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A UNIQUE EXAMPLE OF DICHLORODINITRATOCUPRATE(II) COMPLEX: SYNTHESIS AND MOLECULAR STRUCTURE OF 1,1′-METHYLENEDIPYRIDINIUM DICHLORODINITRATOCUPRATE(II)

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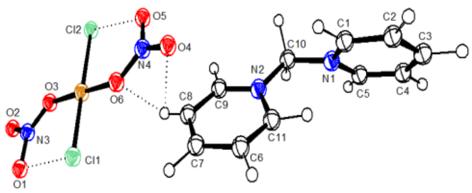
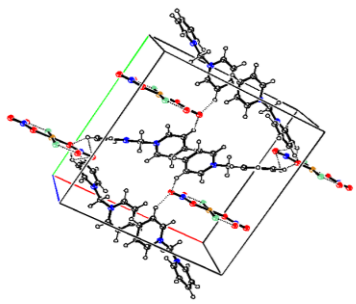
The unique organic-inorganic hybrid salt $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ was synthesized and isolated as pure green powder and fully characterized by multinuclear NMR, FTIR and UV–vis spectroscopy and powder-X-ray diffraction studies. The molecular structure of the salt shows separate organic dications $[(C_5H_5N)_2CH_2]^{2+}$ and distinctive inorganic $[CuCl_2(NO_3)_2]$ anions. The copper centre lies in a distorted square planar environment with two Cl atoms are trans- to each other with the Cl-Cu-Cl bond angle and mean Cu-Cl bond distance of 178.8(1)^o and 2.23(6) Å respectively. While the two bonded, O atoms (NO_3) to Cu are also trans- to each other with O-Cu-O bond angle and average bond length of 178.7(9)^o and 1.80(1) Å respectively. Interestingly, short Cl---O (halogen bond) distances (2.92(5) Å) between each Cl atom and the nearest adjacent O atom of (NO_3) group within the $[CuCl_2(NO_3)_2]$ ion are also identified. These intra-molecular Cl---O short contacts are more likely the reason for the stability of this unusual $[CuCl_2(NO_3)_2]$ anion. $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ is somewhat a rare example of a complex of the anion $[CuCl_2(NO_3)_2]$ with Cl---O(NO_2) halogen bonding.





INTRODUCTION

The demand of novel compounds is always a big challenge to researchers working in various research fields.[1] Recently, organic–inorganic hybrid salts are considered as promising compounds in diverse domains such as of crystal engineering, supramolecular chemistry and materials science,[2-5] and also for optical semiconductor materials.[6,7] Combination of organic and inorganic parts in hybrid organic-inorganic salts gives these types of compounds the desired modified properties, which are more likely unavailable in the neat organic or inorganic parts. Countable 1,1′-methylenedipyridinium hybrid salts of form $[(C_5H_5N)_2CH_2][OsF_nCl_{6-n}]$ (n = 0-6) were previously reported to investigate the order structure of octahedral mixed halo-osmium(IV) complexes.[8-11] In the late years, the dication 1,1′-methylenedipyridinium $[(C_5H_5N)_2CH_2]^{2+}$ was exploited by us to synthesize many organic-inorganic hybrid salts of form; $[(C_5H_5N)_2CH_2]$ $[MCl_4]$, (M = Zn,[12] Cd,[12] Cu,[13] Pt[14]), $[(C_5H_5N)_2CH_2]$ $[AuCl_4]_2$,[13] $[(C_5H_5N)_2CH_2]$

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$[PtCl_6]$,[14] $[(C_5H_5N)_2CH_2][Cu(NO_4)_4]$[15] and $[(C_5H_5N)_2CH_2]$ $[Fe(CN)_5NO]$.[16] Furthermore, the optical nonlinearity of $[(C_5H_5N)_2CH_2]$ $[Fe(CN)_5NO]$,[16] $[(C_5H_5N)_2CH_2][CuCl_4]$[17] and $[(C_5H_5N)_2CH_2][AuCl_4]_2$[18] were also investigated, suggesting them to have potential applications in optical domain.

This was an incentive for us to synthesize the novel and unique organic-inorganic mixed chloronitrato-hybrid salt: 1,1′-Methylenedipyridinium dichlorodinitratocuprate(II). So, the preparation, the spectroscopic characterization and the molecular structure investigations of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ by powder X-ray diffraction studies are the subject of the present article.

RESULTS AND DISCUSSION

The titled compound $[(C_5H_5N)_2CH_2]$ $[CuCl_2(NO_3)_2]$ (Figure 1) was obtained by treatment of $[(C_5H_5N)_2CH_2]Cl_2{\cdot}H_2O$ with $Cu(NO_3)_2$ in an aqueous solution. The obtained product was isolated as pure green salt, which was insoluble in common organic solvents, but it has a good solubility in water or dimethyl sulfoxide (DMSO).

