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Hydrolysis Reactions of 2,4,6-Tris(2-pyrimidyl)- and 2,4,6-Tris(2-pyridyl)-1,3,5-triazines with Divalent Copper. Structure of a Bis(2-pyrimidylcarbonyl)aminatocopper(II) Complex

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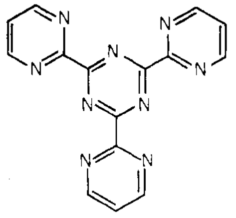
The compounds 2,4,6-tris(2-pyrimidyl)- and 2,4,6-tris(2-pyridyl)-1,3,5-triazine were found to undergo hydrolysis reactions in the presence of divalent copper. The products of these reactions are bis(arylcarbonyl)aminatocopper(II) complexes and the free arylamides. Crystals of bis(2-pyrimidylcarbonyl)aminatotriaquocopper(II) nitrate dihydrate were grown from aqueous solutions of the compound. The blue complex of formula $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3)\cdot 2H_2O$ crystallizes in the triclinic space group $P\bar{1}$ with two formulas per unit cell. Lattice parameters are $a = 13.626$ (3) Å, $b = 6.512$ (1) Å, $c = 10.497$ (2) Å, $\alpha = 101.48$ (1)°, $\beta = 109.32$ (1)°, and $\gamma = 94.83$ (1)°. By use of 3385 unique observed reflections collected by diffractometer, the structure was solved and refined to a final value of 0.030 for the discrepancy factor R_1. The copper atom is coordinated by a distorted octahedral array of ligand atoms. Three nitrogen atoms from the new ligand and one water molecule form a distorted square plane around the copper while two weakly bound water molecules occupy the axial positions. Angular strain at the carbonyl carbon atoms in the coordinated bis(2-pyrimidylcarbonyl)aminato ligand suggests a mechanistic role by which copper(II) assists the hydrolysis of the normally stable 2,4,6-triaryl-1,3,5-triazines.

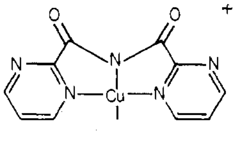
Introduction

During the course of preparing and characterizing heavy-metal complexes of the ligand 2,4,6-tris(2-pyrimidyl)-1,3,5-triazine, TPymT, described in the preceding paper,[1]



TPymT

an interesting reaction was observed with divalent copper. In particular, copper(II) was found to promote the hydrolysis of the TPymT ligand to form a novel bis(2-pyrimidylcarbonyl) aminato chelate complex[2]



A similar reaction takes place with the related 2,4,6-tris(2-pyridyl)-1,3,5-triazine ligand, TPyT, resulting in a bis(2-pyridylcarbonyl)aminatocopper(II) complex. Crystals of both complexes were obtained. The present article describes their properties and the x-ray structure determination of bis(2-pyrimidylcarbonyl)aminatotriaquocopper(II) nitrate dihydrate. As discussed in a preliminary report,[2] several other metal ions promote the hydrolysis of these triazines, but their chemistry has not been further investigated.

Experimental Section

The materials for this study were of reagent grade and were used without further purification. 2,4,6-Tris(2-pyrimidyl)-1,3,5-triazine was synthesized as previously described.[1,2] Infrared spectra were taken on JASCO IRA-1 and Perkin-Elmer 137 and 621 spectrophotometers and were calibrated with polystyrene. Mass spectra were taken on a JEOL JMS-07 EI mass spectrometer.

Hydrolysis of TPymT with Copper to Form $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3)\cdot 2H_2O$. The synthesis and analytical data for this compound were reported previously.[2] It has the following bands in the infrared spectrum (Nujol mull): 3450 (br, m), 3060 (w), 1726 (s), 1663 (w), 1623 (m), 1578 (s), 1562 (w), 1380 (br, under Nujol peak), 1200 (m), 1114 (w), 1076 (w), 1044 (w), 1030 (w), 1005 (w), 855 (w), 830 (w), 715 (m), 675 (m) cm^{-1}.

Hydrolysis of TPyT with Copper to Form $[Cu(C_{12}H_8N_3O_2)(H_2O)_3](NO_3)\cdot 1.5H_2O$. The synthesis, analytical data, and dehydration weight loss of this compound were described previously.[2] Its infrared spectral bands (Nujol mull) appear at 3400 (br, m), 1710 (s), 1665 (m), 1640 (m), 1600 (s), 1570 (m), 1380 (br, under Nujol peak), 1150 (w), 1090 (w), 1045 (w), 1025 (m), 1000 (w), 968 (w), 815 (m), 792 (w), 753 (m), and 698 (m) cm^{-1}.

Extraction of the blue reaction mixture with benzene yielded, upon drying and removal of the benzene, a white powder. The infrared spectrum and mass spectrum (M^+ 122) identified the major product as 2-picolinamide. IR ($CHCl_3$ solution): 3559 (w), 3413 (w), 3030 (m), 1689 (s), 1592 (w), 1555 (s), 1515 (w), 1462 (w), 1433 (m), 1414 (sh), 1370 (m), 1078 (w), 1033 (m), 991 (w), 920 (m) cm^{-1}. MS at 75 V: most intense peak, parent ion, m/e 122 (100), 123 (29, possibly picolinic acid), 106 (9), 105 (6), 104 (7), 80 (18), 79 (56), 78 (93), 77 (10), 76 (13), 75 (9), 53 (9), 52 (43), 51 (49), 50 (41).

Structure Determination of $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3)\cdot 2H_2O$

Collection and Reduction of the X-Ray Data. The crystals used in the structure determination were cut with a razor blade from long needlelike crystals of the compound grown from an aqueous solution by slow evaporation. The crystals were sealed in quartz capillary tubes saturated with water vapor to prevent loss of water of crystallization.

