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A Two-Dimensional Self-Assembled Proton Transfer Compound Containing Pyridinium-2,6-bis(monothiocarboxylate) and Creatinium Ion Pair: Synthesis, Characterization, Crystal Structure, Solution and *Ab initio* Studies

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A two-dimensional self-assembled proton-transfer compound, $(creatH)^+(pdtcH)^-$, **L**, was synthesized from the reaction of pyridine-2,6-bis(monothiocarboxylic) acid, ($pdtcH_2$), and creatinine, creat, and characterized using IR, NMR, UV spectroscopy and X-ray crystallography. The anionic and cationic components self assemble two-dimensionally *via* ion-pairing, H-bonding and π-π stacking and, therefore, parallel sheets are formed. The spectrometric and potentiometric pH titrations indicate that the abundant proton transfer species present at pH < 4.5 is $(creatH)^+(pdtcH)^-$, in support of the single crystal X-ray structure. *Ab initio* method, DFT (B3LYP), was applied for achievement of the barrier energies of proton transfer processes and geometric parameters of transition states.

Keywords: Proton transfer, X-ray, *Ab initio*, Pyridine-2,6-bis(monothiocarboxylic) acid, Creatinine, Solution

INTRODUCTION

Chemists have been interested in preparing self-assembling systems in recent years [1]. Molecular self-assembling involves the spontaneous association of molecules into stable aggregates, joined by non-covalent bonds, with well-defined composition and structure. Self-assembling of 5-(guanidinecarboxyl)-1H-pyrol-2-carboxylate in DMSO [2] and bis(imidazolium)-2,6-pyridine dicarboxylate [3] are example in this regard. Proton transfer from appropriate H-donors to H-acceptors is a potentially applicable, as one of the strategies, method in the preparation of such systems if the starting components of the self-assembling process are correctly and logically chosen from the molecular engineering point of view. Proton transfer is one of the most important elementary in physics, chemistry and biochemistry, as it is the key process in important reactions such as ionization in water, anomalously high proton mobility in water (Von Grotthuss mechanism), acid-base neutralization reactions, proton pumping through membrane protein channels and enzyme catalysis [4-10].

During our recent efforts regarding proton transfer compounds (PTCs) we realized that such self-assembled systems can be synthesized upon the reaction of 2,6-pyridinedicarboxylic acid and amines [11]. In some cases, when the resulting PTCs did not allow us to evaluate their solid phase structures, because of the lack of crystallinity, it became apparent to us that their corresponding transition metal complexations can result in the formation of self-assembling systems [12]. In order to develop new types of PTCs with self-

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assembling capability we have recently investigated influence of pyridine-2,6-bis(monothiocarboxylic) acid, ($pdtcH_2$), on the structural properties of the resulting PTCs. The first $pdtcH_2$-based PTC reported recently from our research group has been the one prepared from $pdtcH_2$ and 2-aminopyridine. Here we report the synthesis of a novel PTC obtained from $pdtcH_2$ and creatinine, creat, and demonstrate the generation of self-assembled supramolecular layers *via* proton transfer process. Creatinine is a biologically important proton acceptor having a number of functional groups suitable for hydrogen bonding [13], which has previously been used in the synthesis of some proton-transfer compounds such as those with nitrobenzoic acids, 3,5-dinitrobenzoic acid, 5-nitrosalicylic acid, 3,5-dinitrosalicylic acid and pyrazine-2,3-dicarboxcylic acid [14]. $pdtcH_2$ is a unique and powerful metal chelator produced by *Pseudomonas stutzeri* and *Pseudomonas putida.* The physiological role of $pdtcH_2$ is that it acts as a siderophore, an antibiotic, or both [15].

EXPERIMENTAL

Materials

Creatinine was purchased from Merck and $pdtcH_2$ was prepared according to the reported procedure [22]. HCl, KOH, KCl, acetonitrile (AN) and methanol were used without any further purification (all from Merck). Carbonate free KOH solution was standardized with potassium hydrogen phthalate. The HCl solution was standardized with standard KOH. All solutions were prepared in doubly distilled deionized water. The solutions used for the calibration of the pH meters were pH 4.00 (±0.01), 7.00 (±0.01) and 10.00 (±0.01) standard buffers.

Instruments

IR spectra were recorded on Perkin-Elmer 343 Spectrometer, using the KBr disc technique. Melting points were determined with an Electrothermal IA-900. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker 250 (250 and 62.5 MHz, respectively) spectrometer. Chemical shifts were reported on the δ scale relative to TMS. The absorption spectra were recorded using a UV-Vis 2100 Shimadzu spectrophotometer (controlled to ±0.1 ºC).

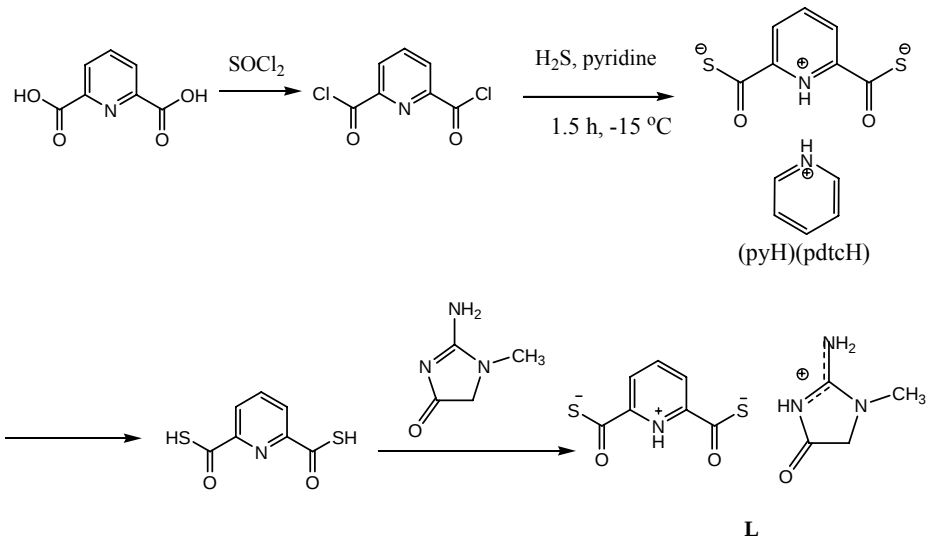
Synthesis of $(creatH)^+$ $(pdtcH)^-$, L

