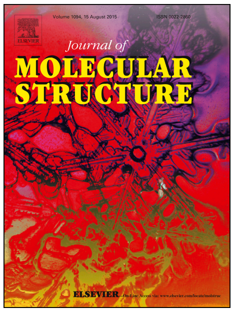

A piperidinium-carbodithioate salt: Synthesis, crystal structure, spectral, cation-interaction and electrochemical studies

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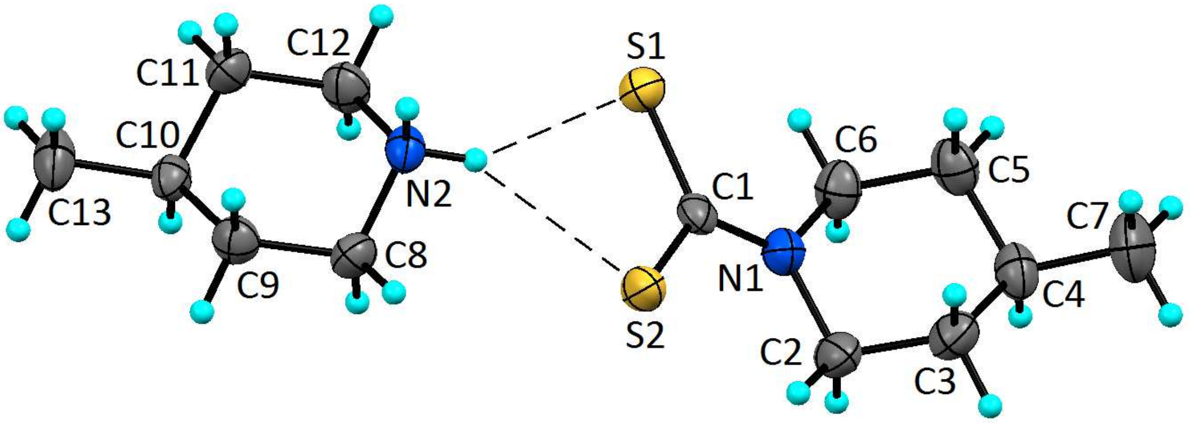
Graphical Abstract (Picture)



Re-revised Manuscript

A piperidinium-carbodithioate salt: Synthesis, crystal structure, spectral, cation-interaction and electrochemical studies

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ABSTRACT

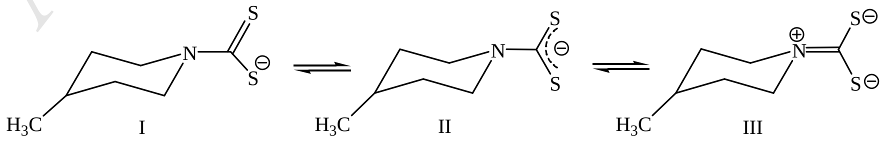
An ionic compound 4-methyl-piperidinium 4-methyl-piperidinecarbodithioate (MPMP) $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ has been synthesized from the one pot reaction of 4-methylpiperidine and carbon disulfide. The compound is well characterized on the basis of elemental analysis, IR, NMR, UV-visible and single crystal X-ray diffraction data. The compound introduces the concept of hydrogen bonding interactions in two ionic species and its effect on crystal packing. The asymmetric unit of the compound consists of 4-methyl-piperidinium cation and 4-methyl-piperidinecarbodithioate anion. Inter and intramolecular N–H···S contacts link piperidinium cation and carbodithioate anion and stabilize the crystal packing in solid state. The compound crystallizes in monoclinic system with space group $P\,2_1/c$. The interaction of the compound with different metal ion solutions is studied and it shows interesting red shifts with Co^{2+}, Cu^+, Cu^{2+} and Ni^{2+} ions which suggests that MPMP may be a useful probe for sensing of these ions. Cyclic voltammetric analysis of the compound exhibits quasi-reversible redox behaviour.

Keywords: piperidinium; carbodithioate; salt; ionic compound; cation interaction;

1. Introduction

Dithiocarbamate represents an interesting class of dithio compounds with a strong chelating ability towards various transition metal ions and forms interesting coloured complexes. The dithiocarbamate derivatives have been widely used in analytical chemistry as complexing agents [1]. The qualitative analysis of metal complexes can be spectrophotometrically performed on the basis of their UV-Vis absorptions [2]. Dithiocarbamates have been used as pesticide since long ago but attracted the interests of medicinal chemists due to their metal binding capacity and exhibit a broad-spectrum of biological activities such as antimicrobial, anticancer, etc. [3]. They are also applicable as anti-tubercular [4] anti-alcoholic drug [5] and agent for the treatment of Alzheimer's disease [6]. Piperidine is an important pharmacophore and an excellent heterocyclic scaffold in the field of drug discovery which provides numerous opportunities exploring this moiety as an anticancer and antimicrobial agent by acting on various receptors [7,8]. Dithiocarbamates can serve as antioxidants for increasing the durability and photo-stability of a variety of polymers, oils and other materials [9]. The piperidine dithiocarbamato ligands generally form four membered *S*,*S*-chelate ring and bridge two metal centres due to the dominant contribution of the resonance form III (Scheme 1) [10-13].

