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Synthesis and crystal structure of Cu(II) and Co(II) complexes with the 1,3-dimethylpyrazole-5-carboxylic acid ligand

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Abstract: In the reaction of 1,3-dimethylpyrazole-5-carboxylic acid (HL) with $M(OAc)_2\cdot 4H_2O$, (M = Cu or Co), two novel complexes were prepared, the square-planar $[CuL_2(H_2O)_2]$ and the octahedral $[CoL_2(MeOH)_4]$. The crystal structures were determined by single-crystal X-ray diffraction. In both complexes, the deprotonated acid displays monodentate coordination to the metal ions. According to the results of a CSD survey, this is the first structural report on the metal complexes with an N^1-substituted pyrazole-5-carboxylic ligand.

Keywords: pyrazole-based ligand; transition metal complex; crystal structure.

INTRODUCTION

Pyrazole-based compounds and their transition metal complexes have attracted considerable research interest because of their potentially beneficial biological properties. The wide biological activity of this class of compounds (anticancer, antimicrobial, antiviral, anti-inflammatory and others) is described in several reviews.[1] Apart from the investigation of the biological activity of pyrazole derivatives, they have been extensively used as ligands or synthons in coordination chemistry[2] and crystal engineering including the metal organic frameworks.[3] The most of these valuable functions of pyrazole ligands originate in their various bonding modes to metal ions that can be further influenced and rationally designed by the attachment of substituents with additional coordination sites.[3–5] Another important property of pyrazole derivatives is the presence of hydrogen bonding sites, either on the pyrazole ring (pyrrolic N–H donor and pyridinic N

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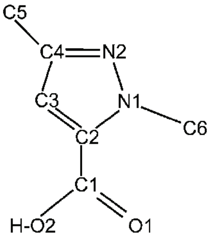
acceptor) or its substituents, which facilitates molecular association into the hydrogen-bonded supramolecular structures.

Ligands derived from pyrazole-5-carboxylic acid also display various bonding modes as they can coordinate in mono- or dianionic form through the pairs of *N*- and *O*-donors from the heterocyclic ring and carboxyl groups. Despite this coordination variety, the Cambridge Structural Databank (CSD)[6] does not contain information about metal complexes with *N*^{1}-substituted derivatives of pyrazole-5-carboxylic acid. Herein, the syntheses, IR characterization and crystal structures of Cu(II) and Co(II) complexes with 1,3-dimethylpyrazole-5-carboxylate (Scheme 1) are presented, whereby the X-ray experiments revealed the not very common monodentate coordination of this pyrazole-5-carboxylic acid based ligand.



Scheme 1. 1,3-Dimethylpyrazole-5-carboxylic acid (HL) with atom numbering.

EXPERIMENTAL

Preparation of the complexes

The $[CuL_2(H_2O)_2]$ complex was synthesized in the reaction of a warm methanolic solution (10 cm^3 CH_3OH) of 0.25 mmol (0.049 g) $Cu(OAc)_2\cdot4H_2O$ with a warm methanolic solution (5 cm^3 CH_3OH) of 0.5 mmol (0.070 g) 1,3-dimethylpyrazole-5-carboxylic acid (HL) mixed in a 1:2 mole ratio. After two days, the blue single crystal product was filtered off and washed with methanol. The yield was 84.29 % (0.080 g).

The $[CoL_2(MeOH)_4]$ complex was synthesized in the reaction of a warm methanolic solution (3 cm^3 CH_3OH) of 0.125 mmol (0.031 g) $Co(OAc)_2\cdot4H_2O$ with a warm methanolic solution (3 cm^3 CH_3OH) of 0.25 mmol (0.035 g) 1,3-dimethylpyrazole-5-carboxylic acid (HL) mixed in a 1:2 mole ratio. After two days, the single crystal product was filtered off and washed with methanol. Yield was 32.75 % (0.019 g). The synthesis resulted in the mixture of reactants, HL and $Co(OAc)_2\cdot4H_2O$, and a very small amount of the $[CoL_2(MeOH)_4]$ complex. After filtering off, the purple crystals of the complex were mechanically separated for IR and X-ray analysis.

For both syntheses, the 1,3-dimethylpyrazole-5-carboxylic acid was used as purchased from Sigma–Aldrich.

