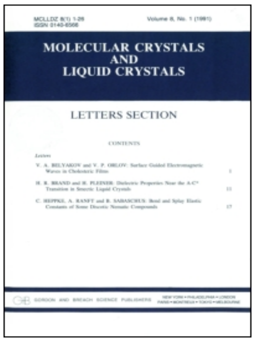

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The assembly of phenazine with metal complexes: Coordination-driven self-assembly vs. hydrogen-bonded cocrystallization

Nenad Judaš, Kristina Habijanec, and Gordan Trajbar

Department of Chemistry, Faculty of Science, University of Zagreb, Zagreb, Croatia

ABSTRACT
In this paper we report two different modes of self-assembly of phenazine with metal complexes. In particular, the solution reaction of phenazine with the sterically encumbered copper(II) benzoate (**BzO**) padelwheel unit, [Cu_2(**BzO**)$_4$], yielded a monomeric complex [Cu_2(**BzO**)$_4$](**phz**)$_2$ in which the paddelwheel unit is flanked on both sides with phenazine molecules acting as monodentate ligands. In contrast, the solution reaction of bis(pentane-2,4-dionato)oxovanadium(IV), VO(**acac**)$_2$, with phenazine yielded cocrystals of composition [VO(**acac**)$_2$(H_2O)]$_2$ · **phz**, held together *via* hydrogen bonds.

KEYWORDS
Phenazine; Copper(II) benzoate; Bis(pentane-2,4-dionato)oxovanadium(IV); Building blocks; Crystal engineering

Introduction

In contrast to simple pyridine-based bridging ligands, such as pyrazine, 4,4’-dipyridyl, or bis(4-pyridyl)ethylene, that have been extensively used in the synthesis of coordination polymers [1–6] and metal-organic frameworks (MOFs) [7–9], the coordination chemistry of more sterically demanding species, such as phenazine (**phz**, Scheme 1) has been less explored [10,11]. Our research program is directed toward utilizing phenazine and associated molecule such as acridine, quinoline and quinoxaline, as coordinatively non-innocent ligands that can be utilized to actively control and design the growth of coordination polymers. In particular, we are interested in challenging the ability of phenazine to act as a bridging ligand in the assembly of coordination polymers based on conventional metal-based building blocks, such as carboxylate-based paddlewheel units and metal β-diketonates. As a part of this research program, we now report two different modes of self-assembly of phenazine with metal complexes. In particular, the solution reaction of phenazine with the sterically encumbered copper(II) benzoate (**BzO**) padelwheel unit, [Cu_2(**BzO**)$_4$], yielded a monomeric complex [Cu_2(**BzO**)$_4$](**phz**)$_2$ in which the paddelwheel unit is flanked on both sides with phenazine molecules acting as monodentate ligands. In contrast, the reaction of bis(pentane-2,4-dionato)oxovanadium(IV), VO(**acac**)$_2$, with phenazine yielded cocrystals of composition

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CONTACT N. Judaš judas@chem.pmf.hr Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, 10 000 Zagreb, Croatia.

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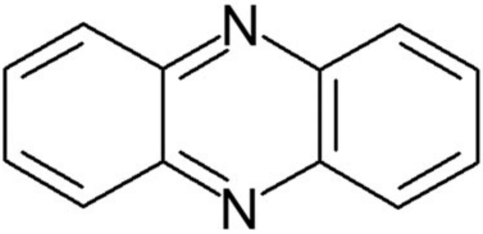
CCDC 1489198 ([Cu2(**BzO**)4](**phz**)2) and CCDC 1489199 ([VO(**acac**)2(H2O)]2 × **phz**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.



Scheme 1.

$[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$, held together *via* hydrogen-bonded $R_2^2(8)$ supramolecular synthons formed between **phz** molecule and hydrated metal complexes.

