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Azine bridged silver coordination polymers: Powder X-ray diffraction route to crystal structure determination of silver benzotriazole

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Abstract

In continuation of our interest in solid-state structures of silver complexes of photographic importance, the structure for silver benzotriazole (AgBZT), has now been obtained. The preferred method for solving crystal structures is via single-crystal X-ray diffraction (XRD). However, for some materials, growing single crystals of appropriate size and quality is often difficult or even impossible. AgBZT is an example of such a silver complex with poor solubility. The usual routes to preparing single crystals using recrystallization from a cooperating solvent resulted in polycrystalline powder samples. We propose a crystal structure for AgBZT, solved from synchrotron X-ray powder diffraction data, using a direct-space Monte Carlo simulated annealing approach. AgBZT crystals are monoclinic, ($P2_1/c$), with unit cell dimensions, $a = 14.8052(3)\,\text{Å}$, $b = 3.7498(4)\,\text{Å}$, $c = 12.3495(12)\,\text{Å}$, and $\beta = 114.200(6)^\circ$. The AgBZT complex is constructed from all three of the Benzotriazole (BZT) nitrogens bonding to a separate silver atom. As a consequence of this bonding mode, the structure is a highly cross-linked, coordination polymer.

Keywords: Silver benzotriazole; Silver complex; Benzotriazole; Structure; Powder X-ray diffraction; Monte Carlo simulated annealing; Photothermographic material; NMR; DFT; Synchrotron

1. Introduction

The routine structure determination from single-crystal X-ray diffraction (XRD) is one of the principal triumphs of crystallography. However, many crystalline solids can be obtained only as microcrystalline powders, and they are not suitable for investigation by single-crystal diffraction methods. There is clearly a pressing need to exploit techniques for solving crystal structures from powder diffraction data. Powder XRD has been used routinely as a fingerprinting technique for decades, and it has also been used in studies related to polymorph identification and to calculate unit cell parameters. Despite the loss of information, which is due to peak overlap, a high-quality powder diffraction pattern often contains enough information for unambiguously determining the corresponding crystal structure. In fact, there has been a rapid development of techniques for structure determination from powder diffraction data [1–5]. The general methodology is to index the diffraction pattern, to solve the crystal structure and to carry out a final Rietveld refinement.

Benzotriazole (BZT), Fig. 1, has a high affinity for silver, which has been the mainstay of its successful use in conventional photographic systems for many years [6]. Silver benzotriazole (AgBZT) has been reported to be an efficient silver source in black and white photothermographic (PTG) imaging systems [7]; and more recently, it has been investigated as the silver source to be used in color PTG materials designed for very high photographic speed

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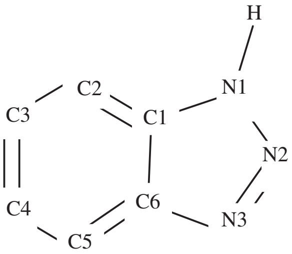

Fig. 1. Benzotriazole.

applications [8,9], compared to "conventional" PTG materials. Contemporary PTG films are not very light sensitive compared to silver halide-based photographic materials, by about four orders of magnitude. Normally, commercial films like Kodak DryView recording film require about 1000 erg/cm^2 [10,11] for exposure, although sensitivity to 1 erg/cm^2 has been demonstrated [12].

In addition to the requirements of photographic sensitivity, the silver source in any PTG material must be stable in the presence of the additional components in imaging chemistry since the entire film retains these components after thermal processing [13]. A better understanding of the physical and chemical properties of AgBZT would contribute to improvements in various aspects of the imaging properties of PTG film construction, such as photographic speeds, improved shelf life, image stability, etc.

