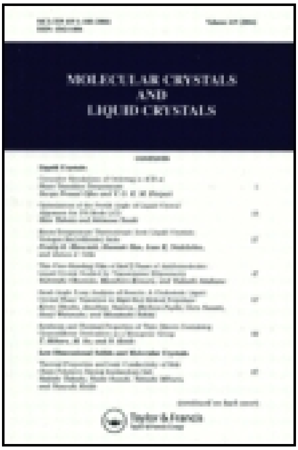

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# Design of a New Reactive Phase using Ammonia as an Ancillary Ligand: Structure and Reactivity of Diamminebis(propynoato)zinc

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# Design of a New Reactive Phase using Ammonia as an Ancillary Ligand: Structure and Reactivity of Diamminebis(propynoato)zinc

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Addition of a 2M solution of $NH_3$ in ethanol to solid tetraaquabis(propynoato)zinc **1** leads directly to the title complex **2.** Formation of hydroxides is eliminated using this procedure. The structure of **2** differs markedly from the octahedral structure observed for the analogous octahedral aqua complex **1.** The structure of **2** is monomeric and tetrahedral, with monodentate carboxylate ligands. The crystal structure consists of isolated molecules interconnected by two strong N-H···O hydrogen bonds and one C-H···O hydrogen bond. Infinite sets of short -C≡C- ··· -C≡C- contacts are also present in the crystal structure. Accordingly, $^{60}Co$ $\gamma$-irradiation of **2** leads to the analogous dark brown polypropynoate complex.

*Keywords:* Metal carboxylates; solid-state reaction

## INTRODUCTION

A possible design strategy[1] for the construction and engineering of reactive phases, using unsaturated ligands pendant to metal complexes, must include the use of compact ligands. Thus, a ligand of small size will not prevent the approach of pendant reactive groups in an efficiently packed crystal structure. In many of the studies we have carried out, the complexes contain either water or no additional ligand, both natural consequences of crystallization from aqueous solution.[2-4] Inspection of the Cambridge Structural Database revealed that there were only nine metal complexes that contained at least one carboxylate and two ammine ligands.[5] Three of these involve Co(III), five Cu(II), and one Zn(II). In an effort to understand and explore the packing and solid-state reactivity of a thus structurally novel series of complexes, we first synthesized a zinc complex containing propynoate and ammonia. This approach parallels our initial study of metal propynoates, which began with tetraaquabis(propynoato)-zinc.[2] In the latter case we used the structure of tetraaqua-bis(acetato)nickel[6] to *design* the reactive phase **1**. In the present case we did not consider the structure of bis(acetato)diamminezinc[7] as a design motif for the first compound to be synthesized, diamminebis(propynoato)-zinc (**2**). We surmised that C–H···O hydrogen bonding, expected for complexes involving the propynoate moiety, would promote the formation of a different structure for **2**.[4] This paper reports the synthesis, X-ray crystal structure determination, and a preliminary study of the solid-state reactivity of compound **2**.

## EXPERIMENTAL SECTION

### Instrumentation

IR spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrometer. A Gammacell 220 Irradiator (Atomic Energy of Canada, Ltd.) equipped with a $^{60}$Co source was used for all γ-irradiation experiments (nominal activity 350 Gy/h).

Diamminebis(propynoato)zinc (**2**)

In order to prevent the formation of hydroxides, a synthesis was carried out in nonaqueous (but not water-free) solution. To 1.00 g ($3.63 \cdot 10^{-3}$ mol) of solid tetraaquabis(propynoato)zinc **1** was added a 2.0 M solution of $NH_3$ in ethanol (3.63 mL, $7.26 \cdot 10^{-3}$ mol, Aldrich). The slurry was stirred until the solid dissolved; the solution was allowed to evaporate, leaving a colorless powder: IR(KBr) 3370, 3242, 3203, 2099, 1620, 1352, 1272, 1231, 897, 776, 685, 642, 592 $cm^{-1}$. Exposure of **2** to $^{60}$Co γ-rays (176 kGy) led to a dark brown solid. The analogous polypropynoate was isolated by repeated extraction of unreacted monomer from the irradiated material using methanol: IR (KBr) 3348, 2100, 1576, 1374, 781, 668 $cm^{-1}$. The $-C{\equiv}C-$ stretching frequency was greatly diminished in the isolated product; no attempt has been made at this time to establish whether further extraction would cause it to disappear.

X-ray Structure Determination

Single crystals were grown by diffusion of acetone into a solution containing 1.00 g of **1** and 7.26 mL ammonia-EtOH solution (2.0M). These crystals were used for the data collection and had a calculated powder pattern similar to the experimental pattern of the colorless powder. The crystal was mounted on a Pyrex fiber affixed to a brass pin, transferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously.[8] The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering were included in the calculations.[9] The structure was solved using by the heavy-atom method; preliminary computational work was carried out using the Enraf-Nonius MolEN software package.[10] Final refinement and drawings were carried out using the Oxford University CRYSTALS-PC [11] package and CAMERON,[12] respectively. At the conclusion of least-squares refinement of positional and anisotropic displacement parameters for all nonhydrogen atoms (isotropic displacement parameters for H atoms), $R = 0.0333$ and $R_w = 0.0341$. A summary of experimental detail is presented in Table I and selected bond lengths and angles in Table II. Tables of atomic coordinates, anisotropic displacement parameters and all bond lengths and angles are available from the authors as a CIF file.

