Diazosulfonate Substituents: A Route to Transition-Metal Complexes with Switchable Water Solubility

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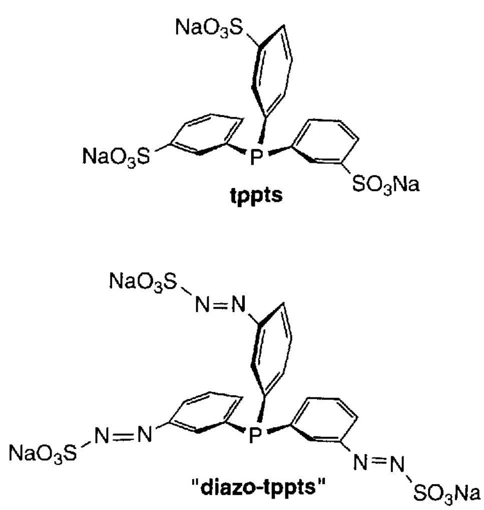
The single-crystal X-ray structure analysis of the diazosulfonate p-$H_2N-C_6H_4-N=N-SO_3Na$ **3** features a Z configuration of the diazo moiety and a nitrogen–sulfur bond. Each sodium atom is coordinated by one diazosulfonate substituent in a chelating manner. Upon reaction of **3** with excess salicylaldehyde, the highly water-soluble Schiff base ligand **6** is obtained in good yield. Treatment of $ZnCl_2$ with 2 equiv. of **6** gives the zinc complex **7**. In all cases, the solubilizing diazosulfonate groups can be cleaved off photolytically, which offers an opportunity to precipitate the molecules from their aqueous solutions.

The introduction of tris(m-sulfonatophenyl)phosphane (tppts, Figure 1), a highly water-soluble analog of the ubiquitous transition-metal ligand triphenylphosphane, immediately initiated the rapid development of homogeneous two-phase catalysis[1]. A prominent example for its successful commercial realization is the rhodium-catalyzed hydroformylation of propylene (Ruhrchemie/Rhône-Poulenc)[2].

Figure 1. The water-soluble ligand tppts and its hypothetical analog "diazo-tppts"



Ligand design, however, is generally hampered by the drastic conditions required for the sulfonation reaction (fuming sulfuric acid), which is quite often accompanied by oxidative degradation processes. Moreover, in many cases the introduction of sulfonate groups into the ligand framework does not occur with the desired selectivity. Varying degrees of sulfonation and the formation of inseparable mixtures of regioisomers are common problems with considerable impact on the usability of the products obtained.

The purpose of this paper is to suggest a modification of conventional sulfonate substituents by formally inserting a diazo group into the $C_{Aryl}-SO_3^-$ bond. In the case of tppts, for example, this manipulation would result in a hypothetical "diazo-tppts" ligand (Figure 1). Several advantages may be anticipated when diazosulfonates are substituted for sulfonates to generate water-soluble transition-metal complexes. New ways of tackling the selectivity problem are provided, since there are a multiplicity of options for placing amino functions at specific positions into a molecular skeleton[3] and also for transforming them into diazonium salts under mild conditions[4]. Starting from these readily available precursors, the aimed-for diazosulfonates are obtained in a spontaneous reaction upon addition of Na_2SO_3.

Another feature of the thermally stable Aryl-$N=N-SO_3^-$ group is its photolytic cleavability (Scheme 1), which provides a means for releasing the anionic substituents from the body of the complex and thereby for switching off its water-solubility at will. This behavior is without parallel in the chemistry of arylsulfonates and may be used for the selective precipitation of metal ions from their aqueous solutions. Nuyken et al. have already exploited the photosensitivity of diazosulfonates in macromolecular chemistry for the creation of water-soluble polymers and photoresins[5,6]. It is worth mentioning that, despite their sensitivity to UV irradiation, diazosulfonates may be handled without problems in diffuse daylight.