The study of the 4-methyl-piperidinium 4-methyl-piperidine-carbodithioate is interesting because it introduces the concept of hydrogen bonding in two ionic species and its effect on crystal packing. A few ionic compounds of piperidine with CO_2, NO_2 and SO_2 are reported but no single crystal X-ray analysis is yet available on compound having piperidinium-carbodithioate cation-anion pair [14-16]. In view of the above importance, we report herein the synthesis, spectral and structural characterization of an ionic compound containing a piperidinium cation and a piperidine-dithiocarbamate anion.



Scheme 1. Resonance structures of 4-methyl-piperidine-carbodithioate

2. Experimental

2.1. *Chemicals and starting materials*

Commercial reagents were used without further purification. 4-Methyl-piperidine was purchased from Sigma Aldrich. Other chemicals were of reagent grade and used as purchased without further purification. All the synthetic manipulations were carried out in open atmosphere and at room temperature. The solvents were dried and distilled before use following the standard procedure.

2.2. *Physical measurements*

The carbon, hydrogen, nitrogen and sulfur contents were determined on a CHN Model CE-440 Analyzer and on an Elementar Vario EL III Carlo Erba 1108. Infrared spectra were recorded in the 4000–400 cm^{-1} region as KBr pellets on a Varian Excalibur 3100 FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL JNM-ECZ500R/S1 FT NMR spectrometer using TMS as an internal reference. The UV-vis absorption spectra were recorded at 2x10^{-5} M solution in MeOH on a SIMADZU 1700 UV–Vis spectrophotometer and emission spectrum was recorded on Agilent Technologies Cary Eclipse Fluorescence Spectrophotometer. Electrochemical studies were performed on a Metrohm (Netherlands) Instrument (Autolab PGSTAT204) attached with NOVA 1.11 software at room temperature under N_2 atmosphere. A three electrode, one compartment cell with solid Pt electrode as working electrode, platinum wire as counter electrode and Ag/AgCl as reference electrode was used.

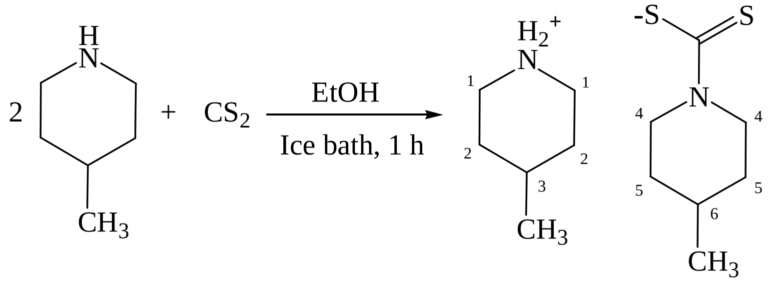
2.3. *X-ray crystallography*

Single crystal X-ray diffraction data collection for $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ were performed on an Xcalibur, Eos, Gemini diffractometer equipped with CrysAlis Pro., using a

Copper monochromated Cu Kα (λ = 1.54178 Å) radiation source at 173(2) K was used. Multi-scan absorption correction was applied to the X-ray data of both compounds. The structure was solved by direct methods (*SHELXL*-2013) and refined by full matrix least-square on F^2 (*SHELXL*) using anisotropic displacement parameters for all non-hydrogen atoms. All hydrogen atoms were included in calculated position and refined with a riding model [17-19]. Figures were drawn using the programs MERCURY and ORTEP-3 [20,21].

2.4. Synthesis of 4-methyl-piperidinium 4-methyl-piperidine-carbodithioate (MPMP)

4-Methyl-piperidinium 4-methyl-piperidine-carbodithioate was prepared by the drop-wise addition of carbon disulfide (0.7 mL, 10 mmol) into a cold ethanolic solution of 4-methylpiperidine (2.4 mL, 20 mmol). The mixture stirred for 1 h in an ice bath. The white solid obtained was filtered off, washed with ethanol and dried under reduced pressure. The compound was dissolved in methanol and kept for crystallization. Colourless crystals suitable for X-ray analysis were obtained after the slow evaporation of the solvent over a period of 15 days (Scheme 2). MPMP is easily soluble in common solvents including water. Yield: 80%; Mp. 188-190 °C. Anal. Calc. for $C_{13}H_{26}N_2S_2$ 274.48 (%): C, 56.88; H, 9.54; N, 10.20; S, 23.36. Found: C, 56.55; H, 9.40; N, 10.56; S, 23.42. IR (KBr, cm^{-1}): 3187 ν(N–H), 2952-2906 ν(C–H), 1586 ν(C–N), 1015 ν(C=S). ^{1}H NMR (δ, ppm): 0.92 (two d, 6H, CH_3,), 1.12–1.22 (m, 2H, H-3, H-6), 1.54–1.72 (m, 8H, H-2, H-5), 2.79 (t, 2H, H-1_{axial}, J = 12 Hz), 2.99 (t, 2H, H-4_{axial} J = 12 Hz), 3.72 (d, 2H, H-$1_{equatorial}$, J = 12.5 Hz), 5.62 (d, 2H, H-$4_{equatorial}$, J = 12.5 Hz), 7.45 (2H, NH) (Scheme 2). ^{13}C NMR (δ, ppm): 21.4 (CH_3), 29.0 (C2), 30.8 (C3, C5), 34.2 (C6), 44.5 (C1), 51.1 (C4), 208.6 (C=S) (Scheme 2).



