

1,1'-METHYLENEDIPYRIDINIUM TETRANITRATOCUPRATE(II): A RARE EXAMPLE OF ORGANIC-INORGANIC HYBRID SALT OF FORM [ORGANIC DICATION][Cu(NO₃)₄], SYNTHESIS, SPECTROSCOPIC CHARACTERIZATIONS AND MOLECULAR STRUCTURAL INVESTIGATIONS

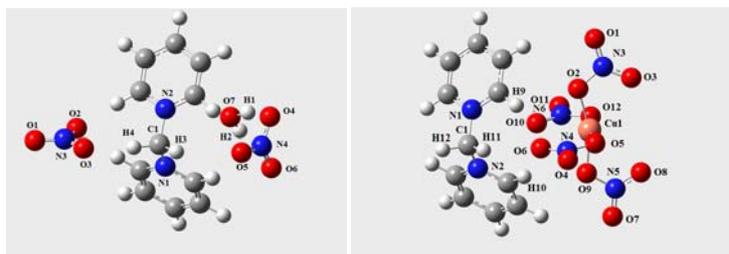
Mahmoud M. AL-KTAIFANI^{*a} and Mohammad K. SABRA^b

^aDepartment of Radioisotopes, Atomic Energy Commission, P.O. Box 6091, Damascus, Syrian Arab Republic

^bDepartment of Physics, Atomic Energy Commission, P.O. Box 6091, Damascus, Syrian Arab Republic

Received April 24, 2018

The ionic compound [(C₅H₅N)₂CH₂](NO₃)₂·H₂O and its novel copper complex [(C₅H₅N)₂CH₂][Cu(NO₃)₄] were synthesized, isolated as pure salts and characterized by multinuclear NMR, FTIR spectroscopies and elemental analysis. Their molecular structures and IR absorption frequencies were also investigated by *ab initio* quantum chemical calculations using Hartree-Fock theory and different basis sets. The calculated structures of [(C₅H₅N)₂CH₂](NO₃)₂·H₂O and [(C₅H₅N)₂CH₂][Cu(NO₃)₄], each consisting of discrete organic dication [(C₅H₅N)₂CH₂]²⁺ and two NO₃⁻ ions or inorganic anion [Cu(NO₃)₄]²⁻ respectively. For the [(C₅H₅N)₂CH₂][Cu(NO₃)₄], the Cu centre has pseudo square planar geometry with Cu–O bond lengths lie in the range (1.819–1.835 Å). The calculated IR characteristic absorption bands for both salts are found to be also in good agreement with those experimentally observed.



INTRODUCTION

Designing of new organic-inorganic hybrid ionic materials is of current interest in materials science.^{1,2} Rich-oxygen compounds have potential applications as oxidizers in Pyrotechnic field. The essential ingredients of a pyrotechnic device are the oxidizer and the reductant. Tetranitratocuprate containing compounds are common oxidisers in pyrotechnic applications.³ Although two organic-inorganic hybrid salts of [Cu(NO₃)₄] anions with monovalent organic cations have been reported and structurally characterized, specifically (C₆H₅CH₂NH₃)₄[Cu(NO₃)₄](NO₃)₂,⁴ and (CH₃NH₃)₂[Cu(NO₃)₄].⁵ To the best of our

knowledge there is no report concerning organic-inorganic hybrid compounds of the [Cu(NO₃)₄] anions and the organic dication [(C₅H₅N)₂CH₂]²⁺. Very recently, in view of the potential affinity of 1,1'-methylenedipyridinium [(C₅H₅N)₂CH₂]²⁺ to form organic-inorganic hybrid salts by treatment with appropriate halide metal, a series of ionic compounds of 1,1'-methylenedipyridinium with halo-metal anion have been reported [(C₅H₅N)₂CH₂][MCl₄] (M = Zn, Cd or Cu),^{6,7} [(C₅H₅N)₂CH₂][AuCl₄]₂,⁷ and [(C₅H₅N)₂CH₂][PtCl_n] (n = 4 or 6).⁸ Since we are interested in expanding the hybrid salts of [(C₅H₅N)₂CH₂]²⁺ to include nitro-derivatives, the syntheses and spectroscopic

* Corresponding author: cscientific3@aec.org.sy

characterizations, and molecular structures of $[(C_5H_5N)_2CH_2](NO_3)_2 \cdot H_2O$ and its copper complex $[(C_5H_5N)_2CH_2][Cu(NO_3)_4]$ are the subject of this work.

RESULTS AND DISCUSSION

The available ionic compound $[(C_5H_5N)_2CH_2]Cl_2 \cdot H_2O$ was readily converted into 1,1'-methylenedipyridinium dinitrate monohydrate $[(C_5H_5N)_2CH_2](NO_3)_2 \cdot H_2O$ (**1**) by substitution reaction utilizing $AgNO_3$. The new sky blue hybrid salt $[(C_5H_5N)_2CH_2][Cu(NO_3)_4]$ (**2**) was obtained by treatment of $[(C_5H_5N)_2CH_2](NO_3)_2 \cdot H_2O$ (**1**) with $Cu(NO_3)_2$ in an aqueous solution. It is worth mentioning that (**2**) is a rare example of organic-inorganic hybrid salt containing $[Cu(NO_3)_4]^{2-}$ anion of type [organic dication] $[Cu(NO_3)_4]$. Both (**1**) and (**2**) were isolated as purely salts and fully characterized by multinuclear NMR, FTIR spectroscopy and elemental analyses. The molecular structures of (**1**) and (**2**) are shown in Figure 1. Products (**1**) and (**2**) are both water

soluble, each is very insoluble in familiar organic solvents, but each has a good solubility in dimethyl sulfoxide (DMSO). Their composition and properties are summarized in Table 1.