Infrared spectra

The infrared spectra (IR) of the synthesized complexes and corresponding uncoordinated ligand were recorded as KBr pellet on a Thermo Nicolet Nexus 670 FT-IR instrument in the wavenumber range of 4000–400 cm^{-1}. As expected, the IR spectra of complexes show rather similar features, especially concerning the position of the relevant absorption band $\nu(COO^-)$. The spectrum of the uncoordinated ligand displayed $\nu(COOH)$ at 1712.27 cm^{-1}, while in spectra of the complexes, the band was replaced with $\nu_{as}(COO^-)$ at *ca*. 1600 cm^{-1} and $\nu_s(COO^-)$

at *ca*. 1350 cm^{-1}. The approximate $\Delta\nu$ of 250 cm^{-1} is in accordance with monodentate coordination of the carboxyl ligand.[7] IR (cm^{-1}): 2926.26, 2578.64, 2481.96, 1712.27, 1542.66, 1471.80, 1245.67; $[CuL_2(H_2O)_2]$: 3434.32, 2926.48, 1600.12, 1538.44, 1460.62, 1354.18, 1293.23; $[CoL_2(MeOH)_4]$: 3380.68, 2927.31, 1605.24, 1536.72, 1459.10, 1350.08, 1287.29.

X-ray crystal structure determination

The diffraction data from selected single crystals of $[CuL_2(H_2O)_2]$ and $[CoL_2(MeOH)_4]$ were collected at 200 and 150 K, respectively on a Nonius Kappa CCD diffractometer equipped with a monocapillary optics collimator, MoK_α radiation (λ = 0.71073 Å). The data were corrected for absorption by evaluation of multi-scans. The crystal structure was solved by direct methods, using SHELXS and refined with SHELXL.[8] The H atoms attached to C atoms were placed at geometrically calculated positions with the C–H distances fixed to 0.93 and 0.96 Å from aromatic and methyl C atoms, respectively. The corresponding isotropic displacement parameters of the hydrogen atoms were equal to $1.2U_{eq}$ and $1.5U_{eq}$ of the parent C atoms. The H atoms attached to O atoms were located in the final electron density maps and refined isotropically. The geometrical calculations were performed with PARST[9] and PLATON.[10] The programs ORTEP[11] and Mercury[12] were used for molecular graphics. The details of the X-ray structural analysis are given in Table S-I of the Supplementary material to this paper.

RESULTS AND DISCUSSION

Coordination modes of pyrazole-5-carboxylic acid ligands in metal complexes extracted from CSD

The CSD analysis[6] focused only on the donor abilities of the pyrazole-5-carboxylic acid ligands (with four potential coordination sites in total) and hence, the crystal structures of complexes with derivatives comprising additional donor sites were not considered. In the complex compounds extracted from CSD, the pyrazole-5-carboxylic ligands displayed seven different ways of coordination. In over 70 % of the structures (40 of 56 extracted), the ligands derived from pyrazole-5-carboxylic acid coordinate only as N^1, *O* bidentates forming the five membered chelate rings. The coordination of the remaining donors leads to the formation of bi- or polynuclear metal complexes, while the formation of a chelate ring is still preferential. There are only two examples of monodentate coordination of pyrazole-5-carboxylic ligands.[13,14] In both of these complexes, the monodentate coordination can be related to the possible steric hindrance between the ligands in the coordination spheres of the corresponding metal ions. Up to now, the crystal structures of complexes with N^1-substituted derivatives of pyrazole-5-carboxylic acid have not been reported.

In the case of the ligand present in the title complexes (Scheme 1), the methyl substituent on the N^1-pyrazole prevents the most frequently occurring chelating form and confines the coordination to the carboxyl oxygen donor. Moreover, the steric hindrance that this substituent produces on the third donor site, N^2-pyrazole, significantly reduces the coordination ability of this donor, consequently monodentate coordination could be expected. It should be mentioned that the crystal structures of complexes comprising N^2-substituted pyrazole-5-carboxylic ligands are also scarce in the literature. In several reported cases with phenyl substituents on pyrazole N^2, the corresponding ligands coordinate in the N^1O-chelating mode.[15]

