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Syn versus *Anti* Conformation in Monodentately Coordinated Sulfonate Groups. Crystal Structure Determination and MMX Force-Field Calculations for *trans*-Di(4-methylbenzenesulfonato)bis(1,3-diaminopropane)-copper(II), $C_{20}H_{34}CuN_4O_6S_2$

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The structure of the title compound was determined by single-crystal X-ray methods. The compound crystallizes in the orthorhombic crystal system (space group $Pbca$, No. 61) with $a = 25.282(2)$, $b = 11.318(2)$, $c = 8.765(2)$ Å, $V = 2508(1)$ Å^3 and $Z = 4$. The Cu(II) ion lies at a centre of symmetry and displays elongated pseudo-octahedral stereochemistry. The equatorial Cu–N distances are Cu–N1 = 2.036(5) and Cu–N2 = 2.021(5) Å. The axial 4-methylbenzenesulfonate ion is monodentately coordinated to the Cu(II) ion, displaying an *anti* conformation. The Cu–O distance is 2.581(5) Å and the Cu1–O1–S1 angle is 129.6(2)°. The chelate ring, consisting of a 1,3-diaminopropane ligand coordinated to the Cu(II) ion, has a chair conformation with puckering values close to those calculated using semiempirical MMX force-field calculations. The calculations also predict that the *anti* conformation is the most stable coordination mode for the 4-methylbenzenesulfonate anion.

The coordination modes of differently substituted benzoate anions have been studied by X-ray diffraction in a number of bis(tn)M(II)X_2 complexes (where tn is 1,3-diaminopropane, M is either Cu or Ni and X is a benzoate anion).[1,2] In every compound both of the benzoate anions are coordinated monodentately to the metal ion, except in aqua-3-iodobenzoatobis(tn)Cu(II) 3-iodobenzoate, where only one of the two anions is coordinated.[3] The predominant coordination mode in Cu(II) carboxylates in general is the *syn* mode, which has been observed in 73.6% of the structures.[4] This has also been the unique coordination mode in the series studied so far. A sulfonate anion would be a likely candidate to display *anti* coordination because of steric hindrance caused by two additional oxygen atoms. As far as the present authors know, there is no review of the coordination mode of sulfonate anions, and only two aromatic sulfonate Cu(II) complexes have been studied structurally.[5,6] In catena(diaqua-bis-μ-2-pyridine-3-sulfonato-*N*,*O*)-copper(II)[5] one of the sulfonate oxygens is in an axial position forming an O–Cu–O′ bridge, while in $[Cu_2(tos)_2(tcoa)(ClO_4)_2 \cdot 4H_2O$ (tos = paratoluenesulfonate or 4-methylbenzenesulfonate anion, tcoa = 1,5,8,12,15,19,22,26-octaazatricyclo[17.9.2.2^{5,15}]dotriacontane)[6] the central copper(II) atom displays five-coordination and the 4-methylbenzenesulfonate anion is in the axial position. In the latter compound the copper(II) ion is displaced from the basal plane towards the axial oxygen and the Cu–O distance is quite short, 2.153(6) Å. Consequently there is probably sterical hindrance for one of the two other sulfonate oxygens to coordinate to Cu(II) ion. In bis(tn)Cu(II) benzoates the axial bond Cu–O is rather long, at least 2.47 Å, and thus causes only minor steric hindrance. In addition, the four nitrogens around the central Cu(II) atom are potential hydrogen-bonding sites, and thus they could bend the sulfonate group to the *syn* mode. We report here the synthesis and structure determination of Cu(tn)$_2$(4-methylbenzenesulfonate)$_2$. Moreover, MMX force-field calculations were performed to study what kind of conformation is the most stable.

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Table 1. Crystal data and experimental details of the structure determination of *trans*-di(4-methylbenzenesulfonato)bis(1,3-diaminopropane)copper(II).

