 1-z; B = 1-x, 2-y, -z; C = 1-x, 1-y, 1-z.

In the solids **3a**, **3b** and **3c**, solvent molecules fill the voids between the large  $[Ag_6(HacacPz)_6]$ aggregates. **3a** contains two molecules of ethanol per unit cell or hexanuclear aggregate. In **3b**, eight molecules of ethanol per unit cell occupy two voids. A more complex situation was encountered in the case of **3c**: The compound contains a well-localized  $CH_2Cl_2$  with halfoccupied atom sites in general position, *i. e.* one  $CH_2Cl_2$  per unit cell and three strongly disordered molecules of 2-butanol in two voids per unit cell (see Experimental).

A decision concerning keto-enol tautomerism in **3** is less obvious because the structure models for these solids have to account for larger asymmetric units, comprise chlathrated solvent molecules and hence are associated with higher standard uncertainties. The IR spectra of **3**, however, closely match those of **1** and **2** for which the diffraction results are unambiguous. A synopsis of the IR spectra of H<sub>2</sub>acacPz, **1**, **2** and **3** is provided in the Supporting Information. The Ag-Ag vibrations in **3** are difficult to assign; they will necessarily be observed at low wave numbers in the Raman spectra and probably not correspond to pure Ag-Ag stretching. A resonance at 83 cm<sup>-1</sup> has been associated with a metal··· metal contact slightly shorter than 3 Å.<sup>37</sup> Our experimental Raman spectrum of **3** (Fig. S12) shows a broad band with a shoulder between 100 and 50 cm<sup>-1</sup> but we do not have sufficient information from Raman spectra of related compounds to suggest a reliable assignment.

Table 1: Ag···Ag distances in Ag<sub>6</sub>(HacacPz)<sub>6</sub> aggregates in compounds 3a, 3b and 3c.

Compound	ligand support	direct
Compound	interaction range $(Å)$	interaction $(Å)$
3a	3.329 - 3.477	2.905
3b resd. 1	3.419 - 3.436	2.969
3b resd. $2$	3.376 - 3.474	2.911
3c resd. 1	3.420 - 3.432	3.006
3c resd. 2	3.370 - 3.499	2.906

In all compounds discussed so far, the acetylacetone part is protonated but the hydroxyl group is not involved in any short intermolecular interactions. Rather, intramolecular O- $H \cdot \cdot \cdot O$  hydrogen bonds with donor  $\cdot \cdot \cdot$  acceptor distances between 2.4 and 2.5 Å occur within each Hacac moiety.

In the absence of soft coordination partners, more drastic conditions are required for deprotonation in the O donor part of the ditopic ligand. Magnesium methoxide proved a suitable reagent, combining the oxophilic nature of the cation with the required basicity of the anion. Crystals of the target product **4** could be directly isolated from the reaction mixture. The diffraction experiment revealed that **4** crystallizes in the orthorhombic space group *Pbca* with the central Mg cation located on a crystallographic center of inversion. It is coordinated by six oxygen atoms in a slightly distorted octahedral geometry. Four oxygen atoms from two O, O' chelating HacacPz ligands are coplanar, and two coordinated apical MeOH molecules complete the coordination sphere with slightly longer Mg-O bonds (Fig. 4 left). In addition, **4** contains two molecules of uncoordinated MeOH per Mg complex. The NH group of the pyrazolyl ring and the hydroxyl groups of the coordinated and the uncoordinated methanol molecules act as donors, the unprotonated pyrazolyl N, one of the Mg-coordinated HacacPz oxygen atoms and the oxygen of the uncoordinated MeOH as

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acceptors for classical hydrogen bonds; they subtend a three-dimensional network (Fig. 4 right and Table S2 in Supporting Information).



Figure 4: Left: Mg(II) complex in the crystal structure of **4**; ellipsoids are drawn at 50 % probability, only the H atoms at N2 and O3 are shown. Symmetry operation: A = 1-x, 1-y, 1-z. Right: N-H···O and O-H···O interactions (dashed blue lines) in the crystal structure of **4**.

