

Mono- and Dinuclear Complexes of a Flexible Schiff Base Ligand – Crystal Structures of a Bishelicate and Two Acentric Monohelicates

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Neutral Ni^{II}, Pd^{II}, Cu^{II}, Ag^I, Zn^{II}, Cd^{II}, and Pb^{II} complexes of *N,N'*-bis(2-tosylaminobenzylidene)-1,4-diaminobutane (H₂SB) have been prepared. The Schiff base seems to exist in a helically coiled state around nickel, copper and zinc ions, but not in Pd(SB)·3H₂O·MeCN, Ag₂(SB)·2H₂O, Cd(SB)·3H₂O, and Pb(SB)·3H₂O, the metal ions of which seem to show planar geometries. The determination of the absolute structures of Cu(SB)·MeCN and Zn(SB)·2MeCN, which crystallise as non-centrosymmetric racemic compounds, shows that these metal(II) ions assume distorted tetrahedral coordination

geometries involving the four N atoms of the dianionic ligand. X-ray structural characterisation also shows that this ligand behaves as a N₂+N₂ donor in the [4+4] bishelicate Ni₂(SB)₂·5MeCN. Secondary interactions between metal centres and one of the O atoms of each tosyl group are detected in these three crystal structures, being especially intense in the dimeric one.

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Introduction

Among other reasons, helical metal complexes^[1–4] have attracted physicists' and chemists' attention due to their potential optical activity.^[5] As achiral ligands are unable to induce predetermined chirality, helicates crystallise as racemic compounds or as mechanical mixtures of enantiopure crystals (racemic mixtures or conglomerates).^[6–7] Of these two types of crystalline racemates, conglomerates are far easier to resolve, but much rarer.

The obtaining of non-centrosymmetric inorganic materials with nonlinear optical properties is undoubtedly a challenge in chemistry.^[8] Since the inverse of a left-handed helix is a right-handed one, a helical compound may crystallise with an inversion centre if both types of handedness appear in a crystal. Thus, with achiral ligands, the heterochiral interaction required to form racemic compounds takes place in centrosymmetric space groups, the overwhelming majority, whereas the minority homochiral crystallisation required to obtain conglomerates exclusively occurs in non-centrosymmetric space groups.

We have recently reported the crystal structures of the two compounds Zn₂(SB¹)₂·1.5H₂O·MeCN^[9] (a typical racemic compound) and Λ -Zn(SB²)·H₂O,^[10] which homochirally crystallises as a conglomerate. Despite the intrinsic

similarities between these two symmetric *N*-tosyl-substituted Schiff bases, which contain (CH₂)₃ and CH₂CH(OH)CH₂ groups, respectively, as spacers (Scheme 1), their behaviour in their corresponding helical Zn^{II} complexes is either binucleating (N₂+N₂ donor) or mononucleating (N₄ donor), respectively. Another ligand with a three-membered spacer, although a more rigid one, in the form of H₂SB³ (Scheme 1), only yielded racemic monohelicates.^[11]

In an effort to understand the behaviour of this type of helical thread, we wished to explore how the higher flexibility of a (CH₂)₄ spacer might influence the coordination behaviour and spatial arrangement of the potential helical H₂SB ("S" arranged, for a classic bisbidentate conduct, in Scheme 1) in several main group and transition (first and second row) metal complexes.

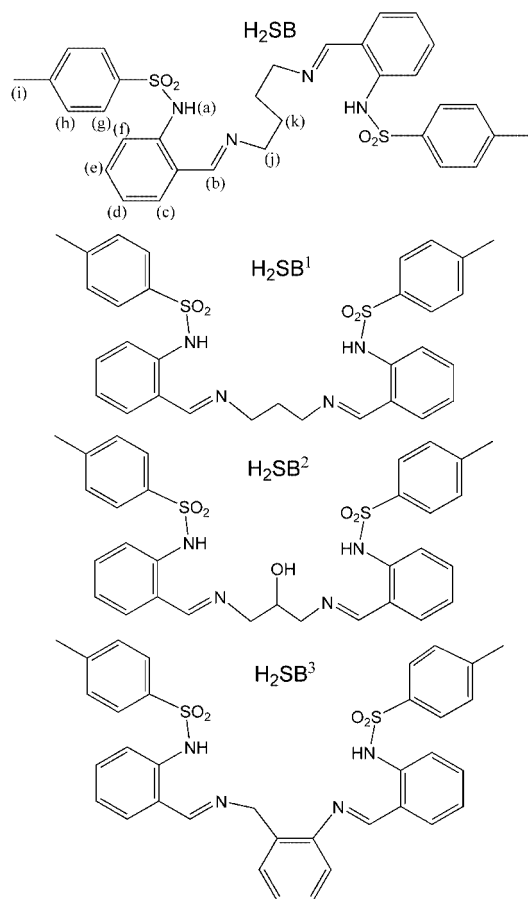
Results and Discussion

Mass and IR Spectroscopic Data

The mass spectra of these complexes exhibit medium- to high-intensity signals, with satisfactory isotopic profiles, attributable to [M(SB) + H]⁺ species, as expected for mononuclear and monomeric compounds. This kind of species is more in accordance with a solvated nature than with coordinating behaviour of the water molecules present in these complexes. With respect to the ESI MS spectrum of the Ag^I complex, a group of peaks assignable to [Ag₂(SB) + H]⁺ species could be notable, since it seems to corroborate the Ag₂(SB)·2H₂O formula found by elemental analysis.

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Scheme 1. Schematic representation of the *N*-tosyl-substituted Schiff bases H_2SB^1 , H_2SB^2 , H_2SB^3 , and H_2SB (with labelling scheme for 1H NMR studies)

It may also be worth mentioning that no peaks with intensities higher than 4% can be detected in the spectra of these complexes in those regions in which dimeric species could appear, even in the case of the dimeric Ni^{II} complex. This prevents the use of the ESI-MS technique to determine whether these complexes are of the type $M(SB)$ or $M_2(SB)_2$.

The IR spectra of these complexes contain absorptions consistent with the presence of the N_4 donor ligand. The CN stretching frequencies show shifts to lower wavenumber values with respect to those observed for the free ligand.^[12] The slight shifts of the $\nu(C=N)$ bands to lower wavenumber (in the $1-15\text{ cm}^{-1}$ range) contrasts with the substantial shifts observed for the $\nu(C-N)$ stretching frequencies ($30-45\text{ cm}^{-1}$). These facts, together with the absence of the $\nu(N-H)$ band, are in agreement with double deprotonation of the ligand, as well as with the participation of both the amide and imine N atoms in the coordination to the metal centres.^[9-12]

Other bands attributable to $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ vibration modes also experience significant decreases in their frequencies. This behaviour could be a sign of interaction between the metal centre and the O atoms belonging to the tosyl groups.

