

IR ANALYSIS OF THE CARBOXYLATE FORMS IN STRUCTURALLY DETERMINED $[\text{Cu}^{\text{II}}(\kappa^3\text{-L})_2]$ SPECIES ISOLATED FROM DIFFERENT ACIDIC SOLUTIONS[♦]

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Several copper(II) coordination compounds with the tridentate $\kappa^3\text{-N,N,O}$ bisligand (L = bis(3,5-dimethylpyrazol-1-yl)acetate or its molecular acid form HL = Hbdmpza) were synthesized from different starting metal salts in appropriate acidic water solutions as reported. The XRD single crystal structural analysis reveals neutral acidic ligand form in $[\text{Cu}(\text{HL})_2] \cdot 2(\text{HSO}_4)$ (**1**) and $[\text{Cu}(\text{HL})_2] \cdot 2\text{Cl}$ (**2**), while ionic in $[\text{Cu}(\text{L})_2] \cdot (\text{CH}_3\text{COOH}) \cdot (\text{H}_2\text{O})$ (**3**), and $[\text{Cu}(\text{L})_2] \cdot 2(\text{H}_2\text{O})$ (**4**). The molecular structures of **2** and **3** are first reported herein, thus enabling a clearer insight for the IR-structural analysis. Two carboxylate C–O bond lengths ranges, namely differing 1.29/1.22 Å for **2**, and the same 1.24/1.24 Å for **3**, respectively, are in agreement with the single (longer)/double (shorter) character of both bonds for the neutral carboxylic HL in **2**, and the same character of both bonds for the carboxylate anionic L^- in **3**, as seen for the related **1** (HL) and **4** (L^-). The most distinguished IR spectra difference for the molecular (HL) / ionic (L^-) is at the 1700 cm^{-1} carboxylate band. The C=O free ligand (HL) double bond position at 1740 cm^{-1} is most similar with 1702 cm^{-1} in **1**, while a split band at 1697, 1665 cm^{-1} is seen for **2**. On the other hand, the anionic asymmetric carboxylate stretching IR band ($\nu_{\text{as}}(\text{COO}^-)$) for **3** (1642 cm^{-1}) and **4** (1635 cm^{-1}) is found at lower energy region. Thus, the additional band within the same region, as seen only for **3** at 1716 cm^{-1} , is assigned to the network neutral acetic acid C=O double bond.

Keywords: Hbdmpza; copper; IR; structure; carboxylate

ИЦ АНАЛИЗА НА КАРБОКСИЛАТНИТЕ ФОРМИ ВО $[\text{Cu}^{\text{II}}(\kappa^3\text{-L})_2]$ ПРИМЕРОЦИ СО ОПРЕДЕЛЕНА СТРУКТУРА, ИЗОЛИРАНИ ОД РАЗНИ КИСЕЛИ РАСТВОРИ

Презентирани се резултатите од синтезата на неколку координациони соединенија на бакар(II) со тридендатниот $\kappa^3\text{-N,N,O}$ бислиганд (L = бис(3,5-диметилпиразол-1-ил)ацетат или неговата молекуларна киселинска форма HL = Hbdmpza), поаѓајќи од различни метални соли во погодни кисели водни раствори. Рендгенската структурна анализа на монокристал докажа неутрална киселинска лигандна форма во $[\text{Cu}(\text{HL})_2] \cdot 2(\text{HSO}_4)$ (**1**) и во $[\text{Cu}(\text{HL})_2] \cdot 2\text{Cl}$ (**2**), а јонска во $[\text{Cu}(\text{L})_2] \cdot (\text{CH}_3\text{COOH}) \cdot (\text{H}_2\text{O})$ (**3**), и во $[\text{Cu}(\text{L})_2] \cdot 2(\text{H}_2\text{O})$ (**4**). Молекуларните структури **2** и **3** се овде презентирани за првпат, овозможувајќи притоа појасен увид при ИЦ-структурната анализа. Карбоксилатните C–O растојанија, кои во **2** варираат (1.29/1.22 Å), а во **3** се исти (1.24/1.24 Å), се во согласност со единичен (подолгото)/двоен (пократкото) карактер на двете врски за неутрален HL во **2**, и ист карактер на двете врски за карбоксилатниот анјонски L^- во **3**, како што е најдено и за соодветните **1** (HL) и **4** (L^-). Најизразена ИЦ-спектрална разлика за молекуларен (HL) / јонски (L^-) се забележува кај карбоксилатната лента на 1700 cm^{-1} . Положбата на лентата на 1740 cm^{-1} што се должи на вибрацијата на двојната C=O врска од слободниот лиганд (HL) е најслична со 1702 cm^{-1} во **1**, додека кај **2** се забележани две расцепени ленти на 1697, 1665 cm^{-1} . Од друга страна, лентата што се должи на анјонската антисиметрична карбоксилатна валентна вибрација ($\nu_{\text{as}}(\text{COO}^-)$) на 1642 cm^{-1} кај **3** и на 1635 cm^{-1} кај **4**, е најдена во пониско енергетско подрачје. Според тоа, дополнителната лента најдена во истото подрачје на 1716 cm^{-1} кај **3** е припишана на вибрација на двојната C=O врска од неутралната оцетна киселина.