$pdtcH_2$ (0.20 g, 1 mmol) was added to a vigorously stirred suspension of creat (0.11 g, 1 mmol) in water (15 ml) over a period of 1 min. The mixture was heated to obtain a homogenous solution. The solution was slowly concentrated and cooled to room temperature. The resulting orange-color crystals were filtered to obtain 0.15 g **L** in 50% yield, m.p.: 172 °C.

^{1}H NMR (DMSO-d_6) δ_H 3.03 (s, 3H, CH_3 creat), 4.17 (s, 2H, CH_2, creat), 8.43 (d^3, J = 7.5 Hz, 2H, $H_{3,5}$ pdtcH), 8.64 (t, ^{3}J = 15.5 Hz, 1H, H_4 pdtcH), 8.88 (2H, NH_2) ppm. ^{13}C NMR (DMSO-d_6) δ_C 31.1(C'$_3$), 54.0(C'$_2$), 122.9(C_3), 144.3(C_1), 147.6(C_4), 157.6(C'$_4$), 171.8(C'$_1$), 193.5(C_1) ppm. IR(KBr) 3341(m), 3145(m), 3071(m), 2987(m), 2689(w), 1756(m), 1691(s), 1639(m), 1621(w), 1593(m), 1553(s), 1497(s), 1412(m), 1395(m), 1338(m), 1273(m), 1248(m), 1233(m), 1187(w), 1151 (m), 1102(s), 1034(m), 979(m), 947(s), 934(s), 891(m), 826(m), 779(w), 737(m), 689(w), 662(m), 608(m), 593(m), 569(m), 555(m), 497(m), 455(w), 410(w) cm^{-1}.

Potentiometric pH Titrations

All potentiometric pH measurements were made on solutions in a 50-ml double-walled glass vessel using a Model 686 Metrohm Titroprocessor equipped with a combined glass-calomel electrode. The sample holder was washed several times with de-ionized water and dried thoroughly before each experiment. The temperature was controlled at 25.0 ± 0.1 °C by circulating water through the jacket, from a constant-temperature bath (MLW thermostat). The solutions were placed in the thermal jacketed sample holder that was connected to a temperature bath and were allowed several minutes to reach thermal equilibrium. The cell was equipped with a magnetic stirrer and a tightly fitting cap, through which the electrode system and a 20-ml capacity Metrohm piston burette were inserted and sealed with clamps and O-rings. Atmospheric CO_2 was excluded from the titration cell with a purging steam of purified nitrogen gas. The pH electrode was calibrated in the thermostated cell with standard buffers to read p[H] directly (p[H] = -log[H^+]). The concentrations of creat were 2.5×10^{-3} M, for the potentiometric pH titrations of $pdtcH_2$ and $pdtcH_2$ + creat. The accurate and excess of HCl was added to porotonation of total sites on the ligands. A



Scheme 1

standard carbonate-free KOH solution (0.098 M) was used in all titrations. The ionic strength was adjusted to 0.1 M with KCl. Before an experimental point (pH) was measured, sufficient time was allowed for the establishment of equilibrium. Ligands protonation constants and their metal complexes protonation, stability and hydrolysis constants were evaluated using the program BEST described by Martell and Motekaitis [19]. The value of $K_w = [H^+] [OH^-]$ used in the calculations was $10^{-13.78}$ [23]. The concentration distribution diagrams were obtained with the programs SPE and SPEPLOT [19].

Spectrophotometric Titration

The solutions of creat (3.0×10^{-5} M) were prepared in AN. Titrations were performed at 25.0 ± 0.1 °C using a $pdtcH_2$ solutions. A step by step increase of a $pdtcH_2$ solution of 5.0×10^{-3} M, prepared in the same solvent, to the titration cell was carried out using a micro syringe and the absorbance of the solution was measured after each addition.

X-ray Structural Analysis

X-ray structural analysis on single crystal **L** was carried out on a STOE IPDS-II diffractometer with graphite monochromated Mo-K_α radiation. The data were collected at a temperature of 100(2) K to a maximum 2θ value of 27.93° and in a series of ω scans in 1° oscillations with 150 second exposures. The crystal-to-detector distance was 110 mm. The data were corrected for Lorentz and polarizing effects. A numerical absorption correction was applied [24,25]. The structure was solved by direct/heavy-atom Patterson method [26] using SHELXL-97. All of the non-hydrogen atoms were refined anisotropically. All of hydrogen atoms were located in the difference Fourier map. The final cycle of full-matrix least-squares refinement [26] on F^2 was based on 2990 unique reflections.

Computational Method

The *ab initio* calculation was carried out with HF/6-31+G** level to access initial optimization by BERNNY optimizer with unrestricted symmetry. Intra and intermolecular proton transfer process were performed with ADDREDUNDANT option by scanning in B3LYP/6-31+G (2d, p) level to access final optimization. QST2 option was used to investigate the transition structure between primitive and final structure. The energies of all the structures and geometric properties were also, calculated. All calculations were performed with the GASSIAN 98W series of program [27].

