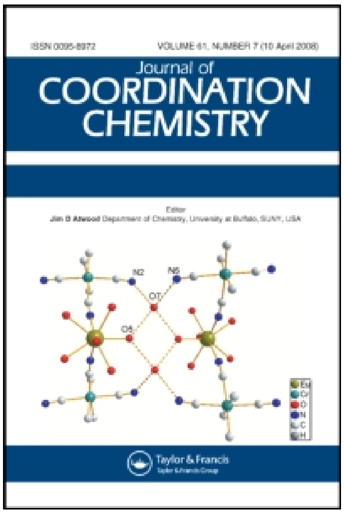

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$K(H_9O_4)$[*CIS*-DINITRO-Co(*TRANS*-N, N-GLYCINATO)$_2$]$_2$ (I)—A NOVEL CLASS OF HYDRONIUM ION TRAPS, OF WHICH (I) CONTAINS AN UNUSUAL FORM OF THE H_9O_4 CATION

Fernando Somoza[a]; Jiwen Cai[a]; Ivan Bernal[a]
[a] Chemistry Department, University of Houston, Houston, TX

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$K(H_9O_4)$[*CIS*-DINITRO-Co(*TRANS*-N,N-GLYCINATO)$_2$]$_2$ (I)—A NOVEL CLASS OF HYDRONIUM ION TRAPS, OF WHICH (I) CONTAINS AN UNUSUAL FORM OF THE $H_9O_4^+$ CATION

FERNANDO SOMOZA, JIWEN CAI and IVAN BERNAL

Chemistry Department, University of Houston, Houston, TX 77204-5641

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When $K[Co(gly)_2(NO_2)_2]$ is recrystallized from deionized water, crystals of (**I**) are isolated which contain an interesting new variant of the classical $H_9O_4^+$ cation. The cation is polymeric and, thus, qualifies for a description of being a proton wire.

Keywords: hydronium, $H_9O_4^+$, crystal structure, cobalt complex

Classification Categories *Note*: gly = glycinato anionedda = ethylenediaminediacetato anion and pddpda = propylenediaminediacetato anion.

We recently examined the structure of a compound with composition $(H_3O^+)[Co(en)_2oxalato]Cl_2{\cdot}H_2O$(**II**) which was obtained as a double salt from a slightly acidified (HCl) solution while attempting to grow x-ray quality crystals of the salt $[Co(en)_2oxalato]Pb_2Cl_5$. [1] Soon thereafter, we obtained crystals of $(H_5O_2^+)$[*cis*-α-Co(edda)ox](**III**) [2] (edda = ethylenediaminediacetato ligand) from an acidified solution(HCl) of the potassium salt and, in both cases, we attributed the change of cation to the additional acid added [1, 2]; however, more recently, we come across two additional cases of entrapped hydronium ions, namely $K(H_5O_2)[Co(pddpda)]_2{\cdot}4H_2O$(**IV**), [3] as well as the current case, (**I**), whose hydronium ion is most unusual, having never been observed in that stereochemical form before. Interestingly, crystals of compounds (**I**) and (**IV**) were grown from solutions of their potassium salts in deionized water, at *ca.* 22°C.

It is striking that all four compounds share the common feature of being Co(III) amine carboxylates in which the amine and the carboxylate moieties may be linked as a multidentate ligand (*e.g.*, glycine, pddpda or edda) or they may be independent of one another, as in the case of (**II**). Finally, we note that of the four classical hydronium ions known (H_3O^+, $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$) we have trapped three of them by use of these cobalt amine carboxylates.

A compound of composition $K[Co(gly)_2(NO_2)_2]$ was prepared by the method of Matsuoka, *et al.* [4] who did not study its crystal structure. We have verified, by elemental analysis [5] that the compound isolated by this procedure is, indeed, the salt of composition $K[Co(gly)_2(NO_2)_2]$. In that synthesis [4] the ratio of KNO_2:Co is (3.5:1). However, upon recrystallization from deionized water, even in the presence of excess (3.5:1) KNO_2, the crystals obtained are of compound (**I**). This has been verified by elemental analysis [5] and by x-ray examination of its crystals (see below for crystallographic details). Finally, an identical situation arises upon crystallizing K[Co(pddpda)] from deionized water since the crystals obtained are those of (**IV**) which also contains one potassium and one hydronium cation ($H_5O_2^+$) for every two cobalt anions.

