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# A new silver–silver-bonded dimer complex: solid-state structure of bis[$\mu$-2*H*-1,3-benzoxazine-2,4(3*H*)-dionato]disilver(I)

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**Key indicators**

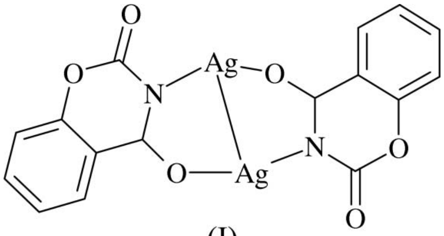
Single-crystal X-ray study
*T* = 293 K
Mean $\sigma$(C–C) = 0.010 Å
*R* factor = 0.039
*wR* factor = 0.102
Data-to-parameter ratio = 8.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The first structure of a silver complex of an aromatic cyclic amide has been determined. The complex is a centrosymmetric dimer, $[Ag(C_8H_4NO_3)_2]$, with the same eight-membered ring construction as silver carboxylates, including a significantly short Ag—Ag bond [2.8042 (12) Å].

## Comment

There is very little information in the literature relating to the solid-state structures of silver cyclic amide complexes, silver glutaramide being the only one of which we are aware (Michalska *et al.*, 1994). Poor solubility, and the corresponding inability to obtain suitable quality single crystals, are the main reasons the solid-state structures of silver complexes such as silver-[2*H*-1,3-benzoxazine-2,4(3*H*)-dione], AgBOD, and silver-1(2*H*)-phthalazinone, AgPAZ, have never been reported. These complexes are extremely difficult to crystallize in sizes suitable for conventional X-ray diffraction techniques. Utilizing slow ligand exchange between 2*H*-1,3-benzoxazine-2,4(3*H*)-dione (HBOD) and AgPAZ, we have now successfully obtained crystals of the title AgBOD dimer, $[AgBOD]_2$, (I). Thus, the first structure of a silver aromatic cyclic amide complex has been resolved and the results are presented here.



(I)

The asymmetric unit of (I) contains one AgBOD unit, with the other AgBOD unit being inversion-related by $(2-x, 2-y, -z)$ (Fig. 1). The molecule of (I) contains an eight-membered ring, analogous to the well known feature exhibited by the solid-state structure of silver carboxylates. As seen in Table 1, the Ag—Ag separation observed is 2.8042 (12) Å, which is well within the normal bonding distance for metallic silver of 2.89 Å (Pauling, 1960). While this distance is normal behavior for silver carboxylate complexes, in which Ag—Ag bonds are commonly observed in the 2.85–3.0 Å range (Cowdery-Corvan & Whitcomb, 2002), it is not very common with other ligands. One silver carboxylate complex has held the record for the shortest Ag—Ag bond of 2.778 (5) Å (Coggon & McPhail, 1972) for 30 years, although a shorter bond of

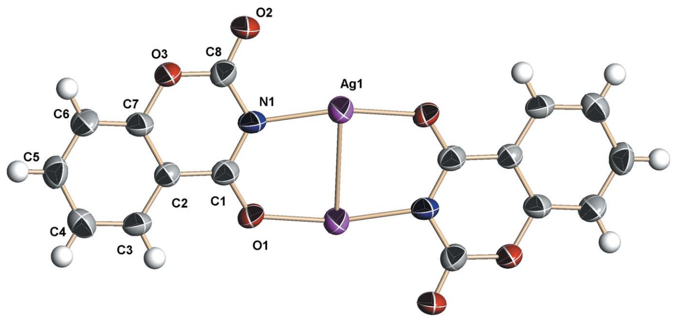


**Figure 1**
The structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary size. Unlabeled atoms are related to labeled atoms by the symmetry operation (2 − $x$, 2 − $y$, −$z$).

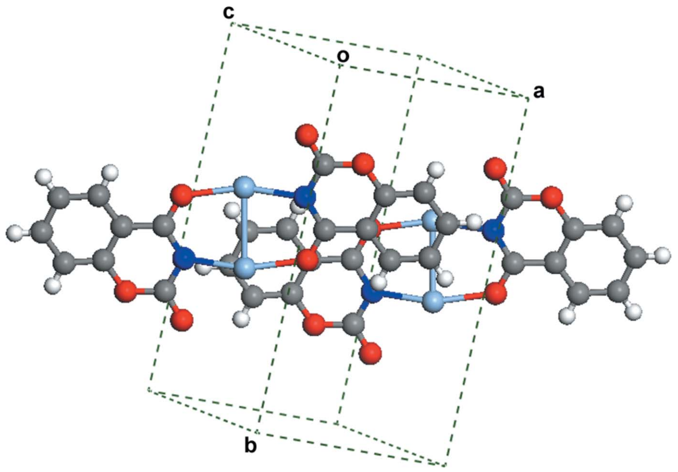


**Figure 2**
The crystal packing of (I), illustrating the parallel but displaced arrangement of benzoxazinone rings.

2.7529 (16) Å has recently been observed for the silver complex of mono-methylphthalate (Whitcomb & Rajeswaran, 2006*a*). The Ag—Ag bond in the title complex is among the shortest such bonding distances ever reported for silver and illustrates the argentophilicity possible when suitable ligands are present. It is worth noting the drastic difference in bonding when the strongly bonding tri-*p*-tolylphosphine (Ptol$_3$) ligand is involved with the normal coordination of the BOD (deprotonated HBOD) ligand (Whitcomb & Rajeswaran, 2006*b*). Without the Ptol$_3$ ligand, not only has the Ag—N distance decreased from 2.254 (3) to 2.147 (6) Å, but the Ag—O bond length has dropped by nearly 0.8 Å, a drastic increase in bond strengths for both bonds. In the title AgBOD dimer, the Ag—N and Ag—O bonds are normal and demonstrate the highly stable nature of this silver complex.