The crystals were investigated on Weissenberg and precession cameras using Cu Kα radiation and shown to belong to the triclinic system. $P\bar{1}$ was chosen as the space group, a choice that seems justified in view of the subsequent successful refinement of the structure. A systematic search failed to reveal any higher symmetry.

Intensity data were collected on a crystal of dimensions 0.20 × 0.53 × 0.33 mm mounted approximately along the needle (b) axis. The mosaicity of the crystal was surveyed by ω and 2θ scans on several strong, low-angle reflections using a wide-open (6.3 mm × 6.3 mm) counter receiving aperture. The mosaic spread was found to be acceptable with the width at half-height of the ω scans ranging from 0.07 to 0.15°. Details of the data collection and reduction are given in Table I.

Solution and Refinement of the Structure. The position of the copper atom was determined from a sharpened, origin-removed, three-dimensional Patterson map. Least-squares refinement of the atom positional parameters, an isotropic temperature factor for the copper atom, and an overall scale factor gave discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)^{1/2}$ of 0.45 and 0.51, respectively. The function being minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weights, w, were set equal to $1/\sigma^2(F_o)$. Subsequent difference Fourier maps and least-squares refinements revealed the positions of all the nonhydrogen atoms. Refinement of the positional and isotropic thermal parameters for these 27 atoms resulted in lowering of the discrepancy factors to $R_1 = 0.111$ and $R_2 = 0.127$. Refinement of the structure with anisotropic temperature factors for all atoms further lowered the discrepancy factors to $R_1 = 0.053$ and $R_2 = 0.090$. Nonhydrogen atom scattering factors for neutral atoms used in these calculations were taken from the compilation of Cromer and Waber,[3] hydrogen atom scattering factors were taken from the compilation of Stewart et al.,[4] and anomalous dispersion was included for the copper atom.[5]

Until this point no correction had been made for the absorption of x rays by the crystal. The linear absorption coefficient for Mo Kα radiation was calculated to be 13.47 cm^{-1}. An absorption correction was made (Table I). Use of the absorption corrected data in the least-squares refinement lowered the discrepancy factors to $R_1 = 0.043$ and $R_2 = 0.074$. A difference Fourier map now revealed the positions of all of the hydrogen atoms. These atoms were included in the structure factor calculation and their positional and isotropic temperature factors were varied in the least-squares refinement.

At this stage it was noticed that, for the 20 strongest reflections, the observed structure factor was considerably smaller than the calculated structure factor. Since this result is symptomatic of secondary extinction effects, the refinement of the structure was continued including an extinction parameter and using Zachariasen's β function.[6,7] The extinction parameter refined to a value of 4.6 (2) × 10^{-7} and the strong reflections no longer exhibited the systematic disagreement between F_o and F_c.

Until this point all refinements had been done by the block-diagonal method. Two cycles of full-matrix refinement on the structure were carried out. The refinement converged with $R_1 = 0.030$ and $R_2 = 0.043$. The final value of the extinction parameter was 4.6 (2) × 10^{-7} and the standard deviation of an observation of unit weight was 1.74 compared with the ideal value of 1.0.[8] On the final cycle no parameter shifted by more than 0.07 of its estimated standard deviation. The final difference Fourier map showed no peak higher than 0.59 e/Å^3 on a scale where all carbon atoms were greater than 4.9 e/Å^3.

Results

Figure 1 shows a computer drawing of the structure along with the numbering scheme to which all subsequent discussion will refer. Table II contains the final positional and thermal parameters for all atoms in an asymmetric unit. Table III lists all pertinent bond distances and angles in the complex. Table IV contains close nonbonding intermolecular interactions, and Table V lists the hydrogen-bonding interactions. Available as supplementary material are Table S1 listing the observed and calculated structure factor amplitudes, Table S2 which gives the root-mean-square amplitudes of thermal motion along the principal axes for each atom refined with anisotropic temperature parameters, and Table S3 which contains the

Table I. Experimental Details of the X-Ray Diffraction Study of $[(C_{10}H_6N_5O_2)Cu(H_2O)_3](NO_3)\cdot 2H_2O$

(A) Crystal Parameters at 23 °C[a]

$a = 13.626$ (3) Å	$V = 849.97$ Å^3
$b = 6.512$ (1) Å	Mol wt 443.86
$c = 10.497$ (2) Å	Space group $P\bar{1}$
$\alpha = 101.48$ (1)°	$Z = 2$
$\beta = 109.32$ (1)°	ρ(calcd) = 1.734 g/cm^3
$\gamma = 94.83$ (1)°	ρ(obsd)[b] = 1.732 (7) g/cm^3

(B) Measurement of Intensity Data

Instrument: Picker FACS-I-DOS diffractometer
Radiation: Mo Kα (λ_{α_1} 0.7093 Å), graphite monochromatized
Takeoff angle: 2.7°
Receiving aperture: 6.33 × 6.33 mm
Crystal-detector distance: 33 cm
Scan technique: coupled θ(crystal)–2θ(counter)
Scan range: 1.75° (symmetric, plus Kα_1–Kα_2 dispersion)
Scan rate: 1.0°/min
Maximum 2θ: 55°
Background measurements: stationary crystal, stationary counter; 20-s counts at each end of 2θ scan range
Standards: three reflections [$(\bar{9}11)$, $(7\bar{3}\bar{3})$, $(\bar{3}1\bar{5})$] measured every 50 data reflections; data corrected later for the approximately 8% crystal decomposition
No. of unique reflections collected: 3924 ($\pm h, +k, \pm l$)

(C) Treatment of Intensity Data[c]

