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Synthesis and X-ray characterization of a polymeric 1:3 complex of copper(II) nitrate with pyrazine

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The structure of poly-μ-pyrazine-bis(pyrazine)(dinitrato-O)copper(II), $Cu(pyz)_3(NO_3)_2$, has been investigated by X-ray diffraction. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 6.8040$ (10), $b = 7.2860$ (10), $c = 9.289$ (2) Å, $\alpha = 69.65$ (2), $\beta = 68.51$ (2), $\gamma = 67.51$ (2)°, and $Z = 1$. The structure consists of linear chains of copper ions bridged by bidentate pyrazine groups, with monodentate terminal pyrazine and nitrate groups completing the distorted octahedral geometry about the copper ions.

KEY WORDS: Copper(II); pyrazine; coordination polymer.

Introduction

The study of coordination polymers has become an area of significant research interest. The inclusion of metal ions in the polymeric backbone offers materials with, for example, novel structural,[1,2] magnetic,[3–6] electrical,[7,8] and liquid crystalline properties.[2,9] Pyrazine (pyz) is a ligand capable of bridging metal centers that has been widely used in the preparation of polymeric materials.[10–18] Coordination polymers are often formed via self-assembly reactions of metal and ligand building blocks. However, other factors such as solvent, temperature, inorganic counterion, metal coordination geometry preference, or metal to ligand mole ratio may influence the reaction, leading to the formation of multiple structural types from a single set of components. To investigate the structural effect of copper(II) nitrate to pyrazine mole ratio, we treated the copper(II) salt with a large excess of the diazine. We report here a single crystal X-ray study of the resultant polymeric 1:3 complex of copper(II) nitrate with pyrazine and compare its structural characteristics with those of the 1:1 complex.[10]

Experimental

$Cu(NO_3)_2{\cdot}2.5H_2O$ and pyrazine (pyz) were obtained from commercial sources and used as received. Blue crystals of $Cu(pyz)_3(NO_3)_2$ were obtained by slow evaporation of an aqueous solution made up of $Cu(NO_3)_2{\cdot}2.5H_2O$ (1.00 g, 4.30 mmol, 2 mL) and pyrazine (4.20 g, 52.4 mmol, 5.5 mL). The compound decomposes to $Cu(pyz)(NO_3)_2$ if left in the open, as discussed below. Infrared spectra were recorded as hexachloro-1,3-butadiene mulls sandwiched between KRS-5 plates (International Crystal Laboratories) on a Bio-Rad Model FTS3000 FT-IR spectrometer.

X-ray crystallographic data were collected at 173 K on a Nonius KappaCCD diffractometer.

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Reflections were indexed and scaled using the Denzo-SMN software package.[19] The structures were solved with SHELXS and refined with SHELXL from the SHELX97 program package.[20] All hydrogen atoms were found in difference maps and refined using suitable riding models with isotropic U tied to the corresponding heavy atom. The largest difference map peak was within close proximity to the copper atom but it is insignificant. Details of the data collection and refinement are summarized in Table 1. The atomic coordinates and isotropic displacement parameters are listed in Table 2 and selected bond lengths and angles are given in Table 3.

Table 1. Crystal Data and Structure Refinement

Compound	$Cu(pyz)_3(NO_3)_2$
CCDC deposit no	174951
Color, shape	Blue, plate
Empirical formula	$C_{12}H_{12}CuN_8O_6$
Formula weight	427.84
Temperature, K	173
Wavelength (Mo $K\alpha$), Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	6.8040(10)
b, Å	7.2860(10)
c, Å	9.289(2)
α,°	69.65(2)
β,°	68.51(2)
γ,°	67.51(2)
Volume, Å^3	384.19(11)
Z	1
Density (calculated), g cm^{-3}	1.849
Absorption coefficient, mm^{-1}	1.478
$F(000)$	219
Crystal size, mm	0.24 × 0.20 × 0.06
Diffractometer	Nonius KappaCCD
θ range for data collection, °	2.43–27.47
Index ranges	$-8 \leq h \leq 8$ $-9 \leq k \leq 9$ $-11 \leq l \leq 12$
Number of reflections measured	3244
Unique data ($R_{int} = 0.0360$)	1753
Absorption correction	Multiscan
Max. and min. transmission	0.9166 and 0.7181
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1753/0/124
Goodness-of-fit on F^2	1.089
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0394$, $wR_2 = 0.0862$
R indices (all data)	$R_1 = 0.0487$, $wR_2 = 0.0914$
Largest diff. peak and hole, e · Å^{-3}	1.053 and −0.537

Note. $R = \sum ||F_o - |F_c|| / \sum |F_o|$. $Rw = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3)

