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Copper(II) Complexes of 1,2,3-Triazolecarboxylic Acids[†]

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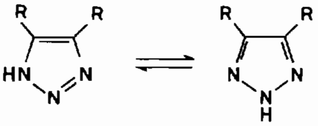
Abstract

The synthesis and characterization of four complexes of copper(II) with 1,2,3-triazolecarboxylic acid derivatives are described. The ligand 1,2,3-triazole-4,5-dicarboxylic acid forms either a 1:1 or a 2:1 complex with copper(II) as a function of pH and ligand concentration. A crystal structure of the 2:1 complex, diaqua-bis(1,2,3-triazole-4,5-dicarboxylato)copper(II) dihydrate, has been determined. It crystallizes in the triclinic space group $P\bar{1}$ with a = 5.203(1) Å, b = 6.583(2) Å, c = 11.835(2) Å, α = 77.99(2)°, β = 98.92(2)°, γ = 105.84(2)°, and R = 0.029 for 1660 observations with $I > 3\sigma(I)$. The copper is in an elongated tetragonal geometry with equatorial coordination through two triazole nitrogens and two water molecules. The axial sites are occupied by carbonyl oxygens of the carboxylic acid substituents. The 1:1 and 2:1 copper(II) complexes with 1,2,3-triazole-4-carboxylic acid and 1-methyl-1,2,3-triazole-4-carboxylic acid, respectively, have also been studied. Thermogravimetric analysis, infrared, and magnetic susceptibility were used to predict the coordination environment of the three complexes not amenable to X-ray crystallography.

Introduction

1,2,3-Triazoles are unique ligands that can potentially coordinate metal ions in a variety of different ways. Since the un-ionized triazole can exist in either of two tautomer forms, there are three possible modes of monodentate coordination and two modes of bridging bidentate coordination. In addition to these modes, the ionized triazole may also function as a bridging tridentate ligand.



Examples of monodentate coordination of Cu^{2+} by 1,2,3-triazoles have shown coordination to occur through both the middle [1] and outer [2] ring nitrogens. Bridging bidentate [3] and tridentate [4] coordinations have recently been reported in copper complexes of 1,2,3-benzotriazole.

We report here the synthesis and characterization of copper(II) complexes of 1,2,3-triazolecarboxylic acids. The ligands chosen for study (Fig. 1) have increased binding sites by virtue of their carboxylic acid substituents and vary in structure in a systematic way that allow for useful comparisons of their metal complexes to be made.

Experimental

Ligands

Literature procedures were used to prepare the requisite ligands. The reactions of hydrazoic acid with acetylene dicarboxylic acid and propiolic acid were used to prepare 1,2,3-triazole-4,5-dicarboxylic acid ($TDAH_3$) [5] and 1,2,3-triazole-4-carboxylic acid (TAH_2) [6], respectively. The ligand 1-methyl-1,2,3-triazole-4-carboxylic acid (MTAH) was prepared from the reaction of methyl azide with propiolic acid [6].

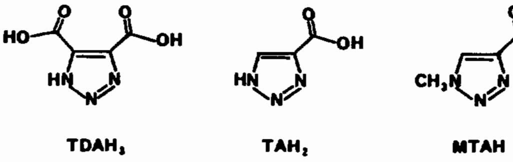


Fig. 1. Ligands and their abbreviations.

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Copper(II) Complexes

The complexes prepared here were found to be the same regardless of whether copper(II) nitrate, copper(II) perchlorate, or copper(II) sulfate was used as the source of the copper(II) ion. The yields for these preparations were quite good, as essentially quantitative precipitation of the respective copper(II) complexes from solution were obtained.

$Cu(TDAH_2)_2(H_2O)_4$

Copper(II) perchlorate (2.5 mmol) was added to a stirred solution of $TDAH_3$ (9.5 mmol) in 100 ml of 3 M $HClO_4$ at room temperature to produce a dark blue solution. Within 5 to 10 min, a heavy blue precipitate began to appear and after 3 days the product was recovered by filtration. Crystals of the complex suitable for X-ray crystallography were obtained from the slow evaporation of a solution of copper(II) perchlorate (1.5 mmol) and $TDAH_3$ (19 mmol) in 350 ml of 3 M $HClO_4$. *Anal.* Calcd for $C_8H_{12}CuN_6O_{12}$: C, 21.46; H, 2.70. Found: C, 21.40; H, 2.73.

