STRUCTURAL STUDY OF MONO- AND BINUCLEAR 2,6-DIACETYLPYRIDINE BIS(NICOTINOYLHYDRAZONE) COORDINATION COMPOUNDS

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Abstract

2,6-Diacetylpyridine bis(nicotinoylhydrazone) (H_2L) represents a Schiff base condensation product of 2,6-diacetylpyridine and nicotinic acid hydrazide and may represent a versatile ligand for a variety of research objectives because it has multiple coordination sites. In this review, the design of seven coordination compounds of the title ligand H_2L with some transition metals-V(II, IV), Fe(III), and Co(II)-is reported. The V(IV), Fe(III), and Co(II) metals give rise to the mononuclear compounds where the metal cations form pentagonal bipyramids, while V(II) forms a binuclear compound with the metal in a tetragonal pyramid environment. The characteristic IR oscillations of H_2L in all complexes and promising adsorption properties are analyzed.

1. Introduction

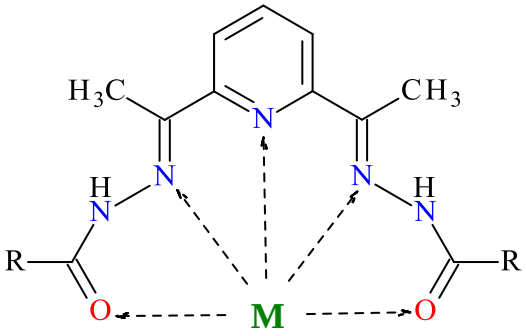
A Schiff base is a condensation product of an aldehyde/ketone and a primary amine [1], which was first reported by Hugo Schiff in 1864. The general formula for a Schiff base is $RN=CR_1R_2$ where R, R_1, and R_2 could be alkyl, aryl, heteroaryl, or cycloalkyl, etc. The complexation of a Schiff base with transition metals leads to the enhancement of their biological activities and a decrease in the cytotoxicity of both the metal ion and the Schiff base ligand [2–4]. These ligands show their versatility of coordinating with a variety of metal ions in different coordination geometries and oxidation states. Schiff bases have been known to form complexes with all transition metals and with lanthanides, which have made them attractive as analytical reagents for spectrophotometric and sensitive spectrofluorimetric determination of trace amounts of these cations [5].

The imine nitrogen atom is capable of acting as a Lewis base toward metal ions; stable coordination is achieved if the metal ion is coordinated with other electron donating groups of the molecule. This condition is generally met when the azomethine bond is present in the vicinity of other electron donating groups/atoms either as ring heteroatoms or as side chains on the molecular scaffold. Hence, the azomethine linkage provides much flexibility in the design of Schiff base ligands with superior and, in some cases, even selective metal ion coordination properties.

Hydrazones represent an important class of compounds that contain an azomethine bond and, similar to Schiff bases, are versatile compounds with vast synthetic utility. Both nitrogen atoms of hydrazones are nucleophilic; however, the amino group nitrogen is more reactive. The azomethine carbon atom has both electrophilic and nucleophilic character; thus, hydrazones have

been known to react with both nucleophilic and electrophilic reagents [6]. The introduction of different functional groups adjacent to the hydrazone linkage further expands the scope of these compounds as chemical reagents [7].

2,6-Diacetylpyridine (dap) is an excellent precursor for the synthesis of a number of complexing agents [8] which can act as planar pentadentate ligands and contribute to the formation of heptacoordinated pentagonal-bipyramidal complexes [9–14]. The dap ligands, due to their multiple coordination sites (Scheme 1), are capable of efficiently stabilizing the metal center forming unique geometries [15].



Scheme 1. Representation of 2,6-diacetylpyridine hydrazone multiple coordination sites (R = several organic groups).

Coordination compounds derived from dap hydrazones and transition metal ions have yielded a surprisingly rich chemistry. The retrieval of Cambridge Structural Database (CSD) [16] revealed over 100 complexes, reported for R = methyl, amine, pyridine, phenyl, phenol, aniline, imidazole or thiosemicarbazone and their derivatives, only 5 of them being 1D and 2D coordination polymers, while all the other represent discrete compounds, mono-, bi-, tri-, tetra-, and pentanuclear ones.

