Dansylated Polyamines as Fluorescent Sensors for Metal Ions: Photophysical Properties and Stability of Copper(II) Complexes in Solution

by **Luca Prodi***, **Marco Montalti**, and **Nelsi Zaccheroni**

Dipartimento di Chimica 'G. Ciamician', Università degli Studi di Bologna, Via Selmi 2, I-40126 Bologna

and **Francesco Dallavalle***, **Guiseppina Folesani**, and **Maurizio Lanfranchi**

Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università degli Studi di Parma, Parco Area delle Scienze 17/A, I-43100 Parma

and **Roberto Corradini**, **Sara Pagliari**, and **Rosangela Marchelli**

Dipartimento di Chimica Organica e Industriale, Università degli Studi di Parma, Parco Area delle Scienze 17/A, I-43100 Parma

Protonation and the Cu^{II} complexation constants of the dansylated polyamines *N*-dansylethylenediamine (**1**), *N*-dansyldiethylenetriamine (**2**), *N*-dansyltriethylenetetramine (**3**), *N'*-[2-(dansylamino)ethyl]diethylenetriamine (**4**), and tris(2-dansylaminoethyl)amine (**5**) were determined by glass-electrode potentiometry in $MeOH/H_2O$ 9:1 (*v*/*v*) solution. For ligands **3** and **4**, the determinations were also performed in aqueous solution. The complexes formed by these ligands in neutral form correspond to those observed for the analogous unsubstituted monoprotonated amines, whereas, when the ligands are deprotonated at the sulfonamide moiety, the species parallel those of the corresponding amines. The molecular structures of the complexes were deduced from the VIS absorption spectra. The crystal structure of the $[CuL_2H_{-2}]$ complex **6** of ligand **1** (L) was determined by X-ray diffraction. The study of the photophysical properties of the ligands **3**–**5** showed that they are good fluorescent sensors for copper(II), which induced fluorescence quenching. Time-resolved fluorescence measurements allowed us to clarify the sensing mechanism. The pH dependence of the quenching effect demonstrated that it occurs for all Cu^{2+} complexes, even for species in which the sulfonamide moiety is not deprotonated. Sensing of Cu^{2+} was compared with that of other metal ions (Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}), and selectivity was studied as a function of pH. Ligands **3** and **4** were found to be selective chemosensors for Cu^{2+} in weakly acidic solution (pH *ca.* 4–5).

1. Introduction. – The need of sensors for different target analytes is well-recognized and has already stimulated considerable research devoted to the preparation of sensitive and selective sensory devices. Fluorescent chemosensors are of particular interest because of their high sensitivity and selectivity [1] in the detection of metal ions [2], anions [3], and organic bioactive molecules [4].

The increasing awareness of the detrimental role that certain transition-metal ions play in human health (see, *e.g.*, [5]) has stimulated the development of transition metal ion sensors for applications in environmental sciences, medical diagnostics, and food technology. For these reasons, many fluorescent sensors for these metal ions have been lately synthesized and characterized [1][2][6].

In this context, we used *N*-dansylethylenediamine¹) (**1**) and *N*-dansyldiethylenetriamine¹) (**2**) (*Fig. 1*; dansyl = [5-(dimethylamino)naphthalen-1-yl]sulfonyl) as compo-

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¹) For systematic names, see *Exper. Part.*

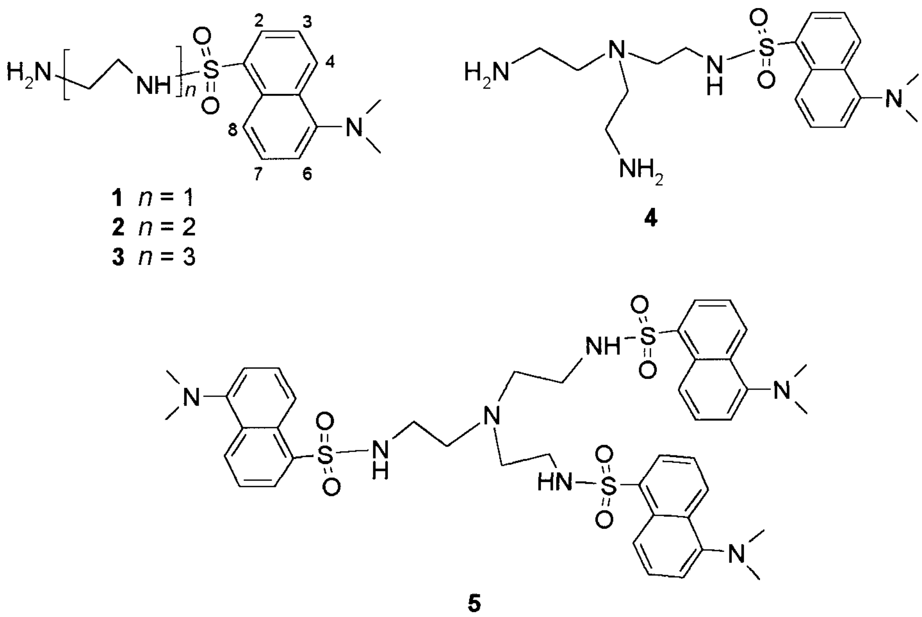

Fig. 1. *Ligands* **1**–**5**

nents in the synthesis of supramolecular sensors based on cyclodextrins, which showed different behavior in their sensing properties towards copper(II) [7][8]. Moreover, we have recently reported the photophysical properties of tris(2-dansylaminoethyl)-amine[1]) (**5**) and of its complexes with different transition-metal ions [9]. The results obtained suggested a possible use of this type of ligands as luminescent chemosensors for copper(II) ions.

The stability, structure, and optical and magnetic properties of the copper(II) complexes with dansylated amino acids were extensively studied [10]; many of these works refer to the dansyl group as a fluorescent probe for protein conformational changes [11][12] and as an identifier of *N*-terminal residues of peptides [13][14]. Zinc(II) and copper(II) complexes of macrocyclic polyamines containing a dansylated side-arm have been recently investigated by *Kimura* and co-workers [15].

In this paper, we report a systematic study of the complexation equilibria of copper(II) with a series of dansylated polyamines, *i.e.* **1**, **2**, *N*-dansyltriethylenetetra-amine[1]) (**3**), *N'*-[2-(dansylamino)ethyl]diethylenetriamine[1]) (**4**), and **5** (*Fig. 1*), with the aim of detecting the species potentially involved in the sensing processes. These ligands were chosen to have access to a different number of amine and sulfonamide N donor atoms and different geometries (linear or branched). Photophysical properties of the two novel ligands **3** and **4** and of their metal complexes were studied as a function of pH to identify the species responsible for the quenching effect and, in particular, to establish if the deprotonation of the sulfonamide group is required for the sensing process, as previously reported for dansylated macrocyclic polyamines with copper(II) and zinc(II) ions [16]. All these data are important to provide a rationale for the design of new ion-sensitive luminophores.

2. Results. – 2.1. *Synthesis.* All ligands were synthesized, according to previously reported procedures [7–9], by reaction of dansyl chloride with the corresponding amine. For the ligands **1**–**4**, mono-functionalization was achieved with an excess of the amine.

2.2. *Solution Equilibria.* 2.2.1. *Ligand Protonation.* Protonation equilibria of the linear Dns-polyamines Dns-en (**1**), Dns-dien (**2**), and Dns-trien (**3**) and of the branched Dns-polyamines Dns-tren (**4**) and Dns_3-tren (**5**) were studied in $MeOH/H_2O$ 9 : 1 (*v*/*v*) at 25° and $I = 0.1$M (KCl). The acidic character of the sulfonamide moiety was found to be quite weak for all ligands (pK_a range 12.5–13.0), and their pK_a could be determined with low precision (±0.2 log units). Therefore, the potentiometric data used in the calculations were limited at pH *ca.* 11.2, and this dissociation was neglected. The results are reported in *Table 1.*

Table 1. *Stepwise Protonation Constants* (log *K*) *for the Ligands* **1**–**5** *in* $MeOH/H_2O$ *9 : 1 and for* **3** *and* **4** *in* H_2O[a]). *T* 25°, $I = 0.1$M (KCl). Standard deviations are given in parentheses.