Even though aryldiazosulfonates have been known for about a hundred years[7], their structural properties have long been under some debate[8]. We have therefore performed the first single-crystal X-ray structure analysis of a diazosulfonate derivative (Figure 2) to determine unequivocally whether (i) the $-N=N-$ moiety indeed adopts a Z

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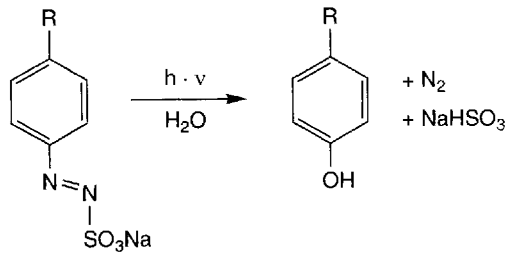
Scheme 1. Regioselective formation of phenols upon photolytic cleavage of aryldiazosulfonates with UV light in aqueous solution

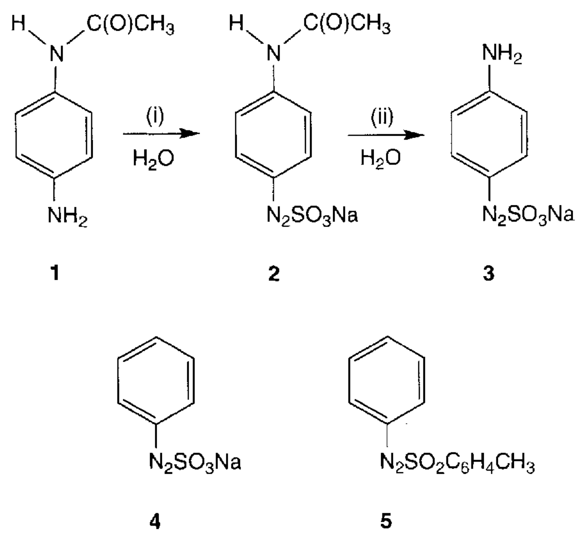


configuration in its electronic ground state as indicated by IR and UV/Vis spectroscopy, and (ii) the coupling reaction between aryldiazonium salts and sulfite ions occurs with N–O or N–S bond formation.

Results and Discussion

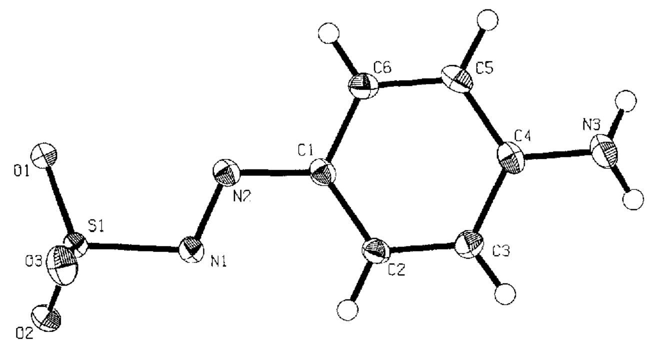
The general route from commercially available **1** to compounds **2** and **3** (Scheme 2) has already been described by Nuyken; however **3** was used in situ for further reactions and was not isolated[6].

Scheme 2. Reagents: (i) $HCl/NaNO_2$, 0°C, 10 min; $Na_2SO_3/Na_2CO_3 \cdot 10\,H_2O$, ambient temp., 1 h. (ii) NaOH, 50°C, 1.5 h; HCl, 0°C



Orange needles of **3** crystallize from its aqueous solution with 2 equiv. of water in the monoclinic space group $P2_1/c$; a plot of the anionic moiety only is given in Figure 2. The diazosulfonate substituent features a *Z* configuration of the –N=N– fragment and a nitrogen–sulfur bond (as opposed to a nitrogen–oxygen bond) in the solid state. Both the O(1)–S(1) bond and the –N=N–S– backbone are located essentially in the plane of the aryl ring, thereby inviting π overlap between these components [dihedral angles: O(1)–S(1)–N(1)–N(2) = –14.6(1)°; N(1)–N(2)–C(1)–C(2) = –5.5(2)°]. However, the N(1)–N(2) bond length of 1.260(2) Å, which lies in the range normally observed for substituted *E* and *Z* azobenzenes [*d*(NN) = 1.25–1.26 Å][9], indicates an unperturbed double bond. For N(2)–C(1) and S(1)–N(1), the bond lengths [1.415(2) Å and 1.730(1) Å, respectively] do not appear to be significantly shortened[10]. Thus, there is no structural evidence for π delocalization between the –N=N– linker and either the SO_3 moiety or the aryl ring.