We have favored 2,6-diacetylpyridine bis(nicotinoylhydrazone) for design and synthesis of vanadium(II, IV), iron(III) and cobalt(II) coordination complexes. Herein, we summarize our recent results on synthesis and single-crystal X-ray structural study of a series of homometallic mono- and binuclear compounds with the following compositions: $[V^{IV}(=O)(H_2L)(SO_4)]\cdot 5H_2O$ (**1**), $[V^{II}_2(H_2L)_2](NO_3)_4\cdot H_2O$ (**2**), $[(Fe(H_2L)(H_2O)_2](NO_3)_3\cdot 5H_2O$ (**3**), $[Co(H_2L)(NCS)_2]\cdot CH_3OH$ (**4**), $[Co(H_2L)(NCS)(H_2O)]NCS$ (**5**), $[Co(H_4L)(NCS)_2][Co(NCS)_4]\cdot 1.75H_2O$ (**6**), $[Co(H_2L)(NCS)(CH_3OH)]_2[Co(NCS)_4]\cdot 2CH_3OH$ (**7**) [17–20].

2. Discussion

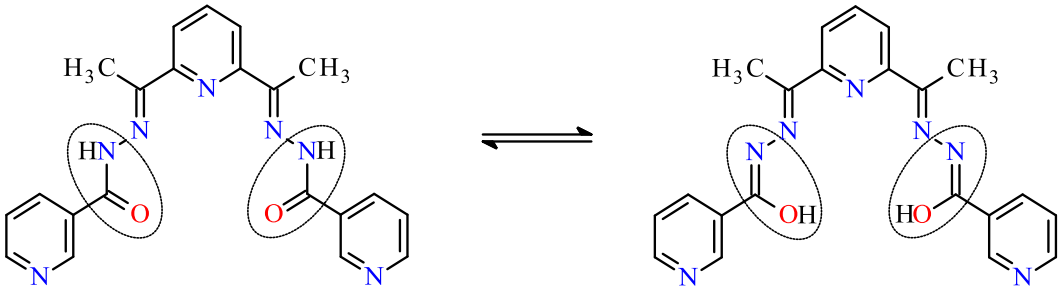
The condensation of 2,6-diacetylpyridine and different hydrazides leads to the formation of the flexible Schiff bases possessing at least five potential donors, such as one pyridine and two azomethine N atoms and two carbonyl O atoms, which can be coordinated in neutral, mono- and/or doubly-deprotonated modes. The coordination of N_3O_2 atom donors provides the

formation of pentagonal-bipyramidal complexes with a stabilized nearly planar system in the equatorial plane of the bipyramid comprised of four five-membered chelate rings and monodentate ligands in the apical positions [21–24]. This geometry depends on the conformational flexibility of the ligand, the coordination capacity of the metal ion, and reaction conditions [25].

Hydrazones play an important role in inorganic chemistry, because they readily form stable complexes with many transition metal ions and many of these complexes may serve as models for biologically important species [26]. It is known that hydrazones derived from condensation of isonicotinic acid hydrazide and pyridine aldehydes exhibit better antitubercular activity than that of hydrazide [27–29].

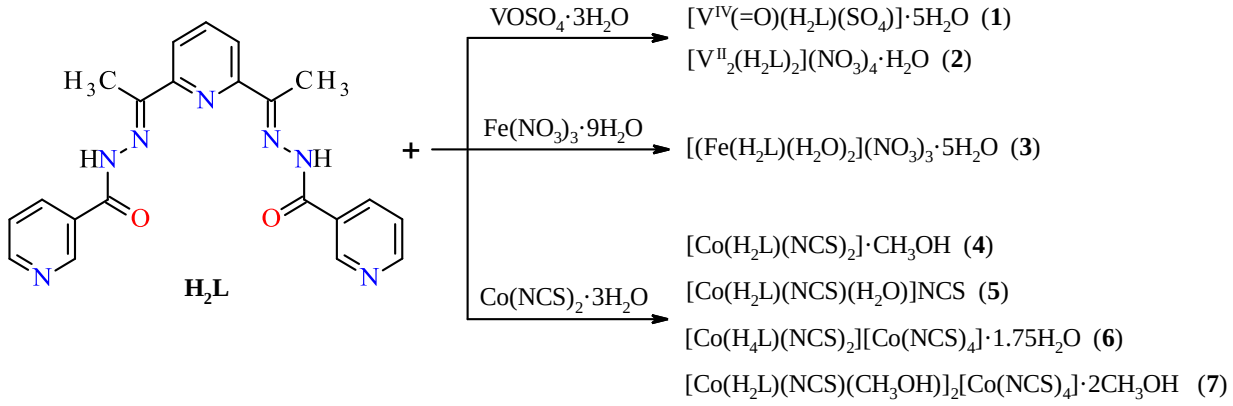
2,6-Diacetylpyridine bis(pyridine-*n*-carbonylhydrazones) (*n* = 2, 3, 4) are versatile ligands for a variety of research objectives. Analysis of the Cambridge Structural Database [16] reveals that, of the three isomeric Schiff bases, 2,6-diacetylpyridine bis(pyridine-3-carbonylhydrazone) is the least commonly used ligand system, since 2,6-diacetylpyridine bis(pyridine-2-carbonylhydrazone) forms mono- [30–32] and tetranuclear complexes with Mn(II), Co(II), Cu(II) and Sn(IV) cations [33–34], while 2,6-diacetylpyridine bis(pyridine-4-carbonylhydrazone) gives rise to mononuclear compound [35] and bidimensional coordination polymer in combination with Mn(II) and Sn(II) cations [36].

