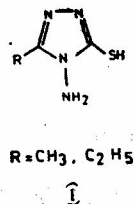


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(EAMT) derivatives of 4-amino-5-mercapto-1,2,4-triazole (I).



All the chemicals used were of AR or CP grade. The ligands were prepared by the methods given in literature⁶. Aqueous solution of methyl derivative and ethanolic solution of ethyl derivative were used in the syntheses of the complexes.

Preparation of the complexes — To a hot aqueous solution of the metal chloride (~6 mmoles) containing 2g of ammonium chloride and a few drops of ammonia (to make the solution basic) was added hot aqueous or ethanolic solution of the ligand (~13 mmoles). The mixture was digested on a water-bath for 3 hr when yellowish-green Ni(II) or chocolate-red Co(II) complex separated. The products were centrifuged, washed with hot water, warm ethanol and ether. The residues were finally dried at 100-105° and kept *in vacuo* over-night. The complexes were found to be almost insoluble in most common solvents.

The method of analysis of sulphur in the ligands and the complexes was similar to the one reported earlier⁶. The metals were estimated by standard methods⁷ while carbon, hydrogen and nitrogen were analysed on micro scale.

The electronic spectra of Ni(II) and Co(II) complexes were recorded in nujol on a Cary 14 spectrophotometer in the range of 350-1500nm. Infrared spectra (in KBr phase) of the ligands and the complexes were recorded on a Perkin - Elmer 521 grating infrared spectrophotometer in the range 4000-250 cm⁻¹.

Analytical data (Table 1) show that Ni (II) and Co(II) form ML₂.2H₂O type of complexes. The diaquo complexes begin to lose water on heating and become anhydrous beyond 150°. This indicates that the water molecules are probably coordinated.

The magnetic moments of Ni(II) complexes with MAMT and EAMT are 3.05 and 3.1 B.M. respectively at room temperature which are characteristic of high-spin Ni(II) complexes in octahedral fields. The values are slightly higher than the spin-only value of 2.83 B.M. probably due to a slight distortion from the pure O_h to D_{4h} symmetry. This is not uncommon in d⁸ system because of Jahn-Teller effect. Since, for a T_d symmetry which gives triplet state as the ground state, the magnetic moments due to orbital contribution would have been much more⁸ than what are actually observed, we prefer a distorted O_h to T_d symmetry for the Ni(II) complexes as supported by the electronic spectral data (Table 2).

The electronic spectra of the Ni(II) complexes show three distinct bands around 9000, 15000 and 23000 cm⁻¹ which can be assigned to the transitions ³T_{2g}(F) ← ³A_{2g}(F), ²T_{1g}(F) ← ³A_{2g}(F) and ³T_{1g}(P) ← ³A_{2g}(F) res-

Complexes of Ni(II) & Co(II) with 3-Methyl & 3-Ethyl Derivatives of 4-Amino-5-mercapto-1,2,4-triazole

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Complexes of Ni(II) and Co(II) with 3-methyl-4-amino-5-mercapto-1,2,4-triazole and 3-ethyl-4-amino-5-mercapto-1,2,4-triazole have been prepared and characterised on the basis of analytical, magnetic and spectral data. The Ni(II) and Co(II) chelates seem to be of high-spin octahedral type.

A GREAT deal of interest has been shown in recent years in the study of substituted 1,2,4-triazoles as complexing agents¹⁻⁴. The 3-alkyl-4-amino-5-mercapto-1,2,4-triazoles are particularly interesting since they contain four donor atoms (three nitrogen and one sulphur). Therefore they are expected to behave as mono-, bi-, tri- or tetradentate ligands. Bonding through nitrogen of the amino group and sulphur of the thiol group could result in the formation of stable metal complexes involving highly favoured five membered ring system. In continuation of our earlier work⁵ in this field, we report here the syntheses and characterization of Ni(II) and Co(II) complexes with 3-methyl (MAMT) and 3-ethyl

TABLE 1 — ANALYTICAL DATA OF THE LIGANDS AND THE COMPLEXES

Compound	Calc. (Found), %				
	C	H	N	S	Metal
C ₃ H ₆ N ₄ S	27.68 (27.81)	4.65 (3.94)	43.03 (42.80)	24.63 (24.45)	—
Ni(C ₃ H ₅ N ₄ S) ₂ ·2H ₂ O	20.41 (20.52)	3.99 (3.81)	31.74 (31.56)	18.16 (18.02)	16.63 (16.44)
Co(C ₃ H ₅ N ₄ S) ₂ ·2H ₂ O	20.40 (20.27)	3.97 (4.24)	31.94 (31.51)	18.13 (17.86)	16.70 (16.94)
C ₄ H ₅ N ₄ S	33.32 (32.57)	5.59 (5.87)	38.86 (38.57)	22.24 (22.08)	— —
Ni(C ₄ H ₇ N ₄ S) ₂ ·2H ₂ O	25.21 (24.94)	4.76 (4.96)	29.40 (29.60)	16.83 (16.50)	15.41 (15.62)
Co(C ₄ H ₇ N ₄ S) ₂ ·2H ₂ O	25.21 (24.80)	4.76 (4.71)	29.41 (28.81)	16.81 (16.59)	15.47 (15.11)

