PRELIMINARY COMMUNICATION

The Presence of Iron(III) Salts of Oxo Acids Can Result in Protonation of Amino Groups

[a]M. BOČA*, [b]G. KICKELBICK, and [c]H. FUESS

[a]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-845 36 Bratislava, Slovakia*
e-mail: uachboca@savba.sk

[b]*Institute of Materials Chemistry, Vienna University of Technology, A-1060 Wien, Austria*

[c]*Institute of Materials Science, Darmstadt University of Technology, D-64289 Darmstadt, Germany*

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The unusual behaviour of ligands containing basic amine sites in systems of iron(III) salts of oxo acids in protic solvents is described. In these mixtures a protonation of the basic centres can take place without addition of other acidic species. This protonation is explained by the hydrolysis of hexaqua iron(III) cation providing protons capable for the protonation of amino groups.

There is an enormous amount of examples of complex compounds consisting of protonated ligands or counter anions of the type $[ML^H]^+[E_{-H}]^-$ or $[ML_{-H}]^-[E^H]^+$ where M is metal, L is ligand (L^H protonated and L_{-H} deprotonated) and E is a counteranion (E^H protonated and E_{-H} deprotonated) of organic origin. Also plenty of organic compounds crystallize in hydroacidic form of the scheme E·HX what can be rewritten in a structural point of view as $[E^H]X$ where X is an anion of the acid. All these products arise from the hydrogen reactions between organic species themselves or by the addition of acids. In the former case the involvement of the metal ion in the reaction scheme seems to be unlikely. The protonation requires the presence of base centres like oxygen or nitrogen.

In some cases the metal ion is involved in the reaction scheme of the protonation of some organic compounds. In literature at least two examples are reported: In the system composed of iron(III) perchlorate and ligand 2,6-bis(benzimidazol-2-yl)pyridine (bzimpy) in ethanolic solution a single crystal X-ray analysis of the resulting compound $(Hbzimpy)(ClO_4)\cdot H_2O$ [1] showed that base nitrogen of benzimidazol site was protonated in the ligand. In a similar reaction of iron(III) perchlorate with the ligand 2,6-bis(benzthiazol-2-yl)pyridine (bztpy) in methanolic solution a single crystal X-ray analysis of $(Hbztpy)(ClO_4)\cdot H_2O$ [2] revealed again a protonated nitrogen atom.

Here we present the preparation of another compound – four times protonated triethylenetetramine (3,6-azaoctane-1,8-diamine), which was prepared without adding any acid. The ethanolic solution of the ligand TAP (condensation product of the 2-pyridinecarboxaldehyde *N*-oxide with triethylenetetramine [3, 4]) was mixed with an aqueous solution of iron(III) sulfate. After filtration of the solid product a mother liquor rested for two weeks and single crystals were obtained as colourless needles.

Single crystals were mounted on SMART diffractometer (Siemens) with a CCD area detector. Graphite-monochromated MoK_α radiation was used. The crystal-to-detector distance was 4.40 cm. A hemisphere of data was collected by a combination of three sets of exposures at 294 K. Each set had a different ϕ angle for the crystal, and each exposure took 20 s and covered 0.3° in ω. The data were corrected for polarization and Lorentz effects and an empirical absorption correction (SADABS) was applied [5]. The cell dimensions were refined with all unique reflections.

The structure was solved by direct methods (SHELXS-86) [6]. Refinement was carried out with the full-matrix least-squares method based on F^2 (SHELXL-93) [7] with anisotropic thermal parame-

*The author to whom the correspondence should be addressed.