2,6-Diacetylpyridine bis(pyridine-3-carbonylhydrazone), also known as 2,6-diacetylpyridine bis(nicotinoylhydrazone) (H_2L), may display keto-enol tautomerism interconversion related with the coordination through either nitrogen or oxygen atoms, or both atoms, and diversifies the coordination to metal centers. It should be noted that the keto–enol equilibrium is possible, especially when the hydrazone hydrogen is abstracted, as shown in Scheme 2.



Scheme 2. Structures of the H_2L ligand and tautomeric forms of it.

Coordination compounds of V(II, IV), Fe(III), and Co(II) with the condensation product of dap and nicotinic acid hydrazide were prepared using the direct method of synthesis in the reaction of the H_2L ligand and the corresponding metal salt in a molar ratio of 1 : 1. Thus, seven transition metal complexes were obtained; their crystal structures were determined by single-crystal X-ray diffraction. Compound **1** represents a binuclear compound, while compounds **2–7** are mononuclear complexes (Scheme 3).



Scheme 3. Synthetic route to the reported coordination compounds.

The crystal structures of **1** and **3–7** are built from molecular mononuclear complexes (**1** and **4**) and cations (**3**, **5–7**), where the coordination polyhedra of the metal cations represent pentagonal bipyramids formed by N_3O_2 set of donor atoms going from the pentadentate Schiff base ligand in the equatorial plane, while the axial vertices are occupied by anions (SO_4^{2-}, NCS^-) and/or solvent molecules (H_2O, CH_3OH) both coordinated in a monodentate fashion (Fig. 1).