$Cu(TDAH)(H_2O)_3$

The complex was prepared by the addition of $TDAH_3$ (3.7 mmol) to a solution of copper(II) nitrate (3.7 mmol) in 15 ml of 0.1 M HNO_3. A blue precipitate appeared after 5 to 10 min.

$Cu(TA)(H_2O)_2$

A hot solution of TAH_2 (24 mmol) in 50 ml of H_2O was added to a stirred hot solution of copper(II) nitrate in 250 ml of 0.1 M HNO_3. Within minutes a fine precipitate appeared which had a light blue-green color.

$Cu(MTA)_2(H_2O)_2$

The addition of MTAH (4 mmol) to a warm solution of copper(II) nitrate (2 mmol) in 20 ml of 0.1 M HNO_3 produced a deep blue solution. Precipitation of the blue complex was found to be extremely variable, with times ranging from minutes to weeks.

Analyses

The C, H analysis was performed by the Chemical Analysis Service Group at the University of New Mexico in Albuquerque.

The copper analyses were carried out by atomic absorption on a Perkin-Elmer 403 atomic absorption spectrophotometer.

Physical Measurements

Infrared spectra were recorded with a Beckman IR-12 spectrophotometer from KBr discs. Room temperature magnetic susceptibilities were measured by the Gouy method [7] on powdered samples [8] with $CuSO_4 \cdot 5H_2O$ used as a calibrant ($\chi = 6.05 \times 10^{-6}$ cgs) [9] and were corrected for diamagnetism with Pascal constants. Thermogravimetric analyses were conducted on a DuPont 900 Thermal Analyzer equipped with the 950 accessory unit. These measurements were carried out under a nitrogen atmosphere and at a heating rate of 5 °C per minute. X-ray powder patterns using CuKα radiation were measured on a Phillips Electronic (Norelco) diffractometer and recorder unit. The density of $Cu(TDAH_2)_2(H_2O)_4$ was obtained by the flotation method.

TABLE I. Crystallographic Data.

Formula	$CuC_8H_{12}N_6O_{12}$
Formula weight	447.76
Space group	$P\bar{1}$
a, Å	5.203(1)
b, Å	6.583(2)
c, Å	11.835(2)
α, degrees	77.99(2)
β, degrees	98.92(2)
γ, degrees	105.84(2)
V, Å^3	379.3(1)
Z	1
d_{obs}, g/cm^3	2.05
d_{calc}, g/cm^3	1.96
Abs. coeff., cm^{-1}	15.2
Data collected	1872
$I > 3\sigma(I)$	1660
R^a	0.029
$R_w{}^b$	0.032

${}^aR = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ${}^bR_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Crystal Structure Determination

A Syntex $P2_1$ automated, four-circle diffractometer with graphite-monochromated Mo$K\bar{\alpha}$ radiation was used to collect the diffraction data. Unit cell parameters were determined by a least-squares fitting of the setting of 15 reflections obtained from an automatic centering routine. Integrated intensities were measured for all (+h, +k, ±l) reflections to 55° in 2θ, by the $\theta-2\theta$ scan technique. A consistency in the intensities of three standard reflections checked every 50 reflections throughout the data collection was taken as evidence that crystal decomposition had not occurred. The intensities of 1872 unique reflections were collected. Lorentz and polarization corrections were applied to the data. No correction for absorption was made. A total of 1660 observations with $I > 3\sigma(I)$ was used in the structure determination. Crystallographic data are listed in Table I.