Single-Crystal X-ray Diffraction Studies

$Cu(SB) \cdot MeCN$ and $Zn(SB) \cdot 2MeCN$

Slow evaporation of saturated acetonitrile solutions of $Cu(SB) \cdot 4H_2O$ and $Zn(SB) \cdot H_2O$ yielded brown and yellow X-ray-quality crystals of $Cu(SB) \cdot MeCN$ and $Zn(SB) \cdot 2MeCN$, respectively. The crystallographic analyses reveal that in both asymmetric units, a solvated acetonitrile molecule (with 0.5 and 1 occupancy sites, respectively) coexists with half a molecule of the symmetric helical complex $M(SB)$ ($M = Cu$ or Zn), the metal ion of which is situated on a twofold axis positioned along z . The whole complex molecules can be generated by the same symmetry operation ($-x, -y, z$). All the atoms so generated have been labelled with #1.

Although both helical enantiomers (Λ and Δ) are present in the unit cell, only the molecular structure of the single-stranded helix corresponding to Λ - $Cu(SB)$ is represented in Figure 1, whereas Δ - $Zn(SB)$ is shown in Figure 2, with the atom labelling schemes used in Table 1. This table lists the most significant bond lengths and angles.

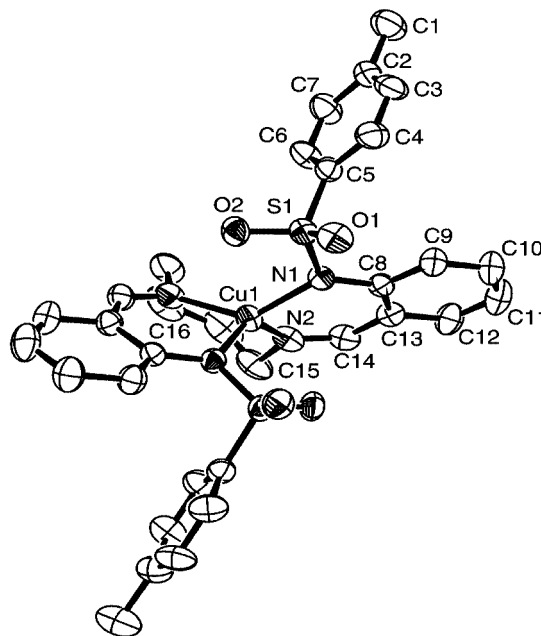


Figure 1. ORTEP view of Λ - $Cu(SB)$, contained in the $Cu(SB) \cdot MeCN$ unit cell; symmetry transformations used to generate equivalent atoms: #1 $-x, -y, z$

The ions in both complexes are symmetrically tetra-coordinated to the four N atoms of the Schiff base, with bond lengths in the ranges typical for this sort of complex. Both coordination environments can be regarded as distorted tetrahedra, especially that corresponding to the Cu^{II} ion, in that the dihedral angles between the two $N-M-N$ terminal planes (θ) are $65.79(14)^\circ$ and $73.31(7)^\circ$ for the Cu^{II} and Zn^{II} complexes, respectively. Moreover, one of the O atoms of each tosyl group [O(2) and O(2)#1] is weakly interacting with the Cu^{II} and Zn^{II} ions, although these $M \cdots O$ distances (ca. $2.8\text{ \AA}$) are too long to be viewed as true coordinated bonds. The $S(1) \cdots S(1)^{\#1}$ distance (about

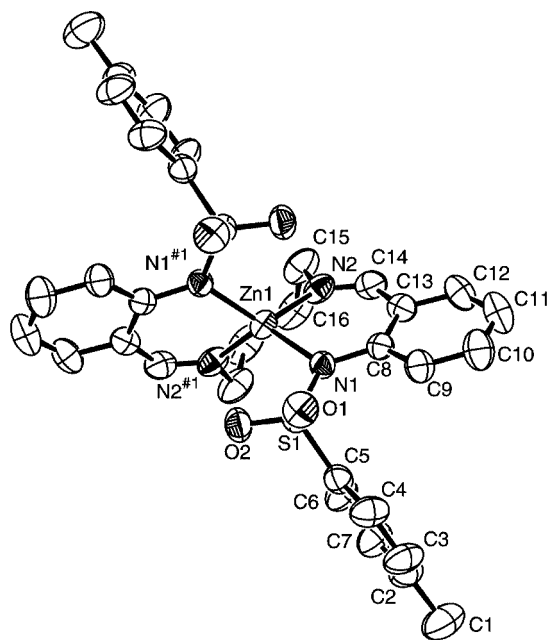


Figure 2. ORTEP view of Δ -Zn(SB), contained in the Zn(SB)·2MeCN unit cell; symmetry transformations used to generate equivalent atoms: $\#1 -x, -y, z$

4.34 and 4.62 Å for the copper and zinc complex, respectively) could in both cases be regarded as a rough estimate of the pitch.^[3] As also occurs in other related monohelicates,^[9–12] if we consider the whole ligand, the wrapping angle would exceed 360°.

The chemical species concerned here, Cu(SB)·MeCN and Zn(SB)·2MeCN, are intrinsically chiral due to their helicity, crystallising in the non-centrosymmetric space group $Fdd2$ of the orthorhombic system, belonging to the $mm2$ crystal class. Although this class is not qualified as chiral or enantiomorphic, it does present a polar axis direction (z),^[13]

which means that the unit-cell origin may be arbitrarily placed along this axis. In these cases, the values found for the Flack parameter^[14] [0.03(19) and 0.021(11) for the Cu^{II} and Zn^{II} complexes, respectively] determine a correct absolute structure, as well as a closely coincident orientation of the structure with respect to the polar axis, more than the enantiopurity or racemic twinning evaluation related with homochiral crystals.

Both crystal packings, which we can see in Figure 3 for Zn(SB)·2MeCN, are based on feeble C–H···O, C–H/ π and π – π stacking interactions. They clearly show both types of helical molecules, with right- and left-handedness (Δ and Λ enantiomers, respectively) arranged on infinite sheets parallel to their C faces, indicative of their non-linearity. This heterochiral crystallisation satisfactorily explains the lack of global optical activity exhibited by crystalline samples of these racemic compounds in acetonitrile solution.