Experimental

Materials

The paddlewheel complex copper(II) benzoate dihydrate, $[Cu_2(\mathbf{BzO})_4](H_2O)_2$, was prepared by mixing hot equimolar aqueous solutions of copper(II) sulphate pentahydrate and sodium benzoate. Slow evaporation of mother liquor resulted in needle-like turquoise crystals that were filtered off and used in further preparations. Bis(pentane-2,4-dionato)oxovanadium(IV), $VO(\mathbf{acac})_2$, (Merck, for synthesis), **phz** (Aldrich, 98%), and absolute ethanol (Claro-prom d.o.o., p.a.) were used as received.

Synthesis of tetrakis(μ_2-benzoato)bis(phenazine)dicopper(II), $[Cu_2(BzO)_4](phz)_2$

Copper(II) benzoate dihydrate (323.5 mg, 0.5000 mmol) and **phz** (90.1 mg, 0.500 mmol) were dissolved in 25.0 and 5.0 mL of warm absolute ethanol, respectively. Transparent solutions were mixed while hot. Slow evaporation of mother liquor over few days resulted in the formation of dark green plates of $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$, from which a single crystal specimen was selected and used in the X-ray diffraction experiment.

Synthesis of diaqua di[bis(pentane-2,4-dionato)oxovanadium(IV)] phenazine cocrystal, $VO(acac)_2(H_2O)\cdot phz$

Bis(pentane-2,4-dionato)oxovanadium(IV) (132.5 mg, 0.5000 mmol) and **phz** (90.1 mg, 0.500 mmol) were both dissolved in two 20 mL portions of absolute ethanol (EtOH). Warm solutions were mixed after complete dissolution of reagents. The resulting green solution was filtered and left to slowly evaporate at room temperature. After few days grayish green plate-like crystals of $[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$ appeared and were used in subsequent crystal-structure determination experiments.

Instrumentation

The single crystal X-ray diffraction data for $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$ and $[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$ were collected at a temperature of 298 K on an Oxford Xcalibur diffractometer equipped with 4-circle κ-geometry goniometer, charge-coupled device (CCD) Spahire 3 detector, and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using the ω-scan mode. Data reduction and empirical absorption correction were done with the CrysAlis software package [12]. The structures were solved by direct methods. The refinement procedure by a weighted full-matrix least-squares methods based on F^2 values against all reflections included anisotropic displacement parameters for all non-H atoms. All hydrogen atoms were positioned geometrically and refined applying the riding model [C—H = 0.93–0.98 Å and with $U_{iso}(H) = 1.2$ or $1.5U_{eq}(C)$], except hydrogen atoms of the water molecules in compound $[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$, whose coordinates were determined from the difference Fourier map. Those hydrogen atoms were included in the refinement process with an isotropic thermal parameter. All calculations were performed using SHELXS97 [13] and SHELXL97 [14] (within the WinGX program package) [15]. Molecular graphics were done using ORTEP [16], Mercury CSD 3.8 [17], RASTOP [18], and POVRay [19].

Results and discussion

The crystallographic and structure refinement data for compounds $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$ and $[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$ are given in Table 1 and ORTEP representations of their asymmetric units are shown in Figs. 1 and 2, respectively.

The crystal structure of $[Cu_2(BzO)_4](phz)_2$

The crystal structure of $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$ is monoclinic, space group $P2_1/c$ with unit cell containing two formula units. The structure consists of copper(II) benzoate paddlewheel buildingenlrg blocks decorated with two molecules of **phz**, held *via* Cu–N bonds of 2.358(2) Å. The copper(II) ions in each paddlewheel unit are five-coordinated, with four benzoate oxygen atoms (atoms O11, O21, O31 and O41) forming the base of a square pyramid and the nitrogen atom of the **phz** ligand forming its apex. Bond distances, d(Cu—O11), d(Cu—O21), d(Cu—O31) and d(Cu—O41), are 1.963(2) Å, 1.964(2) Å, 1.958(2) Å and 1.963(2) Å, respectively, and bond angles ∠(O11—Cu—O21), ∠(O11—Cu—O31) and ∠(O11—Cu—O41) are

Table 1. General and crystallographic data for compounds $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$ and $[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$.

