Investigations on Structural and Electrochemical Properties of Some Disulfides Prepared by Schiff Base Reactions

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Dedicated to Prof. Dr. Egon Uhlig on the Occasion of his 70th Birthday

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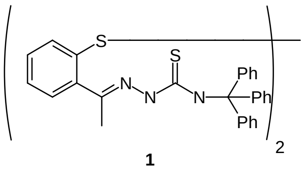
Abstract. Four different disulfides, [2,2'-dithiobis-(2-mercaptoacetophenone)]-4-triphenylmethylthiosemicarbazone (**1**), [5,5'-dithiobis-(4-formyl-3-methyl-1-phenylpyrazole)]-4-triphenylmethylthiosemicarbazone (**2**), bis[1-(2-mercaptophenyl)-2-(4-(1-phenyl-3-methyl)pyrazole)-azaethene]di-sulfide (**3**) and bis[1-phenyl-2-(4-(1-phenyl-3-methyl-5-mer-capto) pyrazole)-azaethene]disulfide (**4**) were synthesized by Schiff base reactions. Their electrochemical behaviour was examined by cyclic voltammetry. The results show low potentials for the disulfide reduction so that these compounds are suitable for the syntheses of tridentate thiolate ligands from disulfides by electrochemical cleavage. In addition compounds **2** and **4** were characterized by X-ray structure determination. The structures show significant differences of the S–S bonds and angles as compared to other disulfides without bulky substituents.

In recent years the investigations on new complexes exhibiting a metal-disulfide bond have been reinforced caused by their probable relevance to certain redox processes in biological systems. It has been postulated that in stellacyanin a disulfide sulfur atom occupies the fourth coordination site of the copper ion [1], whereas the oxidized form of the two-electron copper oxidase ceruplasmin contains a RSSR[Cu^{I}_2] unit [2]. Copper(II)-thiolate interactions have also attracted considerable interest because they are present in the low symmetry copper sites of blue copper proteins such as azurin and plastocyanin [3]. Due to the presence of the distorted tetrahedral N_2SS' coordination around the metal centre in these proteins a number of copper(II) complexes with mixed nitrogen and sulfur donor ligands, such as Schiff bases, have been synthesized as model compounds [4]. The synthetic problems in the development of these model complexes are associated with the instability of the copper(II)-thiolate bond with respect to the formation of copper(I) and disulfide [5]. Castro *et al.* have shown that these difficulties may be overcome by using an electrochemical reductive cleavage of the disulfide bond present in preformed Schiff bases, whereas the resulting Cu^{II}, Zn^{II}, Ni^{II} and Cd^{II} complexes contain the reduced Schiff base ligand [6]. Moreover, disulfide compounds have been proposed as candidates for high energy cathodes in lithium batteries [7]. A series of compounds having –SH groups in molecules are thought to serve as energy storage material, whereby energy exchange occurs according to the reversible polymerisation-depolymerisation process (2HS ↔ S–S). This concept of energy storage is based on an analogy to the reversible protein folding–unfolding process.

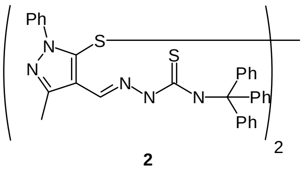
We have become interested in the syntheses of tridentate thiolate ligands from disulfides by electrochemical cleavage because this is a convenient way to form complexes with transition metals. Accordingly structure analysis, spectroscopic (IR, NMR) and cyclic voltammetry studies of four disulfides were undertaken to gain a better insight into the structural and electrochemical features of these compounds.

Results and Discussion

We synthesized the disulfides [2,2'-dithiobis-(2-mercaptoacetophenone)]-4-triphenylmethylthiosemicarbazone (**1**), [5,5'-dithiobis-(4-formyl-3-methyl-1-phenylpyrazole)]-4-triphenylmethylthiosemicarbazone (**2**), bis[1-(2-mercaptophenyl)-2-(4-(1-phenyl-3-methyl)pyrazole)-azaethene]disulfide (**3**) and bis[1-phenyl-2-(4-(1-



1



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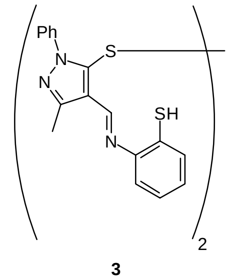

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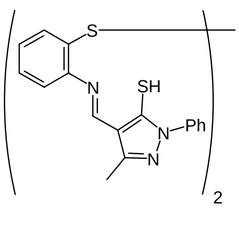

4

phenyl-3-methyl-5-mercapto)pyrazole)-azaethene]disulfide (**4**) by Schiff base reactions. The single crystal X-ray structures were determined for **2** and **4** while the electrochemical properties of **1**–**4** were studied by cyclic voltammetry.