Since significant insight into various silver containing components of PTG media has been achieved by resolving the solid-state structure of the corresponding silver complex with ligands such as stearic acid, mercaptobenzimidazole, phenylmercaptotetrazole, and phthalic acid [14–18], we have attempted to apply this approach to the preparation of single crystals of AgBZT for X-ray crystal structure determination. However, the poor solubility of the complex, $K_{sp} = 13.4$ [19], prevents formation of suitable single crystals of AgBZT. The earliest report on the preparation of AgBZT included a comment regarding its solubility in dilute nitric acid [20], and our efforts to utilize this approach simply incorporated the nitrate as the counterion [21] while the BZT ligand was found to coordinate to the silver as a neutral donor ligand. A related complex, $\{Ag(HBZT)_2(NO_3)\}$, has been reported in the literature [22]. In this case, the BZT is bound to the silver as a neutral donor and the residual nitrate is a weakly coordinating counterion. In general, other silver complexes of ligands containing an azine coordination option similar to BZT contain six-membered ring bridged species, –Ag–N–N–Ag–N–N– [22–28]. In these cases, the Ag–N distances range 2.20–2.27 Å.

Considering the importance of BZT in copper corrosion prevention [29], there is surprisingly little published on the coordination chemistry of this ligand with various metals. The reactivity with copper illustrates the different bonding modes one might expect with this ligand. For example, the copper BZT complexes exhibit the fully deprotonated version, $Cu(BZT)_2$; its opposite, as a fully neutral donor version, $Cu(HBZT)Br_2$; and the intermediate, mixed-ligand bonding modes, $Cu_2(HZT)(HBZT)(NO_3)_2$ [29]. However, the poor crystallinity of these compounds could not provide the metal–ligand bonding details, which can be obtained from crystal structure analysis. The limited additional literature related to BZT coordination chemistry is similar to these. That is, the M-BZT complexes are metal coordination polymers, which are typically poorly soluble in non-coordinating solvents [30,31]. In many cases, such solids are highly amorphous and difficult to crystallize [32].

The only non-silver complexes of BZT whose structures have been reported are those for thallium [32], and nickel [33]. The solid-state structure of TlBZT is a cross-linked polymeric network resulting from each nitrogen being bonded to a Tl^+ atom. In this case, the stoichiometry of the thallium complex is TlBZT, but is better abbreviated as $[TlBZT]_n$. The nickel complex also exhibits the same azine bridge between metal atoms, although the additional complexity of this structure can be attributed to the supplemental ligands.

Despite the inability to grow AgBZT crystals having sufficient size and quality for structure determination via conventional single-crystal X-ray, structure-determination techniques, we now report a crystal structure determined by combining laboratory and synchrotron powder diffraction data supported by density function theory calculations. The highly polymeric structure of the AgBZT complex obtained from powder diffraction data is analogous to the TlBZT complex and is described below.

2. Experimental section

2.1. Preparation of AgBZT

BZT, 2.43 g, was dissolved in 100 mL H_2O containing 0.76 g NaOH. Silver nitrate, 3.45 g dissolved in 10 mL H_2O, was added to produce an immediate white precipitate. The mixture was stirred 30 min, filtered, re-dispersed in water, stirred 15 min, filtered, and air-dried. Elemental analysis—Found (theory): C = 31.93 (31.86), H = 1.75 (1.78), N = 18.84 (18.54) [34]. For specific NMR experiments requiring different levels of Ag^+ present, this preparation procedure was repeated with 75% and 125% of the original silver level.

2.2. X-ray powder data collection

Initial XRD powder patterns were collected using a Rigaku D2000 Bragg–Brentano diffractometer equipped with a copper rotating anode X-ray source, diffracted beam-curved graphite monochromator tuned to Cu$K\alpha$ radiation (1.54184 Å), and a scintillation detector. The specimen for analysis was prepared by passing an aliquot of the title compound through a 325-mesh sieve and sprinkling the sieved sample onto a zero-background