	Dns-en (**1**)	Dns-dien (**2**)	Dns-trien (**3**)		Dns-tren (**4**)		Dns_3-tren (**5**)
	$MeOH/H_2O$	$MeOH/H_2O$	H_2O	$MeOH/H_2O$	H_2O	$MeOH/H_2O$	$MeOH/H_2O$
$L = [LH_{-1}] + H^+$			–10.74(1)		–10.92(1)		
$L + H^+ = [HL]^+$	8.46(1)	9.18(1)	9.46(1)	9.51(1)	9.83(1)	9.86(1)	3.88(1)
$[HL]^+ + H^+ = [H_2L]^{2+}$	2.00(1)	5.43(1)	7.79(1)	7.88(1)	8.86(1)	8.48(1)	2.33(2)
$[H_2L]^{2+} + H^+ = [H_3L]^{3+}$		2.01(1)	4.05(1)	3.39(1)	3.52(1)	2.07(1)	1.91(5)
$[H_3L]^{3+} + H^+ = [H_4L]^{4+}$			3.32(1)	1.98(1)			

[a]) In the mixed solvent, the dissociation of the sulfonamide group was ignored (see text), and the neutral ligands are indicated as L. In H_2O, however, ligands **3** and **4** dissociate, and this process is indicated as $L = LH_{-1} + H^+$ to have the same formulae for the protonated and complex species in both solvents.

The basicity of the amino groups varies only slightly with respect to that of the corresponding amines in H_2O, and the tertiary aliphatic amino group of Dns-tren (**4**) and Dns_3-tren (**5**) cannot be protonated, as observed for tren [17]. The protonation constants of the Me_2N groups present values around log $K = 2$, while those of the other two groups of Dns_3-tren (**5**) show higher values. The protonation equilibria of Dns-trien (**3**) and Dns-tren (**4**), which are H_2O-soluble, were also studied in aqueous solution where the acidity of the sulfonamide group was strongly increased ($pK_a = 10.74$ and 10.92, resp.). However, hereafter, these ligands in neutral form will be indicated as L to have the same formulae for protonated and complex species in both solvents (see footnote in *Table 1*). The observed increase of acidity is in agreement with that reported for other neutral acids (*e.g.*, acetic acid in $MeOH/H_2O$ 8 : 2 (*w*/*w*), $pK_a = 6.57$, and in H_2O, $pK_a = 4.73$ [18]).

2.2.2. *Cu^{II} Complexation.* The stability constants obtained for copper(II) complexes of the Dns-amines **1**–**5** in $MeOH/H_2O$ and of **3** and **4** in H_2O are given in *Table 2.* When neutral, all these ligands form the same complexes with copper(II) as the corresponding monoprotonated amines, whereas, when anionic, they parallel the behavior of the amines [17]. It is worth noting that, in both solvents, Dns-trien (**3**) forms also the species $[CuLH]^{3+}$, in which the cationic ligand is terdentate, with the residual proton on the tertiary amino group of the dansyl moiety (see *Sect. 3.1*). In the

Table 2. *Formation Constants log* β_{pqr} ($\beta_{pqr} = [Cu_pL_qH_r]/[Cu]^p[L]^q[H]^r$) *of the* Cu^{II} *Complexes of Dansylated Polyamines* **1**–**5**. *T* 25°, $I = 0.1$M (KCl). Standard deviations are given in parentheses.

Dns-en (**1**)		Dns-dien (**2**)		Dns-trien (**3**)			Dns-tren (**4**)			Dns$_3$-tren (**5**)	
	MeOH/ H_2O		MeOH/ H_2O		MeOH/ H_2O	H_2O		MeOH/ H_2O	H_2O		MeOH/ H_2O
$[CuLH_{-1}]^+$	−0.98(1)	$[CuL]^{2+}$	9.87(1)	$[CuLH]^{3+}$	18.57(4)	17.94(1)	$[CuL]^{2+}$	14.61(1)	13.76(1)	$[CuLH_{-2}]$	−7.72(1)
$[CuL_2H_{-2}]$	−2.95(1)	$[CuLH_{-1}]^+$	4.91(2)	$[CuL]^{2+}$	16.47(1)	14.60(1)	$[CuLH_{-1}]^+$	7.91(3)	8.03(2)		
		$[CuLH_{-1}(OH)]$	−5.32(3)	$[CuLH_{-1}]^+$	11.08(2)	10.22(1)	$[CuLH_{-1}(OH)]$	−3.00(4)	−1.85(3)		
		$[CuL]^{2+}$	17.60(6)				$[CuL_2]^{2+}$	22.18(4)	[b])		
		$[CuL_2H_{-1}]^+$	10.12(7)				$[CuL_2H_{-1}]^+$	13.39(5)	[b])		
s^2 [a])	2.19		3.24		3.06	3.72		2.69	4.08		1.30
n [a])	282		168		371	296		208	274		107

[a]) $s^2 = \Sigma w_i\,(E^{i}_{obs} - E^{calc}_{i})^2/(n - m)$ = sample variance; $w_i = 1/\sigma_i^2$ where σ_i is the expected error on each experimental *e.m.f.* value (E_i^{obs}); n = number of observations, m = number of parameters to be refined. [b]) Precipitate; see *Exper. Part*

case of Dns$_3$-tren (**5**), two sulfonamide protons are released simultaneously in the presence of Cu^{2+} to give the species $[CuLH_{-2}]$, in agreement with what was already found by means of photophysical studies [9]. The hydroxo species $[CuLH_{-1}(OH)]$ was found only for Dns-dien (**2**) and Dns-tren (**4**), as reported for dien and tren [17].

The complexation equilibria of Dns-trien (**3**) and Dns-tren (**4**) were investigated also in aqueous solution, and the species formed by the former were the same as those found in the mixed solvent (*Table 2*). Representative speciation diagrams for Dns-trien (**3**) and Dns-tren (**4**) in aqueous solution are reported in *Figs. 2* and *3*, respectively.

2.2.3. *Spectrophotometry.* A spectrophotometric study in the VIS region was carried out with the aim of confirming the speciation models obtained by potentiometry and of establishing the coordination modes of the various Cu^{2+} complexes. The spectroscopic parameters ($\lambda_{max}(\varepsilon)$) of the complexes are reported in *Table 3*, together with the literature data for the analogous species of the corresponding amines [19–21]. There is general agreement for λ_{max} of complexes with the same number of N donor atoms (either N or N^-) of the two series of ligands.

2.3. *Single-Crystal Structure of [*CuL_2H_{-2}*]* (**6**) *of Dns-en* (**1**). The crystal structure of **6** consists of centrosymmetric square planar Cu^{II} complexes in which the ligands chelate through the amine and deprotonated sulfonamide N-atoms (Cu−N(1) 1.978(2) and Cu−N(2) 2.028(2) Å). The complex, depicted in *Fig. 4*, shows only the predominant image of the disordered CH_2 and Me C-atoms. Selected bond distances and angles are listed in *Table 4*[2]).

The sulfonamide groups interact through an O-atom with two other Cu atoms determining an elongated octahedral coordination (Cu−O(2′) 2.599(2) Å). The whole structure consists of polymeric chains, in which the sulfonamide groups form a double

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[2]) Crystallographic data (excluding structure factors) for structure **6** have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-147783. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

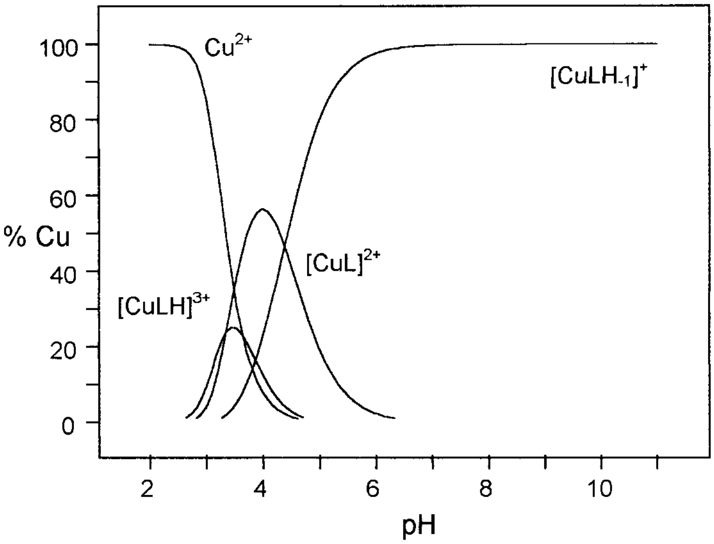

Fig. 2. *Species distribution for the Cu^{II}/Dns-trien* (**3**) *1:1 system in H_2O.* $C_{Cu} = 1 \cdot 10^{-3}$ M.

