

Synthesis of bis-substituted symmetrical compounds, 1,5-bis((1*H*-imidazol-2-yl)methylene)carbonohydrazide (1) and 1,5-bis(((1*H*-imidazol-3-ium)-2-yl)methylene)carbonohydrazide monochloride monohydrate (2) : Spectroscopic characterization and X ray diffraction structure of (2)

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Abstract

The condensation of 1*H*-imidazole-2-carbaldehyde and 2-carbonohydrazide in methanol yielded white solid formulated as $C_9H_{10}N_8O$ (1,5-bis((1*H*-imidazol-2-yl)methylene)carbonohydrazide). The use of the above compound in the tentative of the preparation of a cobalt complex with $CoCl_2 \cdot 6H_2O$ (I) leads to the formation of a 1:1 salt. The crystal structure reveals that both the sp^2 -nitrogen atoms of the imidazole ring are partially protonated with a half-occupied hydrogen atom yielding a monoprotinated hydrated compound formulated as $[C_9H_{11}N_8O] \cdot Cl \cdot H_2O$ (1,5-bis(((1*H*-imidazol-3-ium)-2-yl)methylene)carbonohydrazide monochloride monohydrate)(2). The crystal packing is stabilized by intramolecular hydrogen bonds of type $N(\text{carbohydrazide})-H \cdots Cl$ and $N(\text{imidazolium})-H \cdots Cl$ and intermolecular $N(\text{carbohydrazide})-H \cdots O(\text{carbohydrazide})$, $N(\text{imidazolium})-H \cdots N(\text{imidazolium})$ and $N(\text{imidazolium})-H \cdots O(\text{water})$ hydrogen bonds which form layer parallel to *c* axis. The dihedral angle between the mean planes of the two imidazolium is 3.78°. The dihedral angle formed by the mean planes of two arms of the carbonohydrazide moiety O1/C5/N5/N6/C6 and O1/C5/N4/N3/C4 is 2.68°. The imidazolium fragment form a dihedral angle with its related carbonohydrazide moiety of 4.99° and 5.61°.

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I. Introduction

Schiff bases imines and bis-imines are widely used as ligands of choice in coordination chemistry. The *d*-block metals generate complexes with widely varying properties. The catalytic activities of these complexes [1] are widely used to enhance many chemical reactions such as oxidation [2, 3], reduction [4, 5] and coupling reaction [6, 7]. Enantioselective catalytic reactions are a good example [8, 9]. The use of imidazole carbaldehyde has made it possible to prepare many five-membered heterocyclic compounds with nitrogen atoms in position 1 and 3 [10–12]. The condensation products of imidazole-2-carbaldehyde substituted with aliphatic or aromatic amines are widely reported in the literature [13]. Many compounds derived from imidazole carbaldehyde are used as precursors in the preparation of heterocyclic drugs containing nitrogen atoms [14–16]. Drugs development with a broad spectrum of biological activities is ensured by the above compounds. Antimicrobial [17], anticancer [18, 19], antifungal [20], antioxidant [21] and analgesic [22] properties are reported for compounds derived from imidazole carbaldehyde. These Schiff bases derived from imidazole carboxaldehyde are also known as multitopic ligands for the controlled construction of complex architectures with particular properties such as magnetism [23, 24]. We have recently begun to examine the coordination behavior of a series of Schiff bases containing imidazole moieties. In this paper, we report the synthesis and the characterization of 1,5-bis((1*H*-imidazol-2-yl)methylene)carbonohydrazide and its protonated derivative 1,5-bis(((1*H*-imidazol-3-ium)-2-yl)methylene)carbonohydrazide monochloride monohydrate.

II. Experimental

2.1. Starting materials and instrumentations

1*H*-imidazole-2-carbaldehyde and carbonohydrazide were purchased from Sigma-Aldrich and used as received without further purification. All solvents used were of reagent grade. Melting points were determined on a Büchi 570 melting-point apparatus and were uncorrected.

Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on an FTIR Spectrum Two of Perkin Elmers spectrometer in the 4000–400 cm⁻¹ region. The ¹H and ¹³C NMR spectra were recorded in DMSO-*d*₆ on a BRUKER 500 MHz spectrometer at room temperature using TMS as an internal reference.