Formula	$C_{20}H_{34}CuN_4O_6S_2$
M_r	554.18
Space group (orthorhombic)	*Pbca* (No. 61)
Cell parameters at 291(1) K	
a/Å	25.282(2)
b/Å	11.318(2)
c/Å	8.765(2)
V/Å^3	2508(1)
Calculated density/g cm^{-3}	1.467
Z	4
μ(Mo$K\alpha$)/cm^{-1}	10.72
Crystal dimensions/mm	0.08 × 0.21 × 0.25
Maximum 2Θ/°	55
hkl ranges	h = 0-33 k = 0-15 l = 0-11
Corrections	Lp, abs., sec. extinc., decay (0.25%)
No. of reflections measured	3303 unique
No. of observations [$I > 2\sigma(I)$]	1411
Parameters refined	194
$R = \Sigma(\|F_o\| - \|F_c\|)/\Sigma\|F_o\|$	0.050
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/w\Sigma\|F_o\|^2]^{1/2}$	0.048
E.s.d. of obs. of unit weight	1.33
Least-squares weights	$w = [\sigma^2(F_o)]^{-1}$
Max./min. in final difference map/e Å^{-3}	0.42/−0.38

Experimental

Synthesis. The title compound was synthesised by adding 2.00 mmol of *p*-toluenesulfonic acid (Fluka) in H_2O (50 ml) to a suspension of 1.00 mmol $CuCO_3$ (Baker's Analyzed) in EtOH/H_2O (1/1 100 ml). The suspension was heated and stirred until a homogeneous light green precipitate appeared. The addition of 2.00 mmol of 1,3-diaminopropane (Fluka) in EtOH resulted in a deep blue solution. Deep blue crystals obtained after 5 h cooling were separated by filtration. Anal. Cu 11.5%, calc. for $C_{20}H_{34}CuN_4O_6S_2$ 12.0%.

X-Ray structure determination. The unit-cell parameters were obtained by least-squares refinement of 25 automatically centred reflections ($20.0 < 2\Theta < 32.0°$). Intensity data were collected at 23(1)°C with a Rigaku AFC5S diffractometer in the ω–2Θ scan mode with an ω scan rate of 8.0° min^{-1} and a scan width of 1.22 + 0.30tan Θ using graphite monochromated Mo$K\alpha$ radiation (λ = 0.710 69 Å). The weak reflections [$I < 10\sigma(I)$] were rescanned up to two times. Further details are given in Table 1. An empirical absorption correction, based on azimuthal scans of several reflections, was applied. Also a correction for secondary extinction (Zachariasen type; coefficient 0.36×10^{-6}) was made. The structure was solved by direct methods and refined by standard full-matrix least-squares techniques and Fourier procedures to an R-value of 0.050 ($R_w = 0.048$). The heavy atoms were refined anisotropically and the hydrogen atoms isotropically with fixed temperature factors (1.2 times the temperature factor of the host atom), except for the methyl hydrogens, which were included in the calculated positions.

Neutral atomic scattering and dispersion factors were taken from Ref. 7. Calculations were performed using the Texsan crystallographic software[8] installed on a Vaxstation 3520 computer. The molecular illustrations were drawn with ORTEP.[9] The final atomic positional coordinates for the non-hydrogen atoms and their equivalent isotropic temperature factors are listed in Table 2. Tables

Table 2. Atomic positional parameters of the non-hydrogen atoms and their equivalent isotropic temperature factors for *trans*-di(4-methylbenzenesulfonato)bis(1,3-diaminopropane)copper(II).

Atom	x	y	z	B_{eq}/Å^{2a}
Cu(1)	1/2	1/2	1/2	2.92(4)
S(1)	0.57681(6)	0.4321(1)	0.8459(2)	3.14(6)
O(1)	0.5538(1)	0.5224(3)	0.7485(4)	3.7(2)
O(2)	0.5444(1)	0.3256(3)	0.8503(4)	3.8(2)
O(3)	0.5920(2)	0.4750(3)	0.9948(4)	4.7(2)
N(1)	0.4413(2)	0.5555(4)	0.6420(6)	3.1(2)
N(2)	0.4810(2)	0.3318(4)	0.5549(6)	3.2(2)
C(1)	0.3893(2)	0.4971(5)	0.6407(7)	3.2(3)
C(2)	0.3941(3)	0.3663(6)	0.6727(7)	3.5(3)
C(3)	0.4252(3)	0.2984(5)	0.5547(7)	3.5(3)
C(4)	0.6363(2)	0.3887(5)	0.7545(6)	3.1(2)
C(5)	0.6391(2)	0.2861(5)	0.6701(7)	3.4(3)
C(6)	0.6862(3)	0.2557(6)	0.6013(8)	4.2(3)
C(7)	0.7307(3)	0.3236(6)	0.6113(7)	4.1(3)
C(8)	0.7272(3)	0.4262(7)	0.6934(9)	5.2(4)
C(9)	0.6805(3)	0.4599(6)	0.7650(9)	4.7(3)
C(10)	0.7817(3)	0.2842(7)	0.5362(8)	6.2(4)

[a] The equivalent isotropic temperature factors are of the form $B_{eq} = 4/3\Sigma_i\Sigma_j\beta_{ij}\boldsymbol{a}_i \cdot \boldsymbol{a}_j$.

of anisotropic thermal parameters, and observed and calculated structural factors, may be obtained from the authors upon request.

