rate constant k_1, determined from the linear portion of the rate curves at high [bisulfite], showed the same bell-shaped pH dependence as previously reported (cf. Figure 1).[2,3] Extrapolation of these rates to low concentrations of bisulfite ion showed an intercept (Figure 2). The intercept has a strong dependence on pH as shown in Figure 3. The inflection point at pH = 4.7 corresponds to the pK of the pyrimidine portion of thiamine (4.7). A more complete explanation of the pH dependence of k_2 and k_3 is not possible since the acid-base properties of the intermediate(s) are not known.

Thus the pH dependence of k_1 is in agreement with the mechanism proposed and the pH dependence of the intercept is at least consistent.

These results show clearly that two bisulfite ions are involved in thiamine cleavage as proposed by Zoltewicz and Kauffman.

Our results at low concentrations of bisulfite clearly show a rate-determining attack of bisulfite ion on the bisulfite-thiamine adduct. S_N2 reactivity at the methylene carbon could be expected to increase the bisulfite-thiamine adduct due to the increased electron-donating properties of the bisulfite-thiamine adduct relative to thiamine.

These results certainly rule out both the S_N1 mechanism and the sultone mechanism. Zoltewicz and Kauffman did not support the sultone mechanism but preferred the S_N1 mechanism over the S_N2 mechanism. They point out that the S_N2 mechanism encounters more steric hindrance in the adduct II over I even though electronically S_N2 would be favored in II over I. The electronic effects may compensate for the steric hindrance in compound II.

Zoltewicz and Kauffman have proposed that this mechanism may be functioning in certain enzyme-catalyzed reactions such as the thiaminase reaction. We concur and add that a two-step reaction was considered for the thiamine reaction in 1963.[5] The thiaminase-catalyzed rate of cleavage of thiamine by substituted anilines increased with the value of Hammett's σ constant for negative values of σ constants but decreases with positive values of σ constants. A change in rate-determining step was proposed between negative and positive values of σ constants which requires a two-step mechanism.

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(5) Mazrimas, J. A.; Song, P. S.; Ingraham, L. L.; Draper, R. D. *Arch. Biochem. Biophys.* **1963**, *100*, 409.

Communications to the Editor

$C_3H_5^+$ Isomers: Evidence for the Existence of Long-Lived Allyl and 2-Propenyl Cations in the Gas Phase

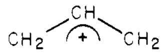
Sir:

Several years ago Aue, Davidson, and Bowers[1] suggested that reactions 1 and 2 formed, at least in part, the 2-propenyl cation

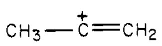
$$BH^+ + CH_2{=}C{=}CH_2 \rightleftarrows C_3H_5^+ + B \qquad (1)$$

$$BH^+ + CH_3C{\equiv}CH \rightleftarrows C_3H_5^+ + B \qquad (2)$$

II rather than the more stable[2] allyl cation I. The suggestion



I



$CH_3{-}\overset{+}{C}{=}CH_2$

II

was based on the measured proton affinities of $CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$ which yield[1-3] $\Delta H_f°(C_3H_5^+) = 230 \pm 2$ kcal/mol, a value 4 kcal/mol greater than the well-known[3,4] heat of formation of allyl cation I and on the fact that $C_3H_5^+$ ions formed from protonation of allene and propyne protonate CH_3OH while those formed from electron-impact-induced fragmentation of allyl chloride do not.

In order to further investigate this problem we have formed $C_3H_5^+$ ions in the source of a high-performance ZAB-2F mass spectrometer[5] either by electron-impact-induced fragmentation of a molecular ion or by selected ion-molecule reactions. The ions are analyzed by collision-induced dissociation spectroscopy (MIKES-CID).[6] A large number of product ion peaks result from collisional excitation of $C_3H_5^+$.[7] The ion peaks that show most clearly differences in MIKES-CID spectra are those containing two carbon atoms. A summary is given in Table I.

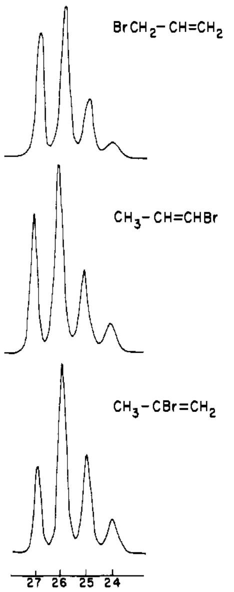


Figure 1. MIKES-CID spectra of $C_3H_5^+$ ions in the region C_2^+ to $C_2H_3^+$. The $C_3H_5^+$ ions were generated by electron impact on the three isomeric bromopropenes shown.