Клучни зборови: Hbdmpza; бакар; ИЦ; структура; карбоксилат

[♦] Dedicated to Academician Gligor Jovanovski on the occasion of his 70th birthday.

1. INTRODUCTION

As two methods namely, the infrared (IR) spectroscopy and the single crystal XRD structural analysis are well established and relatively accessible, they often serve as the principal characterization techniques for the standard laboratory work [1–3]. Sole IR spectrum is generally used as a finger print method, as an exact assignment is vague also for the dominant bands and the molecular structures determined [4, 5]. Nevertheless, a more exact assignment may be achieved by the isotope labeling rather than theoretical/computational methods. Due to a demanding procedure, only a small proportion of the compounds are analyzed this way, *e.g.* some general examples as copper acetate hydrate [6, 7]. Alternatively, a group of relatively similar species may be isolated instead and their spectra compared, enabling thus an easier path to the IR band assignment. One of the challenges is also the hydrogen ion positioning at the molecular structure determination, as the XRD method is based on the electron scattering, and only one electron per each proton. This is most commonly indirectly solved *via* the net neutrality and H-bonding orientation. During our investigation with the scorpionate type ($\kappa^3\text{-N,N,O}$) of ligand bis(3,5-dimethylpyrazol-1-yl)acetate (L^-) [8–10], we managed to isolate several related copper compounds with the bisligand coordination species [11, 12]. The compounds were isolated from different acidic water solutions, rising to a differentiation of the network connections. Thus far, the proton position determination remained an issue not unambiguously confirmed classified, as the isolated species could be either with HL or L^- . Only recently we managed to isolate the last single crystals within this system, giving us an opportunity to reevaluate the IR analysis.

Herein we represent four compounds, having $[\text{Cu}^{\text{II}}(\kappa^3\text{-L})_2]$ coordination building blocks, along with different net solvent and counter ions. They are playing direct role *via* the H-bonding on the nature of the carboxylic/carboxylate group inside the coordination sphere, these latter analyzed *via* the IR/molecular structure correlation.

2. EXPERIMENTAL

2.1. Materials and synthesis

All commercial starting compounds and solvents were of analytical grade quality and used as received. Hbdmpza and the metal compounds were prepared following previously reported procedures

(**1**: calcd./found C 38.2/37.3, H 4.54/4.31, N 14.9/14.6; **2**: calcd./found C 45.7/45.8, H 5.11/4.99, N 17.8/17.8; **3**: calcd./found C 49.1/48.9, H 5.70/5.39, N 17.6/17.5; **4**: calcd./found C 48.5/48.5, H 5.77/5.46, N 18.9/18.9. The chlorido yield was not measured) [11–14]. The single crystals for **2** and **3** were isolated by the same procedure.

2.2. Physical measurements

The infrared spectra of the solid samples were measured in a region $4000\text{--}600\text{ cm}^{-1}$ using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with Specac Golden Gate ATR as a sample support.

X-ray crystallographic study: Single crystal diffraction data were collected on an Agilent SuperNova (Dual, Mo at zero, Atlas) diffractometer using $\text{Cu K}\alpha$ (1.54184 \AA) radiation at 150 K for **2** and **3**. Data reduction and integration were performed with the software package *CrysAlis PRO* [15]. The coordinates of all non-hydrogen atoms were found *via* direct methods using the *SIR97* structure solution program [16]. A full-matrix least-squares refinement on F^2 magnitudes with anisotropic displacement parameters for all non-hydrogen atoms using *SHELXL2013* was employed [17]. All hydrogen atoms were initially located in the difference Fourier maps and were subsequently treated as riding atoms in geometrically idealized positions with bond lengths C–H of 0.98 \AA for methyl, 1.00 \AA for methine and 0.95 \AA for aromatic C–H bonds. The corresponding displacement parameters $U_{\text{iso}}(\text{H})$ were 1.5-times higher than those of the carrier methyl carbon atoms and 1.2-times higher than all other hydrogen bearing carbon atoms. In **2** the carboxylic group hydrogen atom was refined as riding on its carrier atom using an AFIX 4 command (*i.e.* allowing the change of the O2–H2 distance, while the direction towards the acceptor chloride ion did not change, and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$). In **3**, the water molecule and the carboxylic group hydrogen atoms were refined using AFIX 3 command (*i.e.* not allowing the change of their positions, thus refining only their isotropic displacement parameters as $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$). Figures depicting the structures were prepared by *Platon* [18]. Crystal data and information on data collection and refinement can be seen in Table 1.