Crystal structures of **2** *and* **4**

Crystals of **2** and **4** suitable for single crystal X-ray diffraction were obtained from a 1:1 mixture of *N*-methylimidazole and diethylether after two days. Intensity data for **2** were collected on a Siemens CCD diffraction system (synchrotron radiation, $\lambda = 0.41270$ Å) with a scan range from 1.60 to 27.00°. For **4** the intensity data were collected on a STOE imaging-plate diffraction system (Mo K_α radiation, $\lambda = 0.71073$ Å) with a sample-to-plate distance of 60 mm. A scan range from 10.10 to 50.00° with an exposure time of 2 minutes per 2° increment was used. Further details on the data collections are summarized in Table 1. The structures were solved using the Patterson method (program XS) [8]. A series of full-matrix least squares refinement cycles on F^2 (program SHELXL 93) [9] followed by Fourier syntheses gave all the remaining atoms. The hydrogen atoms were included at fixed positions with a common isotropic temperature factor. All non-hydrogen atoms of **2** and **4** were refined anisotropically.

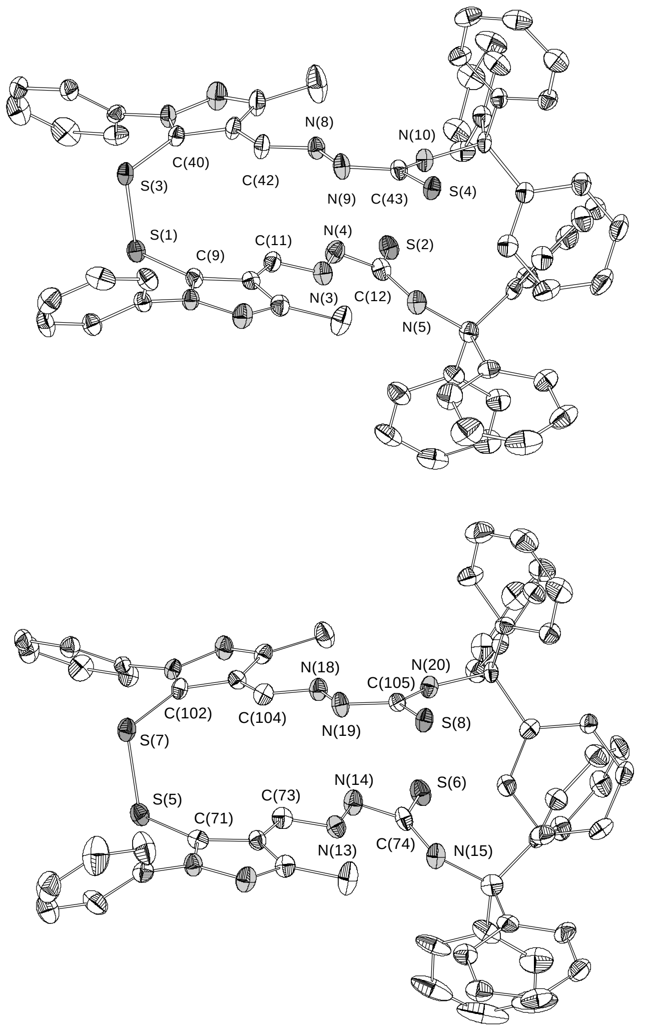

Fig. 1 Molecular structures of the two independent molecules of [5,5'-dithiobis-(4-formyl-3-methyl-1-phenylpyrazole)]-4-triphenylmethylthiosemicarbazone (**2**). Displacement ellipsoids are shown at 30% probability level.