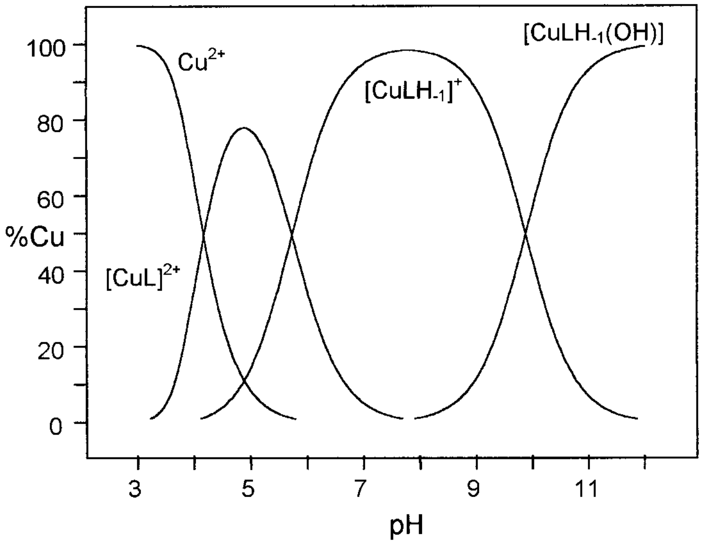

Fig. 3. *Species distribution for the Cu^{II}/Dns-tren* (**4**) *1:1 system in H_2O.* $C_{Cu} = 1 \cdot 10^{-3}$ M.

linking, and octaatomic dimetallacycle rings running parallel to *b*. The amine N-atom exchanges only one H-bond with a centrosymmetric sulfonamide O-atom so that the polymeric chains are linked together only by *van der Waals* interactions.

2.4. *Photophysical Studies.* 2.4.1. *Ligands.* The photophysical properties of compounds **3** and **4** (*Table 5*) do not show any pH dependence in the range 4–10 in

Table 3. *Spectral Properties* (λ_{max} (ε) in nm (cm^{-1} M^{-1})) *and Coordinated Atoms for Copper(II) Complexes of Dansylated Polyamines* **1**–**5** *and of the Corresponding Amines.* O_w = O-Atom of H_2O.

Dns-en (**1**)		Dns-dien (**2**)		Dns-trien (**3**)			Dns-tren (**4**)			Dns_3-tren (**5**)	
	MeOH/ H_2O		MeOH/ H_2O		MeOH/ H_2O	H_2O		MeOH/ H_2O	H_2O		MeOH/ H_2O
$[CuLH_{-1}]^+$ ($N,N^-, 2O_w$)	715 (95)	$[CuL]^{2+}$ ($2N,2O_w$)	710 (78)	$[CuLH]^{3+}$ ($3N,O_w$)	656 (95)	625 (118)	$[CuL]^{2+}$ ($3N,O_w$)	651 (109)	638 (109)	$[CuLH_{-2}]$ ($N,2N^-,O_w$)	638 (127)
$[CuL_2H_{-2}]$ ($2N,2N^-$)	588 (121)	$[CuLH_{-1}]^+$ ($2N,N^-,O_w$)	636 (96)	$[CuL]^{2+}$ ($3N,O_w$)	642 (149)	608 (129)	$[CuLH_{-1}]^+$ ($3N,N^-, O_w$)	856 (170)	881 (160)		
		$[CuLH_{-1}(OH)]$ ($2N,N^-,OH$)	614 (118)	$[CuLH_{-1}]^+$ ($3N,N^-$)	596 (181)	588 (166)	$[CuLH_{-1}(OH)]$ ($3N,N^-, OH$)	807 (175)	822 (174)		
en [a])		dien [a])		trien [b])[c])			tren [c])				
$[CuL]^{2+}$ ($2N,2O_w$)	660	$[CuL]^{2+}$ ($3N,O_w$)	615	$[CuLH]^{3+}$ ($3N,O_w$)	610		$[CuL]^{2+}$ ($4N,O_w$)	870			
$[CuL_2]^{2+}$ (4N)	550	$[CuL(OH)]^+$ (3N,OH)	605	$[CuL]^{2+}$ (4N)	575		$[CuL(OH)]^+$ (4N,OH)	840			
				$[CuL(OH)]^+$ (3N,OH)	587						

[a]) From [19], in H_2O. [b]) From [20], in H_2O. [c]) From [21], in H_2O.

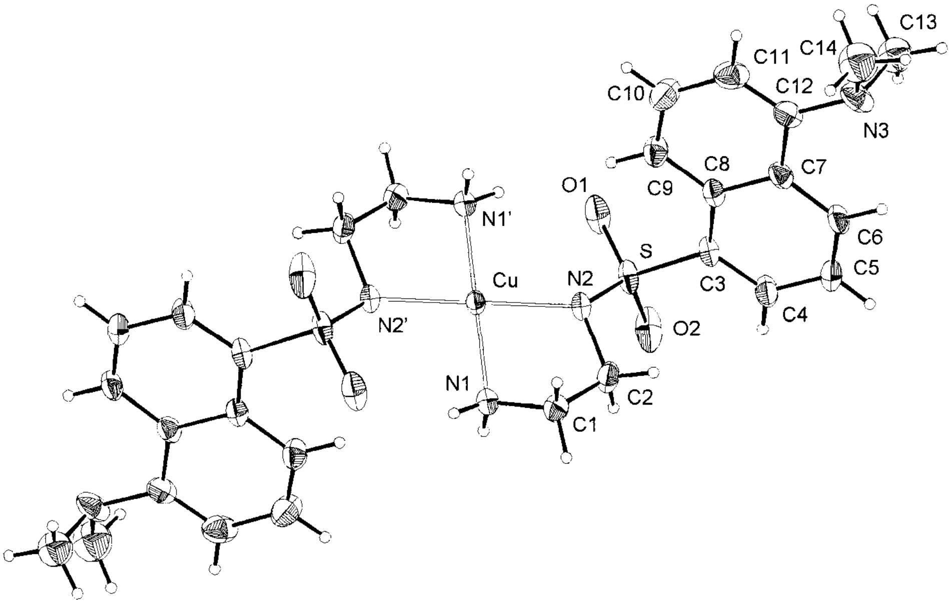

Fig. 4. *Perspective view of* $[CuL_2H_{-2}]$ (**6**) *of Dns-en* (**1**). Only one of the two disordered positions of the CH_2 and Me groups are shown. The thermal ellipsoids are drawn at the 30% probability level.

Table 4. *Selected Bond Lengths* [Å] *and Angles* [deg] *for the Complex [CuL$_2$H$_{-2}$]* (**6**) *of Dns-en* (**1**)

Cu–N(1)	1.978(2)	S–C(3)	1.791(2)
Cu–N(2)	2.028(2)	N(1)–C(1)	1.454(5)
Cu–O(2′)a)	2.599(2)	N(2)–C(2)	1.496(7)
S–O(1)	1.443(2)	C(1)–C(2)	1.507(11)
S–O(2)	1.445(2)	C(3)–C(4)	1.373(3)
S–N(2)	1.566(2)	C(3)–C(8)	1.429(3)
N(1)–Cu–N(2)	83.40(8)	C(1)–N(1)–Cu	107.5(2)
N(1)–Cu–O(2′)a)	88.92(8)	C(2)–N(2)–S	108.8(3)
N(2)–Cu–O(2′)a)	88.20(6)	C(2)–N(2)–Cu	110.4(3)
O(1)–S–O(2)	114.8(1)	S–N(2)–Cu	129.3(1)
O(1)–S–N(2)	109.5(1)	N(1)–C(1)–C(2)	107.6(6)
O(2)–S–N(2)	113.5(1)	N(2)–C(2)–C(1)	107.2(5)
O(1)–S–C(3)	107.7(1)	C(4)–C(3)–C(8)	120.8(2)
O(2)–S–C(3)	104.4(1)	C(4)–C(3)–S	117.0(2)
N(2)–S–C(3)	106.4(1)	C(8)–C(3)–S	122.2(2)

a) Symmetry transformations used to generate equivalent atoms: *x*, *y – 1*, *z*.

aqueous solution. At lower pH values, we observed the disappearance of the absorption band in the 300–400 nm region and the appearance of the structured band typical of naphthalene derivatives with λ_{max} at 295 nm. Similar behavior was observed in the fluorescence spectrum, where the unstructured band in the 400–600 nm region disappeared and a new structured band appeared with λ_{max} at 345 nm. In contrast, at high pH values, a blue shift and an intensity increase was observed both for the absorption and the luminescence bands.

2.4.2. *Complexes with Cu^{2+}.* We already reported [9] that addition of a Cu^{2+} solution to a neutral H_2O/MeCN 1:1 (*v*/*v*) solution of **5** induced a strong decrease in the fluorescence intensity and excited-state lifetime of the ligand. Ligands **3** and **4** showed an analogous behavior in aqueous solution. Titrating aqueous buffered solutions (pH 9.5, borate) of ligands **3** and **4** with Cu^{2+}, an almost complete fluorescence quenching was obtained after the addition of 1 equiv. of Cu^{2+}. The observed changes for compounds **3** and **4** (*Figs. 5* and *6*) were very sensitive to the pH conditions, as it was already reported for **5** [9]. This pH-dependent behavior was fully reversible in the range 3–11.