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(1) D. H. Aue, W. R. Davidson, and M. T. Bowers, *J. Am. Chem. Soc.*, **98**, 6700 (1976).

(2) Revisions in the proton affinity scale and double-resonance experiments with allene and propyne yield proton affinities (PA) of these species of 182 kcal/mol on a scale where PA(NH_3) = 205 kcal/mol (ref 3). The uncertainty in the heat of formation of 2-propenyl ion could be as great as 3-5 kcal/mol, however; see ref 3 and F. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 4071 (1979).

(3) D. H. Aue and M. T. Bowers, Basicity Measurements in "Gas Phase Ion Chemistry", Vol. II, M. T. Bowers, Ed., Academic Press, New York, 1979, pp 1-52.

(4) F. P. Lossing, *Can. J. Chem.*, **50**, 3973 (1972); **49**, 356 (1971). See also D. W. Berman, V. G. Anicich, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 1239 (1979).

(5) Manufactured by V. G. Micromass. For a working description, see R. P. Morgan, J. H. Beynon, R. H. Bateman, and B. N. Green, *Int. J. Mass Spectrom. Ion Phys.*, **28**, 171 (1978).

(6) R. G. Cooks in "Collision Spectroscopy", R. G. Cooks, Ed.; Plenum Press, New York, 1978. For a more general reference, see R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, "Metastable Ions", Elsevier, Amsterdam, 1973. See also N. M. M. Nibbering, T. Nishishita, C. C. van de Sande, and F. W. McLafferty, *J. Am. Chem. Soc.*, **96**, 5668 (1974); F. W. McLafferty, *ACS Symp Ser.*, **No. 70**, 45-47 (1978); K. Levsen, "Fundamental Aspects of Organic Mass Spectrometry", Verlag Chemie, Weinheim, West Germany, 1978.

(7) A. Maquestiou, Y. van Hoverbeke, R. Flamming, C. de Meyer, and A. Menu, *Org. Mass Spectrom.*, **12**, 707 (1979).

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Table I. MIKES–CID Spectra for $C_3H_5^+$ Ions from Various Sources

source of $C_3H_5^+$	*m/e* product ion 27	26	25	24	ZAB-2F 26/27	MS-50[a] 26/27	isomeric %[b] I	II
$ClCH_2CH{=}CH_2$[c]	82	100	42	12	1.22		100	0
$BrCH_2CH{=}CH_2$[c]	84	100	42	14	1.19	1.0	100	0
$CH_2{=}CH_2$[d]	83	100	41	13	1.20	0.95	100	0
$CH_2{=}CHCH_2CH_3$[c]	73	100	41	12	1.37		73	27
c-C_3H_6[c]	73	100	42	13	1.37		73	27
$CH_3CH{=}CHBr$[c]	73	100	44	14	1.37	1.4	73	27
$CH_3CH{=}CH_2$[c]	70	100	46	17	1,43		65	35
$CH_3C{\equiv}CH$[e]	51	100	49	15	1.96	2.0	14	86
$CH_3C{\equiv}CH + H_2O$[f]	51	100	51	17	1.96		14	86
$CH_3C{\equiv}CH + CH_4$[g]	58	100	47	17	1.72		30	70
$CH_2{=}C{=}CH_2$[e]	54	100	48	15	1.85	2.0	22	78
$CH_2{=}C{=}CH_2 + H_2O$[f]	54	100	51	18	1.85		22	78
$CH_2{=}C{=}CH_2 + CH_4$[g]	70	100	40	13	1.43		65	35
$CH_2C(CH_3)CH_2NH_2$[c]	62	100	46	16	1.61		43	57
$CH_3CBr{=}CH_2$[c]	46	100	50	17	2.17	2.5	0	100