Atom	x	y	z	U_{eq}[a]
Cu	0	10000	0	13(1)
N(1)	2981(3)	9969(3)	−5(2)	9(1)
C(1)	4151(4)	11100(4)	−1232(3)	12(1)
C(2)	3839(4)	8864(4)	1225(3)	12(1)
N(2)	−1358(3)	10832(3)	2160(2)	13(1)
N(3)	−3311(4)	12041(4)	5041(3)	21(1)
C(3)	−1593(4)	9447(4)	3580(3)	15(1)
C(4)	−2569(4)	10070(4)	4996(3)	17(1)
C(5)	−2066(5)	12809(4)	2192(3)	20(1)
C(6)	−3030(5)	13381(5)	3632(3)	24(1)
N(4)	1819(4)	4915(3)	2015(3)	19(1)
O(1)	462(3)	6502(3)	1391(2)	18(1)
O(2)	2100(4)	4838(3)	3291(2)	31(1)
O(3)	2816(4)	3494(3)	1350(3)	39(1)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Results and discussion

The structure of $Cu(pyz)_3(NO_3)_2$ with the atom labeling scheme is shown in Fig. 1. It consists of linear chains of copper ions bridged by bidentate pyrazine groups, with coordination number of 6 for each copper completed by monodentate terminal pyrazine and nitrate groups. The coordination geometry about each copper(II) ion is that of a distorted octahedron consisting of four nitrogen atoms and two oxygen atoms. The Cu—N bond length involving the bridging pyrazine ligands is equal to 2.018(2) Å while that involving the terminal pyrazine ligands is 2.075(2) Å. The oxygen atoms of the nitrate groups are considerably further from the copper(II) ion with a Cu—O bond length of 2.3790(19) Å. The Cu—N bond lengths in $Cu(pyz)_3(NO_3)_2$ are comparable to those observed for the equatorially bound pyrazine ligands in $Cu(pyz)(NO_3)_2$ (1.984(4) Å),[10] $Cu(pyz)(NO_2)_2$ (1.993(5) Å),[11] $Cu(pyz)_2(CH_3SO_3)_2$ (2.058(2) Å),[15] and $Cu(pyz)_2(ClO_4)_2$ (2.062(3) Å),[14] and much shorter than those observed for the axially bound pyrazine ligands in $Cu(pyz)_2(CH_3SO_3)_2$

Table 3. Selected Bond Lengths (Å) and Angles (°)[a]

Cu—N(1)	2.018(2)	Cu—N(1)#1	2.018(2)
Cu—N(2)	2.075(2)	Cu—N(2)#1	2.075(2)
Cu—O(1)#1	2.3790(19)	Cu—O(1)	2.3790(19)
N(1)—Cu—N(1)#1	180.0	N(1)—Cu—N(2)	89.24(8)
N(1)#1—Cu—N(2)	90.76(8)	N(1)—Cu—N(2)#1	90.76(8)
N(1)#1—Cu—N(2)#1	89.24(8)	N(2)—Cu—N(2)#1	180.0
N(1)—Cu—O(1)#1	85.96(7)	N(1)#1—Cu—O(1)#1	94.04(7)
N(2)—Cu—O(1)#1	90.21(8)	N(2)#1—Cu—O(1)#1	89.79(8)
N(1)—Cu—O(1)	94.04(7)	N(1)#1—Cu—O(1)	85.96(7)
N(2)—Cu—O(1)	89.79(8)	N(2)#1—Cu—O(1)	90.21(8)
O(1)#1—Cu—O(1)	180.0		

[a] Symmetry transformations used to generate equivalent atoms, #1: $-x, -y+2, -z$; #2: $-x+1, -y+2, -z$.

(2.692(3) Å)[15] and Cu(pyz)(hfac)$_2$ (2.529(3) Å).[13] This indicates strong coordination of the pyrazine ligands in the title complex. The axial coordination sites in Cu(pyz)$_3$(NO$_3$)$_2$ are occupied by two oxygen atoms from monodentate nitrate groups and the Cu—O bond distance is identical, within experimental error, to that found in Cu(pyz)$_2$(ClO$_4$)$_2$ (2.373(12) Å)[14] but shorter than the axial Cu—O bond distances in Cu(pyz)(NO$_3$)$_2$ (2.490(5) Å)[10] and Cu(pyz)(NO$_2$)$_2$ (2.462(5) Å).[11] The greater elongation of the axial Cu—O bonds in the latter two complexes is a reflection of the constraint imposed by the geometry of the nitrate group when it acts as a bidentate ligand. This constraint is also manifested in the degree of angular deviation of the axial Cu—O bond from the equatorial plane. The deviation is 34° and 36° in Cu(pyz)(NO$_3$)$_2$ and Cu(pyz)(NO$_2$)$_2$, respectively, but only 4° in Cu(pyz)$_3$(NO$_3$)$_2$.