2.4.3. *Complexes with Other Metal Ions.* Addition to a $5 \cdot 10^{-5}$ M solution of **3**, **4**, or **5** of up to 100 mol-equiv. of Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Eu^{3+}, Tb^{3+}, Mn^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, and Cr^{3+} did not lead to any change in the absorption and emission spectra of the ligands in the pH range 3–11. Furthermore, no effects were found on the absorption and luminescence spectra upon addition of up to 10 equiv. of the aforementioned metal ions to a solution of equimolar amounts of these ligands and Cu^{2+}. Instead, the photophysical properties of **5** were affected by Co^{2+}, Zn^{2+}, and Cd^{2+} [9], and those of **3** and **4** also by Ni^{2+} and Hg^{2+} (*Figs. 5* and *6*). In particular, a quenching of the fluorescence band was observed with Co^{2+}, Ni^{2+}, and Hg^{2+}, while a blue shift and an intensity increase were caused by Zn^{2+} and Cd^{2+} (*Table 5*).

3. Discussion. – 3.1. *Solution Structures of the Cu^{II} Complexes.* Involvement of the sulfonamide N-atom in metal coordination takes place only upon deprotonation

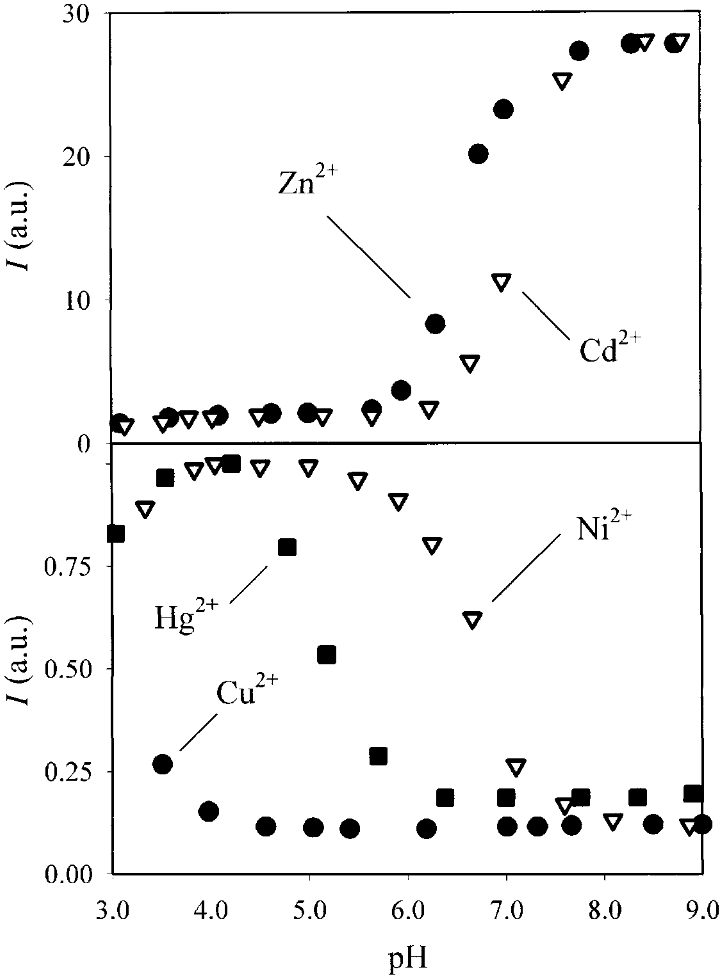

Fig. 5. *pH Dependence of the fluorescence intensity* (λ_{exc} 326 nm) *of aqueous solutions containing equimolar amounts* ($5 \cdot 10^{-5}$ M) *of Dns-trien* (**3**) *and various metal ions.* Upper panel: Zn^{2+} (●), λ_{em} 518 nm, Cd^{2+} (▽), λ_{em} 518 nm. Lower panel: Ni^{2+} (▽), superimposed on Co^{2+} (not shown), λ_{em} 565 nm, Cu^{2+} (●), λ_{em} 565 nm, Hg^{2+} (■), λ_{em} 565 nm. The fluorescence intensity was normalized to that of the ligand at the same wavelength.

assisted by an adjacent anchoring group (*e.g.* $-COO^-$ for *N*-tosyl- and *N*-dansyl-protected α-amino acids) with formation of a chelate ring [10]. In $MeOH/H_2O$ solution, Cu^{2+} promotes a remarkable acidity increase of the sulfonamide group in $[CuL]^{2+}$ of ligands **2**–**4**, which present at least one anchoring amino group ($pK_a = 4.90$ for Dns-dien (**2**), 5.39 for Dns-trien (**3**), and 6.70 for Dns-tren (**4**)). These values are in agreement with that reported for the Cu^{2+} complex of a tetraazamacrocyclic ligand with a dansylated side arm ($pK_a = 5.6$) [15].

The molecular structures of the various species can be inferred from the spectrophotometric data (*Table 3*). The complexes of the linear dansyl amines **1**–**3**

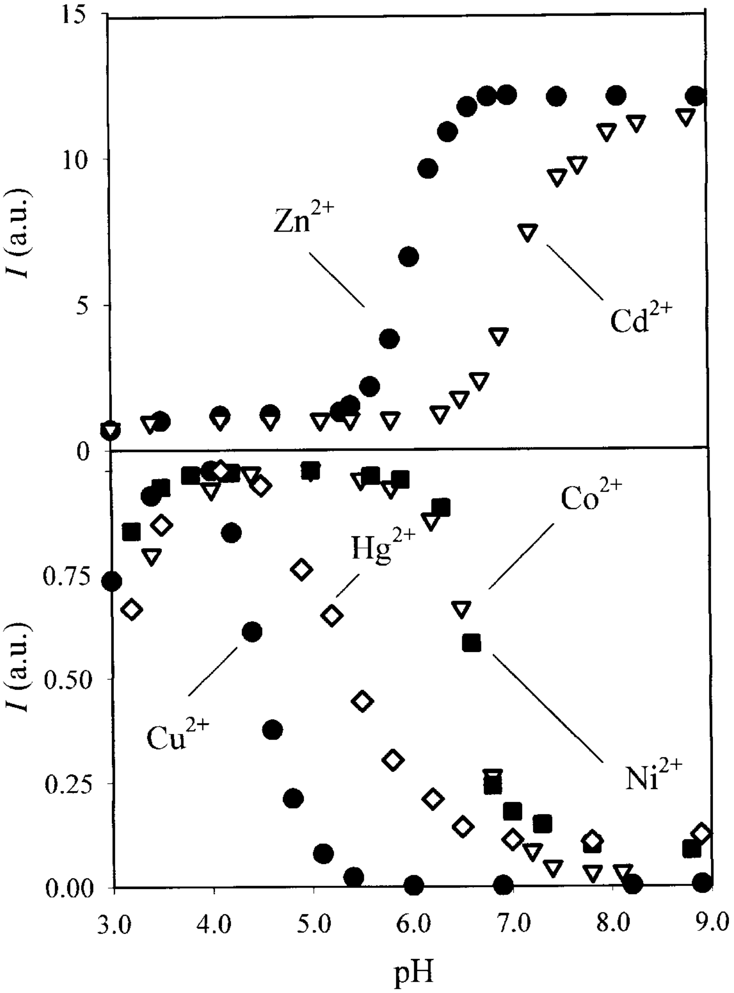

Fig. 6. *pH Dependence of the fluorescence intensity* (λ_{exc} 326 nm) *of aqueous solutions containing equimolar amounts* ($5 \cdot 10^{-5}$ M) *of Dns-tren* (**4**) *and various metal ions.* Upper panel: Zn^{2+} (●), λ_{em} 525 nm; Cd^{2+} (▽), λ_{em} 525 nm. Lower panel: Co^{2+} (▽), λ_{em} 555 nm, Ni^{2+} (■), λ_{em} 555 nm, Cu^{2+} (●), λ_{em} 555 nm; Hg^{2+} (◇), λ_{em} 555 nm. The fluorescence intensity was normalized to that of the ligand at the same wavelength.

most probabily present the square planar coordination geometry generally accepted for the corresponding amines [22]. The species $[CuLH]^{3+}$ of Dns-trien (**3**) shows a λ_{max} value (625 nm in H_2O) similar to that of $[Cu(dien)]^{2+}$ (λ_{max} 615), which implies the same donor atoms (3N, O_w). Therefore, a molecular structure with the Me_2N group protonated can be proposed (*Fig. 7,a*). This hypothesis is also supported by the acidity of this complex ($pK_a = 2.10$ in $MeOH/H_2O$ and 3.34 in H_2O), which is very close to that of the Me_2NH^+ group of the ligand (*Table 1*). As a result, it is reasonable that $[CuL]^{2+}$, having the same donor atoms, presents a similar λ_{max} (608 nm). Finally, the complex

Table 5. *Photophysical Properties* (τ/ns, fluorescence lifetime; I_{rel}, relative intensity) *of Ligands* **3**–**5** *and of their Metal Complexes at pH 9.5*. Solvent: H_2O for **3** and **4**; $MeCN/H_2O$ 1 : 1 (*v*/*v*) for **5**.