The crystal structure was solved and refined using the MULTAN [10] and SHELX [11] programs,

TABLE II. Position Parameters and their e.s.d.s

Atom	x	y	z
Cu	0.0	0.0	0.0
C(1)	−0.0308(3)	−0.1610(3)	0.2468(1)
C(2)	0.1012(3)	−0.1387(3)	0.3548(2)
C(3)	−0.3040(4)	−0.2798(3)	0.2065(2)
C(4)	0.0198(4)	−0.2283(3)	0.4739(2)
N(1)	0.1378(3)	−0.0388(2)	0.1679(1)
N(2)	0.3658(3)	0.0575(3)	0.2206(1)
N(3)	0.3424(3)	−0.0038(2)	0.3333(1)
O(1)	−0.3746(3)	−0.2586(2)	0.1013(1)
O(2)	−0.4530(3)	−0.3939(2)	0.2861(1)
O(3)	−0.2139(3)	−0.3512(3)	0.4804(1)
O(4)	0.1804(3)	−0.1775(2)	0.5579(1)
O(5)	−0.1352(3)	0.2376(3)	0.0204(1)
O(6)	0.0065(3)	0.3806(3)	0.2217(1)
H(1)	0.497(6)	0.059(5)	0.381(2)
H(2)	−0.095(6)	0.288(4)	0.084(2)
H(3)	−0.296(5)	0.231(5)	−0.018(2)
H(4)	0.162(5)	0.453(4)	0.229(3)
H(5)	−0.035(7)	0.319(5)	0.285(2)

TABLE III. Selected Bond Distances (A) and Angles (Deg.) with their e.s.d.s

Distances			
Cu–N(1)	1.994(1)	C(3)–O(1)	1.232(2)
Cu–O(5)	1.952(2)	C(3)–O(2)	1.291(2)
Cu–O(1)	2.490(2)	C(4)–O(3)	1.267(2)
C(1)–N(1)	1.358(2)	C(4)–O(4)	1.235(2)
N(1)–N(2)	1.312(2)	N(3)–H(1)	0.96(2)
N(2)–N(3)	1.326(2)	O(5)–H(2)	0.86(2)
C(2)–C(1)	1.370(2)	O(5)–H(3)	0.88(2)
C(1)–C(3)	1.482(2)	O(6)–H(4)	0.82(2)
C(2)–C(4)	1.489(2)	O(6)–H(5)	0.81(2)
N(3)–C(2)	1.351(2)		
Angles			
N(1)–Cu–O(5)	89.3(1)	O(1)–C(3)–O(2)	125.0(2)
N(1)–Cu–O(1)	74.6(1)	C(2)–C(4)–O(3)	116.3(2)
O(1)–Cu–O(5)	89.9(1)	C(2)–C(4)–O(4)	118.7(2)
C(2)–C(1)–C(3)	133.0(2)	O(3)–C(4)–O(4)	125.0(2)
C(2)–C(1)–N(1)	107.1(1)	C(1)–N(1)–N(2)	110.6(1)
C(3)–C(1)–N(1)	119.8(2)	N(1)–N(2)–N(3)	105.8(1)
C(1)–C(2)–C(4)	132.3(2)	C(2)–N(3)–N(2)	112.3(1)
C(1)–C(2)–N(3)	104.3(1)	C(2)–N(3)–H(1)	134.1(2)
C(4)–C(2)–N(3)	123.4(2)	N(2)–N(3)–H(1)	113.6(2)
C(1)–C(3)–O(1)	118.4(2)	H(2)–O(5)–H(3)	119.9(2)
C(1)–C(3)–O(2)	116.5(2)	H(4)–O(6)–H(5)	108.4(3)

respectively. Atomic scattering factors and the anomalous scattering coefficients for copper were taken from 'International Tables for X-Ray Crystallography' [12]. The ORTEP-II [13] program was used to draw the structures.

Isotropic refinement of the structure with corrections for anomalous scattering by the copper gave $R = 0.096$ and $R_w = 0.109$. A difference Fourier map gave the positions of all but one of the hydrogen atoms. The hydrogen atom not located is presumed to be part of a strong intramolecular hydrogen bond between the two carboxylic groups of the ligand. Addition of the hydrogen positions and anisotropic refinement of the nonhydrogens yielded $R = 0.038$ and $R_w = 0.042$. An additional refinement of the nonhydrogen positions anisotropically and the hydrogen positions isotropically with a restraint of 0.95 ± 0.04 Å gave final values of $R = 0.029$ and $R_w = 0.032$. A final difference map was essentially featureless with two copper residuals of 0.39 and 0.49 e/Å^3 and all other peaks below 0.29 e/Å^3.

