

Stability Constants of Neodymium(III), Samarium(III), Gadolinium(III), Terbium(III), Dysprosium(III) & Holmium(III) Complexes with 2-Amino- 5-mercapto-1,3,4-thiadiazole

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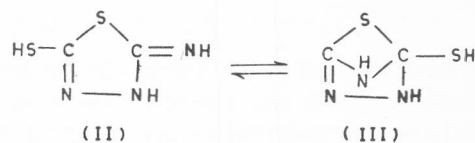
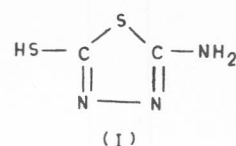
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Neodymium(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III) form 1:1, 1:2 and 1:3 (metal-ligand) complexes with 2-amino-5-mercapto-1, 3, 4-thiadiazole (AMTDA) in aq. ethanol (50%, v/v) and at ionic strength of 0.1 M (NaClO₄). The stability constants of these complexes have been determined potentiometrically. The changes in free energy, enthalpy and entropy have also been reported. The order of stabilities of the chelates is: Gd > Tb > Nd > Ho > Sm > Dy.

The complexes of 2-amino-5-mercapto-1, 3, 4-thiadiazole (AMTDA) with the first and second row transition metal ions have been reported¹ but no work has been done on its complexes with rare earths. In continuation of our earlier work on bismuthiol(I)², we report herein the formation constants of AMTDA complexes of Nd(III), Sm(III), Gd(III), Tb(III), Dy(III) and Ho(III) in aq. ethanol (50%, v/v) employing Bjerrum-Calvin³ pH-titration technique as adopted by Irving and Rossotti⁴. A solvent correction factor was applied in the pH-meter reading for the non-aqueous solvent used⁵.

Anhydrous rare earth chlorides (NdCl₃, TbCl₃, DyCl₃, HoCl₃) were used as such or prepared from their oxides (Sm₂O₃, Gd₂O₃)⁶. The appropriate amounts of these rare earth chlorides were dissolved in perchloric acid of desired normality to prevent hydrolysis. The solution of AMTDA (m.p. 245°, Koch-light, AR) was prepared in ethanol. Sodium hydroxide (BDH), sodium perchlorate (Reidel) and perchloric acid (E. Merck) solutions were prepared in CO₂-free triply distilled water.

For pH measurements an Elico L₁₋₁₀ pH-meter (accuracy ± 0.05 pH unit) equipped with glass-calomel electrode assembly was employed. The calibration of pH electrode system was done with the help of standard buffers (pH 4 and 9.2). The titrations of the following solutions (total volume 50 ml) were carried out under purified N₂ atmosphere in ethanol-water (50%, v/v) against carbonate-free NaOH (1.6 × 10⁻¹ M) at constant ionic strength of 0.1 M



(NaClO₄): (a) 5 ml of perchloric acid, (b) 5 ml perchloric acid + 25 ml AMTDA and (c) 5 ml perchloric acid containing metal ion + 25 ml AMTDA.

The ligand exists in three forms⁷, (I) yellowish prismatic needle (m.p. 245°), (II) transparent white cubes (m.p. 232°) and (III) brownish yellow rectangular plates (m.p. 224°). Janniah and Guha^{8,9} have shown that in solution, it exists in two forms (II and III) in equilibrium with each other, one form being in slight excess over the other. Their interconversion involves the formation of a bridged structure (III). The ligand is amphoteric in character; it accepts a proton at the amino group and loses a proton at the mercapto group thereby showing its potentialities of forming complexes with the metal ions.

In the present work the acid ligand curve deviates from pure acid curve near $B=2.7$. The values of \bar{n}_A were calculated at $B=2.7$ and 6.8 and were found to be 0.838 and 0.274 respectively, indicating the dissociation of one proton only. $\log K_1^H$ was obtained from the proton-ligand formation curve by half-integral method. This value was compared with that calculated by pointwise method.

For the calculation of metal-ligand stability constants of rare earths, very dilute solutions were used to prevent hydrolysis. The pL values were calculated at various \bar{n} values and the metal-ligand formation curves were obtained by plotting \bar{n} against pL . From these curves, the values of the stability constants, $\log K_1$, $\log K_2$ and $\log K_3$ could be directly read by half-integral method (Table 1). The values were also calculated by pointwise method. The highest \bar{n} values obtained at $pH=6.6$ in all the cases were less than 3.5, suggesting the formation of 1:1, 1:2 and 1:3 metal ligand complexes. The abrupt change in \bar{n} value above $pH=6.6$ was not considered due to the possibility of hydrolysis. Standard deviations were also calculated by the known equation.

Table 1—Metal Ligand Stability Constants at $\mu=0.1 M$ (NaClO₄)

| | Nd | Sm | Gd | Tb | Dy | Ho |
|---------------|------------|------------|------------|------------|------------|------------|
| log K_1 25° | 6.416±0.29 | 6.375±0.25 | 6.500±0.27 | 6.375±0.26 | 6.475±0.17 | 6.425±0.24 |
| 35° | 6.176±0.31 | 6.176±0.15 | 6.240±0.25 | 6.120±0.06 | 6.220±0.02 | 6.240±0.20 |
| log K_2 25° | 5.200±0.22 | 5.200±0.26 | 5.400±0.08 | 5.250±0.13 | 5.225±0.25 | 5.275±0.02 |
| 35° | 5.000±0.27 | 5.010±0.24 | 5.180±0.25 | 5.035±0.27 | 5.015±0.26 | 5.095±0.26 |
| log K_3 25° | 4.200 | 4.175 | 4.275 | 4.200 | 3.900 | 4.055 |
| 35° | 4.040 | 4.005 | 4.015 | 4.025 | 3.735 | 3.905 |
| log K_n 25° | 15.816 | 15.750 | 16.175 | 15.825 | 15.60 | 15.755 |
| 35° | 15.216 | 15.191 | 15.515 | 15.280 | 14.970 | 15.240 |

The overall changes in free energy (ΔG) at 25° and 35°C, enthalpy (ΔH) and entropy (ΔS) have been calculated using the standard equations and the values are given in Table 2. ΔG values are almost similar while ΔH and ΔS values differ considerably. The positive values of enthalpy change and increase in entropy^{10,11} have been attributed to the presence of metal chelate bond causing greater steric strain. The formation of 1:2 and 1:3 complexes appears to be less endothermic and the values of ΔH and ΔS are less positive than those of the 1:1 complex. This is completely in agreement¹² with the expectation of less dehydration of the cation and probable degree of covalency in the metal-ligand bonding. The greater the steric hindrance of the complex, the greater will be the values of $\log K_1/K_2$. The deviation in the stability order is also caused by the π -bonding tendency¹³ of the sulphur atom with the metal ion.

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Table 2—Changes in Free Energy, Enthalpy and Entropy

| | Nd | Sm | Gd | Tb | Dy | Ho |
|--------------------------------------------|--------|--------|--------|--------|--------|--------|
| $-\Delta G$ 25° | 21.500 | 21.400 | 21.980 | 21.510 | 21.190 | 21.420 |
| 35° | 21.371 | 21.306 | 21.785 | 21.318 | 21.020 | 21.400 |
| (kcal/mol ⁻¹) | | | | | | |
| ΔH | 25.125 | 23.407 | 27.633 | 27.013 | 26.381 | 21.127 |
| (kcal/mol ⁻¹) | | | | | | |
| ΔS | 153.43 | 147.67 | 163.46 | 159.94 | 156.54 | 140.14 |
| (cal deg ⁻¹ mol ⁻¹) | | | | | | |

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