	Absorption		Fluorescence			
	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	τ/ns	I_{rel} (at r.t.)	I_{rel} (at 77 K)
Dns-trien (**3**)	327	4200	565	3	1.00	1.00
Cu^{2+}	317	5600	565	2.5	0.06	< 0.01
Ni^{2+}	320	4700	538	< 0.5	0.10	< 0.01
Co^{2+}	321	6200	560	< 0.5	0.20	< 0.01
Hg^{2+}	322	5300	536	0.8	0.13	–
Zn^{2+}	318	4500	518	10	1.81	–
Cd^{2+}	317	4600	518	10	1.81	–
Dns-tren (**4**)	326	4200	555	2.5	1.00	1.00
Cu^{2+}	310	5500	555	< 0.5	0.01	< 0.01
Ni^{2+}	318	5200	555	< 0.5	0.01	< 0.01
Co^{2+}	324	5600	555	< 0.5	0.01	< 0.01
Hg^{2+}	323	5000	525	0.7	0.14	–
Zn^{2+}	325	4100	525	8.4	3.38	–
Cd^{2+}	325	4300	525	9.1	3.05	–
Dns-tren (**5**)[a]	334	12700	540	10	1.00	1.00
Cu^{2+}	324	16300	540	10	0.01	0.02
Co^{2+}	327	16900	540	10	0.01	0.03
Zn^{2+}	326	16000	500	12	3.70	2.50
Cd^{2+}	326	16500	500	12	3.70	2.50

[a]) From [9].

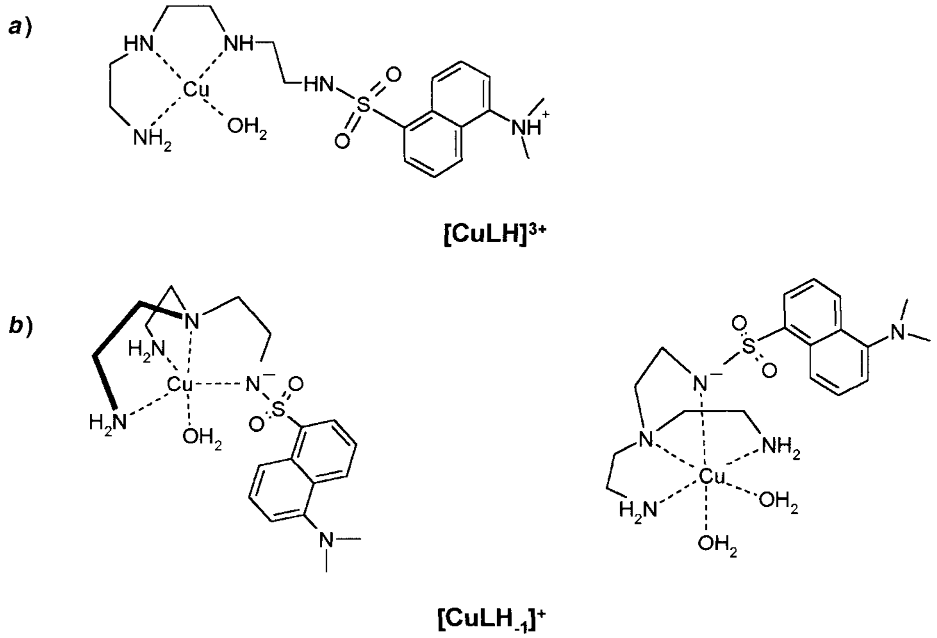

Fig. 7. *Molecular structures proposed for* a) *the complex [CuLH]$^{3+}$ of Dns-trien* (**3**) *and* b) *the complex [CuLH$_{-1}$]$^{+}$ of Dns-tren* (**4**)

$[CuLH_{-1}]^+$ (λ_{max} 588 nm) contains, in addition, the deprotonated sulfonamide N-atom with formation of three five-membered chelate rings as $[Cu(trien)]^{2+}$ (4 N, λ_{max} 575 nm [20]).

The tripodal Dns-tren (**4**) acts as a terdentate ligand in $[CuL]^{2+}$ with three amine N-atoms in a square planar arrangement, as suggested by the λ_{max} (638 nm in H_2O) which is close to those of $[Cu(dien)]^{2+}$ and of $[CuLH_{-1}]^+$ for Dns-dien (**2**) (*Table 3*). The ligand **4** becomes tetradentate in $[CuLH_{-1}]^+$ (*Fig. 7,b*), which has a λ_{max} (881 nm) similar to that of $[Cu(tren)]^{2+}$. The solution structure of the latter was reported as being a *cis*-diaqua-coordinated octahedron on the basis of spectroscopic and calorimetric studies, although a trigonal bipyramidal geometry could not be ruled out [21]. Also the transformation of $[CuLH_{-1}]^+$ into $[CuLH_{-1}(OH)]$ resembles that of $[Cu(tren)]^{2+}$ into $[Cu(tren)(OH)]^+$, both presenting a blue shift (59 and 30 nm, resp.). This is consistent with the proton dissociation of the equatorial H_2O ligand in the hypothetical *cis*-diaqua-coordinated complex of octahedral geometry or of the axial H_2O ligand in the case of a bipyramidal geometry (*cf. Fig. 7,b*).

As regards Dns_3-tren (**5**), the species $[CuLH_{-2}]$ presents a λ_{max} (638 nm) similar to those of $[CuLH_{-1}]^+$ of Dns-dien (**2**) and of $[CuL]^{2+}$ of Dns-trien (**3**), suggesting a planar (N, $2N^-$, O_w) coordination.

3.2. *Photophysical Studies.* 3.2.1. *Ligands.* The photophysical properties of compounds **3**–**5** (*Table 5*) are very similar to those observed with other dansyl derivatives [6] [9] [16] [23–31]. At neutral pH, the dansyl chromophores typically show a large absorption band in the 300–400 nm region and an intense and large luminescence band in the 400–600 nm region. These bands have considerable charge-transfer character, caused by mixing the ^1L_a and ^1L_b states of naphthalene with a charge-transfer state arising from the promotion of a lone-pair electron of the amino group into a π antibonding orbital of the naphthalene ring [29].

As previously described, the photophysical properties of compounds **3** and **4** do not show any pH dependence in the range 4–10. At lower pH values, protonation of the Me_2N group occurs (*Table 1*), and this process shifts the charge-transfer transition towards much higher and inaccessible energy. Under these conditions, the chromophore can be reasonably treated as a substituted naphthalene ring, the absorption and luminescence spectra changing accordingly.

Under very basic conditions, the deprotonation of the sulfonamide group of **3** and **4** increases the electronic density at the aromatic rings, which shifts the amine-to-naphthalene charge-transfer state towards higher energy. Therefore, a blue shift and an intensity increase were observed for both the absorption and the luminescence bands. The constancy of the fluorescence intensity and excited-state lifetime in the pH range where the aliphatic amine groups of **3**–**5** undergo protonation indicate that these groups are not able to quench the fluorescence by electron-transfer processes, in agreement with a sufficiently high reduction potential (*e.g.*, 2.09 V *vs.* SCE in MeCN for dansylamide) [32].

3.2.2. *Complexes with Cu^{2+}*. The strong quenching effect observed for the ligands **3**–**5** with Cu^{2+} can be ascribed to either a dansyl-to-metal energy-transfer (ET) or to a metal-to-dansyl electron-transfer (eT) mechanism. The data obtained also at 77 K suggested that at least a contribution from the ET mechanism was operating for **5** [9]. Similar conclusions can be drawn for **3** and **4** from data of *Table 5*. In addition, the presence of a metal-centred absorption band at lower energy for all the copper(II) complexes demonstrates that a dansyl-to-metal ET mechanism is thermodynamically feasible.

The equilibrium results for Cu^{II} complexes of **1**, **2**, and **5** confirm our previous fluorescence studies [8][9]. In particular, the fluorescence quenching observed for **5** is due to the formation of $[CuLH_{-2}]$ involving the simultaneous deprotonation of only two sulfonamide groups.