Figure 2. PLATON plot of the anionic moiety of **3**. Elements are represented by thermal ellipsoids at the 50% probability level. Selected bond lengths (Å), angles and dihedral angles (deg): Na(1)–O(1)a 2.354(1), the other Na(1)–O distances fall in the range 2.303(2)–2.415(2), Na(1)–N(2)a 2.677(2), S(1)–O(1) 1.447(1), S(1)–O(2) 1.452(1), S(1)–O(3) 1.447(1), S(1)–N(1) 1.730(1), N(1)–N(2) 1.260(2), N(2)–C(1) 1.415(2), N(3)–C(4) 1.386(2); O(1)a–Na(1)–N(2)a 65.4(1), O(1)–S(1)–N(1) 110.0(1), S(1)–N(1)–N(2) 112.6(1), N(1)–N(2)–C(1) 114.9(1), N(2)–C(1)–C(2) 124.3(2), N(2)–C(1)–C(6) 116.1(1); N(1)–N(2)–C(1)–C(2) –5.5(2), N(1)–N(2)–C(1)–C(6) 173.8(2), S(1)–N(1)–N(2)–C(1) –175.5(1), O(1)–S(1)–N(1)–N(2) –14.6(1)

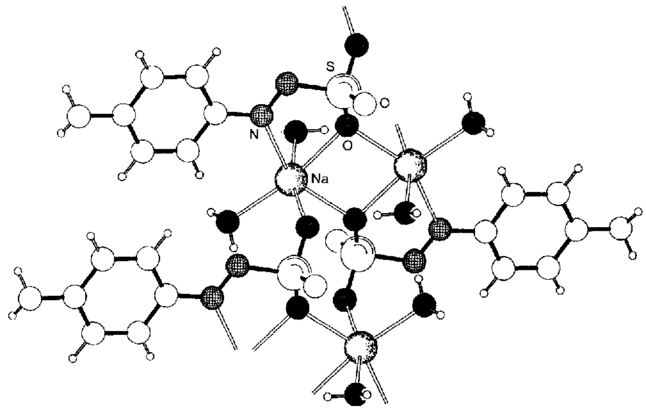


For the amino group (which acts as a weak hydrogen bond acceptor towards a water molecule in the crystal lattice [contact distance: N···H–O = 2.945(2) Å], a pyramidal configuration is found, the sum of angles around the nitrogen atom being 342°. The N(3)–C(4) bond length [1.386(2) Å] has a value intermediate between that of the electron-rich *p*-phenylenediamine (1.43 Å)[11] and the electron-poor derivative *p*-nitroaniline (1.36 Å)[12]. Moreover, in contrast to *p*-nitroaniline, no systematic alteration of C–C bond lengths within the aromatic ring is observed in **3**, which excludes a quinoid character of this molecule. These cited observations all indicate that the diazosulfonate substituent behaves electronically as an "innocent spectator", which has neither pronounced π-donating nor π-accepting properties.

Six donor atoms are arranged in a distorted octahedral configuration around each sodium atom (Figure 3), which in turn connects three different 4-aminophenyldiazosulfonates: **3**, **3a** and **3b**. O(1) and N(2) of anion **3a** bind to two adjacent coordination sites of the same Na^+ ion, thereby testifying to the fact that the diazosulfonate moiety may behave as a chelating ligand towards metal atoms. **3** and **3b** are each bound to sodium via one oxygen atom of their sulfonate units. The remaining coordination sites at the Na^+ ion are occupied by two *cis*-configured water molecules. One oxygen atom of each RSO_3^- fragment bridges two sodium ions [Na···Na distance: 3.518(1) Å], which results in the formation of Na_2O_2 four-membered ring arrangements. In general, the crystal lattice of **3** is composed of alternating hydrophobic and hydrophilic layers; the latter are stabilized by an intricate network of hydrogen bonds

N−H···O, O−H···O and O−H···N with contact distances varying between 2.788(2) and 3.052(2) Å.