[a] Obtained by B/E linked scan on Kratos MS-50 mass spectrometer. See ref 10. [b] Obtained from the *m/e* 27 intensity. Isomer I is the allyl ion $(CH_2CHCH_2)^+$ and isomer II the 2-propenyl ion $CH_3C^+{=}CH_2$. A detailed analysis using all peaks in the CID spectrum indicates an accuracy of ±15%. [c] $C_3H_5^+$ obtained from electron impact. The data reported in the table were for 70-eV electron energy. When the electron energy was lowered to ~10 eV, systematic changes in the MIKES–CID spectra curve were observed for some species. For example, the percent allyl increased for $CH_3CH{=}CHBr$, $CH_3CH_2CH{=}CH_2$ and c-C_3H_6. There was no change in the MIKES–CID spectra of $CH_3CBr{=}CH_2$, which suggests that this system generates only 2-propenyl ion at all energies. The $CH_2{=}CHCH_2Br$ system did show some variation with electron energies, however, indicating that this system may form some 2-propenyl isomer at high electron energies. A more detailed study will be reported elsewhere. [d] $C_3H_5^+$ obtained from the reaction $C_2H_4^+ + C_2H_4 \rightarrow C_3H_5^+ + CH_3$. [e] $C_3H_5^+$ obtained from the reaction $C_3H_4^+ + C_3H_4 \rightarrow C_3H_5^+ + C_3H_3$: M. T. Bowers, D. D. Elleman, R. M. O'Malley, and K. R. Jennings, *J. Phys. Chem.*, 74, 2583 (1970). [f] $C_3H_5^+$ obtained from the reaction $H_3O^+ + C_3H_4 \rightarrow C_3H_5^+ + H_2O$. [g] $C_3H_5^+$ obtained from the reaction $RH^+ + C_3H_4 \rightarrow C_3H_5^+ + R$, where R = CH_4 or C_2H_4.

There are definite reproducible differences in the spectra, particularly in the intensity of the *m/e* = 27 peak relative to the *m/e* 26 base peak (the *m/e* 25 and 24 peaks show consistent, reproducible differences as well but are of lesser magnitude). This fact is dramatically evident in the MIKES–CID spectra of Figure 1 for the three isomeric bromopropenes. The *m/e* 26/*m/e* 27 ratio from the ZAB-2F instrument is listed in Table I and compared with data taken on the Kratos MS-50 mass spectrometer[8] by using a first field-free region collision cell and a B/E linked scan technique.[9] The semiquantitative agreement is satisfying considering the substantial difference in method.[10]

The simplest interpretation of the data in Table I is that fragmentation of 3-chloro- and 3-bromopropenes yields pure allyl cation I, while fragmentation of 2-bromopropene gives pure 2-propenyl cation II. Since a substantial barrier to isomerization between I and II is predicted theoretically,[11] it is probable that I and II do not interconvert at low energies on the mass spectrometric time scale (10^{-6} s). Using these assumptions it is possible to assign percentages of I and II to the $C_3H_5^+$ ions formed via various pathways (Table I).[12]

Given the assumptions of the above paragraph, it is apparent that methallylamine cleaves predominantly by direct loss of CH_2NH_2 to yield the 2-propenyl cation II and a lesser amount of allyl cation I. Similarly, 1-butene fragments by direct loss of $CH_3\cdot$ to yield predominantly the allyl cation I, and a lesser amount of 2-propenyl cation II. Propene loses H· to form substantial amounts of both I and II, as does cyclopropane with rearrangement. Another system that must rearrange is 1-bromopropene where direct loss of Br· would form the high-energy $CH_3CH{=}CH^+$ ion. It is somewhat surprising that more 2-propenyl cation is not formed since this ion would result from a simple 1,2-hydrogen shift either before or after Br· loss.[11,13]

The data for protonated allene and propyne are most interesting. When these $C_3H_5^+$ ions are formed from mild protonation[14] by H_3O^+ or $C_3H_4^+$, the dominant resultant structure is 2-propenyl (86% for propyne and 78% for allene). These results confirm the conclusions of Aue et al.[1] about the structures of these ions. When the higher energy protonating agents[14] CH_5^+ and $C_2H_5^+$ from methane are used, the percentage of 2-propenyl cation decreases dramatically for allene (to 35%) and somewhat for propyne (to 70%). For propyne, the 2-propenyl cation must be formed initially by protonation, and even when a significant amount of energy (up to 44 kcal/mol)[14] is available, this ion does not readily rearrange to the allyl structure. The fact that protonation of allene by strong acids yields mainly allyl cation indicates that allene can undergo direct protonation on the central carbon but that a barrier to protonation at this center must exist since weak acids generate primarily 2-propenyl ion by protonation on the terminal carbon.