CCDC 1040871 (**2**) and 1040872 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1

Crystal data, data collection and refinement for **2** and **3**

Crystal data	2	3
Formula	$\text{C}_{24}\text{H}_{32}\text{Cl}_2\text{CuN}_8\text{O}_4$	$\text{C}_{26}\text{H}_{36}\text{CuN}_8\text{O}_7$
M_r	631.02	636.17
Cell setting, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
a (Å)	7.5137(3)	13.9966(2)
b (Å)	9.5313(8)	13.2851(2)
c (Å)	10.5036(7)	16.2404(2)
α (°)	67.004(7)	90
β (°)	83.527(4)	110.312(2)
γ (°)	84.819(5)	90
V (Å ³)	687.15(8)	2832.06(8)
Z	1	4
D_x (Mg m ⁻³)	1.525	1.492
μ (mm ⁻¹)	3.308	1.602
$F(000)$	327	1332
Crystal form, colour	Prism, light blue	Prism, blue
Crystal size (mm ³)	0.10 × 0.20 × 0.25	0.15 × 0.25 × 0.30
Data collection method	ω scans	ω scans
Absorption correction	multi-scan	multi-scan
No. measured, independent and observed reflections	6132, 2771, 2512	30039, 5795, 4894
Observed reflections	$F^2 > 2.0 \sigma(F^2)$	$F^2 > 2.0 \sigma(F^2)$
R_{int}	0.0475	0.0243
θ range (°)	4.59–74.32	3.602–74.476
$h/k/l$	–7,9/–11,11/–13,13	–17,17/–16,16/–20,19
R (on F_{obs}), wR (on F_{obs}), S	0.0482, 0.1292, 1.048	0.0525, 0.1631, 1.097
No. contributing reflections	2771	5795
No. parameters/restraints	183/0	388/0
$(\Delta/\sigma)_{\text{max}}$, $(\Delta/\sigma)_{\text{ave}}$	0.007, 0.000	0.001, 0.000
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (eÅ ⁻³)	0.520, –0.999	1.361, –1.228

3. RESULTS AND DISCUSSION

The crystal structure of $[\text{Cu}(\text{HL})_2] \cdot 2\text{Cl}$ **2** consists of centrosymmetric homoleptic $[\text{Cu}(\text{HL})_2]^{2+}$ coordination cations, while the chlorido anions completes the net neutrality (Fig. 1). The ligand bis(3,5-dimethylpyrazol-1-yl)acetic acid (HL) is coordinated *via* carbonyl oxygen atom and two pyrazole nitrogen atoms, *i.e.* $\kappa^3\text{-N,N,O}$. The central Cu(II) ion lying at an inversion centre is thus six-coordinated in a shape of an elongated octahedron. The relevant distances and angles are given in Table 2. The carboxylic moiety bonds show that the coordinated O1 is closer to C2 than the noncoordinated O2 by 1.218(3) Å and 1.297(3) Å, respectively. The molecular structure mostly resembles to $[\text{Cu}(\text{HL})_2] \cdot 2(\text{HSO}_4)$ (**1**) with the distinctive carboxylic acid C–O bond lengths differentiation (1.206(4), 1.298(4) Å), though the Jahn-Teller axis O–Cu–O is there longer (Cu–O

2.540(2) Å (2.336(2) Å, **2**) [12]. The latter may probably be related to the H-bonding, as the chlorido anion in **2** is not involved in further H-network bridging, while the hydrogensulfate in **1** is.