$Ni_2(SB)_2 \cdot 5MeCN$

This crystal structure shows the double helical assembly of this neutral dinuclear Ni^{II} complex (Figure 4), in which the ligand assumes a N_2+N_2 bisbidentate coordinating behaviour. As is the case for many other homotopic double-stranded helicates, this one crystallises as a racemate in the most frequently occurring space group for metallohelicates: the centrosymmetric $C2/c$.^[3] The X-ray structural characterisation reveals that its asymmetric unit contains half the bishelicate, with a crystallographically imposed twofold symmetry, which allows the other half molecule to be generated by use of the symmetry operation $-x, y, -z + 1/2$. All the atoms related in this way have been denoted with $\#1$. Additionally, two and a half molecules of solvated acetonitrile are also present, with some disorder, in the asymmetric unit.

Table 1. Selected bond lengths and angles for $Ni_2(SB)_2 \cdot 5MeCN$, Cu(SB)·MeCN, and Zn(SB)·2MeCN

Ni ₂ (SB) ₂ ·5MeCN ^[a]		Cu(SB)·MeCN ^[b]		Zn(SB)·2MeCN ^[b]	
Bond lengths					
Ni(1)–N(21)	1.965(6)	Cu(1)–N(1)	1.965(3)	Zn(1)–N(1)	1.978(2)
Ni(1)–N(11)	1.973(8)	Cu(1)–N(1) ^{#1b}	1.965(3)	Zn(1)–N(1) ^{#1b}	1.978(2)
Ni(1)–N(12)	1.987(6)	Cu(1)–N(2)	1.961(4)	Zn(1)–N(2)	2.009(2)
Ni(1)–N(22)	2.030(5)	Cu(1)–N(2) ^{#1b}	1.961(4)	Zn(1)–N(2) ^{#1b}	2.009(2)
N(11)–C(108)	1.418(11)	N(1)–C(8)	1.393(5)	N(1)–C(8)	1.405(3)
N(11)–S(1)	1.588(9)	N(1)–S(1)	1.612(3)	N(1)–S(1)	1.605(2)
N(12)–C(114)	1.316(9)	N(2)–C(14)	1.273(6)	N(2)–C(14)	1.274(4)
N(21)–S(2)	1.605(5)	N(2)–C(15)	1.455(6)	N(2)–C(15)	1.475(4)
N(21)–C(208)	1.408(9)	S(1)–O(1)	1.436(3)	S(1)–O(1)	1.444(2)
N(22)–C(214)	1.267(9)	S(1)–O(2)	1.447(3)	S(1)–O(2)	1.444(2)
Bond angles					
N(11)–Ni(1)–N(22)	104.0(3)	N(1)–Cu(1)–N(1) ^{#1b}	108.2(2)	N(1)–Zn(1)–N(1) ^{#1b}	119.02(13)
N(11)–Ni(1)–N(12)	91.3(3)	N(1)–Cu(1)–N(2)	93.90(14)	N(1)–Zn(1)–N(2)	94.47(9)
N(11)–Ni(1)–N(21)	151.9(3)	N(1)–Cu(1)–N(2) ^{#1b}	132.99(14)	N(1)–Zn(1)–N(2) ^{#1b}	124.55(9)
N(12)–Ni(1)–N(21)	107.0(2)	N(2)–Cu(1)–N(2) ^{#1b}	100.5(2)	N(2)–Zn(1)–N(2) ^{#1b}	101.07(15)
Torsion angles					
N(12)–C(115)–C(116)–C(16) ^{#1a}	45.7(6)	N(2)–C(15)–C(16)–C(16) ^{#1b}	–77.8(7)	N(2)–C(15)–C(16)–C(16) ^{#1b}	–78.3(4)
N(22)–C(215)–C(216)–C(216) ^{#1a}	75.7(6)				

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

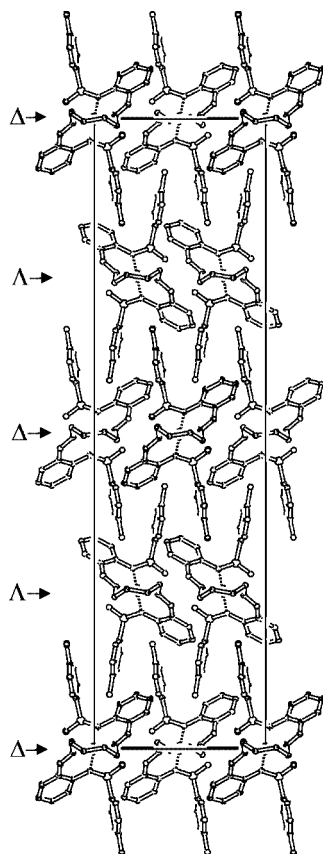


Figure 3. View normal to the *C* face of the crystal packing of $\text{Zn}(\text{SB})\cdot 2\text{MeCN}$, showing the lamination of both types of helical enantiomers (Δ and Λ); acetonitrile molecules have been omitted for clarity

The [4 + 4] bis-helical nature of $\text{Ni}_2(\text{SB})_2\cdot 5\text{MeCN}$ is not common for dinuclear Ni^{II} complexes with bis-bidentate ligands, which mostly give rise to [6 + 6] triple-stranded helicates.^[3–4,15] However, so far the X-ray evidence available indicates, this sort of *N*-tosyl-substituted ligand only yields four coordinate complexes, both in double-stranded helicates^[9,16] and monohelicates.^[9–12] This even occurs with metal ions that characteristically display pseudooctahedral geometries, such as Mn^{II} or Fe^{II} , in that they exhibit unfamiliar tetrahedral geometries with H_2SB^3 .^[11]

The explanation for this low coordination number may lie in the bulky tosyl groups. On one hand, they appear to exert such substantial steric hindrance as apparently to avoid the presence of exogenous coordinating groups, solvent molecules or additional ligand units suitable for achieving an actual hexa-coordination. On the other hand, this uncommon tetra-coordination of the Ni^{II} ions may be easier to understand if we also consider that significant secondary $\text{Ni}\cdots\text{O}$ interactions (ca. 2.5 Å) exist between the Ni^{II} ion and an O atom of each adjacent tosyl group [O(2) and O(4)]. As a result, each N_4 pseudotetrahedral Ni^{II} environment (Figure 4) suffers a substantial seesaw-shaped distortion that the value of θ (ca. 80.15°) does not reveal at first sight, but the N–Ni–N angles do (Table 1). Although these minor $\text{M}\cdots\text{O}$ contacts are typical of metal complexes containing this type of *N*-tosyl-substituted Schiff-base