Compound	$[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$	$[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$
Empirical formula	$C_{52}H_{36}Cu_2N_4O_8$	$C_{32}H_{40}V_2N_2O_{12}$
Formula weight (g/mol)	971.95	746.54
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions		
a (Å)	10.080 (1)	8.438 (1)
b (Å)	16.279 (2)	9.964 (1)
c (Å)	13.184 (2)	11.447 (1)
α (°)	90	105.12(1)
ß (°)	92.24 (1)	104.51(1)
γ (°)	90	101.96(1)
V (Å^3)	2161.7 (5)	860.4(1)
Z	2	2
μ (mm^{-1})	1.047	0.607
Calculated density, D (g/cm)	1.493	1.441
T (K)	298	298
Crystal dimensions (mm^3)	0.78 × 0.61 × 0.49	0.43 × 0.18 × 0.21
$F(000)$	996	388
Reflections unique	8225	3736
Reflections $I > 2\sigma(I)$	5845	3077
Number of parameters	298	229
R, $[(F^2) > 2\sigma(F^2)]$	0.067	0.038
$wR(F^2)$	0.177	0.103
GOOF (S)	1.107	1.051

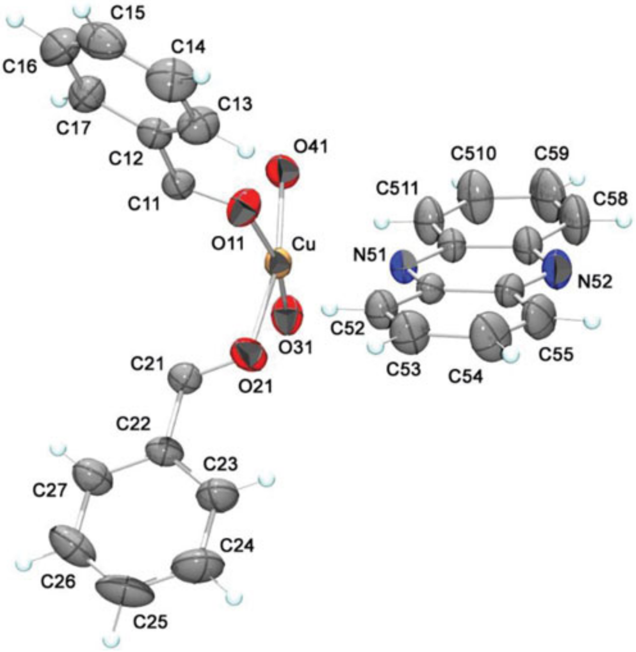


Figure 1. ORTEP representation of the asymmetric unit of $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$ with atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are presented as spheres of arbitrary small radius.

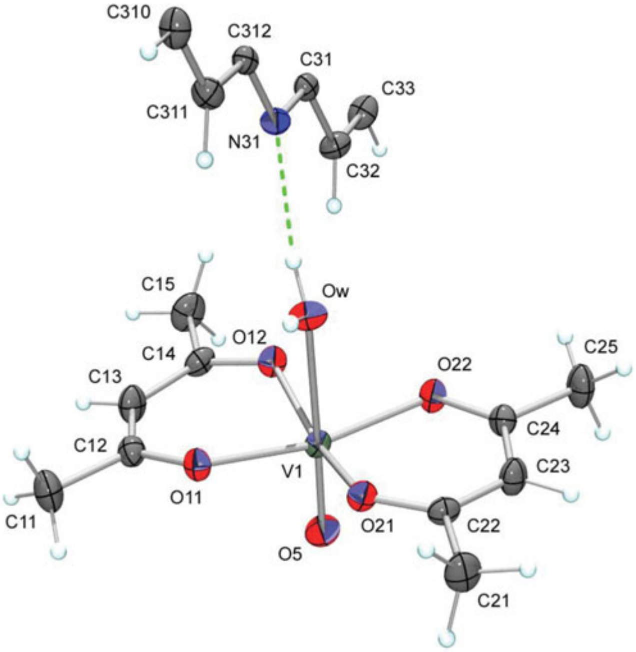


Figure 2. ORTEP representation of the asymmetric unit of $[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$ with atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are presented as spheres of arbitrary small radius.