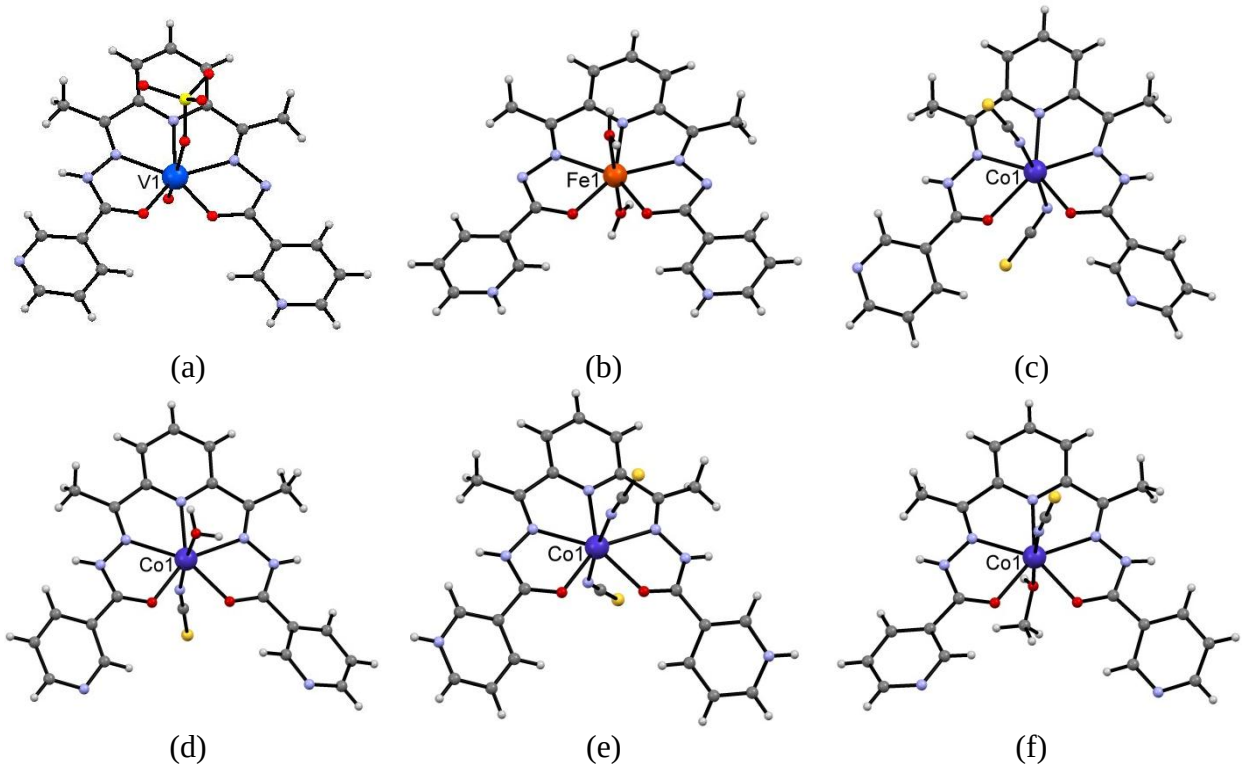


Fig. 1. View of the structure of mononuclear compounds in **1** (a) and **4** (c) and cations in **3** (b) and **5–7** (d–f).

In the molecular complex in **1** and complex cation in **3**, the axial positions are held by two O atoms of the SO_4^{2-} anion and oxo ligand O^{2-} in **1**, while in **3** the O atoms come from two water molecules. In compounds **4–7**, the axial vertices arise from: two N atoms of the NCS^- anions (in **4** and **6**); one N atom of the NCS^- anion and O atom of the water or methanol molecules (in compounds **5** and **7**). In coordination complexes **1**, **3–5**, and **7**, the Schiff base ligand coordinates in the neutral mode, while in complex cation **6**, the organic ligand is protonated at the nitrogen atoms of the terminal pyridine fragments. Analysis of the positioning of the hydrogen atoms from the H_2L ligand in **3** demonstrates the proton transfer from the N atoms of the amide group to the pyridine N atoms. In compounds **6** and **7**, the $[Co(NCS)_4]^{2-}$ complex cation compensates for the positive charge of the Co^{2+} complex cation.

Complex **2** has an ionic structure; the crystals of it are composed of centrosymmetric binuclear cations $[V^{II}_2(H_2L)_2]^{4+}$ (Fig. 2), NO_3^- anions, and crystal water molecules in a ratio of 1 : 4 : 1. The $[V^{II}_2(H_2L)_2]^{4+}$ binuclear complex cation has a double helical structure in which two organic neutral H_2L ligands are coordinated to two metal atoms and lie along the V(1)-V(1') axis. The neutral H_2L ligand is coordinated to the V atom in a pentadentate mode: in a tridentate fashion through the electron-donating N,N,O-atoms and to the V(1') atom in a bidentate fashion through the N,O atoms. The coordination polyhedron of the V atom in complex **1** is a tetragonal pyramid. The basal plane of it is composed of the O and N atoms of one H_2L molecule and the one N atom of the symmetry-related counterpart; the pyramid is completed with the O atom of the other H_2L molecule as an apex. In the crystal, the complex cations and the anions are linked by intermolecular hydrogen bonds and by electrostatic interactions.

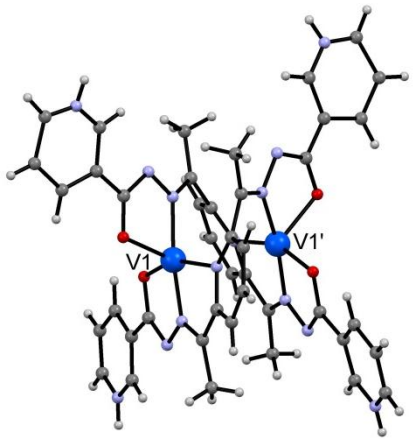


Fig. 2. View of the structure of the binuclear $[V^{II}_2(H_2L)_2]^{4+}$complex cation in **2**.

Except for compound **5**, all other solids contain voids in the crystal lattice filled with solvent guest molecules (H_2O, CH_3OH). The lattice solvents are held in the pores via hydrogen bonds with the coordination complex. The solvent accessible voids (SAVs) of the crystal unit cells were calculated by the PLATON program and are summarized in Table 1. The cumulative solvent volume varies from 5.4% in **6** to 18.2% in **1**. The SAVs assume the shapes of open channels in **1** and **4** and discrete cages in **2**, **3**, **6**, and **7**. Despite the fact that structure **5** represents a solvent-free solid, it contains negligible SAVs (~2.4% of the unit cell volume, V). The mass portions of the entrapped solvent along with numerical characteristics for the volume occupied by

the solvent molecules in the structures indicate that these solids may be considered to be possible sponge materials.

