Triazoles as Complexing Agents: Synthesis and Structural Studies of Some Bivalent Metal Ion Complexes with Bi- and Tridentate Ligands

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Summary. Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of 4-amino-5-mercapto-3-trifluoro-methyl-*s*-triazole (*AMTT*) and 5-mercapto-4-salicylideneamino-3-trifluoromethyl-*s*-triazole (*MSTT*) have been synthesized and characterized on the basis of elemental analyses, magnetic measurements, infrared and electronic spectral data. The ligands *AMTT* and *MSTT* were characterized by elemental analyses, infrared and ^{1}H NMR spectral studies. *AMTT*, involving N and S as donor atoms, and *MSTT*, involving N, O and S as donor atoms, act as bi- and tridentate ligands, respectively. The geometry of the complexes has been assigned on the basis of magnetic and electronic spectral data. EPR parameters for copper (II) complexes have been calculated. Thermal stabilities of the complexes are also reported. Due to insolubility in water and common organic solvents and infusibility at higher temperatures, all the complexes are thought to be polymeric in nature.

Keywords. Metal complexes; Triazoles.

Triazole als Komplexierungs-Agentien: Synthese und Strukturuntersuchungen an einigen bivalenten Metallionenkomplexen mit zwei- und dreizähnigen Liganden

Zusammenfassung. Es wurden Co(II)-, Ni(II)-, Cu(II)-, Zn(II)- und Cd(II)-Komplexe von 4-Amino-5-mercapto-3-trifluormethyl-*s*-triazol (*AMTT*) und 5-Mercapto-4-salizylidenamino-3-trifluormethyl-*s*-triazol (*MSTT*) hergestellt und mittels Elementaranalyse, magnetischen Messungen, Infrarot- und Elektronenspektroskopie charakterisiert. Die Liganden *AMTT* und *MSTT* wurden elementaranalytisch und spektroskopisch (IR und ^{1}H-NMR) charakterisiert. *AMT* wirkt über die N- und S-Donoratome als zweizähniger Ligand, *MSTT* über N, O und S als dreizähniger Ligand. Die Geometrie der Komplexe wurde auf der Basis von magnetischen und elektronenspektroskopischen Daten zugeordnet. Für die Cu(II)-Komplexe wurden die EPR-Parameter berechnet. Die thermischen Stabilitäten der Komplexe wurde ebenfalls untersucht. Wegen ihrer Unlöslichkeit in Wasser und gängigen organischen Lösungsmitteln und der Unschmelzbarkeit bei höheren Temperaturen wird eine polymere Natur der Komplexe angenommen.

Introduction

Schiff bases are an important class of ligands in coordination chemistry and have been studied extensively [1–3] due to various reasons like manifestation of novel structural features, abnormal magnetic properties and relevance to biological

processes. A number of Schiff base complexes [4, 5] have been tested for anti-microbacterial activities and they have found to exhibit bacteriostatic and fungistatic activities. The formation of stable complexes is facilitated with the presence of functional groups such as SH and/or OH sufficiently near to the azomethine moiety.

A survey of the literature has revealed that some studies [6–8] on the metal derivatives of Schiff bases derived from 3-substituted (R)-4-amino-5-mercapto-s-triazoles ($R = CH_3, C_2H_5$ and C_3H_7) are reported in which attempts were made to characterize the complexes by IR and electronic spectral data, and magnetic measurements. However, metal derivatives with *AMTT* and *MSTT* have not been investigated so far. It was therefore thought of interest to synthesize and characterize *AMTT* and *MSTT*, and their metal complexes with some bivalent metal ions.

Experimental Part

Preparation of the Ligands AMTT and MSTT

4-Amino-5-mercapto-3-trifluoromethyl-s-triazole (*AMTT*) was prepared following the literature method [9]. The Schiff base *MSTT* was prepared by refluxing equimolar quantities of *AMTT* and salicylaldehyde in ethanol for about 2 h. On keeping the reaction mixture at room temperature for some time, the product obtained in the form of fine needle-like crystals was filtered and recrystallized from ethanol. *AMTT* was obtained as colourless crystals, m.p. 144° (45%) and *MSTT* as light yellow shining crystals. m.p. 184–86° (85%).

AMTT: Found C 19.40, H 1.45, S 16.98. Required for $C_3H_3F_3N_4S$: C 19.56, H 1.64, S 17.39%. IR (Nujol) cm^{-1}: 3200 ($vN-H$), 1075 ($vC=S$). PMR(*Acetone-d_6*): δ 5.57 (s, 2H, NH$_2$) and 13.25 (s, 1H, NH or SH). On D$_2$O exchange, the proton was absconded whereas a broad peak appeared at δ 4.3 for NH$_2$ protons. This may be due to intramolecular hydrogen bonding.