Structure optimization. The semiempirical force-field calculations were carried out with the program PCModel[10] installed on a PC.

Spectroscopic measurements. The solid-state IR spectra were recorded on a Mattson Galaxy FT infrared instrument using the Nujol mull technique. The characteristic bands with their tentative assignments are as follows: the N–H stretching modes are at 3302 m, 3273 s, 3254 s, 3223 sh and 3171; the aromatic C=C stretching mode is at 1626 m, the NH_2 scissorings are at 1597 m, S–O stretching modes are at 1231 s, 1171 s and 1032 s, and S–C stretching is at 667 cm^{-1}.[11] The UV–VIS spectrum (recorded as described in Ref. 2) displayed a broad band at 550 nm.

Results and discussion

The molecular structure of the compound is shown in Fig. 1. The bond lengths and angles are given in Table 3. The basic structural unit displays the typical CuN_4O_2 coordination mode with the central Cu(II) ion lying at a centre of symmetry. The Cu–N1 and Cu–N2 distances of 2.036(5) and 2.020(5) Å, respectively, are very near to the values found in *trans*-dibenzoatobis(tn)Cu(II) (**1**) [2.043(3) and 2.028(3) Å] and *trans*-di-3-iodobenzoatobis(tn)Cu(II) (**2**) [2.041(3) and 2.029(3) Å]. It is not possible to establish any difference between the Cu–N1 and Cu–N2 bonds for the title compound in terms of standard deviations, although a difference is predicted by the second order Jahn–Teller effect.[12]

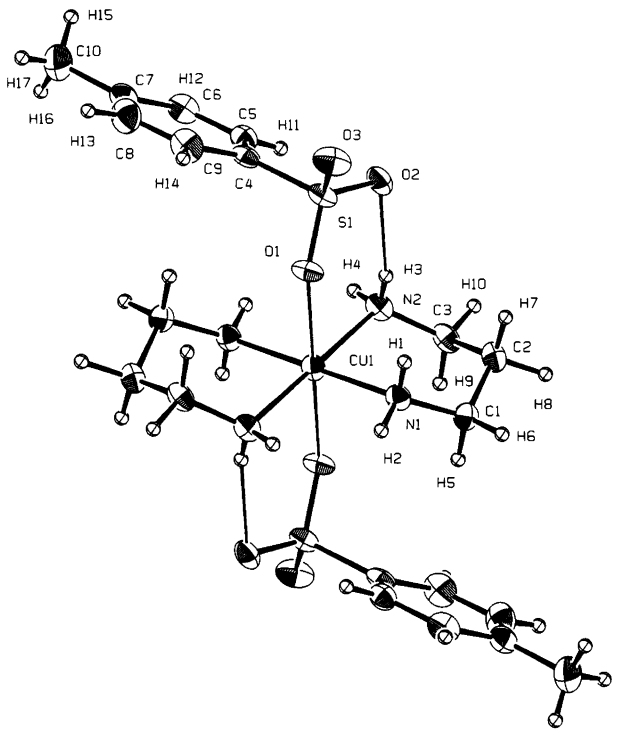

Fig. 1. ORTEP drawing of the molecular unity of the title compound, including the atomic labelling scheme. The asymmetric unit is completely labelled. In this figure 30% probability ellipsoids are drawn.

Table 3. The bond lengths (in Å) and angles (in °) with their standard deviations in parentheses.

