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Stabilities and Structure of Metal Complexes with Sulfur σ-Donor Ligands

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ABSTRACT

Stability constants of VO(II), UO_2(II), and Be(II) complexes with N-aryl substituted-3-mercaptopropionamides have been determined in a 70% (v/v) dioxane-water mixture at constant ionic strength, 0.1 M $NaClO_4$, at 30 ± 1°C in an inert atmosphere of nitrogen using the Irving-Rossotti pH titration technique. Structures of metal complexes of N-aryl substituted-3-mercaptopropionamides have been proposed on the basis of infrared spectroscopic studies. Stabilities of metal chelates have been found to be in the order VO(II) > UO_2(II) > Be(II). The stability sequence has been interpreted on the basis of the charge-radius ratio of the cation and M-S π-interaction.

INTRODUCTION

Analytical aspects of N-(naphthyl)-2-mercaptoacetamide and N-aryl substituted mercaptoacetamide ($R{-}NHCOCH_2SH$) have been extensively studied and reported [1] in the literature. The present communication deals with stabilities and their possible structures on the basis of IR spectral studies of VO(II), UO_2(II), and Be(II)

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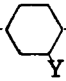
complexes wherein the –SH group acts as an acidic functional group and the carbonyl oxygen, rather than the amino nitrogen, acts as a donor atom in metal complexes of N-aryl substituted 3-mercaptopropionamides (R–NHCOCH$_2$CH$_2$SH).

EXPERIMENTAL

Ligands

N-Phenyl-3-mercaptopropionamide and its analogs (X––NH.CO.CH$_2$.CH$_2$.SH; X = Cl, Y = H; X = CH$_3$, Y = H; X = OCH$_3$; Y = H; X = H, Y = Cl; X = H, Y = CH$_3$) were prepared by the method given by Guha Sircar [2]. The purity of the compounds was checked by the iodine titration method, thin-layer chromatography for single spots, and elemental analyses.

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Solutions

All chemicals used were of analytical grade. Dioxane was purified by Weissberger's method [3]. Metal solutions were prepared from their respective metal salts and were estimated by standard methods. Carbonate-free 0.1 M sodium hydroxide solution was prepared in double distilled water.

Instruments

E.C. model expanded scale pH meter (accuracy ± 0.02) with glass and saturated calomel electrodes assembly was used for pH measurements. Perkin-Elmer infrared spectrophotometer model 537 was used to obtain the spectra of the compounds.

Procedure

Stability Constants

The Irving-Rossotti pH titration technique [4] was adopted to determine the stepwise stability constants of metal complexes at 30 ± 1°C. The following solutions (total volume, 50 mL), prepared in a 70% (v/v) dioxane-water mixture, were used:

1. 0.006 M perchloric acid, 0.1 M NaClO$_4$
2. 0.006 M perchloric acid, 0.1 M NaClO$_4$, 0.002 M ligand

3. 0.006 M perchloric acid, 0.1 M $NaClO_4$, 0.002 M ligand, 0.0004 M metal ion solution

The ionic strength was maintained at 0.1 M $NaClO_4$ in each case and the titrations were carried out in an inert atmosphere using 0.1 M NaOH solution.

Solid Complexes

Vanadyl sulfate (1.0 g, 0.005 mol) or uranyl nitrate (2.5 g, 0.005 mol) was dissolved in about 7.5 mL double distilled water. The pH of the solution was adjusted between 4.50-5.00 for VO(II) and 5.00-5.50 for UO_2(II) by adding 10% hydrochloric acid/10% sodium acetate solution. Hot ethanolic solution containing 2 g of the ligand (N-phenyl-3-mercaptopropionamide), a slight excess over that required for a 1:2 metal-to-ligand ratio, was gradually added with constant stirring to the warm solution of the metal ion. Green and yellow granular complexes were obtained for VO(II) and UO_2(II), respectively. The precipitate was digested on a hot water bath for nearly half an hour and filtered under suction. It was washed two to three times with ethanol and water. The precipitate was dried.

