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Crystal Structures, Thermal Degradation, and Biological Activities of Some New Ammonium and Hydrazinium Salts of Cyclohexanediaminetetraacetic Acid

C. Sonia ^a & B. N. Sivasankar ^a

^a Department of Chemistry, Government Arts College, Udhagamandalam, The Nilgiris, Tamilnadu, India

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Crystal Structures, Thermal Degradation, and Biological Activities of Some New Ammonium and Hydrazinium Salts of Cyclohexanediaminetetraacetic Acid

C. Sonia and B. N. Sivasankar

Department of Chemistry, Government Arts College, Udhagamandalam, The Nilgiris, Tamilnadu, India

Neutralization reaction in aqueous medium between cyclohexanediaminetetraacetic acid (H₄CDTA) and weak bases such as hydrazine hydrate and aqueous ammonia yielded a series of new salts such as N₂H₅H₃CDTA.H₂O, (N₂H₅)₃HCDTA.H₂O, NH₄H₃CDTA.2H₂O, and N₂H₅NH₄H₂CDTA.H₂O. The type of salt formed depends on the ratio of H₄CDTA to base used and the pH of the medium. The compositions of the previous compounds were determined by hydrazine and microanalyses. The infrared spectra of the salts reveal the presence of free carboxylic acid groups. The Xray single-crystal structures of N2H5H3CDTA and NH4H3CDTA clearly reveal that these salts exist as zwitterions in solid state. The simultaneous TG-DTA profiles show the multistep degradation with almost 100% mass loss indicating the complete decomposition. The biological screening of the aqueous solution of these salts reflects the enhanced activities of the hydrazinium salts than the free acid and the ammonium salts.

Keywords antibacterial and antifungal activities, H₄CDTA, hydrazinium and ammonium salts, monoclinic, thermal degradation, X-ray crystal structure

INTRODUCTION

Aminopolycarboxylic acids are effective chelating agents and forms stable complexes with transition metal ions and lanthanide ions.^[1,2] These simple and bridged binuclear and poly nuclear complexes are known for their optical, magnetic, and biological applications in many areas of recent interest.^[3–7] Among the aminopolycarboxylic acids, iminodiacetic acid (IDA), nitrilotriacetic acid (NTA), ethylenediaminediacetic acid (EDDA), and ethylenediaminetraacetic acid (EDTA) have been widely used as a multidentate ligands during the syntheses and structural investigation of simple salts, simple metal complexes and their sodium, potassium, ammonium and hydrazinium derivatives.^[1,2,8–10] Though few simple complexes were prepared and well characterized with H_4CDTA , the corresponding ammonium and hydrazinium complexes have not been reported in the literature.^[11,12] The interest in these complexes lies in the fact that, these complexes obtained at particular pH conditions could yield complexes with desired number of coordinated water molecules. Hence, one can control the water of hydration, which makes these complexes as a possible potential precursor for hydroxy and hydrazine bridged poly nuclear cluster which in turn can be utilized for the hydrolysis of DNA and RNA.^[13] As the initiation of the previous investigations some new ligands, the hydrazinium and ammonium salts of H_4CDTA , which can be used for the preparation of complexes, have been prepared and characterized by analytical, spectral, thermal, Xray single-crystal, and biological studies. The results of these studies are presented in this article.

EXPERIMENTAL

The chemicals used were of AR grade. The solvents were distilled before use and double distilled water was used for the preparation and analyses. Hydrazine hydrate (99–100%) was used as received.

The hydrazine content in the salts was determined by volumetric analysis under Andrew's conditions using 0.025 M KIO₃.^[14] The C, H, and N analyses were performed on a Perkin-Elmer (model 1240) CHN analyzer. The infrared spectra of the solid samples in the range 4000–500 cm⁻¹ were recorded on a Perkin-Elmer 597/1650 spectrophotometer using KBr pellets of the samples. Simultaneous TG-DTA experiments in air were carried out using a STA 1500 thermal analyzer using 8–10 mg of the samples with the heating rate of 10°C per minute and the platinum cups as sample holders.

