

1,1'-[(Ethane-1,2-diylldioxy)di-*o*-phenylene]bis(indoline-2,3-dione) (*L*) and a novel [Ag₂L₂]²⁺ metallocycle based on coordination-driven Ag—O and Ag— π bonds

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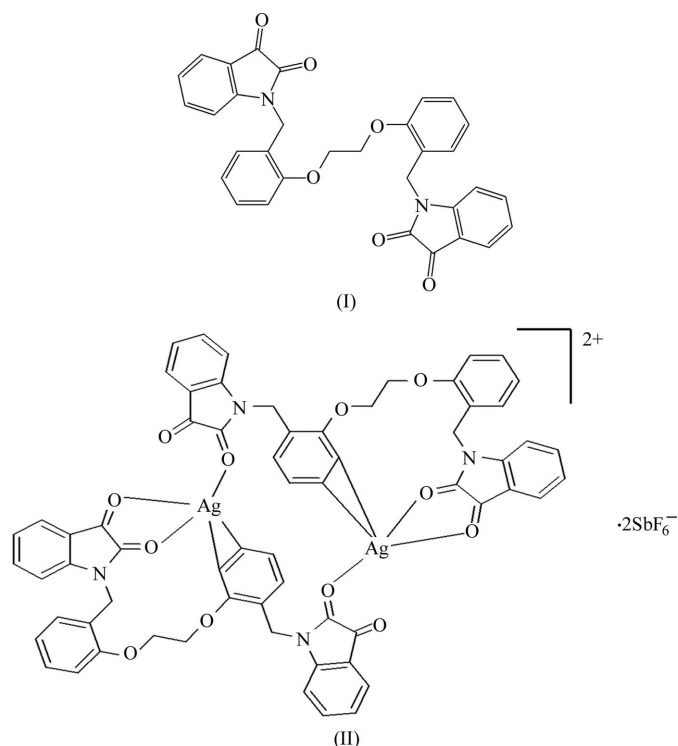
1,1'-[(Ethane-1,2-diylldioxy)di-*o*-phenylene]bis(indoline-2,3-dione), C₃₂H₂₄N₂O₆, *L* or (I), adopts a *trans* conformation with the two terminal indoline-2,3-dione groups located on opposite sides of the central ether bridge, as required by a centre of inversion located at the mid-point of the ethane C—C bond. However, in the discrete binuclear Ag^I metallocycle complex salt bis{ μ -1,1'-[(ethane-1,2-diylldioxy)di-*o*-phenylene]bis(indoline-2,3-dione)}disilver(I) bis(hexafluoroantimonate), [Ag₂(C₃₂H₂₄N₂O₆)₂][SbF₆]₂, (II), synthesized by combination of *L* with AgSbF₆, *L* adopts a *gauche* conformation to bind Ag^I *via* the two indolinedione O atoms and two C atoms from the phenoxy ring. One dione O atom from the opposite side of the ether bridge completes the irregular coordination environment of each Ag^I atom. The complex is on a centre of inversion located between the Ag^I atoms. In the solid state, these binuclear [Ag₂L₂]²⁺ metallocycles stack together *via* intermolecular π - π interactions to generate a one-dimensional chain motif, with the [SbF₆]⁻ counter-ions, which are disordered, located between the chains.

Comment

The design and construction of molecular architectures based on transition metals and organic spacers is currently attracting significant attention (Leininger *et al.*, 2000; Moulton & Zaworotko, 2001; Kitagawa *et al.*, 2004). Over the past decade, numerous supramolecular networks based on metal-containing molecular building blocks linked through weak intermolecular interactions have successfully been achieved (Liu *et al.*, 2006; Reger *et al.*, 2009). Compared with hydrogen-

bond-driven networks, supramolecular networks driven by π - π stacking have received less attention. The π - π interaction undoubtedly plays an important role in determining the arrangement of discrete molecular complexes in the solid state (Khavasi & Fard, 2010).

In order to investigate further how π - π interactions participate in the arrangement of molecular complexes in self-assembled aggregates, we synthesized a new ethylene glycol ether bridging ligand, namely 1,1'-[(ethane-1,2-diylldioxy)di-*o*-phenylene]bis(indoline-2,3-dione), *L* or (I), in which two large aromatic indoline-2,3-dione groups are introduced. The combination of (I) with AgSbF₆ afforded [Ag₂L₂][SbF₆]₂, (II), which features a π - π -stacking-driven one-dimensional chain consisting of novel dinuclear [Ag₂L₂]²⁺ complexes.