A comparison of 4 with the only prior structural result obtained for the ligand HacacPz, its complex with the lighter congener Be,<sup>17</sup> reveals clear differences. The alkaline earth cation in the latter is only four-coordinated, in agreement with general trends: a search in the CSD<sup>32</sup> resulted in 109 structures with BeO<sub>4</sub> fragments whereas only one example of hexa-coordinated Be with dubious charge balance has been reported. In contrast, sixfold coordination for Mg cations is unexceptional. The oxygen atoms in the BeO<sub>4</sub> core investigated by Boldog *et al.*<sup>17</sup> subtend an almost undistorted tetrahedron, with Be-O distances of 1.60 Å, whereas the Mg-O distances in **4** range between 2.0 and 2.1 Å and the bite angle of the HacacPz ligand amounts to 86°.

With respect to Crystal Engineering, the N coordinated complexes 1 - 3 and the O coordinated compound 4 show distinctly different behaviour: our attempts to crosslink the dangling acetylacetone moieties in the former did not yet lead to isolated crystalline reaction products whereas further N coordination of 4 was successful. In the following section, we will discuss the resulting mixed-metal coordination compound 5.

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The Mg-O bonds to the coordinated MeOH molecules represent the predetermined breaking points in 4: equimolar reaction with cadmium acetate gives additional coordination of a Cd coordinated acetate oxygen to the alkaline earth cation. In parallel, the pyrazolic N donor completes the octahedral coordination about a symmetry-equivalent Cd(II). The reaction stoichiometry and a first interpretation of the single crystal diffraction experiment on solid 5 suggest the overall composition Mg(HacacPz)<sub>2</sub>Cd(OOCCH<sub>3</sub>)<sub>2</sub>. In line with this hypothesis, a coordination sphere with  $\bar{1}$  site symmetry made up entirely of oxygen atoms is observed for Mg (Fig. 5 left) whereas the softer Cd cation is situated on a twofold axis in a mixed nitrogen-oxygen N<sub>2</sub>O<sub>4</sub> environment (Fig. 5 right). In the introduction, we suggested an approximate cation  $\cdots$  cation distance subtended by the HacacPz ligand of *ca.* 9 Å, and we can now confirm this estimate: the ditopic ligand in 5 bridges a Mg $\cdots$ Cd of 9.1 Å.



Figure 5: Coordination of an Mg(II) cation (left) and Cd(II) (right) in the crystal structure of **5**. Ellipsoid are drawn at 50 % probability level. Symmetry operation: A = 0.5 - x, 1.5-y, 1-z; B = 0.5 + x, 0.5 + y, z; C = 0.5 - x, 0.5 + y, 1.5-z; D = 1 - x, y, 1.5-z.

Closer inspection of the diffraction results, however, indicated a slightly more complicated situation: refinement of the well-ordered structure model as described above converged with an unrealistically small displacement parameter for the Mg cation. This exclusively O coordinated site is not completely occupied by the alkaline earth cation but also to a minor extend by Cd(II). Fig. S2 in the Supporting Information compiles displacement parameter plots for tentative variations in the occupancy factors: visual inspection confirms a low Cd(II) content. Our final structure model is based on site occupancy refinement in which

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the sum of the occupancies was constrained to unity; it converged for 93.5(3)% of Mg and 6.5(3)% of Cd. We recall that the solid thus characterized, **5a**, was obtained from a reaction with 4:  $Cd(OOCCH_3)_2 = 1$ : 1 stoichiometry. Our interpretation of the disordered cation site is corroborated by the existence of an isomorphous solid: **5b** crystallizes in the presence of an excess of cadmium actetate and shows a Mg : Cd = 86.3(4) : 13.7(4) ratio for the occupancy of the oxygen-coordinated cation. The information about partial occupancy of the O six-coordinated cation site by Cd stems mostly from the very pronounced difference in electron density between Mg and Cd; we also note, however, that cation-oxygen distances in **5b** are slightly longer than in **5a**, in agreement with the more pronounced site occupancy by the larger Cd(II) cation. 5a and 5b represent two individual compositions of a solid solution 5 in which the Mg(II) cation may be partially replaced by Cd(II). How surprising is this type of substitutional disorder? The elements Mg and Cd both adopt hexagonal close packing but clearly differ in their intermetal distances. As for their divalent cations, Cd(II) (1.09 Å) is significantly larger than Mg(II) (0.86 Å)<sup>38</sup> and much softer with respect to Pearson hardness.<sup>39</sup> Towards oxygen, both cations prefer coordination number 6; a compilation of CSD-based<sup>32</sup> frequencies for different coordination numbers is provided in the Supporting Information (Fig. S20). We are aware of only one crystal structure for which substitutional disorder between Mg(II) and Cd(II) has been reported: Yao and coworkers<sup>40</sup> have encountered a related case of a six-coordinated cation site preferentially occupied by Mg(II), together with a small (7%) Cd(II) content.

