Coordination Chemistry of Proton. In Situ Synthesis and X-Ray Structural Analysis of 2-Hydroxyethanaminium Picrate, $HOCH_2CH_2NH_3^+ \cdot C_6H_2N_3O_7^-$

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(Received May 26, 1989)

2-Hydroxyethanaminium picrate, $HOCH_2CH_2NH_3^+ \cdot C_6H_2N_3O_7^-$, is prepared through a metathetical reaction of $Mg(Pic)_2$ and $HOCH_2CH_2NH_2$ (2-aminoethanol, MEA) in ethanol through in situ generation of HPic. Orange yellow crystals ($MEAH^+Pic^-$) (mp 163 °C) of the "Salt" are produced alongwith the colorless $Mg(CH_2NH_2CH_2O^-)_2$, even when MEA is less than 1:1 with respect to $Mg(Pic)_2$. The crystals are monoclinic, space group $P2_1/c$, $a=11.797(4)$, $b=14.288(3)$, $c=7.124(2)$ Å, $\beta=97.63(2)°$, $Z=4$, $D_{cal}=1.62$ g cm^{-3}. Structural analysis from the 1617 reflection data ($R=0.059$, $R_w=0.056$) reveals that the picric acid proton is formally transferred to the MEA nitrogen (N-H, 0.968 Å) and is merely bonded to the phenoxide of Pic (H···O$^-$, 1.951 Å) and weakly also to an oxygen of *o*-nitro group of the anion (H···ONO, 2.379 Å). The transferred proton becomes an integral part of the cation $MEAH^+$ and completes the fourth covalent bond of the sp^3 N of MEA, and does not show any special affinity for the anionic oxygen of Pic; the N-H···O$^-$ (142.8°) and N-H···ONO (141.6°) angles are closely comparable.

During in vitro chemical studies of alkali (M^+) and alkaline earth (M^{2+}) cations (general abbr. M^{z+}), which are being exectuted to throw light on the in vitro functions[1,2] of Na^+, K^+, Mg^{2+}, and Ca^{2+}, we frequently use a foreign proton donor, HL, in the ML_z-ligand reaction mixtures, where L is an organic charge neutralizer and HL its parent acid. The aim is usually to stabilize L through homoconjugation, formation of L···$(HL)_n$, so that M^{z+}-ligand interaction is favored to enable the synthesis of the ML_z-ligand. Such studies with 1,10-phenanthroline,[3] 2,2′-bipyridine,[4] *N,N,N′,-N′*-tetramethylethylenediamine (TMED),[5] and *N*-donor ligands in general, led frequently to the synthesis of HL-ligand by products which have constantly been of the 1:1 stoichiometry. In the meantime we developed interest in the study of interaction chemistry of the proton so that the trends in the interaction chemistry of small alkali and alkaline earth cations, Li^+ and Mg^{2+}, are understood more confidently and hence the H^+-complexes such as the title compound.

For the ML_z–MEA systems, wherein MEA denotes 2-aminoethanol and L is 2-nitrophenolate (Onp), 2,4-dinitrophenolate (Dnp), or 2,4,6-trinitrophenolate (picrate; Pic), each ML_z–MEA reaction gave rise to a metathetical reaction (in the order $M^+<M^{2+}$, Ca<Sr<Ba<Mg, Onp<Dnp<Pic) so that $M(CH_2NH_2CH_2O^-)_z$ salt plus HL-MEA were obtained even when amount of MEA in the reaction was not more than the equivalent of ML_z.[6] For $Mg(Pic)_2$, as also evident from the foregoing efficiency orders, metathetical reaction and hence the production of HPic–MEA (instead of the Mg^{2+}-complex) was only noted. Because of our interest in the coordination chemistry of the proton, we undertook X-ray analysis of HPic-MEA which in fact proved to be $MEAH^+$ Pic^-.