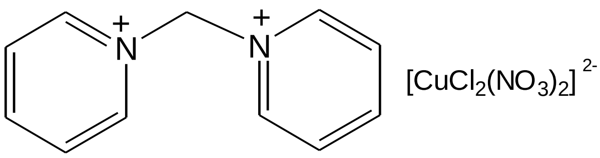

Fig. 1 – Molecular structure of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$.

The product is characterized by the ^{1}H and ^{13}C{^{1}H} NMR spectroscopies. Expectedly, the ^{1}H and ^{13}C{^{1}H} NMR spectra for $[(C_5H_5N)_2CH_2]$ $[CuCl_2(NO_3)_2]$ (Figure 2) have similar features to their corresponding ones of the related organic-inorganic hybrid salts $[(C_5H_5N)_2CH_2][CuX_4]$ (X = Cl^{-}[13] or NO_3^{-}[15]). The ^{1}H NMR spectrum showed the anticipated four resonances (broadening peaks) corresponding to four different proton environments. The obtained peaks are in their expected intensity ratio. Broadening peaks are also observed in ^{1}H NMR spectra of the $[(C_5H_5N)_2CH_2][CuX_4]$ (X= Cl^{-} or NO_3^{-}), which most probably due to the electric quadruple effects of the paramagnetic Cu(II). The ^{13}C{^{1}H} NMR spectrum also gives the expected four resonances consistent with four environmentally different C centres.

The FTIR spectrum of the product is shown in Figure 3. It is readily noticeable the presence of the characteristic absorption bands at 1186 cm^{-1} (C–N), 1492 cm^{-1} (CH_2), 1631 cm^{-1} (C=N) and also the distinctive stretching band of NO_3 group at 1384 cm^{-1}. The obtained bands are quite informative and consistent with the molecular structure in Figure 1.

The UV-Vis spectrum of $[(C_5H_5N)_2CH_2]$ $[CuCl_2(NO_3)_2]$ (Figure 4) gave a broad absorption band at λ_{max}= 267.5 nm extending in the range 250–400 nm. The distinguished broad spectral feature is more likely associated with the combination of $\pi - \pi^*$, (d$\rightarrow$d*) transition and/or ligand-to-metal charge-transfer (LMCT) in the complex. Since the measurement of UV-Vis spectrum was carried out in a very dilute DMSO solution (40×10^{-6} M), no absorptions in the visible region of the spectrum were detected.

The molecular structure of $[(C_5H_5N)_2CH_2]$ $[CuCl_2(NO_3)_2]$ was also confirmed by powder X-ray diffraction study (Figure 5). It shows discrete organic dications $[(C_5H_5N)_2CH_2]^{2+}$ and inorganic $[CuCl_2(NO_3)_2]$ anions. The copper atom lies in a distorted square planar environment with two Cl atoms are trans- to each other with the Cl-Cu-Cl angle is 178.8(1)^o. In similar manner, the two bonded O (NO_3) atoms to Cu are also trans- to each other with O-Cu-O angle of 178.7(9)^o. The mean Cu-Cl and Cu-O(NO_3) bond distances are 2.23(6) Å and 1.80(1) Å respectively (Table 1). Both of them are lying in their expected range and comparable to their corresponding ones of the related structurally characterized salts $[(C_5H_5N)_2CH_2][CuCl_4]$,[13] $(CH_3NH_3)_2[Cu(NO_3)_4]$[19] and $(C_6H_5CH_2NH_3)_4[Cu(NO_3)_4](NO_3)_2$.[20] Noteworthy, the Cu centre within $[CuCl_2(NO_3)_2]$ anion is an inversion centre (Figure 5).

For the two coordinated NO_3 groups, the N–O bond lengths lie within 1.20(1)-1.24(6) Å and the O–N–O bond angles within 113.6(0) – 126.4(0)° (Table 1). Both are consistent with the average N–O bond distance and planarity of nitrate ions respectively.[21] The C–C, C–N bond distances as well as C-N-C and C-C-C angles within the organic dication $[(C_5H_5N)_2CH_2]^{2+}$ unit of the $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ did not show any significant changes from those of parent salt $[(C_5H_5N)_2CH_2]Cl_2{\cdot}H_2O$.[22]