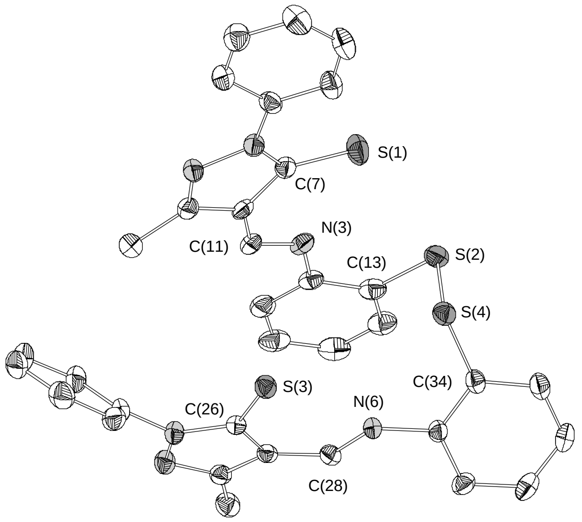

Fig. 2 Molecular structure of bis[1-phenyl-2-(4-(1-phenyl-3-methyl-5-mercapto)pyrazole)-azaethene]disulfide (**4**). Displacement ellipsoids are shown at 30% probability level.

Projections of the structures of compounds **2** and **4** are depicted in Figures 1 and 2. The asymmetric unit of compound **2** contains two disulfide molecules and one molecule of diethylether. Due to the high similarity of both disulfides the following discussion uses the data of only one of these molecules. Information about relevant bond lengths and bond angles information is given in Table 2. Structural properties of similar disulfide compounds have been discussed previously by Íde *et al*. [10] and Delgado *et al*. [11]. By comparing different disulfides Allen *et al*. found that S–S bond distances are bimodally distributed; for torsion angles in the ranges 75–105 and 0–20°, S–S bond distances were found to be 2.03(1) and 2.07(2) Å, respectively [12]. With 83.1(1) and 73.1(1)° for the C–S–S–C dihedral angles and the corresponding S–S bond distances of 2.079(1) and 2.068(2) Å, respectively, compounds **2** and **4** show significantly differences to the bimodal distribution of the mentioned values. This anomalous behaviour could be explained by the presence of the bulky substituents.

For **2** the dihedral angle between the pyrazole ring and the C(9)–S(1)–S(3) plane is 77.6° while the corresponding angle for the second half of the molecule is 83.9°. For **4** the dihedral angles between the phenyl rings

Table 1 Crystallographic data for **2** and **4**

	2	**4**
Formula	$C_{128}H_{114}N_{20}S_8O$ [a])	$C_{34}H_{26}N_6S_4$
Formula weight	2208.95	646.85
Temperature (K)	213(1)	213(1)
Diffractometer	Siemens CCD	STOE IPDS
Crystal size (mm)	0.06 × 0.02 × 0.02	0.07 × 0.12 × 0.25
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	12.024(2)	8.545(2)
b (Å)	55.860(1)	11.583(2)
c (Å)	18.236(4)	16.181(3)
α (°)		92.76(3)
β (°)	107.60(3)	98.68(3)
γ (°)		100.87(3)
V (Å^3)	11676(2)	1549(1)
Z	4	2
D_c (g cm^{-3})	1.257	1.386
2θ range (°)	$1.60 \leq 2\theta \leq 27.00$	$10.10 \leq 2\theta \leq 50.00$
λ (Å)	0.41270	0.71073
hkl range	$-15 \leq h \leq 15$ $-69 \leq k \leq 69$ $-22 \leq l \leq 22$	$-10 \leq h \leq 10$ $-12 \leq k \leq 13$ $-19 \leq l \leq 19$
No. data collected	235748	9915
No. unique data	24068	5103
R1 ($I>2\sigma(I)$)	0.1136	0.0705
wR2 (all data)	0.1643	0.1900
GOF	1.184	1.106
Residual density (e Å^{-3})	0.296, −0.287	0.545, −0.431

[a]) One formula unit contains two molecules of the disulfide and one molecule of diethylether