X-Ray Structure Determination

The X-ray intensity data was collected on a Kappa-Apex II CCD diffractometer with graphite monochromated M-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SIR92 program and completed using Fourier techniques. Refinement was carried out using SHELXL-97 program.^[15,16] All the hydrogen atoms can be located in different Fourier map. The C-H distance in methylene (CH₂)

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Address correspondence to B. N. Sivasankar, Department of Chemistry, Government Arts College, Udhagamandalam, The Nilgiris 643002, Tamilnadu, India. E-mail: sivabickol@yahoo.com

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and ring (CH₂) were constrained to 0.97 Å. The O-H distances in water molecules were constrained as 0.900(0.001) Å with H-O-H angle restrained to be near tetrahedral. The N-H distances of hydrazinium cations were restrained to be 0.89Å for NH₃ moiety, 0.85 Å for NH₂ moiety, and 0.84 Å for NH₄⁺ moiety. The packing is stabilized through intermolecular hydrogen bonding interactions.

Preparation of Salts

An aqueous suspension (50 mL) of H_4 CDTA. H_2O (18.2 g, 0.05 mol) was neutralized with an aqueous solution (20 mL) of the respective bases such as hydrazine hydrate, aqueous ammonia, or the mixture of two in appropriate ratio. During the addition of base, the acid slowly dissolved and after the complete addition the resulting solutions were slightly heated on a water bath for the completion of the reaction. The solutions thus obtained were filtered and evaporated on the water bath to one third of their original volumes. The concentrated solutions were then kept at room temperature for crystallization. After a week time the colorless crystals formed were removed, washed quickly with ice cold water and dried in air.

Biological Screening

Six pathogenic micro-organisms such as *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Bacillus subtilis*, *Aspergillus niger*, and *Candida albicans* were used to test the biological potential of the newly synthesized hydrazinium and ammonium salts. These were obtained from the stock cultures of the Microbiology Laboratory of Ramakrishna Hospital, Coimbatore, India.

Activity Testing

The anti-bacterial activities of all the salts were studied by the usual cup-plate-agar-diffusion method. The compounds were screened for their anti-bacterial activity against Gram-positive and Gram-negative microorganism. The method comprises the following steps:

- 1. Preparation of media, sterilization, and tubing;
- 2. Sterilization of the cleaved glass apparatus;
- Pouring of the seeded medium into sterilized Petri dishes and cutting of the cups;
- 4. Pouring of the dilute solution of the compounds into the tubes;
- 5. Incubation at a particular temperature; and
- 6. Determination of zone of inhibition.

The composition of test media is the factor, which often exerts a great effect on the drug activity. This is particularly true for these salts, since the inhibitors of these compounds appear to be present in the common bacteriological culture medium. Efficient media of known chemical composition are available for many species such as *S. aureus* and *E. coli*. In addition to the composition of the test media, its pH also directly or indirectly influences the activity. The pHs of the media taken are adjusted to 7.6 ± 0.1 . The composition of the test media used

in the experiment was the following: (a) NaCl = 6 g, (b) peptone = 10 g, (c) beef extract = 3 g, (d) yeast extract = 2 g, (e) sucrose = 1.5 g, (f) agar-agar = 3%, and (g) distilled water = 1 L. The zones of inhibition around the discs were measured after 24 h. Ciprofloxacin was used as a standard positive control.

RESULTS AND DISCUSSION

The hydrazinium, ammonium or hydrazinium-ammonium salts of cyclohexanediaminetetraacetic acid were obtained by acid-base neutralization reaction between the acid and respective bases in required ratios. It was observed that excess of base than required for the formation of the respective salts should be added for the isolation of the salts. The replacement of the acidic protons could be possible only with the addition of excess amount of bases. The reaction with 1:1 acid to base ratio always resulted in the partial dissolution of acid.