## RESULTS AND DISCUSSION

Diamminebis(propynoato)zinc (**2**) crystallizes as discrete tetrahedral monomeric complexes; the structure of a single molecule is shown in Figure 1. Complex **2** has crystallographic $C_s$ symmetry; all atoms except the nitrogen atom and the three associated hydrogen atoms lie on the crystallographic mirror plane. Distances and angles (Table II) lie within normal ranges for tetrahedral zinc carboxylates containing two ammine, pyridine or imidazole ligands.[13]

The crystal structure contains six N-H···O and C-H···O interactions worthy of mention (Table II). As can be seen in Table II, there are two bifurcated pairs of N-H···O hydrogen bonds; the stronger of each pair is

Table I. Data for the X-ray Diffraction Study of $Zn(NH_3)_2(O_2CC{\equiv}CH)_2$

(A) Crystal Data at 21(1) °C.

Crystal system : Monoclinic
Space group : $P2_1/m$ [$C^2_{2h}$; No. 11]
$a = 7.089(2)$ Å
$b = 7.010(2)$ Å
$c = 9.465(3)$ Å
$\beta = 93.88(3)°$
$V = 469.3(4)$ Å$^3$

$Z = 2$
Crystal Size : 0.084 x 0.170 x 0.840 mm.
Formula Wt : 237.51
$\rho_{obs}{}^{a} = 1.67(1)$ g·cm$^{-3}$
$\rho_{calc} = 1.681$ g·cm$^{-3}$
$\mu = 2.66$ mm$^{-1}$ (MoK$\bar{\alpha}$)

Radiation : MoK$\bar{\alpha}$, graphite monochromator
Reflections measured : $h, k, \pm l$ (3° ≤ 2θ ≤ 55°)
No. of reflections measured : 1248, 1159 in unique set
Absorption correction : empirical, trans. factors 0.865 - 1.00
Refinement[b] : full-matrix least-squares, with:
anisotropic displacement parameters for Zn, N, C and O atoms;
isotropic displacement parameters for H atoms;
$R = 0.0333$; $R_w = 0.0341$; $S = 1.13$

---

[a] Measured by neutral buoyancy in *n*-hexane/1,1-dibromomethane.

[b] $R_{av} = \Sigma|I-I_{av}|/\Sigma I$; $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ ; $R_w = \{\Sigma w[|F_o|-|F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$
SDU = $\{\Sigma w[|F_o|-|F_c|]^2/(m-n)\}^{1/2}$ where m (=1014) is the number of observations and n (=95) is the number of parameters.

Table II. Bond Lengths (Å) and Angles (°) for $Zn(NH_3)_2(O_2CC{\equiv}CH)_2$ **2**

| | | | |
|---|---|---|---|
| Zn(1) - O(1) | 1.947(2) | O(4) - C(4) | 1.216(5) |
| Zn(1) - O(3) | 1.970(2) | C(1) - C(2) | 1.458(5) |
| Zn(1) - N(1) | 1.996(3) | C(2) - C(3) | 1.175(6) |
| O(1) - C(1) | 1.273(4) | C(4) - C(5) | 1.469(5) |
| O(2) - C(1) | 1.217(4) | C(5) - C(6) | 1.172(6) |
| O(3) - C(4) | 1.265(4) | | |

| | | | |
|---|---|---|---|
| O(1)-Zn(1)-O(3) | 108.7(1) | O(1)-C(1)-O(2) | 125.7(3) |
| O(1)-Zn(1)-N(1) | 113.6(1) | O(1)-C(1)-C(2) | 113.9(3) |
| O(3)-Zn(1)-N(1) | 103.6(1) | O(2)-C(1)-C(2) | 120.5(3) |
| O(1)-Zn(1)-N(1) | 113.6(1) | C(1)-C(2)-C(3) | 179.0(4) |
| O(3)-Zn(1)-N(1) | 103.6(1) | O(3)-C(4)-O(4) | 127.4(3) |
| N(1)-Zn(1)-N(1) | 112.6(2) | O(3)-C(4)-C(5) | 113.5(3) |
| Zn(1)-O(1)-C(1) | 116.8(2) | O(4)-C(4)-C(5) | 119.1(3) |
| Zn(1)-O(3)-C(4) | 130.5(2) | C(4)-C(5)-C(6) | 179.5(5) |

| X -- H .. Y | D...A | D-H..A | Symm Operation |
|---|---|---|---|
| N(1)--H(11)..O(1) | 3.100(3) | 117(4) | -x,1/2-y,1-z |
| N(1)--H(11)..O(4) | 3.082(4) | 163(5) | -x,1/2-y,1-z |
| N(1)--H(12)..O(4) | 3.224(4) | 143(5) | 1+x,y,z |
| N(1)--H(12)..O(2) | 3.230(4) | 126(5) | 1-x,1/2+y,1-z |
| C(3)--H(31)..O(3) | 3.152(6) | 162(6) | x,y,1+z |
| C(6)--H(61)..O(2) | 3.525(6) | 173(7) | -1+x,y,-1+z |