Cu(1)–N(1)	2.036(5)	C(1)–C(2)	1.511(8)
Cu(1)–N(2)	2.021(5)	C(2)–C(3)	1.510(8)
Cu(1)–O(1)	2.581(5)	C(4)–C(5)	1.378(7)
S(1)–O(1)	1.453(4)	C(4)–C(9)	1.381(8)
S(1)–O(2)	1.457(4)	C(5)–C(6)	1.378(9)
S(1)–O(3)	1.444(4)	C(6)–C(7)	1.367(9)
S(1)–C(4)	1.774(6)	C(7)–C(8)	1.370(9)
N(1)–C(1)	1.473(7)	C(7)–C(10)	1.513(8)
N(2)–C(3)	1.461(8)	C(8)–C(9)	1.39(1)
N(1)–Cu(1)–N(2)	88.4(2)	O(2)–S(1)–C(4)	105.0(2)
N(1)–Cu(1)–N(2)′	91.6(2)	O(3)–S(1)–C(4)	106.0(3)
N(1)–Cu(1)–O(1)	80.7(2)	N(1)–C(1)–C(2)	111.5(5)
N(1)–Cu(1)–O(1)′	99.3(2)	C(1)–C(2)–C(3)	114.4(5)
N(2)–Cu(1)–O(1)	91.0(2)	C(5)–C(4)–C(9)	119.1(6)
N(2)–Cu(1)–O(1)′	89.0(2)	S(1)–C(4)–C(9)	119.6(5)
Cu(1)–N(1)–C(1)	120.5(4)	C(4)–C(5)–C(6)	119.3(6)
Cu(1)–N(2)–C(3)	118.2(4)	C(5)–C(6)–C(7)	122.9(6)
Cu(1)–O(1)–S(1)	129.6(2)	C(6)–C(7)–C(8)	117.1(6)
O(1)–S(1)–O(2)	111.9(2)	C(6)–C(7)–C(10)	120.5(6)
O(1)–S(1)–O(3)	113.6(2)	C(8)–C(7)–C(10)	122.4(6)
O(1)–S(1)–C(4)	105.6(2)	C(7)–C(8)–C(9)	121.8(6)
O(2)–S(1)–O(3)	113.8(3)	C(4)–C(9)–C(8)	119.8(6)

Symmetry code: i = 1 − *x*, 1 − *y*, 1 − *z*.

Instead, there is more variation in the axial bond length Cu–O. The present compound has the value 2.580(5) Å, whereas it is 2.468(3) in **1** and 2.500(3) Å in **2**. The axial elongation in the CuN_4X_2-type coordination polyhedra has gained much interest. The usual concept to explain the elongation is *d–s* mixing.[13,14] However, the most stable deformation predicted by this concept leads to a polyhedron of the type CuN_4OO', where the axial bonds are different.[15] Only one structure in the series of $[Cu(tn)_2]^{2+}$ has been found to correspond to this type so far. Instead, compounds 1 and 2 are of the type CuN_4O_2, and sulfatobis(tn)Cu(II) and selenatobis(tn)Cu(II) display the type CuN_4O.[16]

The chelate rings of the title compound have the usual chair conformation. Some parameters describing the puckering of the chelate ring are listed in Table 4. The

Table 4. Geometrical parameters describing bis(tn)CuO_2 chromophores. The symbols have their original meaning given in Ref. 17.

Compound	z_1/Å[a]	z_2/Å[a]	z_3/Å[a]	Φ/[b]	*Q*/Å[c]	Cu–O/Å
1	1.05	0.870	1.04	11.0	0.662	2.468
2	1.04	0.828	1.01	21.1	0.646	2.500
This work	0.886	0.635	0.931	55.1	0.600	2.580

[a] z_i is the distance of a C_i atom from the corresponding CuN_4 plane. [b] 0° refers to the chair and 90° to the half-chair conformation. [c] the *Q* is the total puckering of a chelate ring.

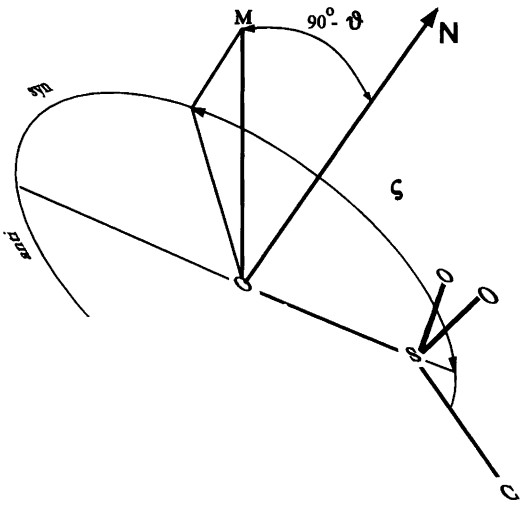

Fig. 2. The definition of the *syn–anti* coordination modes (adapted from Refs. 4 and 19) applied to a metal sulfonate fragment. The positive and negative values of ς refer to *anti* and *syn* coordination, respectively. The parameter $90° - \vartheta$ describes deviation of the metal from the normal vector ***N*** drawn to the CSO plane.