NMR spectroscopic details of (**1**) and (**2**)

Since the dication $[(C_5H_5N)_2CH_2]^{2+}$ is the same for both $[(C_5H_5N)_2CH_2](NO_3)_2 \cdot H_2O$ (**1**) and $[(C_5H_5N)_2CH_2][Cu(NO_3)_4]$ (**2**), as expected the 1H and $^{13}C\{^1H\}$ NMR spectra for (**1**) and (**2**) are very similar, and they have the same features to their corresponding ones of the related organic-inorganic hybrid salts $[(C_5H_5N)_2CH_2][MCl_4]$ ($M = Zn, Cd$ or Cu),^{6,7} $[(C_5H_5N)_2CH_2][AuCl_4]_2$ ⁷ and the parent molecule $[(C_5H_5N)_2CH_2]Cl_2$.⁹ The 1H and $^{13}C\{^1H\}$ NMR spectra of (**1**) and (**2**), each showed the expected four resonances corresponding to four different proton environments and four singlets of four environmentally different C centres respectively. The NMR spectroscopic data of (**1**) and (**2**) are presented in Table 2.

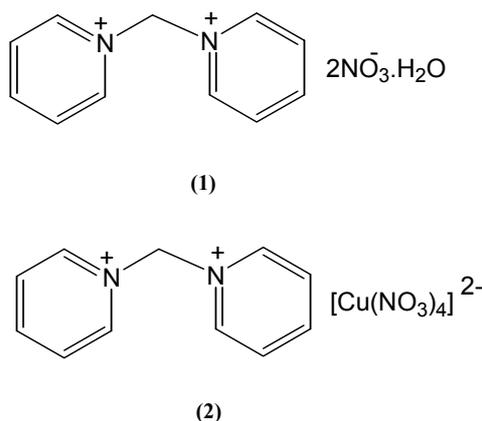


Fig. 1 – Molecular structures of (**1**) and (**2**).

Table 1

Characterization data of (**1**) and (**2**)

Compound	Formula	M_r	$w_i(\text{calc.})/\%$			Yield	M.p.
			C	H	N		
(1)	$C_{11}H_{14}N_4O_7$	314.25	42.04	4.49	17.82	70	205
			42.09	4.62	18.36		
(2)	$C_{11}H_{12}O_{12}N_6Cu$	483.79	27.31	2.50	17.37	65	195
			27.88	1.71	16.45		

Table 2

The NMR spectroscopic data of (**1**) and (**2**)

Compound	Spectral data
(1)	1H NMR (DMSO- d_6), δ : 7.26 (s, 2H, CH ₂), 8.33 (m, 4H, py), 8.81 (m, 2H, py), 9.46 (m, 4H, py) $^{13}C\{^1H\}$ NMR (DMSO- d_6), δ : 77.61 (CH ₂), 129.18 (Py), 146.34 (Py), 149.24 (Py)
(2)	1H NMR (DMSO- d_6), δ : 7.26 (s, 2H, CH ₂), 8.31 (m, 4H, py), 8.78 (m, 2H, py), 9.44 (m, 4H, py). $^{13}C\{^1H\}$ NMR (DMSO- d_6), δ : 77.58 (CH ₂), 129.15 (Py), 146.32 (Py), 149.21 (Py)

Infrared spectroscopic details of (1) and (2)

The two FTIR spectra of $[(C_5H_5N)_2CH_2](NO_3)_2 \cdot H_2O$ (**1**) and $[(C_5H_5N)_2CH_2][Cu(NO_3)_4]$ (**2**) are fairly similar (Figure 2), but the slightly considerable variations in the intra-molecular environment around each group in the two compounds give rise to informative different shifts and broadening of absorption bands. To make the comparison of the two spectra more obvious, the spectra are subdivided into different regions. The FTIR spectra of (**1**) and (**2**) in the range $400\text{--}600\text{ cm}^{-1}$ are depicted in Figure 3.

By comparing the two spectra in this part of FTIR fingerprint region, they look almost similar except a distinctive absorption band at 503 cm^{-1} . This band is very informative and readily attributed to the symmetric stretching mode of the Cu–O bond in the complex.^{10,11}

Figure 4 shows the FTIR spectra of (**1**) and (**2**) in the region $1000\text{--}2000\text{ cm}^{-1}$. It is noticeable the presence of the characteristic absorption band at 1581 cm^{-1} and also the broadening of main stretching band of NO_3^- group (centred at 1383 cm^{-1}) in the spectrum of (**1**). The band at 1581 cm^{-1} is readily assigned to the (O–H) bending vibrations

for H_2O molecules of (**1**),¹² while the band broadness might be attributed to inter-molecular hydrogen bonding that takes place between H_2O molecules and NO_3^- groups.¹³ As the H_2O molecules are involved in the crystal lattice structure of (**1**), the O–H stretching band around 3450 cm^{-1} is also splitting into distinctive three absorption bands (Figure 2) corresponding to different donor (H_2O) and acceptor (NO_3^-) hydrogen bonds.^{13,14}

Ab initio calculation

Ab initio quantum chemical methods are used to find the optimized geometries of the ground state energies and infrared spectra of both (**1**) and (**2**). Hartree–Fock level of theory and different basis sets (from STO up DZ), as implemented in the Firefly package (A. Granovsky; <http://classic.chem.msu.su/gran/firefly/index.html>), are employed to perform the calculations. This package is partially based on the GAMESS (US) source code.¹⁵ The structures of all starting molecules are built using the GABEDIT code,¹⁶ a graphical user interface for computational chemistry software.