The positions of the atoms are listed in Table II. Selected bond distances and angles are given in Table III. All computations were carried out on an Amdahl 5860 computer at the University of Michigan. Observed and calculated structure factors and anisotropic thermal parameters are available as supplementary material from the Editor.

Results and Discussion

Stoichiometry

The simplest formulas for the four copper(II)–triazole complexes are listed in Table IV and were calculated from the percent copper found in each complex with the assumptions that the complexes are mononuclear, neutral, and contain only water in addition to the ligand and metal ion. That the same complexes are isolated regardless of the counter anion of the initial copper(II) is consistent with the formation of neutral complexes. The number of water molecules predicted for each complex on the basis of the copper analyses was confirmed through the measurement of the water loss from these complexes by thermogravimetric analysis, as shown in Table IV. For the case of the $Cu(TDAH_2)_2(H_2O)_4$ complex, a carbon, hydrogen analysis (*cf.* Experimental) also concurs with the deduced formula. X-ray powder patterns were used for qualitative identification of the complexes. Characteristic *d*-spacings for the four complexes are listed in Table IV.

The formation of two different complexes of $TDAH_3$ with Cu(II) is remarkable in that both complexes are prepared in relatively acidic solutions. The 2:1 complex, $Cu(TDAH_2)_2(H_2O)_4$, precipitates quantitatively from solutions with excess ligand and 1–3 M in strong mineral acid, while the 1:1 complex, $Cu(TDAH)(H_2O)_3$, precipitates quantitatively from 0.1 M acid solutions that contain a slight excess of metal ion. Thus, factors which seem to favor the precipitation of the 2:1 complex

TABLE IV. Analytical Data.

Complex	%Cu calcd	%Cu found	$\%H_2O$ calcd	$\%H_2O$ found	d-spacings, Å (rel. int.)
$Cu(TDAH_2)_2(H_2O)_4$	14.2	14.2	16.1	17.0	3.14(36), 2.98(41), 2.51(34), 2.27(21), 1.70(20), 1.59(100)
$Cu(TDAH)(H_2O)_3$	23.3	22.5	19.8	19.7	3.25(89), 2.63(45), 2.35(46), 1.58(100), 1.56(20)
$Cu(TA)(H_2O)_2$	30.1	28.8	17.1	16.8	2.88(100), 2.07(16), 1.63(22), 1.57(94)
$Cu(MTA)_2(H_2O)_2$	18.0	18.2	10.2	10.3	4.57(76), 4.43(100), 2.31(28), 2.28(25), 2.06(20), 1.57(29)

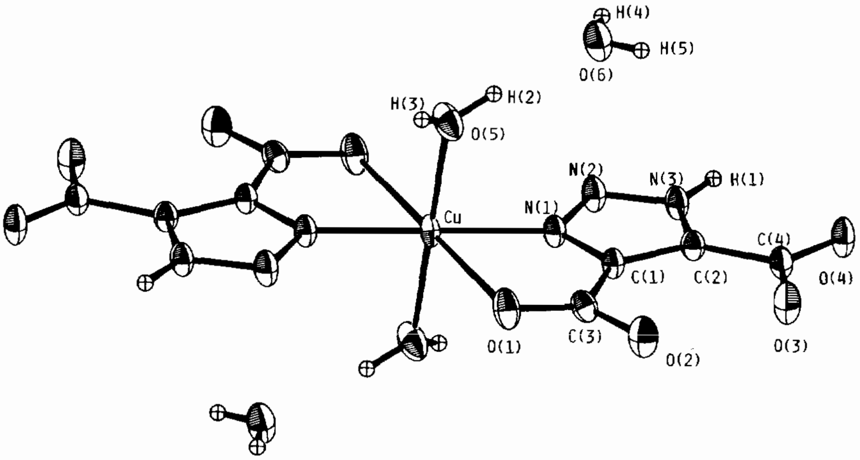


Fig. 2. ORTEP view of $Cu(TDAH_2)_2(H_2O)_4$, showing the atomic numbering scheme, with 50% probability ellipsoids and hydrogen spheres of arbitrary size.