Scheme 2. Synthesis of $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ (MPMP)

3. Result and discussion

3.1. IR spectrum

The IR spectrum of $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ showed absorptions due to the stretching modes of N-H ν(3187), C-N ν(1586) and C=S ν(1015), respectively. The absorption bands around 2925 cm^{-1} are attributed to aliphatic C–H stretches (Supplementary Fig. 1). Compound shows a slight lower stretching vibration in ν N-H (3187) as compared to other compound, indicating that the dithio sulfur is involved in hydrogen bonding [16]. The compound exhibits a band at 1586 cm^{-1} with a positive shift of 115 cm^{-1} for C-N stretching, when compared to 4-methyl piperidine which confirms the conjugation of CS_2 with piperidine nitrogen [12]. Compound showed two absorptions bands at 1462 and 1379 cm^{-1} due to asymmetric symmetric bending vibrations of CH_3 group.

3.2. NMR spectra

The ^1H NMR spectrum of $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ showed double doublet signals at δ 0.92 ppm due to methyl protons. The multiplet signals were observed in the range of δ 1.12–1.22 and 1.54–1.72 ppm due to H-3, H-6 and H-2, H-5 protons, respectively (Scheme 2). In the carbdithioate anion the axial and equatorial H-4 protons appeared at 2.99 (t) and 5.62 (d) ppm, respectively while the axial and equatorial protons (H-1) in the piperidinium cation appeared at 2.79 (t) and 3.72 (d) ppm. For the axial protons both the geminal coupling with the equatorial protons as well as the vicinal coupling with the adjacent axial protons were large but in case of equatorial protons, only the geminal coupling with the axial protons was large. The deshielding of equatorial and axial protons was due to high electron density at nitrogen atom [22, 23]. However, the equatorial protons were more deshielded than the axial protons (Supplementary Fig. 2) [24]. A small broad signal at δ 7.45 ppm for N-H protons is observed which is highly deshielded when compared to N-H protons of 4-methyl piperidine (δ 2.32 ppm). This suggests strong interaction between N-H protons and dithio sulfur atoms.

The ^{13}C NMR spectrum of $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ showed a signal at δ 208.6 ppm due to the CS_2 carbon attributed to the considerable double bond character in the C-N bond of the dithiocarbamato group which supports the formation of the compound (MPMP). In the piperidine ring, carbon atoms adjacent to the nitrogen were more deshielded than other carbon atoms. The signals for C1, C2 and C3 in cation were observed at δ 44.5, 29.0 and 30.8 ppm, respectively (Scheme 2). Whereas the signals for C4, C5, C6 in anion appeared at δ 51.1, 30.8 and 34.2 ppm, respectively. The methyl carbons appear δ 21.4 at ppm (Supplementary Fig. 3) [11, 12].

3.3. Electronic absorption and emission spectra

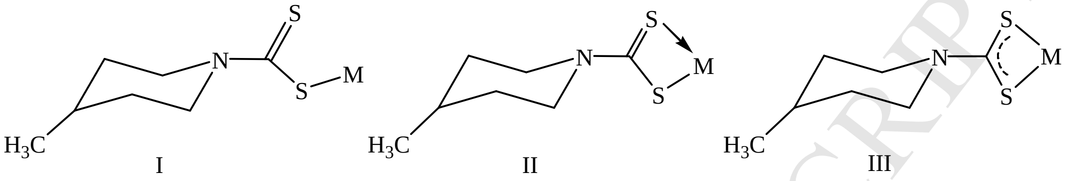
The compound MPMP displays two high energy bands at at 34800 and 39000 cm^{-1} which may be assigned to $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$ transitions which are attributed to the NCS_2 chromophore (Fig. 1). Upon excitation at 34800 cm^{-1}, the compound MPMP exhibited maximum emission at 30500 cm^{-1} (Fig. 3).