2.2. Synthesis of 1,5-bis((1H-imidazol-2-yl)methylene)carbonohydrazide (H₂L) and its protonated derivative

To a mixture of 20 mL of methanol and 10 mL of distilled water was added carbohydrazide (3 g, 0.0333 mol). The mixture was refluxed for 30 minutes. A solution of 1H-imidazole-2-carbaldehyde (3.19 g, 0.0330 mmol) dissolved in 20 mL of methanol was slowly dropwise over a period of one hour. The resulting mixture was heated under reflux for 2 hours. The suspension was filtered, and the white precipitate obtained was washed with (2 × 10 mL) of cold methanol and dried under vacuum over P₂O₅. MP. 254°C. Yield: 92 %. FT-IR (ATR, ν, cm⁻¹): 3248 (N—H), 3086 (=C—H), 1666 (C=O), 1621 (C=N), 1573 (C_{im}=C_{im}), 1547 (C_{im}=C_{im}), 1466 (C_{im}=C_{im}), 1141 (N—N). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 7.00–7.52 (m, 4H, H-Imidazole), 8.01 (s, 2H, N=C—H), 10.78 (s, 2H, N—H), 12.58 (s, 2H, N—H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm): 151.50 (C=O), 141.32 (C_{ipso imidazol}), 129.57 (C=N), 118.67 (C_{imidazol}). Anal. calcd. for C₉H₁₀N₈O: C, 43.90; H, 4.09; N, 45.51. Found: C, 43.88; H, 4.07; N, 45.53 %.

In our attempt to synthesize a complex with the ligand and cobalt chloride, a hydrated organic chloride salt (H₃L·Cl·H₂O) is isolated as a crystal suitable for X-ray analysis. Yield: 57 %. FT-IR (ATR, ν, cm⁻¹): 3242 (N—H), 3085 (=C—H), 1669 (C=O), 1621 (C=N), 1571 (C_{im}=C_{im}), 1548 (C_{im}=C_{im}), 1465 (C_{im}=C_{im}), 1143 (N—N). Anal. calcd. for C₉H₁₃N₈O₂Cl: C, 35.95; H, 4.36; N, 37.26; Cl, 11.79. Found: C, 35.92; H, 4.31; N, 37.22; Cl, 11.75 %.

2.3. Crystal Structure Determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compound, was grown by slow evaporation of EtOH solution of the compound. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a XtaLAB Synergy, Dualflex Hypix diffractometer with graphite monochromatized CuKα radiation (λ = 1.54184 Å). All data were corrected for Lorentz and polarization effects. The structure was solved and refined using the Bruker SHELXTL Software Package [25]. All the structures were refined on *F*² by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [26]. H atoms of the NH group was located in the Fourier difference maps and refined without restraints. Other H atoms were geometrically optimized and refined as riding on their carriers. Molecular graphics were generated using ORTEP-3 [27].

Table 1 : Crystallographic data and refinement parameters for compound (2).