axial bond length Cu–O and twisting of the ring seem to correlate with the total puckering of the ring. When the axial bond length increases there is simultaneous flattening and twisting of the ring. This is unexpected, since a contradictory report has been published by Kupka *et al.* When *trans*-$[Co(CN)_2(tn)_2]Cl \cdot 3H_2O$ was irradiated with polarised light, analysis of the vibronic structure supported by results of normal-coordinate analysis gave the opposite result.[18] The conformation of the chelate ring seems to shift from chair to half-chair upon axial elongation of the Cu–O bond. However, these findings must be considered preliminary; work is going on to determine more structures in the series of bis(tn)Cu(II) benzoates.

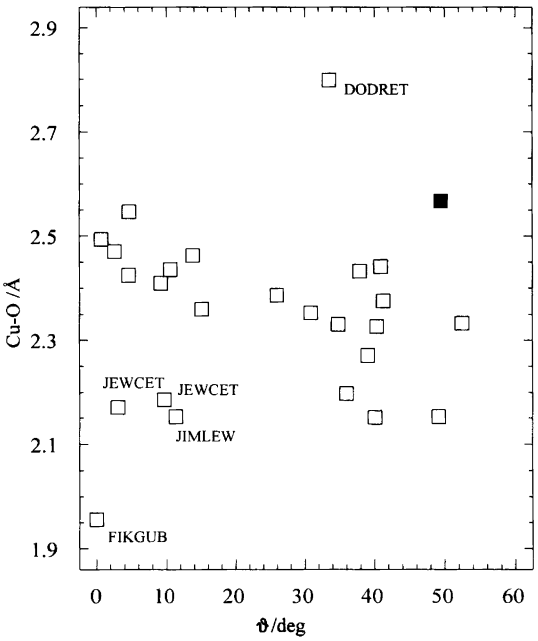

Fig. 3. Correlation between the Cu–O distance (in Å) and the angle ϑ (in °). The fragment names refer to the compounds found from CSD. The complete listing of the references is given in Table S1 (Supplementary material). The filled square corresponds to the title compound.

The 4-methylbenzenesulfonate anion is monodentately coordinated to the Cu(II) ion. There are 16 structures in the CSD (Cambridge Structural Database) with a sulfonate anion coordinated monodentately to a copper ion (with oxidation state I or II). A list of the corresponding references is given in Table S1 (Supplementary material). Of these, all but one contain an aliphatic sulfonate anion. There are in total 25 independent (not related by symmetry) Cu-sulfonate fragments.

The definition (according to the usage given in Ref. 19) for the *syn* and *anti* coordination modes is shown in Fig. 2. As can be seen, two parameters are required to describe the coordination mode explicitly. Unfortunately, the usual IUPAC recommendation[20] is not applicable here because it is restricted to one value only (the torsion angle).* In our definition the reference plane in the IUPAC sense consists of sulfur and the two oxygens not coordinated to a central metal atom. To study further the coordination mode of a sulfonate anion, two parameters (ϑ and ς) were calculated for the compounds found from CSD. The angle ϑ describes the deviation from the CSO plane and the angle ς position in the plane. During the calculations the values for ϑ were given their absolute values. Both ς and ϑ show wide variation. The present compound has the values 49.4 and 168.3° for ϑ and ς, respectively.

There seems to be a correlation between the angle ϑ and the Cu–O distance (Fig. 3). When the Cu–O distance approaches 2.5, the fragment C–S–O–Cu displays increasing convergence towards planarity. There are, however, some outliers. Obviously the distance of about 2.8 Å (DODRET) is too long to indicate any coordination between a copper ion and an oxygen. As for FIKGUB and JEWCET,† the sulfonate anion occupies an equatorial position, whereas in all the other complexes it lies axially. JIMLEW is the only compound having an aromatic sulfonate anion. Interestingly, the title compound also contains an aromatic sulfonate anion and seems to be an outlier. The difference between JIMLEW and the present compound lies in the coordination; JIMLEW displays five coordination, while there is six coordination in our compound.