Divalent metal salts typically form 1:1 or 1:2 polymeric complexes with pyrazine. Examples of such complexes that have been structurally characterized by X-ray crystallography include the pyrazine-bridged chain polymers Cu(pyz)(NO$_3$)$_2$,[10] Cu(pyz)(NO$_2$)$_2$,[11] Cu(pyz)Cl$_2$,[12] Cu(pyz)Br$_2$[12] and Cu(pyz)(hfac)$_2$ (hfacH = hexafluoroacetylacetonate),[13] and the sheet polymers Cu(pyz)$_2$(ClO$_4$)$_2$,[14] Cu(pyz)$_2$(CH$_3$SO$_3$)$_2$,[15] Fe(pyz)$_2$(NCS)$_2$,[16] Co(pyz)$_2$(NCS)$_2$,[17] and Co(pyz)$_2$Cl$_2$.[18] Thus, Cu(pyz)$_3$

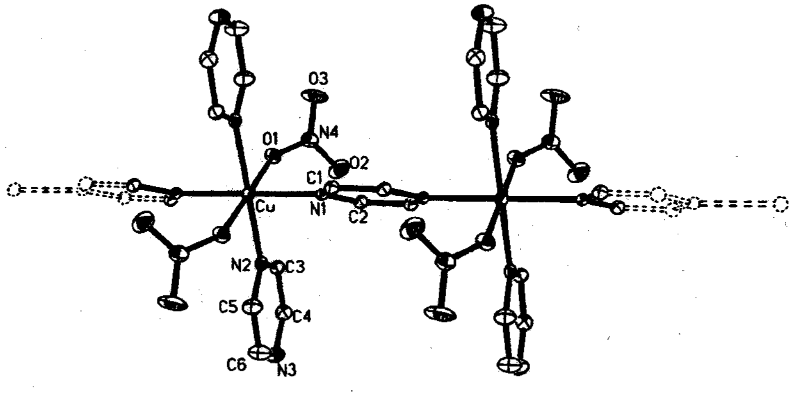

Fig. 1. Chain structure of Cu(pyz)$_3$(NO$_3$)$_2$. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity.

$(NO_3)_2$ is unique in having a 1:3 metal to pyrazine ratio. A 1:3 nickel(II)-pyrazine complex, $Ni(pyz)_3(CH_3SO_3)_2$, has been reported but the structure was not confirmed by X-ray diffraction studies.[5]

The structure of $Cu(pyz)(NO_3)_2$ consists of linear chains of copper ions bridged by bidentate pyrazine ligands, with four oxygen atoms from two bidentate chelating nitrate groups completing the distorted octahedron geometry about each copper ion.[9] $Cu(pyz)_3(NO_3)_2$ contains the same -Cu-pyz-Cu- polymeric backbone, but coordination number of 6 about each copper ion is achieved through two nitrogen atoms from monodentate pyrazine ligands and two oxygen atoms from monodentate nitrate groups. The different bonding modes of the pyrazine and nitrate groups in $Cu(pyz)(NO_3)_2$ and $Cu(pyz)_3(NO_3)_2$ are readily inferred from their infrared spectra. The infrared spectrum of uncoordinated pyrazine exhibits a band at 417 cm^{-1} which shifts to higher energies when the ligand coordinates to a metal center.[21] The corresponding band is observed at 491 cm^{-1} in the spectrum of $Cu(pyz)(NO_3)_2$, consistent with the presence of only bidentate pyrazine ligands in this compound. In the case of $Cu(pyz)_3(NO_3)_2$ two bands are observed at 490 cm^{-1} and 459 cm^{-1} and are attributed to the bidentate and monodentate pyrazine ligands, respectively. Both monodentate and bidentate nitrate groups exhibit three NO stretching bands, typically in the 960–1630 cm^{-1} range. In general, the separation of the two highest-frequency bands is larger for bidentate than for monodentate coordination for similar complexes and this feature can be used to distinguish between the two modes of nitrate group coordination.[22] The separation is 196 cm^{-1} (bands observed at 1488 and 1292 cm^{-1}) for $Cu(pyz)(NO_3)_2$ and 98 cm^{-1} (bands observed at 1401 and 1303 cm^{-1}) for $Cu(pyz)_3(NO_3)_2$. These results are indicative of bidentate nitrate coordination in $Cu(pyz)(NO_3)_2$ and monodentate coordination in $Cu(pyz)_3(NO_3)_2$, consistent with their structures as determined by X-ray crystallography.

When left in open containers, whether exposed to air or an inert atmosphere, $Cu(pyz)_3(NO_3)_2$ readily lose 2 molecules of pyrazine per formula unit to yield $Cu(pyz)(NO_3)_2$. This is indicated by the change in color from blue to indigo, the color of $Cu(pyz)(NO_3)_2$. In addition, the infrared spectrum of the decomposition product is identical to that of $Cu(pyz)(NO_3)_2$ prepared directly by the reaction of aqueous solutions of $Cu(NO_3)_2 \cdot 2.5H_2O$ and pyrazine in a 1:1 molar ratio. The decomposition of $Cu(pyz)_3(NO_3)_2$ can be minimized by storing the sample in a sealed vial with a small head space.

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