Crystal data for $Co_2KO_{20}N_8C_8H_{25}$(**I**): monoclinic system, C2/c, z = 4, a = 20.056(4), b = 15.375(3), c = 8.135(3) Å, β = 101.71(2) °, V = 2456.41 Å^3, $2\Theta_{max}$(Mo-Kα) = 55°, F(000) = 1452. Number of reflections: 3118; number of unique reflections: 2814; number of data with I(hkl) $\geq 2.5\sigma$(I): 2439; number of variables: 177; number of atoms: 33; μ = 16.1 cm^{-1}. Transmission coefficients range from 0.7963 to 0.9979. $R(F)$ = 0.0528 and $R_w(F)$ = 0.0702. The hydrogens of the anions were placed at calculated positions (N-H = C-H = 0.95 Å; B = 5.0 Å^2); those of the hydronium cation were found in a final difference map and fixed there (B = 5.0 Å^2). Data were obtained with an Enraf-Nonius diffractometer and processed with the programs provided. Further details of the structural analysis may be obtained from the authors.

Reference to the figures show the following features present in the component parts of (**I**): (a) Figure 1 shows two asymmetric units necessary to depict the entire $(H_2O)(H_5O_2^+)(H_2O)$ cation (which sits at an inversion center) and its relation to the cobalt anions. The large open circle, inside a Co(glycinato) ring, is the potassium cation. Labels were left out since they obscure the structural details under discussion. A labeled view of the asymmetric unit is available from I. Bernal (b) The hydronium cation is in reality an infinite polymeric string of composition $[(H_2O)(H_5O_2^+)(H_2O)]_n$ which runs along the entire length of the c-axis, see Figures 2 and 3. (c) the hydronium cation in (I) is a structural isomer of the classically characterized $H_9O_4^+$ species observed in studies of ordered

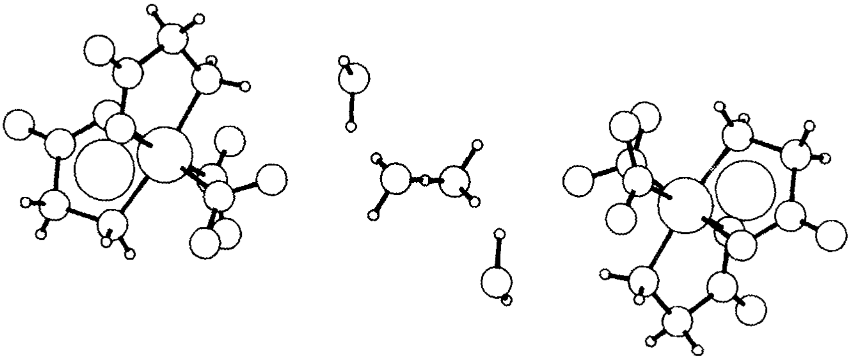

FIGURE 1 Two asymmetric units linked by the central H^+ ion which lies at an inversion center of the space group. Note the central $H_5O_2^+$ cation has hydrogens which are staggered as well as pyramidal oxygens whose non-bonded pairs are directed to water hydrogens. The view was selected to emphasize that feature of the structure.

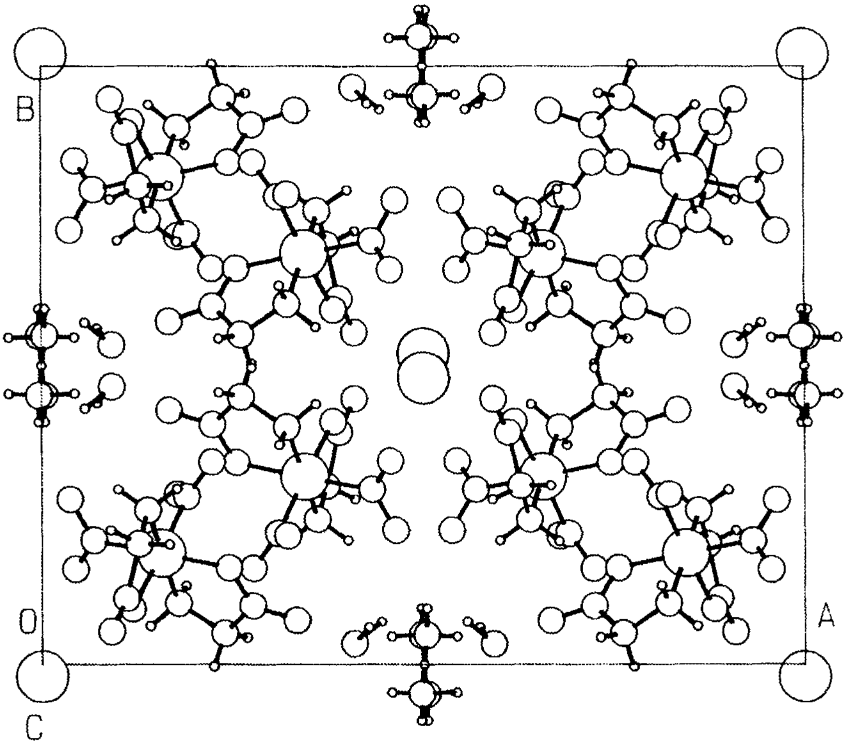

FIGURE 2 A *c*-projection of the unit cell showing the packing mode of the cations and anions. Note that the cobalt anions form two types of cages: the central one contains potassium cations bonded to the $-NO_2$ and glycinato ligand oxygens, whereas the cages at the four edges of the cell contain the hydronium cations.