RESULTS AND DISCUSSION

Synthesis and Characterization of L

The procedure adopted in the synthesis of **L** is outlined in Scheme 1. The reaction between $pdtcH_2$ and creatinine at a 1:1

molar ratio lead to the formation of the orange-color crystalline compound **L**. The melting point of **L** was sharp and different from that of the starting materials. The characterization of **L** was performed using NMR, IR spectroscopy and X-ray crystallography.

NMR spectroscopy study was conducted to characterize the chemical structure of **L**. A comparison between ^{1}H and ^{13}C NMR spectra of **L** and those of the corresponding dithiocarboxylic acid and creatinine, clearly indicated the presence of both starting materials; dithiocarboxylic acid and creatinine in **L**. The ^{1}H NMR spectrum showed two characteristic sets of resonances at 3.02 and 4.17 ppm due to methyl and methylene hydrogens in $creatH^{+}$ and at 8.44 and 8.64 ppm due to $pdtcH^{-}$. The ^{13}C NMR spectrum of **L** presented eight resonances at 31.1, 54.0, 122.9, 144.3, 147.6, 157.6, 171.8, 193.5, ppm as expected. Considering the peak assignments reported for $pdtcH_2$ (123.9, 138.8, 150.0, and 190.4 ppm), the resonances at 31.1, 54.0, 157.6 and 171.8 ppm can be definitely correlated to creatinium ion [16].

The infrared spectrum of **L** confirmed the absence of the two well-defined SH bands of medium intensity at 2566 and 2521 cm^{-1} corresponding to $pdtcH_2$. The expected strong asymmetry C=O stretching for $pdtcH_2$ at 1668 cm^{-1} has been replaced by a distinct strong band at 1553 cm^{-1} which is due to the thiocarboxylate C=O stretching. These two changes indicate that proton transfer has occurred and an ionic adduct has been formed. Two characteristic frequencies at 3071 and 3341 cm^{-1}, corresponding to the asymmetric and symmetric stretching frequencies of NH_2 group of creatinine, respectively, indicate that this group has not been protonated. The IR spectrum showed absorptions characteristics of the amide C=O and $C=NH_2^{+}$, at 1691 and 1497 cm^{-1}, respectively. Therefore, the endocyclic imine N atom of creatinine has to be protonated.

With respect to the IR and NMR data presented, one can conclude that **L** consists of $(creatH)^{+}$ and $(pdtcH)^{-}$ fragments resulting from a mono proton transfer process. The formation of the 1:1 proton transfer compound **L** was further confirmed by solution studies and X-ray crystal structure.

Single Crystal X-ray

The numbering scheme and ORTEP diagram of (creatH)(pdtcH) are presented in Fig. 1. A summary of X-ray crystallographic data for **L** is given in Table 1 while some selected bond lengths, bond angles and torsion angles data are given in Table 2. Table 3 lists H-bonding data for the compound **L**. As is seen in Fig. 2, the lattice is composed of ion pairs $creatH^{+}$ and $pdtcH^{-}$ produced upon two different proton transfers from two -COSH functional groups. The intra- and intermolecular proton transfers take place to two different destinations, i.e. pyridine and creatinine nitrogens. The two sulfur atoms of the two resulting $-COS^{-}$ anions are oriented differently, one toward the pdtc nitrogen and the other one far from it. The selected torsion angles involving the thiocarboxylato groups and the pyridine frameworks, given in Table 2, indicate that both thiocarboxylato groups are coplanar with the corresponding pyridine frames. From Fig. 2 it is clear that anionic and cationic components of the ion-pair compound self-assemble into parallel layers. Three obvious factors causing the formation of such two-dimensional self-assembled supramolecular system are: i) intermolecular H-bonding between ion pairs, ii) electrostatic attractions between opposite ions and iii) π-π interactions between the components of two neighboring sheets. The two neighboring sheets distance is about 3.32 Å indicating π-π stacking in lattice. Another interesting aspect of the solid phase structure of **L** is generation of a supramolecular macrocycle in the lattice, as shown in Fig. 3. The resulting macrocycle involves two pdtcH and two creatH components. Each component is H-bonded to the two neighboring components carrying opposite charge. The generated macrocycle is then extended through H-bonding to build the two-dimensional self-assembled supramolecular system noticed earlier.

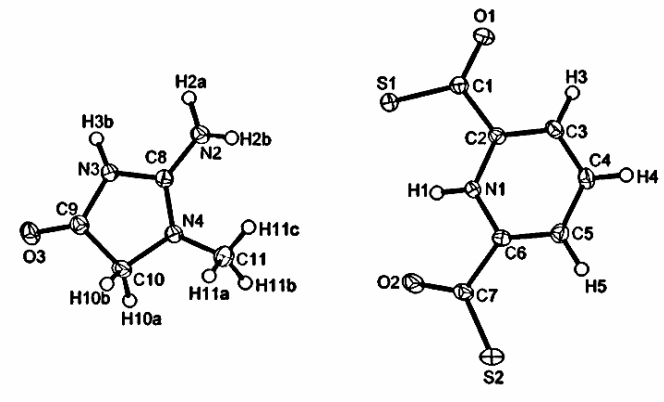


Fig. 1. ORTEP diagram for **L**.