The molecule of compound (I) is on a centre of inversion located at the mid-point of the central C16—C16ⁱ bond [symmetry code: (i) $-x, -y + 1, -z$] (Fig. 1) and consequently adopts a *trans* conformation in the solid state, with the two terminal indoline-2,3-dione groups located on opposite sides of the central bridging ether group. The results are similar to previously reported ethylene glycol ether bridging molecules, which typically adopt *trans* conformations in the free state (Han & Zhen, 2005). In addition, the plane of the terminal indoline-2,3-dione group is nearly perpendicular to that of the adjacent phenoxy arene ring; the corresponding dihedral angle is 83.39 (6)°. In the crystal structure, the molecules of (I) are arranged in chains running along the *a* axis, with π - π interactions involving overlapping benzene and five-membered rings [centroid-centroid distance = 3.648 (2) Å] from adjacent parallel indoline-2,3-dione groups (Fig. 2).

In (II), two *L* ligands connect to each of two Ag^I centres, leading to a discrete binuclear Ag^I metallocycle complex,

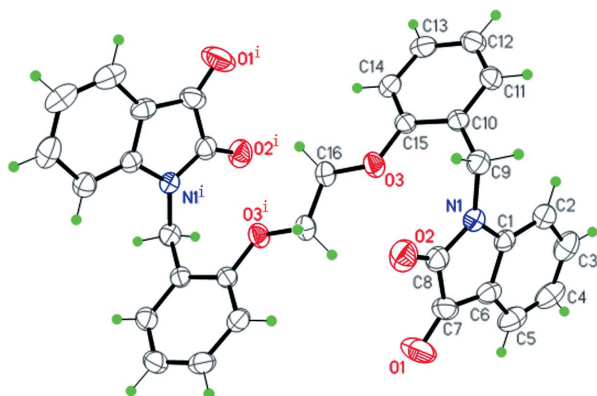


Figure 1
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level. [Symmetry code: (i) $-x, -y + 1, -z$.]

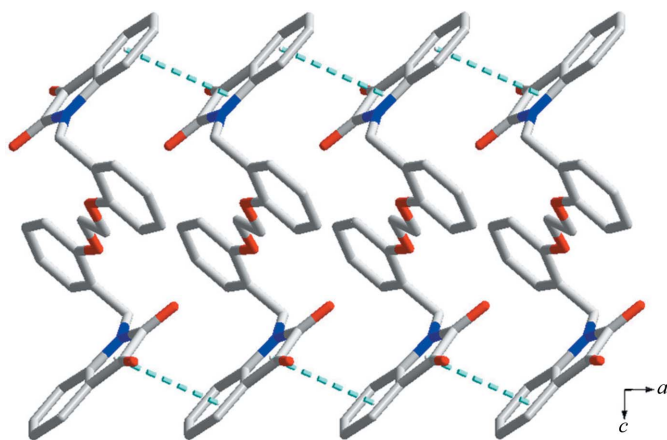


Figure 2
The packing of (I), showing one-dimensional chains driven by π - π interactions (dashed lines).

$[\text{Ag}_2\text{L}_2]^{2+}$, with a centre of inversion located between the Ag^{I} atoms [$\text{Ag}1 \cdots \text{Ag}1^i = 4.749(1) \text{ \AA}$; symmetry code: (i) $-x, -y + 1, -z + 1$] (Fig. 3). The symmetry-unique Ag^{I} centre lies in a five-coordinated environment defined by three O-atom donors ($\text{O}2^i, \text{O}5$ and $\text{O}6$) from two ligands and two π -donor C atoms from a phenoxy arene ring. The $\text{Ag}-\text{O}$ [$2.372(4)$ – $2.577(4) \text{ \AA}$] and $\text{Ag}-\text{C}$ [$2.458(6)$ and $2.572(6) \text{ \AA}$] distances are consistent with those we have previously observed in related complexes (Dong *et al.*, 2006). In the metallacycle formed by each Ag^{I} atom and its primary coordinating *L* ligand, an open rectangular-like loop of dimensions $ca\ 4.74(1) \times 7.60(4) \text{ \AA}$ is found.