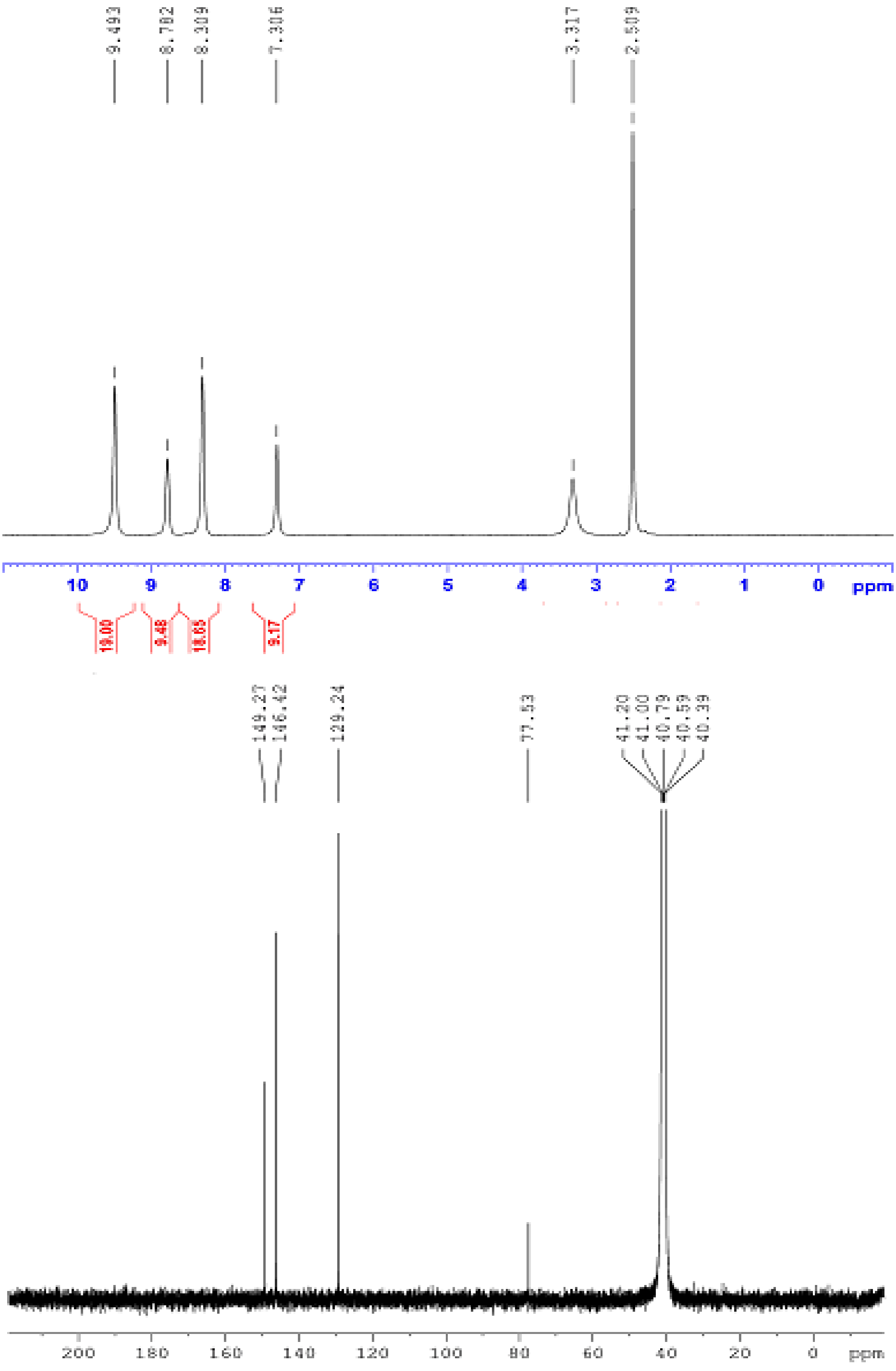

Fig. 2 – ^{1}H (above) and $^{13}C\{^{1}H\}$NMR (below) spectra of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ (DMSO-d_6, 25^{o}C).