A very interesting feature can be inferred from the comparison of the pH dependence of the fluorescence intensity of **3** and **4** (*Figs. 5* and *6*) with the corresponding speciation diagrams (*Figs. 2* and *3*). The fluorescence is quenched along with the Cu^{II} complexation, even in a pH range (3.5–4.5 for **3** and 4–6 for **4**) where the sulfonamide group is not yet completely deprotonated. This finding is particularly important for the possible design of new chemosensors based on the dansyl chromophore, since Cu^{2+} sensing can be performed in a pH range much wider than that in which the deprotonation of the sulfonamide group occurs. At higher pH, no measurable changes of fluorescence intensity can be observed, neither when the sulfonamide group of **3** and **4** is deprotonated ($[CuLH_{-1}]^+$), nor when the hydroxy species of **4** is formed. Some changes are instead observed in the UV spectra: the large absorption band in the 300–400 nm region undergoes a hypsochromic shift after the deprotonation of the sulfonamide group. This can be ascribed to the increase in electron density on the aromatic rings caused by this deprotonation process, that moves the amine-to-naphthalene charge-transfer state towards higher energy, as observed for the complex $[CuLH_{-2}]$ of **5**. It is important to note that the formation of the Cu^{II} complexes, and, hence, the quenching of the ligand fluorescence, occurs at different pH values for the three ligands, in the order **3** < **4** < **5**. This indicates that ligand **3** can signal the presence of copper ions in the widest pH range.

3.2.3. *Complexes with Other Metal Ions.* To test the possible use of the ligands **3**–**5** as chemosensors for copper ions, it was necessary to investigate their complexing properties towards many other metal ions that could interfere during copper(II)-concentration measurements. The results obtained both by direct and by competition experiments with Na^+, K^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Eu^{3+}, Tb^{3+}, Mn^{2+}, Pb^{2+}, Fe^{2+}, Fe^{3+}, and Cr^{3+} indicated that these metal ions do not significantly interfere with Cu^{2+}.

Effects on the photophysical properties were instead caused by the complexation of **5** with Co^{2+}, Zn^{2+}, and Cd^{2+} [9], and of **3** and **4** with Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} (*Table 5*; *Figs. 5* and *6*). In particular, the blue shift observed with Zn^{2+} and Cd^{2+} for ligands **3**–**5** can be ascribed to the formation of a complex containing the deprotonated ligand. In fact, complexation with Zn^{2+} and Cd^{2+} d^{10} ions does not usually introduce low-energy metal-centered or charge-separated excited states into the molecule, so that ET and eT processes cannot occur. However, the deprotonation/complexation process increases the electronic density on the naphthalene ring, moving the charge-transfer state responsible for the dansyl luminescence towards higher energy. The complexation of these two ions with the neutral ligands does not affect the fluorescence properties, as was instead observed for Cu^{2+}.

It is important to underline that Zn^{2+} and Cd^{2+} cause a negligible interference in the copper analysis performed with ligands **3**–**5**, since the contribution of their complexes to the fluorescence spectra occurs at different wavelengths. Moreover, there is a large pH range in which sensing of Cu^{2+}, but not of Zn^{2+} and Cd^{2+} can be obtained (*Figs. 5* and *6*).

Complexation of ligands **3**–**5** with Co^{2+}, Ni^{2+}, and Hg^{2+} ions leads to fluorescence quenching, and the data obtained suggest that at least a contribution from the ET mechanism should be operating for Co^{2+} and Ni^{2+}. As it was found for Cu^{2+}, the quenching rate constants, calculated from the data in *Table 5* are very high ($k_q > 1 \cdot 10^{10}$ s^{-1}) both at room and low temperature. For Hg^{2+} complexes, the quenching rate constants at room temperature are instead lower ($3 \cdot 10^9$ s^{-1} and $9 \cdot 10^8$ s^{-1} for **3** and **4**, resp.), and a blue shift (30–40 nm) was again observed. In this case, a contribution to fluorescence quenching from the 'heavy-atom effect' cannot be excluded, while the ET mechanism cannot be effective for this d^{10} ion.

The ions Co^{2+}, Ni^{2+}, and Hg^{2+} quench the ligand fluorescence and could, therefore, interfere in a quantitative analysis performed by means of **3**–**5** as Cu^{2+} chemosensors. This problem can be, however, overcome because there is a pH range in which all ligands are able to bind efficiently only Cu^{2+}.

4. Conclusions. – Photophysical measurements show that Cu^{II} induces fluorescence quenching of ligands **3**–**5** by a mechanism involving energy transfer. The equilibrium data demonstrate that quenching occurs along with Cu^{2+} coordination, and that the deprotonation of the sulfonamide group is not necessary.

The photophysical studies also suggest a possible use of ligands **3**–**5** as luminescent chemosensors for Cu^{2+}, because for each of them there is a pH range in which sensing of Cu^{2+} is selective. These features make them a suitable set for the design of a multisensory system for the determination of several metal ions at once in real time. The realization of such a device requires the immobilization of an array of the chemosensors on a surface, and work in this direction is currently in progress in our laboratories.

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Experimental Part

General. The 5-(dimethylamino)naphthalene-1-sulfonyl chloride and triethylenetetramine dihydrochloride (= *N,N'*-bis(2-aminoethyl)ethane-1,2-diamine dihydrochloride) were from *Fluka*, 96% tris(2-aminoethyl)amine (= *N,N*-bis(2-aminoethyl)ethane-1,2-diamine) from *Aldrich*, and MeCN and $CHCl_3$ from *Carlo Erba*. M.p.: *Gallenkamp* melting-point apparatus; uncorrected. IR Spectra (cm^{-1}). *Nicolet 5PC* FT-IR spectrometer. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AC300* spectrometer at 300 MHz; chemical shifts δ in ppm, coupling constants J in Hz. Mass Spectra (C I): *Finnigan-Mat SSQ-710* mass spectrometer; m/z (rel. %).

N-*(2-Aminoethyl)-5-(dimethylamino)naphthalene-1-sulfonamide* (Dns-en; **1**), N-*{2-[(2-Aminoethyl)amino]ethyl}-5-(dimethylamino)naphthalene-1-sulfonamide* (Dns-dien; **2**) and N,N',N''-*(Nitrilotriethan-2,1-diyl)-tris[5-(dimethylamino)naphthalene-1-sulfonamide]* (Dns_3-tren; **5**) were synthesized as reported previously [7–9]. Elemental analyses (C, H, N, S) of all the ligands gave acceptable results.

N-*{2-{{2-[(2-Aminoethyl)amino]ethyl}amino}ethyl}-5-(dimethylamino)naphthalene-1-sulfonamide* (Dns-trien; **3**). To a stirred soln. of triethylenetetramine dihydrochloride (5.0 g, 22.9 mmol) in H_2O/MeCN 1:1 (*v*/*v*) (100 ml), 5-(dimethylamino)naphthalene-1-sulfonyl chloride (dansyl chloride; 1.2 g, 4.5 mmol) in MeCN (50 ml) was added at 0°. The mixture was stirred at r.t. for 3 h. Unreacted dansyl chloride was eliminated by means of acidification (pH 4) and extraction with Et_2O. The aq. layer was made basic with aq. NaOH soln.

(pH 11) and extracted with CH_2Cl_2. Evaporation yielded a green-yellow oil, to which HCl was added. Crystallization from MeOH and Et_2O gave 0.5 g (25%) of **3** · 2 HCl. Yellow solid. TLC (MeOH/32% NH_3 soln. 9 : 1 (*v*/*v*)): R_f 0.26. M.p. 165 – 167°. IR (KBr): 3500 – 3300, 3304, 3070 – 3000, 2941, 2832, 1616, 1575, 1456, 1329, 1143, 783. ^1H-NMR ((D_6)DMSO): 2.78 – 2.96 (*m*, 10 H, CH_2); 2.82 (*s*, Me_2N); 3.16 (*t*, *J* = 6.5, 2 H, CH_2); 7.26 (*d*, *J* = 7.4, H−C(6)); 7.60 (*t*, *J* = 8.4, H−C(3)); 7.64 (*t*, *J* = 7.4, H−C(7)); 8.14 (*d*, *J* = 7.3, H−C(8)); 8.30 (*d*, *J* = 8.7, H−C(2)); 8.48 (*d*, *J* = 8.5, H−C(4)). ^{13}C-NMR ((D_6)DMSO, assignments by DEPT): 37.94 (CH_2); 38.78 (CH_2); 44.05 (CH_2); 44.92 (Me_2N); 45.96 (CH_2); 46.40 (CH_2); 54.77 (CH_2); 115.09 (CH); 118.87 (CH); 123.47 (CH); 127.92 (CH); 128.37 (CH); 128.80 (C); 128.93 (C); 129.52 (CH); 135.10 (C); 151.27 (C). CI-MS: 380 (100, M^+), 349 (26, $[Dns-C_5H_{12}N_3]^+$), 306 (16, $[Dns-C_3H_7N_2]^+$), 293 (11, $[Dns-C_2H_6N_2]^+$), 235 (8, Dns^+). Anal. calc. for $C_{18}H_{29}N_5O_2S \cdot 2\,HCl$ (452.45): C 47.78, H 6.91, N 15.47, S 7.08; found: C 47.91, H 6.77, N 15.12, S 6.92.