Description of crystal structures

The $[CuL_2(H_2O)_2]$ complex crystallizes in the space group $P2_1/c$. The Cu atom is placed in a nearly ideal square planar environment formed by pairs of oxygen donors from the deprotonated carboxylic acid and H_2O molecules, Fig. 1a. The lengths of the two types of Cu−O bonds coincide within the s.u. values, while the angle O2−Cu1−O1w of 91.09(6)° actually shows the largest deviation from the ideal square-planar geometry (Table S-II of the Supplementary material). The Cu(II) ion lies on an inversion center. The Cu−O1w and Cu−O1 bond lengths are within the ranges of previously reported square-planar Cu(II) complexes comprising monodentately-coordinated carboxyl and H_2O ligands.[16] In comparison to the crystal structure of the uncoordinated 1,3-dimethylpyrazole-5-carboxylic acid (HL),[17] the geometry of the coordinated ligand is slightly altered (Table S-II). Apart from the expected changes in the carboxyl fragment due to the acid deprotonation, the dihedral angle between COO^- and pyrazole planes increases upon the ligand coordination form 4.0 to 8.7(2)°. Concerning the coordination plane of the four oxygen donors, the pyrazole ring is rotated by 69.2(1)°.

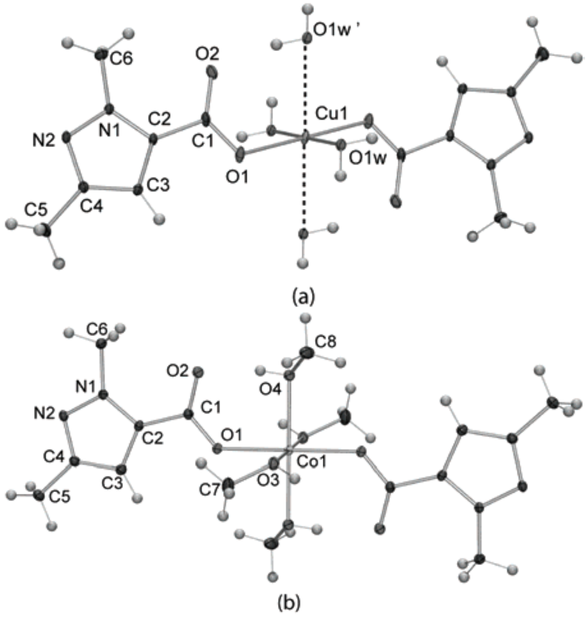


Fig. 1. Molecular structures of: a) $[CuL_2(H_2O)_2]$ with indicated positions of pseudo-coordinated O1w atoms (dashed lines) and b) $[CoL_2(MeOH)_4]$, independent molecule A. The displacement ellipsoids are drawn at the 40 % probability level.

Two types of rather strong hydrogen bonds having H···A distances shorter than 2.0 Å stabilize the crystal structure of the $[CuL_2(H_2O)_2]$ complex (Table I). The O1w−H1w···O1 interaction between the H_2O molecule and the uncoordinated carboxyl oxygen atom links the complex units into a chain extending along the *a* axis (Fig. 2a). It should be noticed that within this chain, each H_2O oxygen atom is closely adjacent to the Cu(II) ions of the neighboring complex unit. The Cu1···O1w^i ($i = x–1, y, z$) distance is 2.802(1) Å, which is significantly shorter than the sum of the van der Waals radii of these two atoms (3.84 Å).[18] Taking into account these short Cu···O1w^i contacts, the environment of each Cu(II) ion could be described as pseudo-octahedral. The positions of pseudo-coordinated O1w^i atoms are shown in Fig. 1a. The angles formed between the atom O1w^i and the O2 and O1w donor atoms from the Cu(II) coordination sphere are 87.9 and 105.8°, respectively. The separation distance between two Cu(II) in the chain is 3.826(1) Å and coincides with the length of the shortest *a* axis. Both H_2O molecules coordinated to Cu(II) further engage as hydrogen bonding donors to the non-substituted pyrazole *N* atoms of the neighboring chain (O1w−H2w···N2), leading to cross-linkage and the formation of a three-dimensional network. A fragment of this three-dimensional crystal packing is shown in Fig. 2a.