Table 1. Crystallographic Data of Compound **L**

Formula	$C_{11}H_{12}N_4O_3S_2$	
Formula weight	312.39	
Crystal system	Triclinic	
Space group	P - 1	
Unit cell dimensions	a = 6.2868(17)Å	α = 95.06(2)º
	b = 7.408(2) Å	*β* = 91.69(2)º
	c = 14.810(4) Å	γ = 95.16(2)º
Unit cell volume ($Å^3$)	683.8 (3)	
Z, Calculated density (g cm^{-3})	2, 1.517	
Temperature (K)	100 (2)	
Wavelength	0.71073 A	
Absorption coefficient (mm^{-1})	0.402	
F(000)	324	
Crystal size (mm)	0.35 × 0.20 × 0.07	
θ range for data collection	2.76 to 27.93º	
Limiting indices	-8 <= h <= 8, -9 <= k <= 9, 0 <= l <= 19	
Reflections collected/unique	2990	
Completeness to θ = 27.93	91.3%	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2990/0/229	
Goodness-of-fit on F^2	1.055	
Final R indices [I > 2sigma(I)]	R1 = 0.0299, wR2 = 0.0771	
R indices (all data)	R1 = 0.0328, wR2 = 0.0790	
Largest diff. peak and hole (e A^{-3})	0.290 and -0.225	

Table 2. Selected Bond Lengths (Å), Angles (º) and Torsion Angles (º) of Compound **L**

C(1)-O(1)	1.2468(16)	C(7)-O(2)	1.2461(17)
C(1)-S(1)	1.7026(14)	C(7)-S(2)	1.6874(14)
C(1)-C(2)	1.5169(17)	C(6)-C(7)	1.5229(17)
C(2)-N(1)	1.3424(16)	C(6)-N(1)	1.3467(16)
C(8)-N(2)	1.3064(17)	C(8)-N(4)	1.3261(17)
C(8)-N(3)	1.3757(17)	C(9)-O(3)	1.2114(17)
C(9)-N(3)	1.3806(17)	C(9)-C(10)	1.5162(19)
C(10)-N(4)	1.4578(16)	C(11)-N(4)	1.4577(17)
O(1)-C(1)-C(2)	115.13(11)	O(2)-C(7)-C(6)	113.59(11)
O(1)-C(1)-S(1)	128.17(10)	O(2)-C(7)-S(2)	127.70(10)
C(2)-C(1)-S(1)	116.69(9)	C(6)-C(7)-S(2)	118.71(10)
N(2)-C(8)-N(4)	127.51(12)	N(2)-C(8)-N(3)	121.97(12)
N(4)-C(8)-N(3)	110.51(11)	O(3)-C(9)-N(3)	126.16(12)
O(3)-C(9)-C(10)	127.76(12)	N(3)-C(9)-C(10)	106.06(11)
N(4)-C(10)-C(9)	102.68(10)	C(2)-N(1)-C(6)	124.64(11)

Table 2. Continued

C(8)-N(3)-C(9)	110.37(11)	C(8)-N(4)-C(11)	126.92(11)
C(8)-N(4)-C(10)	110.28(11)	C(11)-N(4)-C(10)	121.85(11)
O(1)-C(1)- C(2)-N(1)	179.02(12)	N(1)-C(6)-C(7)-S(2)	-175.80(10)
S(1)-C(1)-C(2)-N(1)	-1.85(17)	N(1)-C(6)-C(7)-O(2)	4.86(18)
O(1)-C(1)-C(2)-C(3)	-2.4(2)	C(5)-C(6)-C(7)-S(2)	5.1(2)
S(1)-C(1)-C(2)-C(3)	176.69(11)	C(5)-C(6)-C(7)-O(2)	-174.21(14)
C(3)-C(2)-N(1)-C(6)	-1.2(2)	C(5)-C(6)-N(1)-C(2)	0.1(2)
N(2)-C(8)-N(3)-C(9)	-177.77(13)	N(4)-C(8)-N(3)-C(9)	3.28(16)
O(3)-C(9)-N(3)-C(8)	179.45(14)	C(10)-C(9)-N(3)-C(8)	-1.93(15)
N(2)-C(8)-N(4)-C(11)	9.0(2)	N(3)-C(8)-N(4)-C(11)	-172.11(13)
N(2)-C(8)-N(4)-C(10)	177.91(14)	N(3)-C(8)-N(4)-C(10)	-3.21(16)
C(9)-C(10)-N(4)-C(8)	1.89(15)	C(9)-C(10)-N(4)-C(11)	171.45(13)

Table 3. Hydrogen Bonds of Compound **L**

D–H···A	**d(D–H)**	**d(H···A)**	**d(D···A)**	**<(DHA)**
N(1)–H(1)···S(1)	0.8600	2.4600	2.9351	116.00
N(1)–H(1)···O(2)	0.8600	2.1500	2.5533	108.00
N(2)–H(2A)···S(1)	0.9100	2.3700	3.2824	175.00
N(3)–H(3B)···O(1)	0.8900	1.8500	2.7341	173.00

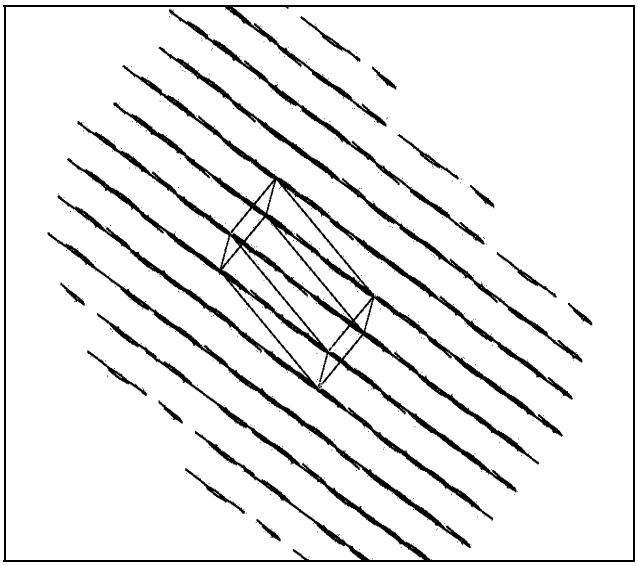


Fig. 2. Crystal packing diagram for **L**.