Figure 3. Coordination sphere of Na^+ in **3** · 2 H_2O



The chemical behavior of any metal complex is largely dependent on the σ-donating/π-accepting ability of its constituent ligands. These properties should therefore be influenced as little as possible by the presence of the solubilizing substituents. The X-ray crystal structure of **3** already indicates that this condition is met by the diazosulfonate group. Further evidence can be gained with the help of ^{13}C-NMR spectroscopy. The term $\Delta\pi = \delta(^{13}C)_{para} - \delta(^{13}C)_{meta}$[13] will be used to quantify electronic substituent effects on the π-electron density of the aryl ring, with negative values of Δπ indicating electron-releasing and positive values electron-withdrawing groups. Since Δπ values are only valid for monosubstituted benzene rings, we have investigated sodium phenyldiazosulfonate **4** as well as the sulfone **5**, which no longer bears a negative charge (Scheme 2). The Δπ values of **4** and **5**, together with those of selected compounds for comparison[14], are summarized in Table 1. From these data it may be concluded that the electron-withdrawing power of the diazosulfone substituent equals that of the nitro group. In contrast, the diazosulfonate moiety is an extremely weak π donor, causing only minor perturbation of the aromatic ring. In comparison, conventional sulfonate substituents have moderate electron-withdrawing properties.

Table 1. Δπ values of the monosubstituted benzenes **4** and **5** and of selected C_6H_5R compounds for comparison

R	δ(*para*)	δ(*meta*)	Δπ	Solvent
N_2^+ [14]	144.5	134.2	+10.3	$CDCl_3$
$N_2SO_2C_6H_5CH_3$	135.8	130.3	+5.5	[D6]DMSO
NO_2 [14]	134.6	129.4	+5.2	$CDCl_3$
SO_3^- [14]	131.5	128.9	+2.6	[D6]DMSO
$N_2C_6H_5$ [14]	130.7	128.8	+1.9	$CDCl_3$
H [14]	128.5	128.5	±0	$CDCl_3$
$N_2SO_3^-$	129.7	131.0	−1.3	[D6]DMSO
CH_3 [14]	125.4	128.4	−3.0	$CDCl_3$
$N(CH_3)_2$ [14]	117.0	129.4	−12.4	$CDCl_3$

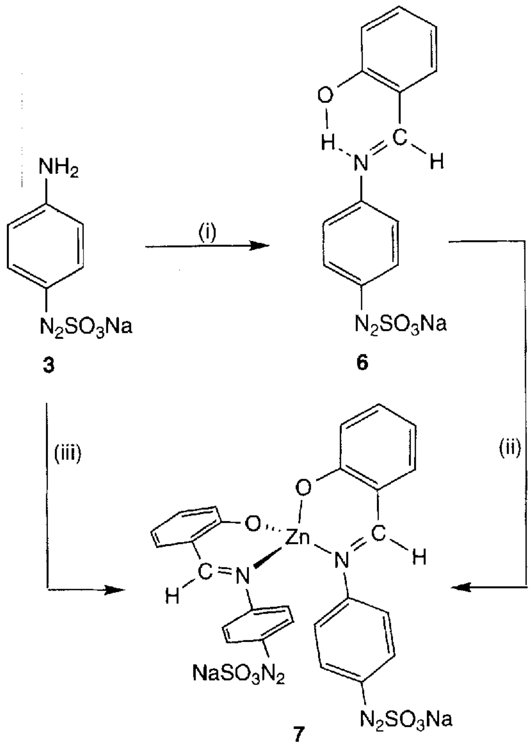
Certain transition-metal ions are known to break down aryldiazonium cations, with dinitrogen being liberated in the course of the reaction[4]. A similar reactivity of the diazosulfonate substituent would obviously mean a considerable restriction of its usability in transition-metal ligands. To obtain information about this, a water solution of **3** was treated with Fe^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, $Cu^{+/2+}$, Ag^+ and Zn^{2+} and the characteristic absorption of the diazosulfonate moiety (λ_{max} = 376 nm) was monitored in the UV/Vis spectrum. The presence of copper ions, which are catalysts for the Sandmeyer reaction[4], also led to rapid destruction of **3**. In the case of Pd^{2+}, the experiments did not give fully reproducible results, therefore some negative effect of this metal cannot be ruled out. All other ions had no impact on the diazosulfonate moiety.

Compound **3** provides access to organic imines, which are well known for their excellent ligand properties. Treatment of **3** with salicylaldehyde in refluxing methanol gave the Schiff base **6** in good yield. However, a large excess of the aldehyde is required to draw the reaction to completion. **6** was obtained as a yellow powder (λ_{max} = 358 nm). When an aqueous solution of **6** is irradiated with the light of a mercury lamp for 1 min, the absorption at λ = 358 nm vanishes, thereby testifying to the photolytic cleavage of the diazosulfonate unit (Scheme 1). Both an absorption at 1622 cm^{-1} in the infrared spectrum of **6** and a resonance at δ = 9.04 in its ^{1}H-NMR spectrum are indicative of the presence of an imino function in this molecule.