Among the structures, there are in total six fragments displaying an *anti* conformation and 19 a *syn* conforma-

* In the representation of stereochemical relationships '*anti*' means 'on opposite sides' of a reference plane, in contrast to '*syn*', which means 'on the same side'. Conformations are described as synperiplanar, synclinal, anticlinal, or antiperiplanar according as the torsion angle is within ±30° of 0°, ±60°, ±120° or ±180°, respectively.

† There are two independent fragments (not related by symmetry) in the structure.

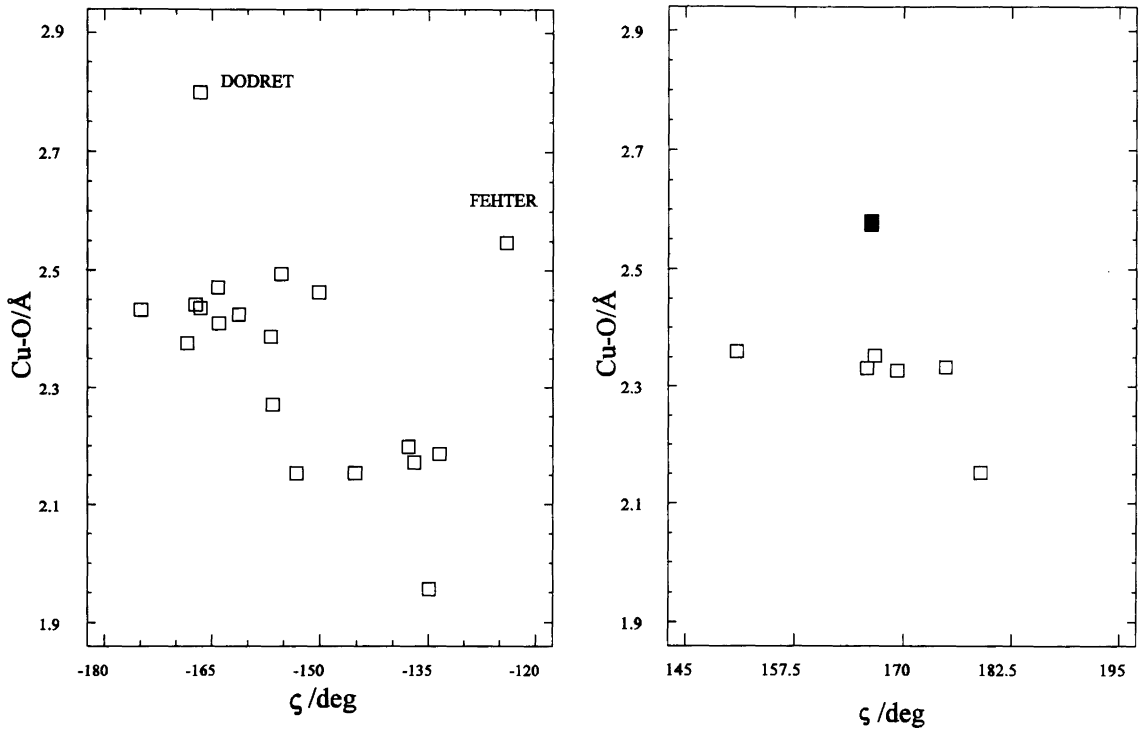

Fig. 4. Correlation between the Cu–O distance (in Å) and the angle ς (in °). The fragment names refer to the compounds found from CSD. The filled square corresponds to the title compound.

tion (Fig. 4). For the compounds displaying a *syn* mode, there are seemingly two outliers. Here also, the long axial distance for DODRET may be an explanation. As for FEHTER, the steric influence of 1,2:5,6:9,10-tribenzocyclododeca-1,5,9-triene-3,7,11-triyne ligand may be a reason for a deviation. Upon elongation, the coordination mode for the *syn* forms changes towards a *meso* mode, where the copper atom would lie approximately along the S–O bond. Surprisingly, the opposite seems to hold true for the *anti* forms. However, there are so few compounds in this category that it is too early to establish a definite correlation.

Formally, there should be two double bonds and one single bond between the sulfur atom and three oxygen atoms. However, resonance will very likely average the geometry. In the title compound the S1–O1 and S1–O2 bonds are slightly longer, 1.453(4) and 1.457(4) Å, respectively, than S1–O3 bond, 1.444(4) Å. This is understandable since O1 is coordinated and O2 accepts three hydrogen bonds. The angles around S1 are almost tetrahedral (Table 3) and the angle Cu1–O1–S1 is 129.6(2)°.