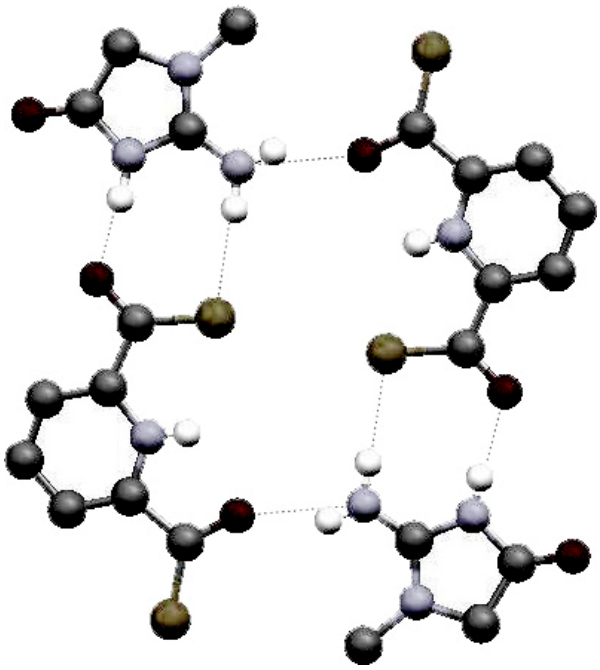


Fig. 3. Macrocycle generated by the H-bonding between two pdtcH_2 and two creatH ionic fragments.

Solution Studies

Spectrophotometry. In order to investigate the stoichiometry and stability of the proton transfer compound **L** in solution, the interaction between $pdtcH_2$ and creat was studied in acetonitrile (AN) spectrophotometrically. The electronic spectra of $pdtcH_2$, creat and the resulting in AN solution are shown in Fig. 4. As is obvious, while $pdtcH_2$ shows a maximum absorbance at 267 nm and creat does not have any absorbance in 250-450 nm (at 3.0×10^{-5} M), the resulting PTC possesses two absorption maxima at 279 and 355 nm. The observed red-shift and appearance of a new peak are due to the proton transfer from the diacid to the amine and the consequent interaction of the resulting oppositely charged species [17].

The electronic spectra of a 3.0×10^{-5} M of creat in the presence of increasing amount of $pdtcH_2$ recorded in AN solution are shown in Fig. 5 and a corresponding absorbance *vs*. $pdtcH_2$/creat mole ratio plot at 355 nm is illustrated in Fig. 6. From Fig. 6, it is seen that the increased absorbance of creat solution with increasing concentration of $pdtcH_2$ shows a distinct inflection point at a mole ratio of about 1 emphasizes the formation of 1:1 proton transfer complex in solution. This

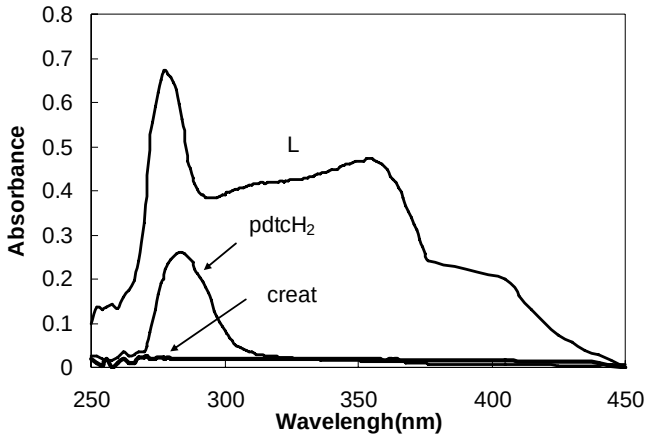


Fig. 4. Electronic spectra of 3.0×10^{-5} M of creat, 4.0×10^{-5} M of $pdtcH_2$ and 6.0×10^{-5} M of **L** in AN.

was further confirmed by excellent computer fitting of the resulting absorbance-mole ratio data to a 1:1 stoichiometry, using a non-linear least-squares curve fitting program KINFIT [18]. The formation constant of **L** thus evaluated was found to be $\log K_f = 4.03 \pm 0.01$.

Potentiometric pH titration. In preliminary experiments,

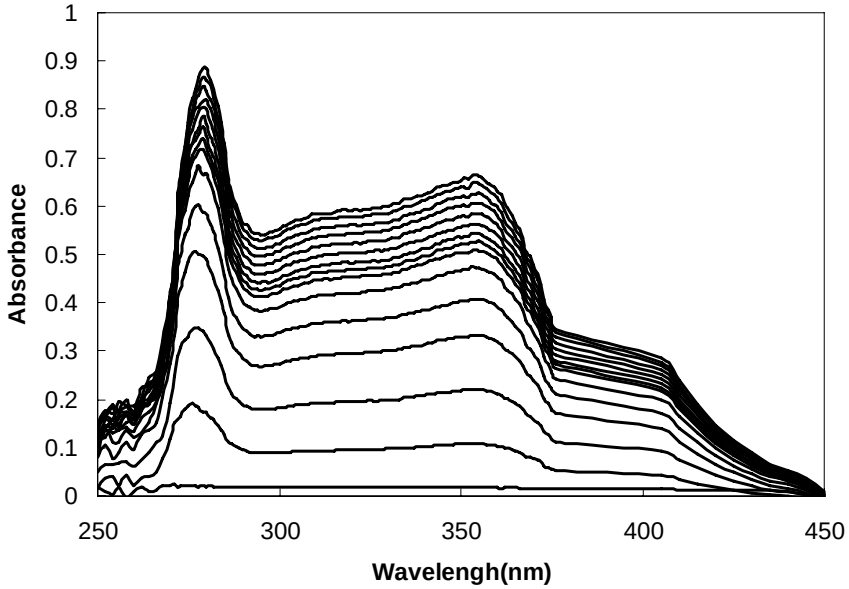


Fig. 5. Electronic spectra of 3.0×10^{-5} M of creat in the presence of increasing concentration of $pdtcH_2$ (5.0×10^{-5} M) in AN.