**5** forms a three-dimensional coordination network (Fig. 6 left). With respect to topology, each Mg and Cd dication may be perceived as a 4-connected node. The resulting binodal (4,4) net can be assigned the vertex symbol  $(4.4.8_2.8_2.8_8.8_8)(4.4.8_7.8_7.8_7.8_7)$ ,<sup>41</sup> which corresponds to a **pts** net.<sup>42</sup> A simplified view of the topology is shown in Fig. 6 right.<sup>43</sup>

The Raman spectra for solids **4** and **5** show a band at *ca.* 400 cm<sup>-1</sup> which is absent in those of **1-3**. We tentatively assign this resonance to Mg-O stretching.



Figure 6: Perspective view of the 3D network of the bimetallic coordination polymer 5. Six coordinated Cd is drawn in polyhedron mode (left); schematic illustrating the 3D topology in 5. Color code: pink node, Mg(II) center; black node, Cd(II) center; pink stick, acetate linker; black stick, HacacPz<sup>-</sup> linker (right).

# Conclusion

Employing cations of different Pearson hardness, we have been able to selectively deprotonate the soft N and the hard O donor site of the pyrazolyl-substituted acetylacetone H<sub>2</sub>acacPz. Future work will be dedicated to the fluorescence properties of the discrete molecular species **3**. We will also attempt to synthesize mixed-metal coordination polymers involving Ag and Yb cations: decomposition of such compounds has led to catalytically active agglomerates of silver nanoparticles and rare-earth oxide.<sup>44</sup>

# Experimental

## Materials and Methods

All chemicals were used without further purification:  $\text{ZnCl}_2$  (99%, Grüssing), AgNO<sub>3</sub> (KMF), silver benzoate (99%, Acros), Mg (99.8%, Fluka), cadmium acetate (97%, Kraft Bernd) and dimethyl sulfoxide-d<sub>6</sub> (99.9 atom %D, Aldrich).

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IR spectra were recorded on a Nicolet Avatar 360 E.S.P. spectrometer in KBr windows. Raman spectra were obtained with a Horiba LABRAM HR instrument equipped with a 633 nm HeNe excitation laser. The electron-impact mass spectrum of H<sub>2</sub>acacPz was recorded on a Finnigan MAT-95 at a nominal electron energy of 70 eV. CHN microanalyses were carried out at the Institute of Organic Chemistry, RWTH Aachen University, using a HERAEUS CHNO-Rapid. Powder diffraction experiments were performed at room temperature on flat samples with a Stoe & Cie STADI P diffractometer equipped with an imageplate detector with constant  $\omega$  angle of 55° using germanium-monochromated Cu-K<sub> $\alpha$ 1</sub> radiation ( $\lambda = 1.54051$  Å). <sup>1</sup>H NMR spectra were measured with a Bruker Avance II UltrashieldTM plus 400 instrument (400 MHz, referenced to TMS).

### **Syntheses**

#### Synthesis of H<sub>2</sub>acacPz.

The H<sub>2</sub>acacPz ligand was prepared according to the literature method by W. L. Mosby.<sup>45–47</sup> Spectroscopic data: <sup>1</sup>H NMR (d<sub>6</sub>-DMSO):  $\delta = 16.98$  (s, 1H, -OH), 12.33 (s, 1H, -NH), 2.06 (s, 6H, -CH<sub>3</sub>), 1.87 (s, 6H, -CH<sub>3</sub>). Broadening of the signal at 2.06 ppm associated with the methyl groups in the acetylacetone part of the ligand (Fig. S21) is due to keto-enol tautomerism. Deprotonation of this part of the ligand as in **4** results in a narrow line.<sup>48–51</sup> MS-EI: m/z calcd for  $[C_{10}H_{14}N_2O_2]^+$ : 194.1055; found: 194.1.

#### Synthesis of $Zn(H_2acacPz)_2Cl_2$ , 1.

 $H_2acacPz$  (9.7 mg, 0.05 mmol) and  $ZnCl_2$  (3.4 mg, 0.025 mmol) were dissolved in methanol (2 mL) and stirred for 10 min at ambient temperature. The clear solution was left unperturbed for slow evaporation. Colorless crystals grew over a period of one week. Yield: 10.2 mg (0.019 mmol, 76%). Phase purity of the product was confirmed by powder diffraction of the bulk material (see Fig. S15, Supporting Information).