structures in which the hydrogens were identified at sensible places; for instance, in the case of HCl·6H_2O(V) [6] in which the authors showed a very clear picture of $H_9O_4^+$. However, in (V) the hydronium ions form infinite cages containing the halide counteranion, unlike (I) which is an infinite polymer located in tunnels running along the *c*-axis (see Figures 2 and 3) and whose walls are formed by the cobalt anions (d) in (V), the cation is asymmetric in that on one side of its central ($H_5O_2^+$) portion two of its hydrogens form bonds with the oxygens of an adjacent pair of ($H_5O_2^+$) cations; on the other side, each of the hydrogens is linked to two waters which are hydrogen bonded to one another as well. All hydrogens of (V), thus far not accounted for, form hydrogen bonds to chloride anions. [6] (e) in (I), all four hydrogen bonds (see Figures 1 and 3) are formed by hydrogens of the waters to oxygens of the central ($H_5O_2^+$) portion of the cation. This is opposite

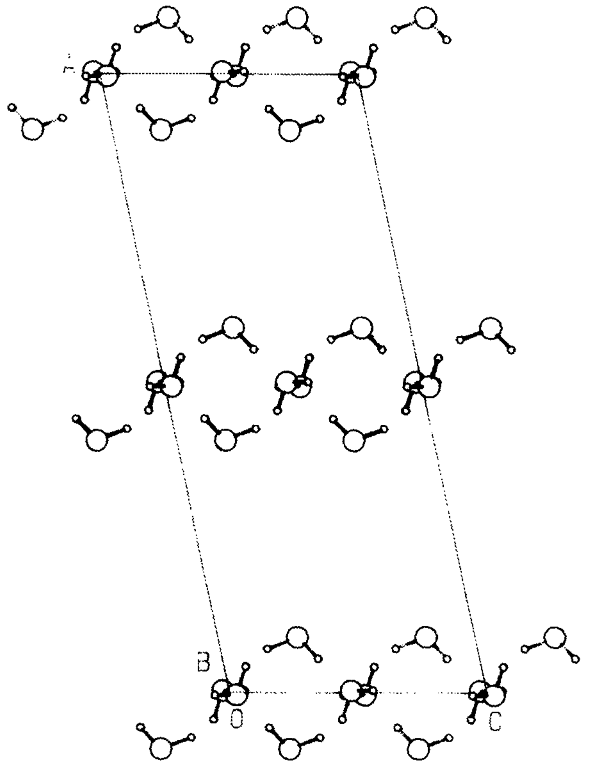

FIGURE 3 A *b*-projection of the unit cell showing only the infinitely hydrogen-bonded strings of cations, whose repeating unit is of composition $H_9O_4^+$. Note that four symmetrically arranged waters act as hydrogen-bonded bridges between cationic species of composition $H_5O_2^+$, the waters providing the hydrogen required.

to the picture described for those bonds found in (**V**). Thus, while (**V**) [6] and (**I**) contain a cation of composition $H_9O_4^+$, their structures differ markedly.

Many of the other crystal structures in the literature describing $H_5O_2^+$ and $H_9O_4^+$ cations are partially disordered or lack hydrogens and no conclusions can be drawn as to their exact nature except by informed guesses based on O...O distances and comparisons with those which have resolved hydrogens. Of those with well-ordered cations, the most instructive ones are those of $HCl{\cdot}2H_2O$ [7] which contains very well defined $H_5O_2^+$ cations similar to the relevant fragment of (**I**), and the structures of crystalline hydrates of hexafluorosilicic acids [8] which contain $H_5O_2^+$ and $H_7O_3^+$. All of these species contain asymmetrically-bonded hydronium cations in which some of their hydrogens are linked to adjacent oxygens and to their counteranions.

Reference to Figure 2 shows that the cobalt anions form large cages of two types: one (in the center of the figure) contains potassium cations; the other cage (at the top and bottom as well as at the left and right edges of the cell) contain the hydronium cations. Finally, the true nature of the hydronium cations is best appreciated in Figure 3, which is a packing diagram showing the polymeric strings. Note that the holes in cages shown in Figure 2 are infinite channels. This is the unique feature of the hydronium ion present in (**I**), never before observed.

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