3.4. Cation Interaction Behaviour

UV-Vis absorption spectra were recorded at 2 x 10^{-5} M in methanol. The absorption spectral bands observed for MPMP at 34850 and 39050 cm^{-1} may be assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions due to NCS moiety (Fig. 1). The potassium derivative of the same anion (potassium 4-methylpiperidine-carbodithioate) showed absorption maxima at 33650 and 37700 cm^{-1}. Thus MPMP shows blue shift of 1800 and 1650 cm^{-1}, respectively regarding its potassium derivative. We detected the colour change and new *d-d* absorption bands upon addition of different metal(II) acetates due to coordination between metal ion and sulfur donor atom (Fig. 1.a). Upon addition of cobalt acetate solution the colour changed to green and a new band was observed at 30800 cm^{-1} whereas upon addition of copper(II) acetate solution showed brown colour and absorption band at 23000 cm^{-1}. These values are close to the absorption maxima reported in their metal complexes with 4-methylpiperidine-carbodithioate [12]. The band around 23000 cm^{-1} for Cu-MPMP may be assigned to the envelope of the $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$ and $^2\mathrm{E_g}$ transitions and suggests a square planar geometry for the complex [12,25]. Upon adition of manganese(II) acetate in MPMP solution colour changed to brown and a band was observed at 21900 cm^{-1} which is the characteristic of six coordinate Mn(III) and may be assigned to the $^5E_g \rightarrow {}^5T_{2g}$ transition [24,26]. Ni-MPMP solution gives spectral bands at 25550 and 18350 cm^{-1} and it is the characteristic of square-planar Ni(II) complex [24,27]. The diamagnetic Zn(II) complex did not show *d-d* transition. The interaction behaviour was also studied with cuprous chloride, ferrous chloride, ferric sulphate, chromium acetate and mercuric chloride besides above metal(II) acetates (Fig. 1.b). Upon addition of Cu(I) chloride in MPMP, colour changed into greenish-brown and a new broad band at 26000 cm^{-1} was observed. Ferrous chloride and ferric sulphate gave dark red and brown colour, respectively in MPMP solution, while Cr(III) acetate and Hg(II) chloride ions did not showed any significant colour change (Fig. 2). This study suggests that Co^{2+}, Cu^{+}, Cu^{2+} and Ni^{2+} ions showed significant red shift in UV-visible spectra, hence MPMP may be a good probe for sensing these ions in solution [2].

The high energy absorption maxima in the range of 39000-30800 cm^{-1} can be attributed to the NCS_2 chromophore. It is noteworthy that free MPMP showed two bands at

34850 and 39050 cm^{-1} due to NCS_2 moiety while upon addition of metal ions the former band either disappeared or its intensity decreased. It also suggests the interaction of metal ions with NCS_2 moiety. Some possible modes of cation interactions are depicted in scheme 3. M^{2+} and M^{3+} are at the border line of hard and soft lewis acid, therefore they may exist with slight different in their stability (Scheme 3, III).



Scheme 3. Possible modes of interactions of MPMP with various cations

3.5. *Crystal structure description of $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$*

The molecular structure of $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ with atom numbering scheme is shown in Fig. 4. The details of data collection, structure solution and refinement are listed in Table 1. Selected bond lengths and angles are given in Tables 2 and hydrogen bonding parameters are given in Table 3.

The molecule $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ consists of 4-methyl-piperidinium and 4-methyl-piperidinecarbodithioate cation-anion pair. In the piperidinium cation, the C–C and C–N single bonds are similar to those reported in other piperidinium cation [14,15] while in anion the C–N bond lengths [C8–N2 = 1.487(3), C12–N2 = 1.485(3) Å] are shorter than C–N single bond suggesting partial double bond character [12,28]. The C–S bond lengths [C1–S1 = 1.717(2) and C1–S2 = 1.721(2) Å] have well agreement with other reported piperidinecarbodithioate anion [12,29]. These C–S bond distances are intermediate between C–S single and C=S double bond distances which attribute to the delocalization of the π-electrons in the NCS_2 moiety [12,30].

In the crystal structure, N2–H2D···S1 [2.53 Å] andN2–H2D···S2 [2.65 Å] contacts link the dithiocarbamate anion to the piperidinium cation in the asymmetric unit (Fig. 4). In addition, intermolecular N–H···S [N2-H2C···S1#1 = 2.54 Å; N2-H2C···S2#1 = 2.75 Å] contacts generating $R_1^2(4)$ ring motifs are also observed (Fig. 5). These hydrogen bonding cantacts are working between cationic and anionic species and stabilize the crystal structure of compound in solid state. The hydrogen bonds between S···H successfully disperse the energy-rich electronic density at the sulfur atoms of the dithiocarbamate ion in combination with the electronic attraction between N^+···S; thus the dithiocarbamate ion in the complex acquires a stable state. The crystal structure of the compound is also stabilized by intramolecular C–H···S contacts (Table 3).