The bond between an aromatic ring and a carboxylate carbon shows elongation in the series of *trans*-dibenzoato-bis(tn)Cu(II) complexes compared with the values found in the corresponding acids.[1,2] An analogous effect is found also in the title compound, where the S1–C4 distance 1.774(6) Å is longer than the value in the acid, 1.752(2) Å.[21] Also the average value of 1.799(8) Å found in the fragments obtained from CSD shows elongation. Obviously coordination plays an important role in the elongation.

Perhaps owing to the *anti*-conformation, the anions are packed in a different way than the *para*-substituted benzoate anions,[1] which have the propensity to form pairwise oriented parallel planes. The closest interplanar distances here are between C4···C6* and C5···C6*, 3.672(9) and 3.99(1) Å, respectively (* refers to symmetry operator $x, 1/2-y, 1/2-z$). These values are too long to indicate any intermolecular interaction, as was suggested for **2**.[2]

The possible hydrogen bonds are listed in Table 5. The wavenumbers given in the Experimental section for N–H vibrations can be explained by hydrogen bonding and complexation, as discussed in Ref. 2. As can be seen from Fig. 2, two of them can be described as intramolecular. The possible bond from O1 is questionable because of the unfavourable N–H···O angle of 121(5)°. The statistical expectation value reported by Taylor and Kennard is

Table 5. Distances (in Å) and angles (in °) related to hydrogen-bond formation (standard deviations in parentheses).

	N–H	H···O	N···O	N–H···O
N(1)–H(1)···O(1)	0.78(5)	2.53(6)	3.017(6)	122(5)
N(1)–H(2)···O(2^{ii})	0.91(5)	2.20(5)	3.079(6)	163(5)
N(2)–H(3)···O(2)	0.79(5)	2.27(5)	3.046(7)	168(5)
N(2)–H(4)···O(2^{iii})	0.81(5)	2.19(5)	2.994(6)	172(5)

Symmetry codes:; $^{ii} = 1-x, \frac{1}{2}+y, \frac{3}{2}-z$; $^{iii} = x, \frac{1}{2}-y, z-\frac{1}{2}$.

162°.[22] Moreover, the O···H distance is quite long compared with the expectation value of 1.96 Å.

Theoretical calculations. MMX calculations were performed to determine whether it was possible to synthesise an isomer with the *syn* conformation of the sulfonate anions. The force field MMX was derived from the MM2 force field by N. L. Allinger. The program has the ability to handle transition metals. The structure was optimised by the following strategy. The bis(tn)Cu complex was optimised with the central copper atom requiring planar coordination and the Cu–N distances fixed (the force constant had a value of 10 000 mdyn $Å^{-1}$) at 2.028 Å. The chelate rings were already in the chair conformation at the start of the optimization. After the minimisation was complete, the 4-methylbenzenesulfonate anions were added in the axial position with a fixed Cu–O distance of 2.580 Å. The Cu–N distances were kept fixed as before. All the hydrogen atoms connected to the nitrogen atoms were activated to be able to form intramolecular hydrogen bonds during the optimizations. Several different starting positions for the anions always produced the *anti*-conformation for the sulfonate anions, even when the axial bond was given the value of 2.90 Å.

The bond lengths and angles for the optimised structure are given in Table S2 (Supplementary material). The semiempirical calculations made earlier by Gollogly and Hawkins predict that the bite angle N–Cu–N should be 90° or even wider.[23] The present optimization gives the value of 87.5°, which is reasonably close to the observed value of 88.4(2)°. The total puckering value Q has the value 0.616 Å, which is reasonably close to the observed value of 0.600(6) Å. The conformational angles ϑ and ς for the optimized structure are 28.9° for ϑ and 144.2° for ς.† These values deviate clearly from the observed values of 49.4 and 168.3°, respectively. It is interesting to note that these optimized values are closer to the range expected on the basis of the correlation illustrated in Figs. 3 and 4. Obviously intermolecular interactions may play an important role. As for the optimized value of ς, the *anti* coordination mode is even more pronounced. It should be remembered that the intermolecular interactions were excluded in the calculations, and thus the differences may be due to by additional intermolecular hydrogen bonding and stacking of the aromatic rings. These in turn are very likely to affect the electronic properties of the whole sulfonate group and also bonding to copper.

† PCMODEL is unable to make use of symmetry operators. Thus the central copper atom does not lie exactly at the centre of symmetry. Accordingly, average values are given in the text.

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