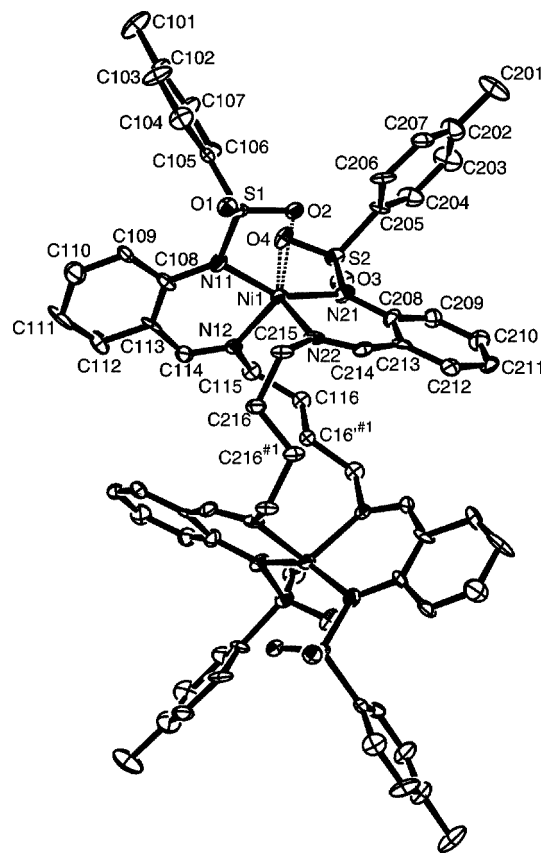


Figure 4. ORTEP view of $\Delta, \Delta\text{-Ni}_2(\text{SB})_2$ contained in the $\text{Ni}_2(\text{SB})_2\cdot 5\text{MeCN}$ unit cell, with the secondary $\text{Ni}\cdots\text{O}$ interactions shown as dotted lines; symmetry transformations used to generate equivalent atoms: #1 $-x, y, -z + 1/2$

ligand,^[9–12,16] it could be worthy of mention that these interactions seem to be significantly shorter when the ligand behaves as N_2+N_2 -bisbidentate (about 2.5 Å),^[9,16] than as merely N_4 -tetradentate (usually about 2.8 Å),^[9–12] as in the preceding Cu^{II} and Zn^{II} complexes (vide supra).

The bis-helical arrangement of $\text{Ni}_2(\text{SB})_2\cdot 5\text{MeCN}$ with metal coordination environments that could be also regarded as severely distorted N_4O_2 pseudooctahedral (Figure 4), therefore seems to be more appropriate than simple mononucleating N_4 donor behaviour for satisfying the stereochemical requirements of Ni^{II} (preferably octahedral). This tendency of Ni^{II} to achieve a pseudooctahedral coordination through secondary $\text{Ni}\cdots\text{O}$ contacts had also been indicated for some mesohelicates containing bisbidentate ligands designed to provide tetrahedral coordination environments.^[17] Something similar also occurred in the case of $\text{Ni}_2(\text{SB}^1)_2\cdot \text{MeCN}$,^[16] whereas the rigid H_2SB^3 (Scheme 1), designed to be N_4 -mononucleating, is able to impose a distorted tetrahedral geometry, though also exhibiting $\text{Ni}\cdots\text{O}$ interactions (2.5 and 2.8 Å).^[11] In contrast, a simple N_4 -compartment can adequately fulfil the tetrahedral coordination preferences of Cu^{II} ions. Unlike Cu^{II} and Ni^{II} , the spherical Zn^{II} ions (d^{10}) allow both monohelicates to be obtained, with H_2SB , H_2SB^2 [10] or H_2SB^3 , and also a bis-helicate,^[9] when interacting with H_2SB^1 (Scheme 1). Hence, while the spacer length has a significant influence on the

stereochemistry of some types of helicates,^[18] it does not appear to be a crucial factor for providing single- or double-stranded helicates with *N*-tosyl-substituted Schiff bases.

Ideally, homotopic helicates should give rise to palindromic helices; this means with constant pitch,^[3] as occurs in $\text{Ni}_2(\text{SB}^1)_2 \cdot \text{MeCN}$,^[16] in which both $(\text{SB}^1)^{2-}$ threads are similarly arranged, the centroids of their benzyldiene groups being at about 10 Å. In principle, the ligand array in $\text{Ni}_2(\text{SB})_2 \cdot 5\text{MeCN}$ could appear similar to that, even also showing a minor and a major groove. However, a thorough inspection allows it to be established that the higher flexibility of SB^{2-} seems to tolerate a clear disparity of both helical strands, with substantially different arrangements (Figure 5). Thus, we can see that the $\text{C101}-\text{C101}^{\#1}$ ligand strand (shaded in Figure 5) seems more stretched than the $\text{C201}-\text{C201}^{\#1}$ one, which shows a pronounced folding. Hence, the theoretical pitch must be longer for the first one. In fact, the distances between their benzyldiene centroids are about 10.9 and 8.6 Å, respectively. Although the two coilings are fairly different, their assembly, lacking significant intra- or intermolecular $\pi-\pi$ or $\text{C}-\text{H}/\pi$ interactions, produces a symmetric, even crystallographically, homotopic double-helix.^[3] Consequently, their also different wrapping angles could compensate for their differences, and result in an intramolecular $\text{Ni}\cdots\text{Ni}$ distance of about 6.8 Å. This is only slightly longer than that reported for $\text{Ni}_2(\text{SB}^1)_2 \cdot \text{MeCN}$ (6.2 Å).^[16] Similitude in the intramolecular $\text{M}\cdots\text{M}$ distances with $(\text{CH}_2)_2$ and $(\text{CH}_2)_3$ bridging groups has also been observed for some [6+6] Fe^{II} bishelicates.^[19]

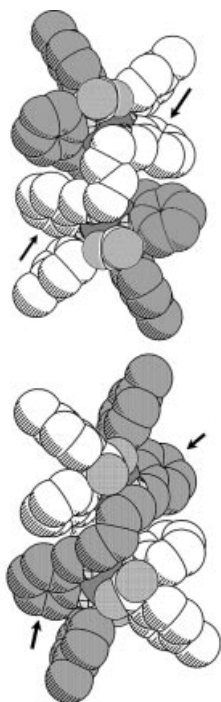


Figure 5. Two opposite views of a compact ball scheme for $\text{Ni}_2(\text{SB})_2 \cdot 5\text{MeCN}$ with the helical axis parallel to left margin; the more stretched ligand strand ($\text{C101}-\text{C101}^{\#1}$) is shaded; the intramolecular distances between those ring centroids signed by arrows are: 8.6 Å (top) and 10.9 Å (bottom)