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Spectra

Infrared absorption spectra of the ligand and its VO(II) and UO_2(II) complexes were obtained in KBr disk. A few important characteristic absorption bands with their relative intensities and assignments are given in Table 1.

Calculation

Proton-ligand stability constants were evaluated from the formation curve, a plot of $\bar{n}A$ vs pH values, obtained from the titration curves of Solutions 1 and 2 by the Irving-Rossotti method. Similarly, metal ligand stability constants were evaluated from the formation curves, a plot of $\bar{n}$ and pA values obtained from the titration curves of Solutions 2 and 3. Hydrolysis correction was made while calculating $\bar{n}$ values.

Stability constants, calculated by Bjerrum's half integral method [5], are in agreement with the values obtained by the least squares [6], Schroder [7], and Block and McIntyre [8] methods. The results are given in Table 2.

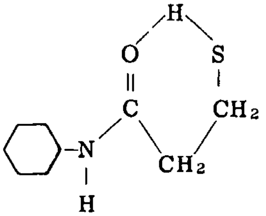
TABLE 1. Infrared Absorption Frequencies of Vanadyl(II) and Uranyl(II) Complexes of N-phenyl-3-mercaptopropionamide ($C_6H_5NH.CO.CH_2CH_2SH$)

Compounds	νN-H trans		νSH		Amide I	Amide II	Amide III
Ligand	3290	3190	3125	2560	1655	1575	1270
Vandyl complex	3290	-	3090	-	1645	1520	1250
Uranyl complex	3290	3190	3120	-	1650	1545	1255

DISCUSSION

Infrared absorption spectral analyses of N-phenyl-3-mercaptopropionamide and its related compounds have been reported from our laboratories [9].

Absorption bands at 3290 and 3180 cm^{-1} in the spectrum of the ligand have been assigned to bonded –NH stretching vibrations in which the –NH group is trans with respect to the carbonyl group. Amido carbonyl and SH stretching vibrations have been found to occur at 1655 and 2560 cm^{-1}, respectively (cf. Table 1). Brown and Corbridge [10] have observed that the CH_3CO– group in the acetanilide molecule makes an angle of 37° 54' with the C_6H_5NH– plane and that C=O and NH groups are in the trans-position to each other. On the basis of analogy, $-COCH_2CH_2SH$ is not likely to lie in the anilino plane of 3-mercaptopropionalide. This situation brings mercapto- and the carbonyl groups closer to each other and forms the intramolecular hydrogen-bonded Structure I:



I

The involvement of C=O as the proton acceptor group has also been concluded on the basis of its lowering by 20 cm^{-1} from its observed value of 1670 cm^{-1} in N-phenyl-2-mercaptoacetamide where it is not involved in such bonding. Similar lowering of C=O absorption frequency by 10-25 cm^{-1} have been reported [11] in other compounds where it acts as a proton acceptor group. This rules out the possibility of the mercapto group being involved in intramolecular hydrogen

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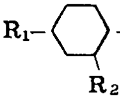
TABLE 2. Proton-Ligand Stability Constants of N-Aryl Monosubstituted-3-mercaptopropionamides,



$R_1-C_6H_3(R_2)-NH.CO.CH_2.CH_2SH$, and Their Metal Ligand Stability Constants

Compounds		H⁺	Be(II)			UO₂(II)			VO(II)		
R_1	R_2	Log K	Log K_1	Log K_2	Log K_1K_2	Log K_1	Log K_2	Log K_1K_2	Log K_1	Log K_2	Log K_1K_2
H	H	10.90	9.92	7.05	16.97	9.27	8.53	17.80	9.97	9.48	19.45
			9.92	7.05	16.97[a]	8.93	8.87	17.80[a]	-	-	19.40[c]
			9.89	7.02	16.91[b]	8.93	8.87	17.80[b]	-	-	-
								17.49[c]	-	-	-
Cl	H	10.56	8.85	6.51	15.16	8.91	8.15	17.06	9.50	8.70	18.20
			8.64	6.52	15.16[a]	-	-	-	9.22	8.98	18.20[a]
			8.64	6.52	15.16[b]	-	-	17.00[c]	9.22	8.98	18.20[b]
											18.22[c]
CH_3	H	10.98	8.95	7.96	16.91	9.55	8.81	18.36	9.80	9.20	19.00
			8.86	7.85	16.71[a]	9.21	9.15	18.36	-	-	19.01[c]
			8.85	7.85	16.70[b]	9.20	9.15	18.35[b]	-	-	-
			-	-	-	-	-	18.24[c]	-	-	-
OCH_3	H	11.04	8.96	7.05	16.01	9.56	8.77	18.33	9.81	9.16	19.01

