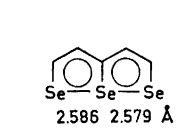
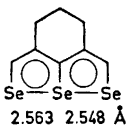
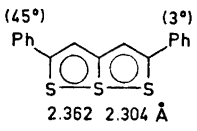


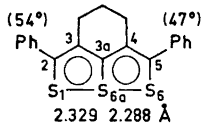
(I)



(II)



(III)



(IV)

The sulphur-sulphur distances in (IV) are S(1) – S(6a) = 2.329(1) Å and S(6a) – S(6) = 2.288(1) Å, and the sum of the S – S distances, 4.617(1) Å, is 0.049 Å smaller than the sum of the S – S distances in 2,5-diphenyl-6a-thiathiophthene (III),[3] 4.666(3) Å. Hence, a 3,4-trimethylene bridge has the same effect on the S – S bonding in 6a-thiathiophthenes as it has on the Se – Se bonding in 6a-selenaselenophthenes.

Other bond lengths in the 6a-thiathiophthene system of IV are: S(1) – C(2) = 1.709(3) Å, S(6a) – C(3) = 1.755(3) Å, S(6) – C(5) = 1.710(3) Å, C(2) – C(3) = 1.378(4) Å, C(3) – C(3a) = 1.425(4) Å, C(3a) – C(4) = 1.426(4) Å, and C(4) – C(5) = 1.381(4) Å.

A sample of 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene was generously supplied by M. Stavaux.[4] The crystals are dark red and belong to the monoclinic space group $P2_1/c$. The cell dimensions are $a = 6.882(1)$ Å, $b = 12.871(1)$ Å, $c = 19.049(1)$ Å, and $\beta = 94.98(2)°$. There are four molecules per unit cell; $D_c = 1.393$ g cm^{-3}, $D_m = 1.38$ g cm^{-3}.

The structure analysis is based on X-ray data collected on a paper-tape controlled Siemens AED diffractometer using Cu$K\alpha$ radiation. 2546 refractions were observed within $\theta = 71°$.

The structure was solved by the heavy atom method and refined by full matrix least squares. The present R factor is 0.036.

We thank Dr. M. Stavaux, Département de Chimie, Université de Caen, France, for a sample of 2,5-diphenyl-3,4-trimethylene-6a-thiathiophthene.

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Spectrophotometric Studies of Copper(II) Chelates of 1-Nitroso-2-naphthol-6-sulphonic and 2-Nitroso-1-naphthol-6-sulphonic Acids in Aqueous Solution

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The formation of copper(II) chelates by some *o*-nitrosonaphtholsulphonic acids has been discussed in previous papers.[1,2] As rather strong complexes are formed by ligands of this type with copper(II), only spectrophotometric methods can be used in general to study the complex formation reactions.

In the present paper, results for copper(II) chelates of two ligands, 1-nitroso-2-naphthol-6-sulphonic and 2-nitroso-1-naphthol-6-sulphonic acids, are reported. This ligand pair is well suited for a comparison of the chelation abilities of two isomeric *o*-nitrosonaphthols.

1-Nitroso-2-naphthol-6-sulphonic acid forms an orange yellow copper(II) chelate and 2-nitroso-1-naphthol-6-sulphonic acid a less stable chelate, which, however, is bright red in colour.

The absorption spectra of the 1 : 1 copper(II) chelates CuL are reproduced in Figs. 1 and 2. Application of Job's

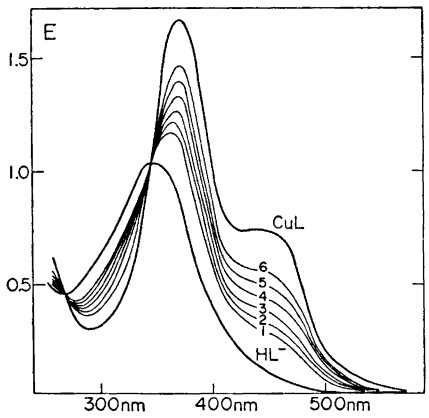

Fig. 1. Absorption spectra of the 1-nitroso-2-naphthol-6-sulphonate anion and the copper chelate CuL in aqueous solutions at 25°C; $c_{HL^-} = 1.95 \times 10^{-4}$ M, $c_{Cu} = 2.13 \times 10^{-3}$ M, $I = 0.161$.

The pH values of the solutions were: (1) 1.08, (2) 1.19, (3) 1.32, (4) 1.49, (5) 1.61, (6) 1.92.

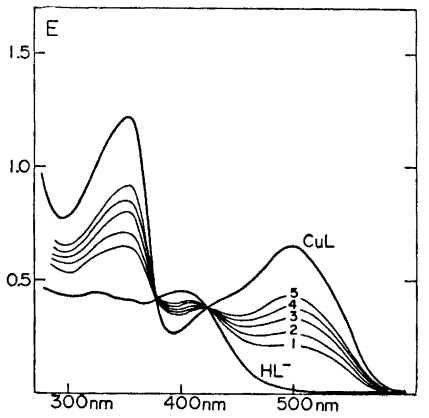

Fig. 2. Absorption spectra of the 2-nitroso-1-naphthol-6-sulphonate anion and the copper chelate CuL; $c_{HL^-} = 1.11 \times 10^{-4}$ M, $c_{Cu} = 1.12 \times 10^{-3}$ M, $I = 0.106$.

The pH values of the solutions were: (1) 2.44, (2) 2.59, (3) 2.76, (4) 2.87, (5) 3.04.

method of continuous variations indicated clearly that 2 : 1 chelates are formed at a high pH and a high ligand : metal ratio.