Anal. Calcd. for  $C_{20}H_{28}Cl_2N_4O_4Zn$ : C: 45.78, H: 5.38, N: 10.68.

Found: C: 45.04, H: 5.95, N: 10.20.

## Synthesis of $[Ag(H_2acacPz)_2]NO_3 \cdot H_2O, 2.$

AgNO<sub>3</sub> (4.2 mg, 0.025 mmol) was dissolved in one drop of water and 1 mL of methanol was added. H<sub>2</sub>acacPz (9.7 mg, 0.05 mmol) was dissolved in MeOH (1 mL). These two solutions were combined and stirred for 10 min at ambient temperature. The clear reaction mixture was left unperturbed for slow evaporation. Colorless crystals grew over a period of one week. Yield: 7.2 mg (0.012 mmol, 48%). Phase purity of the product was confirmed by powder diffraction of the bulk material (see Fig. S16, Supporting Information).

Anal. Calcd. for  $C_{20}H_{30}AgN_5O_8$ : C: 41.68, H: 5.25, N: 12.15.

Found: C: 42.01, H: 5.67, N: 11.61.

# Synthesis of $[Ag_6(HacacPz)_6] \cdot 2EtOH$ , 3a, $[Ag_6(HacacPz)_6] \cdot 4EtOH$ , 3b and $[Ag_6(HacacPz)_6] \cdot 0.5CH_2Cl_2 \cdot 1.5C_4H_{10}O$ , 3c.

Solutions of Ag(PhCOO) (11.5 mg, 0.05 mmol) in THF (2 mL) and H<sub>2</sub>acacPz (9.7 mg, 0.05 mmol) in MeOH (2 mL) were combined. The mixture was stirred for 12 h at ambient temperature and the phases were separated by centrifugation. The supernatant liquid was discarded and the solid residue was washed twice with MeOH (2 mL). Yield: 9.6 mg of Ag<sub>6</sub>(HacacPz)<sub>6</sub> (0.0053 mmol, 64%). Colorless block-shaped crystals of **3a** and **3b** were obtained by slow diffusion of EtOH into a CH<sub>2</sub>Cl<sub>2</sub> solution of Ag<sub>6</sub>(HacacPz)<sub>6</sub> within two days. Crystals of **3c** were prepared in an analogous way using 2-butanol instead of EtOH as antisolvent in diffusion. All solvates of **3** lose solvent very fast as evidenced by powder diffraction. When solid **3a** is freshly isolated, hardly ground and subjected to powder diffraction with the protection of perfluoropolyallyether, the powder pattern of the bulk is in agreement with the expectation from the single crystal structure (see Supporting Information Fig. S17). No fully satisfactory elemental analysis has been obtained for **3**.

Anal. Calcd. for  $C_{60}H_{78}Ag_6N_{12}O_{12}$ : C: 39.89, H: 4.35, N: 9.30.

Found: C: 37.43, H: 4.37, N: 9.34.

## Synthesis of [Mg(HacacPz)<sub>2</sub>(MeOH)<sub>2</sub>]·2MeOH, 4

Magnesium methoxide was prepared by reaction of Mg (23.9 mg, 1 mmol) with dry MeOH (10 mL) at room temperature; standard Schlenk technique was used to exclude moisture and oxygen. This magnesium methoxide solution was combined with a solution of H<sub>2</sub>acacPz (388.5mg, 2 mmol) in dry MeOH and stirred for 3 h. The colorless precipitate consisted of larger crystals. It was recovered by filtration and washed with *ca.* 0.5 mL of cold MeOH and dried in a desiccator. Yield: 299.3 mg (0.63 mmol, 63%). The methanol solvate 4 undergoes fast desolvation as evidenced by powder diffraction. When solid 4 is freshly isolated, hardly ground and subjected to powder diffraction with the protection of perfluoropolyallyether, the powder pattern indicates concomitant presence of solvated and desolvated material (see Supporting Information Fig. S18).

Anal. Calcd. for  $C_{22}H_{34}MgN_4O_6$  (desolvation of uncoordinated MeOH): C: 55.65, H: 7.22, N: 11.80.