(continued)

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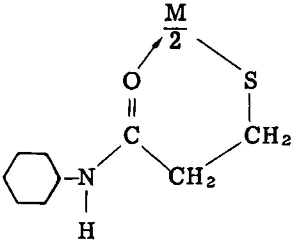
TABLE 2 (continued)

Compounds		H^+	Be(II)			UO_2(II)			VO(II)		
R_1	R_2	Log K	Log K_1	Log K_2	Log K_1K_2	Log K_1	Log K_2	Log K_1K_2	Log K_1	Log K_2	Log K_1K_2
			8.94	7.07	16.01[a]	9.23	8.97	18.30[a]	-	-	-
			8.94	7.07	16.01[b]	9.28	9.05	18.33[b]	-	-	18.98[c]
			-	-	-	9.28	9.05	18.33[c]	-	-	-
H	Cl	10.75	8.62	7.29	15.91	9.57	8.25	17.82	10.02	9.10	19.12
			8.53	7.38	15.91[a]	9.50	8.32	17.82[a]	9.83	8.29	19.12[a]
			8.53	7.38	15.91[b]	9.55	8.32	17.87[c]	9.75	8.25	19.00[c]
H	CH_3	11.10	9.08	7.50	16.58	9.63	9.05	18.68	9.69	8.87	18.56
			9.05	7.54	16.59[a]	-	-	18.72[c]	9.43	9.13	18.56[c]
			9.04	7.55	16.59[b]	-	-	-	-	-	18.59[c]

[a] Stability constants by Schroder's method.
[b] Stability constants by Block and McIntyre's method.
[c] Stability constants by the least squares method.

bonding with the acceptor amino nitrogen atom, although nitrogen, like oxygen, could interact through its p-electrons.

Infrared absorption spectra of metal complexes, as expected, do not show any absorption band in the unambiguous region 2600-2550 cm^{-1} reported [12] for –SH stretching vibrations. The amide C=O absorption band has been lowered to some extent in both complexes, probably due to interaction with heavy metal. Absorption bands due to other vibrations in the remaining parts of the organic ligand molecule have been identified in the spectra; they stay almost constant. Absorption bands due to metal-oxygen and metal-sulfur bonds in UO_2(II) and VO(II) complexes could not be identified because they occur in a very low region of the spectrum. The metal complexes can therefore be assigned Structure II:



II

Effect of Substituents on Stability Constants

Titration curves of the ligands as such and in the presence of metal ion did not indicate the attachment of a third molecule of the bidentate ligand although higher coordination numbers in UO_2(II) and VO(II) are known. Table 2 shows that the stability constants calculated by different methods are in close agreement. Substituents in the phenyl ring at nitrogen atom in the ligand molecule are not likely to influence proton-ligand or metal-ligand stability constants significantly because these groups are far from the reaction center.

The stabilities of metal complexes are in the order VO(II) > UO_2(II) > Be(II). The sequence can be explained in terms of the ionic potential, i.e., the charge-radius ratio of the cations. The metal-ligand stability constants decrease with a decrease in the charge-radius ratio of the cations.

Beryllium(II), being a nontransition metal, does not have $d\pi$ electrons to donate to the vacant $d\pi$ orbitals of the sulfur atom of ligands, and hence no M-S π-interaction can take place. However, such M-S π-interactions are possible in VO(II) and UO_2(II) complexes, and this imparts extra strength to the M-S σ-bond. Consequently these metal ions form more stable complexes than Be(II).

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