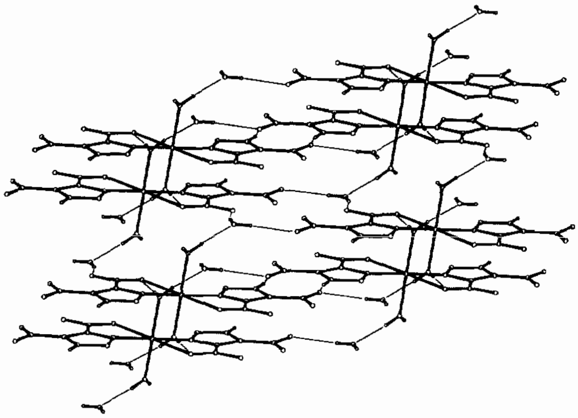


Fig. 3. Hydrogen bond network in lattice of $Cu(TDAH_2)_2(H_2O)_4$.

are a large excess of ligand and more acidic solutions. This dependency of the stoichiometry on the amount of ligand and the pH is similar to that reported for copper(II) complexes of pyrazine-2,3-dicarboxylic acid [14], in which 2:1 and 1:1 complexes were isolated at 1.2 and 2.5 pH, respectively. In both systems, the increased acidity seems to impede the loss of a second proton from the ligand and thus inhibits formation of a 1:1 complex.

Crystal Structure of $Cu(TDAH_2)_2(H_2O)_4$

An ORTEP view of the structure of $Cu(TDAH_2)_2(H_2O)_4$ is shown in Fig. 2. The complex is mononuclear and contains the copper(II) in the commonly found six-coordinate elongated tetragonal geometry [15], where the copper(II) is coordinated through four short in-plane donors at ~2 Å and also cooordinated through two longer out-of-plane donors at ~2.5 Å. The ratio of the in-plane to out-of-plane distance is ~0.8, which is definitive for the tetragonal geometry [15]. The equatorial coordination plane is defined by two triazole nitrogens [N(1)] and two water molecules [O(5)]. The more distant axial sites are occupied by the carbonyl oxygens [O(1)] of a carboxylic acid substituent.

The lattice is composed of parallel layers that pass through the Cu(II)–triazole coordinate plane. In each layer, triazoles of adjacent complexes are hydrogen bonded to each other in a dimer fashion. The layers are 'stitched' together by hydrogen bond interactions through both the coordinated and lattice water molecules. A view of the hydrogen bond

TABLE V. Hydrogen Bonds in $Cu(TADH)_2(H_2O)_4$: A–B Distances and Angles for A—H- - -B.

A	H	B	Å	Deg.	Transformation of Coordinates of B
N(3)	H(1)	O(4)	2.698	166.8	1 – x, –y, 1 – z
O(5)	H(2)	O(6)	2.667	175.8	x, y, z
O(5)	H(3)	O(1)	2.751	172.2	–1 – x, –y, –z
O(6)	H(4)	O(2)	2.867	167.1	1 + x, 1 + y, z
O(6)	H(5)	O(4)	2.857	172.9	–x, –y, 1 – z

network is shown in Fig. 3 and hydrogen bond distances and angles are given in Table V. The hydrogen bond distances are all ~2.7–2.8 Å with bond angles of ~165–175°.

The intricate hydrogen bond network of $Cu(TDAH_2)_2(H_2O)_4$ contains a dimer-like hydrogen bonding between coplanar complexes that occurs through the H(1) atom of the N(3) ring nitrogen of one complex to the O(4) carboxylate oxygen of another complex, while the H(1) atom of the latter complex interacts with the O(4) of the former complex. The coordinated water has hydrogen bonds to both the lattice water and the O(1) carbonyl oxygen of a nearby complex. The lattice water, in addition to its interaction with the coordinated water, forms hydrogen bonds with an O(2) carboxyl oxygen and an O(4) carboxylate oxygen of two different nearby complexes.