Table 1. Selected geometrical and crystal packing parameters in compounds **1**-**7**

Compound	Space group	V, Å^3	SAVs, Å^3 (%)	Solvent uptake, %	Reference, refcode in CSD
1	$P2_1/n$	2727.6(2)	497.0 (18.2)[a]	13.75[b,c]	[17], IXEYAN
2	$C2/c$	5463.1(8)	750.7 (13.7)[a]	1.54[b,c]	[17], IXIGED
3	$P2_1/n$	3265.39(8)	408.5 (12.5)[a]	16.37[b]; 11.70[c]	[18, 19], JAPLIY
4	P-1	1296.98(12)	108.0 (8.3)[a]	5.26[b,c]	[20], YECZIS
5	$C2/c$	2631.1(3)	63.6 (2.4)	3.03[b]; –[c]	[20], YEFBIX
6	P-1	1872.22(19)	101.7 (5.4)[a]	3.50[b,c]	[20], YEDBER
7	$C2/c$	6719.3(19)	895.8 (13.3)[a]	8.79[b]; 4.39[c]	[20], YEFBOD

[a] SAVs calculated with the removal of guest molecules.
[b] Total solvents' gravimetric uptake.
[c] Non-coordinated solvents' gravimetric uptake.

IR spectra of the free H_2L ligand and compounds **1–7** were recorded in a range of 400-4000 cm^{-1}; the assignments of wavenumbers observed in the recorded spectra of the complexes, together with the wavenumbers of the ligand, are listed in Table 2. Some spectroscopic similarities are evident in the IR spectra of the ligand and all the compounds. In all complexes, the amide I, amide II, and amide III vibrational bands have undergone a slight shift upon the coordination effect. The displacement of the amide I band by 18-31 cm^{-1} in compounds **4–7** in the direction to the low-frequency region against the ligand spectrum is probably the result of the coordinating C=O group effect at the metal. The spectra of compounds **1–3** exhibit broad bands in the region of 2700-2300 cm^{-1}, which can be attributed to $\nu(=NH^+)$ vibrations [37] resulting from the proton migration from the NH groups to the nitrogen atoms of the terminal heterocycles.

Table 2. Vibrational wavenumbers of H_2L in compounds **1–7** (cm^{-1})

Compound	ν(OH), ν(N–H)	amide I, ν(C=O)	ν(C=N) azomet.	ν(CN) ring	amide II, $\delta_{NH}+\nu_{C-N}$	amide III
H_2L	3182	1663	1617	1591	1567	1258
1	3384	1540	1633	1593	1571	1275
2	3348	1595	1617	1583	1558	1274
3	3381	1532	1632	1595	1566	1272
4	3467, 3180	1632	1646	1594	1538	1268
5	3331, 3155	1635	1657	1590	1570	1273
6	3346	1639	1605	1588	1572	1287
7	3551, 3445	1645, 1635	1661	1590	1570	1272

In compounds **1**–**3**, the Schiff base H_2L coordinates in the enol-form, while in **4**–**7** in the keto-form. The negative charges of the N atoms after proton migration probably cause the formation of pseudometallocycles MNNCO, where distances of C⋯O bonds have intermediate values between single and double bonds (1.288 and 1.302 Å in **1**; 1.278 and 1.290 Å in **2**; 1.272 and 1.273 Å in **3**) similar to V(IV) and Fe(III) acetylacetonates [38, 39] and ammine-(*N*-(1-(4-chlorophenyl)-4,4,5,5,6,6,6-heptafluoro-3-oxyhex-2-en-1-ylidene)benzene carbohy-drazonato-N,O,O')-nickel(II) [40], which explain the different spectral behavior of C⋯O groups in the studied complexes.

3. Conclusions

The combination of 2,6-diacetylpyridine bis(nicotinoylhydrazone) (H_2L) with V(IV), Fe(III), and Co(II) salts has given rise to six mononuclear compounds (V(IV), Fe(III), Co(II)) and one binuclear complex (V(II)); in three of them, H_2L coordinates in the enol-form; in the other four compounds, the ligand exists in the keto-form. Six solids accommodate solvent molecules in the crystal lattice, while the mononuclear $[V^{IV}(=O)(H_2L)(SO_4)]\cdot 5H_2O$ compound exhibits the most promising adsorptive properties.

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