3.6 *Electrochemical characterization*

The electrochemical behaviour of the compound MPMP $\{C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-\}$ was studied using cyclic voltammetry and is depicted as Fig. 6 and 7. The cyclic voltammograms were recorded in 10^{-3} M MPMP solution in CH_3CN at a platinum electrode using 0.1M TBAP as supporting electrolyte. MPMP exhibited two sets of cathodic-anodic peaks at 0.530 V, 0.460 V and -0.100 V, -0.250 V, respectively at 0.020 V.s^{-1} scan rate and the separation between the cathodic and anodic peak potentials ($\Delta E_p = E_{pa} - E_{pc}$) of 0.070 V and 0.150 V indicate quasi-reversible redox behaviours. The peack separation potential of 0.070 V for cathodic and anodic peak at 0.536 V, 0.460 V is slightly high as compared to that expected for one-electron process and hence it can be assumed that the redox process is coupled with some chemical reaction accompanied with the charge transfer from piperidinium to carbodithioate moiety with a formal redox potential $E = (E_{pa} + E_{pc})/2 = 0.495$ V (Fig. 7). On scaning at higher scan rates the cathodic peak potential slightly shifted and separation between cathodic and anodic peaks increased which indicated that the redox process is not completely reversible. At scan rates 0.020, 0.050, 0.100, 0.150 and 0.200 V, the peak separation was 0.070, 0.076, 0.080, 0.092 and 0.100 V, respectively (Fig. 6) [12,31].

4. Conclusions

In this paper we reports the synthesis and structure of an organic salt $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$. The compound was synthesized using 4-methylpiperidine and carbon sulfide in one step. The compound is characterised by various physicochemical methods. The molecule crystallizes in monoclinic system with space group $P\ 2_1/c$. The asymmetric unit of molecule $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ consists of 4-methyl-piperidinium and 4-methyl-piperidinecarbodithioate cation-anion pair which are linked *via* inter and intramolecular piperidinium N-H···S carbodithioate interactions. In the UV-Vis absorption spectrum of the compound bands observed at 34800 and 39000 cm^{-1} may be assigned to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in NCS moiety. While upon excitation at 34800 cm^{-1} it exhibited maximum emission at 30500 cm^{-1}. The behaviour of the compound in different metal ion solutions is studied and it shows interesting red shifts with Co^{2+}, Cu^+, Cu^{2+} and Ni^{2+} ion which suggests that the compound $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ may be useful in sensing of these ions in solution. Cyclic voltammetric analysis of the compond at 20 mV.s^{-1} showed peak separation potential of 0.070 V between cathodic and anodic peak with a formal redox potential $E = (E_{pa} + E_{pc})/2 = 0.495$ V which is slightly high as compared to that expected for one-electron process and hence the compound exhibits a quasi-reversible redox behaviour.

5. Supplementary material

CCDC 1543175 contains the supplementary crystallographic data for $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ which can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/.................

Acknowledgements

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Table 1. Crystallographic data for $C_6H_{14}N^+ \cdot C_7H_{12}NS_2$

Empirical formula	$C_{13}H_{26}N_2S_2$
Formula weight	274.48
Crystal system	Monoclinic
Space group	$P\ 2_1/c$
T (K)	173(2)
λ, Cu Kα (Å)	1.54178
a (Å)	11.2982(7)
b (Å)	15.5679(6)
c (Å)	9.5884(5)
α, γ(°)	90
β (°)	110.593(6)
	77.597(7)
V, (Å^3)	1578.73(15)
Z	4
ρ_{calcd} (g/cm^3)	1.155
μ (mm^{-1})	2.91
F(000)	600
Crystal size(mm^3)	0.30×0.20×0.15
θ range for data collections(°)	4.180-71.306
Index ranges	-13≤h≤13, -18≤k≤11, -11≤l≤10
No. of reflections collected	5641
No. of independent reflections(R_{int})	2996 (R_{int} = 0.044)
No. of data/restrains/parameters	2996 / 0 / 156
Goodness-of-fit on F^2	1.102
R_1^a, wR_2^b [(I>2σ(I)]	0.0518, 0.1364
R_1^a, wR_2^b (all data)	0.0604, 0.1445
Largest difference in peak /hole (e.Å^{-3})	0.44, −0.33
CCDC	1543175

$^aR_1 = \Sigma||F_o| - |Fc||\Sigma|F_o|$; $^bR_2 = [\Sigma w\,(|F^2{}_o| - |F^2{}_c|)^2/\Sigma w|F^2{}_o|^2]^{1/2}$