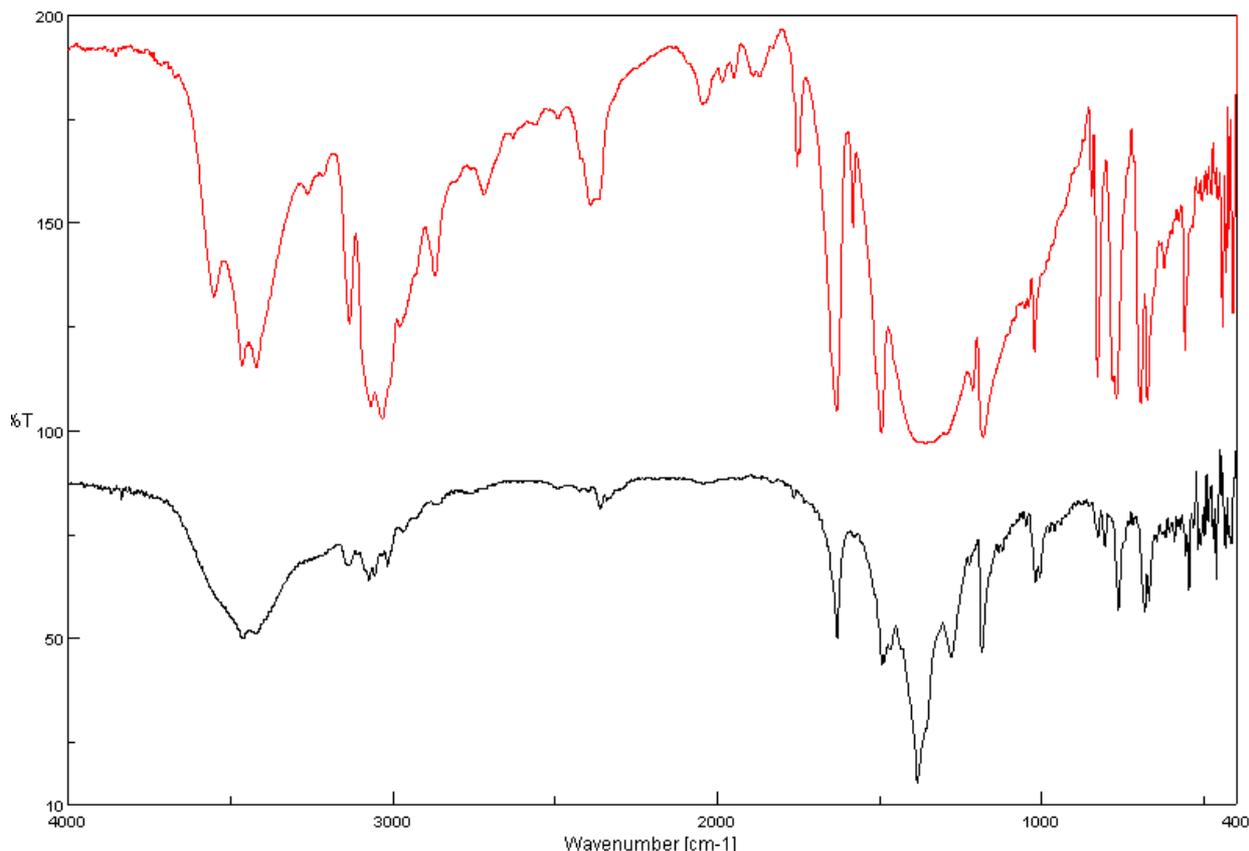


Fig. 2 – Experimental FTIR spectra of (**1**) (top) and (**2**) (bottom) in the range of $400\text{--}4000\text{ cm}^{-1}$.