Experimental

Synthesis of HPic-MEA: $Mg(Pic)_2$ (0.1 mmol) was dissolved with MEA (0.2 mmol) is 5 ml ethanol. Colorless $Mg(CH_2NH_2CH_2O^-)_2$ salt, produced through the metathetical reaction, was filtered after ca. 30 min. The filtrate was subjected to crystallization of the title compound through slow evaporation at ca. 25 °C. Orange yellow single crystals (mp 163 °C) were filtered as produced (6—8 h). The title product can also be synthesized by a direct 1:1 reaction of HPic and MEA in ethanol but it is usually not as nicely crystalline. Elemental analysis of HPic–MEA: Found: C, 33.45; H, 3.38; N, 19.14%; Calcd: C, 33.10; H, 3.44; N, 19.31%.

X-Ray Structural Analysis: Cell parameters were determined by a least square fitting of the settings of 15 reflections ($\pm hkl$) measured on a Syntx diffractometer. Intensity data were collected in the θ–2θ-mode ($2\theta \leqq 50°$) with graphite-monochromatized Mo $K\alpha$ radiation. The structure was solved by direct methods (MULTAN-82)[7] and refined by full-matrix least squares to $R=0.059$, $R_w=[\sum(w|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.056$ for 1617 ($2\theta \leqq 50°$) independent reflections with $F_o^2 \geqq 1{,}5\,\sigma(F_o^2)$ [221 parameters, maximal shift esd=0.24]. Weights were given by the expression $w=k[\sigma^2(F_o)+0.0002F_o^2]^{-1}$. Hydrogen atoms were located in a difference syntehesis and their positions refined freely together with individual isotropic temperature factors in the last cycles of refinement. The non-hydrogen atoms were refined anisotropically. A final difference synthesis was effectively contourless (maximum 0.36 e Å^{-3}).

Results

Molecular Structure: Structure of the molecule is depicted in the labelled Fig. 1 and a projection of the unit cell content perpendicular to [001] in Fig. 2. Final coordinates for the nonhydrogen and hydrogen atoms with equivalent isotropic temperature factors are shown in Table 1.[8] $C_8H_{10}O_8N$ is monoclinic, space

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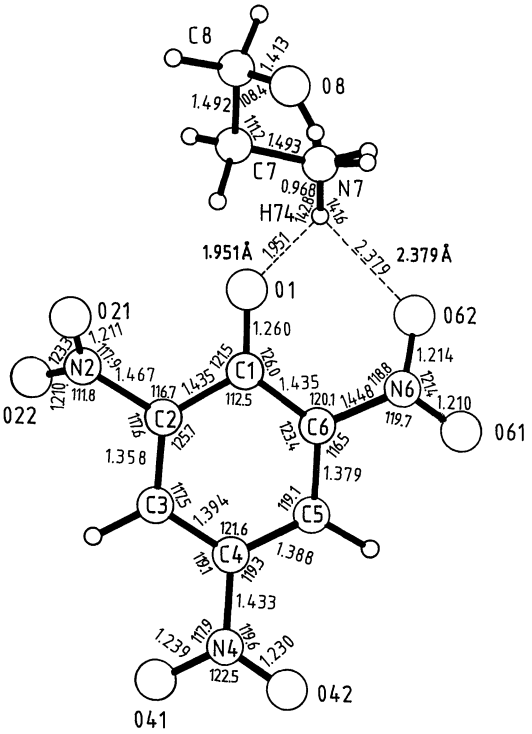

Fig. 1. Labelled diagram of the molecular structure of 2-hydroxyethanaminium picrate, $HOCH_2CH_2$-$NH_3^+C_6H_2N_3O_7^-$ with their bond distances and angles.