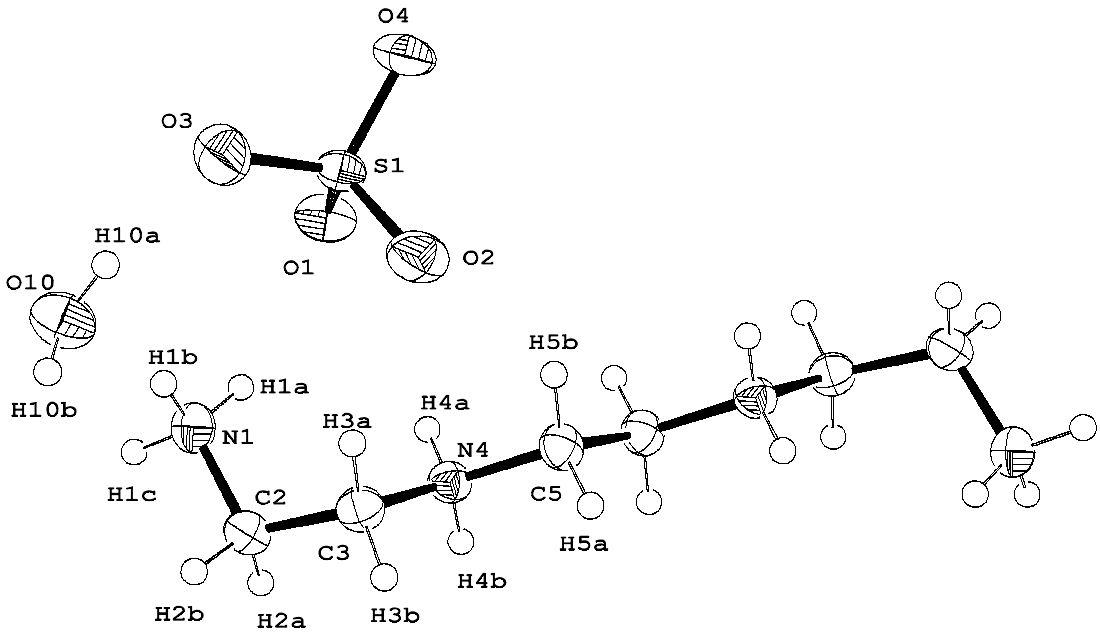

Fig. 1. The structure of the $(NH_3^+(CH_2)_2NH_2^+(CH_2)_2NH_2^+(CH_2)_2NH_3^+)(SO_4^{2-})_2 \cdot 2H_2O$, only one sulfate group and one water molecule are included (thermal ellipsoids of 50 % probability level).

Table 1. Crystal Data and Structure Refinement for $(NH_3^+(CH_2)_2NH_2^+(CH_2)_2NH_2^+(CH_2)_2NH_3^+)(SO_4^{2-})_2 \cdot 2H_2O$

Empirical formula	$C_6H_{26}N_4O_{10}S_2$
M_r/(g mol^{-1})	378.42
Colour	colourless
Cryst. system	triclinic
Space group	P-1
a/Å	7.2423(10)
b/Å	7.3177(9)
c/Å	8.4209(11)
α/°	90.150(2)
β/°	100.206(2)
γ/°	112.563(2)
V/Å^3	404.38(9)
T/K	294(2)
Z	1
λ/Å	0.71073
ρ(calc.)/(Mg/m^3)	1.554
Crystal size/mm	0.58 × 0.50 × 0.28
μ/mm^{-1}	0.384
hkl ranges	−9, 9; −7, 9; −11, 11
No. of data collected	2734
Indep. reflections	1944 (R_{int} = 0.0289)
$R(F)$ [$I > 2\sigma(I)$]	2.98 %
$R_w(F^2)$ (all data)	8.25 %
Goodness of fit on F^2	1.035
Largest peak and hole/e Å^{-3}	0.286, −0.376
Data, restraints, parameters	1944, 0, 135

ters for all nonhydrogen atoms. The positions of the amine and water H atoms were refined freely together with individual isotropic displacement parameters. All other H atoms were included in the refinement at the geometrically calculated positions and refined using a riding model with U_{iso} constrained to be $1.2U_{eq}$ of the parent C atom. No unacceptable displacement parameters were observed.

The crystal data and structure refinement are shown in Table 1. The structural formula of the compound can be written as $(NH_3^+(CH_2)_2NH_2^+(CH_2)_2NH_2^+(CH_2)_2NH_3^+)(SO_4^{2-})_2 \cdot 2H_2O$ and its structure is shown in Fig. 1. In the literature, plenty of structures of the same cation with different counteranions are reported [8—17]. Explanation for the missing pyridine *N*-oxide fragment is a decomposition of the ligand in the aqueous environment of the initial condensation compounds.