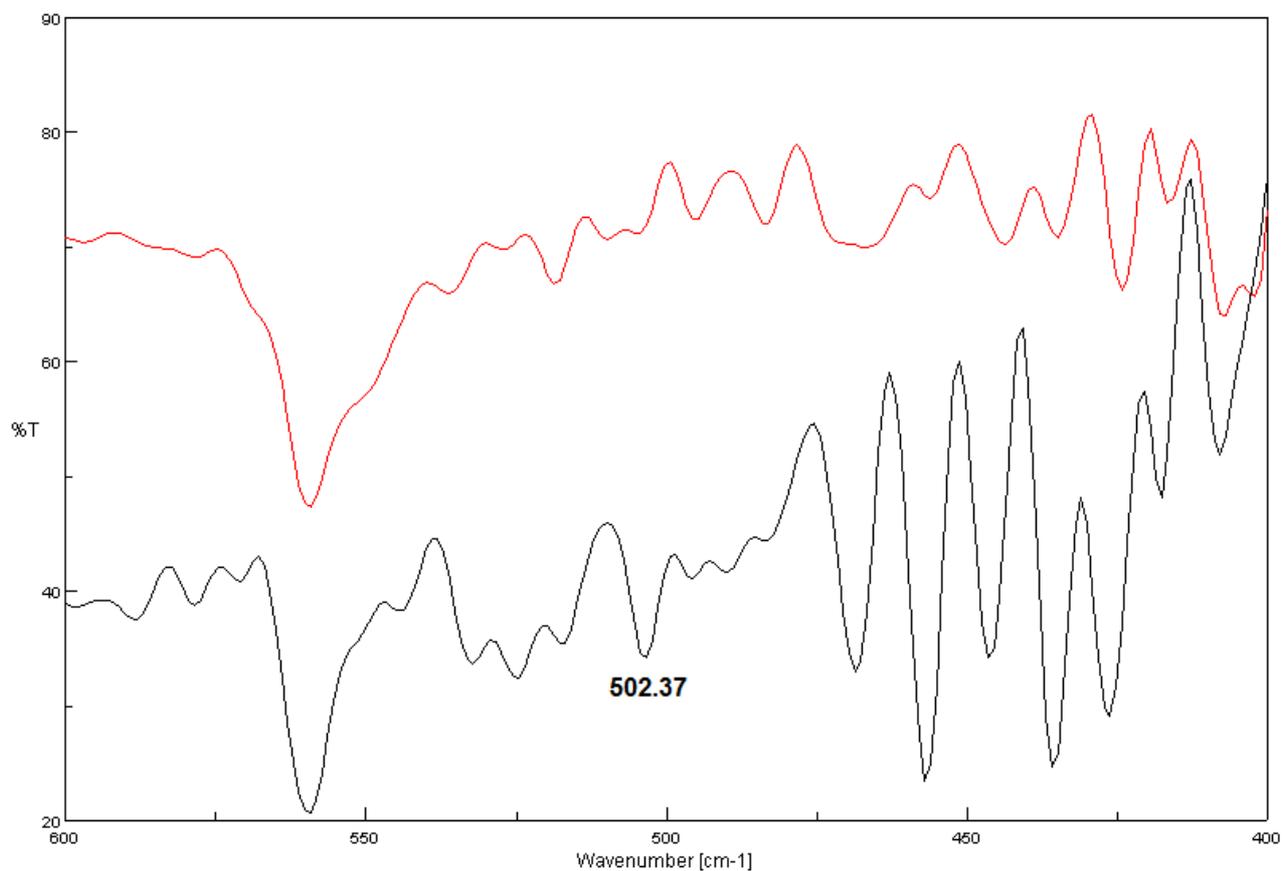


Fig. 3 – Experimental FTIR spectra of (1) (top) and (2) (bottom) in the range of 400-600 cm^{-1} .