Finally, the $\text{C}-\text{N}$ distances found confirm those observed in the IR spectroscopy section. Thus, the $\text{C}=\text{N}_{\text{imine}}$ and $\text{C}-\text{N}_{\text{imine}}$ distances show values similar to those reported for the free ligand,^[12] whereas the $\text{C}-\text{N}_{\text{amide}}$ distances are significantly longer. The $\text{M}-\text{N}$ distances (Table 1) are in the usual range reported for Ni^{II} , Cu^{II} , and Zn^{II} complexes containing N_{amide} and N_{imine} donor atoms.^[9–12,16,20] As was also suggested by the IR techniques, $\text{M}\cdots\text{O}$ interactions seem to affect the $\text{S}-\text{O}$ bonds, since these are slightly longer than those found for the free ligand.^[12]

¹H NMR Studies

$\text{Zn}(\text{SB}) \cdot \text{H}_2\text{O}$

In order to investigate the solution behaviour of $\text{Zn}(\text{SB}) \cdot \text{H}_2\text{O}$, we have studied its ¹H NMR spectra in CDCl_3 at temperatures ranging between 323 and 218 K (deposited as Electronic Supporting Information, see footnote on the first page of this article). From these results, and in view of the ligand symmetry, the observation of two signals each for H_j and H_k (Scheme 1), must be a consequence of the diastereotopic natures of the geminal protons of each methylene group. This is consistent with a helical arrangement,^[21] as also occurred in the solid state. Since both methylene protons are non-equivalent even at 323 K, $\text{Zn}(\text{SB}) \cdot \text{H}_2\text{O}$ seems to preserve its helical conformation in chloroform solution on the NMR timescale, which is also indicative of a strong coordination of the N atoms to the metal centre. On the basis of the kinetic stability of this complex, the results obtained at room temperature can be used as a diagnostic probe for helicity.

Both COSY and NOESY experiments at room temperature in chloroform, acetonitrile or dimethyl sulfoxide solutions allow a full assignment of the ¹H NMR signals (see Experim. Section). They clearly show AB spin behaviour of the methylene protons on the NMR timescale, since those protons situated near to equatorial positions with respect to the $\text{C}(15)\text{N}(2)\text{C}(14)$ or $\text{C}(15^{\#1})\text{N}(2^{\#1})\text{C}(14^{\#1})$ planes, H_{jeq} and H_{keq} , are observed at higher field than those situated close to axial positions (H_{jax} and H_{kax}).

A NOESY experiment (Figure 6) shows coupling of H_b with H_c and H_{jeq} (but not with H_{jax}), as well as between H_g and H_f . Consequently, these intramolecular $\text{H}\cdots\text{H}$ distances should be lower than ca. 3.1 Å in solution. The X-ray crystal studies determined that the $\text{H}_b\cdots\text{H}_c}$, $\text{H}_b\cdots\text{H}_{\text{jeq}}$ and $\text{H}_g\cdots\text{H}_f$ distances in the solid state are in the 2.2–2.7 Å range, whereas $\text{H}_b\cdots\text{H}_{\text{jax}}$ is higher (3.1 Å). These facts seem to indicate that the spatial arrangement of the helical ligand in the zinc complex is analogous, both in the solid state and in solution (even in a coordinating solvent such as dmso).

$\text{Pb}(\text{SB}) \cdot 3\text{H}_2\text{O}$

A NOESY experiment was a key element in the full assignment of the proton signals (deposited as Electronic Supporting Information). Since the H_b and H_i signals are two clear references in the spectrum, the H_i-H_b} , H_b-H_c} and H_b-H_j couplings allow the unequivocal identification

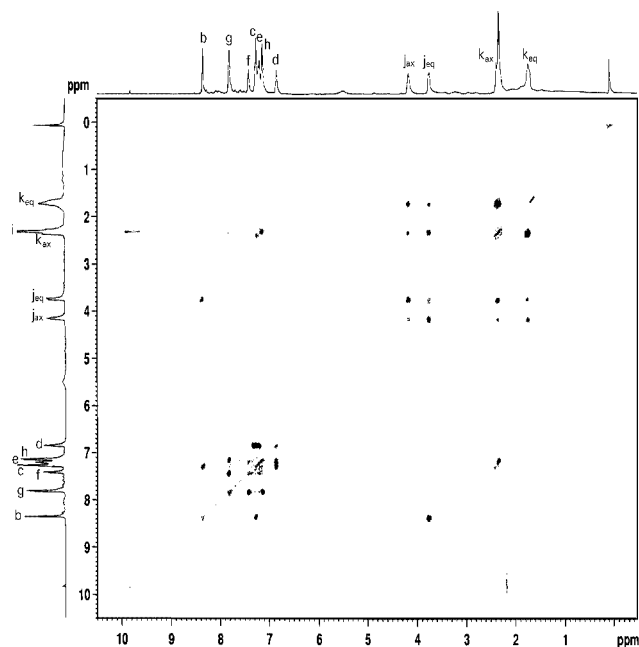


Figure 6. NOESY experiment for $\text{Zn}(\text{SB})\cdot\text{H}_2\text{O}$ in CDCl_3 at 300 K

of H_h , H_c , and H_j , respectively. Similarly, the $\text{H}_c\text{--H}_d$, $\text{H}_d\text{--H}_e$, and $\text{H}_e\text{--H}_f$ couplings provide evidence of the H_d , H_e , H_f , and H_g positions, whilst the absence of coupling between H_g and H_f seems to indicate that the spatial arrangement of the tosyl groups, with respect to benzylidene rings, is not equivalent to that observed in $\text{Zn}(\text{SB})\cdot\text{H}_2\text{O}$.

The experiment mentioned also shows the enantiotopic nature of the geminal protons in each methylene group on the NMR timescale at room temperature. This could rule out a helical arrangement of SB^{2-} in this complex. Although the observation of one signal each for H_j and H_k (in $[\text{D}_6]\text{DMSO}$ or Cl_3CD at room temperature) could be due to a fast exchange between helical and non-helical arrangements of SB^{2-} in the Pb^{II} complex, a series of ^1H NMR spectra in the 323–218 K range reveals the kinetic stability of this complex in chloroform solution, even at high temperatures.