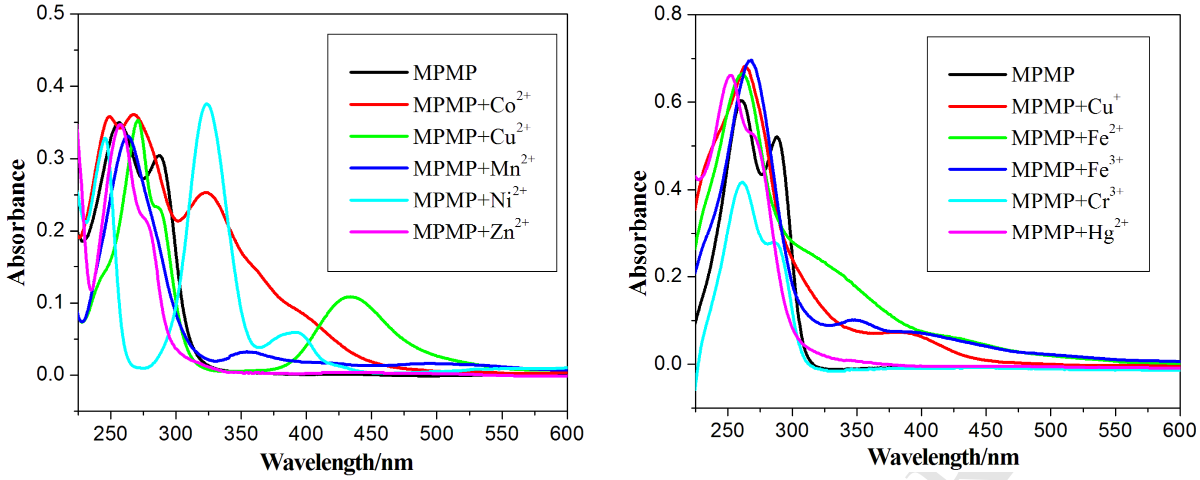
Table 2 Selected bond lengths and angles for $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$

Bond lengths (Å)		Bond angles (°)	
S1-C1	1.717(2)	C1-N1-C6	123.30(19)
S2-C1	1.721(2)	C1-N1-C2	123.69(19)
N1-C1	1.349(3)	C6-N1-C2	112.78(18)
N1-C6	1.463(3)	C12-N2-C8	112.11(17)
N1-C2	1.465(3)	N1-C1-S1	120.29(16)
N2-C12	1.485(3)	N1-C1-S2	120.21(16)
N2-C8	1.487(3)	S1-C1-S2	119.49(12)
C2-C3	1.509(3)	C3-C4-C7	111.9(2)
C10-C13	1.521(3)	C3-C4-C5	109.00(19)
C3-C4	1.520(3)	C7-C4-C5	110.8(2)
C4-C7	1.526(4)	C13-C10-C11	111.3(2)
C4-C5	1.527(4)	C13-C10-C9	111.5(2)
C5-C6	1.516(3)	C11-C10-C9	108.80(17)

Table 3. Inter and intramolecular hydrogen bonds [Å and º] for $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$

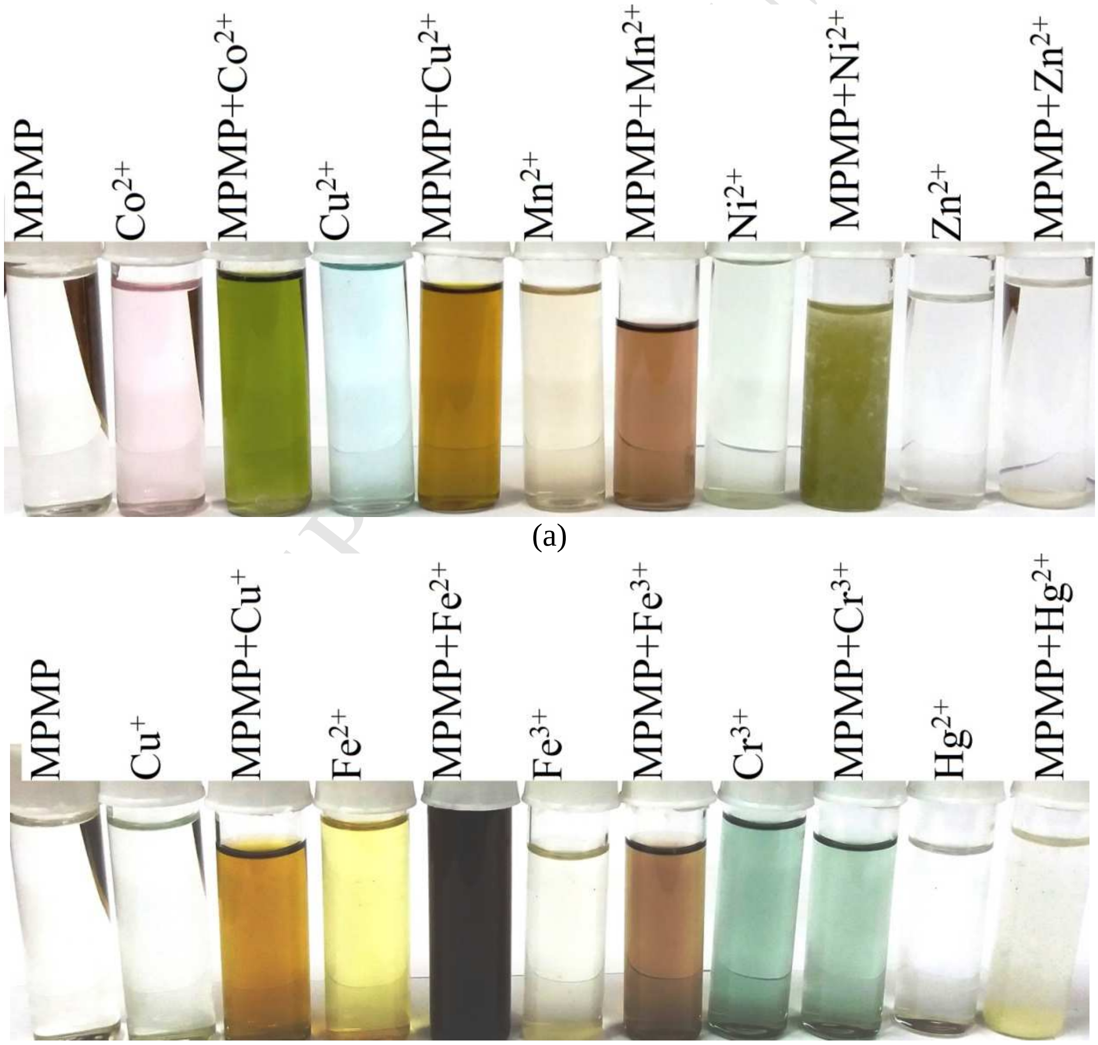
D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
N2-H2C···S1#1	0.91	2.54	3.3570(19)	149.9
N2-H2C···S2#1	0.91	2.75	3.499(2)	140.7
N2-H2D···S1	0.91	2.53	3.3423(18)	148.8
N2-H2D···S2	0.91	2.65	3.4018(18)	140.5
C2-H2B···S2	0.99	2.49	3.040(2)	114.5
C6-H6A···S1	0.99	2.48	3.030(2)	114.6