The crystal structure is centrosymmetric and consists of triethylenetetrammonium (fourfold protonated triethylenetetramine) cations, sulfate anions, and water molecules. The cations are chains of zig-zag form (Fig. 1). All C—C and N—C distances are of expected lengths. N1—C2 is shorter than N4—C3 and N4—C5 (Table 2). In addition, angles N—C—C and C—N—C are of expected value in the range of 110—113°. The distance of N1—H1a is the shortest hydrogen contact in polyamine. Also both distances between water oxygen and hydrogen differ. The sulfate groups form distorted tetrahedra. The reason for such distortion and differences in above-mentioned bonds can arise from a very extended hydrogen bonds network. Not only N—H...O and O—H...N but also C—H...O contacts were observed and are summarized in Table 3.

For an explanation of the above results we offer the following hypothetical reaction scheme. In the alcoholic solution of the iron(III) perchlorate, cations $[Fe(H_2O)_6]^{3+}$ are present because the initial iron(III)

Table 2. Bond Distances/Å

S1—O3	1.4575(10)	C5—H5a	1.522(2)
S1—O2	1.4721(10)	N4—H4a	0.877(17)
S1—O4	1.4788(9)	N4—H4b	0.874(18)
S1—O1	1.4833(9)	O10—H10b	0.79(3)
N1—C2	1.4884(16)	O10—H10a	0.91(2)
C2—C3	1.5097(17)	N1—H1a	0.89(2)
C3—N4	1.4976(16)	N1 —H1c	0.93(2)
N4—C5	1.4891(15)	N1—H1b	0.93(2)

Table 3. Hydrogen Bond and Short Contact Distances and Angles with Operations of Symmetry

Donor—H...Acceptor	H...A/Å	D...A/Å	D—H...A/°
N1—H1b...O10	1.89(2)	2.7906(17)	163.0(18)
O10—H10a...O3	1.89(3)	2.7828(17)	168(2)
N1—H1a...O1^{i}	2.04(2)	2.9140(15)	167.8(19)
N4—H4a...O1^{i}	1.900(18)	2.7751(14)	175.2(16)
N4 –H4b...O4^{ii}	1.836(18)	2.7028(14)	171.1(16)
N1—H1c...O2^{iii}	1.85(2)	2.7674(15)	169.3(17)
N1—H1c...O4^{iii}	2.592(19)	3.2442(16)	127.5(14)
O10—H10b...O2^{iv}	1.97(3)	2.7546(16)	174(2)
C2—H2a...O3^{ii}	2.43	3.2066(17)	136.7
C5—H5a...O10^{v}	2.48	3.4143(18)	162.6

i = 1 − *x*, 1 − *y*, −*z*; ii = 1 + *x*, 1 + *y*, *z*; iii = 1 + *x*, *y*, *z*; iv = 1 − *x*, 1 − *y*, 1 − *z*, v = *x*, 1 + *y*, *z*.

perchlorate contains at least ten water molecules and six of them form the primary coordination sphere and are difficult to exchange with alcohol molecules. The situation in aqueous solution of iron(III) sulfate is clear. In the next step the complex cations $[Fe(H_2O)_6]^{3+}$ undergo a hydrolysis according to the well known scheme

$$[Fe(H_2O)_6]^{3+} \rightarrow [Fe(OH)(H_2O)_5]^{2+} + H^+$$

The proton may protonate base centres as happened in all three cases mentioned according to the following schemes

$$H^+ + \text{bzimpy} + ClO_4^- + H_2O \rightarrow$$
$$\rightarrow \text{Hbzimpy}^+(ClO_4)^- \cdot H_2O \text{ (s)}$$

$$H^+ + \text{bztpy} + ClO_4^- + H_2O \rightarrow$$
$$\rightarrow \text{Hbztpy}^+(ClO_4)^- \cdot H_2O \text{ (s)}$$

$$4H^+ + \text{teta} + 2SO_4^{2-} + 2H_2O \rightarrow$$
$$\rightarrow H_4\text{teta}^{4+}(SO_4^{2-})_2 \cdot 2H_2O \text{ (s)}$$

where teta is triethylenetetramine.

This observation seems to be interesting because it may illuminate some problem in biosystems and it may open new ways of investigation of protonation reaction in pure organic or bioinorganic chemistry. It is possible that similar results could be observed in systems with another counteranions of inorganic acids not only of oxo but also nonoxo ones. Also different metals could be considered.

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