July, 1988] © 1988 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 61, 2639—2640 (1988) 2639

Studies of the Stabilities of Scandium, Yttrium, and Lanthanoid-Ion Complexes of 2-Nitroso-5-(*N*-propyl-3-sulfopropylamino)phenol

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(Received December 4, 1987)

Synopsis. The stability constants of the 1:1 complexes formed by 2-nitroso-5-(*N*-propyl-3-sulfopropylamino)phenol (NPSAP: H_2L) with tervalent scandium, yttrium, and lanthanoids, but not promethium, have been determined potentiometrically in aqueous solutions at an ionic strength of 0.1 with potassium nitrate and at 25 °C. The stability constants of the 1:1 complexs increased with the increase in the atomic number of the lanthanoid, with the slight decrease at gadolinium. The stability constant of the 1:1 complex of scandium was the highest among the metal complexes investigated, while that of the yttrium complex was found to be between those of the cerium and praseodymium complexes.

Many studies have been reported on the complexing behavior of *o*-nitrosonaphthols,[1–6] such as 2-nitroso-1-naphthol-4,8-disulfonic acid with tervalent lanthanoid ions, and the stability constants for these complexes, including those for scandium(III) and yttrium(III) complexes,[5] have been discussed with respect to the structures of the ligands, the basicity of the donor atoms, and the relative sizes of central metal ions.[4]

Recently, 2-nitroso-5-(*N*-propyl-3-sulfopropylamino) phenol (NPSAP: H_2L) has been synthesized as a water-soluble nitrosophenol derivative and found to be a useful chromogenic reagent for iron[7] and cobalt.[8] The chelating behavior of the reagent with some bi- and ter-valent metal ions has also been described.[9] This paper will report on the chelating behavior of this particular ligand for tervalent lanthanoid ions, including scandium(III) and yttrium(III) ions, in order to provide more detailed information on the nature of *o*-nitrosophenols as ligands.

Experimental

The apparatus and methods were the same as those described in a recent paper.[9] All the measurements were carried out at 25±0.5 °C and at an ionic strength of 0.1 with potassium nitrate. All of the 0.01 M (1 M=1 mol dm^{-3}) stock solutions of the metal ions, except for those of thulium and lutetium, were prepared by dissolving their chlorides or nitrates in water. As to the two metal ions mentioned, their oxides were dissolved in hydrochloric acid; the solution was then boiled to dryness to expel the excess hydrochloric acid and subsequently diluted with water. The metal-ion concentrations, of the stock solutions were determined by EDTA titration.[10] The mathematical analysis of the chelating behavior of the ligand and the calculations of their stability constants were carried out by the use of the SUPERQUAD program[11] on potentiometric data, using $\log K_1^H=8.23$ and $\log K_2^H=2.61$ as the protonation constants of the ligand.[9]

Results and Discussion

The interpretation of the potentiometric data obtained from the titration of a 3:1 (ligand-to-metal) mixture of NPSAP with each of the lanthanoids, scandium, and yttrium ions indicated that, in most cases, only 1:1 complexes were formed when $-\log[H^+]$ was raised to about 4.8 by adding potaasium hydroxide. The results obtained on the stability constants for the 1:1 complexes are given in Table 1, as $\log \beta_1$, where $\beta_1=[ML^+]/[M^{3+}][L^{2-}]$, together with their computed standard deviations. The formation of the 2:1 complexes was observed on some metal ions; these results are also given in Table 1, as $\log \beta_2$, where $\beta_2=[ML_2^{2-}]/[M^{3+}][L^{2-}]^2$.