Zn^{2+} was chosen for the preparation of the first metal complex of **6**, because it possesses a diamagnetic nature and normally establishes a tetrahedral coordination geometry, which excludes the formation of stereoisomers. The zinc complex **7** is formed from **6**, zinc(II)chloride and NEt_3 in refluxing methanol (Scheme 3). However, a one-pot synthesis employing a mixture of **3**, salicylaldehyde and zinc(II)-acetate also gave satisfactory results. The elemental analysis of the product obtained excludes an octahedral coordination of the zinc ion by three imino ligands. Only one set of signals is found in the NMR spectra of **7**, and all chemical shifts closely resemble those of other tetrahedral Schiff base complexes of Zn(II)[15], which have been structurally characterized by X-ray crystallography. Thus, all data obtained on **7** are consistent with the molecular structure given in Scheme 3, and there is no indication of a contribution of the diazosulfonate moiety to the zinc coordination. Both the free ligand **6** and the zinc complex **7** are readily soluble in water and can be precipitated from their solutions upon irradiation with UV light. While **6** did not show any tendency to hydrolyze over an extended period of time, the half-life time of **7** in aqueous solution is only about 6 h. The hydrolysis of **7** in D_2O was monitored by NMR spectroscopy and found to lead to the liberation of the free ligand **6**.

We conclude that the diazosulfonate substituent represents a promising alternative to conventional sulfonate groups for the generation of water-soluble transition-metal complexes. Our future research will focus on ligand development (e.g. "diazo-tppts") to increase the water stability of the resulting transition-metal complexes. Moreover, the diazosulfonate substituent does not necessarily have to be

Scheme 3. Reagents: (i) salicylaldehyde, methanol reflux, 2 h. (ii) $ZnCl_2/NEt_3$, methanol reflux, 15 min. (iii) salicylaldehyde/$Zn(OC(O)CH_3)_2 \cdot 2\ H_2O$/NaOH, methanol reflux, 15 min



introduced directly into the ligand framework, but may be tied to the complex via a suitable linker. We have already obtained encouraging results using **3** as a solubilizing group, together with transition-metal ligands bearing reactive hydroxy or amino groups and cyanuric chloride as the linker between them.

Helpful discussions with Prof. Dr. *O. Nuyken* and Dr. habil. *B. Voit* (Technische Universität München) are gratefully acknowledged. We are also grateful to Prof. Dr. *W. A. Herrmann* (Technische Universität München) for his generous support and to the *"Bayerischer Forschungsverbund Katalyse"* (FORKAT) for funding.

Experimental Section

General: NMR: Jeol JMN-GX 400 and Bruker DPX 400. – IR: Perkin-Elmer 1650 FTIR. – UV/Vis: Hewlett-Packard 8452 A. – Elemental analyses: Microanalytical laboratory of the Technische Universität München. – Compounds **2** and **4** were synthesized according to literature procedures[5,6].

Preparation of **3**: A solution of 4.86 g (18.32 mmol) of **2** in 30 ml of water was treated at ambient temp. first with 18.4 ml of an aqueous solution of picric acid (1%) and then with 1.45 g (36.25 mmol) of NaOH. The resulting red mixture was kept at 50°C for 1.5 h and then cooled to 0°C in an ice bath. 1.75 ml (18.42 mmol) of aqueous HCl (32%) was added, and the mixture adopted an orange colour. The solution was brought to neutral pH by careful addition of dilute HCl (3%) whereupon a yellow precipitate formed. The solid material was collected on a frit (G3) and dried in vacuo. The filtrate was concentrated to about half its original volume to yield a second crop of **3**. – Yield: 2.64 g (56%). – UV/Vis (H_2O): λ_{max} = 376 nm. – ^1H NMR (400 MHz, $[D_6]DMSO$): δ = 6.04 (s, 2H, NH_2), 6.61 [d, 2H, J(HH) = 8.8 Hz, C_6H_4], 7.49 [d, 2H, J(HH) = 8.8 Hz, C_6H_4]. – ^{13}C NMR (100.5 MHz, $[D_6]DMSO$): δ = 113.4, 125.3, 140.4, 153.3 (C_6H_4). – $C_6H_6N_3NaO_3S$ (223.18) $\cdot$ 2 H_2O (18.02): calcd. C 27.80, H 3.89, N 16.21, S 12.37; found C 27.55, H 3.58, N 16.00, S 11.84.