Found: C: 54.60, H: 6.62, N: 12.70.

## Synthesis of $Mg_{1-x}Cd_x(HacacPz)_2Cd(OOCCH_3)_2$ , 5

In a test tube, 4 (9.5 mg, 0.02 mmol) was dissolved in a mixture of MeOH/CH<sub>2</sub>Cl<sub>2</sub> (1 mL/1 mL). The solution was layered by a mixture of 0.5 mL CH<sub>2</sub>Cl<sub>2</sub> and 0.5 mL MeOH. A top layer of Cd(OOCCH<sub>3</sub>)<sub>2</sub> ·H<sub>2</sub>O (5.3 mg, 0.02 mmol) in 1 mL of MeOH was added and the test tube was left unperturbed at room temperature for crystallization by diffusion. Colorless crystals of **5a** formed within two days. The composition  $Mg_{1-x}Cd_x(HacacPz)_2Cd(OOCCH_3)_2$ , x = 0.065(3) was determined by single crystal X-ray diffraction. Yield: 8.2 mg (0.013 mmol, 65%). Phase purity of the product was confirmed by powder diffraction of the bulk material (see Fig. S19, Supporting Information).

When an excess of cadmium acetate was used by changing the reaction stoichiometry 4 :

 $Cd(OOCCH_3)_2 \cdot H_2O$  to 1 : 2, the solid **5b** was obtained. It is isomorphous to **5a**, with x = 0.137(4). Yield: 9.7 mg (0.015 mmol, 75%). No fully satisfactory elemental analysis was obtained for **5**.

# **Crystallographic Studies**

The diffraction experiments were performed with a Bruker D8 goniometer equipped with an Incoatec microsource (Mo-K<sub> $\alpha$ </sub>,  $\lambda = 0.71073$  Å, multilayer optics) and an APEX CCD detector; a sample temperature of 100(2) K was maintained with an Oxford Cryostream 700 instrument. Intensity data were integrated with  $SAINT + 5^2$  and corrected for absorption by multi-scan methods using the program SADABS.<sup>53</sup>

The crystal structures were solved with Patterson or Direct methods, and refinements were accomplished with full matrix least-squares procedures as implemented in SHELXL- $13.^{54}$  All non-hydrogen atoms were assigned anisotropic displacement parameters; hydrogen atoms were placed in idealized positions and included as riding with constrained isotropic displacement parameters. In **1** - **5**, the hydrogen atoms of the hydroxyl group and secondary amine were located according to the following strategy: 1. tentative assignment of local electron density maxima from Fourier difference maps, followed by refinement with distance restraints; 2. in the absence of geometrically acceptable electron density maxima, positions in the direction of a suitable hydrogen bond acceptor were calculated and also subjected to distance restraints; 3. if neither matching electron density maxima nor suitable hydrogen bond acceptors were available, H atoms were calculated in standard distance in arbitrary orientation.

In 2, the nitrate anion and the water molecule are disordered about a crystallographic center of inversion; the situation is depicted in Fig. S1. For reasons of symmetry and charge balance, the mutually exclusive components were assigned half occupancy and a common isotropic displacement parameter in the least squares refinement. In **3a**, the solvent molecule

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#### **Crystal Growth & Design**

was refined as ethanol with similarity restraints for its displacement parameters. The assignment of EtOH to the electron density in the solvent-containing void was in agreement with a tentative  $SQUEEZE^{55}$  calculation. Electron density in the solvent-accessible voids of **3b** was handled with the  $SQUEEZE^{55}$  algorithm. The <sup>1</sup>H NMR spectra for **3c** confirmed the identity of the chlathrated solvents  $CH_2Cl_2$  and 2-butanol. Distance and displacement similarity restraints were used for the refinement of the  $CH_2Cl_2$  molecule; its occupancy converged to ca. 0.5. No structure model could be obtained for 2-butanol because of severe disorder. Therefore, in the final structure model for 3c, atoms in the CH<sub>2</sub>Cl<sub>2</sub> molecule were assigned half occupancy and the electron density in the remaining solvent-accessible voids was handled with the  $SQUEEZE^{55}$  algorithm. In **5a**, the exclusively O-coordinated cation showed substitutional disorder: in addition to its major occupancy by Mg, a minor site occupancy of Cd was detected. Coordinates and displacement parameters for the alternative cations were constrained to be equal and the sum of their site occupancies was constrained to unity; relative site occupancy converged to a Mg : Cd ratio of 93.5(3) : 6.5(3). The same type of substitutional disorder was detected in **5b**, albeit with a higher Cd content of 13.7(4)%. After refinement of the disorder model for **5b**, a list of disagreeable reflections showed a clear tendency for  $F^2(obs.) \gg F^2(calc.)$ . A test with the TwinRotMat option in PLATON<sup>56</sup> confirmed non-merohedral twinning for this sample, with 375 out of 3066 reflections overlapping. An appropriately modified set of intensity data taking the partially overlapped diffraction of both domains into account (HKLF5 format in SHELXL97<sup>57</sup>) gave significantly improved convergence results and relative domain fractions of 0.82 and 0.18.