Reduction to preliminary $F_o{}^2$ and $\sigma(F_o{}^2)$: correction for background, attenuators, and Lorentz–polarization effects of monochromatized x radiation in the usual manner,[d,e] ϵ[f] = 0.04; Picker scalar truncation handled by adding 0.45 to each counted value and multiplying by 10; extra term of 24.75 added to $\sigma^2(I)$ to account for the errors in this roundoff[g]
Absorption correction: $\mu = 13.47$ cm^{-1}; transmission factors varied between 0.68 and 0.80; program also calculated Zachariasen's β function for use in a refinement of an extinction correction[c]
Averaging: done over zero-level Friedel pairs; R_{av}[h] = 0.019
Scaling: Wilson's method[i]
Observed data: 3385 unique reflections for which $F_o{}^2 > 3\sigma(F_o{}^2)$

[a] From a least-squares fit to the setting angles of 25 reflections having $2\theta > 30°$. [b] By flotation in mixtures of bromoform and carbon tetrachloride. [c] Programs for an IBM 360-91 computer used in this work: UMAT, the local version of the Brookhaven diffractometer setting and cell constant and orientation refinement program; ORABS, the local version of the absorption correction program by D. J. Wehe, W. R. Busing, and H. A. Levy modified for the Picker FACS-I geometry; further modified by E. I. Lerner to calculate Zachariasen's β function[6] modified for the Picker FACS-I geometry;[7] XDATA, the Brookhaven Wilson plot and scaling program; FORDAP, the Zalkin Fourier program; CUGLS, the local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS) modified by Ibers and Doedens for rigid-body refinement; ORFFE, the Busing–Martin–Levy molecular geometry and error function program; TRACER II, the Lawton lattice transformation–cell reduction program; ORTEP, the Johnson thermal ellipsoid plotting program; in addition, various local data-processing programs. [d] B. G. Segal and S. J. Lippard, *Inorg. Chem.*, **13**, 822 (1974). [e] L. V. Azaroff, *Acta Crystallogr.*, 8, 701 (1955). [f] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967). [g] M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, **12**, 525 (1973). [h] $R_{av} = \Sigma^N|F^2(\text{av}) - F^2|/\Sigma^N F^2$; N is the number of reflections measured more than once. [i] A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

Table II. Final Positional and Thermal Parameters[a]

ATOM	X	Y	Z	β11 OR B	β22	β33	β12	β13	β23
CU	0.238316(17)	0.21495(4)	0.00861(2)	2.677(17)	21.06(9)	6.40(3)	2.19(2)	2.186(15)	4.28(3)
O1B	0.04104(12)	0.2179(3)	0.22316(16)	4.12(9)	27.8(5)	8.72(17)	2.48(17)	3.77(11)	4.6(2)
O1A	-0.06544(11)	0.2659(3)	-0.05130(16)	3.06(8)	25.3(5)	9.91(18)	2.48(15)	2.92(10)	5.7(2)
O2	0.36716(12)	0.1617(3)	-0.03115(16)	3.56(9)	21.7(5)	8.78(17)	2.19(16)	3.25(10)	3.2(2)
O5	0.38100(14)	-0.2314(3)	-0.18915(17)	5.23(11)	35.0(6)	8.48(19)	6.0(2)	1.68(12)	3.4(3)
O6	0.23721(16)	-0.1876(4)	-0.3383(2)	5.84(13)	58.6(10)	11.8(2)	10.1(3)	1.95(15)	6.2(4)
O7	0.35478(18)	-0.3139(5)	-0.4071(2)	7.65(16)	72.5(12)	9.8(2)	8.0(4)	3.67(16)	0.1(4)
O3	0.32105(14)	0.5943(3)	0.0888(2)	5.05(11)	23.5(5)	10.3(2)	3.33(19)	3.01(13)	5.6(3)
O4	0.19481(14)	-0.1821(3)	-0.0890(2)	4.23(11)	26.2(5)	12.5(2)	2.82(18)	4.65(13)	6.9(3)
O8	0.45867(16)	0.3707(4)	-0.1669(2)	4.63(12)	27.6(6)	11.5(2)	0.9(2)	2.90(13)	6.4(3)
O9	-0.25212(17)	0.3140(4)	-0.3057(2)	4.83(12)	35.5(7)	10.5(2)	4.7(2)	2.71(14)	2.9(3)
N3B	0.24193(15)	0.2025(3)	0.40075(19)	5.11(12)	26.3(6)	6.88(19)	2.8(2)	2.79(12)	4.6(3)
N1B	0.29451(13)	0.1927(3)	0.20644(17)	3.43(10)	18.6(5)	6.76(17)	2.07(16)	2.24(10)	3.9(2)
N2	0.11070(12)	0.2360(3)	0.05039(17)	3.01(9)	17.8(4)	6.83(17)	1.94(16)	2.33(10)	3.1(2)
N3A	-0.03312(14)	0.2783(3)	-0.29369(19)	3.56(10)	22.4(5)	8.40(20)	2.01(18)	1.81(11)	5.2(3)
N1A	0.14471(13)	0.2525(3)	-0.17697(17)	3.18(9)	18.9(5)	6.92(17)	2.04(16)	2.26(10)	3.9(2)
N4	0.32360(14)	-0.2462(3)	-0.31322(20)	4.20(11)	23.7(6)	8.5(2)	2.08(20)	2.20(12)	2.4(3)
C2B	0.22330(15)	0.2016(3)	0.26921(20)	3.89(12)	15.3(5)	6.9(2)	1.56(19)	2.61(12)	3.0(2)
C4B	0.3420(2)	0.1979(5)	0.4769(2)	5.91(16)	32.7(8)	6.9(2)	3.2(3)	2.35(16)	5.7(3)
C5B	0.42083(19)	0.1953(5)	0.4237(3)	4.26(14)	33.8(8)	8.4(3)	3.1(3)	1.37(15)	6.5(4)
C6B	0.39423(17)	0.1883(4)	0.2847(2)	3.47(12)	26.8(7)	8.7(2)	2.4(2)	2.39(14)	6.0(3)
C7B	0.11265(15)	0.2194(3)	0.1791(2)	3.43(11)	14.9(5)	7.2(2)	1.32(18)	2.59(12)	2.5(2)
C7A	0.02278(14)	0.2550(3)	-0.0524(2)	3.17(10)	13.0(5)	8.0(2)	1.17(17)	2.40(12)	3.2(2)
C2A	0.04556(14)	0.2634(3)	-0.1833(2)	3.00(10)	14.3(5)	7.5(2)	1.09(17)	1.95(12)	3.2(2)
C4A	-0.01103(19)	0.2827(4)	-0.4078(2)	4.95(15)	29.6(8)	8.0(2)	3.4(3)	1.64(15)	6.2(3)
C5A	0.0886(2)	0.2739(4)	-0.4120(3)	5.86(16)	30.2(8)	8.2(2)	3.9(3)	3.47(16)	6.7(3)
C6A	0.16583(17)	0.2598(4)	-0.2930(2)	4.21(13)	24.7(6)	8.1(2)	2.8(2)	3.29(14)	5.6(3)
H1O2	0.371(2)	0.042(5)	-0.074(3)	3.9(6)					
H2O2	0.403(3)	0.233(5)	-0.058(4)	5.6(9)					
H1O3	0.315(2)	0.630(5)	0.164(3)	4.1(7)					
H2O3	0.292(2)	0.649(5)	0.042(3)	3.2(6)					
H1O4	0.197(3)	-0.194(5)	-0.177(4)	6.4(9)					
H2O4	0.152(2)	-0.196(5)	-0.078(3)	3.8(7)					
H1O8	0.447(2)	0.483(5)	-0.168(3)	4.2(8)					
H2O8	0.516(3)	0.379(6)	-0.145(4)	5.6(9)					
H1O9	-0.203(4)	0.290(7)	-0.280(4)	7.1(12)					
H2O9	-0.280(3)	0.307(6)	-0.380(4)	5.8(10)					
HC4B	0.352(2)	0.211(4)	0.574(3)	4.1(6)					
HC5B	0.485(2)	0.206(4)	0.477(3)	3.9(6)					
HC6B	0.438(2)	0.196(4)	0.244(3)	3.6(6)					
HC4A	-0.067(2)	0.296(4)	-0.483(3)	3.5(5)					
HC5A	0.105(2)	0.288(5)	-0.496(3)	4.9(7)					
HC6A	0.234(2)	0.255(5)	-0.285(3)	4.6(7)					