The $C_3H_5^+$ ion formed in reaction 3 is 100% allyl. This is an

$$C_2H_4^{+}\cdot + C_2H_4 \rightarrow C_3H_5^+ + CH_3\cdot \qquad (3)$$

important result because of the substantial interest in the mechanisms of $C_3H_5^+$ ion formation from various $C_4H_8^{+}\cdot$ ions.[15]

Consideration of all of the above cases indicates that I and II are stable, long-lived isomers at low energies and the probability of forming I or II depends rather strongly on the mechanism of formation of the $C_3H_5^+$ ion. The isomeric integrity appears to break down at high internal energies, however, as evidenced by the variation in isomer percentage when propyne is protonated by reagents of different proton affinity. It is also evidenced in the metastable (MIKES) peak shape for reaction 4 observed in

$$C_3H_5^+ \rightarrow C_3H_3^+ + H_2 \qquad (4)$$

the absence of collision gas. In all cases the peak shapes and widths are identical and reproduce literature shapes[16] (attributed to the allyl cation). The implication is that all $C_3H_5^+$ ions with enough energy to decompose via (4) have rearranged to a common structure, presumably I. Since isomerization has preceded decomposition in some cases, but not all, the barrier to isomerization must be less than the barrier to decomposition via (4).[17]

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(8) For a discussion of the technique, see K. R. Jennings, *ACS Symp. Ser.*, No. **70**, 3-17 (1978).

(9) A. P. Bruins, K. R. Jennings, and S. Evans, *Int. J. Mass Spectrum. Ion Phys.*, **26**, 395 (1978). See also J. H. Beynon and R. K. Boyd, *Org. Mass Spectrom.* **12**, 163 (1977).

(10) In a B/E linked scan a narrow peak is recorded whose height corresponds to ion intensity at the energy corresponding to the theoretical center of a product ion peak. In reality, a collision-induced peak is shifted slightly to lower energy; hence a B/E scan does not always record maximum ion intensity.

(11) L. Radom, P. C. Hariharna, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 6531 (1973).

(12) The fact that the *m/e* 27 peak in the vinylic $C_3H_5^+$ systems is suppressed relative to the allyl systems forms the basis for assigning the percentages in Table I and makes chemical sense.

(13) The possibility exists that other $C_3H_5^+$ isomers contribute, such as $CH_3CH{=}CH^+$ and $\underline{CH_2CH_2CH}^+$. The first of these is a primary cation and will be at much higher energy than I or II and the second is predicted to rearrange to I without a barrier[11] although there is still some question on this issue.[1] It is possible that $(CH_3CH_2{=}CHBr)^+$ initially forms $CH_3CH{=}CH^+$ from loss of Br·, but if this $C_3H_5^+$ isomer is long-lived it does not generate a distinct MIKES–CID pattern.

(14) The exothermicities of the proton transfer reactions are 44 kcal/mol ($CH_5^+ + C_3H_4$), 19 kcal/mol ($C_2H_5^+ + C_3H_4$), 9 kcal/mol ($H_3O^+ + C_3H_4$), 16 kcal/mol ($CH_3C{\equiv}CH^{+}\cdot + CH_3C{\equiv}CH$), and 5 kcal/mol ($CH_2{=}C{=}CH^{+}\cdot + CH_2{=}C{=}CH_2$); see ref 3.

(15) T. Baer, D. Smith, B. P. Tsai, and A. S. Werner, *Adv. Mass Spectrom.*, **7A**, 56 (1977); S. T. Ceyer, P. W. Tiedemann, C. Y. Ng, B. H. Mahan, and Y. T. Lee, *J. Chem. Phys.*, **70**, 2138 (1979); G. G. Miesels, M. J. Weiss, T. Hsieh, and G. M. L. Verboom, *J. Am. Chem. Soc.*, **101**, 7189 (1979); W. J. Chesnavich, L. Bass, T. Su, and M. T. Bowers, to be published.

(16) J. L. Holmes and J. K. Terlouw, *Org. Mass Spectrom.*, **10**, 787 (1975); J. L. Holmes, A. D. Osborn, and G. M. Weiss, *ibid.*, **10**, 867 (1975).

(17) For a discussion see R. D. Bowen and D. H. Williams in *ACS Symp. Ser.*, No. **70**, 18-46 (1978).