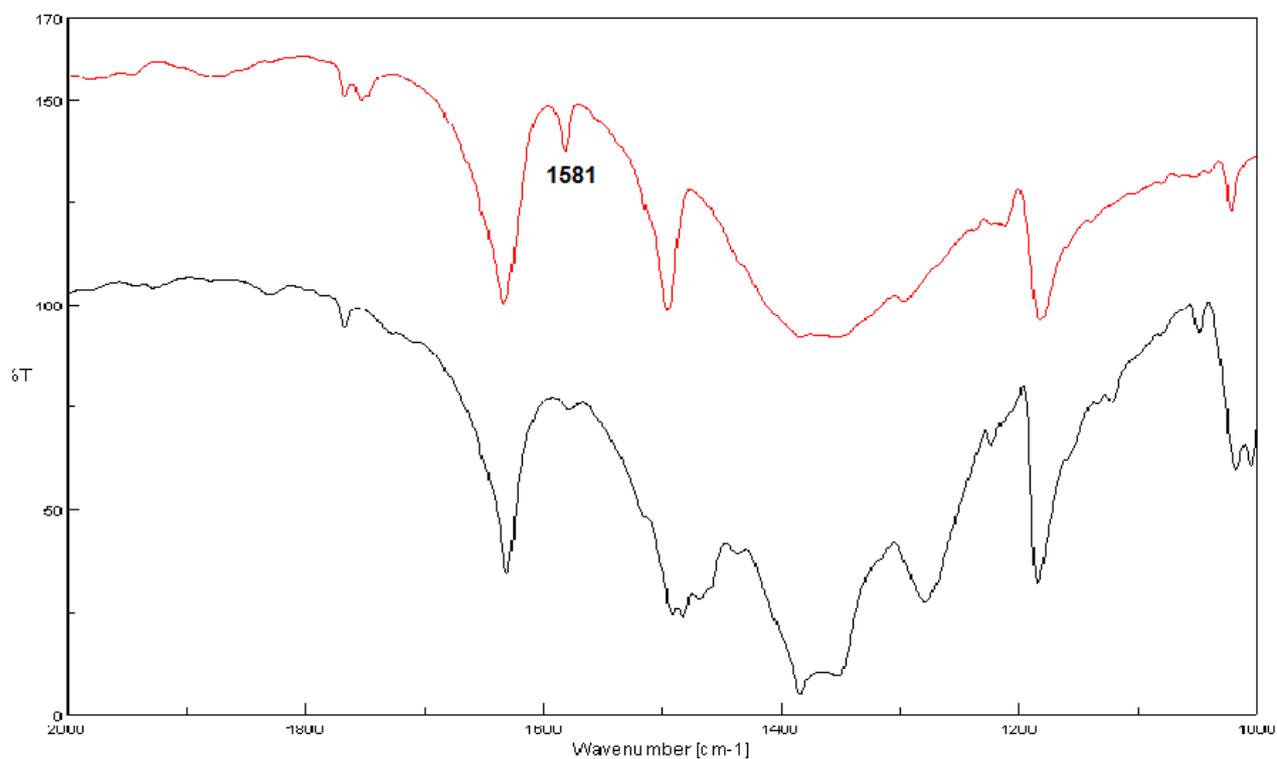


Fig. 4 – Experimental FTIR spectra of (1) (top) and (2) (bottom) in the range of 1000-2000 cm^{-1} .

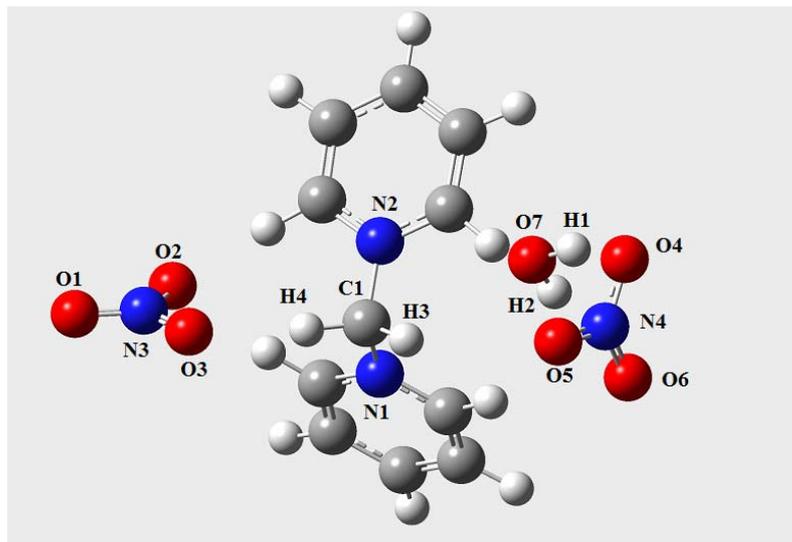


Fig. 5 – The optimized molecular structure of $[(C_5H_5N)_2CH_2](NO_3)_2 \cdot H_2O$ (**1**).

Table 3

Optimized geometrical parameters for the lowest energy structure of (**1**)

Bond	Bond distance (Å)	Bond	Bond angle (°)
N3–O1	1.194	O1–N3–O2	120.7
N3–O2	1.247	O1–N3–O3	121.5
N3–O3	1.235	O2–N3–O3	117.8
N4–O4	1.225	O4–N4–O5	118.9
N4–O5	1.240	O4–N4–O6	121.2
N4–O6	1.210	O5–N4–O6	119.8
C1–N1	1.475	N1–C1–N2	112.3
C1–N2	1.473	H3–C1–H4	112.1
C1–H3	1.075	H1–O7–H2	104.7
C1–H4	1.075		
O7–H1	0.950		
O7–H2	0.943		
O4–H1	2.029		

The geometrical structure of (**1**), which is optimized using Hartree-Fock level of theory and 6311 basis, is shown in Fig. 5, where the dication $[(C_5H_5N)_2CH_2]^{2+}$ is sited between nitrate anions. The N–O bond distances lie within 1.19–1.24 Å and the O–N–O angles within 117.8 – 121.5° (Table 3). Both are consistent with the average N–O bond distance and planarity of nitrate ions respectively.¹⁷ The mean bond distances and angles of the dication $[(C_5H_5N)_2CH_2]^{2+}$ are also comparable with their corresponding ones of related structurally characterized salt $[(C_5H_5N)_2CH_2]Cl_2 \cdot H_2O$.¹⁸ The water molecule lies between the dication and one NO_3^- group with average H–O bond distance of 0.94 Å and H–O–H bond angle of 104.7°. The relatively short (O7–H1 ...O4) of 2.03 Å indicates a hydrogen bond between the water molecule and the mentioned NO_3^- group.

The optimized molecular structure of $[(C_5H_5N)_2CH_2][Cu(NO_3)_4]$ (**2**) is shown in Fig. 6 for LANL2DZ basis set. It contains distinctive separated organic dication $[(C_5H_5N)_2CH_2]^{2+}$ and