Compared with (I), the torsion angle of the central ether group, $\text{O}3-\text{C}16-\text{C}17-\text{O}4$, has changed from 180 to $76.1(5)^\circ$ in (II). Thus, *L* adopts a *trans* conformation about its central core in the free state, (I), but a *gauche* conformation after coordinating to the Ag^{I} centre in (II). The freedom of rotation around the central C–C single bond gives rise to varied conformations which may be frozen by metal-directed interactions. It is well known that flexible ethylene glycol ether bridging ligands with two terminal coordination donors can adopt different conformations under different conditions. For

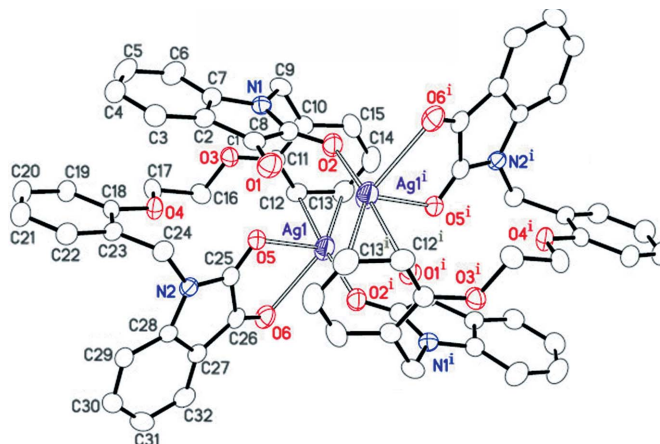


Figure 3
The molecular structure of the $[\text{Ag}_2\text{L}_2]^{2+}$ cations in (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry code: (i) $-x, -y + 1, -z + 1$.]

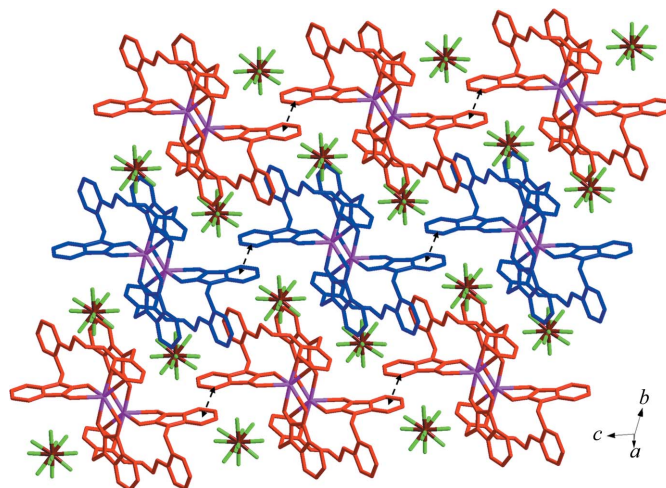


Figure 4
The one-dimensional chains of $[\text{Ag}_2\text{L}_2]^{2+}$ cations in (II), driven by intermolecular π - π interactions (dashed lines). Both orientations of the rotationally disordered $[\text{SbF}_6]^-$ counter-ions, located in the space between the chains, are shown.

example, we have reported previously a study of a flexible ethylene glycol ether bridging ligand adopting different conformations at different temperatures (Dong *et al.*, 2007). The relationship between the planes of the indoline-2,3-dione rings and the adjacent phenoxy rings is similar to that observed in the free ligand, as the corresponding dihedral angles are $89.1(1)$ and $81.9(1)^\circ$.

In the solid state, the dinuclear complexes of (II) are linked to each other through π - π interactions between the benzene rings (atoms $\text{C}27-\text{C}32$) of indoline-2,3-dione groups from two different $[\text{Ag}_2\text{L}_2]^{2+}$ units [centroid-centroid distance = $3.825(5) \text{ \AA}$; slippage of centroids = 1.77 \AA], resulting in one-dimensional chains along the crystallographic *c* axis (Fig. 4). These π - π -interaction-driven one-dimensional chains are stacked in an $\dots AA \dots$ parallel fashion in the *b* direction. Although there appear to be π - π interactions between arene

rings in different chains, the corresponding centroid–centroid distance is 5.503 (8) Å, which is far too long for such interactions. The uncoordinated [SbF₆][−] counter-ions, which are rotationally disordered, are located in the spaces between the chains (Fig. 4).

In summary, the flexible ligand *L* with terminal indoline-2,3-dione groups can be used as a polydentate or chelating ligand to coordinate transition metal ions. A novel one-dimensional supramolecular chain was obtained based on such coordination. This study demonstrates that π – π interactions play an important role in constructing aggregate supramolecular compounds. We are currently extending this study by preparing new ligands of this type with different substituted functional groups. We anticipate this approach to be useful for constructing novel superamolecular complexes.