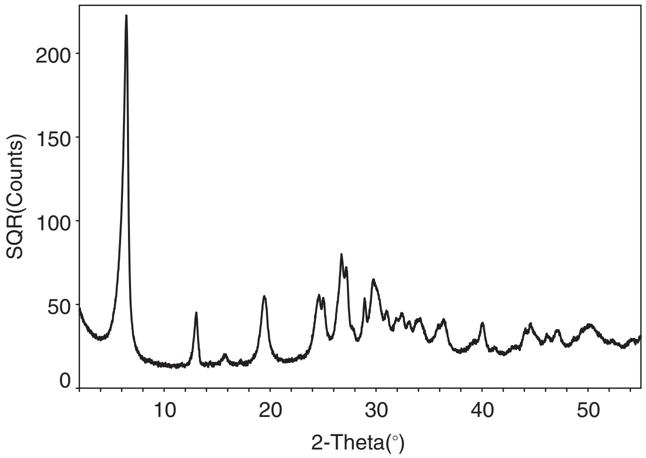

Fig. 2. X-ray powder pattern for AgBZT, Cu$K\alpha$ laboratory source (plotted as square root of intensity to enhance low-intensity diffraction peaks).

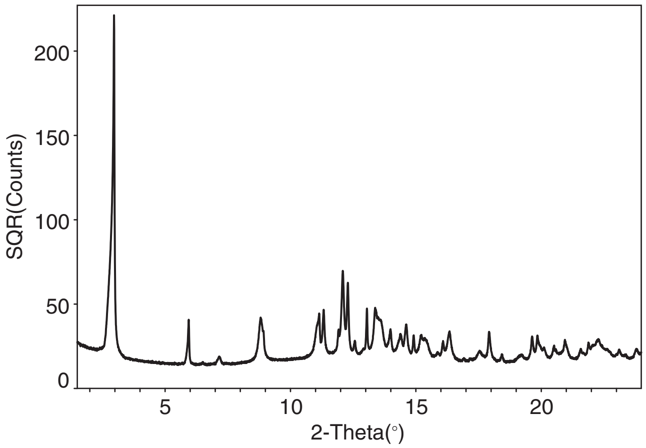

Fig. 3. X-ray powder pattern for AgBZT, synchrotron source (plotted as square root of intensity to enhance low-intensity diffraction peaks).

quartz plate [35]. Data were collected using a step scan, 0.01° 2θ/step, 2 s/step. The resulting diffraction pattern is shown in Fig. 2.

The data from this pattern show two low-angle diffraction peaks, indicative of at least one axis in the unit cell with a length of ~14.5–15 Å. Further evaluation of the data in Fig. 2 reveals several diffraction peaks in the range of 20–50° 2θ that have acceptable intensity but contain several overlapped peaks. Using Jade 6.1 [36], peak positions were determined by using a Pearson VII peak profile fitting routine, and unit cell parameters were determined using pattern indexing. However, attempts to solve the structure using the laboratory data were unsuccessful. Therefore, it was determined that a high-resolution diffraction pattern would be required in order to proceed with structure solution.

Synchrotron XRD [37] data were collected at Brookhaven National Laboratories on beamline X3B1. The powder diffractometer associated with this beamline comprises a Huber goniometer equipped with a diffracted beam Ge (111) analyzer crystal and a NaI scintillation detector. The angular resolution for this configuration is less than 0.01° full width at half maximum. The wavelength was 0.70025 Å, calibrated using an NIST SRM 1976 α-Al_2O_3 plate. The specimen for analysis was prepared by passing an aliquot of AgBZT powder through a 325-mesh sieve and packing the sieved sample into a 0.7 mm I.D. glass capillary. Data were collected with the sample spinning, using a step scan, 0.005° 2θ/step, 1 s/step. The resulting diffraction pattern is shown in Fig. 3.

The diffraction pattern in Fig. 3 clearly demonstrates the superior quality obtained using a synchrotron-based diffractometer for data collection. In particular, the enhanced peak resolution increases the probability of obtaining a successful structure solution from powder XRD data. Pattern indexing of the synchrotron data gave the same unit cell as was obtained from the laboratory-source XRD data.

2.3. Structure determination

The synchrotron XRD powder pattern (Fig. 3) was indexed using the Jade 6.1 [36] algorithm, as a monoclinic cell having $a = 14.835$, $b = 3.740$, $c = 12.360$ Å, and $\beta = 114.6°$. The systematic absences unambiguously determined the space group of AgBZT to be $P2_1/c$. Pawley refinement [38,39] was used to fit the peak profiles and adjust various parameters to minimize the weight profile R-factor R_{wp}. Ten cycles of Pawley refinement resulted in $R_{wp} = 6.42\%$, confirming the choice of unit cell and space group.