^{13}C-NMR Data of **4**: The compound was synthesized as described by Nuyken[5] to obtain the missing ^{13}C-NMR data. – ^{13}C NMR (100.5 MHz, D_2O): δ = 128.0 (o-C_6H_5), 129.7 (p-C_6H_5), 131.0 (m-C_6H_5), 146.2 (i-C_6H_5).

Preparation of **5**: A mixture of aniline (0.95 g, 10.20 mmol) and water (10 ml) was treated at ambient temp. with 3.8 ml of aqueous HCl (32%). An aqueous solution of $NaNO_2$ (0.69 g, 10.00 mmol) was added at 0°C, then the yellow mixture was stirred for 10 min and added to a solution of sodium toluenesulfonate (3.46 g, 19.53 mmol) and $Na_2CO_3 \cdot 10\ H_2O$ (11.07 g, 38.69 mmol) in 15 ml of water. Upon stirring for 1 h at ambient temp. an orange solid gradually precipitated, which was collected on a frit (G3), treated with water (2 × 20 ml) and redissolved in 10 ml of diethyl ether. The ether solution was extracted with water (4 × 50 ml), dried over anhydrous $MgSO_4$, filtered and the filtrate slowly concentrated in vacuo. A yellow crystalline solid formed, which was collected on a frit (G3) and dried in vacuo. – Yield: 2.39 g (90%). – UV/Vis (EtOH): λ_{max} = 294 nm. – ^1H NMR (400 MHz, $[D_6]DMSO$): δ = 3.35 (s, 3H, CH_3), 7.53 [d, 2H, J(HH) = 8.5 Hz, C_6H_4S], 7.61 [vtr, 2H, J(HH) = 7.5 Hz, m-C_6H_5], 7.73 [t, 1H, J(HH) = 6.7 Hz, p-C_6H_5], 7.78 [d, 2H, J(HH) = 8.0 Hz, o-C_6H_5], 7.83 [d, 2H, J(HH) = 8.5 Hz, C_6H_4S]. – ^{13}C NMR (100.5 MHz, $[D_6]DMSO$): δ = 21.4 (CH_3), 124.3 (o-C_6H_5), 129.1 (i-C_6H_4S), 130.2 (C_6H_4S), 130.3 (m-C_6H_5), 130.5 (C_6H_4S), 135.8 (p-C_6H_5), 146.6 (H_3CC), 148.6 (i-C_6H_5). – $C_{13}H_{12}N_2O_2S$ (260.31): calcd. C 59.98, H 4.65, N 10.76, S 12.32; found C 60.11, H 4.76, N 11.04, S 12.25.

Preparation of **6**: To a solution of **3** (0.65 g, 2.51 mmol) in 20 ml of methanol was added with stirring 3.56 g (29.15 mmol) of neat salicylaldehyde. The mixture was refluxed for 2 h and then cooled to ambient temp., whereupon a yellow precipitate formed. The solid material was collected on a frit (G3), extracted with benzene (2 × 30 ml) and dried in vacuo. – Yield: 0.79 g (96%). – UV/Vis (H_2O): λ_{max} = 358 nm. – IR (KBr): $\tilde{\nu}$ = 1622 cm^{-1} (C=N). – ^1H NMR (400 MHz, $[D_6]DMSO$): δ = 6.99 (m, 2H, C_6H_4–C=N), 7.43 [vtr, 1H, J(HH) = 8.5 Hz, C_6H_4–C=N], 7.58 [d, 2H, J(HH) = 8.6 Hz, C_6H_4–N=C], 7.69 (d, 1H, J(HH) = 6.5 Hz, C_6H_4–C=N), 7.83 [d, 2H, J(HH) = 8.6 Hz, C_6H_4–N=C], 9.04 (s, 1H, N=CH). – ^{13}C NMR (100.5 MHz, $[D_6]DMSO$): δ = 116.9, 119.4, 119.6, 122.7, 124.1, 132.8, 134.0, 148.8, 151.5, 160.7 (C_{Ar}), 164.7 (N=C). – $C_{13}H_{10}N_3NaO_4S$ (327.29): calcd. C 47.71, H 3.08, N 12.84, S 9.80; found C 47.63, H 3.21, N 12.50, S 9.59.