## Acknowledgement

Financial support by China Scholarship Council (Q. Guo) is gratefully acknowledged. We thank Irmgard Kalf for help with the Raman spectra.

# Supporting Information Available

The following files are available free of charge.

- Crystallographic information in CIF format.
- Illustration of the disordered nitrate anion and water molecule in **2**.
- Illustration of the refinement results with variable minor site occupancy by Cd(II) in
   5a.
- Infrared spectra for H<sub>2</sub>acacPz, 1, 2, 3, 4 and 5.
- Raman spectra for **1-5**.
- Powder patterns for 1-5.
- Histogram showing coordination numbers for Mg(II) and Cd(II) in exclusively Ocoordinated environments.
- <sup>1</sup>H NMR spectrum of  $H_2acacPz$  in  $d_6$ -DMSO.
- <sup>1</sup>H NMR spectrum of 4 in  $d_6$ -DMSO.
- Ag···Ag distances of  $Ag_6(HacacPz)_6$  aggregates in compounds **3a**, **3b** and **3c**.
- hydrogen bond information of **4**.

This material is available free of charge via the Internet at http://pubs.acs.org/.

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# For Table of Contents Use Only

Title: "An acetylacetonate or a pyrazole? Both! 3-(3,5-dimethyl-pyrazol-4-yl)pentane-2,4-dione as a ditopic ligand" Authors: Qianqian Guo and Ulli Englert



The regioselectivity of the ditopic ligand 3-(3,5-dimethyl-pyrazol-4-yl) pentane-2,4-dione can be controlled by the Pearson hardness of the reacting cations. The softer heterocyclic moiety was used as N donor towards Zn(II) and Ag(I). With stronger bases and in the presence of oxophilic Mg cations, the harder hydroxyketone part of the ligand may be deprotonated to a chelating acetylacetonate.

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Compound	1	21	<b>3</b> a	30
Empirical formula	$\mathrm{C}_{20}\mathrm{H}_{28}\mathrm{Cl}_2\mathrm{N}_4\mathrm{O}_4\mathrm{Zn}$	$\mathrm{C}_{20}\mathrm{H}_{30}\mathrm{AgN}_5\mathrm{O}_8$	$ m C_{64}H_{90}Ag_6N_{12}O_{14}$	$C_{68}H_{102}Ag_6N_{12}O_{16}$
Moiety formula	$\mathrm{C}_{20}\mathrm{H}_{28}\mathrm{Cl}_2\mathrm{N}_4\mathrm{O}_4\mathrm{Zn}$	$\mathrm{C}_{20}\mathrm{H}_{28}\mathrm{AgN}_4\mathrm{O}_4,$	$ m C_{60}H_{78}Ag_6N_{12}O_{12},$	$C_{60}H_{78}Ag_6N_{12}O_{12},$
		$NO_3, H_2O$	$2(C_2H_6O)$	$4(C_2H_6O)$
Formula weight (g/mol)	524.73	576.36	1898.69	1990.84
Crystal description	colorless plate	colorless block	colorless rod	colorless block
Crystal size (mm)	$0.29 \ge 0.17 \ge 0.09$	$0.19 \ge 0.18 \ge 0.10$	$0.16 \ge 0.09 \ge 0.08$	$0.27 \ge 0.27 \ge 0.16$
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	C2/c	$P\overline{1}$	$P\overline{1}$	$P\bar{1}$
a (Å)	25.914(3)	6.311(4)	11.250(2)	10.780(4)
b (Å)	7.3777(9)	7.438(5)	14.032(3)	14.439(6)
c $(Å)$	12.9236(16)	13.725(9)	14.434(3)	26.241(10)
$\alpha$ (°)		74.584(12)	117.441(3)	74.511(6)
β (°)	101.076(2)	82.418(12)	110.836(3)	86.050(7)
(°) γ		71.287(11)	90.525(4)	87.599(7)
$V(\hat{A}^3)$	2424.8(5)	587.4(7)	1848.3(6)	3925(3)
Z	4	1	1	7
$\mu \ (\mathrm{mm}^{-1})$	1.266	0.914	1.625	1.537
Total/unique reflections	6570/2215	5371/2399	16103/7252	35904/16091
$R_{int}$	0.0602	0.0530	0.0640	0.0869
$R[F^2 > 2\sigma(F^2)]$	0.0307	0.0450	0.0570	0.0531
$wR_2 \ (F^2)$	0.0983	0.0975	0.1385	0.0972
GOF	1.050	1.019	1.008	0.985
No. of parameters	151	172	454	835
$\Delta_{ ho_{max}}/\Delta_{ ho_{min}}~(e~{ m \AA}^{-3})$	0.442 / -0.579	0.935/-1.237	1.395/-1.227	1.521/-1.379
CCDC	1478683	1478684	1478685	1478686