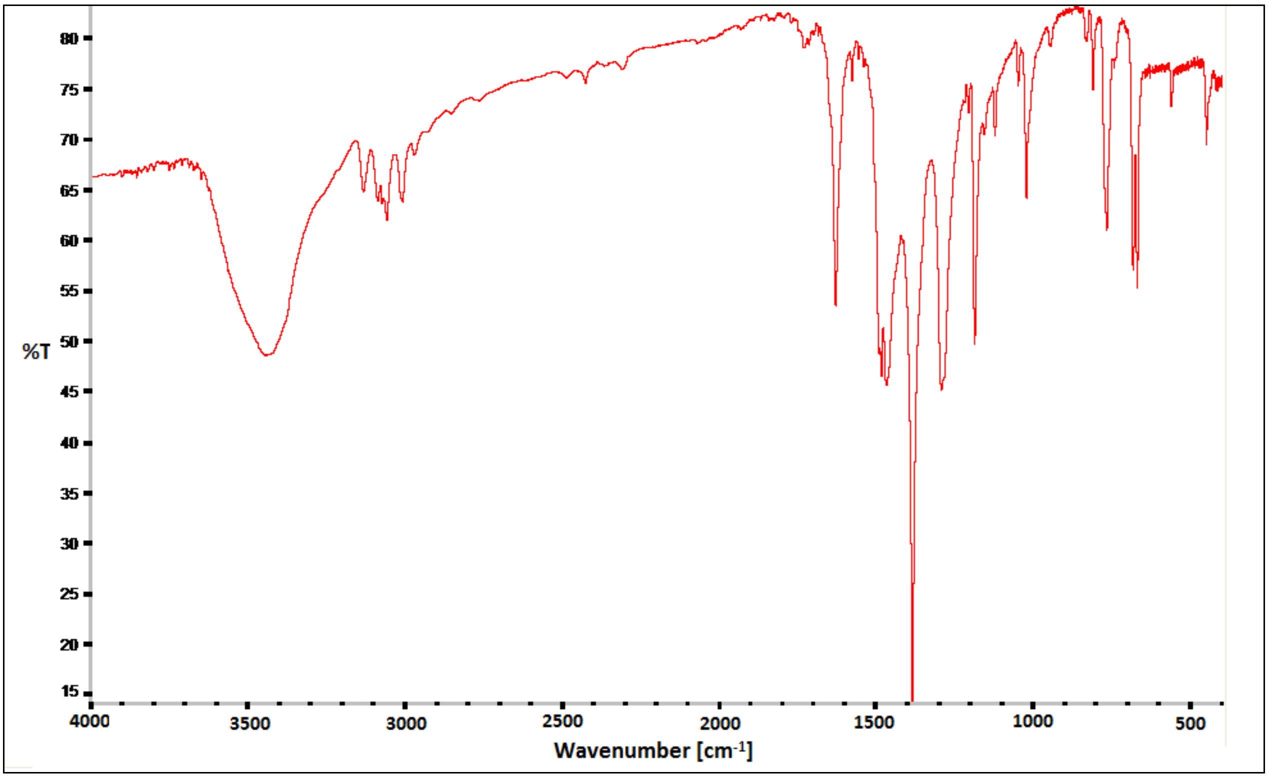

Fig. 3 – FTIR spectrum of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ (KBr disc).

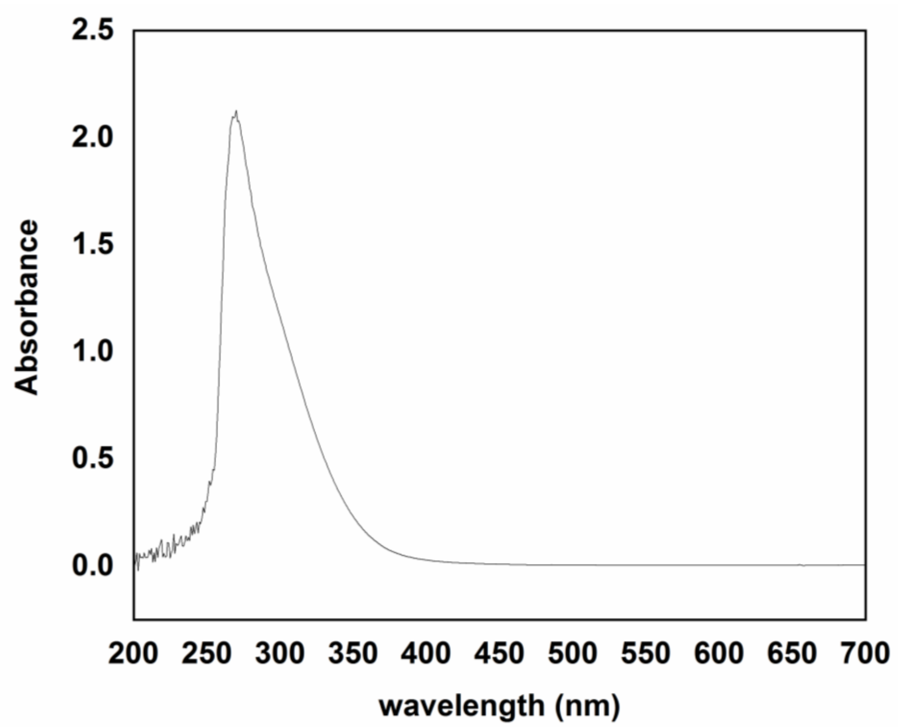

Fig. 4 – UV–Vis spectrum of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ in DMSO at concentration of 40×10^{-6} M.

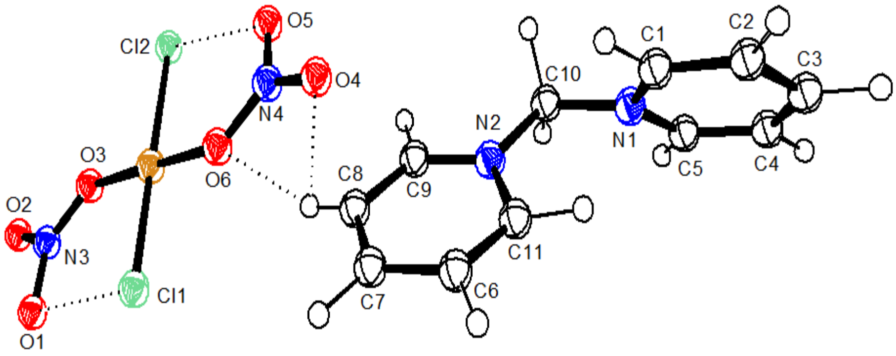

Fig. 5 – Molecular structure of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ with atomic labeling.
Intra-molecular hydrogen bonds and short Cl---O distances (halogen bond) are indicated by dashed lines.