[a] Atom labelling is as in Figure 1. For atoms not shown in that figure the labelling is as follows: Atoms N4, O5, O6 and O7 comprise the nitrate anion. Atoms O8 and O9 are oxygen atoms of water molecules which are not metal coordinated. Hydrogen atoms are labelled 1 or 2 followed by the label of the atom to which they are attached (eg. H2O8 is the second hydrogen atom attached to O8).

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NUMBERS IN PARENTHESES ARE ERRORS IN THE LAST SIGNIFICANT DIGIT(S)
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EXP(-(β11*H**2+β22*K**2+β33*L**2+2*β12*H*K+2*β13*H*L+2*β23*K*L))
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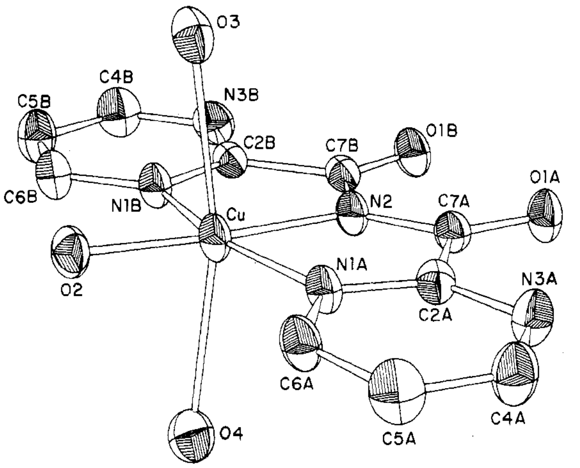

Figure 1. ORTEP drawing of the molecule showing atom-labeling scheme and 50% probability thermal ellipsoids. Hydrogen atoms, the nitrate anion, and noncoordinated water molecules are omitted.

results of least-squares best-plane calculations on various parts of the complex. Figure 2 shows a stereoview of the packing of the molecules in two unit cells.

Discussion

Description of the Structure. The geometry around the copper atom can be described as a distorted octahedron, as shown in Figure 1. An approximate mirror plane passes through atoms Cu, O2, O3, O4, and N2 as can be seen by comparing the geometries of the A and B halves of the ligand (Table III). The copper atom forms four short bonds ranging from 1.938 (2) to 2.020 (2) Å to the three nitrogen atoms and one oxygen atom that make up a distorted square plane and two long bonds of 2.482 (2) and 2.524 (2) Å to axial oxygen atoms. The angles N2–Cu–N1A and N2–Cu–N1B in the equatorial plane are 82.01 (7) and 81.57 (7)°, respectively. They are smaller than the ideal value of 90° because these angles are part of a five-membered planar chelate ring. The other angles in the chelate ring all lie between 110 and 120°, reduced from the ideal value of 120° expected for sp^2-hybridized carbon or nitrogen atoms. Distortion of the angle at the metal atom from 90° is found in related complexes. The corresponding angles in cyano(2,2′,2″-terpyridine)copper(II) nitrate monohydrate[9] are 77.8 (5) and 80.1 (5)° while those in 2-hydroxyethanethiolato(2,2′,2″-terpyridine)platinum(II) nitrate[10] are 80.6 (2) and 80.8 (2)°. Both of these complexes have tridentate chelate structures similar to that of the present compound and have metal–nitrogen bonds of approximately the same length.