The molecular structure shows the occurrence of a strong intramolecular hydrogen bond [16] of 2.471 Å between the O(2) and O(3) atoms of the two carboxyl groups of each triazole. The C–O bond distances of the axially coordinated carboxyl group are indicative of the hydrogen atom being covalently attached to the O(2) atom. In addition, the C–O bond distances of the free carboxyl group are more in accord with a carboxylate anion. Thus the strong intramolecular hydrogen bond is most likely non-centered. An analogous result has been observed in a copper(II) complex of hydrogen phthalate [17].

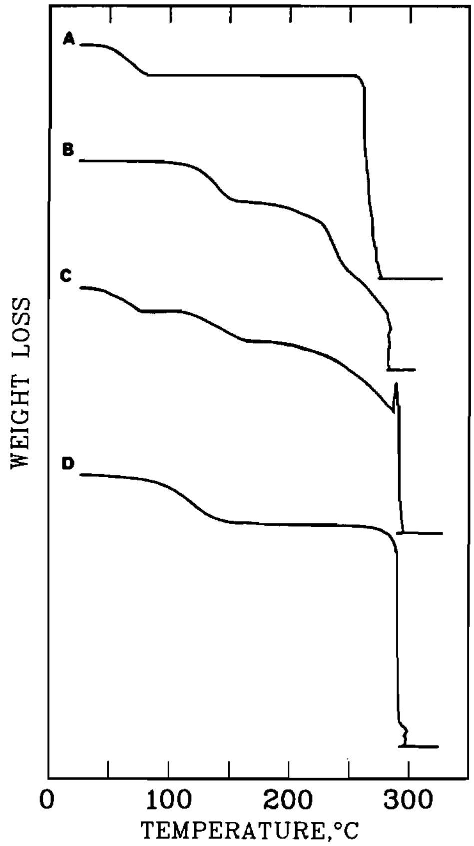


Fig. 4. Thermogravimetric plots of A) $Cu(MTA)_2(H_2O)_2$, B) $Cu(TDAH_2)_2(H_2O)_4$, C) $Cu(TDAH)(H_2O)_3$, and D) $Cu(TA)(H_2O)_2$ obtained at a heating rate of 5 °C/min under a nitrogen atmosphere.

Thermogravimetric Results

Thermogravimetric analysis (TGA) of the four copper(II)–triazole complexes were carried out under a nitrogen atmosphere with a sample size of 8–10 mg and a heating rate of 5 °C/min. The thermograms of these complexes are shown in Fig. 4, where the basic features involve loss of H_2O, loss of CO_2 via decarboxylation, and decomposition to inorganic residue. The temperature ranges for these processes are given in Table VI. Although these

TABLE VI. Thermogravimetric Analysis Data.

Complex	H_2O Loss Temp. Range (°C)	H_2O Loss Number	CO_2 Loss Temp. Range (°C)	% CO_2 Loss		Complex Decomp. (°C)
				Calcd.	Found	
$Cu(TDAH_2)_2(H_2O)_4$	100–160	4	160–280	20	22	280
$Cu(TDAH)(H_2O)_3$	25–75	1	180–285	32	28	285
	100–160	2				
$Cu(TA)(H_2O)_2$	50–150	2	265–287	21	08	287
$Cu(MTA)_2(H_2O)_2$	30–60	2	255–260	13	02	260

TABLE VII. IR Bands within 1750–1340 cm^{-1}.

Complexes $Cu(TDAH_2)_2(H_2O)_4$	$Cu(TDAH)(H_2O)_3$	$Cu(TA)(H_2O)_2$	$Cu(MTA)_2(H_2O)_2$
1665s,sh	1725s	1655vs	1675vs
1590s,sh	1605vs	1570m	1635s
1550vs	1550s	1400s	1560m
1500vs	1450s		1355m
1470s,sh	1365m		
1390s			
1350m			

Free Ligands $TDAH_3$	TAH_2	MTAH
1695vs	1735vs	1700s
1545m	1715vs	1550m
1435m	1540m	1440m
1410m	1460s	1415m
1350m	1345s	1350m

temperature ranges are dependent on such factors as heating rate, sample size, and atmosphere, and cannot be correlated with thermodynamic stability since they represent kinetic processes [18], qualitative assessments of the coordination environment can be made through the comparison of temperatures of H_2O and CO_2 lost from the four complexes under the same experimental conditions.