Table 2 Selected interatomic distances (Å) and angles (°) for **2** and **4**

2		**4**	
S(1)–S(3)	2.079(1)	S(2)–S(4)	2.068(3)
S(1)–C(9)	1.753(3)	S(1)–C(7)	1.680(2)
S(2)–C(12)	1.687(3)	S(2)–C(13)	1.774(2)
S(3)–C(40)	1.742(3)	S(3)–C(26)	1.676(2)
S(4)–C(43)	1.692(3)	S(4)–C(34)	1.773(3)
N(8)–C(43)	1.279(3)	N(3)–C(11)	1.332(3)
N(9)–C(43)	1.351(3)	N(6)–C(28)	1.325(2)
C(9)–S(1)–S(3)–C(40)	83.1(2)	C(13)-S(2)–S(4)–C(34)	83.2(1)

and the C–S–S planes are 75.2 and 83.8°, respectively. This indicates a pπ–dπ interaction between the fully occupied p_z orbital on an aromatic C atom with an empty d orbital on a S atom [13]. The distances of the sulfur atoms connected to the carbon atoms of the pyrazole rings in **2** are with 1.753(3) Å (S(1)–C(9)) and 1.742(3) Å (S(3)–C(40)) in the typical range of a sulfur–carbon single bond, whereas the S(2)–C(12) and the S(4)–C(43) distances are significantly shorter (1.687(3) and 1.692(3) Å) as expected for such kind of double bonds. In compound **4** the S(2)–C(13) and the S(4)–C(34) bond lengths with 1.774(2) and 1.773(3) Å show no significant differences to other known single bond distances [14]. In contrast to compound **2** the bond lengths of the pyrazole carbon atoms to the sulfur atoms of **4** indicate double bonds (S(1)–C(7), 1.680(2) Å and S(3)–C(26), 1.676(2) Å) [15]. All other bond distances are in the normal range.

The atomic coordinates for this work are available on request from the director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this paper.

Cyclic voltammograms of **1** to **4**

The cyclic voltammograms of **1** to **4** were measured in DMF with a scan rate of 50 mV/s starting at 0 V in negative direction. The cyclic voltammogram of **2** is shown in Figure 3 as an typical example of these disulfides. In each voltammogram one irreversible oxidation and one irreversible reduction peak can be observed. The oxidation peak potentials (E_p^{ox}) show the following values: 0.69 V for **1**, 0.67 V for **2** and 0.66 V for **3** and **4**, whereas the reduction peak potentials (E_p^{red}) are at −0.55 V for **1**, −0.56 V for **2** and −0.56 V for **3** and **4** (Table 3). It is difficult to compare these values to the literature, because of the fact that the potentials depend on the solvent and the electrodes. In recent literature the electrochemical properties of disulfides have been studied in detail by cyclic voltammetry in a number of solvent systems [16]. Therein oxidation potentials in the range of 0.05 to 1.52 V and reduction potentials of −0.52 to −2.71 V were described.

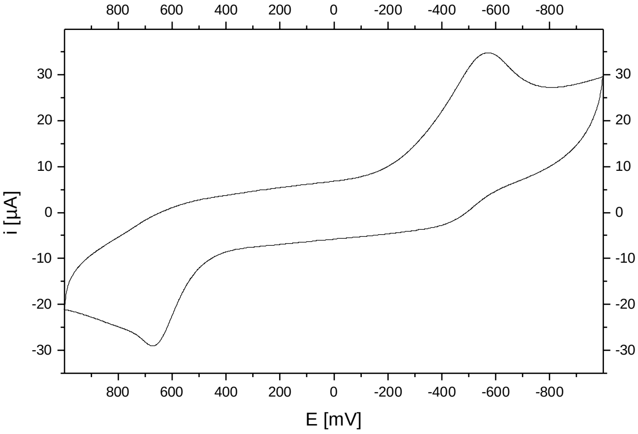

Fig. 3 Cyclic voltammogram of [5,5'-dithiobis-(4-formyl-3-methyl-1-phenylpyrazole)]-4-triphenylmethylthiosemicarbazone (**2**)

Table 3 Peak potentials of compounds **1–4**

	E_p^{ox} (V)	E_p^{red} (V)
1	0.69	−0.55
2	0.67	−0.56
3	0.66	−0.56
4	0.66	−0.56

In aprotic solvents the reduction process of RSSR is, in general, characterized by an irreversible two-electron transfer giving rise to the corresponding thiolate ion RS^- (eqn. (1)).