The four atoms that comprise the equatorial coordination sites of the copper atom do not quite fall on a plane. Atoms O2 and N2 are 0.045 (2) and 0.061 (2) Å above while atoms N1A and N1B are 0.053 (2) and 0.056 (2) Å below the mean plane through the four atoms. The copper atom is 0.0424 (3) Å below this same plane. The individual pyrimidine rings show no deviations from planarity greater than 0.018 (3) Å. The ligand itself is not, however, nicely planar. Best-plane calculations through the ligand, copper, and equatorial water oxygen atoms show several atoms with quite large deviations. The ligand is better described by two planes, one encompassing the "A" half and the other the "B" half. The "A" half shows no deviations from planarity greater than 0.044 (3) Å while the "B" half shows no deviations greater than 0.0740 (18) Å. The dihedral angle between these two planes is 2.9°.

The weakly bonded axial ligands are not perpendicular to

Table III. Bond Distances (Å) and Angles (deg) in the Structure of $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3)\cdot 2H_2O$[a]

Coordination Geometry

Distances

Cu–N2	1.9380 (16)	Cu–O2	1.9764 (15)
Cu–O3	2.482 (2)	Cu–O4	2.524 (2)
Cu–N1A	2.0199 (16)	Cu–N1B	2.0015 (17)

Angles

N2–Cu–N1A	82.01 (7)	N2–Cu–N1B	81.57 (7)
N2–Cu–O2	173.78 (8)	N2–Cu–O3	99.83 (7)
N2–Cu–O4	94.63 (7)	O2–Cu–O3	85.68 (7)
O2–Cu–N1A	100.73 (7)	O2–Cu–N1B	95.77 (7)
O2–Cu–O4	79.90 (7)	N1B–Cu–N1A	163.50 (9)
N1A–Cu–O3	92.65 (7)	N1B–Cu–O3	88.59 (7)
N1A–Cu–O4	89.03 (7)	N1B–Cu–O4	93.87 (7)
O3–Cu–O4	165.54 (8)		

Ligand Geometry

Distances

N1A–C2A	1.339 (2)	N1B–C2B	1.340 (3)
C2A–N3A	1.320 (3)	C2B–N3B	1.318 (3)
N3A–C4A	1.333 (3)	N3B–C4B	1.339 (3)
C4A–HC4A	0.92 (3)	C4B–HC4B	0.97 (3)
C4A–C5A	1.378 (4)	C4B–C5B	1.365 (4)
C5A–HC5A	1.00 (3)	C5B–HC5B	0.86 (3)
C5A–C6A	1.367 (3)	C5B–C6B	1.373 (3)
C6A–HC6A	0.90 (3)	C6B–HC6B	0.85 (3)
C6A–N1A	1.350 (3)	C6B–N1B	1.341 (3)
C2A–C7A	1.516 (3)	C2B–C7B	1.520 (3)
C7A–O1A	1.214 (3)	C7B–O1B	1.210 (3)
C7A–N2	1.356 (3)	C7B–N2	1.369 (3)

Angles

Cu–N1A–C2A	112.57 (13)	Cu–N1B–C2B	114.11 (13)
Cu–N1A–C6A	130.37 (14)	Cu–N1B–C6B	128.25 (15)
C2A–N1A–C6A	117.01 (18)	C2B–N1B–C6B	117.38 (18)
N1A–C2A–C7A	116.53 (17)	N1B–C2B–C7B	115.73 (17)
N1A–C2A–N3A	125.51 (19)	N1B–C2B–N3B	125.85 (19)
C7A–C2A–N3A	117.96 (17)	C7B–C2B–N3B	118.38 (17)
C2A–N3A–C4A	116.62 (19)	C2B–N3B–C4B	115.78 (19)
N3A–C4A–C5A	122.5 (2)	N3B–C4B–C5B	122.8 (2)
N3A–C4A–HC4A	114.9 (1.7)	N3B–C4B–HC4B	112.3 (1.7)
C5A–C4A–HC4A	122.6 (1.7)	C5B–C4B–HC4B	124.6 (1.7)
C4A–C5A–C6A	117.2 (2)	C4B–C5B–C6B	117.7 (2)
C4A–C5A–HC5A	121.8 (1.7)	C4B–C5B–HC5B	120.3 (1.9)
C6A–C5A–HC5A	120.9 (1.7)	C6B–C5B–HC5B	121.8 (1.9)
C5A–C6A–N1A	121.1 (2)	C5B–C6B–N1B	120.4 (2)
C5A–C6A–HC6A	123.8 (1.9)	C5B–C6B–HC6B	124.5 (1.9)
N1A–C6A–HC6A	115.0 (1.9)	N1B–C6B–HC6B	114.7 (1.9)
C2A–C7A–O1A	119.64 (18)	C2B–C7B–O1B	121.25 (18)
C2A–C7A–N2	110.87 (15)	C2B–C7B–N2	110.06 (15)
O1A–C7A–N2	129.49 (19)	O1B–C7B–N2	128.70 (19)
Cu–N2–C7A	117.93 (13)	Cu–N2–C7B	118.39 (13)

Nitrate Anion

Distances

N4–O5	1.257 (3)	O4–H1O4	0.92 (4)
N4–O6	1.229 (3)	O4–H2O4	0.64 (3)
N4–O7	1.218 (3)	O8–H1O8	0.77 (3)
O2–H1O2	0.79 (4)	O8–H2O8	0.73 (4)
O2–H2O2	0.83 (3)	O9–H1O9	0.68 (4)
O3–H1O3	0.81 (3)	O9–H2O9	0.73 (4)
O3–H2O3	0.71 (3)		

Angles

O5–N4–O6	119.5 (2)	Cu–O3–H2O3	108 (2)
O5–N4–O7	119.9 (2)	H1O3–O3–H2O3	111 (3)
O6–N4–O7	120.6 (2)	Cu–O4–H1O4	102 (2)
Cu–O2–H1O2	120 (2)	Cu–O4–H2O4	97 (3)
Cu–O2–H2O2	130 (2)	H1O4–O4–H2O4	122 (3)
H1O2–O2–H2O2	99 (3)	H1O8–O8–H2O8	106 (3)
Cu–O3–H1O3	103 (2)	H1O9–O9–H2O9	123 (5)

[a] See footnotes *a* and *b* of Table II.