The BZT molecule was assumed to be flat (BZT is planar in the structure of the analogous thallium complex, TlBZT [32]) as designated as one motion group, and the silver ion was designated as the second motion group. The PowderSolve algorithm [1,2,38] was used to solve the crystal structure. PowderSolve is a global search algorithm which uses a direct space Monte Carlo simulated annealing approach to generate a large number of trial structures guided by the automatic comparison of the simulated powder patterns to the experimental one. The best match ($R_{wp} = 12.47\%$) was selected as the starting point for further structure refinement. The R_{wp} value at this stage is usually 2–2.5 times larger than the value obtained from the Pawley refinement.

At this stage, the hydrogen atoms were inserted in idealized positions, and the structure was refined by the Rietveld method [38,40]. The final R_{wp} was 9.64% (Fig. 4), for refined unit cell dimensions of, $a = 14.8052(3)$, $b = 3.7498(4)$, $c = 12.3495(12)$ Å, and $\beta = 114.200(6)°$.

Details of unit cell data are summarized in Table 1, atomic coordinates and bonding information are listed in Supplementary Data Tables S-1 and S-2. The bond lengths and bond angles for a BZT moiety were all fixed at chemically reasonable values, atomic temperature factors were all assigned a fixed value of 0.05 Å^2. Crystallographic

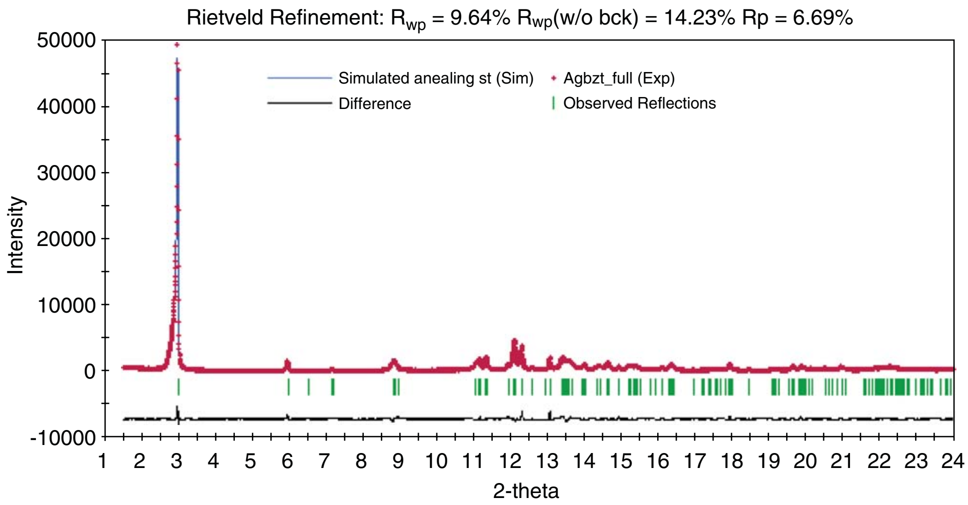

Fig. 4. Comparison of the diffraction pattern calculated from the structure solution after Rietveld Refinement—simulated annealing (blue) overlaid with the experimental synchrotron pattern (red). The observed reflections (green) and difference plot (black) are plotted below the overlaid patterns.

Table 1
Unit cell parameters for AgBZT

Empirical formula	$C_6H_4N_3Ag_1$	
Formula weight	225.99	
Wavelength	0.70025 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	$a = 14.8052(3)$ Å	$\alpha = 90°$
	$b = 3.7498(4)$ Å	$\beta = 114.200(6)°$
	$c = 12.3495(12)$ Å	$\gamma = 90°$
Volume	625.3 Å^3	
Z	4	
$F(000)$	432	
Density (measured)	2.459 mg/m^3	
Density (calculated)	2.400 mg/m^3	
Final R_{wp} (Rietveld refinement)	9.64%	

data for this structure has been deposited with the Cambridge Crystallographic Data Centre as supplementary data no. 293247. Copies of the data may be obtained free of charge upon request from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk; WEB: http://www.ccdc.cam.ac.uk). The Powder pattern is being deposited with ICDD.