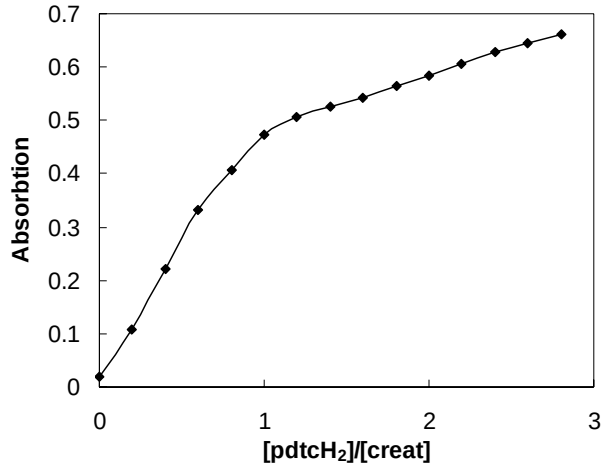


Fig. 6. Absorbance *vs*. $pdtcH_2$/creat plot for the titration of a 3.0×10^{-5} M creat with $pdtcH_2$ in AN at 355 nm and 25.0 ± 0.1 °C.

the fully protonated forms of $pdtcH_2$ and creat, as the building blocks of the self-associated system, were titrated with a standard KOH aqueous solution, in order to obtain some information about their protonation constants. The protonation constants ($K_n^H = [H_mL]/[H_{(m-n)}L][H]^n$) were calculated by fitting the resulting potentiometric data to the program BEST [19] and the results are summarized in Table 4.

The equilibrium constants for reaction of $pdtcH_2$ and creat in aqueous solution were evaluated from the experimental pH profiles obtained with $pdtcH_2$ and creat present, as described before [20,21]. The cumulative stability constants for the resulting complexes, β_{lqh}, are defined by Eq. (1) (charges are omitted for simplicity).

$$lL' + qQ + hH \overset{\beta_{lqh}}{\rightleftharpoons} L'_lQqH_h$$
$$\text{with } \beta_{lqh} = [L'_lQ_qH_h]/[L']^l[Q]^q[H]^h \quad (1)$$

where L′ is $(pdtc)^{2-}$, Q is creat and H is proton, and l, q and h are the respective stoichiometric coefficients. Since the activity coefficients are unknown, the β_{lqh} values are defined in terms of concentrations. The errors are minimized by the use of a high constant ionic strength (0.1 M KCl) and low ligand concentration (1.0×10^{-3} M).

The species distribution diagram obtained for the $pdtcH_2$-creat system shown in Fig. 7 revealed that a variety of binary

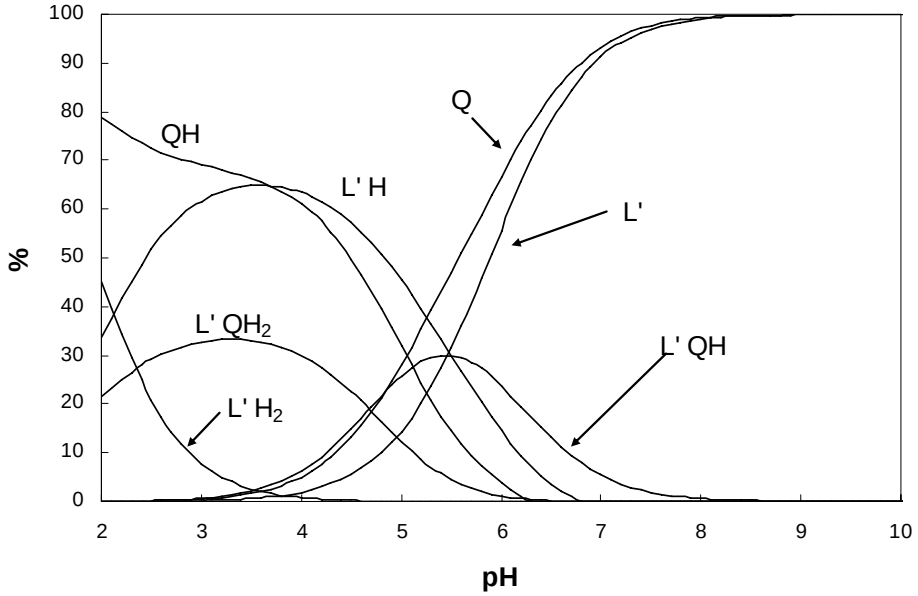


Fig. 7. Species distribution diagram for the mixture of creat (Q) and $pdtcH_2$ ($L'H_2$). The calculated titration curve was computed from protonation constants of creat and $pdtcH_2$. Initial concentration of creat and $pdtcH_2$ are 2.5×10^{-3} M, with experimental conditions of 25 ºC and μ = 0.1 M KCl.

species, including mono- to two protonated species, form through the binding of $pdtcH_2$ by protonated creat can be formed in solution. Meanwhile, the corresponding experimental pH-metric curve was used to evaluate the equilibrium constants for the reactions of protonated forms of the creat and $pdtcH_2$. The stability constants obtained are listed in Tables 4 and 5.