The pKa value of the protons in H_4 CDTA is obviously known to be a vital factor during their replacement by bases. In the present case, weak bases such as hydrazine and ammonia are expected to replace only two protons with lower pKa values, 2.4 and 3.5. Further replacement of other two protons with pKa values 6.1 and 12.4 was not successful and always yielded viscous solutions. The chemical reactions for the formation of salts are represented as follows:

$$\begin{split} H_4 CDTA.H_2O &+ 2N_2H_4.H_2O \rightarrow N_2H_5H_3CDTA.H_2O \\ &+ N_2H_4.H_2O + H_2O \\ H_4 CDTA.H_2O &+ 4N_2H_4.H_2O \rightarrow (N_2H_5)_3H_2CDTA.H_2O \\ &+ N_2H_4.H_2O + 3H_2O \\ H_4 CDTA.H_2O &+ 2NH_3.H_2O \rightarrow NH_4H_3CDTA.2H_2O \\ &+ NH_3.H_2O \\ 2H_4 CDTA.H_2O &+ 3N_2H_4.H_2O \end{split}$$



FIG. 1. TG-DTA of N2H5H3CDTA.H2O.



FIG. 2. TG-DTA of NH₄H₃CDTA.2H₂O.

+
$$3NH_3.H_2O \rightarrow N_2H_5NH_4H_2CDTA.H_2O$$

+ $2N_2H_4.H_2O$ + $2NH_3.H_2O$ + $2H_2O$

The excess of hydrazine and ammonia present in the reaction mixture are usually evolved during the evaporation for concentration. The mono hydrazinium and mono ammonium salts were prepared in the form of single crystals suitable for X-ray singlecrystal study. All the salts derived were highly crystalline and water soluble. The compositions of the salts were assigned on the basis of hydrazine analysis and microanalysis. The analytical data of the salts are summarized in Table 1.

Infrared Spectra

The infrared spectra of the hydrated salts show broad band in the region 3250–3400 cm⁻¹ with several microsplittings, which are assigned to N–H stretching of $N_2H_5^+$, NH_4^+ and H–N⁺ of zwitterions and O–H stretching of water and free carboxylic acid groups. The carbonyl stretching of free carboxylic acid groups are observed at 1700 cm⁻¹. The ν_{asy} and ν_{sym} stretchings of carboxylate ions are seen in the regions of 1600–1610 cm⁻¹ and 1380–1390 cm⁻¹, respectively. The characteristic N-N stretching of N₂H₅⁺ ion is observed at 960 cm⁻¹ for hydrazinium salt while this band is absent in the ammonium salt.^[17]

Thermal Degradation Studies

Monohydrazinium salt undergoes dehydration in the temperature range $80-100^{\circ}$ C followed by the loss of hydrazine molecule in the range $150-200^{\circ}$ C. The free acid thus formed as the intermediate then undergoes gradual and complete degradation from 200 to 650° C. The DTA shows an endotherm for

TABLE 1 Analytical data

Compound		Elemental analysis				
	Color	C% Observed (Calcd.)	H% Observed (Calcd.)	N% Observed (Calcd.)	Hydrazine% Observed (Calcd.)	
N ₂ H ₅ H ₃ CDTA.H ₂ O	Colorless	39.9 (40.18)	7.9 (8.19)	13.10 (13.39)	7.50 (7.65)	
(N ₂ H ₅) ₃ HCDTA.H ₂ O	Colorless	39.9 (40.12)	8.42 (8.70)	22.95 (23.23)	19.00 (19.8)	
NH ₄ H ₃ CDTA.2H ₂ O	Colorless	39.8 (40.18)	8.10 (8.37)	9.69 (9.97)	_	
N ₂ H ₅ NH ₄ H ₂ CDTA.H ₂ O	Colorless	39.78 (40.18)	8.28 (8.56)	15.84 (16.10)	7.00 (7.35)	



FIG. 3. ORTEP diagram of N2H5H3CDTA.H2O.

dehydration, an exotherm for dehydrazination and a broad exotherm for pyrolysis of the acid.