Table IV. Close Nonbonding Intermolecular Distances (Å)

Atom 1[a]	Atom 2	Atom 2 position[b]	Dist, Å
O1A	N3A	$\bar{x}, \bar{y}, \bar{z}$	2.737 (3)
O1A	C7A	$\bar{x}, 1 + \bar{y}, \bar{z}$	3.030 (3)
O1A	C7B	$\bar{x}, \bar{y}, \bar{z}$	3.099 (3)
O9	C2B	$\bar{x}, 1 + \bar{y}, \bar{z}$	3.076 (3)
N3B	C5A	$x, y, 1 + z$	3.311 (3)
C7B	C7A	$\bar{x}, \bar{y}, \bar{z}$	3.240 (3)

[a] See footnotes *a* and *b* of Table II. [b] Symmetry operation applied to coordinates of Table II.

the equatorial coordination plane of the copper atom. The angles O2–Cu–O3 and O2–Cu–O4 are 85.68 (7) and 79.90 (7)°, respectively. The hydrogen atoms bound to oxygen atom O3 are hydrogen bonded to oxygen atom O4 at position x, $1 + y$, z and to oxygen atom O9 at position $\bar{x}$, $1 - y$, $\bar{z}$. Oxygen atom O3 is also the receptor of a hydrogen bond from hydrogen atom H2O8 at position $1 - x$, $1 - y$, $\bar{z}$. The hydrogen atoms on oxygen atom O4 are hydrogen bonded to oxygen atom O1A at position $\bar{x}$, $\bar{y}$, $\bar{z}$ and to the nitrate anion oxygen atom O6 at position x, y, z. Oxygen atom O4 is also the receptor of a hydrogen bond from hydrogen atom H2O3 as mentioned above. These hydrogen bonds are assigned on the basis of the proximity of the hydrogen atoms to possible receptor atoms. The rest of the hydrogen-bonding scheme is outlined in Table IV and can be seen in Figure 2.

The geometry of the ligand is in general normal for nitrogen-containing heterocycles. The average length of a carbon–carbon bond within the pyrimidine rings is 1.37 Å while the average intra-ring carbon–nitrogen bond length is 1.34 Å. These values can be compared with the average carbon–carbon distance of 1.39 Å and carbon–nitrogen distance of 1.34 Å in the pyrimidine rings of $(TPymT)Pb_2(NO_3)_4\cdot 2H_2O$[1] and with the average carbon–carbon distance of 1.37 Å and the average carbon–nitrogen distance of 1.35 Å in cyano(2,2′,2″-terpyridine)copper(II) nitrate monohydrate.[9] The carbonyl carbon atoms are 1.516 (3) and 1.520 (3) Å from their respective ring carbon atoms. Those values compare favorably with the carbonyl carbon atom–ring carbon atom distance of 1.515 (8) Å in picolinamide.[11]

One point of note in the ligand geometry is the angles at the sp^2-hybridized carbonyl carbon atoms C7A and C7B. From Table III one can see that the angles around C7A are 119.6 (2), 110.9 (2), and 129.5 (2)° for C2A–C7A–O1A, C2A–C7A–N2, and O1A–C7A–N2, respectively. The corresponding angles around C7B are 121.2 (2), 110.1 (2), and 128.7 (2)°. The deviation of these angles from the expected value of 120° is clearly caused by the binding of the copper atom. The need for short metal–nitrogen bonds introduces this angular strain. The corresponding intrachelate ring angles in cyano(2,2′,2″-terpyridine)copper(II) nitrate monohydrate,[9] which has an average copper(II)–nitrogen bond length of 2.02 Å, are 111 (1) and 110 (1)°. The corresponding angles in 2-hydroxyethanethiolato(2,2′,2″-terpyridine)platinum nitrate,[10] where the average metal–nitrogen distance is 2.00 Å, are 112.6 and 113.0°. When the metal–nitrogen distances are larger, the angular strain is less. This effect can be seen by comparing the angles just cited with the corresponding angles in (dimethyl diisothiocyanato)(2,2′,2″-terpyridine)tin(IV)[12] and in $(TPymT)Pb_2(NO_3)_4\cdot 2H_2O$.[1] In the former complex the average metal–nitrogen distance is 2.52 Å and the two angles of interest are both 116.0° while in the latter the angles of interest are 115, 116, 116, and 118° with the average metal–nitrogen distance being 2.71 Å. Angular strain may be responsible for the copper-promoted hydrolysis reaction (vide infra).

The geometry of the nitrate anion is as expected. It is planar with no atom deviating more than 0.007 (2) Å from the mean plane of the four atoms. The bond lengths are within 0.04 Å of one another and the intra-anion angles are all within 0.5° of 120°.

