

Short Communications

Stabilities of Lanthanoid Complexes of 2-Nitroso-1-naphthol-4,6-disulfonic and 2-Nitroso-1-naphthol-4,7-disulfonic Acids

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Studies of the lanthanoid complex formation with different sulfonic acid derivatives of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol are in progress in our laboratory. In a previous communication we noted that, compared with other nitrosonaphtholsulfonic acids, 2-nitroso-1-naphthol-4,8-disulfonic acid forms remarkably stable complexes with tervalent lanthanoids.¹ The result was unexpected in view of our observations of nickel(II), zinc(II), and cadmium(II) complex formation with the ligands of 1,2-nitrosonaphthol series.^{2,3}

The object of the present work was to learn more about those factors responsible for the stability of lanthanoid complexes of this type of ligand by investigating additional compounds of similar structure to 2-nitroso-1-naphthol-4,8-disulfonic acid. For this purpose 2-nitroso-1-naphthol-4,6-disulfonic and 2-nitroso-1-naphthol-4,7-disulfonic acids were chosen, and stability constants for their Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), and Dy(III)

complexes were determined. The choice of the lanthanoid ions for the study was directed by the fact that the stability of the 1:1 lanthanoid complexes of several 1,2-nitrosonaphtholsulfonic acids has been found to have a maximum value at samarium or europium; the lanthanoids represented are just those near this region.

Results. Interpretation of the potentiometric data obtained from titrations of both 2-nitroso-1-naphthol-4,6-disulfonic and 2-nitroso-1-naphthol-4,7-disulfonic acids with each of the lanthanoid ions indicates that only two successive complexes are formed. No protonated or polynuclear complex species could be found. It was also impossible to increase the concentrations of the free ligands to such extent that any reliable data for the possible third complexes would have been found. These results confirm our earlier observations of 1-nitroso-2-naphthol-3,6-disulfonic and 2-nitroso-1-naphthol-4,8-disulfonic acids.^{1,4} As pointed out previously, there were no difficulties in producing the third complexes with nitrosonaphthol(mono)sulfonic acids, especially in the case of 1-nitroso-2-naphtholmonosulfonic acids.

The gross stability constants ($\beta_1 = [ML]/[M^{3+}][L^{3-}]$ and $\beta_2 = [ML_2^{3-}]/[M^{3+}][L^{3-}]^2$) of the complexes of 2-nitroso-1-naphthol-4,6-disulfonic and 2-nitroso-1-naphthol-4,7-disulfonic acids are collected in Table 1. The results for the 1:1 complexes are illustrated in Fig. 1, together with the corresponding values for some other nitrosonaphtholsulfonic acids, studied previously. As one can see, the stability order of the lanthanoid

Table 1. Stability constants of the lanthanoid complexes of 2-nitroso-1-naphthol-4,6-disulfonic and 2-nitroso-1-naphthol-4,7-disulfonic acids in aqueous solution at $I=0.100$ and 25°C .^a

	2-Nitroso-1-naphthol-4,6-disulfonic acid		2-Nitroso-1-naphthol-4,7-disulfonic acid	
	$\log \beta_1$	$\log \beta_2$	$\log \beta_1$	$\log \beta_2$
Praseodymium	3.670 ± 0.014	5.893 ± 0.030	3.803 ± 0.012	5.862 ± 0.035
Neodymium	3.759 ± 0.014	6.021 ± 0.023	3.879 ± 0.012	6.000 ± 0.026
Samarium	3.886 ± 0.010	6.383 ± 0.018	4.017 ± 0.014	6.271 ± 0.032
Europium	3.818 ± 0.009	6.349 ± 0.015	3.955 ± 0.016	6.241 ± 0.034
Gadolinium	3.702 ± 0.012	6.259 ± 0.015	3.831 ± 0.017	6.228 ± 0.030
Terbium	3.480 ± 0.011	6.135 ± 0.015	3.651 ± 0.017	6.194 ± 0.033
Dysprosium	3.389 ± 0.009	6.015 ± 0.015	3.589 ± 0.017	6.053 ± 0.026

^a The uncertainties given are three times the computed least squares standard deviations.