MSTT: Found C 41.34, H 2.20, S 11.25. Required for $C_{10}H_7F_3N_4OS$: C 41.66, H 2.43, S 11.11%. IR (Nujol) cm^{-1}: 1615 ($vN=CH$), 1270 ($vC-O$, phenolic), 1090 ($vC=S$). PMR (*DMSO-d_6*): δ 6.5–7.9 (m, 5H, SH and 4 aromatic protons), δ 9.08 (s, 1H, OH, disappeared on D$_2$O exchange), δ 9.5 (s,1H, azomethine proton).

Metal Derivatives of AMTT

Aqueous solution of bivalent metal acetates of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were mixed with *AMTT* in different metal:ligand molar ratios (1:1, 1:2 and 1:excess) slowly and with constant stirring. The products were filtered, washed with hot water, alcohol and acetone, and finally dried. The reactions gave the product in 1:2 stoichiometry except copper where the metal gets reduced from Cu(II) to Cu(I) and thus an 1:1 complex was formed.

Metal Derivatives of MSTT

Bivalent metal salts (BDH, AnalaR) were used as such. The metal derivatives were prepared by adding slowly and with constant stirring aqueous solution of metal acetates to the warm alcoholic solution of the ligand MSTT in different molar ratios. The products were washed and dried as above. With 1:1 and 1:2 (metal:ligand) molar ratios, products were found to be of 1:1 and 1:2 stoichiometry, respectively. The 1:excess reaction yielded the products with only 1:2 stoichiometry.

The yields of the complexes were in the range of 70–80%. The metals in the complexes were estimated using standard procedures [10].

IR spectra of the complexes were recorded on a Beckman IR-20 spectrophotometer. PMR spectra of the ligands were recorded on a Perkin-Elmer 90 MHz spectrometer. Electronic spectra were recorded in the region 200–1800 nm at the IIT, Madras. Magnetic measurements were carried out at room temperature (25 ± 5 °C) with the help of vibrating sample magnetometer, Model 155, at USIC, University of Roorkee, Roorkee. Thermal analyses were carried out on a Derivatograph, Mom-

Budapest, Hungary, type Paulik-Paulik-Erdey, OD-102. The specimens were heated at the rate of $10°/min$ in $20-1000°C$ range and heated alumina was used as the standard. EPR spectra were recorded at IIT, Madras.

Results and Discussion

The analytical and physical data of the complexes are given in Table 1.

Infrared Spectra

The complexing property of RNCS groups with metal ions has been studied [11]. The ligands exhibit thione-thiol isomerism, thione $HNC-(=S)-$ and thiol $-N=C(-SH)-$ groups in thione-thiol equilibrium, and hence give characteristic thioamide bands in their IR spectra. A broad band observed in the region 3400–3100 cm^{-1} centered at 3200 cm^{-1} is assigned to $v(N-H)$ mode. This band is shifted to lower wavenumber (3180–3060 cm^{-1}) in the complexes where coordination through amine nitrogen is inferred. The very weak band in both AMTT and MSTT in the region 2630–2590 cm^{-1} due to $v(S-H)$ is absent in the spectra of the complexes showing deprotonation of the thiol group. A characteristic band appearing in the region 1620–1615 cm^{-1} assigned to $v(-N=CH)$ shifts to lower frequency by 10–25 cm^{-1} in metal complexes showing coordination of the nitrogen atom of the azomethine group [12–14]. Bands at 1075 and 1090 cm^{-1} in the free ligands are due to $v(C=S)$. The IR spectra of respective metal complexes exhibit a band for $v(C-S-)$ in the region 745–700 cm^{-1} [15, 16].