It is worth to mention that the molecular structure investigation exhibits intra-molecular C–H· · ·O and Cl---O short contacts within each unit (Figure 5). C–H· · ·O short contacts are observed where the H center is bridging the closest two O atoms of the same NO_3 within its own unit (Table 2). Noteworthy, short Cl---O distances (2.89(5) Å and 2.94(4) Å) between each Cl atom and the nearest adjacent O atom of NO_3 group within the $[CuCl_2(NO_3)_2]$ ion are also identified. This distance is considerably less than the sum of van der Waals radii of Cl and O atoms (3.4 Å).[23]

Interestingly, $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ is a rather rare example of a complex containing the anion $[CuCl_2(NO_3)_2]$ and Cl---O(NO_3) halogen bonding. This type of interactions, which controls the arrangement of molecules in crystal packing of complexes, was recently recognized by the International Union of Pure and Applied Chemistry (IUPAC) and the Cambridge Structural Database (CSD). This non-covalent interaction is called halogen bond (XB) and defined as intermolecular or an intra-molecular interaction between halogen center acting as Lewis acid (halogen bond donor) and an atom having lone pair as Lewis base (halogen bond acceptor).[24-26]

These intra-molecular Cl---O short contacts as well as the mentioned hydrogen bridging are more likely the reason for the stability of this unusual $[CuCl_2(NO_3)_2]$ anion.

In the crystal packing of the complex weak intermolecular C–H· · ·O hydrogen bonds link the dictions $[(C_5H_5N)_2CH_2]^{2+}$ and anions $[CuCl_2(NO)_3]^{2-}$ to form three dimensional network (Figure 6). These hydrogen bondings may be effective in the stabilization of the crystal packing of the complex. Furthermore, parallel pyridinium rings of two adjacent different $[(C_5H_5N)_2CH_2]^{2+}$ units are also observed with a centroid–centroid distance between pyridinium rings of 3.07(9) Å (Figure 7). This strongly indicates that the crystal packing of the complex is also further stabilized by non-covalent π–π interactions between pyridinium rings of adjacent dications.[27,28] For more details, the atomic coordinates of the complex are presented in Table 4.

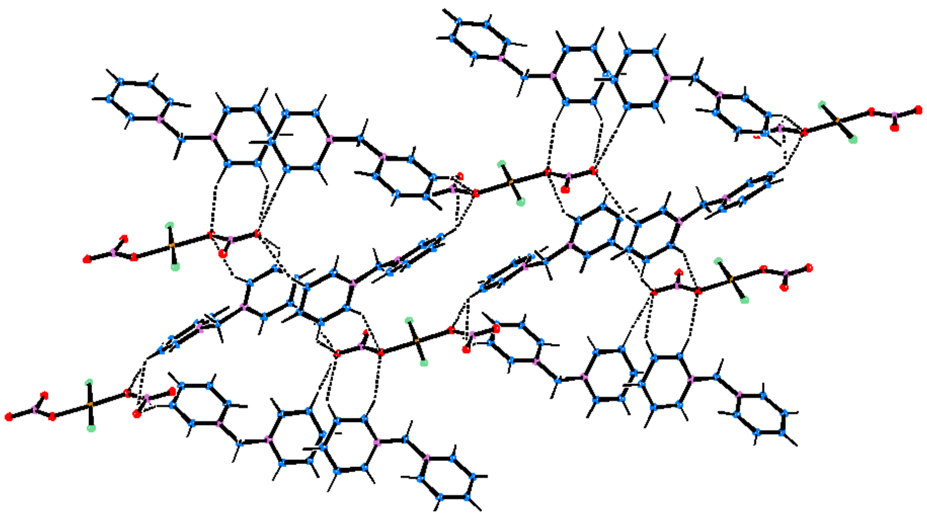

Fig. 6 – Portion of the packing diagram of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$. Hydrogen bonds between molecules are indicated by dashed lines [Symmetry codes: (i) –x, -y, –z; (ii) -x, y +1/2, –z].