Table 2. Representative data for the determination of β_1 and β_2 from an individual titration of disodium 2-nitroso-1-naphthol-4,6-disulfonate with samarium ions. $C_{Sm} = 8.90 \times 10^{-4}$ M, $C_L = 3.153 \times 10^{-3}$ M, $C_H = 1.5 \times 10^{-5}$ M, titrant 0.100 M NaOH, $v_0 = 100.0$ ml, $I^{\frac{1}{2}}(\text{mean}) = 0.333$, $pK_3(\text{mean}) = 5.863$.

Titre (ml)	$-\log [H^+]$	Titre (ml)	$-\log [H^+]$	Titre (ml)	$-\log [H^+]$
0.136	3.981	0.895	4.928	1.658	5.555
0.259	4.174	1.020	5.049	1.780	5.644
0.384	4.351	1.146	5.161	1.912	5.734
0.510	4.514	1.277	5.267	2.039	5.824
0.639	4.661	1.400	5.367	2.160	5.918
0.760	4.799	1.525	5.462		

Calculated values: $\log \beta_1 = 3.823 \pm 0.003$, $\log \beta_2 = 6.313 \pm 0.006$

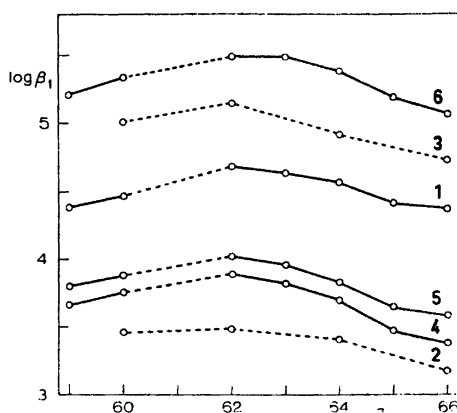


Fig. 1. Stability constants of the first lanthanoid complexes versus atomic number for 1-nitroso-2-naphthol-6-sulfonic (1), 2-nitroso-1-naphthol-4-sulfonic (2), 1-nitroso-2-naphthol-3,6-disulfonic (3), 2-nitroso-1-naphthol-4,6-disulfonic (4), 2-nitroso-1-naphthol-4,7-disulfonic (5), and 2-nitroso-1-naphthol-4,8-disulfonic (6) acids at 25 °C and $I = 0.100$.

complexes of these sulfo-substituted ligands is essentially similar; in each case the most stable complexes are formed by samarium or europium.

2-Nitroso-1-naphthol-4,7-disulfonic acid forms stronger 1:1 complexes than does 2-nitroso-1-naphthol-4,6-disulfonic acid. This mutual order of stability, which has also been found for the nickel(II)² and zinc(II)⁵ complexes of the ligands, is exceptional when one takes the acid strengths of the ligands into consideration (at the ionic strength 0.1, the values of pK_3 for 2-nitroso-1-naphthol-4,7-disulfonic and 2-nitroso-1-naphthol-4,6-disulfonic acids are 5.84 and 5.88, respectively). In producing 1:2 complexes it is no longer valid.

As compared with 2-nitroso-1-naphthol-4,8-disulfonic acid, the complexes of the present ligands are distinctly less stable (Fig. 1). The difference in the stabilities of the complexes is so pronounced that it cannot entirely be explained by the different basicities of the ligand anions (pK_3 for 2-nitroso-1-naphthol-4,8-disulfonic acid at $I = 0.1$ is 6.66⁶).^{2,3} It is obvious that the negative sulfonate group in *peri*-position to the hydroxyl group has a strengthening effect on complex formation with trivalent lanthanoids.

As expected for electrostatic reasons, the 1:1 lanthanoid complexes of nitrosonaphthol(di)sulfonic acids are more stable than those of nitrosonaphthol(monosulfonic) acids. By contrast, it seems evident that the weakened tendency of the disulfonic acid derivatives of 1,2-nitrosonaphthols to form higher complexes also arises from electrostatic reasons rather than any strict steric grounds. Owing to the different ionic charges of the reacting species, however, the concentration stability constants of the complexes are not directly comparable.

It has been shown previously that 1-nitroso-2-naphthols generally form stronger nickel(II), zinc(II), and cadmium(II) complexes than do 2-nitroso-1-naphthols.^{1,2} Since our information about the lanthanoid complexes of these ligands is still quite limited, general conclusions in this respect can hardly be made.