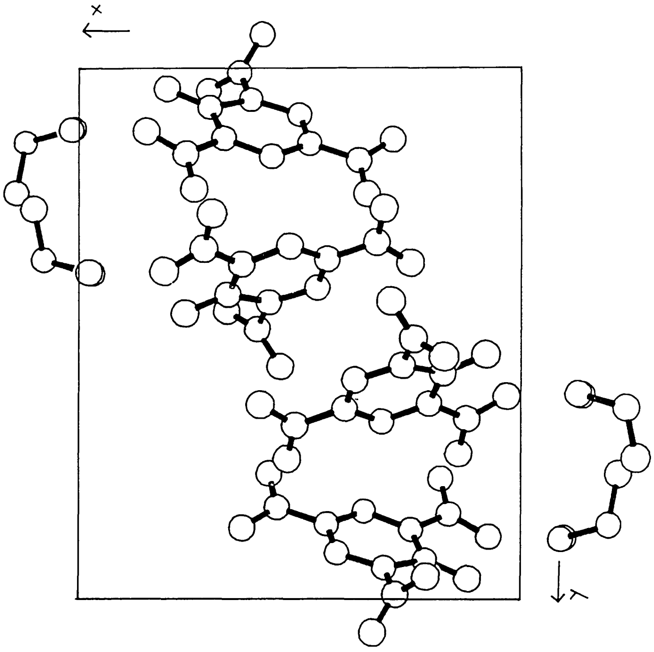

Fig. 2. Projection of the unit cell contents perpendicular to [001].

group $P2_1/c$ with a=11.797(4), b=14.288(3), c=7.124(2) Å, β=97.63(2)°, Z=4, D_{calc}=1.62 g cm^{-3}.

Table 1. Atom Coordinates with Isotropic Temperature Factors (Å^2)

Atom	x/a	y/b	z/c	U_{eq}
O_1	0.1659(2)	0.5387(1)	1.0825(3)	0.040(1)
C_1	0.1659(2)	0.5743(2)	1.0537(4)	0.030(1)
C_2	0.3626(2)	0.5596(2)	1.1825(4)	0.032(1)
N_2	0.3507(2)	0.5091(2)	1.3581(4)	0.044(2)
O_{21}	0.2898(2)	0.5430(2)	1.4641(4)	0.086(2)
O_{22}	0.4052(3)	0.4380(2)	1.3934(4)	0.078(2)
C_3	0.4692(2)	0.5876(2)	1.1547(4)	0.033(2)
C_4	0.4791(2)	0.6417(2)	0.9948(4)	0.030(1)
N_4	0.5900(2)	0.6732(2)	0.9616(3)	0.036(1)
O_{41}	0.6747(2)	0.6344(2)	1.0500(3)	0.045(1)
O_{42}	0.5980(2)	0.7362(2)	0.8466(3)	0.052(1)
C_5	0.3841(2)	0.6659(2)	0.8677(4)	0.032(2)
C_6	0.2782(2)	0.6321(2)	0.7598(4)	0.032(2)
N_6	0.1823(2)	0.6608(2)	0.7598(4)	0.042(2)
O_{61}	0.1923(2)	0.7268(2)	0.6568(4)	0.070(2)
O_{62}	0.0928(2)	0.6183(2)	0.7533(4)	0.086(2)
N_7	−0.0485(2)	0.6159(2)	1.1060(4)	0.038(1)
C_7	−0.0241(2)	0.6138(2)	1.3170(5)	0.043(2)
C_8	−0.1275(3)	0.6399(3)	1.4055(5)	0.047(2)
O_8	−0.1524(2)	0.7351(2)	1.3655(3)	0.031(1)
H_3	0.542(2)	0.570(2)	1.251(3)	0.047(8)
H_5	0.386(3)	0.706(2)	0.745(3)	0.058(9)
H_{71}	0.000(3)	0.545(1)	1.355(5)	0.070(11)
H_{72}	0.044(2)	0.662(2)	1.357(5)	0.066(11)
H_{73}	−0.096(2)	0.664(2)	1.052(4)	0.053(10)
H_{74}	0.020(2)	0.605(3)	1.048(5)	0.094(14)
H_{75}	−0.086(3)	0.675(2)	1.056(6)	0.088(14)
H_{81}	−0.108(3)	0.633(2)	1.552(3)	0.066(11)
H_{82}	−0.198(2)	0.597(2)	1.357(4)	0.041(8)
H_{83}	−0.115(3)	0.773(3)	1.304(6)	0.058(8)