inorganic $[Cu(NO_3)_4]^{2-}$. The Cu(II) centre within the $[Cu(NO_3)_4]^{2-}$ is coordinated by four NO_3^- ions and located in a pseudo square planar environment. In this distorted square planar arrangement, the equatorial positions are occupied by the four O atoms with Cu–O_i (i = 2, 5, 9, 12) bond distance lying in the range (1.819–1.835 Å) (Table 4). Although they are located almost at right angles ($\angle O_2-Cu_1-O_{12} = \angle O_{12}-Cu_1-O_9 = 90.9^\circ$, $\angle O_9-Cu_1-O_5 = \angle O_2-Cu_1-O_2 = 90.5^\circ$), but not in the same plane $O_2-Cu_1-O_9 = 161.4^\circ$, $O_{12}-Cu_1-O_5 = 171.8^\circ$). For the other eight O atoms of NO_3^- groups in the calculated structure, the nearest O atom to the Cu centre has a distance of 2.684 Å. This distance is longer than the sum of the ionic radii of Cu (0.92 Å) and O (1.26 Å)¹⁹ to give a relatively considerable interaction. The same feature of distorted square planar environment and similar average (Cu–O) bond lengths are reported for the structurally related complex $(C_6H_5CH_2NH_3)_4[Cu(NO_3)_4](NO_3)_2$.⁴

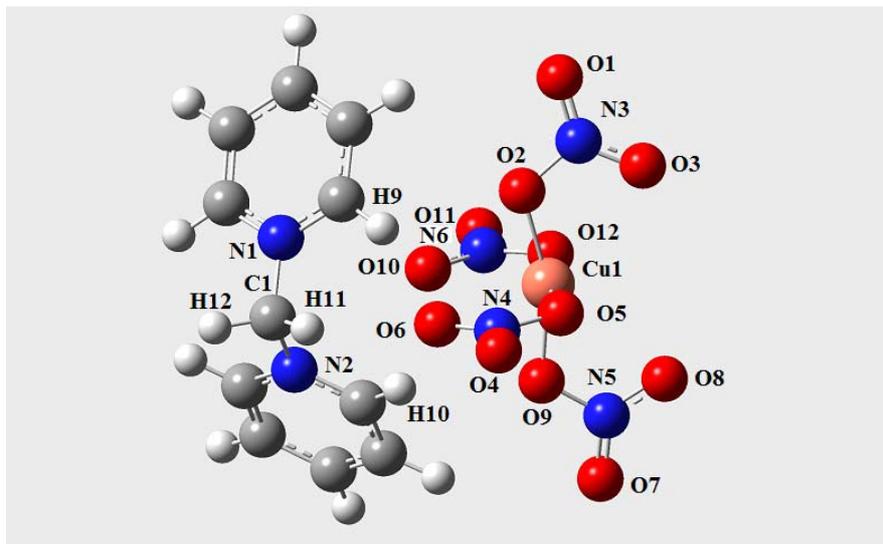


Fig. 6 – The optimized molecular structure of (2).

Table 4

Optimized geometrical parameters of the lowest energies structure of (2)

Bond	Bond lengths (Å)	Bond	Bond angles (°)
Cu1–O2	1.819	O2–Cu1–O5	90.5
Cu1–O5	1.832	O2–Cu1–O12	90.9
Cu1–O9	1.819	O5–Cu1–O9	90.5
Cu1–O12	1.835	O9–Cu1–O12	90.9
Cu1–O1	3.841	O2–Cu1–O9	161.4
Cu1–O3	2.758	O12–Cu1–O5	171.8
Cu1–O7	3.842	Cu1–O2–N3	116.9
Cu1–O8	2.765	Cu1–O9–N5	117.1
Cu1–O4	3.815	Cu1–O12–N5	114.4
Cu1–O6	2.684	Cu1–O5–N4	114.4
Cu1–O11	3.814	O1–N3–O2	116.1
Cu1–O10	2.675	O1–N3–O3	128.4
O1–N3	1.220	O2–N3–O3	115.5
O2–N3	1.355	O4–N4–O5	120.0
O3–N3	1.238	O4–N4–O6	125.1
O4–N4	1.198	O5–N4–O6	114.9
O5–N4	1.330	O7–N5–O8	128.4
O6–N4	1.288	O7–N5–O9	116.1
O7–N5	1.221	O8–N5–O9	115.5
O8–N5	1.238	O10–N6–O11	125.3
O9–N5	1.355	O10–N6–O12	115.4
O10–N6	1.276	O11–N6–O12	119.3
O11–N6	1.204	N1–C1–N2	114.3
O12–N6	1.330	H11–C1–H12	109.2
O10–H9	2.096		
O6–H10	2.099		
C1–H11	1.075		
C1–H12	1.077		

The IR absorption frequencies for the optimized geometries of (1) and (2) (see appendices A and B respectively) were computed at the same levels of theory from analytic second derivatives and verified to be real. We do not use any scaling factor to correct the calculated frequencies (Table 5). For compound (1), the C=N and C–H (CH₂) frequencies are identical to the experimental ones and the frequencies that referred to NO₃ group and C–N are in good

agreement with corresponding experimental ones within ± 0.05 . While for (2), we find that the calculated Cu–O stretching frequency (503 cm⁻¹) is identical to the experimental one. The other important frequencies that referred to (NO₃) group and (C=N) are found to be very close to the experimental ones into (1638 cm⁻¹) and (1383 cm⁻¹) respectively.