TABLE I. The geometry of hydrogen bonding (Å, °) for the Cu(II) and Co(II) complexes; symmetry codes for $[CuL_2(H_2O)_2]$: i) $x+1, y, z$; ii) $–x+1, y–1/2,–z+1/2$; symmetry codes for $[CoL_2(MeOH)_4]$: i) x, y, z; ii) $x, y–1, z$

Structure	*D*–H···*A*	*D*–H	*D*···*A*	H···*A*	*D*–H···*A*
$[CuL_2(H_2O)_2]$	O1w−H1w···O3^i	0.81(3)	2.611(2)	1.82(3)	165(3)
	O1w−H2w···N2^{ii}	0.83(3)	2.716(2)	1.89(3)	170(4)
$[CoL_2(MeOH)_4]$	O4a−H4a···O2a^i	0.79(3)	2.587(2)	1.83(3)	160(3)
	O4b−H4b···O1b^i	0.82(3)	2.582(2)	1.78(3)	167(3)
	O3a−H3a···N2a^{ii}	0.73(3)	2.707(3)	1.98(3)	175(3)
	O3b−H3b···N2b^{ii}	0.79(3)	2.765(2)	1.97(3)	177(3)

The second complex $[CoL_2(MeOH)_4]$ crystallizes in space group *P*-1, with the asymmetric unit containing two halves of the corresponding crystallographically independent complex molecules (A and B). The two Co(II) ions, which are placed in the inversion centers (0,0,0 and 0.5,0.5,0.5), adopt deformed octahedral coordination geometry (Table S-II) built by two monodentately coordinated L ligands and four molecules of methanol, Fig. 1b. The Co−O1 coordination bonds in the two independent molecules are of similar lengths, while the dihedral angles between the carboxyl and pyrazole planes are 8.6(2) and 3.5(2)° for molecules A and B, respectively. The bonds within the L ligand show only small variations with respect to the uncoordinated molecule[17] and the same ligand in the Cu(II) complex. Comparison of the monodentate coordination of the L ligand to the Co(II) and Cu(II) ions in the two complexes revealed a pronounced difference between the Cu1−O1−C1 and each of the two Co1−O1−C1 angles (9.3° on average) (Table S-II). In both molecules of $[CoL_2(MeOH)_2]$, the carboxyl group of L is placed in the level of vicinal MeOH ligand and engages in strong intramolecular (O4−H4···O2) hydrogen bonding (Table I). This is in contrast to the Cu(II) complex in which a carboxyl group points away from the vicinal ligand to engage in intermolecular O−H···O interaction.