Table 2: Crystal data and refinement results for N coordination compounds 1, 2, 3a and 3b.

 $\begin{array}{c} 24 \\ \text{ACS Paragon Plus Environment} \end{array}$ 

Empirical formula ( Moiety formula ( Formula weight (g/mol) 1 Crystal description o		4	วัล	5b
Moiety formula ( Formula weight (g/mol) 1 Crystal description c	C66.5H94Ag6CIN12O13.5	$\mathrm{C}_{24}\mathrm{H}_{42}\mathrm{MgN}_4\mathrm{O}_8$	$C_{24}H_{32}Cd_{1.06}Mg_{0.94}N_4O_8$	$C_{24}H_{32}Cd_{1.14}Mg_{0.86}N_4O_8$
Crystal description c	$C_{60}H_{78}Ag_6N_{12}O_{12}$	$C_{22}H_{34}MgN_4O_6$	$C_{24}H_{32}Cd_{1.06}Mg_{0.94}N_4O_8$	$C_{24}H_{32}Cd_{1.14}Mg_{0.86}N_4O_8$
Formula weight (g/mol) 1 Crystal description c	$0.5(CH_2Cl_2), 1.5(C_4H_{10}O)$	$2(CH_4O)$		
Crystal description c	960.21	538.92	646.52	653.36
	coloress block	colorless block	colorless block	colorless block
Urystal size (mm)	0.23 x 0.23 x 0.17	$0.27 \ge 0.25 \ge 0.20$	$0.16 \ge 0.14 \ge 0.13$	$0.23 \ge 0.18 \ge 0.17$
Crystal system t	riclinic	orthorhombic	monoclinic	monoclinic
Space group	ρĪ	Pbca	C2/c	C2/c
a (Å) 1	-0.8760(11)	14.085(5)	13.494(5)	13.490(3)
b (Å) 1	(4.5740(14))	13.903(5)	15.208(6)	15.129(4)
c $(Å)$ 2	26.271(3)	15.487(5)	15.540(6)	15.529(4)
$\alpha$ (o)	(2, 177(2))			
β (°) 8	(2005(2))		110.905(7)	110.683(4)
γ (°) 8	88.246(2)			
$V\left( \hat{A}^3 \right)$ 3	3966.2(7)	3032.9(19)	2979.3(19)	2965.0(13)
2		4	4	4
$\mu \; ({ m mm}^{-1})$ 1	538	0.106	0.843	0.900
Total/unique reflections 4	13747/14425	8607/3031	12442/2777	8489/3066
$R_{int}$ (	).0557	0.0770	0.1516	0.0939
$R[F^2 > 2\sigma(F^2)] \tag{C}$	0.0539	0.0532	0.0593	0.0714
$wR_2 (F^2)$ $C$	).1679	0.1166	0.1376	0.1892
GOF 1	033	1.016	0.968	1.081
No. of parameters 8	62	184	183	184
$\Delta_{ ho_{max}}/\Delta_{ ho_{min}}~(e~{ m \AA}^{-3})$ 1	601/-0.819	0.274/- $0.286$	0.935/-1.237	$2.403^a/ ext{-}1.564^b$
CCDC 1	478687	1478688	1478689	1478690

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