Loss of water from the four copper(II)–triazole complexes as shown in Fig. 4 occurs for the most part in two distinct regions that are on either side of 100 °C. Our initial tendency was to correlate these regions as below and above 100 °C with the loss of lattice and equatorially coordinated water, respectively, since this type of correlation has been observed in some metal complexes. For example, in the thermogram of the copper(II) complex of nicotinic acid N-oxide, four water molecules are lost below 100 °C and two water molecules are lost above 100 °C, which correspond nicely to the four lattice waters and two coordinated waters present in the crystal structure of the complex [19]. However, the thermogram of $Cu(TDAH_2)_2(H_2O)_4$, which crystallographically contains two equatorially coordinated waters and two lattice waters, shows loss of all four water molecules together in one step from 100–160 °C. Thus, caution must be exercised in the classification of water as lattice or coordinated on the basis of TGA alone.

We speculate that the simultaneous loss of coordinated and lattice water molecules may be due to the hydrogen bond network that permeates the lattice. Of particular importance may be the hydrogen bonding between the two types of water. Indeed, in the copper(II) nicotinic acid N-oxide complex discussed above, none of the lattice waters are hydrogen bonded to the equatorially coordinated waters. Whether or not such criteria are applicable to other copper(II) complexes remains to be seen, since factors other than just bond strengths determine the release of water molecules from a solid, such as the rearrangement of groups that takes place as water is lost [20].

The thermogram of $Cu(TDAH)(H_2O)_3$ shows the loss of one water below 100 °C as a lattice water and the loss of two waters above 100 °C, which according to the above analysis, corresponds to either the loss of two equatorially coordinated waters or the simultaneous loss of one lattice water which is hydrogen bonded to an equatorially coordinated water. The complex $Cu(MTA)_2(H_2O)_2$ is predicted to have two lattice waters since both waters are lost well before 100 °C. The thermogram of $Cu(TA)(H_2O)_2$ is difficult to assess since both waters are lost in one step over a temperature range of 50–150 °C, but may be indicative of a lattice water hydrogen bonded to a coordinated water.

Table VI also gives the temperature ranges for CO_2 evolution from the four copper(II)–triazole complexes. Temperatures of CO_2 evolution below ~240 °C can be correlated with the existence of a 'free' or uncoordinated carboxyl group, since temperatures in the range of 200–240 °C are often used to decarboxyl $TDAH_3$ and TAH_2 [6, 21]. According to this criterion and assuming no drastic rearrangement in the dehydrated complexes, both $Cu(TDAH_2)_2(H_2O)_4$ and $Cu(TDAH)(H_2O)_3$ have one uncoordinated carboxyl group. Loss of CO_2 in both $Cu(TA)(H_2O)_2$ and $Cu(MTA)_2$-

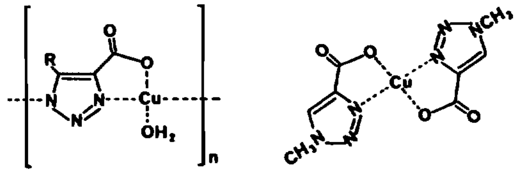
$(H_2O)_2$, on the other hand, occurs just before decomposition at ~260 °C. Therefore, the carboxylate in each of these complexes is involved in coordination. Prediction of the presence of uncoordinated carboxylates or carboxylic acids on the basis of CO_2 elimination prior to decomposition of a complex, has also been demonstrated by Magrí *et al.* [14] in studies of metal ion complexes with pyrazine-2,3-dicarboxylic acid.