Preparation of **7**. – *Method a:* A suspension of **6** (0.05 g, 0.15 mmol) in 10 ml of methanol was treated with 0.02 g (0.20 mmol) of NEt_3 and 0.02 g (0.15 mmol) of zinc(II)chloride. The mixture was refluxed for 15 min and filtered through a frit (G3). The solid residue was extracted with 10 ml of methanol, then 10 ml of diethyl ether and dried in vacuo. – *Method b:* To a solution of **3** (0.41 g, 1.58 mmol) in 20 ml of methanol was added with stirring a solution of 0.20 g (0.91 mmol) of zinc(II)acetate dihydrate in 10 ml of methanol and a solution of 0.22 g (1.80 mmol) of salicylaldehyde in 10 ml of methanol. The mixture was refluxed for 15 min and the hot solution treated dropwise with 0.07 g (1.78 mmol) of NaOH in 5 ml of methanol. Upon cooling to ambient temp. a yellow precipitate formed, which was purified as outlined above. – Yield: 0.52 g (74%). – UV/Vis (H_2O): λ_{max} = 372 nm. – IR (KBr): $\tilde{\nu}$ = 1615 cm^{-1} (C=N). – ^1H NMR (400 MHz, $[D_6]DMSO$): δ = 6.60 [vtr, 2H, J(HH) = 8.0 Hz, C_6H_4–C=N], 6.70 [d, 2H, J(HH) = 8.5 Hz,

C_6H_4–C=N], 7.32 [vtr, 2H, *J*(HH) = 8.0 Hz, C_6H_4–C=N], 7.45 [d, 2H, *J*(HH) = 7.0 Hz, C_6H_4–C=N), 7.51 [d, 4H, *J*(HH) = 8.5 Hz, C_6H_4–N=C], 7.70 [d, 4H, *J*(HH) = 8.5 Hz, C_6H_4–N=C], 8.69 (s, 2H, N=CH). – ^{13}C NMR (100.5 MHz, [D_6]DMSO): δ = 114.5, 119.2, 122.9, 123.2, 123.8, 135.9, 137.5, 148.5, 152.5, 170.5 (C_{Ar}), 171.3 (N=C). – $C_{26}H_{18}N_6Na_2O_8S_2Zn$ (717.94) · 2 H_2O (18.02): calcd. C 41.42, H 2.94, N 11.15, S 8.50, Zn 8.7; found C 41.30, H 2.81, N 11.05, S 8.40, Zn 8.5.

X-ray Crystal Structure Analysis of **3**[16]: An orange crystal of **3** ([$C_6H_{10}N_3NaO_5S$]; M = 259.22) was mounted in a glass capillary on an automatic Four Circle Diffractometer (CAD4, Enraf Nonius). Final lattice parameters were obtained by least-squares refinement of 25 high-angle reflections (graphite monochromator, λ = 0.71073 Å, Mo-K_α). Monoclinic system, space group $P2_1/c$, a = 5.538(1) Å, b = 24.334(4) Å, c = 7.923(2) Å, β = 92.11(1)°, V = 1067.0(4) Å^3, D_{calc} = 1.614 g/cm^3, μ = 0.35 mm^{-1}, Z = 4. Data were corrected for Lorentz and polarization effects. Crystallographic measurement at 163 ± 1 K; range of measurement 1.67° < Θ < 25.97°; 2375 reflections collected: 156 with negative intensity were rejected; all 1953 [1813 with $I > 2\sigma(I)$] independent reflections were used for refinement. The structure was solved by direct methods (SHELXS-86)[17] and refined with standard difference Fourier techniques (SHELXL-93)[18]. All hydrogen atoms were located in the Fourier map and refined freely. Number of parameters refined: 185; 10.6 data per parameter; GOOF: 1.06; residual electron density: +0.33 eÅ^{-3}, –0.40 eÅ^{-3}; $R1$ = 0.0275 [for $I > 2\sigma(I)$], $wR2$ = 0.0743 (all data); minimized function was $\Sigma w(F_o^2 - F_c^2)^2$; $w = 1/[\sigma^2(F_o^2) + (0.0460\ P)^2 + 0.4772\ P)]$ with $P = [\max(F_o^2, 0) + 2\ F_c^2]/3$.

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