$$RSSR + 2e^- \rightarrow 2RS^- \qquad (1)$$

An alternative interpretation is that the process initially involves a slow electron transfer step to produce the radical anion $RSSR^{\bullet -}$, which decays in a fast reaction to RS^- and $RS^\bullet$. Depending on the rate of this cleavage the latter compound would then be further reduced to another thiolate ion RS^- (eqn. (2)) [17].

$$RSSR + 2e^- \rightarrow RSSR^{\bullet -} + e^- \rightarrow RS^\bullet + RS^- + e^- \rightarrow 2RS^- \qquad (2)$$

The oxidation peaks in the cyclic voltammograms correspond to the oxidation of RS^- to $RS^\bullet$ which then couples chemically with another $RS^\bullet$ to form the disulfide (eqn. (3)) [18].

$$2RS^- - 2e^- \rightarrow 2RS^\bullet \rightarrow RSSR \qquad (3)$$

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Experimental

All experiments involving sulfur-containing materials were performed under argon or nitrogen atmosphere using standard Schlenk and glovebox techniques. Solvents were dried by standard methods and degassed prior to use. The compounds 4-triphenylmethyl-thiosemicarbazide [19], 4-formyl-3-methyl-1-phenyl-5-sulfanylpyrazole [20] and 2-mercaptoacetophenone-4-triphenylmethylthiosemicarbazone [21] were prepared according to the literature. Elemental analyses were carried out at the Institute of Organic Chemistry, University of Münster by using a Perkin-Elmer 240 Elemental Analyser. ^{1}H spectra were recorded on a Bruker WH 300 spectrometer (300 MHz.; calibrated relative to the chemical shifts of the solvent protons). A Bruker FT-IR IFS 48 instrument was used to record the IR-spectra (KBr pellets). Cyclic voltammograms were obtained on a normal potentiostat CV-50W (BAS). Potentials were measured with a glassy carbon working electrode with respect to an Ag/AgCl electrode, and the counter electrode was made of platinum. A reagent grade of tetrabutylammonium perchlorate was used as supporting electrolyte.

5,5'-Dithiobis-[4-formyl-3-methyl-1-phenylpyrazole]

A solution of iodine (0.65 g, 5.1 mmol) in ethanol (50 ml) was added dropwise to a solution of 4-formyl-3-methyl-1-phenyl-5-sulfanylpyrazole (1.09 g, 5.0 mmol) in ethanol (50 ml) until the colour of the iodine persisted. After a few minutes water (100 ml) was added, and the mixture was stirred for 2 h. The yellow precipitate was suction filtered, washed with water and dried *in vacuo* (0.86 g, 80%). *m.p.* 55 °C. – ^{1}H NMR (d_6-DMSO): δ/ppm = 2.38 (s, 6H, CH_3), 7.27–7.55 (m, 10H, ArH), 9.54 (s, 2H, CHO). – IR: ν/cm^{-1} = 3 057m, 2 812w, 1 680s, 1 595m, 1 513m, 1 476m, 1 398m, 1 372m, 1 011m, 758s, 692m.

[2,2'-Dithiobis-(2-mercaptoacetophenone)]-4-triphenylmethylthiosemicarbazone (**1**)

A solution of iodine (0.56 g, 2.2 mmol) in ethanol (20 ml) was added dropwise to a suspension of 2-mercaptoacetophenone-4-triphenylmethylthiosemicarbazone (1.00 g, 2.1 mmol) and triethylamine (2 ml) in ethanol (20 ml) until the colour of the iodine persisted. After a few minutes water (100 ml) was added and the mixture was stirred for 2 h. The yellow precipitate was suction filtered, washed with water and dried *in vacuo* (0.90 g, 90%). *m.p.* 217 °C. – ^{1}H NMR (d_6-DMSO): δ/ppm = 3.13 (s, 6H, CH_3), 7.01–7.66 (m, 38H, ArH), 8.02 (s, 2H, NH), 10.02 (s, 2H, SH). – IR: ν/cm^{-1} = 3 070s, 2 491m, 1 954m, 1 695m, 1 595s, 1 560s, 1 490m, 1 302m, 1 206m, 1 170w, 1 160w, 1 034w, 1 002s, 843s, 726s.