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1



(a) (b)

Fig. 1. UV-Vis absorption spectra of $C_6H_{14}N^+\cdot C_7H_{12}NS_2^-$ (MPMP) and interaction with different metal ions (a) Co^{2+}, Cu^{2}+, Mn^{2+}, Ni^{2+}, Zn^{2+} (b) Cu^+, Fe^{2+}, Fe^{3+}, Cr^{3+} and Hg^{2+} in MeOH.



(a)

(b)

Fig. 2. Colour change of MPMP in presence of different metal ions to show the sensing behaviour

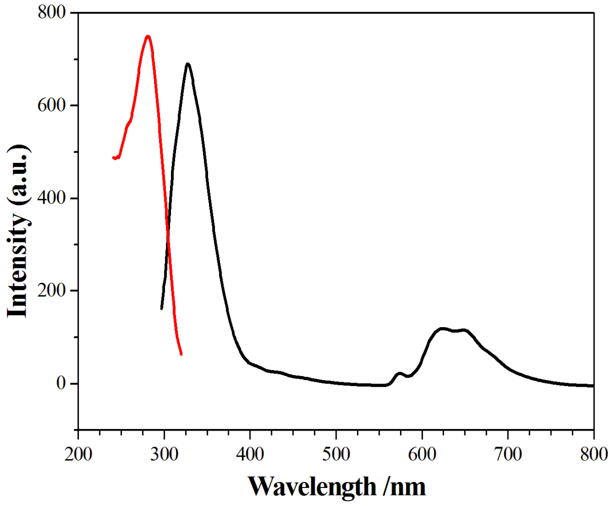


Fig. 3. Emission spectrum of $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$ in MeOH at 10^{-5} M is displayed in black, excitation wave length was 287 nm. Corresponding excitation spectrum is shown in red.

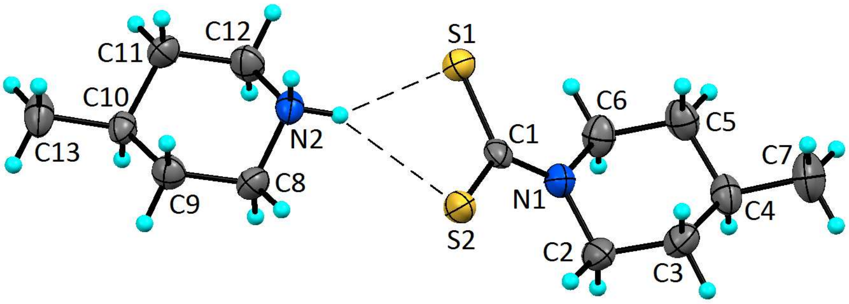


Fig. 4. Molecular structure of $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$

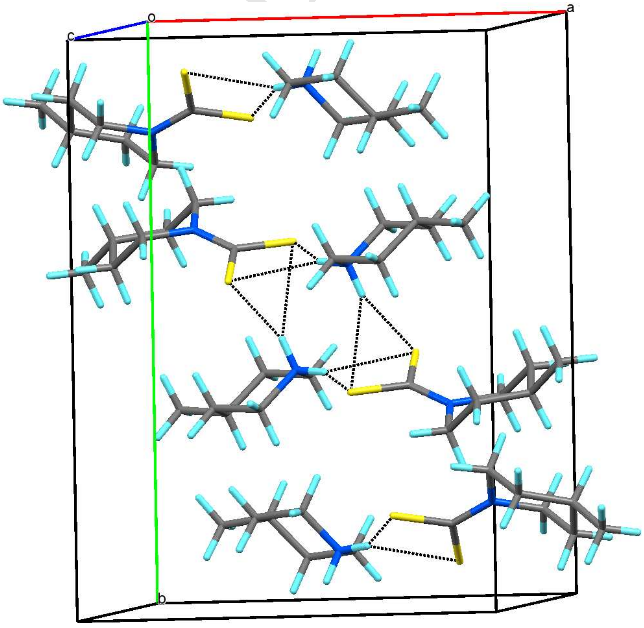


Fig. 5. Molecular packing of $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$ viewed along the *c* axis. Dashed lines indicate piperidinium N-H···S carbodithioate interactions