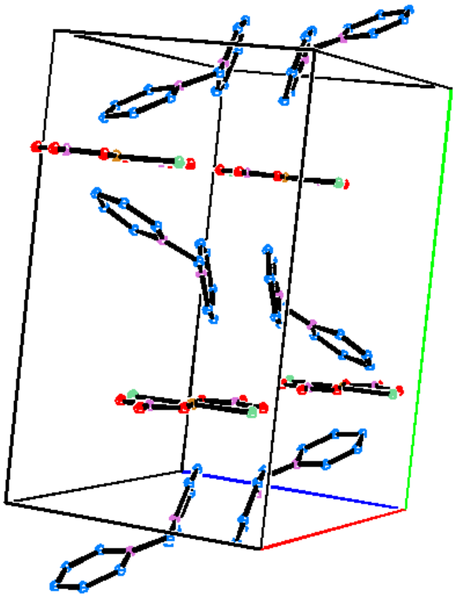

Fig. 7 – Parallel pyridinium rings of two adjacent different $[(C_5H_5N)_2CH_2]^{2+}$ units are observed in the crystal packing of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$. Hydrogen atoms are omitted for clarity.

Table 1

Selected bond lengths (Å) and angles (°) for $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$

C1–C2	1.362(8)	N2–C10	1.467(5)
C1–N1	1.345(5)	Cu–O3	1.818(2)
C2–C3	1.388(3)	Cu–O6	1.785(1)
C3–C4	1.386(3)	Cu–Cl1	2.133(8)
C4–C5	1.363(1)	Cu–Cl2	2.393(9)
C5–N1	1.350(1)	N3–O1	1.263(8)
N1–C10	1.468(8)	N3–O2	1.230(0)
C6–C7	1.385(7)	N3–O3	1.213(1)
C6–C11	1.306(6)	N4–O4	1.201(0)
C7–C8	1.384(0)	N4–O5	1.201(7)
C8–C9	1.370(0)	N4–O6	1.221(0)
C9–N2	1.345(7)	C11–N2	1.426(3)
Cl1–Cu–Cl2	178.8(1)	O4–N4–O5	119.9(9)
O3–Cu–O6	178.7(9)	O4–N4–O6	126.3(9)
Cl1–Cu–O3	106.1(8)	O5–N4–O6	113.6(0)
Cl1–Cu–O6	72.6(0)	Cu–O3–N3	134.9(0)
Cl2–Cu–O3	75.0(0)	Cu–O6–N4	134.9(8)
Cl2–Cu–O6	106.2(0)	N1–C10–N2	113.4(6)
O1–N3–O2	119.6(4)	C1–N1–C5	121.1(4)
O1–N3–O3	120.1(6)	C9–N2–C11	119.6(3)
O2–N3–O3	120.1(9)		

Table 2

Hydrogen bond distances (Å) and bond angles (°) for the complex

	d(D–H)	*d(H···A)*	*d(D···A)*	*Angle(D–H···A)*
C4(vii)–H4(vii)···O2(iv)	1.064	2.394	3.183	129.65
C2(vi)–H3(vi)···O2(iv)	1.136	2.495	3.447	141.49
C5(ix)–H5(ix)···O3(iv)	1.062	2.391	3.339	147.91
C5(vii)–H5(vii)···O3(iv)	1.062	2.391	3.339	147.91
C8(ii)–H8(ii)···O5(ii)	0.877	2.999	3.570	124.53
C8(ii)–H8(ii)···O6(ii)	0.877	1.750	2.528	148.15

Symmetry code: (i) –x, -y, –z; (ii) –x, y +1/2, –z.

EXPERIMETAL

Materials and Measurements

Reactions and manipulations were conducted in air with reagent grade solvents. $Cu(NO_3)_2.3H_2O$ (BDH, Germany) is a commercial sample and it is used as received. $[(C_5H_5N)_2CH_2]Cl_2\cdot H_2O$ was prepared according to literature method.[29] ^1H and $^{13}C\{^1H\}$ NMR spectra were acquired on a *Bruker Bio spin 400* spectrometer (Switzerland). Microanalysis was performed using *EURO EA* (Italy). Powder X-ray diffraction was performed on a *Stoe Transmission diffractometer* (Stadi P) (Stoe & CIE, Germany).

Synthesis of 1,1`-methylenedipyridinium dichlorodinitratocuprate

An aqueous solution of $Cu(NO_3)_2\cdot 3H_2O$ (0.28 g, 1.15 mmol, 3 mL H_2O) was added to a solution of $[(C_5H_5N)_2CH_2]Cl_2\cdot H_2O$ (0.30 g, 1.15 mmol, 3 ml of H_2O). Green precipitate was immediately formed and the resulting mixture was stirred overnight. The solvent was then removed in vacuum to afford quantitatively $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$, which was washed with EtOH to give a green powder (450 mg, yield 90%).