Infrared and Magnetic Measurements

The infrared spectra of the triazole ligands and their complexes with copper(II) were recorded as KBr discs and all of the bands occurring in the frequency range 1740–1340 cm^{-1} are reported in Table VII. It is within this range that the asymmetric and symmetric stretches of the carboxylic acid and its salts occur. Ideally, the location of these bands and the relative difference in frequency between them should permit identification of a carboxylate involved in coordination and assignment of whether the carboxylate is a monodentate or bidentate ligand [22]. In practice this is sometimes difficult due to problems in assignment of the $\nu(OCO)_s$ stretch [22] and to shifts in the bands from strong hydrogen bonding interactions [22, 23]. No doubt such factors contribute to the lack of definitive conclusions that can be drawn from the IR data in Table VII.

It is possible, however, to identify the presence of coordinated carboxylates in the complexes. Both $Cu(TDAH_2)_2(H_2O)_4$ and $Cu(TDAH)(H_2O)_3$ appear to have one coordinated carboxylate and one 'free' carboxylate, while the lone carboxylates of both $Cu(TA)(H_2O)_2$ and $Cu(MTA)_2(H_2O)_2$ are involved in coordination. In the former pair of complexes, the region of 1750–1340 cm^{-1} is quite complex and indicates that more than one type of carboxylate is present in each. On the other hand, in the latter pair of complexes, this region is relatively clean and is indicative of one coordinated carboxylate. These conclusions are consistent with those obtained from the thermogravimetric measurements.

The effective magnetic moments of the four copper(II) complexes were determined at room temperature by the Gouy method. The 2:1 complexes, $Cu(TDAH_2)_2(H_2O)_4$ and $Cu(MTA)_2(H_2O)_2$, gave effective magnetic moments of 2.0 and 1.9 B.M., respectively. Both values are within the accepted range of 1.8–2.0 B.M. for magnetically dilute complexes [24] and indicate that both complexes are probably mononuclear. The 1:1 complex $Cu(TA)(H_2O)_2$ and $Cu(TDAH)(H_2O)_3$ have effective magnetic moments of 1.7 and 1.8 respectively, which may correspond to magnetically non-dilute complexes that are polynuclear.



$Cu(TDAH)(H_2O)_3$ R = CO_2H
$Cu(TA)(H_2O)_2$ R = H
$Cu(MTA)_2(H_2O)_2$

Fig. 5. Possible structures of $Cu(TDAH)(H_2O)_3$, $Cu(TA)(H_2O)_2$ and $Cu(MTA)_2(H_2O)_2$.

Summary and Conclusions

Two copper(II) complexes with 1,2,3-triazole-4,5-dicarboxylic acid ($TDAH_3$) have been prepared and characterized. A X-ray crystal structure of the 2:1 complex $Cu(TDAH_2)_2(H_2O)_4$, which is formed in 1–3 M acid solution with excess $TDAH_3$, shows a mononuclear complex with an elongated tetragonal geometry. Equatorial coordination is through two triazole nitrogens and two water molecules, while the axial sites are filled by carbonyl oxygens. The 1:1 complex $Cu(TDAH)(H_2O)_3$, on the basis of magnetic moment, TGA, and IR, is predicted to be polymeric, to have at least one coordinated water, and to have one coordinated and one uncoordinated carboxyl group. A structure for $Cu(TDAH)(H_2O)_3$ consistent with these data is given in Fig. 5.

Copper(II) complexes of 1,2,3-triazole-4-carboxylic acid (TAH_2) and 1-methyl-1,2,3-triazole-4-carboxylic acid (MTAH) have also been characterized. The 2:1 complex $Cu(MTA)_2(H_2O)_2$ is probably mononuclear since the methyl substituent blocks a '1,3' bridging mode through the triazole and is in accordance with the normal magnetic moment. As shown in Fig. 5, the MTA ligand is thought to be bidentate with coordination through a carboxylate oxygen and a triazole nitrogen. Since the two waters associated with the complex correlate to lattice waters by TGA, the carboxyl oxygens of nearby complexes most likely occupy the axial positions. Lastly, the 1:1 complex $Cu(TA)(H_2O)_2$ is probably polymeric, based on magnetic data, and may have a structure (Fig. 5) similar to that of $Cu(TDAH)(H_2O)_3$ since its IR and TGA data indicate a coordinated carboxylate and a coordinated water.

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