$\text{Pd}(\text{SB})\cdot 3\text{H}_2\text{O}\cdot\text{MeCN}$, $\text{Ag}_2(\text{SB})\cdot 2\text{H}_2\text{O}$ and $\text{Cd}(\text{SB})\cdot 3\text{H}_2\text{O}$

The diamagnetism of the Pd^{II} complex attests to the electronic pairing in the d_{xz} , d_{yz} , d_z^2 , and d_{xy} orbitals, which is consistent with a square planar symmetry for a d^8 ion. Both the spectra of the Pd^{II} and Cd^{II} complexes display only one signal each for H_j and H_k , as would be expected for a planar arrangement of SB^{2-} . NOESY experiments in $[\text{D}_6]\text{DMSO}$ at room temperature allow a rigorous assignment of the ^1H NMR signals for these complexes (see Experm. Section).

The diamagnetism shown by $\text{Ag}_2(\text{SB})\cdot 2\text{H}_2\text{O}$ attests to the presence of Ag^{I} ions and consequently the inability of the ligand to stabilise Ag^{II} even under strongly oxidising conditions (10 V). As in previous cases, the observation of only one signal each for H_j and H_k at room temperature (Electronic Supplementary Material) is indicative of a non-heli-

cal arrangement of SB^{2-} in this complex. Its anomalous stoichiometry and the ligand versatility allows the postulation that the ligand could behave as bisbinucleating, so it could act as a bridge between the two Ag^{I} ions.

Diffuse Reflectance and Magnetism

The diffuse reflectance spectrum of $\text{Ni}_2(\text{SB})_2\cdot 2\text{H}_2\text{O}$ is characterised by a medium intensity broad band around 680 nm, which is attributed to a $d\text{--}d$ transition expected for d^8 ions in tetrahedral fields.^[22] In the spectrum of $\text{Cu}(\text{SB})\cdot 4\text{H}_2\text{O}$, the only absorption attributable to a $d\text{--}d$ transition is observed at about 460 nm, which is also consistent with a tetrahedral geometry.^[23]

The magnetic moment for the Ni^{II} dimer at room temperature (3.0 BM per mol of Ni^{2+}) is quite low for a tetrahedral compound. This could be caused by a considerable distortion from the ideal geometry, resulting in a fall in the orbital contribution to this value.^[24] In fact, we have found a similar value (3.3 BM per mol of Ni^{2+}) for $\text{Ni}_2(\text{SB}^{\text{I}})_2\cdot\text{MeCN}$,^[16] in which the ligand, helical arrangement and the $\text{Ni}\cdots\text{Ni}$ distance (ca. 6.2 Å) are not very different from those observed for $\text{Ni}_2(\text{SB})_2\cdot 2\text{H}_2\text{O}$. No coupling interactions between the two Ni^{2+} ions are to be expected, because these are quite far apart (ca. 6.8 Å) and the ligands seem incapable of transmitting any interaction. Finally, a μ value at room temperature (2.1 BM) in the narrow range expected for a magnetically dilute tetrahedral compound arises from the magnetic susceptibility measurements for $\text{Cu}(\text{SB})\cdot 4\text{H}_2\text{O}$.

Conclusions

The studied N_4 donor ligand displays a helical arrangement around those ions corresponding to the fourth period – Ni^{II} , Cu^{II} , and Zn^{II} – but it appears planar around Pd^{II} , Ag^{I} , Cd^{II} , and Pb^{II} ions, belonging to the fifth and sixth periods. Ionic radii thus seem to play a relevant role in the stereochemistry. Similarly, and in view of the secondary $\text{M}\cdots\text{O}$ interactions, a predilection for pseudooctahedral rather than distorted tetrahedral environments could be responsible for the obtaining of double-stranded Ni^{II} helicates, instead of monohelicates, with *N*-tosyl-substituted Schiff bases containing a pure alkyl chain of three or four members as spacer. Both Cu^{II} and Zn^{II} ions assume distorted tetrahedral coordination geometries involving the four N atoms of the dianionic ligand in their monohelicates, whereas the ligand behaves as a N_2+N_2 donor in $\text{Ag}_2(\text{SB})\cdot 2\text{H}_2\text{O}$ and $\text{Ni}_2(\text{SB})_2\cdot 5\text{MeCN}$.

The studied $(\text{CH}_2)_4$ spacer between the two 2-tosylaminobenzylidene units has not given rise to homochiral crystals of $\text{Ni}_2(\text{SB})_2\cdot 5\text{MeCN}$, $\text{Cu}(\text{SB})\cdot\text{MeCN}$, or $\text{Zn}(\text{SB})\cdot 2\text{MeCN}$. However the last two crystallise in an acentric space group with a polar axis, forming alternative sheets of the two helical enantiomers (Λ and Δ), which is unusual for helical racemic compounds.

Experimental Section

General: Elemental analyses were performed on a Carlo–Erba EA 1108 analyser. NMR spectra were recorded on a Bruker DRX 500 spectrometer in CDCl_3 , CD_3CN , or $[\text{D}_6]\text{DMSO}$ as solvents. Infrared spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the $4000\text{--}600\text{ cm}^{-1}$ range. Electrospray mass spectra were recorded on a LC/MSD Hewlett–Packard 1100 spectrometer with DMSO and methanol with formic acid (2%) as solvent. The FAB mass spectrum was recorded on a Micromass Autospec spectrometer, with *m*-nitrobenzyl alcohol as matrix. Diffuse reflectance spectra were recorded on a Perkin–Elmer Lambda 9 spectrophotometer. Magnetic susceptibility measurements were performed on pulverised samples at room temperature with a Sherwood Scientific magnetic susceptibility balance.

Syntheses: Chemicals of the highest commercial grade available (Aldrich) were used as received. *N,N'*-Bis(2-tosylaminobenzylidene)-1,4-diaminobutane (H_2SB) was prepared^[12] by condensation of 2-(tosylamino)benzaldehyde^[25] with 1,4-diaminobutane. Complexes, except for $\text{Pd}(\text{SB})\cdot 3\text{H}_2\text{O}\cdot \text{MeCN}$, were obtained by an electrochemical method,^[9–12,22] in which a metal anode was oxidised in an acetonitrile solution of H_2SB . The preparation of $\text{Zn}(\text{SB})\cdot \text{H}_2\text{O}$ is outlined below. The cell can be summarised as:



Caution: Although no problem has been encountered in this work, all perchlorate compounds are potentially explosive, and should be handled in small quantities and with great care!