N-{2-[Bis(2-aminoethyl)amino]ethyl}-5-(dimethylamino)naphthalene-1-sulfonamide (Dns-tren; **4**). A soln. of dansyl chloride (1.2 g, 4.5 mmol) in $CHCl_3$ (150 ml) was added dropwise to tris(2-aminoethyl)amine (tren; 2 ml, 13.4 mmol) at 0°, under stirring. The mixture was stirred for 3 h at r.t. After extractions with an aq. acid soln. (pH 4), the aq. layer was treated with NaOH up to pH *ca.* 11 and extracted with CH_2Cl_2. The org. solvent was evaporated and the obtained green-yellow oil treated with HCl and crystallized with MeOH and Et_2O: 1.1 g (51%) of **4** · 2 HCl · 2 H_2O. Yellow solid. TLC (MeOH/32% NH_3 soln. 9 : 1 (*v*/*v*)): R_f 0.10. M.p. 160° (dec.). IR (KBr): 3600 – 3250, 3100 – 2850, 1614, 1464, 1319, 1141, 796. ^1H-NMR ((D_6)DMSO): 2.45 – 2.50 (*m*, 2 H, CH_2N); 2.55 – 2.65 (*m*, 4 H, CH_2N); 2.70 – 2.90 (*m*, 8 H, Me_2N, CH_2); 2.95 – 3.08 (*m*, 4 H, CH_2); 7.30 (*d*, *J* = 7.5, H−C(6)); 7.63 (*t*, *J* = 8.4, H−C(3)); 7.64 (*t*, *J* = 7.9, H−C(7)); 8.10 – 8.25 (*m*, 7 H, NH_3^+, SO_2NH); 8.15 (*d*, *J* = 7.3, H−C(8)); 8.36 (*d*, *J* = 8.6, H−C(2)); 8.49 (*d*, *J* = 8.5, H−C(4)). ^{13}C-NMR ((D_6)DMSO, assignments by DEPT): 36.42 (CH_2); 45.00 (Me_2N); 50.81 (CH_2); 53.66 (CH_2); 54.76 (CH_2); 115.29 (CH); 119.45 (CH); 123.63 (CH); 127.75 (CH); 128.01 (CH); 128.73 (C); 128.83 (C); 129.10 (CH); 136.07 (C); 150.56 (C). CI-MS: 380 (50, M^+), 349 (100, $[Dns-C_5H_{14}N_3]^+$), 250 (8, $[Dns-NH]^+$), 171 (36, [(dimethylamino)naphthalene]$^+$), 116 (20, $C_5H_{14}N_3^+$). Anal. calc. for $C_{18}H_{29}N_5O_2S \cdot 2\,HCl \cdot 2\,H_2O$ (488.48): C 44.26, H 7.22, N 14.34, S 6.56; found: C 44.13, H 6.82, N 14.14, S 6.72.

Potentiometric Measurements. All solns. were prepared with double-distilled H_2O and HPLC-grade MeOH, both freshly boiled. Solns. to be titrated were prepared by weighting the ligand and adding the required volumes of *i*) HCl, *ii*) Cu^{2+}, and *iii*) solvent up to a volume of 50 ml.

The titrations were carried out in MeOH/H_2O 9 : 1 (*v*/*v*) and in aq. soln. at 25° and $I = 0.1$M KCl. The potentiometric apparatus for the automatic data acquisition (vol, *E*) was already described [33]. *Hamilton* (P/N: 238000) combined electrodes (glass and Ag/AgCl, 3M KCl) were used; the one employed in the mixed solvent was modified as recommended by *Fisicaro* and *Braibanti* [34], filling the reference compartment with a 0.1M KCl MeOH/H_2O soln. The electrodic chains were calibrated in terms of $[H^+]$ by titrating HCl solns. with MeOH/H_2O or aq. standard KOH soln. (hereafter pH = − log $[H^+]$), as already described [33]. The pK_w values resulted to be 14.42(1) in the mixed solvent and 13.76(1) in aq. soln.

The protonation constants of each ligand were determined by alkalimetric titration of 3 samples ($1.0 – 1.6 \cdot 10^{-3}$ M). For the copper(II) complexation equilibria, 3 – 5 titrations were carried out with ligand/metal molar ratios 1 : 1 and 2 : 1, except for Dns-en (**1**) (L/M from 2 : 1 to 4 : 1), C_{Cu} ranging between 0.6 and $1.7 \cdot 10^{-3}$ M. In the case of Dns-tren (**4**) in aq. soln., L/M ratios higher than 1.2 : 1 were inaccessible owing to the formation of a precipitate at pH *ca.* 8. Dns_3-tren/Cu^{II} equilibria (MeOH/H_2O) were limited at pH *ca.* 6.8 for the same reason. The overall stability constants were determined by means of the computer program HYPERQUAD 2000 [35]. For each system, the data from different titrations were treated as a unique batch. Distribution diagrams for the various systems were calculated and plotted by the program HYSS [36].

Spectrophotometric Measurements. Absorption spectra: *Kontron Uvikon 941-Plus* or *Perkin-Elmer Lambda-40* spectrophotometers, matched quartz cells of 1- or 5-cm pathlength against 0.1M KCl as reference. Solns. were passed from the potentiometric vessel to the thermostated spectrophotometric cell by a peristaltic pump. The Cu^{II}/Dns-ligand systems (Cu/L 1 : 1 for **2** – **5** and 1 : 2 for **1**, $C_{Cu} = 1.0 – 1.7 \cdot 10^{-3}$ M) were studied by means of 6 – 9 spectra at appropriate pH in the range 400 – 800 nm (ligands **1** – **3** and **5**) or 400 – 1100 nm (**4**). Molar absorptivities (ε) of the various species as a function of λ were calculated by means of the program SQUAD [37] and the formation constants obtained by potentiometry.

*(*SP*-4)-Bis{*N*-[2-(Amino-κ*N*)-ethyl]-5-(dimethylamino)naphthalene-1-sulfonamidato-κ*N*}copper* ($[CuL_2H_{-2}]$; **6**). Blue crystals of **6** separated out from a MeOH/H_2O 8 : 2 (*v*/*v*) soln. containing Cu^{2+} and the ligand (molar ratio 1 : 3, C_{Cu} *ca.* $5 \cdot 10^{-3}$M) at pH *ca.* 9. IR (KBr): 3322, 3261, 2925, 2882, 2828, 2783, 1249, 1119, 975, 784. Anal. calc. for $C_{28}H_{36}CuN_6O_4S_2$: C 51.87, H 5.60, N 12.96, S 9.89; found: C 51.98, H 5.34, N 12.70, S 9.72.

X-Ray Crystallography. An elongated prism of **6** (0.50 × 0.15 × 0.15 mm) was mounted on a glass fiber on a *Bruker AXS-SMART-1000/NT* area detector diffractometer. Graphite-monochromatized MoK_α (λ 0.71073 Å) radiation was used with the generator working at 45 kV and 40 mA. Cell parameters and the orientation matrix were initially determined from least-squares refinement on 92 reflections measured in three different sets of 60 frames each in the range $0 < \theta < 30°$. The intensities were collected by the ω-scan technique, 1321 frames in four different sets (30 s per frame; $\Delta\omega = 0.3°$) within the limits $3 < 2\theta < 57°$, with the sample-detector distance fixed at 5 cm. No crystal decay was observed; an empirical absorption correction was applied with SADABS [38]; transmission factors in the range 0.67–1.00. A total of 8487 reflections were collected (3059 unique, $R_{\text{int}} = 0.0230$; $R_\sigma = 0.0227$). The structure was solved by direct methods (SIR92) [39] and refined with full-matrix least squares (SHELXL-97) [40] on the basis of 2648 independent reflections with $I > 2\sigma(I)$; anisotropic temperature factors were assigned to all non-H-atoms. H-Atoms were riding on their parent atoms. The C-atoms of the en fragment were found disordered and distributed in two positions with δ and λ conformations and with occupancy factors of 0.75 and 0.25, resp. Also the Me groups of Me_2N were found disordered and distributed in two positions with occupancy factors of 0.70 and 0.30. All calculations were carried out on the *Digital AlphaStation 255* of the *Centro di Studio per la Strutturistica Diffrattometrica del CNR*, Parma. The programs Parst [41] and ORTEP [42] were also used. Crystal data and structure refinement parameters are reported in *Table 6*.