Table 1. Analytical and physical data for the complexes

Compounds	Colour and State	Analysis (%) found (calcd.)			μ_{eff} (B.M.) at room temp.
		M	C	S	
$C_3H_3F_3N_4S$ (AMTT)	Colourless solid	–	19.4(19.6)	17.0(17.4)	–
$Co(C_3H_2F_3N_4S)_2·2H_2O$	Pink solid	12.5(12.8)	15.4(15.6)	13.9(13.9)	4.65
$Ni(C_3H_2F_3N_4S)_2·2H_2O$	Green solid	12.5(12.8)	15.2(15.5)	13.8(13.6)	3.14
$Cu(C_3H_2F_3N_4S)·2H_2O$	Colourless solid	25.4(25.8)	14.5(14.6)	12.2(12.6)	diamagnetic
$Zn(C_3H_2F_3N_4S)_2$	White solid	15.3(15.1)	16.3(16.7)	14.7(13.8)	diamagnetic
$Cd(C_3H_2F_3N_4S)_2·2H_2O$	White solid	21.4(21.9)	14.2(14.0)	12.2(12.4)	diamagnetic
$C_{10}H_7F_3N_4OS$ (MSTT)	Light yellow solid	–	41.3(41.7)	11.3(11.1)	–
$Co(C_{10}H_5F_3N_4OS)·3H_2O$	Bluish green solid	14.4(14.8)	29.8(30.1)	8.0(8.0)	3.89
$Ni(C_{10}H_5F_3N_4OS)·3H_2O$	Green solid	14.6(14.8)	30.1(30.0)	7.9(8.0)	2.97
$Cu(C_{10}H_5F_3N_4OS)·H_2O$	Dark green solid	16.9(17.3)	32.7(32.7)	8.5(8.7)	1.72
$Zn(C_{10}H_5F_3N_4OS)·H_2O$	White solid	17.6(17.7)	32.2(32.5)	8.3(8.7)	diamagnetic
$Co(C_{10}H_6F_3N_4OS)_2$	Bluish green solid	9.2(9.3)	37.5(37.9)	10.4(10.1)	5.15
$Ni(C_{10}H_6F_3N_4OS)_2$	Green solid	9.0(9.3)	37.4(37.9)	10.0(10.1)	3.40
$Cu(C_{10}H_6F_3N_4OS)_2$	Colourless solid	10.2(10.0)	37.8(37.6)	9.8(10.0)	diamagnetic
$Zn(C_{10}H_6F_3N_4OS)_2$	White solid	10.0(10.2)	37.3(37.5)	10.3(10.0)	diamagnetic
$Cd(C_{10}H_6F_3N_4OS)_2$	White solid	16.2(16.4)	34.7(35.0)	9.1(9.3)	diamagnetic

In 1:1 complexes of $MSTT$, a higher shift in the region 1310–1290 cm^{-1} was observed for phenolic v(C–O) as compared to the band at 1270 cm^{-1} for $MSTT$. This may be due to deprotonation of the phenolic OH group and formation of a band between metal and oxygen [17]. Similarly in 1:2 complexes of $MSTT$, the shift towards higher region is very small ($\sim$ 5 cm^{-1}) and it may be due to coordination of the phenolic OH group without loss of hydrogen. Bands in the far IR region 380–340, 440–400 and 520–480 cm^{-1} in the spectra of metal complexes of $MSTT$ are indicative of v(M–S), v(M–O) and v(M–N) linkages, respectively [18, 19], whereas in case of $AMTT$ complexes, only two bands for v(M–S) and v(M–N) were observed. The presence of coordinating water in the metal complexes is indicated by a broad band in the region 3500–3200 due to the presence of v(O–H).

Electronic Spectra

Cobalt(II) formed Co$(AMTT)_2 \cdot 2H_2O$, Co$(MSTT) \cdot 3H_2O$ and Co$(MSTT)_2$ complexes. Six coordinated complexes of cobalt(II) generally exhibit three bands in the regions 8000–10000, 15000–18000 and 21000–30000 cm^{-1}. Three main absorption bands at 10750, 15360 and 21600 cm^{-1} along with shoulders and 13500, 14810 and 15100 cm^{-1} were observed for the Co $(AMTT)_2 \cdot 2H_2O$ complex. The three main transitions may be due to three spin-allowed transitions arising from $^4T_{1g}$(F) (ground state term) to $^4T_{2g}$(F) (v_1), $^4A_{2g}$(F) (v_2) and $^4T_{1g}$(P) (v_3) excited states in octahedral field [20]. Shoulders in the spectrum may be due to spin-forbidden transitions.

The reaction between nickel(II) and $AMTT$, and $MSTT$ yielded Ni$(AMTT)_2 \cdot 2H_2O$, Ni$(MSTT) \cdot 3H_2O$ and Ni$(MSTT)_2$ complexes. The absorption spectra of these complexes showed absorption bands in the regions 7000–9000, 11000–15000 and 20000–25000 cm^{-1}, which may be assigned to transitions $^3A_{2g}$(F)$\rightarrow$$^4T_{2g}$(F) ($v_1$), $^3A_{2g}$(F)$\rightarrow$$^3T_{1g}$(F)($v_2$) and $^3A_{2g}$(F)$\rightarrow$$^3T_{1g}$(F) ($v_3$), suggesting octahedral geometry [20].