Characterization and NMR, FTIR and UV–vis spectroscopic data of $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$

Green powder, m.p. 201°C, Yield: 90%; Anal. Calcd for $C_{11}H_{12}Cl_2CuN_4O_6$ (430.69): C, 30.68; H, 2.81; N, 13.01 Found: C, 30.37; H, 2.94; N, 12.48; ^1H NMR (400.1 MHz, DMSO-d_6): δ_H 7.31 (2H, b, CH_2), 8.31 (4H, b, py), 8.78 (2H, m, py), 9.49 (4H, b, py); $^{13}C\{^1H\}$ NMR (100.6 MHz, DMSO-d_6): δ_C 77.53 (s, CH_2), 129.24 (s, Py), 146.42 (s, Py), 149.27 (s, Py). IR (KBr) ν cm^{-1}: 1186 (C–N, *str*), 1384 (NO_3, *str*), 1492 (CH_2, *def*), 1631 (C=N, *str*). UV (DMSO): λ_{max} (ε) = 267.5 nm (2.1).

Powder X-ray diffraction Study:

In our case, all attempts to obtain single crystal of good quality and proper size of the material were unsuccessful. Therefore, the structure was determined using the powder X-ray diffraction data. This was collected using a transmission diffractometer (*STADI-P STOE*, Darmstadt, Germany), with Cu K_α radiation (λ= 1.54060 Å) and a germanium monochromator operated at 50 kV and 30 mA. The scanning angle was from 5º to 100º with a scanning rate of 1º per minute. The structure solution of new hybrid materials exclusively from the indexation of the powder X-ray diffraction patterns using the conventional methods is mostly uneasy tasked. This is due to the poor crystallinity of such materials combined with low symmetries or large unit cells. In order to solve the material structure, a direct calculation method was applied, using the software package *EXPO2014*.[30] A monoclinic cell with satisfactory figure of merit was found for the materiel. The structure can be described as belonging to the space group *P21/m*. The crystal parameters are: a=15.396 (3) Å; b=15.6959 (15) Å; c=9.5449 (12) Å; α= γ = 90.0°; β = 96.160 (7)°. The structure was further refined using Rietveld method as implemented in *GSAS-II* package.[31,32] The final values of the crystallographic data and refinement goodness factors are shown in Table 3. The factors are reliable and reasonably satisfactory to support indexing results M(20)=20.6. The final Rietveld plots of the X-ray diffraction patterns are given in Figure 8.

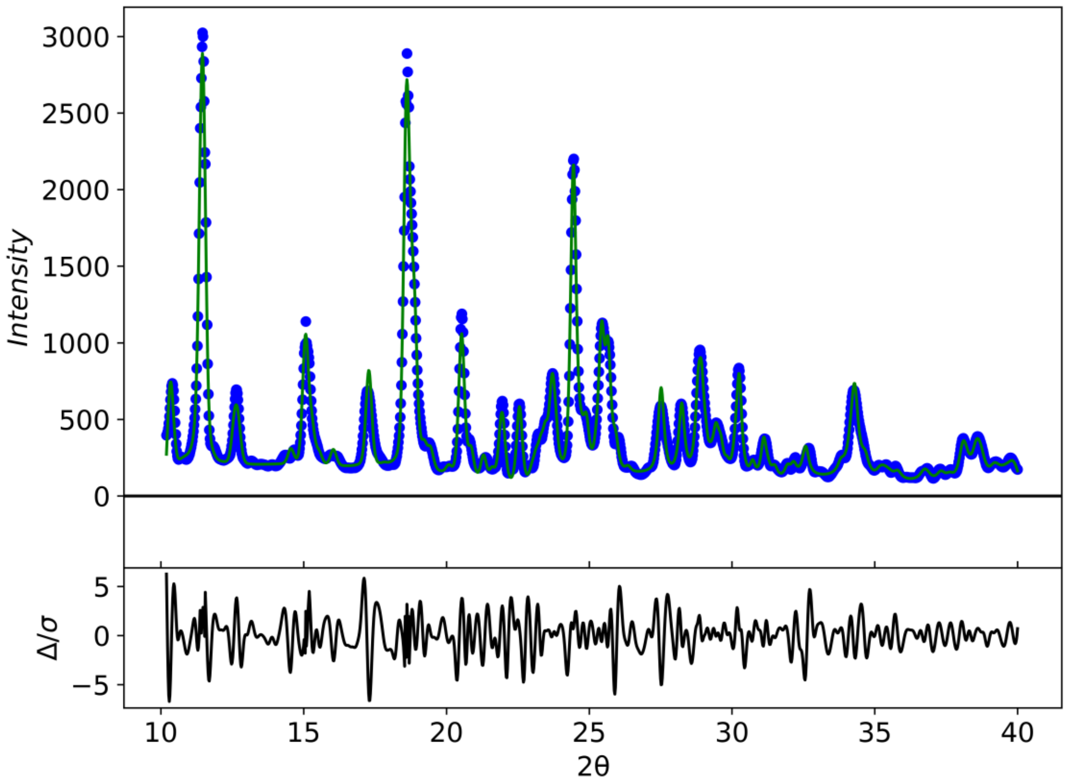

Fig. 8 – The final Rietveld pattern for $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$. The (*) is the observed values and (-) are the fitted ones. (-) is the difference between the observed and the fitted values.