An acetonitrile solution (80 cm^3) of H_2SB (100 mg, 0.166 mmol), containing about 30 mg of tetramethylammonium perchlorate, was electrolysed for 1 h 45', with use of a 5 mA current intensity and an initial voltage of 16 V. Filtration and concentration of the resulting solution yielded a solid that was washed with diethyl ether and dried in vacuo. The ligand amount, current intensity and electrolysis time were identical for all the complexes. Initial voltages were in the 8–16 V range.

$\text{Pd}(\text{SB})\cdot 3\text{H}_2\text{O}\cdot \text{MeCN}$ was obtained by heating of a methanol solution containing H_2SB , NaOH, and $\text{Pd}(\text{AcO})_2$ in 1:2:1 molar ratio at reflux for 6 hours. Filtration of the resulting suspension yielded a solid that was washed with diethyl ether and dried in vacuo. The reaction end was determined by TLC.

$\text{Ni}_2(\text{SB})_2\cdot 2\text{H}_2\text{O}$: Green solid. Yield 81%. M.p. $> 320\text{ }^\circ\text{C}$. $\text{C}_{64}\text{H}_{68}\text{N}_8\text{Ni}_2\text{O}_{10}\text{S}_4$ (1354.91): calcd. C 56.7, H 5.1, N 8.3, S 9.5; found C 56.7, H 5.3, N 8.5, S 9.2. IR (KBr): $\tilde{\nu} = 3440$ (br., O–H), 1626 (s, C=N), 1301 (s, C–N), 1260, 1134 (s, SO_2) cm^{-1} . FAB-MS: m/z (%) = 659.0 (55%) $[\text{Ni}(\text{SB}) + \text{H}]^+$; μ (300 K): 6.0 B.M. UV/Vis (solid): λ_{max} (nm) = 680 [m, $^3\text{T}_1(\text{P}) \leftarrow ^3\text{T}_1(\text{F})$].

$\text{Pd}(\text{SB})\cdot 3\text{H}_2\text{O}\cdot \text{MeCN}$: Brown solid. Yield 82%. M.p. $260\text{ }^\circ\text{C}$. $\text{C}_{34}\text{H}_{41}\text{N}_5\text{O}_7\text{PdS}_2$ (802.27): calcd. C 51.9, H 4.9, N 7.5, S 8.6; found C 51.6, H 4.7, N 7.7, S 8.3. IR (KBr): $\tilde{\nu} = 3441$ (br., O–H), 1632 (s, C=N), 1294 (s, C–N), 1242, 1143 (s, SO_2) cm^{-1} . ESI-MS (100 V): m/z (%) = 707.0 (100) $[\text{Pb}(\text{SB}) + \text{H}]^+$. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.58$ (m, 4 H, H_k), 1.88 (m, 4 H, H_j), 2.07 (s, 6 H, H_i), 7.10 (m, 14 H, $\text{H}_c + \text{H}_d + \text{H}_e + \text{H}_g + \text{H}_h$), 7.20 (d, 2 H, H_f), 7.65 (s, 2 H, H_b) ppm.

$\text{Cu}(\text{SB})\cdot 4\text{H}_2\text{O}$: Brown solid. Yield 87%. M.p. $250\text{ }^\circ\text{C}$. $\text{C}_{32}\text{H}_{40}\text{CuN}_4\text{O}_8\text{S}_2$ (736.36): calcd. C 52.2, H 5.5, N 7.6, S 8.7; found C 52.7, H 5.3, N 7.8, S 8.7. IR (KBr): $\tilde{\nu} = 3442$ (br., O–H), 1621 (s, C=N), 1295 (s, C–N), 1263, 1138 (s, SO_2) cm^{-1} . FAB-MS: m/z (%) = 664.0 (60) $[\text{Cu}(\text{SB}) + \text{H}]^+$. μ (293 K): 2.1 B.M. UV/Vis (solid) λ_{max} (nm) = 460 (m, $^2\text{E} \leftarrow ^2\text{T}$).

$\text{Ag}_2(\text{SB})\cdot 2\text{H}_2\text{O}$: Grey solid. Yield 76%. M.p. $250\text{ }^\circ\text{C}$. $\text{C}_{32}\text{H}_{36}\text{Ag}_2\text{N}_4\text{O}_6\text{S}_2$ (852.52): calcd. C 45.1, H 4.3, N 6.6, S 7.5; found C 45.2, H 4.1, N 7.0, S 7.3. IR (KBr): $\tilde{\nu} = 3453$ (br., O–H), 1633 (s, C=N), 1293 (s, C–N), 1261, 1126 (s, SO_2) cm^{-1} . ESI-MS (150 V): m/z (%) = 603.3 (100) $[\text{H}_2\text{SB} + \text{H}]^+$, 711.2 (25) $[\text{Ag}(\text{HSB}) + \text{H}]^+$, 817.0 (5) $[\text{Ag}_2(\text{SB}) + \text{H}]^+$. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 1.85$ (m, 4 H, H_k), 2.29 (s, 6 H, H_i), 3.62 (m, 4 H, H_j), 6.70 (t, 2 H, H_d), 7.05 (t, 2 H, H_e), 7.16 (d, 4 H, H_h), 7.22 (d, 2 H, H_c), 7.33 (d, 2 H, H_f), 7.67 (d, 4 H, H_g), 8.47 (s, 2 H, H_b) ppm.

$\text{Zn}(\text{SB})\cdot \text{H}_2\text{O}$: Beige solid. Yield 70%. M.p. $210\text{ }^\circ\text{C}$. $\text{C}_{32}\text{H}_{34}\text{N}_4\text{O}_5\text{S}_2\text{Zn}$ (684.15): calcd. C 56.2, H 5.0, N 8.2, S 9.4; found C 56.8, H 5.0, N 8.6, S 8.9. IR (KBr): $\tilde{\nu} = 3442$ (br., O–H), 1634 (s, C=N), 1299 (s, C–N), 1261, 1140 (s, SO_2) cm^{-1} . FAB-MS: m/z (%) = 665.3 (72) $[\text{Zn}(\text{SB}) + \text{H}]^+$. ^1H NMR (500 MHz, Cl_3CD): $\delta = 1.76$ (m, 2 H, H_{keq}), 2.35 (s, 6 H, H_i), 2.39 (m, 2 H, H_{kax}), 3.76 (m, 2 H, H_{jeq}), 4.19 (m, 2 H, H_{jax}), 6.82 (t, 2 H, H_d), 7.12 (d, 4 H, H_h), 7.18 (t, 2 H, H_e), 7.25 (d, 2 H, H_c), 7.40 (d, 2 H, H_f), 7.75 (d, 4 H, H_g), 8.32 (s, 2 H, H_b) ppm.