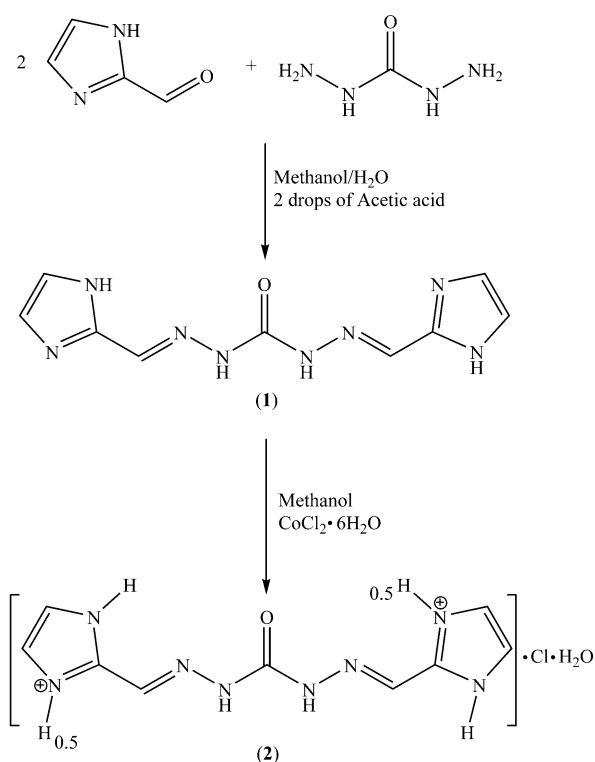
Chemical formula	C ₉ H ₁₁ N ₈ O·Cl·H ₂ O
<i>M_r</i>	300.72
Crystal system	Monoclinic
Space group	<i>P</i> 2/ <i>n</i>
Temperature (K)	100
<i>a</i> (Å)	13.9010 (2)
<i>b</i> (Å)	4.88869 (11)
<i>c</i> (Å)	21.1219 (4)
β (°)	93.7039 (16)
<i>V</i> (Å ³)	1432.39 (5)
<i>Z</i>	4
Radiation type	Cu <i>K</i> α
μ (mm ⁻¹)	2.53
Crystal size (mm)	0.14 × 0.05 × 0.04
T _{min} , T _{max}	0.826, 1.000
No. of measured reflections	17665

No. of independent reflections	2702
No. of observed [$I > 2\sigma(I)$] reflections	2549
R_{int}	0.026
$R[F^2 > 2\sigma(F^2)]$	0.057
$wR(F^2)$	0.178
S	1.08
No. of reflections	2702
No. of parameters	184
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ ($e \text{ \AA}^{-3}$)	0.59, -0.99

III. Result and discussion

3.1. General study

The ligand H_2L (**1**) is obtained by performing a condensation reaction between carbonohydrazide and two equivalents of imidazole carbaldehyde. It was characterized by infrared and NMR spectroscopies. Elemental analysis confirms the formation of the compound with the formula $\text{C}_9\text{H}_{10}\text{N}_8\text{O}$. The FTIR spectrum shows bands at 3248 cm^{-1} , 1666 cm^{-1} and 1621 cm^{-1} which are assigned to $\nu_{\text{N-H}}$, $\nu_{\text{C=O}}$ and $\nu_{\text{C=N}}$, respectively. Between 1573 and 1466 cm^{-1} , bands corresponding to the $\nu_{\text{C=C}}$ and $\nu_{\text{C=N}}$ vibrations of the imidazole ring are pointed. The band which appears at 1141 cm^{-1} is due to the $\nu_{\text{N-N}}$ vibration. The ^1H and ^{13}C NMR spectra are in accordance with the formulation. A signal at 8.02 ppm attributed to the proton of the azomethine group correlated with the signal at 129.57 ppm attributed to the azomethine carbon atom confirms the condensation. At 9.3 ppm , a signal characteristic of the presence of HN— appears. The signals at 10.78 ppm and 12.58 ppm are respectively attributed to the protons of the C=N—N—H groups and NH of the imidazole moieties. The signal at 151.50 ppm is attributed to the carbon atom of the carbonyl group. In our tentative to synthesize a cobalt complex by reacting the ligand H_2L (**1**) and the cobalt chloride salt, a hydrated chloride organic salt in which the ligand is monoprotonated was isolated and formulated as $\text{H}_2\text{L}\cdot\text{Cl}\cdot\text{H}_2\text{O}$ (**2**). The elemental analyze agree with the formulation. Its FTIR spectrum is similar to those of the H_2L (**1**).



Scheme 1. Synthetic scheme for the ligand (**1**) and (**2**).