Table 5

Experimental and calculated IR absorption frequencies (cm^{-1}) of (1) and (2)

		$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{CH}_2)$	$\nu(\text{NO}_3)$	$\nu(\text{Cu}-\text{O})$
		(str)	(str)	(def)	(str)	(str)
(1)	Exp	1633	1183	1495 782	1383	-
	Theoretical calculations	1633	1244	1494 782	1408.68	-
(2)		$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{CH}_2)$	$\nu(\text{NO}_3)$	$\nu(\text{Cu}-\text{O})$
		(str)	(str)	(def)	(str)	(str)
(2)	Exp	1630	1185	1491 680	1384	502
	Theoretical calculations	1638	1103	1473 780	1383	503

It is worth mentioning that, many attempts were carried out to confirm the molecular structures of **1** and **2** using powder X-ray diffraction studies. Although the expected overall molecular structures of **1** and **2** were established, unfortunately they could not satisfactorily be refined owing to disorder of some bonds and angles within both structures.

EXPERIMENTAL

Materials

All procedures were conducted in air with reagent grade solvents. AgNO_3 (PROLABO, EEC) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (BDH, Germany) are commercial samples and they are used as received. $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ was prepared according to literature method.⁹ ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were acquired on a Bruker Bio spin 400 spectrometer (Switzerland). FTIR spectra were recorded on Thermo-Nicolet 6700 FT-IR spectrometer taken as KBr disk with a resolution of 4 cm^{-1} . Microanalysis was performed using EURO EA (Italy).

Synthesis of 1,1'-methylenedipyridinium dinitrate monohydrate (1)

A solution of $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (0.20 g, 0.76 mmol) in H_2O (3 ml) was treated with a solution of AgNO_3 (0.26 g, 1.52 mmol) in H_2O (3 mL) with rapid stirring at ambient temperature. A precipitation of AgCl was immediately observed. The resulting mixture was left stirring for 3 h and then filtered to exclude insoluble AgCl . After that, solvent was removed *in vacuum* to afford quantitatively product (**1**), which was washed with EtOH to give a white powder (170 mg, yield 70%).

Synthesis of 1,1'-methylenedipyridinium tetranitratocuprate (2)

A solution of $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (0.15 g, 0.48 mmol) in H_2O (3 ml) was added to a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.12 g, 0.48 mmol) in H_2O (3 mL), the resulting solution was heated to $60\text{ }^\circ\text{C}$ overnight. The solvent was then removed *in vacuum* to afford quantitatively product (**2**), which was washed with EtOH to give a pale blue powder (150 mg, yield 65%).

CONCLUSIONS

The ionic compound $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, which has a potential propensity to form organic-inorganic hybrid ionic compounds of type $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2][\text{M}(\text{NO}_3)_4]$ by treatment with the appropriate $\text{M}(\text{NO}_3)_2$, was prepared. Its novel copper salt $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2][\text{Cu}(\text{NO}_3)_4]$, which is a remarkable case of the organic-inorganic hybrid salt of form $[(\text{organic dication})][\text{Cu}(\text{NO}_3)_4]$, was synthesized. Both salts were characterized by NMR and FTIR spectroscopies. The molecular structures of both salts were optimized by *ab initio* quantum chemical calculations using Hartree-Fock theory and different basis sets. Then the IR frequencies were obtained at the same level of theories for both salts. We found that the characteristic frequencies of each salt in good agreement with the corresponding experimental ones.

Appendix A

List of the xyz coordinates of the optimized $[(\text{C}_5\text{H}_5\text{N})_2\text{CH}_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ at HF and 6311 basis set level of theory.

Atom	x	y	z
C	1.21728500	-1.67193000	0.46752400
C	1.05609800	-2.80648100	1.21680000
C	-0.15813200	-3.48003900	1.17445200
C	-1.18246500	-2.99787400	0.38030900
C	-0.97466100	-1.85213800	-0.34812100
N	0.20220900	-1.21163200	-0.28993600
H	-0.29759900	-4.37560100	1.75244200
H	2.14272800	-1.12160300	0.44858500

Appendix A (continued)

H	1.87724500	-3.15527300	1.81172300
H	-2.13784300	-3.47962100	0.31404700
H	-1.72745100	-1.43927200	-0.99110300
C	1.24110000	1.72122200	0.40083400
C	1.08850300	2.87388800	1.12262900
C	-0.13022700	3.53997400	1.08629300
C	-1.16515800	3.03463700	0.32165100
C	-0.96631900	1.87164400	-0.38045500
N	0.21439400	1.23704800	-0.32596000
H	-0.26536000	4.44675900	1.64727400
H	2.16669400	1.17125900	0.38300600
H	1.91771100	3.24027600	1.69535300
H	-2.12473700	3.50900300	0.26611600
H	-1.73295800	1.43443100	-0.99146800
C	0.41178300	0.00113300	-1.10296300
H	1.42797300	-0.01128600	-1.46335800
H	-0.30202500	-0.00800400	-1.90734800
N	4.25507100	-0.04847000	-0.53369000
O	5.43238800	-0.06339600	-0.72817100
O	3.80175200	0.00859400	0.62650200
O	3.44676300	-0.08948800	-1.46693600
N	-3.67815400	-0.05439500	-0.88487500
O	-3.98690000	0.98895900	-0.32242800
O	-2.90827400	-0.00715900	-1.85552800
O	-4.06271200	-1.12588800	-0.47428100
O	-2.32134100	0.15991700	1.90453800
H	-2.69358100	-0.57959300	2.35668400
H	-3.04569700	0.53414600	1.41600700