The results of the determinations of the equilibrium constants of the first chelation reactions

$$Cu^{2+} + HL^- \overset{K_I}{\rightleftharpoons} CuL + H^+ \qquad (1)$$

are presented in Table 1. All the values reported are mean values of determinations carried out by measuring the spectra of several solutions with different pH values in the buffer range.

Table 1. pK_I values of copper(II) chelation reactions in aqueous solutions of varying ionic strength (KCl), the thermodynamic values at 25°C and the corresponding values of the parameters of the Debye-Hückel equation (2).

1-Nitroso-2-naphthol-6-sulphonic acid as ligand

I	pK_I (430–460 nm)	
0.227	−1.540	$pK_I^\circ = -1.85$
0.342	−1.395	
0.402	−1.361	$\alpha = 1.9$
0.496	−1.310	$B = 0.2$
0.702	−1.160	

2-Nitroso-1-naphthol-6-sulphonic acid as ligand

I	pK_I (346–358 nm)		pK_I (490–506 nm)	
0.089	−0.458		−0.480	
0.236	−0.333		−0.339	
0.325	−0.264		−0.278	
0.453	−0.147	[a]	−0.204	[b]
0.552	−0.151		−0.168	
0.710	−0.056		−0.097	

[a] $pK_I^\circ = -0.61$, $\alpha = 2.9$, $B = 0.2$

[b] $pK_I^\circ = -0.62$, $\alpha = 3.1$, $B = 0.1$

Table 1 contains also the values of the thermodynamic constants (at 25°C) evaluated by fitting the following extended form of the Debye-Hückel equation to the experimental data:

$$pK_I = pK_I^\circ + 2.036\sqrt{I}/(1 + \alpha\sqrt{I}) - BI \qquad (2)$$

The dependence of pK_I on the square root of ionic strength is shown in Fig. 3. The stability constants $\beta_1 = [CuL]/[Cu^{2+}][L^{2-}]$ of the chelates are listed in Table 2.

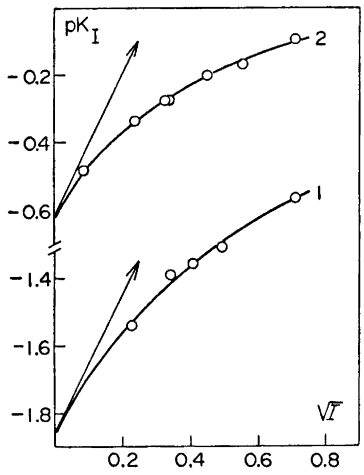

Fig. 3. pK_I as a function of the square root of ionic strength. Curve (1) refers to 1-nitroso-2-naphthol-6-sulphonic acid as ligand and curve (2) to 2-nitroso-1-naphthol-6-sulphonic acid as ligand in copper chelate formation. Note: One additional value $pK_I = -0.284$ ($\sqrt{I} = 0.348$) for the copper(II) chelate of 2-nitroso-1-naphthol-6-sulphonic acid, determined also spectrophotometrically in this laboratory, is included in the figure.[6]

Table 2. Stability constants of the copper(II) chelates CuL of the two nitrosonaphtholsulphonic acids in aqueous solution at 25°C. $\beta_1 = [CuL]/[Cu^{2+}][L^{2-}]$

Ligand	$pK_{a(2)}^{\circ}$	$\log \beta_1^{\circ}$	$\log \beta_1$ ($I = 0.1$)
1-Nitroso-2-naphthol-6-sulphonic acid	7.60	9.45	8.66
2-Nitroso-1-naphthol-6-sulphonic acid	7.39	8.01	7.30

The following values of stability constants of the first copper(II) chelates of other *o*-nitrosonaphtholsulphonic acids at zero ionic strength and 25°C have been reported previously: $\log \beta_1^{\circ}(CuL^-) = 9.9$ for the chelate of 1-nitroso-2-naphthol-3,6-disulphonic acid ("Nitroso R-acid"; $pK_{a(3)}^{\circ} = 7.51$,[1] $\log \beta_1^{\circ}(CuL) = 7.8$ for the chelate of 2-nitroso-1-naphthol-4-sulphonic acid ($pK_{a(2)}^{\circ} = 6.50$)[1] and $\log \beta_1^{\circ}(CuL) = 8.64$ for the chelate of 2-nitroso-1-naphthol-8-sulphonic acid ($pK_{a(2)}^{\circ} = 8.19$).[2]

Data on the stabilities of the zinc and cadmium chelates of these ligands are also available.[3] The stability constants of the copper, zinc, or cadmium chelates of these two isomeric ligands exhibit a good linear correlation.

Experimental. The preparation and purification of sodium 1-nitroso-2-naphthol-6-sulphonate and sodium 2-nitroso-1-naphthol-6-sulphonate have been described in earlier papers.[4,5]

The copper salt was copper(II) perchlorate; the copper concentration of the prepared stock solution was determined electroanalytically. Dried potassium chloride was added as neutral salt to increase the ionic strengths of the solutions.

A Perkin-Elmer Model 402 Ultraviolet Spectrophotometer equipped with calibrated 10 mm quartz cells and connected to a Digital Voltmeter MkIII (Weis Electronics, Ltd.) was used.

The methods used to evaluate the equilibrium constants of the metal chelation reactions from spectrophotometric data have been described in detail previously.[1-5] The values of the dissociation constants of the ligands were calculated by means of equations presented in earlier papers.[4,5]

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