3.2. Structural comment of compound (2)

The compound (2) crystallizes in Monoclinic space group $P2_1/n$. The asymmetric unit contains one ligand molecule of the monoprotonated Schiff base ligand one chloride anion and one free water molecule. The molecular structure of the title compound (2) with the atomic-labeling scheme is shown in Figure 1. Partial protonation (50%) of 1,5-bis((1*H*-imidazol-2-yl)methylene)carbonohydrazide : $C_9H_{10}N_8O$ molecule has occurred at the N1 and N8 atoms with a site occupancy of 0.5 for H1 and H8 atoms, resulting in the formation of 1,5-bis(((1*H*-imidazol-3-ium)-2-yl)methylene)carbonohydrazide monochloride monohydrate : $[C_9H_{11}N_8O] \cdot Cl \cdot H_2O$. One of the(((1*H*-imidazol-3-ium)-2-yl)methylene)imine groups adopt a *trans* conformation with respect to the carbonyl O atom across the respective C5—N4 bond, while the second (((1*H*-imidazol-3-ium)-2-yl)methylene)imine groups adopt a *cis* conformation with respect to the carbonyl O atom across the respective C5—N5 bond. The N3 and O1 atoms adopt *trans* conformation with respect to C5—N4, while the O1 and N6 atoms assume *cis* conformation with respect to C5—N5. The N6/N5/C5/O1/N4/N3 carbonohydrazide moiety is almost planar with a maximum deviation from least-squares plane of 0.0015 Å for the O1 atom. Additionally, the dihedral angle formed by the mean planes of two arms of the carbonohydrazide moiety O1/C5/N5/N6/C6 and O1/C5/N4/N3/C4 is 2.68° and the torsion angles C6—N6—N5—C5 (179.9(2)°) and C4—N3—N4—C5 (-177.3(2)°) confirm that the central part of the molecule is almost linear. The dihedral angle between the two imidazolium moieties is 3.78°. The imidazolium fragment form a dihedral angle with its related carbonohydrazide moiety of 4.99° and 5.61°, respectively. The O1—C5 [1.235(3) Å], N3—C4 [1.278(3) Å] and N6—C6 [1.281(3) Å] distances indicate that these correspond to double bonds and are comparable to those reported for 1-(2'-hydroxybenzylidene)-5-(1'-pyridylethylidene)carbonohydrazide [1.227 (3) Å for O—C; 1.282 (3) Å and 1.284(3) Å for N—C][28]. The C5—N4 and C5—N5 bond lengths [1.361 (3) and 1.368 (3) Å] are in the normal range observed for a single C—N bond [29]. The N—N bond length values [1.364(3) and 1.363(3) Å] are indicative of single bond character as observed in the literature[30].

Table 2: Selected bond lengths (Å) and angle (°).

O1—C5	1.235 (3)	N6—N5	1.367 (3)
N4—N3	1.364 (3)	N6—C6	1.281 (3)
N4—C5	1.361 (3)	N5—C5	1.368 (3)
N8—C7	1.331 (3)	N8—C9	1.374 (3)
N7—C7	1.341 (3)	N7—C8	1.374 (3)
N1—C1	1.374 (3)	N1—C3	1.328 (3)
N2—C2	1.371 (3)	N2—C3	1.347 (3)
N3—C4	1.278 (3)	O1—C5—N5	123.4 (2)
O1—C5—N4	121.5 (2)	N4—C5—N5	115.1 (2)