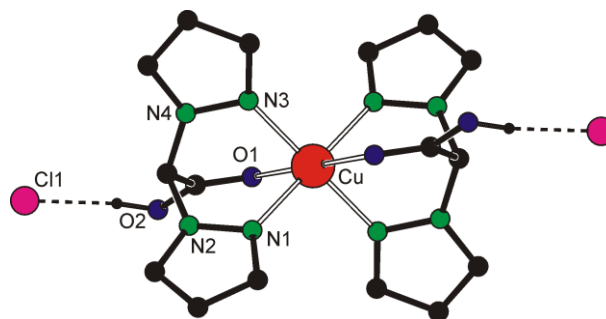


Fig. 1. A molecular structure of $[\text{Cu}(\text{HL})_2] \cdot 2\text{Cl}$ **2**. Only the carboxylate hydrogen atoms are visible. All other hydrogen atoms, along with the methyl carbon atoms, are omitted for clarity [18].

Table 2

The relevant bond distances and angles [\AA , $^\circ$] around the central Cu(II) ion in **2**

Cu1–O1	2.336(2)	N1–Cu1–O1	85.48(6)	
Cu1–N1	2.038(2)	N1–Cu1–N3	86.02(8)	
Cu1–N3	2.004(2)	N3–Cu1–O1	84.17(7)	
C2–O1	1.218(3)	C2–O2	1.297(3)	
D–H \cdots A	D–H [\AA]	H \cdots A [\AA]	D \cdots A [\AA]	<D–H–A [$^\circ$]
O2–H2 \cdots Cl1	0.84	2.03	2.8653(18)	172.1

Contrary to compound **2**, where the carboxylic group of the ligand HL remains undisturbed, in $[\text{Cu}(\text{L})_2] \cdot (\text{CH}_3\text{COOH}) \cdot (\text{H}_2\text{O})$ **3**, the ligand deprotonates showing anionic L^- bis(3,5-dimethylpyrazol-1-yl)acetate. As the ligand remains $\kappa^3\text{-N,N,O}$, the neutral coordination moiety $[\text{Cu}(\text{bdmpza})_2]$ with an elongated octahedral chromophore is obtained as well, while the acetic acid and water molecules extend the crystal structure via H-bonding (Fig. 2). The relevant distances and angles are listed in Table 3. The

major carboxylate difference between **3** and **2** is not at the Cu–O coordination bond, with almost the same value 2.311(2), 2.326(2) \AA (**3**) (2.336(2) \AA ; **2**), but to both C–O lengths. In **3**, these bonds are almost of the same lengths 1.239(3) – 1.243(3) \AA , thus the situation obviously differs with **1** and **2**, by 1.206(4), 1.298(4) \AA and 1.218(3), 1.297(3) \AA , respectively. These bond lengths of **3** thus clearly better resembles to $[\text{Cu}(\text{L})_2] \cdot 2(\text{H}_2\text{O})$ (**4**) with the carboxylate C–O 1.245(4), 1.241(4) and the Jahn-Teller axis with Cu–O 2.293(2) [11].

Table 3

The relevant bond distances and angles [\AA , $^\circ$] around central Cu(II) ion in **3**

Cu1–O1	2.311(2)	O1–Cu1–O3	177.98(6)	
Cu1–O3	2.326(2)	N1–Cu1–N7	178.36(7)	
Cu1–N1	2.021(2)	N3–Cu1–N5	177.79(7)	
Cu1–N3	2.055(2)	O1–Cu1–N1	85.41(6)	
Cu1–N5	2.038(2)	O1–Cu1–N3	85.33(7)	
Cu1–N7	2.034(2)	O1–Cu1–N5	94.79(6)	
C2–O1	1.242(3)	O1–Cu1–N7	93.88(7)	
C2–O2	1.242(3)	N1–Cu1–N3	85.16(8)	
C14–O3	1.243(3)	N3–Cu1–N7	96.27(8)	
C14–O4	1.239(3)	O3–Cu1–N1	96.61(6)	
C25–O5	1.261(7)	O3–Cu1–N3	94.69(7)	
C25–O6	1.231(7)	O3–Cu1–N5	85.27(6)	
N1–Cu1–N5	92.65(8)	O3–Cu1–N7	84.11(7)	
N5–Cu1–N7	85.93(8)			
D–H \cdots A	D–H [\AA]	H \cdots A [\AA]	D \cdots A [\AA]	<D–H–A [$^\circ$]
O7–H7W1 \cdots O5	0.79	1.96	2.736(6)	165
O7–H7W1 \cdots O6	0.79	2.40	3.026(6)	137
O7–H7W2 \cdots O2	0.96	1.81	2.759(3)	170