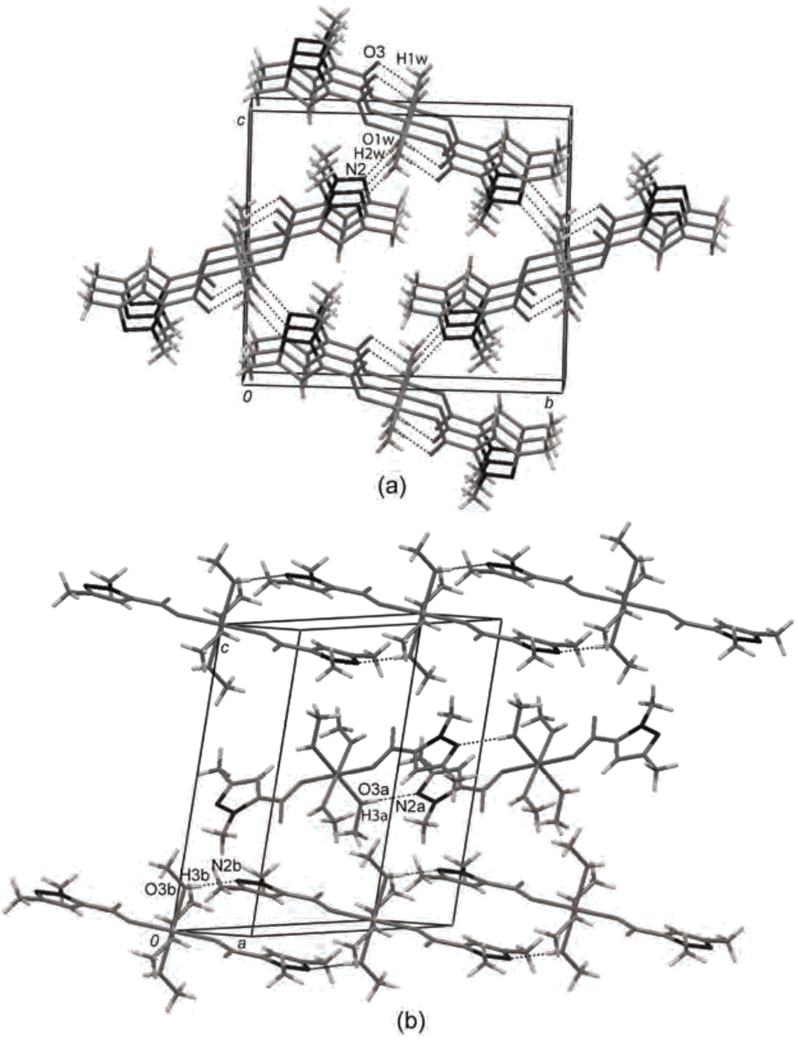


Fig. 2. Crystal packing of: (a) $[CuL_2(H_2O)_2]$ and (b) $[CoL_2(MeOH)_4]$. Intermolecular interactions are indicated by dashed lines.

The MeOH ligands mostly contribute to the dissimilarity of the two independent [$CoL_2(MeOH)_4$] molecules. Thus, the Co−O coordination bonds involving MeOH ligands (Table S-II) are both longer in molecule B by 0.04Å on average. A closer comparison of the coordinated MeOH also showed marked differences in the orientation of their methyl groups. Considering the MeOH ligands that form strong intramolecular hydrogen bonds, it could be observed that their C8 methyl atoms deviate from corresponding O1/O1′/O4/O4′ planes by 0.18(1) and 0.96(1) Å in A and B, respectively. In both type of molecules another pair of MeOH serves as donor in the O3−H3···N2 intermolecular hydrogen bond to the pyrazole acceptor from the neighboring molecule (Table I). These interactions lead to the formation of two distinct chains composed of the same type of molecules, A or B. Both chains run in the direction of the *b* axis; the mutual inclination between the pyrazole rings belonging to different chains is 47.4(1)°. The chains composed of A and B molecules mutually interact by van der Waals interactions (Fig. 2b).

CONCLUSION

The report describes the synthesis, IR characterization and crystal structures of Cu(II) and Co(II) complexes with 1,3-dimethylpyrazole-5-carboxyle ligand (HL), the square-planar [$CuL_2(H_2O)_2$] and the octahedral [$CoL_2(MeOH)_4$]. The presence of a methyl substituent on the N^1 atom of HL prevents bidentate coordination common for pyrazole-5-carboxylic acid-based ligands; therefore, in both complexes the ligand is monodentately coordinated to the metal ion. The crystal structures of the complexes are stabilized by extensive O−H···O and O−H···N hydrogen bonds, in which H_2O and methanol ligands play a significant role as hydrogen bonding donors.

SUPPLEMENTARY DATA

Crystallographic data of the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC No. 1015253 and 1015254. The data are available free of charge *via* www.ccdc.cam.ac.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk). The crystallographic data, and selected bond lengths and angles for the Cu and Co complexes are given in Tables S-I and S-II, respectively, of the Supplementary material to this paper, which is available electronically from http://www.shd.org.rs/JSCS/ or from the corresponding author on request.

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ИЗВОД

СИНТЕЗА И КРИСТАЛНА СТРУКТУРА КОМПЛЕКСА Cu(II) И Co(II) СА 1,3-ДИМЕТИЛ-ПИРАЗОЛ-5-КАРБОКСИЛНОМ КИСЕЛИНОМ

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У реакцији 1,3-диметилпиразол-5-карбоксилне киселине (HL) и $M(OAc)_2 \cdot 4H_2O$ (M = Cu или Co) синтетисана су два нова комплекса, квадратно-планарни $[CuL_2(H_2O)_2]$ и октаедарски $[CoL_2(MeOH)_4]$. Некоординовани лиганд и синтетисани комплекси су окарактерисани инфрацрвеним спектрима. Кристалне стуктуре комплекса су одређене рендгенском стуктурном анализом. У оба комплекса депротонована киселина се координује за јон метала као монодентатни лиганд. Према резултатима претраге Кембричке банке података ово је први стуктурни опис комплекса метала са N^1-супституисаним дериватом пиразол-5-карбоксилне киселине.

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