The trihydrazinium salt undergoes endothermic dehydration up to 95° C followed by the loss of three hydrazine molecules as a broad exotherm splitting in the region $150-200^{\circ}$ C. The intermediate, the free acid decomposes similar to the case of monohydrazinium salt in the temperature range 200–650°C.

The ammonium salt loses two water molecules at $60-120^{\circ}$ C for which the DTA shows a broad and weak endotherm. The anhydrous salt loses ammonia molecule in the temperature range $200-250^{\circ}$ C for which a sharp endotherm is observed. Subsequent pyrolysis of acid takes place up to 600° C leaving no residue in the sample holder indicating complete decomposition.

The ammonium hydrazinium salt shows two endotherms at 90°C and 100°C for the removal of water and ammonia and an exotherm at 150°C for dehydrazination. However, the TG shows continues weight loss for these two processes. Further



FIG. 4. Packing diagram of N2H5H3CDTA.H2O.

TABLE 2Crystal data and structure refinement

	N ₂ H ₅ H ₃ CDTA.H ₂ O	NH ₄ H ₃ CDTA.2H ₂ O
CCDC No.	799930	800071
Identification code	N ₂ H ₅ H ₃ CDTA.H ₂ O	NH ₄ H ₃ CDTA.2H ₂ O
Empirical formula	$C_{14}H_{28}N_4O_9$	$C_{14}H_{29}N_3O_{10}$
Formula weight	396.40	399.40
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, P21/c	Monoclinic, P21/c
Unit cell dimensions	A = 8.6297(4) Å	A = 8.6297(4) Å
	$lpha=90^\circ$	$lpha=90^\circ$
	B = 9.4882(3) Å	B = 11.5016(5) Å
	$\beta = 102.1660(10)^{\circ}$	$eta=90^\circ$
	C = 21.7697(8) Å	C = 18.3935(9) Å
	$\gamma = 90^{\circ}$	$\gamma = 90^{\circ}$
Volume	1818.18(15) Å ³	1860.78(11) Å ³
Z, Calculated density	4, 1.448 Mg/m^3	4, 1.426 Mg/m^3
Absorption coefficient	0.121 mm^{-1}	0.121 mm^{-1}
F (000)	848	856
Crystal size	$0.30 \times 0.30 \times 0.20$ mm	$0.22 \times 0.16 \times 0.16$ mm
Theta range for data collection	$2.09-29.65^{\circ}$	$1.91 - 33.60^{\circ}$
Limiting indices	$-11 \le h \le 12,$	$-12 \le h \le 14,$
	$-15 \le k \le 15,$	$-14 \le k \le 10,$
	$-25 \le 1 \le 19$	$-33 \le 1 \le 32$
Reflections collected / unique	21877 / 5083	26096 / 6778
	[R (int) = 0.0258]	[R (int) = 0.0240]
Completeness to theta $= 25.00$	100.0%	100.0%
Absorption correction equivalents	Semiempirical from equivalents	Semiempirical from
Max, and min, transmission	0.9762 and 0.9646	0.9809 and 0.9739
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F
Data / restraints / parameters	5083 / 0 / 278	6778 / 3 / 297
Goodness-of-fit on F^2	1.032	1.033
Final <i>R</i> indices $[I > 2 \text{sigma}(I)]$	R1 = 0.0421,	R1 = 0.0456,
	wR2 = 0.1071	wR2 = 0.1288
<i>R</i> indices (all data)	R1 = 0.0617,	R1 = 0.0625,
× •	wR2 = 0.1222	wR2 = 0.1422
Largest diff. Peak and hole	0.474 and -0.210 e. Å ⁻³	$0.446 \text{ and } -0.260 \text{ e.} \text{\AA}^{-3}$

decomposition of the acid takes place up to 600°C with 100% weight loss.