Table 2. List of hydrogen bonds for $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$ and $[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$.

Hydrogen bond	*d*(D—H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	∠(DHA) (°)
$[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$				
C24–H24···N52^i	0.93	2.93	3.797(4)	156(1)
$i = 2 - x, 0.5 + y, 0.5 - z$				
$[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$				
Ow–H2···O11^i	0.83(3)	2.16(3)	2.966(2)	163(3)
Ow–H1···N31	0.87(3)	2.09(3)	2.938(2)	168(2)
C32–H32···O12	0.93	2.58	3.455(3)	157.9
C311–H311···O21^i	0.93	2.47	3.313(3)	150.3
C33–H33···O12^{ii}	0.93	2.63	3.563(3)	176.1
C310–H310···O5^{iii}	0.93	2.68	3.316(3)	122.3
$i = 2 - x, 2 - y, 2 - z$; $ii = 1 - x, 1 - y, 1 - z$; $iii = x, y, 1 + z$				

91.8(1)°, 166.2(1)° and 87.3(1)°, respectively. This indicates a slightly distorted coordination polyhedron. A survey of the Cambridge Structural Database (version 5.37, update of February 2016) [20] completed using ConQuest (version 1.18) [21] confirmed that all these bonds and bond angles are in good agreement with analogous values found in other Cu(II) benzoato complexes. As expected, **phz** ligands succesfully bonded to the apical (axial) positions of the copper-benzoato paddlewheels but this did not resulted with bridging and formation of a linear polymer (chain) structure. Instead, **phz** ligands act as acceptors of weak C24—H24···N52^i hydrogen bonds (Table 2, Figure 3). In this manner molecular ribbons are formed that stack to each other forming plates with folded surfaces that overlay each other like LEGO® blocks (Figure 4). This is in accordance with similar cases when copper-benzoato paddlewheel building blocks were decorated with 6-methylquinoline [22], quinoxaline [23] and 4-methylquinoline [24] but, in our structure, in contrast to those aforementioned, the face-to-face overlap of **phz** molecules is much less pronounced.

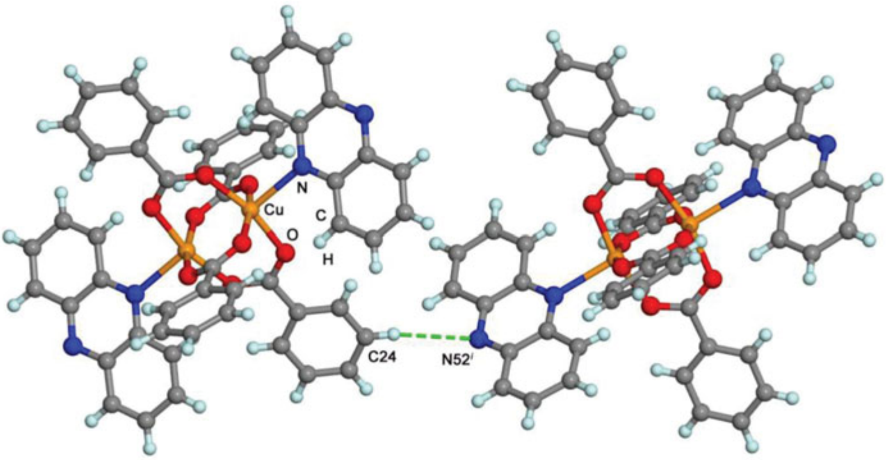


Figure 3. A view of two paddlewheel building blocks connected by a C24—H24···N52^i hydrogen bond in $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$.