A simple low-molecular-weight species such as (I) might be expected to exhibit some organic solubility. Previously, we proposed that extensive coordination *via* the multiple Ag-bonding groups in the BOD ligand would produce a high-molecular-weight polymer (Whitcomb & Rajeswaran, 2006*b*), not unlike that observed in silver benzotriazole (Rajeswaran *et al.*, 2006) or silver mercaptobenzimidazole (Whitcomb & Rogers, 2006), thereby explaining the poor solubility of the title complex. A packing diagram (Fig. 2) shows that the BOD ligands are packed parallel to each other, and the perpendicular distance between the benzoxazinone rings is 3.246 Å. This distance is common for π–π interactions (Nozary *et al.*, 2002; Yajima *et al.*, 2003; Subramanian *et al.*, 2004; Moers *et al.*, 2002; Blake *et al.*, 1997) and indicates that the π-electronic systems of the BOD ligands can interact with each other. However, in this case there is no π–π overlap, as the benzoxazinone rings are displaced. Instead, a long Ag—O bond of 2.712 (5) Å is observed between the carbonyl and the Ag$^+$ ion in adjacent [AgBOD]$_2$ dimers. The eight-membered ring is constrained to accommodate this bond. Such a bond yields a distorted tetrahedral coordination environment around the Ag atom, satisfying both its coordination number and steric constraints. This interdimer Ag—O bond length is quite common, particularly in silver carboxylate complexes, where it produces a high-molecular-weight coordination polymer which inhibits solvent solubility. While the dimeric interactions between the [AgBOD]$_2$ units in the solid state may contribute toward lowering solubility, the added Ag—O bonding interaction between [AgBOD]$_2$ dimers is likely the main reason for its overall poor solubility.

## Experimental

Crystals of the title compound suitable for single-crystal X-ray diffraction were obtained by slow ligand exchange of HBOD for phthalazinone from the insoluble AgPAZ complex [prepared separately from equimolar amounts of 1(2*H*)-phthalazinone, KOH and silver nitrate in water]. Simply allowing a tetrahydrofuran solution of HBOD (7 ml, 0.20 g) to stand over AgPAZ (0.21 g) for 60 d resulted in the slow growth of colorless crystals of (I) directly on top of the AgPAZ. Decanting the solvent and allowing the product to dry produced crystals. Examination of the crystals under a microscope revealed they were of adequate size for single-crystal X-ray diffraction analysis. However, defects were visible, indicating that the quality of the crystals could affect the overall quality of the single-crystal data.

*Crystal data*

[Ag(C$_8$H$_4$NO$_3$)$_2$]
$M_r$ = 539.98
Monoclinic, $P2_1/c$
$a$ = 7.3677 (9) Å
$b$ = 13.0995 (19) Å
$c$ = 7.4839 (10) Å
$\beta$ = 95.430 (7)°
$V$ = 719.05 (17) Å$^3$
$Z$ = 2

$D_x$ = 2.494 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4643 reflections
$\theta$ = 1.0–23.3°
$\mu$ = 2.77 mm$^{-1}$
$T$ = 293 (2) K
Block, colorless
0.07 × 0.07 × 0.05 mm

*Data collection*

Nonius KappaCCD area-detector diffractometer
$\omega$ scans
Absorption correction: integration (Coppens, 1970)
$T_{\min}$ = 0.068, $T_{\max}$ = 0.200
4643 measured reflections

1022 independent reflections
749 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.080
$\theta_{\max}$ = 23.3°
$h$ = −7 → 8
$k$ = −14 → 14
$l$ = −8 → 8

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.102$
$S = 1.07$
1022 reflections
118 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.288P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.62$ e Å$^{-3}$
$\Delta\rho_{min} = -0.63$ e Å$^{-3}$

### Table 1
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Ag1—N1 | 2.147 (6) | Ag1—O2$^{ii}$ | 2.712 (5) |
| Ag1—O1$^{i}$ | 2.170 (5) | O1—Ag1$^{i}$ | 2.170 (5) |
| Ag1—Ag1$^{i}$ | 2.8042 (12) | | |
| N1—Ag1—O1$^{i}$ | 161.17 (19) | C1—N1—Ag1 | 125.9 (5) |
| N1—Ag1—Ag1$^{i}$ | 81.68 (13) | C8—N1—Ag1 | 113.0 (5) |
| O1$^{i}$—Ag1—Ag1$^{i}$ | 83.01 (13) | | |

Symmetry codes: (i) $-x+2, -y+2, -z$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$. The crystals were weakly diffracting, resulting in a low data-to-parameter ratio. All further attempts to grow better quality single crystals were unsuccessful.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* and *Materials Studio* (Accelrys, 2002); software used to prepare material for publication: *SHELXTL*.

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