Table 3

Crystallographic data and refinement parameters for $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$

Chemical formula	$C_{11}H_{12}Cl_2CuN_4O_6$
Mr	430.69
Crystal colour	Green
Crystal system	Monoclinic
Space group	$P2_1/m$
Temperature (K)	298
Unit cell parameters	
a (Å)	15.3960 (3)
b (Å)	15.6959 (15)
c (Å)	9.5449 (12)
β (°)	96.160 (6)
V (Å^3)	2293.3 (6)
Z	2
Radiation type	Cu $K\alpha_1$
λ	1.54059 Å
Specimen shape, size (mm)	Fine powder
Data collection	
Diffractometer	*STOE transmission STADI-P*
Specimen mounting	powder loaded between two Mylar foils
Data collection mode	transmission
Scan method	step
2θ *min*	5.08°
2θ *max*	80.06°
2θ step =	0.02°
Refinement	
R factors and goodness of fit R_p	0.067
R_{wp}	0.088
R_{exp}	0.051
$R(F^2)$	0.00000
χ^2	3.024
Number of data points	3750
Number of parameters	30
Number of restraints	0

Background function: "chebyschev" function with 20 terms: 76(6), 5.8(4)e2, 1.5(30)e2, -1.32(19)e4, -1.3(6)e4, 8.1(29)e4, 1.9(6)e5, -1.3(21)e5, -1.10(30)e6, -6(9)e5, 3.2(8)e6, 3.1(22)e6, -5.3(14)e6, -6(3)e6, 5.0(14)e6, 6.3(30)e6, -2.4(8)e6, -3.3(15)e6, 4.9(18)e5, 7(3)e5,

Profile function: Finger-Cox-Jephcoat function parameters U, V, W, X, Y, SH/L: peak variance(Gauss) = Utan(Th)^2+Vtan(Th)+W: peak HW(Lorentz) = X/cos(Th)+Ytan(Th); SH/L = S/L+H/L U, V, W in (centideg)^2, X & Y in centideg -1.83(12)e3, 1.2(3)e2, 101(7), 9.9(4)e2, -73(7), 0.001, Crystallite size in microns with "isotropic" model: parameters: Size, G/L mix 1.000, 1.000, Microstrain, "isotropic" model (10^6 * delta Q/Q) parameters: Mustrain, G/L mix 1000.000, 1.000,

Preferred orientation correction: March-Dollase correction coef. = 1.000 axis = [0, 0, 1]

Table 4

Atomic coordinates of the complex

Atom	x	y	z
C1	0.37949	0.42330	1.38888
C2	0.46180	0.44211	1.35835
C3	0.49329	0.52441	1.38079
C4	0.44100	0.58593	1.43360

Table 4 (continued)

C5	0.35922	0.56389	1.46280
N1	0.32927	0.48375	1.43937
H1	0.55721	0.54038	1.35802
H2	0.35365	0.36070	1.37667
H3	0.50261	0.39019	1.31562
H4	0.46279	0.64961	1.45257
H5	0.31784	0.60905	1.50422
C6	0.16170	0.36413	1.13873
C7	0.08003	0.33572	1.16629
C8	0.05276	0.34944	1.29796
C9	0.10722	0.39078	1.39878
N2	0.18610	0.41860	1.37023
H6	0.03871	0.30398	1.08610
H7	0.18443	0.35571	1.03891
H8	0.00162	0.33474	1.32156
H9	0.09014	0.40214	1.50207
C10	0.24441	0.45847	1.48326
H10	0.25582	0.41517	1.56956
H11	0.21226	0.51344	1.51758
C11	0.21252	0.40626	1.23295
H12	0.27589	0.43055	1.23295
Cu	−0.17067	0.25000	1.42628
N3	−0.35417	0.25000	1.39855
O1	−0.35944	0.25000	1.26550
O2	−0.42133	0.25000	1.45768
O3	−0.28325	0.25000	1.46754
N4	0.01122	0.25000	1.44888
O4	0.08024	0.25000	1.40100
O5	0.00902	0.25000	1.57435
O6	−0.06095	0.25000	1.38190
Cl1	−0.17654	0.25000	1.20191
Cl2	−0.16084	0.25000	1.67829

CONCLUSION

The novel organic–inorganic hybrid ionic compound $[(C_5H_5N)_2CH_2][CuCl_2(NO_3)_2]$ was synthesized. It is a remarkable case of hybrid salt containing dichlorodinitratocuprate(II) $[CuCl_2(NO_3)_4]$ with Cl---O(NO_2) halogen bond. The obtained complex was fully characterized by spectroscopic methods and its identity was confirmed by powder X-ray diffraction study.

SUPPLEMETARY INFORMATION

CCDC 1981718 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/ conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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