As is obvious from Fig. 7 and Table 5, the most abundant specie present at pH < 4.5 is (creatH)(pdtcH) (log$K$ = 2.50). Thus, the aqueous solution studies are in support of a 1:1 association between $(creat\ H)^+$ and $(pdtcH)^-$, being similar to that observed for **L** by NMR spectroscopy. The proposed 1:1 stoichiometry of **L** was also found to be in agreement with thatfor **L** in crystalline form, as shown in Fig. 1.

Computational Details

The *ab initio* B3LYP/6-31+G(2d, p) calculations were performed for the barrier energy of both proton transfers (i.e. single and double) as well as for tautomerization in creatinine. The results have been schematically shown in Figs. 8-11. As shown in Fig. 8, the barrier energy for an intramolecular proton transfer from thiocarboxylic acid functional group to nitrogen atom of $pdtcH_2$ was calculated to be about 8 kcal mol^{-1}. The barrier energy for the C=O group rotation around C-C bond was 0.72 kcal mol^{-1}. This rotation takes place most

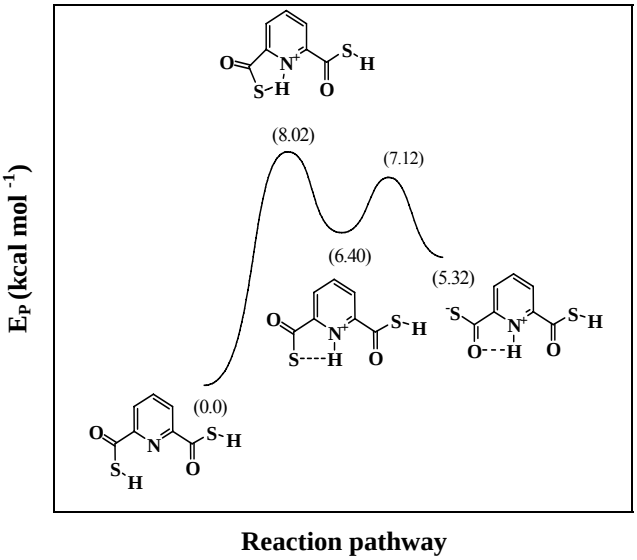


Fig. 8. The barrier energy (kcal mol^{-1}) for intramolecular proton transfer in $pdtcH_2$.

Table 4. Overall Stability Constants, β, for the Interaction of H^+ with $[pdtc]^{2-}$, Creat and their 1:1 Mixture

System	l	q	h	logβ	Max (%)	at pH
$pdtcH_2$	1	0	1	5.59	45	2
	1	0	2	7.62	65	4
creat	0	1	1	5.04	78	2
pdtc-creat	1	1	1	8.06	30	5.5
	1	1	2	13.13	33	3.3

Table 5. Overall Stability Constants, β, and Stepwise Recognition Constants, K, for Interaction of $pdtcH_2$ with Creat at μ = 0.1 M KCl

Stoichiometry			Logβ	Equilibrium quotient K	log$K$
creat	$pdtcH_2$	H			
1	1	1	8.06	[creat.pdtcH]/[creat][pdtcH]	2.47
1	1	2	13.13	[creat.$pdtcH_2$]/[creatH][pdtcH]	2.50

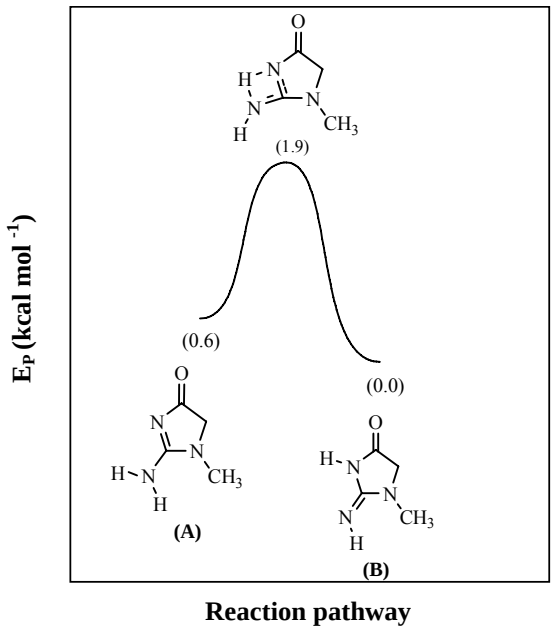


Fig. 9. The barrier energy (kcal mol^{-1}) for tautomer structures of creat.

probably because of the stronger intramolecular H-bonding between thiocarboxylate oxygen and N-H hydrogen. Also, the large size of sulfur atom in the five member ring which is formed after proton transfer may be another factor influencing the rotation.

Creat has two tautomeric structures A and B; the barrier energy for tautomer structure of creat was calculated to be 1.3 kcal mol^{-1} (Fig. 9). The structure A was found to be 0.6 kcal mol^{-1} more stable than B. Therefore the structure of tautomer A was used to follow the corresponding calculations for single and double proton transfer.