TABLE 2 — ELECTRONIC SPECTRAL DATA OF Ni(II) AND Co(II) COMPLEXES

Complexes	Band positions (cm ⁻¹)	ν_2/ν_1	10Dq (cm ⁻¹)	B (cm ⁻¹)	β
Ni(C ₃ H ₅ N ₄ S) ₂ ·2H ₂ O	9400 15400 23800	1.63	9960	830	0.8
Ni(C ₄ H ₇ N ₄ S) ₂ ·2H ₂ O	9855 15870 23350	1.61	10260	855	0.82
Co(C ₃ H ₅ N ₄ S) ₂ ·2H ₂ O	8200 21740 25000	1.99	9020	820	0.84
Co(C ₄ H ₇ N ₄ S) ₂ ·2H ₂ O	8475 21250 23800	2.03	9330	848	0.87

pectively in the case of octahedral complexes of Ni(II). The ν_1 band expected around 9000 cm⁻¹ is split into two bands. This splitting can be ascribed⁹ to lowering of the symmetry from O_h to D_{4h} because of Jahn-Teller distortion and also because of the difference in strengths of the fields at equatorial and axial positions. The values of 10Dq and B were calculated as described in literature¹⁰. Since configuration interaction between the high spin $T_{1g}(P)$ and $T_{1g}(F)$ excited states in O_h symmetry lowers the ratio ν_2/ν_1 from about 1.8 to around 1.6 for Ni(II) complexes, the values of 1.63 and 1.61 actually got for these complexes support the octahedral symmetry. The yellowish-green colour of the diaquo complexes also supports the O_h symmetry.

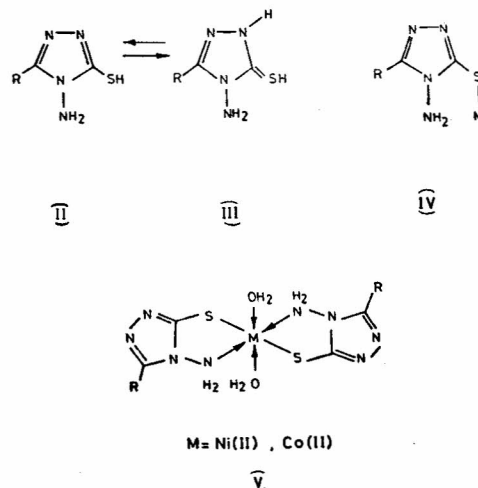
The magnetic moments of Co(II) complexes with MAMT and EAMT are 4.95 and 4.8 B.M. respectively which are much higher than the spin-only value of 3.87 B.M. These can be explained on the basis of O_h symmetry involving a high degree of orbital contribution due to the three-fold orbital degeneracy of the $^4T_{1g}$ ground state. It is not surprising that the ligands in the equatorial position being less hindered bidentate monoanions, favour an O_h symmetry⁸. Further support to this view comes from electronic spectral results.

The electronic spectra of Co(II) complexes of the MAMT and EAMT show two distinct bands around 8000 and 21000 cm⁻¹ due to the transitions $^4T_{2g}(F) \leftarrow ^4T_{1g}(F)$ and $^4T_{1g}(P) \leftarrow ^4T_{1g}(F)$ respectively. These bands are typical of high-spin octahedral Co(II) complexes. Besides these bands, a shoulder is seen around 25000 cm⁻¹ which is of considerable intensity and may be due to the spin-orbit coupling in the $^4T_{1g}(P)$ state. The increased intensity indicates some tetragonal distortion. The chocolate-red colour of these complexes supports an octahedral geometry. The values of 10Dq and B were calculated in the same way¹⁰ as described for Ni(II) complexes.

As already reported⁵, the ligands exist in thiol and thione forms (II and III) respectively. The occurrence of a medium intensity band around 2540 cm⁻¹

due to $\nu(S-H)$ and a strong band around 750 cm⁻¹ due to $\nu(C=S)$ in the spectra of the ligands supports the view that the ligands exist in tautomeric forms. As the ligand molecules contain thioamide groups, shifts in positions of thioamide bands can be expected as a result of bonding through sulphur of the thiol form and/or nitrogen of the amino group.

If the bonding scheme as proposed above is valid, the charge delocalised between N, C and S in the thioamide group of the ligand molecules would get localised between N and C (IV). As a result, $\nu(C=N)$ would shift towards higher wave number side while $\nu(C=S)$ would shift towards lower wave number side in the spectra of complexes. Both these shifts are actually observed because thioamide band II ($\nu C=N$) + $\nu C-N$ appearing at 1295 cm⁻¹ in the spectra of the ligands shifts to 1340 ± 5 cm⁻¹ in the spectra of the complexes. Similarly the thioamide band III ($\nu C=S$)¹¹ around 750 cm⁻¹ in the ligands shifts to 675 ± 10 cm⁻¹ in the spectra of the complexes. In addition, new bands are seen in the spectra of Ni(II) and Co(II) complexes at 3440-3300, 1625 ± 5 and 880 cm⁻¹ which are characteristic of coordinated water. Bands around 400 and 360 cm⁻¹ are seen in



the spectra of all the complexes which can be assigned to $\nu(M-N)$ and $\nu(M-S)$ modes respectively. Based on the above mentioned evidences, structure (V) is assigned to the Ni(II) and Co(II) complexes.