In between the adjacent coordination building blocks in **3**, one water molecule and one acetic acid molecule are present. By the assistance of hydrogen bonds, pseudo-chains (Fig. 2) are formed. Herein, the main difference is seen between $[\text{Cu}(\text{L})_2] \cdot (\text{CH}_3\text{COOH}) \cdot (\text{H}_2\text{O})$ **3** and $[\text{Cu}(\text{L})_2] \cdot 2(\text{H}_2\text{O})$ **4**, as acetic acid replaces one water molecule. A decision to distinct between the double and the single bond (HL) and the intermediate (both equal lengths, each partly with double and partly with

single bond character in L^-) within the carboxylic/carboxylate moieties, and simultaneously a position of the acidic proton, either at acetic acid or bis(3,5-dimethylpyrazol-1-yl)acetic acid, is crystallographically based mainly on their C–O lengths. At **3**, larger difference in acetic acid 1.231(7)/1.261(7) \AA prevails over shorter one in bis(3,5-dimethylpyrazol-1-yl)acetate 1.239(3)–1.243(3) \AA . The latter is thus determined anionic and the acetic acid remains molecular as initially.

The Figure 2 shows the hydrogen bonding network of the compound **3**. The O4...O7 short distance 2.843(2) Å (the non-coordinated carboxylate oxygen atoms and the water molecule) clearly suggests a proton between them. However, we have not found any better refinement solution, as the presented one, to support the option of the O4...O7 H-bond. Possibly, an H-bonding potential

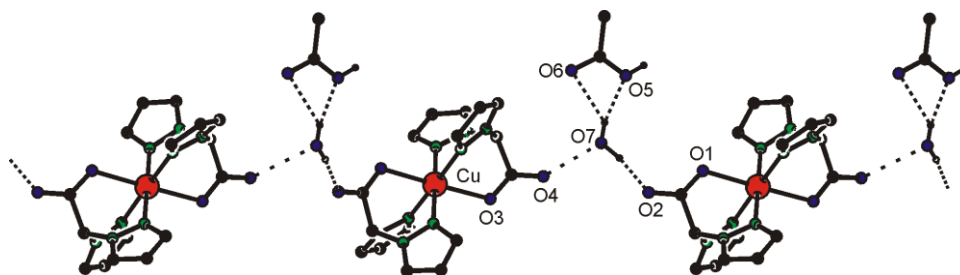


Fig. 2. Pseudo-chains in $[\text{Cu}(\text{L})_2] \cdot (\text{CH}_3\text{COOH}) \cdot (\text{H}_2\text{O})$ **3** formed by the assistance of hydrogen bonding. Only the water and acetic acid hydrogen atoms are visible. All other hydrogen atoms, along with the methyl carbon atoms, are omitted for clarity. For a close O4...O7 contact 2.843(2) Å, see text [18].

3.3. IR spectroscopy

The most representative IR spectrum section for **1–4** is at the 1800–1500 cm^{-1} area, as the potential origins for such energy vibrations are clearly limited, this being ‘the double/single bond region’ for C–O, C–C and C–N bonds, *e. g.* carboxylates, benzoates and pyrazoles [4, 5]. The characteristic pyrazole IR band at 1550 cm^{-1} is seen in Figure 3, where only for the free acetic acid no signal is found. The free ligand (bis(3,5-dimethylpyrazol-1-yl)acetic acid) carboxylic acid moiety with its C=O double bond position at 1740 cm^{-1} is most similar with 1702 cm^{-1} in **1** (Fig. 3) [12]. The corresponding free ligand carboxylic C–O(H) single bond stretching bands are at 1252, 1219 cm^{-1} , thus giving a difference $\Delta = [v_{\text{as}}(\text{C}=\text{O}) - v_{\text{as}}(\text{C}-\text{O})] \sim 400 \text{ cm}^{-1}$ being indicative for a presence of both, the single and the double carboxylic C–O bonds of the acidic –COOH ligand form. A deprotonation of the carboxylic acid, giving a carboxylate anion, shows also two principal bands within the IR spectrum, namely for the asymmetric and the symmetric carboxylate stretching, together enabling similar difference calculation $\Delta = [v_{\text{as}}(\text{OOC}) - v_{\text{as}}(\text{OOC})]$ [19], though it is smaller than for the free (acidic) ligand. The asymmetric carboxylate band is usually expected at 1600 cm^{-1} , while the symmetric carboxylate band at 1400 cm^{-1} . A monodentate carboxylate anion is thus more similar to the free ligand, while for the bidentate (chelate or bridging), this difference is even shorter. The other compound among **2–4**, that most resembles the energy of the free ligand C=O band, is **2** with a dominant

of the mother liquid species incorporated in a crystal structure of the solids as non-coordinated counter ions or neutral molecules, cannot be applied in more than one direction (restrictions of the crystal packing). The compounds thus can precipitate, but a kind of disorder outside coordination sphere remains.