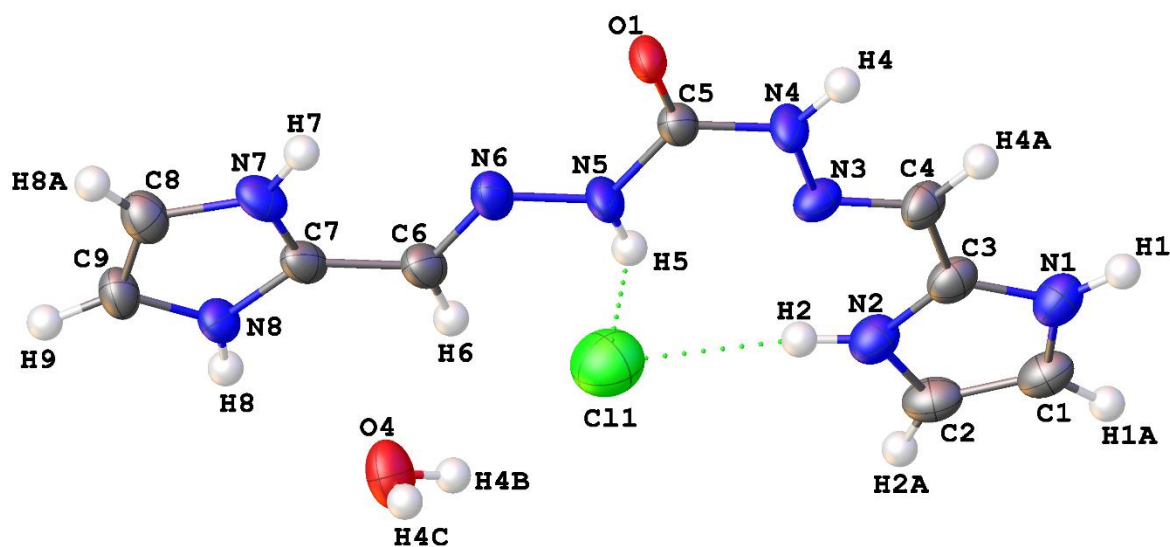


Figure 1. The molecular structure of the title molecular salt (I), with atom labelling for the asymmetric unit.

The intramolecular hydrogen bonds of type N(carbohydrazide)—H...Cl (N5—H5...Cl) and N(imidazolinium)—H...Cl (N2—H2...Cl) form a $s(10)$ ring motif (Table 3, Figure 2). The intermolecular hydrogen bonds results in the formation of $R_2^2(8)$, $R_2^2(7)$ and $R_2^2(5)$ ring motifs as shown in Figure 2. The crystal packing of compound **2** is stabilized by intermolecular N(carbohydrazide)—H...O(carbohydrazide) (N4—H4...O1ⁱ; $-x+1, -y+2, -z+1$), N(imidazolinium)—H...N(imidazolium), O(water)—H...O(carbonyl) (O4—H4B...O1ⁱ; $-x+1, -y+2, -z+1$), O(water)—H...N(imine) (O4—H4B...N6ⁱ; $-x+1, -y+2, -z+1$) and (N8—H8...N8ⁱⁱ; $x, y+1, z$) N(imidazolinium)—H...O(water) (N7—H7...O4ⁱⁱⁱ; $-x, -y, -z+1$) hydrogen bonds which form layers parallel to *c* axis (Table 3, Figure 3).

Table 3: Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H4B...O1 ⁱ	0.87	2.17	3.023(3)	167.6
O4—H4B...N6 ⁱ	0.87	2.49	3.022(3)	120.2
N4—H4...O1 ⁱⁱ	0.88	1.93	2.803(3)	171.2
N8—H8...N8 ⁱⁱⁱ	0.88	1.85	2.727(4)	172.4
N7—H7...O4 ^{iv}	0.88	1.98	2.852(3)	172.0
N5—H5...Cl1	0.88	2.48	3.289(2)	153.5
N2—H2...Cl1	0.88	2.25	3.127(2)	172.3

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x, -y, -z+1$; (iv) $x, y+1, z$.