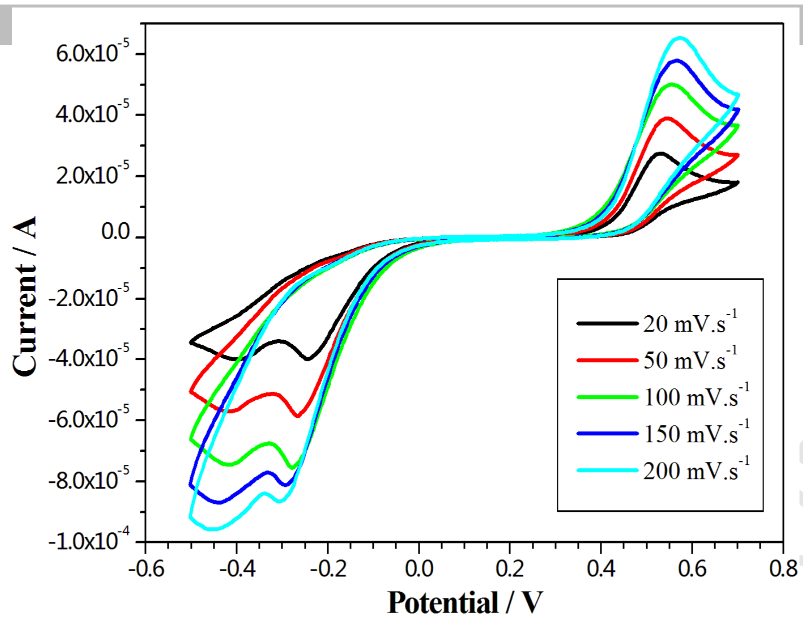


Fig. 6. The cyclic voltammograms obtained for $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$ at different scan rates

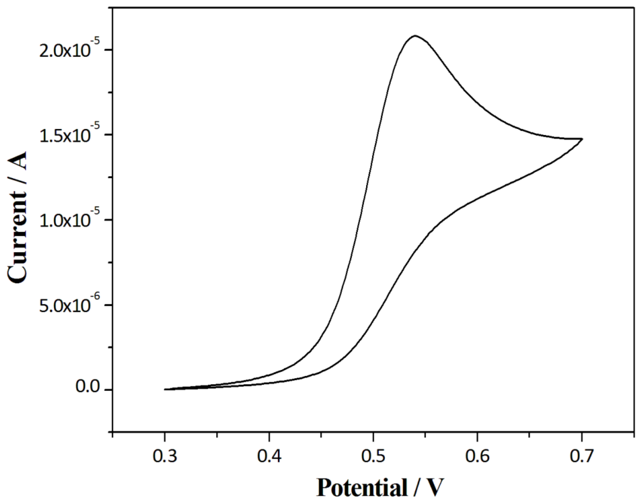


Fig. 7. The cyclic voltammogram obtained for $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$ at 20 mVs^{-1} scan rates

Research Highlights

- Crystal structure of an ionic compound piperidinium-carbodithioate is reported.
- The compound consists of $C_6H_{14}N^+$ cation and $C_7H_{12}NS_2^-$ anion pair.
- Cyclic voltammetric study of the compound shows quasi-reversible redox behaviour.
- The compound showed interesting red shifts with Co^{2+}, Cu^+, Cu^{2+} and Ni^{2+} ions.
- Inter and intramolecular N–H···S contacts link cation-anion pairs.

Graphical Abstract (Synopsis)

The ionic compound 4-methyl-piperidinium 4-methyl-piperidinecarbodithioate $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$ has been synthesized from the one pot reaction of 4-methylpiperidine and carbon disulfide. The asymmetric unit of the compound consists of 4-methyl-piperidinium cation and 4-methyl-piperidinecarbodithioate anion which are linked *via* inter and intramolecular N–H···S contacts. The compound is well characterized on the basis of IR, NMR, UV-visible and single crystal X-ray diffraction data. The behaviour of the compound in different metal ion solutions is studied and it shows interesting red shifts with Co^{2+}, Cu^+, Cu^{2+} and Ni^{2+} ions which suggests that $C_6H_{14}N^+ \cdot C_7H_{12}NS_2^-$ may be useful in sensing of these ions in solution. Cyclic voltammetric analysis of the compond exhibits quasi-reversible redox behaviour.