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Studies on Formation Constants of UO_2^{2+} , VO_2^{2+} , Ce^{3+} & Nd^{3+} Chelates with Substituted Salicylaldehydes

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The complexation of UO_2^{2+} , VO_2^{2+} , Ce^{3+} and Nd^{3+} ions with salicylaldehyde, 3-chloro-, 4-hydroxy-, 5-methyl- 5-iodo-, 6-chloro-, 3-methyl-5-nitro and 5-methyl-3-nitro-salicylaldehydes has been investigated in 75% (v/v) dioxane-water medium at $\mu = 0.1M(NaClO_4)$ employing Calvin-Bjerrum titration technique. The validity of $\log K = a.pK + b$ relation is examined for these complexes.

A LITERATURE survey reveals that the stability constants of the complexes of UO_2^{2+} , VO_2^{2+} , Ce^{3+} and Nd^{3+} with salicylaldehyde and substituted salicylaldehydes have not been determined. The present note, therefore, deals with the determination of stability constants of these complexes in 75% (v/v) dioxane-water medium employing Calvin-Bjerrum potentiometric technique.

All the reagents used were of AR quality. Except for salicylaldehyde and 4-hydroxysalicylaldehyde, the other ligands listed in Table I were prepared and purified by the methods described previously¹. The method of purification of dioxane, the procedure

employed and the methods used for the calculations of \bar{n}_A , \bar{n} , pK and $\log K$ are the same as given earlier¹.

The proton-ligand stability constants of substituted salicylaldehydes reported in an earlier paper¹ are presented in Table I.

pK_2 for 4-hydroxysalicylaldehyde could not be determined by either the half-integral or the point-wise method as \bar{n}_A in this case remains almost constant above B (pH meter reading) 10.6. The higher value of B could not be used with accuracy because of limitations of the sodium ion error. pK_2 was determined employing the equation $pK_1 + pK_2 = 2B$, which holds at $\bar{n}_A = 1.00$. Kabadi *et al.*², followed a similar procedure to calculate pK_2 for salicylic acid in 75% (v/v) dioxane-water medium.

The values of \bar{n} , the average number of ligands attached per metal ion and the free ligand exponent pL were calculated from the titration curves of the ligands and complexes. The values of n selected were between 0.2 to 0.8 and between 1.2 to 1.8 for calculation of $\log K_1$ and $\log K_2$. The stepwise stability constants of the UO_2^{2+} , VO_2^{2+} , Ce^{3+} and Nd^{3+} complexes were determined by analysing the formation curves (\bar{n} versus pL) and using methods such as half-integral and point-wise calculations^{3,4}. For greater accuracy, when the difference of $\log K_1$ and $\log K_2$ was less than 1.78, the method of least squares was applied. The values of $\log K_1$ and $\log K_2$ are given in Table I.

The maximum values of \bar{n} up to the point of precipitation are 2.1 for UO_2^{2+} and 1.8 to 1.9 for VO_2^{2+} indicating the formation of 1:1 and 1:2 uranyl and vanadyl complexes respectively. The significant deviation of the metal complex curve from the ligand curve begins at $B = 2.2$ to 2.5 for UO_2^{2+} and $B = 2.5$ for VO_2^{2+} chelates with different substituted salicylaldehydes. Precipitation in these systems occurs at $B = 5.0$ to 7.0, ruling out the possibility of formation of polynuclear complexes.

The metal complex curve and the ligand curve start deviating from each other for Ce^{3+} and Nd^{3+} complexes at $B = 2.6$ and 3.5 respectively. From the \bar{n} values it is evident that 1:1 and 1:2 complex formation takes place.

The B values of hydrolysis of uranyl ion and vanadyl ion obtained from the deviation of uranyl and vanadyl curves from their corresponding acid curves are 5.0 and 5.8 respectively. The departure of the metal complex titration curve from the ligand curve in both the cases is observed at $B = 2.2$ for all the substituted salicylaldehydes, indicating that the complexation occurs before hydrolysis sets in. The 1:1 and 1:2 complexes are formed in the case of uranyl and vanadyl systems at $B = 2.3$ to 3.8 and 4.2 to 5.2 respectively. No precipitate is formed in the metal complex titration.

For Ce^{3+} and Nd^{3+} complexes no precipitation occurs up to $B = 6.1$. The metal complex curve and the ligand curve start deviating from each other for Ce^{3+} and Nd^{3+} complexes at 2.6 and 3.5 respectively.