$\text{Cd}(\text{SB})\cdot 3\text{H}_2\text{O}$: White solid. Yield 70%. M.p. $24\text{ }^\circ\text{C}$. $\text{C}_{32}\text{H}_{38}\text{CdN}_4\text{O}_7\text{S}_2$ (767.21): calcd. C 50.1, H 5.0, N 4.9, S 8.3; found C 49.6, H 5.4, N 4.7, S 8.0. IR (KBr): $\tilde{\nu} = 3443$ (br., O–H), 1628 (s, C=N), 1293 (s, C–N), 1261, 1128 (s, SO_2) cm^{-1} . ESI-MS (150 V): m/z (%) = 715.1 (24) $[\text{Cd}(\text{SB}) + \text{H}]^+$. ^1H NMR (500 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 2.27$ (m, 4 H, H_k), 2.31 (s, 6 H, H_i), 3.80 (m, 4 H, H_j), 6.84 (t, 2 H, H_d), 7.20 (m, 4 H, $\text{H}_e + \text{H}_c$), 7.24 (d, 4 H, H_h), 7.37 (d, 2 H, H_f), 7.75 (d, 4 H, H_g), 8.56 (s, 2 H, H_b) ppm.

$\text{Pb}(\text{SB})\cdot 3\text{H}_2\text{O}$: White solid. Yield 80%. M.p. $320\text{ }^\circ\text{C}$. $\text{C}_{32}\text{H}_{38}\text{N}_4\text{O}_7\text{PbS}_2$ (862.00): calcd. C 40.8, H 4.1, N 5.6, S 6.8; found C 41.7, H 4.9, N 5.6, S 6.8. IR (KBr): $\tilde{\nu} = 3442$ (br., O–H), 1635 (s, C=N), 1283 (s, C–N), 1259, 1131 (s, SO_2) cm^{-1} . ESI-MS (150 V): m/z (%) = 809.2 (15) $[\text{Pb}(\text{SB}) + \text{H}]^+$. ^1H NMR (500 MHz, Cl_3CD): $\delta = 1.92$ (m, 4 H, H_k), 7.69 (d, 4 H, H_g), 7.60 (d, 2 H, H_f), 7.25 (m, 4 H, $\text{H}_e + \text{H}_c$), 7.07 (d, 4 H, H_h), 7.00 (t, 2 H, H_d), 3.75 (m, 4 H, H_j), 2.20 (s, 6 H, H_i), 8.31 (s, 2 H, H_b) ppm.

Single-Crystal X-ray Diffraction Studies

$\text{Cu}(\text{SB})\cdot \text{MeCN}$ and $\text{Zn}(\text{SB})\cdot 2\text{MeCN}$: Diffraction intensity data were collected at room temperature on a Bruker SMART CCD-1000 diffractometer with use of graphite-monochromatised Mo- K_α radiation ($\lambda = 0.71073\text{ \AA}$). Absorption correction was carried out from equivalents with the aid of the SADABS program.^[26] The structures were solved by direct methods and refined by full-matrix, least-squares based on F^2 , with the aid of SHELX-97 software.^[27] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at geometrically calculated positions with thermal parameters derived from the parent atoms. Table 2 provides a summary of crystal data, data collection and refinement parameters. Molecular graphics are represented by Ortep-3 for Windows, RasWin, and Platon.^[28]

$\text{Ni}_2(\text{SB})_2\cdot 5\text{MeCN}$: Several green needle crystals from different recrystallisation attempts of $\text{Ni}_2(\text{SB})_2\cdot 2\text{H}_2\text{O}$ were measured at 120 K, showing poor diffracting behaviour. This could be the result of extensive solvation and disorder,^[3] as several low-quality refinements indicated. For the best data set that could be obtained, the measured crystal proved to be a two-component twin [twin ratio: 0.719(5)], arising from a rotation of -179.94° around the vector normal to (1 0 0) in the reciprocal space. The twin law was used to process the data with the aid of the GEMINI program.^[29] The structure was solved with the help of DIRDIF^[30] and then treated as in the two previous cases. The C atoms of one of the methylene

Table 2. Crystal and structure refinement data for Ni₂(SB)₂·5MeCN, Cu(SB)·MeCN, and Zn(SB)·2MeCN

	Ni ₂ (SB) ₂ ·5MeCN	Cu(SB)·MeCN	Zn(SB)·2MeCN
Empirical formula	C ₇₄ H ₇₉ N ₁₃ Ni ₂ O ₈ S ₄	C ₃₄ H ₃₅ CuN ₅ O ₄ S ₂	C ₃₆ H ₃₈ N ₆ O ₄ S ₂ Zn
<i>M</i>	1524.16	705.33	748.21
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>C</i> 2/ <i>c</i> (No. 15)	<i>Fdd</i> 2 (No. 43)	<i>Fdd</i> 2 (No. 43)
<i>a</i> [Å]	34.212(12)	47.029(11)	12.3928(15)
<i>b</i> [Å]	12.443(4)	12.258(3)	47.606(6)
<i>c</i> [Å]	18.114(6)	12.297(3)	12.1526(15)
β [°]	93.234(7)	90	90
<i>U</i> [Å ³]	7699(5)	7089(3)	7169.7(15)
<i>T</i> [K]	120(2)	293(2)	298(2)
<i>Z</i>	4	8	8
μ(Mo- <i>K</i> _α) [mm ⁻¹]	0.659	0.777	0.849
No. ref. col./ no. ref. ind./ <i>R</i> _{int}	12223/12228/0.00	8095/3112/0.0257	3732/3531/0.00
Data/restraints/parameters	12228/6/456	3112/1/223	3531/1/224
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0831, 0.1987	0.0397, 0.1073	0.0304, 0.0690
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1241, 0.2199	0.0565, 0.1167	0.0423, 0.0747
Abs. struct. Flack parameter		0.034(19)	0.021(11)
Residuals [e·Å ⁻³]	0.769, -0.590	0.409, -0.300	0.241, -0.214

chains could be located in two disordered positions [C(115)–C(116) and C(15')–C(16')] with 51.6 and 48.4% occupation sites, respectively], and they were isotropically treated. Some of the solvent molecules also show some disorder, and they were isotropically treated and some restraints applied.

CCDC-189324, -197776, and -197777 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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