The simultaneous TG-DTA traces of $N_2H_5H_3CDTA.H_2O$ and $NH_4H_3CDTA.2H_2O$ are shown in Figures 1 and 2 respectively.

Structure of N₂H₅H₃CDTA.H₂O

This salt crystallizes as monoclinic crystal system with P21/c space group. The observed crystal density from the X-ray single crystal study is 1.448 mg/m³, which is very close to the experimental value of 1.441 mg/m³. The crystal structure of

the compound shows that it is composed of discrete $N_2H_5^+$ and H_3CDTA^{3-} ions along with a water molecule, which are in close packing arrangement held together by hydrogen bonds. The packing diagram reveals the presence of four such molecules in a unit cell. The structure clearly shows that N_2 consists of two free carboxylic acid (CH₂COOH) groups while N_1 has two carboxylate ions (CH₂COO⁻). Among the two acidic protons removed from two carboxylic acid groups, one attached to N_1 so as to give the zwitterion structure while the other attached to hydrazine and present as hydrazinium cation. The acidic proton with pKa = 2.4 is expected to neutralize the hydrazine forming

Bond lengths (Å)			Bond angles (°)		
C(1)-N(1)	1.5194(16)	N(1)-C(1)-C(6)	111.85(10)	N(1)-C(1)-C(2)	110.61(10)
C(8)-O(4)	1.2586(17)	N(1)-C(1)-H(1A)	107.3	N(2)-C(2)-C(1)	110.38(11)
C(10)-O(2)	1.2341(17)	N(2)-C(2)-C(3)	115.36(11)	N(2)-C(2)-H(2A)	107.2
C(11)-N(2)	1.4602(16)	N(1)-C(7)-C(8)	113.35(11)	N(1)-C(7)-H(7A)	108.9
C(12)-O(6)	1.3122(16)	N(1)-C(7)-H(7B)	108.9	O(3)-C(8)-O(4)	126.46(13)
C(14)-O(7)	1.2092(17)	O(3)-C(8)-C(7)	114.40(12)	O(4)-C(8)-C(7)	119.13(11)
N(1)-H(1)	0.910(16)	N(1)-C(9)-C(10)	109.57(10)	N(1)-C(9)-H(9A)	109.8
N(3)-H(5D)	0.89(3)	N(1)-C(9)-H(9B)	109.8	H(9A)-C(9)-H(9B)	108.2
N(3)-H(5E)	0.95(3)	O(2)-C(10)-O(1)	126.05(13)	O(2)-C(10)-C(9)	118.55(12)
N(4)-H(6C)	0.97(3)	O(1)-C(10)-C(9)	115.40(12)	N(2)-C(11)-C(12)	111.79(11)
O(1W)-H(1D)	0.89(3)	N(2)-C(11)-H(11A)	109.3	N(2)-C(11)-H(11B)	109.3
O(8)-H(8)	1.0068	O(5)-C(12)-O(6)	123.70(13)	O(5)-C(12)-C(11)	123.54(12)
C(8)-O(3)	1.2414(16)	O(6)-C(12)-C(11)	112.75(11)	N(2)-C(13)-C(14)	113.50(11)
C(9)-N(1)	1.4988(16)	N(2)-C(13)-H(13A)	108.9	N(2)-C(13)-H(13B)	108.9
C(10)-O(1)	1.2633(17)	O(7)-C(14)-O(8)	123.72(13)	O(7)-C(14)-C(13)	125.66(13)
C(12)-O(5)	1.2061(17)	O(8)-C(14)-C(13)	110.61(12)	C(7)-N(1)-C(9)	112.54(10)
C(13)-N(2)	1.4536(17)	C(7)-N(1)-C(1)	114.21(10)	C(9)-N(1)-C(1)	111.16(10)
C(14)-O(8)	1.3132(17)	C(7)-N(1)-H(1)	108.4(10)	C(9)-N(1)-H(1)	104.1(10)
N(3)-N(4)	1.437(2)	C(1)-N(1)-H(1)	105.6(10)	C(13)-N(2)-C(11)	112.02(10)
N(3)-H(5C)	0.94(2)	C(13)-N(2)-C(2)	113.96(10)	C(11)-N(2)-C(2)	113.71(11)
N(4)-H(6D)	0.91(3)	N(4)-N(3)-H(5D)	113.1(15)	N(4)-N(3)-H(5C)	109.0(14)
O(1W)-H(1C)	0.87(4)	H(5D)-N(3)-H(5C)	104(2)	N(4)-N(3)-H(5E)	106.7(15)
O(6)-H(6)	0.9253	H(5D)-N(3)-H(5E)	108(2)	H(5C)-N(3)-H(5E)	116(2)
		N(3)-N(4)-H(6D)	102.6(18)	N(3)-N(4)-H(6C)	103.5(14)
		H(6D)-N(4)-H(6C)	106(2)	H(1C)-O(1W)-H(1D)	104(3)
		C(12)-O(6)-H(6)	109.5	C(14)-O(8)-H(8)	109.5