$C_{56}H_{48}N_6S_4$	Calcd.:	C 72.07	H 5.18	N 9.00
(933.3)	Found:	C 72.31	H 5.54	N 8.78.

[5,5'-Dithiobis-(4-formyl-3-methyl-1-phenylpyrazole)]-4-triphenylmethylthiosemicarbazone (**2**)

A solution of 5,5'-dithiobis-[4-formyl-3-methyl-1-phenylpyrazole] (0.50 g, 1.2 mmol) in ethanol (80 ml) was added to a suspension of 4-triphenylmethylthiosemicarbazide (0.76 g, 2.3 mmol) in ethanol (80 ml). The mixture was stirred for 24 h at room temperature and then filtered. The resulting solid was washed with ethanol and dried *in vacuo* (0.9 g, 71%). *m.p.* 217 °C. – ^{1}H NMR (d_6-DMSO): δ/ppm = 2.21 (s, 6H, CH_3), 7.18–7.39 (m, 40H, ArH), 7.87 (s, 2H, NH), 8.79 (s, 2H, CH=N), 11.64 (s, 2H, SH). – IR: ν/cm^{-1} = 3 340m, 3 058m, 3 028m, 1 596m, 1 515s, 1 499s, 1 448m, 1 382m, 1 201m, 1 156m, 1 106m, 1 108w, 751s, 698s.

$C_{62}H_{52}N_{10}S_4$	Calcd.:	C 69.90	H 4.92	N 13.15
(1065.4)	Found:	C 69.68	H 5.11	N 12.98.

Bis[1-(2-mercaptophenyl)-2-(4-(1-phenyl-3-methyl)pyrazole)-azaethene]disulfide (**3**)

A solution of 5,5'-dithiobis-[4-formyl-3-methyl-1-phenylpyrazole] (0.86 g, 2.0 mmol) in ethanol (50 ml) was added to a solution of 2-aminobenzenethiol (0.54 g, 4.0 mmol) in ethanol (10 ml). The mixture was stirred for 24 h at room temperature and then filtered. The resulting orange solid was washed with ethanol and dried *in vacuo* (1.12 g, 85%). *m.p.* 198 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.21 (s, 3H, CH_3), 7.12–8.02 (m, 9H, ArH), 8.54 (s, 1H, CH=N). – IR: ν/cm^{-1} = 3 406w, 3 045w, 2 917w, 1 626s, 1 597m, 1 578s, 1 540m, 1 496s, 1 432m, 1 385m, 1 362m, 1 317s, 1 281s, 1230m, 1 143m, 1 026m, 757s, 688m, 630s.

$C_{34}H_{26}N_{10}S_4$	Calcd.:	C 63.13	H 4.05	N 12.99
(646.9)	Found:	C 62.86	H 4.39	N 12.78.

Bis[1-phenyl-2-(4-(1-phenyl-3-methyl-5-mercapto)pyrazole)-azaethene]disulfide (**4**)

A solution of 2,2'-diaminodiphenyldisulfide (1.06 g, 8.0 mmol) in ethanol (100 ml) was added to a solution of 4-formyl-3-methyl-1-phenyl-5-sulfanylpyrazole (3.48 g, 16.0 mmol) in ethanol (50 ml). The mixture was stirred for 24 h at room temperature and then filtered. The resulting orange solid was washed with ethanol and dried *in vacuo* (4.67 g, 90%). *m.p.* 186 °C. – ^{1}H NMR ($CDCl_3$): δ/ppm = 2.20 (s, 3H, CH_3), 7.05–8.13 (m, 9H, ArH), 8.62 (s, 1H, CH=N). – IR: ν/cm^{-1} = 3 448w, 3 061w, 2 917w, 1 627s, 1 597m, 1 578s, 1 496s, 1 432m, 1 386m, 1 317s, 1 281s, 1 143m, 1 048m, 1 026w, 993w, 758s, 690m, 517s.

$C_{34}H_{26}N_{10}S_4$	Calcd.:	C 63.13	H 4.05	N 12.99
(646.9)	Found:	C 63.45	H 4.26	N 12.69.

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