2.4. *Density function theory calculations*

A hybrid method [41] based on density functional theory (DFT) calculations with the VASP program [42–46] was used as part of the final structure refinement. In the first step, a crystal structure optimization with fixed lattice parameters was carried out starting from the structure solution, thus obtaining molecular geometries that take into account deformations related to the crystal environment. In the second step, a Rietveld refinement was performed in which only the molecular positions and orientations were allowed to vary.

3. Discussion of results

3.1. *Description of the structure of AgBZT*

The 1:1 stoichiometry of the AgBZT complex requires all three nitrogens to be involved with silver coordination since there are no additional ligands available to occupy its coordination sphere. Correspondingly, the multiple linkage sites on the single ligand molecule provide for a highly polymeric structure, which is consistent with the solubility properties of the compound.

The crystal structure of AgBZT is a layer structure, very similar to the structure reported for TlBZT [32], with Ag^+ ions and the BZT ligand coordinated in a zigzag fashion. The unit cell packing (Fig. 5) illustrates infinitely linked chains in the structure of AgBZT.

It can be seen that all three nitrogens of the AgBZT are bound to a silver atom. Stoichiometrically, AgBZT is correct, and although $[AgBZT]_n$ is a more accurate descriptor, AgBZT is a simpler abbreviation.

The AgBZT complex is constructed from all three of the BZT nitrogens bonding to a separate silver atom. The important Ag–N bond distances are 1.996(15), 1.979(9), and 2.202(13) Å. As a consequence of this bonding mode, the structure is a highly cross-linked, coordination polymer. From a charge perspective, one can view this structure as six-membered $[Ag\text{-}BZT]_2$ dimers connected by the third silver. The dimer component is based on the N=N bridging capability of the BZT, which is analogous to that observed for the bonding mode of phthalazine with silver [47].

In a previous study where a crystal structure was solved using powder XRD, solid-state NMR measurements were used to help validate the structure [48]. The NMR data and

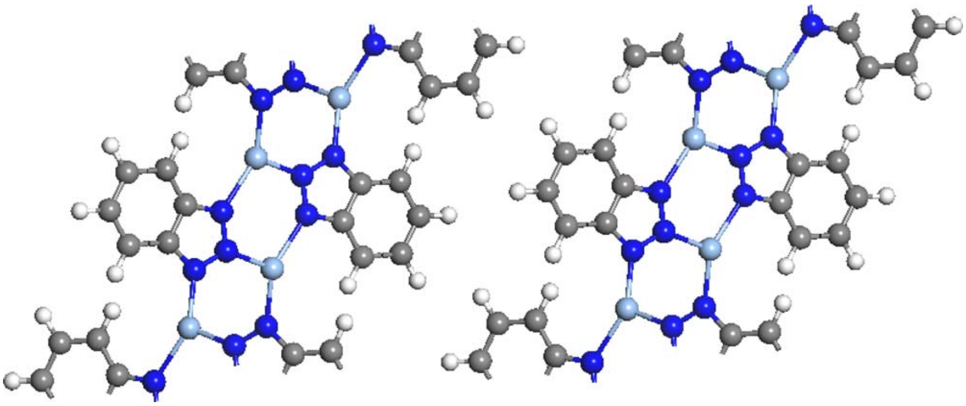

Fig. 5. The unit cell packing showing infinite cross-linked chains in the structure of AgBZT.