Fluorescence Measurements. For spectrofluorimetric measurements, H_2O of millipore grade was used as a solvent. The equipments and procedures were already described [43].

Table 6. *Crystal Data and Structure Refinement for* **6**a)

Empirical formula	$C_{28}H_{36}CuN_6O_4S_2$
M_r	648.29
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit-cell dimensions	$a = 11.315(1)$ Å
	$b = 5.702(1)$ Å
	$c = 22.599(1)$ Å
	$\beta = 95.800(1)°$
Volume	1450.6(3) Å^3
Z, Calculated density	2, 1.484 Mg/m^3
Absorption coefficient	0.943 mm^{-1}
$F(000)$	678
Crystal size	0.50 × 0.15 × 0.15 mm
θ Range for data collection	1.94 to 26.77 deg.
Index ranges	$-14 \leq h \leq 13$, $-7 \leq k \leq 7$, $-28 \leq l \leq 22$
Reflections collected/unique	8007/3059 (R(int) = 0.0230)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3059/0/218
Goodness-of-fit on F^2	1.040
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0374$, $wR_2 = 0.0999$
R indices (all data)	$R_1 = 0.0434$, $wR_2 = 0.1034$
Extinction coefficient	0.0087(10)
Largest diff. peak and hole	0.603 and -0.552 e · Å^{-3}

a) GOOF = $[\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)]^{1/2}$, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

REFERENCES

[1] 'Fluorescent Chemosensors for Ion and Molecule Recognition', Ed. A. W. Czarnik, A. C. S. Symposium Series 538, American Chemical Society, Washington, DC, 1992; A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515 and ref. cit. therein.

[2] G. Grynkiewicz, M. Poenie, R. Y. Tsien, *J. Biol. Chem.* **1985**, *260*, 3440; L. Fabbrizzi, A. Poggi, *Chem. Soc. Rev.* **1995**, *24*, 197; L. Prodi, F. Bolletta, M. Montalti, N. Zaccheroni, *Coord. Chem. Rev.* **2000**, *205*, 59; B. Valeur, I. Leray, *Coord. Chem. Rev.* **2000**, *205*, 3; C. Bargossi, M. C. Fiorini, M. Montalti, L. Prodi, N. Zaccheroni, *Coord. Chem. Rev.* **2000**, *208*, 17.

[3] A. W. Czarnik, *Acc. Chem. Res.* **1994**, *27*, 302 and refs. cit. therein.

[4] A. P. de Silva, H. Q. N. Gunaratne, C. McVeigh, G. E. M. Maguire, P. R. S. Maxwell, E. O' Hanlon, *Chem. Commun.* **1996**, 2191; C. Chen, H. Wagner, W. C. Still, *Science (Washington, D.C.)* **1998**, *279*, 851.

[5] E. Foulkes, 'Biological Effects of Heavy Metals', CRC Press, Boca Raton, FL, 1990, Vols. I and II; H. Sigel, A. Sigel, 'Concepts on Metal Ion Toxicity', Dekker, New York, 1986.

[6] A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, 'Advances in Supramolecular Chemistry', Jai Press, Inc., 1997, Vol. 4, p. 1; M. Shuster, M. Sandor, *Fresenius J. Anal. Chem.* **1996**, *356*, 326.

[7] R. Corradini, A. Dossena, R. Marchelli, A. Panagia, G. Sartor, M. Saviano, A. Lombardi, V. Pavone, *Chem. Eur. J.* **1996**, *2*, 373.

[8] R. Corradini, A. Dossena, G. Galaverna, R. Marchelli, A. Panagia, G. Sartor, *J. Org. Chem.* **1997**, *62*, 6283.

[9] L. Prodi, F. Bolletta, M. Montalti, N. Zaccheroni, *Eur. J. Inorg. Chem.* **1999**, 455.

[10] A. Bonamartini Corradi, *Coord. Chem. Rev.* **1992**, *117*, 45.

[11] N. Ikuta, J. Koga, N. Kuroki, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 228.

[12] G. A. Davis, *J. Am. Chem. Soc.* **1972**, *94*, 5089 and ref. cit. therein.

[13] E. M. Kuroleva, U. G. Maltsen, B. G. Belenkii, M. Viska, *J. Chromatogr.* **1982**, *242*, 145.

[14] G. De Jong, U. G. Hughes, E. Van Wieringen, K. J. Wilson, *J. Chromatogr.* **1982**, *241*, 345.

[15] T. Koike, T. Watanabe, S. Aoki, E. Kimura, M. Shiro, *J. Am. Chem. Soc.* **1996**, *118*, 12696.

[16] E. Kimura, T. Koike, *Chem. Soc. Rev.* **1998**, *27*, 179.

[17] R. M. Smith, A. E. Martell, R. J. Motekaitis, 'NIST Critically Selected Stability Constants of Metal Complexes Database, NIST Standard Reference Database', Version 4, 1997.

[18] D. B. Rorabacher, W. J. MacKellar, F. R. Shu, M. Bonavita, *Anal. Chem.* **1971**, *43*, 561.

[19] H. Gampp, H. Sigel, A. D. Zuberbuhler, *Inorg. Chem.* **1982**, *21*, 1190.

[20] L. Sacconi, P. Paoletti, M. Ciampolini, *J. Chem. Soc.* **1961**, 5115.

[21] P. Paoletti, M. Ciampolini, *Ricerca Sci. A* **1963**, *33*, 399.

[22] P. Paoletti, L. Fabbrizzi, R. Barbucci, *Inorg. Chim. Acta Rev.* **1973**, *7*, 43.

[23] K. Hamasaki, S. Usui, H. Ikeda, T. Ikeda, A. Ueno, *Supramol. Chem.* **1997**, *8*, 125.

[24] M. Nakamura, T. Ikeda, A. Nakamura, H. Ikeda, A. Ueno, F. Toda, *J. Chem. Soc., Chem. Commun.* **1995**, 721.

[25] R. F. Chen, J. Kernohan, *J. Biol. Chem.* **1967**, *242*, 5813.

[26] W.-Y. Lin, H. E. van Wart, *J. Inorg. Biochem.* **1988**, *32*, 21.

[27] R. B. Thompson, E. R. Jones, *Anal. Chem.* **1993**, *65*, 730.

[28] G. K. Walkup, B. Imperiali, *J. Am. Chem. Soc.* **1996**, *118*, 3053; G. K. Walkup, B. Imperiali, *J. Am. Chem. Soc.* **1997**, *119*, 3443.

[29] Y.-H. Li, L.-M. Chan, L. Tyer, R. T. Moody, C. M. Himel, D. M. Hercules, *J. Am. Chem. Soc.* **1975**, *97*, 3118.

[30] G.-P. Xue, J. S. Bradshaw, J. A. Chiara, P. B. Savage, K. E. Krakowiak, R. M. Izatt, L. Prodi, M. Montalti, N. Zaccheroni, *Synlett* **2000**, 1181.

[31] F. Bolletta, L. Prodi, N. Zaccheroni, C. Trombini, M. Lombardo, D. Fabbri, *Organometallics* **1996**, *15*, 2415.

[32] F. Vögtle, S. Gestermann, C. Kauffmann, P. Ceroni, V. Vicinelli, L. De Cola, V. Balzani, *J. Am. Chem. Soc.* **1999**, *121*, 12161.

[33] F. Dallavalle, G. Folesani, R. Marchelli, G. Galaverna, *Helv. Chim. Acta* **1994**, *77*, 1623.

[34] E. Fisicaro, A. Braibanti, *Talanta* **1988**, *35*, 769.

[35] P. Gans, A. Sabatini, A. Vacca, *Talanta* **1996**, *43*, 1739.

[36] L. Alderighi, P. Gans, A. Ienco, D. Peters, A. Sabatini, A. Vacca, *Coord. Chem. Rev.* **1999**, *184*, 311.

[37] D. J. Legget, W. A. E. Mc Bryde, *Anal. Chem.* **1975**, *47*, 1065.

[38] G. M. Sheldrick, 'SADABS, Siemens Area Detector Absorption Correction Software', Universität Göttingen, Germany, 1996.

[39] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualiardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

[40] G. M. Sheldrick, 'SHELXL-97, Program for the Refinement of Crystal Structures', University of Göttingen, Göttingen, Germany, 1997.

[41] M. Nardelli, *Comput. Chem*. **1983**, *7*, 95.

[42] L. Zsolnai, H. Pritzkow, 'ZORTEP, ORTEP Original Program Modified for PC, University of Heidelberg, Germany, 1994.

[43] M. Montalti, L. Prodi, N. Zaccheroni, *J. Fluorescence* **2000**, *10*, 71.

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