No protonated or polynuclear complex species could be found in this system. It was impossible to increase the value for $-\log[H^+]$ to such an extent that any reliable data for the possible higher complexes could be found. The increase in the ligand-to-metal ratio would result in the formation of higher complexes; however, the titrations on such a mixture were not carried out in this experiment. A series of stability constants for the 1:1 complexes with fourteen lanthanoid metal ions is illustrated in Fig. 1, together

Table 1. Stability Constants of 1:1 Metal Complexes of Scandium, Yttrium, and Lanthanoid Ions with 2-Nitroso-5-(*N*-propyl-3-sulfopropylamino)-phenol at 25 °C and at I=0.1 (KNO_3)

Metal ion M^{3+}	$\log \beta_1$ (st. dev.)
Sc	7.48 (0.007)
Y[a]	5.52 (0.006)
La	5.09 (0.003)
Ce	5.43 (0.003)
Pr	5.61 (0.003)
Nd	5.70 (0.003)
Sm	5.86 (0.002)
Eu	5.85 (0.001)
Gd[b]	5.70 (0.006)
Tb	5.81 (0.003)
Dy	5.85 (0.003)
Ho	5.86 (0.003)
Er	5.94 (0.003)
Tm	6.03 (0.005)
Yb	6.13 (0.001)
Lu[c]	6.03 (0.007)

a) $\log \beta_2$=10.06(0.03). b) $\log \beta_2$=10.06(0.15). c) $\log \beta_2$=11.01(0.07).

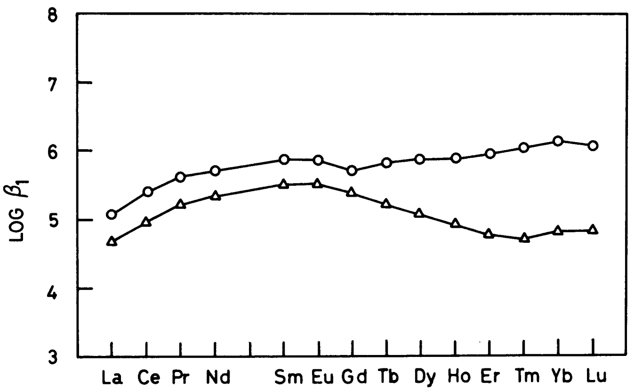

Fig. 1. Stability constants of the 1:1 complexes of lanthanoid ions with NPSAP (-○-) and 2-nitroso-1-naphthol-4,8-disulfonic acid (-△-) at 25 °C and at I=0.1 (KNO_3).

with the corresponding values for 2-nitroso-1-naphthol-4,8-disulfonic acid.[4]

It seems from this figure that the stability trends of the complexes with the earlier half of the series of metal ions resemble each other among the two ligands. However, as to the later half of the series, the stability trends of the complexes with both ligands show a rather noticeable difference. The stability constants of the NPSAP complexes increase very slightly with an increase in the atomic number from gadolinium to ytterbium, whereas those of 2-nitroso-1-naphthol-4,8-disulfonic acid decrease from gadolinium to thulium.

According to Moeller et al., the trends in the stability-constant data for the lanthanoid elements heavier than gadolinium can be divided qualitatively into three groups; a group of ligands for which there is a regular increase in the stability constants, a group of ligands for which the stability constants have nearly the same values, and a group of ligands for which the stability constants decrease slightly.[12] The stability trend of NPSAP may be classified as that of the second group of ligands.

It has also been pointed out by the same authors that the value of the stability constant of the yttrium complex of this group of ligands was among those for light lanthanoid elements. The fact that the position of the stability constant of the yttrium complex with NPSAP was found between cerium and praseodymium complexes also suggests that NPSAP belongs to the second group.

The stability constants of the NPSAP comlexes with all of the lanthanoid ions are higher than that of 2-nitroso-1-naphthol-4,8-disulfonic acid, as is shown in Fig. 1. The relatively higher values of the stability constants of NPSAP compared with those for nitrosonaphthols were also observed on other metal ions, such as zinc(II) and copper(II).[9] Such a high stability of the NPSAP complexes may be ascribed to its higher basicity of phenolic oxygen compared to that of nitrosonaphthols.[9]

The stability constant of the scandium(III) complex is markedly higher than those of the lanthanoid complexes; this may be due to the smaller ionic radius of the scandium ion compared to those of the lanthanoid ions.[13]

The stability constants of the yttrium and lanthanum complexes of NPSAP are found to be in the order of $Cu^{2+}>Ni^{2+}>Y^{3+}>La^{3+}>Zn^{2+}$,[9] just as one can see in the case of the nitroso R acid complexes.[14]

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