split band at 1697, 1665 cm^{-1} [11, 12]. On the other hand, the anionic asymmetric carboxylate stretching IR band ($v_{\text{as}}(\text{COO}^-)$) for **3** (1642 cm^{-1}) and **4** (1635 cm^{-1}) is thus found at lower energy region. The additional band within this region for **1–4** is seen only for **3** at 1716 cm^{-1} , and is assigned to the network neutral acetic acid C=O double bond. Despite the acetic acid is most commonly found within compounds deprotonated as acetate, in this case ($[\text{Cu}(\text{L})_2] \cdot (\text{CH}_3\text{COOH}) \cdot (\text{H}_2\text{O})$ **3**), the net neutrality requires, either the coordinated L or acetic acid needs to be in the neutral acidic or anionic salt form. Within this competition, the acetic acid remains neutral. A comparison of the title compounds IR spectra, along with acetic acid and HL (Fig. 3), clearly shows obvious similarities of **3** $[\text{Cu}(\text{L})_2] \cdot (\text{CH}_3\text{COOH}) \cdot (\text{H}_2\text{O})$ and **4** $[\text{Cu}(\text{L})_2] \cdot 2(\text{H}_2\text{O})$ (with addition of acetic acid) than of **3** and **1** ($[\text{Cu}(\text{HL})_2] \cdot 2(\text{HSO}_4)$) or **2** ($[\text{Cu}(\text{HL})_2] \cdot 2\text{Cl}$) (with addition of HL). Such a distinction between the molecular (HL) / ionic (L^-) is clearly in accordance with the XRD determined C–O distances, as they differ in acetic acid, while are almost the same for L^- . On the other hand, the hydrogen atoms positions within the determined structures are not always unambiguously positioned. As the XRD single crystals analysis final refinement values are practically hydrogen atom independent (electron density is essential for the XRD scattering), thus the XRD C–O data are more reliable than O–H.

Herein we are not focused to the other sections of the IR spectra as they are not as indicative as the described one.

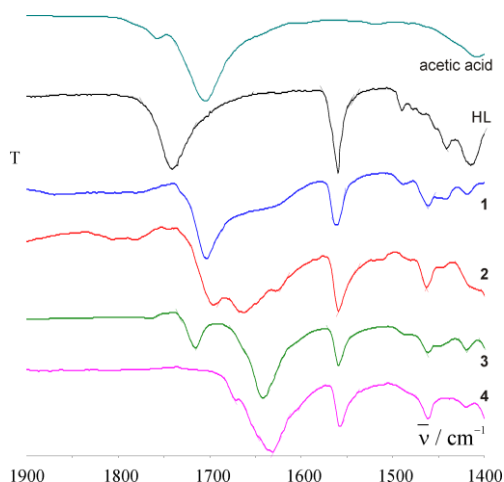


Fig. 3. The IR spectra of the free acetic acid, the tridentate acidic ligand HL and **1–4**.

4. CONCLUSIONS

Four copper(II) coordination compounds with the tridentate κ^3 -*N,N,O* bisligand ($L = \text{bis}(3,5\text{-dimethylpyrazol-1-yl})\text{acetate}$ or its molecular acid form HL) were analyzed by crystallographic data and IR spectroscopy. The XRD single crystal structural analysis reveals neutral ligand form in $[\text{Cu}(\text{HL})_2] \cdot 2(\text{HSO}_4)$ (**1**) and $[\text{Cu}(\text{HL})_2] \cdot 2\text{Cl}$ (**2**), while ionic in $[\text{Cu}(\text{L})_2] \cdot (\text{CH}_3\text{COOH}) \cdot (\text{H}_2\text{O})$ (**3**), and $[\text{Cu}(\text{L})_2] \cdot 2(\text{H}_2\text{O})$ (**4**). A bond length difference at the two carboxylate C–O bonds is in agreement with the single(longer)/double(shorter) character of both bonds for the neutral carboxylic HL in **1** and **2**, and the same character of both bonds for the carboxylate anionic L^- in **3** and **4**. This lengths differentiation is in agreement with the IR spectra difference for the molecular (HL) / ionic (L^-) at the 1700 cm^{-1} region carboxylic / carboxylate band.

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