Appendix B

List of the xyz coordinates of the optimized [(C₅H₅N)₂CH₂][Cu(NO₃)₄]
at HF and LanL2dz basis set level of theory

Atom	x	y	z
C	-1.62503383	1.93824955	0.69052886
C	-1.53372209	3.12536445	-0.02034399
C	-2.66256309	3.61461088	-0.66235494
C	-3.87615324	2.90644194	-0.56878876
C	-3.91400639	1.74609734	0.15615575
N	-2.79458654	1.26433703	0.77243397
H	-2.61542080	4.52722076	-1.21997586
H	-0.78157759	1.52482292	1.19411698
H	-0.59104335	3.62567009	-0.06646048
H	-4.76528749	3.26543941	-1.04033606
H	-4.82082375	1.19641600	0.28082607
C	-1.65523536	-1.91299048	0.67377529
C	-1.58456852	-3.10018327	-0.03939341
C	-2.72689710	-3.57906730	-0.66521492
C	-3.93314804	-2.86107211	-0.55258095
C	-3.95040388	-1.70102463	0.17359374
N	-2.81744340	-1.22869897	0.77257960
H	-2.69579135	-4.49153353	-1.22419650
H	-0.80132480	-1.50850351	1.16665717
H	-0.64722079	-3.60910402	-0.09858747
H	-4.83240001	-3.21260525	-1.01038599
H	-4.85081405	-1.14441353	0.31355394
C	-2.87143825	0.01835467	1.57473881
H	-2.05173524	0.01102195	2.26961598
H	-3.79925322	0.02672969	2.12197761
Cu	1.77643411	-0.00998296	-0.12078274
N	2.53886398	2.57826189	-0.42874869
O	2.31836344	3.77828142	-0.44386368
O	1.51146287	1.78774827	-0.03553063
O	3.58208512	1.98374668	-0.73217595

Appendix A (continued)

N	0.04694103	0.00978386	-2.15743173
O	-0.33178949	0.01654181	-3.30054381
O	1.35338173	-0.00297253	-1.90345118
O	-0.71009256	0.01388693	-1.13012733
N	2.48565410	-2.61491551	-0.44050261
O	2.23599112	-3.80950468	-0.46128226
O	3.54241793	-2.04478851	-0.74222417
O	1.47780364	-1.80265368	-0.04156470
N	1.52890806	-0.01684563	2.54055966
O	0.31253310	-0.00531855	2.11820216
O	1.85844407	-0.02511297	3.69202399
O	2.45149419	-0.01907922	1.58590878

Acknowledgements. We thank Professor I. Othman, Director General, Professor A. H. Al-Rayyes, Head of the Radioisotope department, for their support of this work. We also thank Chem. R. Al Sabeq, Chem. A. Alsharif, A. Habeb and F. Maksoud for their help.

REFERENCES

- N. Kimizuka and T. Kunitake. *Advanced Materials*, **1996**, 8, 89-91.
- D. B. Mitzi, M. T. Prikas and K. Chondroudis, *Chem. Mater.*, **1999**, 11, 542-544.
- G. Steinhauser, K. Tarantik and T. M. Klapötke, *Journal of Pyrotechnics*, **2008**, 27, 3-13.
- M. Rademeyer, *Acta Cryst.*, **2006**, E62, m269-m271.
- G. Steinhauser, K. Karaghiosoff and T. M. Klapötke, *Z. Anorg. Allg. Chem.*, **2008**, 634, 892-894.
- M. M. Al-Ktaifani and M. K. Rukiah, *Chemical papers*, **2011**, 65, 469-476.
- M. M. Al-Ktaifani and M. K. Rukiah, *Acta Cryst.*, **2012**, C68, m246-m250.
- M. M. Al-Ktaifani and M. K. Rukiah, *Chemical papers*, **2012**, 66, 1032-1038.
- B. Almarzoqi, A. V. George and N. S. Isaacs, *Tetrahedron*, **1986**, 42, 601-607.
- K. Helios, R. Wysokinski, A. Pietraszko and D. Michalska, *Vibrational Spectroscopy*, **2011**, 55, 207-215.
- K. Malek, M. Vala, J. Swiatek-Kozłowska and L. M. Proniewicz, *New J. Chem.*, **2004**, 28, 477-483.
- B. H. Stuart, "Infrared Spectroscopy: Fundamentals and Applications", Wiley, 2004, p.49-50.
- J.-J. Max and C. Chapados, *J. Chem. Phys.*, **2009**, 131, 184505.
- W. Kemp, "Organic Spectroscopy", 3rd Edition, MACMILLAN PRESS LTD, London, 1991, p.31-33.
- M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis and J. A. Montgomery, *J. Comput. Chem.*, **1993**, 14, 1347-1363.
- A. R. Allouche, *J. Comput. Chem.*, **2011**, 32, 174-182.
- F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc. Perkin Trans*, **1987**, 2, S1-S19.
- W.-Z. Fu, W.-J. Wang, Y.-Y. Niu and S. W. Ng, *Acta Cryst.*, **2010**, E66, o1211.
- J. E. Huheey, E. A. Keiter and R. L. Keiter, "Inorganic Chemistry: Principle of Structure and Reactivity", 4th Edition, Harper Collins College Publishers, 1993, p. 290-296.