Mechanistic Speculations. The complexes bis(2-pyridylcarbonyl)aminatocopper(II) nitrate–4.5–water and bis(2-

Table V. Hydrogen-Bonding Interactions in $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3)\cdot 2H_2O$[a]

Hydrogen atom	Receptor atom	Receptor atom position[b]	H-O, A	O-O, A	Angle (deg)	
H1O2	O5	x, y, z	1.99 (3)	2.817 (3)	O2-H1O2-O5	174 (3)
H2O2	O8	x, y, z	1.89 (4)	2.665 (3)	O2-H2O2-O8	165 (3)
H1O3	O9	$\bar{x}, 1-y, \bar{z}$	1.94 (3)	2.719 (3)	O3-H1O3-O9	161 (3)
H2O3	O4	$x, 1+y, z$	2.11 (3)	2.818 (3)	O3-H2O3-O4	175 (3)
H1O4	O6	x, y, z	1.95 (4)	2.855 (3)	O4-H1O4-O6	166 (3)
H2O4	O1A	$\bar{x}, \bar{y}, \bar{z}$	2.16 (3)	2.729 (2)	O4-H2O4-O1A	151 (4)
H1O8	O5	$x, 1+y, z$	2.15 (3)	2.903 (3)	O8-H1O8-O5	168 (3)
H2O8	O3	$1-x, 1-y, \bar{z}$	2.09 (4)	2.814 (3)	O8-H2O8-O3	178 (4)
H2O9	O7	$\bar{x}, \bar{y}, -1-z$	2.14 (4)	2.872 (3)	O9-H2O9-O7	175 (4)

[a] See footnotes *a* and *b* of Table II. [b] See footnote *b* of Table IV.

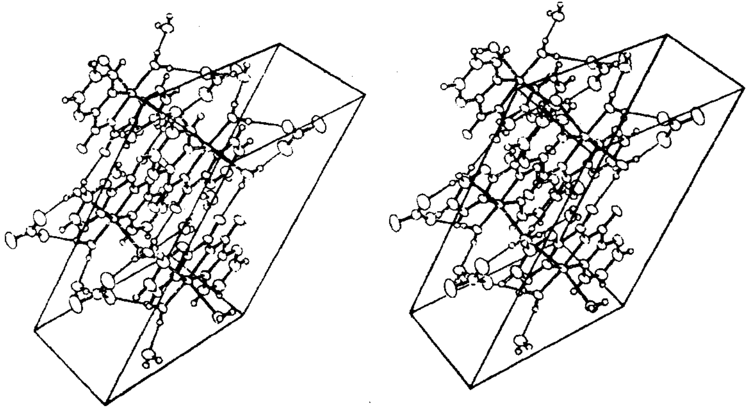

Figure 2. Stereoscopic view of the packing of molecules in two unit cells. The cell outlined extends from $-\frac{1}{2}$ to $+\frac{1}{2}$, in fractional coordinates, along the crystallographic *a*, *b*, and *c* axes. Hydrogen-bonding interactions are indicated by thin lines. Hydrogen atoms are drawn arbitrarily small.

pyrimidylcarbonyl)aminatotriaquocopper(II) nitrate–2–water are formed by a hydrolysis reaction from the corresponding triazines. Simple triazines are known to hydrolyze under relatively mild conditions. The parent compound, *s*-triazine, hydrolyzes completely in water in 10 min at 25 °C. The reaction products are formic acid and ammonia with a formamidine as the initial product.[13] The hydrolysis of *s*-triazine is faster in either acidic or basic solution.[14] 2,4,6-Trisubstituted triazines are more stable toward hydrolysis. Cyanuric chloride hydrolyzes to cyanuric acid with the triazine ring remaining intact. Cyanuric acid itself is quite stable toward hydrolysis, requiring hot mineral acids to hydrolyze it to carbon dioxide and ammonia.[15] 2,4,6-Triaryltriazines, the class to which TPyT and TPymT belong, are usually stable toward hydrolysis. The conditions employed for their hydrolyses are typically concentrated mineral acid and temperatures in excess of 150 °C.[16] Under these conditions the products of the hydrolysis reactions are the corresponding carboxylic acids and ammonia. Both TPymT and TPyT are stable to cold mineral acid, In fact one method of purifying TPymT involves dissolving it in 6 N HCl.[1,2] TPymT and TPyT are also stable to hot water from which they can be recrystallized. It is clear then that the metal atom, in this case copper but as previously reported several other metals too,[2] in some way assists the hydrolysis of the triazine ring.

Metal-catalyzed and -promoted hydrolysis reactions are well-known in organic chemistry and biochemistry. In general the metal acts in one of the following ways:[17] (1) The metal ion may act as a Lewis acid and catalyze reactions that are acid catalyzed. The metal ion may be able to act as an acid even in neutral pH thereby giving it a considerable advantage over the proton. (2) The metal ion may coordinate to the substrate in such a way as to polarize the chemical bonds thereby enhancing nucleophilic attack on the reaction center. (3) The metal may enhance nucleophilic hydrolysis by providing coordinated hydroxide at a pH where free hydroxide could not exist. (4) The metal may enhance the reaction by aligning the reactants which are coordinated to it. (5) The metal may enhance the nucleophilic attack on the substrate by charge neutralization in the ground or transition states. There are many examples of these modes of metal enhancement of hydrolysis in the literature.[17-20]

The metal-assisted hydrolysis of the triazine ring in TPyT and TPymT is effected by a modification of mode (2) and probably some assistance from mode (1). Since, as mentioned previously, TPymT and TPyT are stable to mineral acids, it seems unlikely that the hydrolysis is being caused by the metal acting solely as an acid. Rather, the main effect the metal exhibits is likely to be destabilization of the triazine ring upon coordination. When a copper ion binds in one of the tridentate terpyridine-like sites of TPymT, it causes strain at carbon atoms C7A and C7B. Within the chelate ring the angle at these atoms is compressed from an ideal 120° to a value close to 110°. This angle is therefore very close to the value the angle should have in the "tetrahedral intermediate" of hydrolysis by nucleophilic attack. The hydrolysis is enhanced by this angular strain because the geometry of the triazine–metal complex approaches that of the transition state. As previously mentioned such strain is found in terpyridine complexes. In those complexes, however, no hydrolysis takes place simply because it is much more difficult to hydrolyze a pyridine ring than a triazine ring (just compare the tendency toward hydrolysis of pyridine and *s*-triazine). Attack of water at carbon atoms C7A and C7B would form a tetrahedral intermediate or transition state. Coordination of copper(II) to the remaining nitrogens of the triazine ring would make them better leaving groups. Cleavage of the carbon–nitrogen bonds would leave a coordinated imide (Figure 1) and an amidine product which could release copper and be hydrolyzed to the amide or possibly further to the acid.