TABLE 3 Bond lengths (Å) and bond angles (°) for $N_2H_5H_3CDTA.H_2O$

TABLE 4 Hydrogen bonds for the compound $N_2H_5H_3CDTA.H_2O~(\mbox{\AA and}~^\circ)$

D-H···A	d (D-H)	$d(H\!\cdot\!\cdot\!\cdot A)$	$d(D \cdots A)$	<(DHA)
O(6)-H(6)O(4)#1	0.93	1.69	2.6050(15)	171.5
O(8)-H(8)O(1)#2	1.01	1.56	2.5396(15)	162.7
O(8)-H(8)O(2)#2	1.01	2.59	3.1265(16)	113.0
N(1)-H(1)O(2)	0.910(16)	2.053(16)	2.6257(15)	119.7(12)
N(1)-H(1)N(2)	0.910(16)	2.379(16)	2.8500(15)	112.2(12)
N(4)-H(6D)O(2)#3	0.91(3)	2.34(3)	3.053(2)	134(2)
N(4)-H(6C)O(1W)	0.97(3)	2.03(3)	2.961(2)	161(2)
O(1W)-H(1C)O(2)#4	0.87(4)	2.34(4)	3.0417(19)	139(3)
O(1W)-H(1D)O(1)	0.89(3)	1.93(3)	2.8187(18)	176(3)
N(3)-H(5D)O(7)#3	0.89(3)	2.04(3)	2.9003(18)	160(2)
N(3)-H(5C)O(3)#5	0.94(2)	1.85(2)	2.7890(17)	175(2)
N(3)-H(5E)O(4)#3	0.95(3)	2.00(3)	2.9334(17)	166(2)

Symmetry transformations used to generate equivalent atoms:

 $\#1-x,-y+2,-z+1\ \#2-x,-y+1,-z+1\ \#3\ x+1,\ y,\ z\ \#4-x+1,-y+1,-z+1\ \#5-x+1,-y+2,-z+1.$