Figure 1 shows that the HPic proton is rather formally transferred to the MEA nitrogen, N_7(N–H, 0.968 Å) which infact becomes the integral part of the base molecule yielding $^+H_3N\cdot CH_2CH_2OH$ while completing the fourth tetrahedral valency of sp^3 hydridized N_7 atom. The C_7 and C_8 atoms of MEA are approximately sp^3 with N_7–C^7–C^8 (111.2°) and C_7–C_8–O_8 (108.4°) angles being tetrahedral values. None of the N_7-protons undergoes intramolecular bonding with the MEA oxygen, O_8. However, the H_{74} atom bonds with the *Pic phenoxide* atom, O_1 (1.951 Å) and rather weakly also with an *ortho-nitrooxygen* atom, O_{62} (2.379 Å). The N_7–$H_{74}\cdots O_1$ (142.8°) and N_7–$H_{74}\cdots O_{62}$ (141.6°) angles are, however, comparable.

The Pic moiety displays a detectable quinonoid structure wherein C_1–O_1 (1.260 Å) and C_4–N_4 (1.433 Å) bonds are short enough to show a double-bond character; the bonds adjoining them, viz. C_1–C_2 (1.435 Å) and C_1–C_6 (1.435 Å), and N_4–O_{41} (1.239 Å) and N_4–O_{42} (1.230 Å) are longer than the analogous bonds in the Pic moiety.

Discussion

Chemical Significance: Direct reaction of organic acids with organic nitrogenous bases have led to the recognition of detectable charge transfer towards the acid proton[9] to a formal proton transfer on the base nitrogen.[10] Hpic and HDnp have been noted to form

H^+-transfer complexes with aromatic diamines and been characterized spectrophotometrically.[11] X-Ray structural analysis of the product HPic-serotonin·H_2O[12] has revealed a transfer of the proton to the base (and a charge-transfer stacking of Pic moiety with the protonated base). We report herein the first such product, $MEAH^+$–Pic^-, obtained in situ employing a $M(Pic)_z$–MEA ($M^{z+}=Mg^{2+}$) reaction in a protic medium (ethanol); initial $Mg^{2+}L^-_2$–MEA complexation leads to $Mg^{2+}(L^-)_2$ pair loosening as well as "cationization" of those MEA protons which belongs to the NH_2 and OH functions. This is adequate enough for Pic^- to eliminate H^+ from the complexed molecule of MEA; HPic so produed forms HPic–MEA with unreacted MEA.

A direct reaction of MEA with HOnp, HDnp and HPic leads to the synthesis of complexes with progressively increased melting points (115, 136, 163 °C, respectively). The present X-ray structural results indicate that the H^+ charge transfer with MEA in this order, ultimately ends up in formal H^+-transfer. A progressively increased melting point of the complexes in this order is, therefore, an index of accordingly an enhanced ionicity of the system. The salt $MEAH^+$–Pic^-, in a sense, is a H^+-complex wherein Pic is the charge neutralizer and MEA a monodentate ligand. The $H^+\cdots N$(MEA) is, however, strong to the extent that interatomic penetration takes place yielding a formal H–N (MEA) covalent bond. The lengths of the H_{74}–O_1^- and H_{74}–O_{62} bonds may be different (for structural and conformational reasons) but the proton, because of its hydrogen like nature, does not show any preference for any of the two oxygens; the N_7–H_{74}–O_1 (142.8°) and N_7–H_{74}–O_{62} (141.6°) angles are practically equal. The concerned proton has not only shown an indifference to the MEA-hydroxyl oxygen (MEA moiety being not intramolecularly bonded) but also an exclusive preference for the neutral nitrogen N_7, over the anionic phenoxide, O_1. Also, the $M(Pic)_z$–MEA reactions become favored[6] in the orders Cs to Li and Ba to Mg, so that the most efficient metathetical reaction for $Mg(Pic)_2$, and hence the most highly facilitated generation of HPic, is attributed to the most strong Mg^{2+}–N(MEA) interaction. Both the points collectively suggest that the hard M^{z+} ions are not only O-philic as usually described[13–15] but also N-philic and that the preference of the M^{z+} (M^+ or M^{2+}) for the N-sites increases with the charge density (Charge/radius ratio) of the cation, unlike noted for O-sites.

The author (RC) thankfully acknowledge the University Grants Commission, New Delhi for Research Scientist Award.

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