It would seem that the carbonyl carbon atom is better able to cope with the strained angles around it than is a carbon in the triazine ring, and the reaction stops at this point. More rigorous conditions might further hydrolyze the imide to an amide and a carboxylic acid. Consistent with this proposed mechanism is the fact that metals that form long metal–nitrogen bonds and therefore do not induce large amounts of angular strain do not facilitate the hydrolysis of the triazine ring. Examples of such complexes are (TPymT)$Pb_2(NO_3)_4\cdot 2H_2O$, (TPymT)$Pb_3Cl_6\cdot 3H_2O$, and (TPymT)$UO_2(NO_3)_2\cdot 7H_2O$, all of which can be boiled in water with no apparent decomposition.[1]

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Registry No. $[Cu(C_{10}H_6N_5O_2)(H_2O)_3](NO_3)\cdot 2H_2O$, 62264-17-9; $[Cu(C_{12}H_8N_3O_2)(H_2O)_3](NO_3)$, 62264-16-8; 2-picolinamide, 527-85-5; TPymT, 60681-68-7; TPyT, 3682-35-7.

Supplementary Material Available: Tables S1–S3 giving structure factor amplitudes, rms thermal amplitudes, and least-squares best planes (25 pages). Ordering information is given on any current masthead page.

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Notes

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Comparative Electronic Spectra and Structure of Mononuclear and Binuclear Dioxygen Complexes[1]

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The complexation of molecular oxygen by transition metals has attracted wide interest primarily for its importance as a biological model.[3a] Thus, cobalt–dioxygen complexes have been particularly useful in formulating some of the basic principles of metal–dioxygen chemistry. It is widely accepted that the reaction of cobalt(II) complexes with molecular oxygen leads to an adduct best described as containing formally oxidized cobalt and reduced dioxygen. The stoichiometry of this reaction depends strongly on reaction conditions, so that the 1:1 Co–O_2 "superoxo" complexes initially formed may rapidly react with excess cobalt to give binuclear "μ-peroxo" (Co^{III}–O_2^{2-}–Co^{III}) complexes. Quite recently the electronic structures of some μ-peroxo[3b,c] and μ-superoxo complexes[3c] (formed by the one-electron oxidation of the corresponding peroxo complexes) have been examined in some detail. No such studies have been reported for the analogous mononuclear species, however, perhaps due to the strong ligand → ligand bands generally associated with such systems (e.g., cobalt porphines, and cobalt–Schiff base complexes[3a,4]) which obscure the metal associated bands of interest. Recently, however, the $(Et_4N)_3[Co(CN)_5]$ complex has been shown to react with dioxygen in nonaqueous solvents (e.g., DMF[5]) to generate the mononuclear dioxygen complex $[Co(CN)_5O_2]^{3-}$ for which the crystal structure is now known.[6] This system exhibits well-resolved ligand field spectra which may be interpreted by comparison to analogous $[Co(CN)_5X]^{4-}$ complexes and compared with the corresponding binuclear μ-superoxo complex $[Co(CN)_5O_2Co(CN)_5]^{5-}$ so that the effects of the complex stoichiometry may be evaluated.

Materials and Methods

Tetraethylammonium cyanide was prepared by ion exchange on an Amberlite IR 400 resin, passing tetraethylammonium chloride over a column presaturated with KCN. All chemicals used were reagent grade. All spectra were run in spectral grade solvents which were dried and redistilled before use. $[N(C_2H_5)_4]_3[Co(CN)_5O_2]$ was prepared by the method of White et al.[5] and characterized by ESR. Nonaqueous solutions of $K_5[Co(CN)_5O_2Co(CN)_5]$ were obtained by dissolving the compound in the presence of an external electrolyte, Bu_4NClO_4. ESR spectra were obtained on a Varian E6S spectrometer using a flat quartz cell. Visible spectra were obtained on a Cary 14 spectrophotometer using matched quartz cells.

Conductance measurements were performed on a YSI Model 300 conductance bridge, for which a cell constant was obtained using standard KCl solutions.

Results and Discussion

Spectra of the superoxo complexes $[Co(CN)_5–O_2–Co(CN)_5]^{5-}$ and $[Co(CN)_5O_2]^{3-}$ are presented in Figure 1. Convincing band assignments for the binuclear complex have already been made by Gray and co-workers.[3c] The band at 310 nm corresponds to an LMCT ($\pi_h^*(O_2^-\cdot) \to d_{z^2}$), the shoulder at 380 nm to the $^1A_1 \to {}^1E$ tetragonal component of the "$^1A_{1g} \to {}^1T_{1g}$" (d → d) transition, and the intense band at 526 nm to an MLCT ($d\pi \to \pi_v^*(O_2^-\cdot)$). Attempts at finding a weak π_h^*–π_v^* band at about 10 000 cm^{-1} in the mononuclear complex have not thus far met with success.) Upon examination, the transition energies for the mononuclear complex are found to be quite similar to those for the binuclear complex (Table I). Thus the band assignments made by Gray for the binuclear complex are probably also valid for the mononuclear complex.

The spectra show a substantial medium dependence, as indicated by the solvent variation study summarized in Table I. Since the more negatively charged $[Co(CN)_5–(\mu\text{-}O_2)–Co(CN)_5]^{5-}$ might be expected to be differently solvated from $[Co(CN)_5O_2]^{3-}$, one might expect the various bands in the former complex to be solvent shifted from the corresponding bands in the latter. The observed shifts, however, are too small for a comparison of band positions to be very meaningful. It