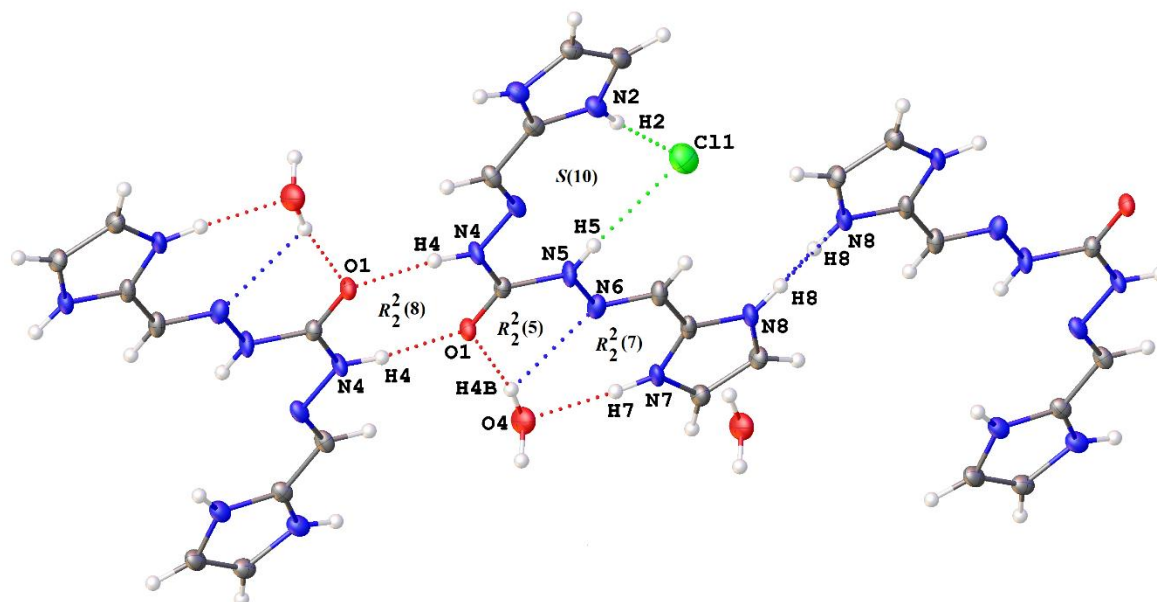


Figure 2. The intramolecular (green dashed lines) and intermolecular hydrogen bonds (red and blue dashed lines) showing the rings motifs formed in the structure.

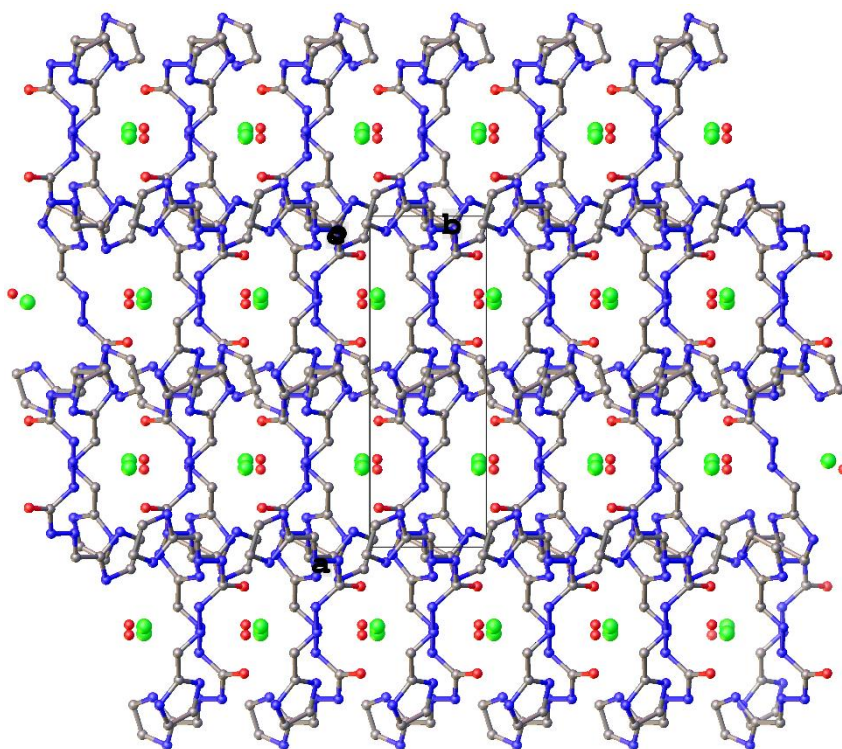


Figure 3. A view along the *c* axis of the O—H...O hydrogen-bonded chain.

IV. Conclusion

The disubstituted carbonohydrazide derivative namely, 1,5-bis((1*H*-imidazol-2-yl)methylene)carbonohydrazide (**1**) was successfully synthesized by condensation of 1*H*-imidazole-2-carbaldehyde and carbonohydrazide. The tentative to prepare a cobalt complex with (**1**) and cobalt dichloride hexahydrate yielded a monoprotonated hydrate compound 1,5-bis(((1*H*-imidazol-3-ium)-2-yl)methylene)carbonohydrazide monochloride monohydrate(**2**). The structures of the compounds were confirmed by elemental analysis and spectroscopic techniques (FT-IR, ¹H and ¹³C NMR). The molecular structure of 1,5-bis(((1*H*-imidazol-3-ium)-2-yl)methylene)carbonohydrazide monochloride monohydrate was also determined using X-ray crystallography technique.

Supplementary Materials

CCDC-2248492 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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