Acknowledgments. The support of the National Science Foundation under Grants CHE76-17573 and CHE77-15449 and the Science Research Council, U.K., is gratefully acknowledged. M.T.B. thanks the Science Research Council, U.K., for an SRC Senior Visiting Fellowship during the early stages of this work. A travel grant from the Royal Society, London, to J.R.G. is also gratefully acknowledged. We also wish to thank a referee for suggesting we perform careful studies of the MIKES-CID spectrum as a function of electron energy.

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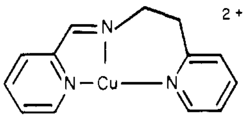
Received February 19, 1980

A Tricopper(II) Complex Containing a Triply Bridging Carbonate Group

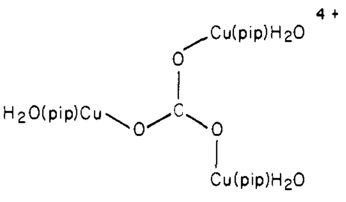
Sir:

In the course of studies on imidazolate-bridged dicopper(II) complexes,[1] we occasionally isolated a crystalline, carbonate-containing compound from basic aqueous solutions of Cu(pip)-$(NO_3)_2 \cdot H_2O$[2] (I) and imidazole. Use of freshly boiled water and



$Cu(pip)^{2+}$, I

minimal solution stirring inhibited the formation of this compound, suggesting that dissolved carbon dioxide was the source of the carbonate ion. X-ray structural work revealed the novel cation II. Although numerous carbonate complexes are known and



$[Cu(pip)(H_2O)]_3CO_3{}^{4+}$, II

exhibit a variety of monodentate, chelating, and bridging geometries,[3,4] to our knowledge II is the first discrete compound to contain a triply bridging carbonate ion. Here we report the syntheses of the perchlorate and nitrate salts of II, their crystal structure, and temperature-dependent magnetic susceptibility studies that reveal ferromagnetic behavior.

Table I. Exchange Coupling Constants for Some Carbonate-Bridged Copper(II) Complexes

complex	*g*	*J*, cm^{-1}	*zJ'*, cm^{-1}	ref
$[Cu(pip)(H_2O)]_3(CO_3)(NO_3)_4$	2.120 (1)	4.82 (3)	−0.079 (1)	*a*
$[Cu(pip)(H_2O)]_3(CO_3)(ClO_4)_4$	2.139 (1)	4.47 (4)	−0.075 (1)	*a*
$Na_2Cu(CO_3)_2$	2.24 (2)	4.1 (7)	*b*	18

[a] This work. Values for g, J, and zJ' were obtained by least-squares fits of the observed data (~220 points) to the expression $\chi_M{}^{cor}T = (\chi' T)/[1 - (2zJ'\chi')/Ng^2\beta^2]$, where $\chi' = [(Ng^2\beta^2)(1 + 5\exp(3J/kT))]/[4kT(1 + \exp(3J/kT))]$, in $\chi_M{}^{cor}T$ vs. T plots for $T \leqslant 290$ K. [b] Not applicable.

Slow cooling of a solution containing 10 mmol of Cu(pip)-$(NO_3)_2 \cdot H_2O$[1,2] and 4 mmol of K_2CO_3 dissolved in 30 mL of hot water produced well-formed, blue hexagonal bipyramids of $[Cu(pip)(H_2O)]_3(CO_3)(NO_3)_4$[5a] in 40% yield. The perchlorate salt[5b] was prepared in 75% yield by substituting Cu(pip)-$(ClO_4)_2 \cdot H_2O$ and using 300 mL of water. Carbonate-related IR-active vibrational frequencies[6] occur at 1460 (ν_3), 840 (ν_2), and 752 (ν_4) cm^{-1} for the perchlorate salt.

Both compounds crystallize in the hexagonal system and are isomorphous. The unit cell parameters[7] for the nitrate salt are $a = b = 13.414$ (3) Å, $c = 16.024$ (2) Å, $Z = 2$, $\rho_{obsd} = 1.585$ g cm^{-3}, and $\rho_{calcd} = 1.578$ g cm^{-3}. Intensity data were collected by diffractometer,[9] and the structure was solved by heavy-atom methods in space group $P\bar{6}2c$ and refined (926 data, 133 parameters) to a current value of 0.054 for the residual R_1.[10] The structure and selected geometric features of the cation II are shown in Figure 1.