As shown in Figs. 10 and 11, the barrier energies for intermolecular proton transfer between creat and the products shown in Fig. 8 were calculated assuming two paths. In the first path, an intermolecular proton transfer from the remaining thiocarboxylic acid functional group to the nitrogen atom of creat was considered. The barrier energy for such a single proton transfer was calculated to be 25.2 kcal mol^{-1} (Fig. 10). In the second path, a double intermolecular proton transfer takes place as shown in Fig. 11. The barrier energy for

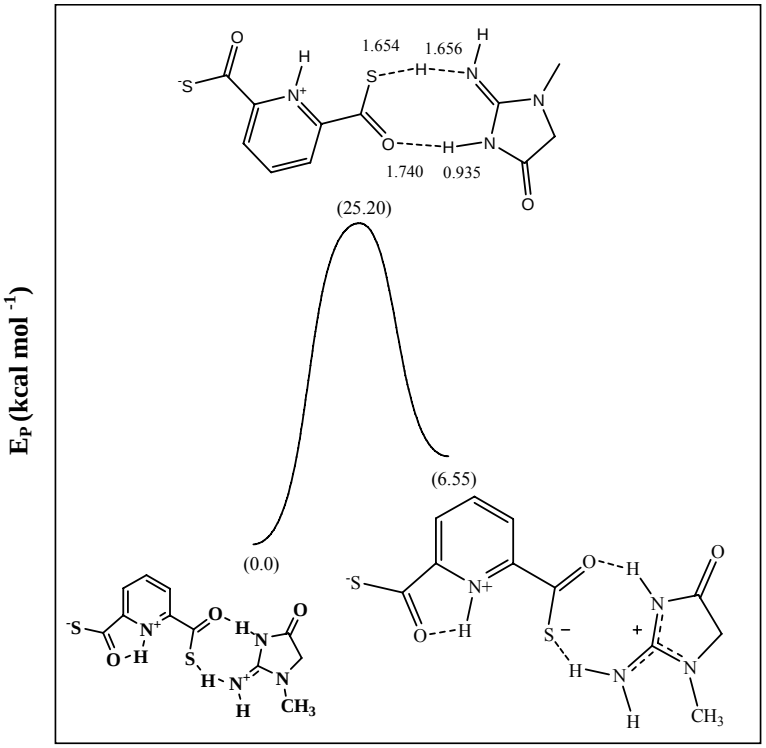


Fig. 10. The barrier energy (kcal mol^{-1}) for intermolecular single proton transfer between pdtcH_2 and creat.

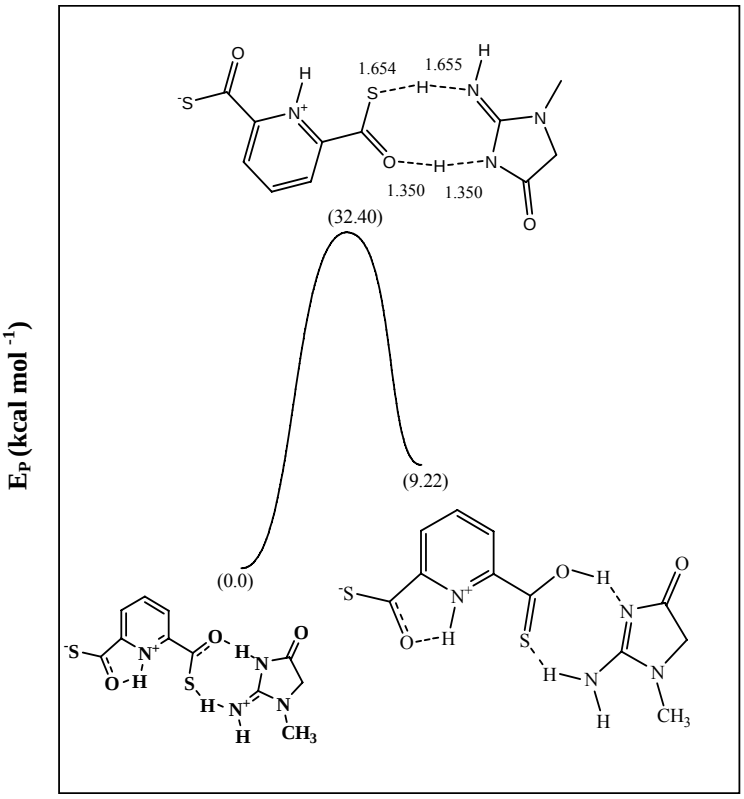


Fig. 11. The barrier energy (kcal mol^{-1}) for intermolecular double proton transfer between pdtcH_2 and creat.

the current transfer was calculated to be 32.4 kcal mol^{-1}. As is clear from Figs. 10 and 11, the SH and NH distances in the transition states of single and double intermolecular proton transfer processes are different. Comparison between the energy barriers for the two discussed intermolecular proton transfers indicates that the first path is more likely because of the lower barrier energy.

CONCLUSIONS

The result and discussion presented indicates that the reaction between pyridine-2,6-bis(monothiocarboxcylic) acid, (pdtcH_2), and creatinine, creat, in water results in an intermolecular and an intramolecular proton transfer of two carboxylic acid protons to the amine group of creatinine and to the nitrogen atom of pdtcH_2, respectively. The single crystal X-ray analysis confirms the generation of a two-dimensional self-assembled proton-transfer compound, $(creatH)^+(pdtcH)^-$. The anionic and cationic components self assemble *via* ion-pairing, H-bonding and π-π stacking. The spectrophotometric and potentiometric pH titrations data are in support of the solid phase structure, indicating the existence of the proton transfer species, $(creatH)^+(pdtcH)^-$, in aqueous solution at pH < 4.5. The results obtained by the application of *ab initio* method, DFT (B3LYP), to the both intramolecular and intermolecular proton transfer processes between creat and pdtcH_2 have also, shown a good agreement with the structural data obtained by X-ray crystallography.

SUPPLEMENTARY DATA

Full crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 622719. These data can be obtained free of

charge *via* www.ccdc.cam.ac.uk or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, CB2, 1EZ, UK, (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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