Experimental

K₂CO₃ (6.91 g, 50 mmol) was added with stirring to a solution of 1,2-bis(2-bromomethylphenoxy)ethane (2.00 g, 5 mmol) and indoline-2,3-dione (1.47 g, 10 mmol) in anhydrous CH₃CN (50 ml). The mixture was stirred for 12 h at ambient temperature and monitored by thin-layer chromatography (TLC). After removal of the solvent under vacuum, the residue was purified on silica gel by column chromatography using CH₂Cl₂–MeOH (30:1 *v/v*) as eluent to afford (I) as a red crystalline solid (1.09 g, 2.05 mmol; yield 41%). IR (KBr pellet, ν , cm^{−1}): 1737 (*s*), 1615 (*s*), 1471 (*s*), 1351 (*s*), 1256 (*m*), 1119 (*w*), 1055 (*w*), 752 (*s*), 630 (*m*), 469 (*m*); ¹H NMR (300 MHz, CDCl₃, 298 K, TMS): δ 7.51 (*d*, 2H, *o*-C₆H₄), 7.31 (*m*, 2H, *m*-C₆H₄), 7.28 (*m*, 2H, *p*-C₆H₄), 7.23–6.98 (*abb*, 8H, –C₆H₄), 6.78 (*d*, 2H, *m*-C₆H₄), 4.91 (*s*, 4H, –CH₂–), 4.42 (*s*, 4H, –CH₂–). Elemental analysis calculated for C₃₂H₂₄N₂O₆: C 72.18, H 4.51, N 5.26, O 18.05%; found: C 72.19, H 4.50, N 5.25, O 18.06%.

A solution of AgSbF₆ (6.46 mg, 0.019 mmol) in benzene (5 ml) was layered on a solution of (I) (10.0 mg, 0.019 mmol) in CH₂Cl₂ (7 ml). The system was left for about one week at room temperature and red crystals of (II) were obtained (7.90 mg, yield 48%). IR (KBr pellet, ν , cm^{−1}): 1712 (*s*), 1611 (*s*), 1491 (*s*), 1343 (*s*), 1245 (*m*), 1119 (*w*), 1062 (*w*), 759 (*s*), 662 (*s*), 472 (*m*).

Compound (I)

Crystal data

C ₃₂ H ₂₄ N ₂ O ₆	$V = 1293.4 (8) \text{ \AA}^3$
$M_r = 532.53$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 4.8272 (17) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 14.194 (5) \text{ \AA}$	$T = 298 \text{ K}$
$c = 18.883 (7) \text{ \AA}$	$0.55 \times 0.14 \times 0.04 \text{ mm}$
$\beta = 91.472 (7)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	2398 independent reflections
6683 measured reflections	1506 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.065$	181 parameters
$wR(F^2) = 0.160$	H-atom parameters constrained
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$
2398 reflections	$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

[Ag ₂ (C ₃₂ H ₂₄ N ₂ O ₆) ₂][SbF ₆] ₂	$\gamma = 100.819 (3)^\circ$
$M_r = 1752.30$	$V = 1533.0 (6) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 10.193 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 11.594 (3) \text{ \AA}$	$\mu = 1.61 \text{ mm}^{-1}$
$c = 14.220 (3) \text{ \AA}$	$T = 298 \text{ K}$
$\alpha = 111.121 (3)^\circ$	$0.30 \times 0.17 \times 0.10 \text{ mm}$
$\beta = 91.073 (3)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	8087 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2003)	5593 independent reflections
$T_{\text{min}} = 0.645$, $T_{\text{max}} = 0.856$	4279 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.053$	3 restraints
$wR(F^2) = 0.134$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 1.07 \text{ e \AA}^{-3}$
5593 reflections	$\Delta\rho_{\text{min}} = -1.02 \text{ e \AA}^{-3}$
481 parameters	

The H atoms in both structures were placed in idealized positions and treated as riding, with C–H = 0.93 (aromatic), 0.97 (CH₂) and, in (II), 0.98 Å (CH with C coordinated to Ag), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The [SbF₆][−] anion was statistically disordered over two orientations, with site-occupation factors set at 0.50:0.50. The Sb1–F3/Sb1–F3', Sb1–F6/Sb1–F6' and Sb1–F4/Sb1–F4' pairs of bond lengths were restrained to be the same within a standard deviation of 0.01 Å. Atom F2' was constrained to have the same anisotropic displacement parameters as atom F2.

For both compounds, data collection: SMART (Bruker, 2003); cell refinement: SMART; data reduction: SAINT (Bruker, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3280). Services for accessing these data are described at the back of the journal.

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