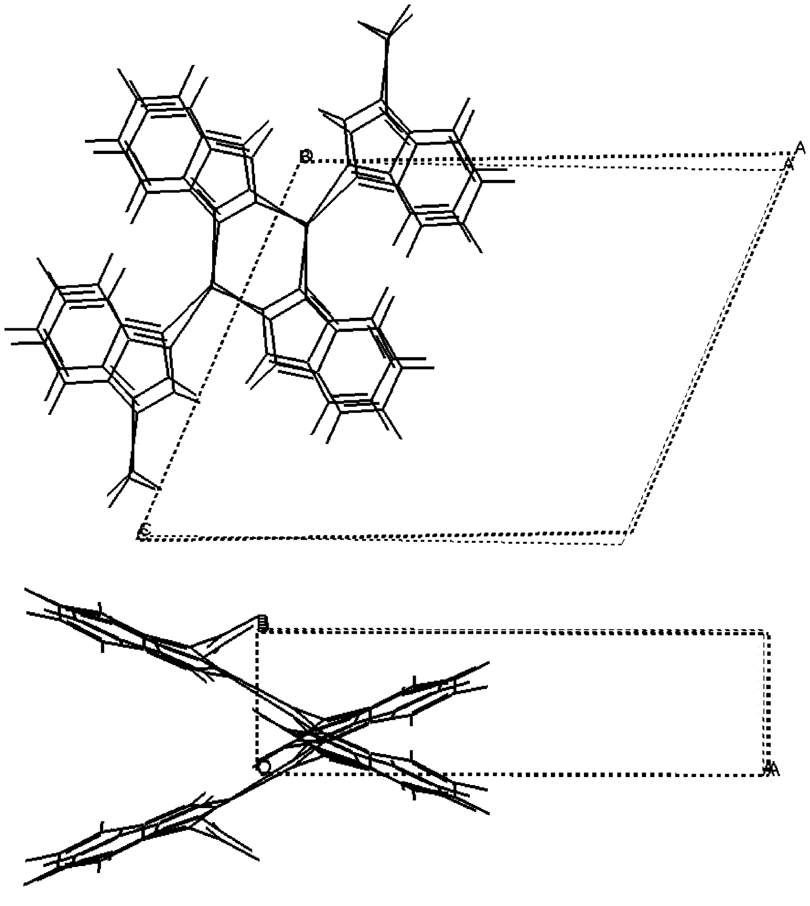

Fig. 6. Superposition of the experimental and the calculated crystal structure seen along the *b*-axis (upper part) and along the *c*-axis (lower part).

results for AgBZT are described in detail in the Supplemental Data section.

3.2. Density functional theory calculations

To complement the experimental structure determination DFT calculations were added to the procedure. It has been shown previously [49] that DFT calculations are a powerful tool for the confirmation and the further refinement of crystal structure solutions from powder diffraction data. In this work, we use a hybrid method [41] that combines DFT calculations by means of the VASP program [42–46] with an empirical van der Waals correction. Correction terms involving the silver atom were discarded since appropriate parameters are currently not available.

A superposition of our experimental crystal structure and the calculated crystal structure is shown in Fig. 6. The crystal structure optimization clearly conserves the overall packing arrangement and results in lattice parameters $a = 14.44$ Å (−2.5%), $b = 3.84$ Å (2.3%), $c = 12.19$ Å (−1.3%) and $\beta = 112.24°$. The cell volume changes by 0.1%. The observed change of the unit cell falls into the range of deviations between experimental and calculated cells reported for a variety of organic compounds [41]. If the experimental unit cell parameters are held constant, the crystal structure optimization moves the silver atom by 0.11 Å, while the ligand is shifted by about 0.4 Å and slightly rotated. The conservation of the packing arrangement and the good agreement between the calculated and the experimental unit cell further supports the validity of our structure solution.

4. Conclusions

The solid-state structure of AgBZT generated from the high resolution synchrotron-generated X-ray powder diffraction data is proposed, which is consistent with the DFT calculations and the analogous, known structure of TlBZT. The AgBZT structure demonstrates the highly bound nature of the silver atoms within the crystal, and the extended, polymeric network of this complex explains the poor solvent solubility as well as its general stability. This structure is another example of how structure determination using powder diffraction data can be used for those cases in which the absence of a suitable crystal prevents the application of standard crystallographic techniques. In this case, the low *R* factors, the match of the calculated X-ray pattern resulting from the calculated structure to the observed X-ray pattern, the good agreement between calculated versus measured density, absence of any unrealistic close contacts, and close similarity to the analogous TlBZT complex, all support the validity of the structure.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.01.022.

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