	Boi	TABL nd lengths (Å) and bond angle	E 5 es (°) for NH ₄ H ₃ CI	DTA.2H ₂ O		
Bond lengths (Å)				Bond angles	Bond angles (°)	
C(1)-N(2)	1.5206(13)	N(2)-C(1)-C(6)	110.24(8)	N(2)-C(1)-C(2)	112.42(8)	
C(7)-N(1)	1.4545	N(2)-C(1)-H(1A)	107.4	N(1)-C(6)-C(1)	110.65(8)	
C(8)-O(1)	1.3189(14)	N(1)-C(6)-C(5)	114.82(8)	N(1)-C(6)-H(6A)	107.4	
C(9)-C(10)	1.5116(16)	N(1)-C(7)-C(8)	111.52(8)	N(1)-C(7)-H(7A)	109.3	
C(10)-O(4)	1.2968(15)	N(1)-C(7)-H(7B)	109.3	O(2)-C(8)-O(1)	123.91(12)	
C(12)-O(5)	1.2282(14)	O(2)-C(8)-C(7)	124.12(10)	O(1)-C(8)-C(7)	111.97(10)	
C(13)-N(2)	1.4937(13	N(1)-C(9)-C(10)	116.63(9)	N(1)-C(9)-H(9B)	108.1(9)	
C(14)-O(7)	1.2471(15)	N(1)-C(9)-H(9B)	112.7(9)	O(3)-C(10)-O(4)	123.69(11)	
O(4)-H(4)	0.99(3)	O(3)-C(10)-C(9)	118.11(11)	O(4)-C(10)-C(9)	118.18(10)	
O(1W)-H(1C)	0.97(3)	N(2)-C(11)-C(12)	111.04(8)	N(2)-C(11)-H(11A)	109.4	
O(2W)-H(2D)	0.854(10)	N(2)-C(11)-H(11B)	109.4	O(5)-C(12)-O(6)	126.52(10)	
N(3)-H(3E)	0.76(3)	O(5)-C(12)-C(11)	120.02(9)	O(6)-C(12)-C(11)	113.45(9)	
N(3)-H(3F)	0.84(4)	N(2)-C(13)-C(14)	113.32(9)	N(2)-C(13)-H(13A)	108.9	
C(6)-N(1)	1.4760	N(2)-C(13)-H(13B)	108.9	O(8)-C(14)-O(7)	126.69(11)	
C(8)-O(2)	1.2054(15)	O(8)-C(14)-C(13)	114.43(10)	O(7)-C(14)-C(13)	118.88(10)	
C(9)-N(1)	1.4544(14)	C(8)-O(1)-H(1)	110.1(17)	C(10)-O(4)-H(4)	112.0(14)	
C(10)-O(3)	1.2235(15)	H(1B)-O(1W)-H(1C)	90(2)	H(2C) O(2W) H(2D)	105(2)	
C(11)-N(2)	1.5005(12)	H(3D)-N(3)-H(3E)	104(2)	H(3D)-N(3)-H(3C)	117(2)	
C(12)-O(6)	1.2780(13)	H(3E)-N(3)-H(3C)	111(2)	H(3D)-N(3)-H(3F)	97(3)	
C(14)-O(8)	1.2474(15)	H(3E)-N(3)-H(3F)	115(3)	H(3C)-N(3)-H(3F)	113(3)	
O(1)-H(1)	0.85(3)	C(9)-N(1)-C(7)	113.80(8)	C(9)-N(1)-C(6)	114.01(8)	
O(1W)-H(1B)	0.85(2)	C(7)-N(1)-C(6)	112.82(8)	C(13)-N(2)-C(11)	111.45(8)	
O(2W)-H(2C)	0.821(9)	C(13)-N(2)-C(1)	114.01(8)	C(11)-N(2)-C(1)	110.99(8)	
N(3)-H(3D)	0.93(3)	C(13)-N(2)-H(1)	109.1(9)	C(11)-N(2)-H(1)	108.2(9)	

TADIE 5

TABLE 6 Hydrogen bonds for the compound $NH_4H_3CDTA.2H_2O~(\text{\AA and}~^\circ)$

102.6(9)

C(1)-N(2)-H(1)