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(1) Kolks, G.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 5804.

(2) Pip is an abbreviation for the tridentate Schiff base ligand 2-[2-(2-pyridyl)ethyliminomethyl]pyridine (see ref 1).

(3) Gagne, R. R.; Gall, R. S.; Lisensky, G. C.; Marsh, R. E.; Speltz, L. M. *Inorg. Chem.* **1979**, *18*, 771 and references cited therein.

(4) (a) Davis, A. R.; Einstein, F. W. B.; Curtis, N. F.; Martin, J. W. L. *J. Am. Chem. Soc.* **1978**, *100*, 6258. (b) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W.; Watkins, K. O. *Inorg. Chem.* **1979**, *18*, 2296. (c) Churchill, M. R.; Davies, G.; El-Sayed, M. A.; El-Shazly, M. F.; Hutchinson, J. P.; Rupich, M. W. *Ibid.* **1980**, *19*, 201.

(5) Anal. (a) Calcd for $Cu_3C_{40}H_{45}N_{13}O_{18}$: C, 40.49; H, 3.82; N, 15.35; O, 24.27; Cu, 16.07; CO_3, 5.06. Found: C, 40.35; H, 4.03; N, 15.53; O (by difference), 24.30; Cu, 15.79; CO_3, 5.62. (b) Calcd for $Cu_3C_{40}H_{45}N_9Cl_4O_{22}$: C, 35.95; H, 3.39; N, 9.43; Cl, 10.61. Found: C, 35.84; H, 3.67; N, 9.16; Cl, 10.33.

(6) Nakamoto, K. "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed.; Wiley-Interscience: New York, 1970; p 98.

(7) Weissenberg and precession photographs of both salts can be indexed according to a hexagonal unit cell in which reflections that obey the condition $h - k = 3n$ are normal, sharp spots; otherwise the reflections appear as weak, diffuse spots. For the *hk0* zone, reflections with $h - k \neq 3n$ are systematically absent. This pattern is indicative of partial ordering, with the disorder occurring along the *c* axis only.[8a,b] The sharp reflections are associated with a fully disordered subcell. The dimensions of the two cells are related by the expressions $a_s = b_s = 3^{1/2}a$, $c_s = c$, and $Z_s = 3Z$, where the subscript s refers to the supercell and *a*, *c*, and *Z* are the values reported here for the subcell. Data have been collected only for the subcell.

(8) "Advanced Methods of Crystallography", Ramachandran, G. N., Ed.; Academic Press: New York, 1964: (a) Wooster, W. A. p 121; (b) Jagodzinski, H., p 181.

(9) The data were collected by the Molecular Structure Corp., College Station, TX. We thank Drs. Bert Frenz and Jan Troup for this courtesy.

(10) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. Although the space group extinction conditions for $P\bar{6}2c$ are not rigorously obeyed (occasional weak violations were observed), interpretation of the Patterson map was possible only in this space group. The two overlapping images of the pip ligand, required as a result of the crystallographic $\bar{6}$ symmetry axis (vide infra), were readily resolved. Although atoms N9 and Cu (Figure 1) were located at $z = {}^1/_4$ on the Patterson and difference Fourier maps, they rapidly refined to their final positions when placed ~0.25 and 0.10 Å, respectively, from this plane to achieve geometry consistent with other structural studies of the $Cu(pip)^{2+}$ moiety.[11] Six nitrate groups were disordered about the mirror planes at $z = {}^1/_4, {}^3/_4$ [position 6(h)] and were refined as rigid bodies with N–O = 1.20 Å, O–N–O = 120°. Two nitrate groups were badly disordered about position 2a. The Cu, OW, carbonate C, carbonate O, and nitrate group atoms were refined with anisotropic temperature factors. The atoms of the pip ligand were refined with isotropic temperature factors. Hydrogen atoms were fixed at calculated positions, and an overall U_{hyd} was refined to 0.10 $Å^2$. The geometry of the $Cu(pip)^{2+}$ moiety is in excellent agreement with that of the four crystallographically independent units found in $[Cu(pip)]_2(imidazolate)(NO_3)_3 \cdot 2.5H_2O$.[11]

(11) Kolks, G.; Lippard, S. J., to be submitted for publication.

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