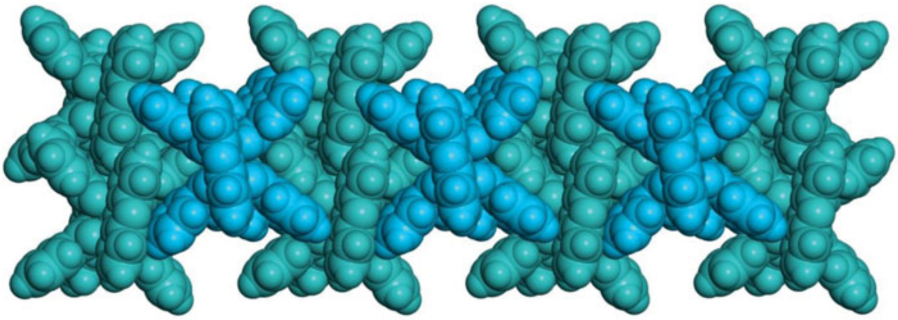


Figure 4. A spacefill representation of the stacking of molecular ribbons in the crystal structure of $[Cu_2(\mathbf{BzO})_4](\mathbf{phz})_2$. For clarity, ribbons are shown in two different colors.

The crystal structure of $[VO(acac)_2(H_2O)]_2 \cdot phz$

Cocrystal of (aqua)bis(pentane-2,4-dionato)oxovanadium(IV) and **phz** is triclinic, space group $P\bar{1}$. Vanadium(IV) ions are at the center of a distorted square-bipyramidal coordination polyhedron built by three ligating molecules (two *O*,*O*'-donating pentane-2,4-dionato ligands and one water molecule) and oxo oxygen atom. Oxygen atoms of pentane-2,4-dionato ligands (O11, O12, O21, and O22) form the base of a distorted square bipyramide whose apices are occupied by oxo oxygen atom (O5) and oxygen atom of coordinated water molecule (Ow).

As in the crystal of *trans*-(aqua)bis(isomaltolato)oxovanadium(IV) [25], CSD code MANPAT, the water molecules coordinated to the bis(pentane-2,4-dionato)oxovanadium(IV) moieties strongly affect the molecular self-assembly. But, there is additional effect of **phz** molecules. The crystal is built by centrosymmetric dimers of (aqua)bis(pentane-2,4-dionato)oxovanadium(IV) coordination units that are held together by pairs of Ow—H2···O11^{i} hydrogen bonds. These centrosymmetric dimers are bridged by **phz** molecules with three hydrogen bonds, Ow—H1···N31, C32–H32···O12, and C311–H311···O21^{i} (Table 2 and Fig. 5).

In this manner molecular chains are formed, which are further interlinked by C33–H33···O12^{ii} and C310–H310···O5^{iii} hydrogen bonds (Fig. 6), resulting in sheets co-planar

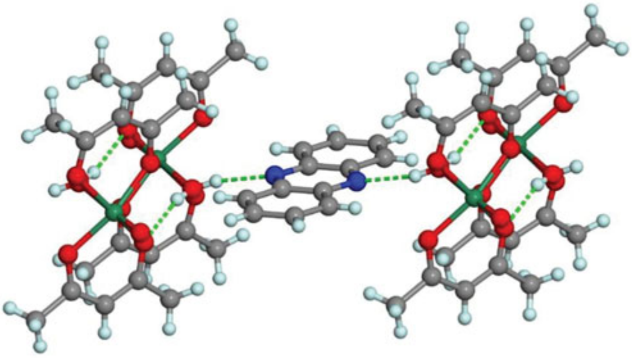


Figure 5. A view of two $VO(\mathbf{acac})_2(H_2O)$ dimers in the crystal structure of $[VO(\mathbf{acac})_2(H_2O)]_2 \cdot \mathbf{phz}$, assembled by pairs of Ow—H2···O11^{i} hydrogen bonds and bridged by a single **phz** molecule through a pair of Ow—H1···N31 hydrogen bonds.