D—H···Ad	(D-H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	<(DHA)
O(4)-H(4),O(6)#1	0.99(3)	1.52(3)	2.5177(12)	179(3)
N(3)-H(3D)O(7)#2	0.93(3)	2.04(3)	2.9329(17)	159(2)
N(3)-H(3D)O(2)#2	0.93(3)	2.55(3)	3.067(2)	115(2)
N(3)-H(3E)O(3)#3	0.76(3)	2.23(3)	2.980(2)	170(3)
O(1)-H(1)O(2W)	0.85(3)	1.76(3)	2.6037(16)	174(3)
N(2)-H(1)N(1)	0.863(14)	2.289(13)	2.8351(12)	121.3(11)
N(2)-H(1)O(2)	0.863(14)	2.637(13)	3.2864(13)	132.9(11)
N(3)-H(3C)O(8)	0.90(2)	1.93(2)	2.8082(16)	163.2(18)
N(3)-H(3F)O(4)#2	0.84(4)	2.28(4)	3.0752(18)	159(4)
O(1W)-H(1C)O(8)	0.97(3)	1.98(3)	2.911(2)	159(2)
O(2W)-H(2D)O(7)#2	0.854(10)	2.07(3)	2.7611(16)	137(4)
O(1W)-H(1B)O(6)#4	0.85(2)2.48(2)	2.9598(17)	116.1(16)	
O(2W)-H(2D)O(3)#3	0.854(10)	2.58(4)	2.8038(17)	96(3)

Symmetry transformations used to generate equivalent atoms:

0.90(2)

0.863(14)

#1 -x + 1, -y + 1, -z #2 -x + 1, -y, -z #3 x, y - 1, z #4 -x + 2, -y, -z.

N(3)-H(3C)

N(2)-H(1)

		Diameter of zone inhibition (mm)						
Compound	Conc. mg/disc	Staphylococcus aureus	Escherichia coli	Pseudomonas aeruginosa	Bacillus subtilis			
N ₂ H ₅ H ₃ CDTA. H ₂ O	500	23	20	15	18			
	250	20	14	11	13			
(N ₂ H ₅) ₃ H CDTA.H ₂ O	500	25	26	21	25			
,.	250	22	21	15	21			
NH ₄ H ₃ CDTA .2H ₂ O	500	16	18	_	13			
	250	13	12	_	11			
NH ₄ N ₂ H ₅ H ₂ CDTA	500	16	18	18	21			
	250	14	15	13	17			
Standard	Ciprofloxacin/ disc	25	27	27	27			

TABLE 7 Antibacterial activity of the CDTA ligands

the hydrazinium salt. The structure is unsymmetrical due to the asymmetry with respect to nitrogen atoms and carboxylic acid groups. The ORTEP diagram and packing diagram of the salt are shown in Figures 3 and 4, respectively. The crystal data of the salt is given in Table 2. The bond lengths and bond angles for this compound are listed in Table 3 and hydrogen bonds are summarized in Table 4.

Structure of NH₄H₃CDTA.2H₂O

The crystal data of this salt is also summarized in Table 2. The ORTEP diagram of the ammonium salt is shown in Figure 5. This salt also crystallizes in monoclinic system with P21/c space group. The unit cell also consists of four molecules. The ORTEP diagram is comparable with that of the hydrazinium salt. The structures are almost similar except the ammonium ion present



FIG. 5. ORTEP diagram of NH₄H₃CDTA.2H₂O.

in the salt instead of hydrazinium ion. This salt has two water molecules in its crystal structure. But the CDTA moiety has exactly same structure as observed in the case of hydrazinium salt. The bond length and bond angle are summarized in Table 5 and hydrogen bonds are given in Table 6.

Antimicrobial Activities of the Salts

The newly synthesized hydrazinium and ammonium salts of CDTA were screened for their antibacterial activities against Gram-positive and Gram-negative organisms by agar diffusion method using ciprofloxacin as the standard. Though all the prepared salts show better activity than the acid, H₄CDTA, hydrazinium, trihydrazinium, and ammonium salts show very good activities as evident from the zone of inhibition. The antibacterial activities of the ligands are summarized in Table 7. Except monohydrazinium and trihydrazinium salts, which show very little activities that too only against *Candida albicans*, other salts hardly show any activity against both *Candida albicans* and *Aspergillus niger*.

SUPPLEMENTARY MATERIAL

Supplementary materials for X- ray crystal structures are available with the following CCDC numbers: $N_2H_5H_3CDTA.H_2O$: CCDC 799930 and $NH_4H_3CDTA.2H_2O$: CCDC 800071.

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