Experimental. The disodium salts of 2-nitroso-1-naphthol-4,6-disulfonic and 2-nitroso-1-naphthol-4,7-disulfonic acids were prepared by treatments of the sodium salts of 1-nitroso-2-naphthol-6-sulfonic and 1-nitroso-2-naphthol-7-sulfonic acids with aqueous $NaHSO_3$ followed by boiling with hydroxylamine hydrochloride in dil. HCl. Methods of the synthesis and analysis of *ortho*-nitrosonaphtholsulfonic acids, including the acids above, have previously been described in detail by the author.²

The lanthanoid salts were perchlorates prepared by dissolving the corresponding oxides into warm perchloric acid. The metal concen-

trations of the stock solutions were controlled by complexometric titrations and the acid contents by titrations of the hydrogen ion liberated from an ion-exchange column (Amberlite IR-120).

Apparatus and methods. The apparatus and methods were the same as described in a recent paper.² All measurements were carried out at 25 °C.

In the determination of the complex stability constants, several titrations were carried out at ionic strengths near 0.1 using different ligand-metal ratios. The initial estimates of the constants calculated from stoichiometric relationships were refined by a modified version of the programme SCOGS⁷ on a Univac 1108 computer. An example of the calculations is presented in Table 2. The final values of the constants given are those obtained by interpolation to the precise value 0.100 of ionic strength.

The values of the naphtholic protonation constants of the ligands needed in the calculations were obtained from the following Debye-Hückel equations: for 2-nitroso-1-naphthol-4,6-disulfonic acid,²

$$pK_3 = 6.507 - 3.054\sqrt{I}/(1 + 1.394\sqrt{I}) + 0.453 I$$

and for 2-nitroso-1-naphthol-4,7-disulfonic acid,²

$$pK_3 = 6.451 - 3.054\sqrt{I}/(1 + 1.591\sqrt{I}) + 0.277 I.$$

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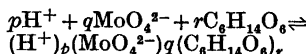
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Multicomponent Polyanions. IX. On the Crystal Structure of a Protonized Mannitolodimolybdate Complex

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Investigations of equilibria



where $C_6H_{14}O_6$ is D-mannitol, have shown that complexes (2,2,1) and (3,2,1) are formed (the complexes are given in (p, q, r) notation).¹ The study covered the $-\log [H^+]$ range $1 < -\log [H^+] < 9$.

In parallel with this investigation crystallization experiments using molar ratios of H^+ , MoO_4^{2-} , and $C_6H_{14}O_6$ corresponding to the composition of the complexes, have also been carried out. Hitherto this preparative work has only resulted in crystals corresponding to a (4, 2, 1) complex, which has not been confirmed in the $-\log [H^+]$ range studied, but is assumed to appear at $-\log [H^+] < 1$.

X-Ray characteristics and a preliminary structure of this crystalline phase is reported in the present communication.

Crystal data.

$H_2Mo_2O_8C_6H_{10}O_6 \cdot 3H_2O$	F.W. = 506.10
Monoclinic $P2_1$	$V = 697.7(1) \text{ \AA}^3$
$a = 12.2342(6) \text{ \AA}$	$D_x = 2.409 \text{ g cm}^{-3}$
$b = 6.9008(4) \text{ \AA}$	$D_m = 2.40 \pm 0.01 \text{ g cm}^{-3}$
$c = 8.3845(5) \text{ \AA}$	(floatation method)
$\beta = 99.740(6)^\circ$	$Z = 2$

Experimental. Accurate unit cell dimensions were determined from X-ray powder photographs taken with a Guinier-Hägg camera using $CuK\alpha_1$ -radiation ($\lambda = 1.54051 \text{ \AA}$) with $Pb(NO_3)_2$ as internal standard ($a_{Pb(NO_3)_2} = 7.8575 \text{ \AA}$, 25 °C). Three-dimensional single crystal X-ray diffraction data were collected by the equi-inclination Weissenberg method, using $CuK\alpha$ -radiation ($\lambda = 1.5418 \text{ \AA}$). The intensities of 1414 independent reflexions from the $h0l-h6l$ layers were estimated visually using multiple film technique. Correction for Lorentz- and polarization effects was then applied.

From a three-dimensional Patterson synthesis the positions of the two Mo atoms were obtained. Since the y -coordinates for both atoms were the same (≈ 0.37), the phase angles computed were equivalent within the layers and restricted to multiples of $\approx \pi/4$. This resulted in a centre of symmetry induced in the space group $P2_1$, making both the complex and its mirror image appear in a following Fourier map.² To obtain non-equivalent phase angle values anomalous scattering was applied, and combined