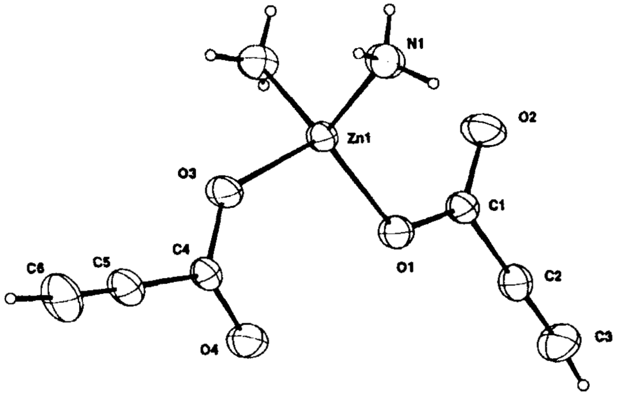

**Figure 1**. Molecular structure of $Zn(NH_3)_2(O_2CC{\equiv}CH)_2$

shown in Figure 2, along with the stronger of the C–H···O hydrogen bonds. The N(1)–H(11)···O(4) hydrogen bond forms an $R_2^2(12)$ ring, while N(1)–H(12)···O(4) and C(3)–H(31)···O(3) form discrete (D) hydrogen bonds. The IR spectrum of **2** shows bands at 3242 and 3203 cm$^{-1}$. It is likely that these arise from the C(6)–H(61)···O(2) and C(3)–H(31)···O(3) interactions, respectively.[14]

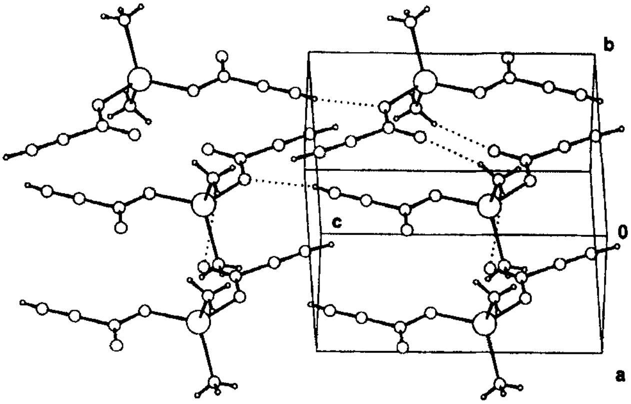

**Figure 2.** Hydrogen bonds in the crystal structure of **2**

The shortest contacts between α and β carbon atoms on different propynoate moieties are: C(2)···C(6)[*1*+*x*, *y*, *1*+*z*], 3.560Å; C(3)···C(5)[*x*, *y*, *1*+*z*], 3.558Å; and C(5)···C(6)[-*1*-*x*, *y*, *z* and -*1*-*x*, *1*-*y*, *z*], 4.030Å. The first two of these form an infinite chain (Figure 3) along the crystallographic *a* direction. A chain of infinite short contacts has been shown to be a requirement for solid-state reactivity of monoacetylenees in solids;[2-4] the angles between the potentially reactive monoacetylenes are

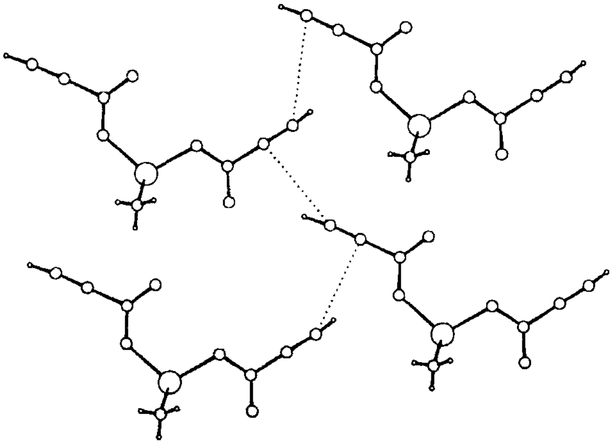

**Figure 3.** Short $-C{\equiv}C- \cdots -C{\equiv}C-$ contacts in the crystal structure of **2**

not important.[3] Accordingly, exposure of compound **2** to $^{60}$Co γ-rays, produces an orange-red color in the solid, and further exposure leads to a dark brown color (176 kGy). As the irradiation proceeds, there is a concomitant loss in intensity of the $-C{\equiv}C-$ stretching mode at 2099 cm$^{-1}$, indicating the likely formation of a polypropynoate. A complete set of time-conversion experiments, as well as synthesis and structural studies of other new metal carboxylates containing ammonia as an additional ligand, are underway. The synthesis, X-ray structure determination and preliminary reactivity study have established that ammine complexes will be useful and interesting targets for the generation of new reactive phases of metal salts and complexes containing unsaturated carboxylates.

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