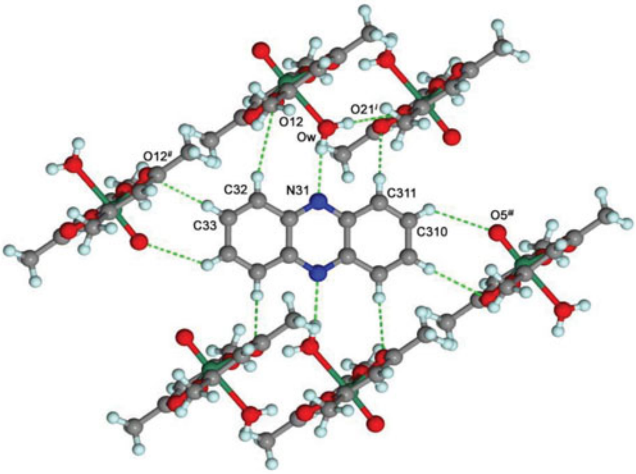


Figure 6. A ball-and-stick representation of hydrogen bonding interactions surrounding a **phz** molecule in the crystal structure of $[VO(\textbf{acac})_2(H_2O)]_2 \cdot \textbf{phz}$. Three hydrogen bonds, Ow—H1···N31, C32–H32···O12, and C311–H311···O21^{i} link VO(**acac**)$_2$(H$_2$O) dimers into chains, whereas C33–H33···O12^{ii} and C310–H310···O5^{iii} hydrogen bonds link these chains further into sheets.

with {001} crystallographic plane (Fig. 7), from which pentane-2,4-dionato moieties protrude on both sides. The sheets are held together by dispersion forces.

Conclusion

In summary, the self-assembly of **phz** with two types of metal-based building blocks, a sterically encumbered paddlewheel unit and a hydrated metal acetylacetonate leads to two qualitatively different results. In the first case, **phz** acts as a monodentate ligand, producing a

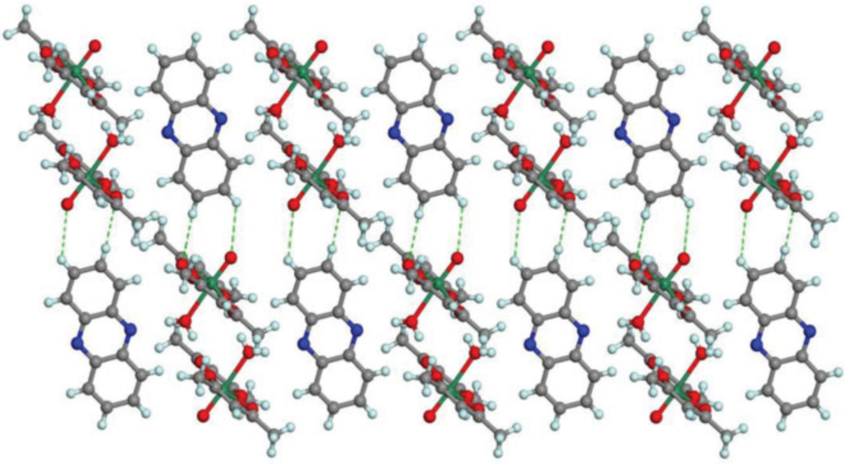


Figure 7. A ball and stick representation of a single sheet coplanar to the {001} crystallographic plane, formed by the assembly of $[VO(\textbf{acac})_2(H_2O)]_2$ dimers and **phz** molecules through sets of C33–H33···O12^{ii} and C310–H310···O5^{iii} hydrogen bonds in the cocrystal $[VO(\textbf{acac})_2(H_2O)]_2 \cdot \textbf{phz}$.

potentially coordinatively unsaturated paddlewheel structure, with sp^2 nitrogen atoms available for metal coordination. In contrast, the assembly of **phz** with (aqua)bis(pentane-2,4-dionato)oxovanadium(IV) coordination units leads to the formation of a cocrystal based on hydrogen-bonded $R_2^2(8)$ synthons involving O—H···N hydrogen bonds from the coordinated water molecule onto a molecule of **phz**, and C—H···O hydrogen-bonding interactions from the **phz** aromatic system onto the oxygen atoms of the pentane-2,4-dionato ligands. A preliminary investigation of the Cambridge Structural Database indicates that the formation of hydrogen-bonded structures, instead of coordination complexes, could be a reliable aspect of **phz** self-assembly in the presence of water. We are currently conducting a detailed database search, accompanied with a systematic structural study of how phenazine interacts with other types of metal complexes.

Acknowledgments

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