The electronic spectrum of Cu$(MSTT) \cdot H_2O$ showed one broad absorption band at 17480 cm^{-1} and a square planar geometry has been proposed.

Magnetic Measurements

The expected ranges of magnetic moments for d^7, d^8 and d^9 systems are 4.3–5.2, 2.8–3.5 and 1.7–2.2 B.M., respectively. The μ_{eff} values of Co(II), Ni(II) and Cu(II) complexes (Table 1) are within the expected ranges. However, in Co$(MSTT) \cdot 3H_2O$ the magnetic moment value of 3.89 B.M. (close to spin only value) may be due to quenching of orbital contribution and ligand effects [21]. The diamagnetic nature of copper in Cu$(AMTT) \cdot 2H_2O$ showed monovalent state of copper having d^{10} configuration. Cu$(MSTT)_2$ was also found to be diamagnetic. The anomalous behaviour of this complex may be attributed to metal–metal interaction, since the complex is polymeric, super-exchange phenomenon and/or high polarizability [22] of the ligand (sulphur donor) which supplies more electron density to copper ion and consequently the ions interact more strongly. The strong spin–spin interaction may take place by overlap of singly occupied d$_{x^2-y^2}$ orbital of two cupric ions which give a δ type bond [23].

All the complexes of zinc(II) and cadmium(II) are diamagnetic as expected for a d^{10} system. $Zn(AMTT)_2$, $Zn(MSTT)\cdot H_2O$ are four coordinated, and $Cd(AMTT)_2\cdot 2H_2O$, $Zn(MSTT)_2$ and $Cd(MSTT)_2$ are six coordinated, as inferred from elemental analyses and IR spectral data.

EPR Spectra

The EPR spectrum of the $Cu(MSTT)\cdot H_2O$ complex has been studied. The $g_{\parallel}$ and $g_{\perp}$ values have been found to be 2.12 and 2.026 respectively. The g_{av} was calculated to be 2.0572. The greater value of $g_{\parallel}$ compared to $g_{\perp}$ indicates the presence of an unpaired electron in the $d_{x^2-y^2}$ orbital. The g values coupled with observations from electronic spectrum support a square planar geometry with covalent nature of the metal-ligand bond [24].

Thermal Analyses

The thermal behaviour of these complexes is almost the same, hence only that of $Cd(AMTT)_2\cdot 2H_2O$ and $Cu(MSTT)_2$ are discussed in detail. The DTG curve of $Cd(AMTT)_2\cdot 2H_2O$ showed that the first and second water molecules were lost at 60° and 160 °C, corresponding losses in mass on TG curves are 3.19% (theoretical 3.42%) and 6.99% (theoretical 7.24%). After 160°, the organic part starts decomposing and finally at 790°, the end product is CdO. The total experimental loss of 74.66% is corroborated by a theoretically calculated mass loss of 75.04%.
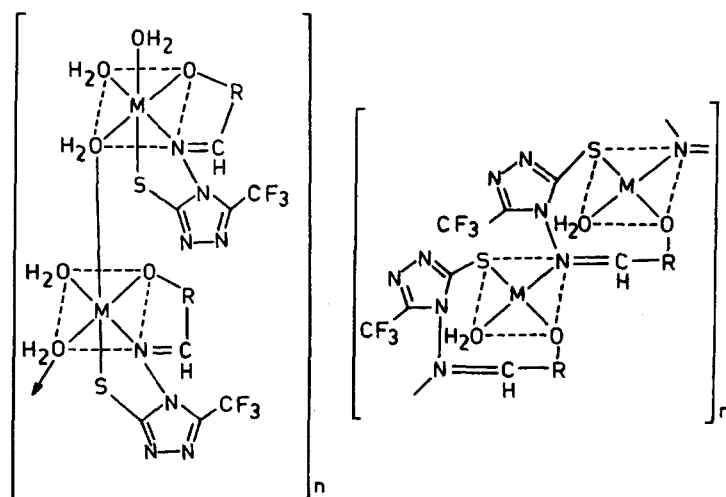
In thermoanalytical curves of $Cu(MSTT)_2$, the formation of CuS and SO_2 was identified at 710° with mass loss of 73.19% (theoretical 74.99%). CuO was the end product with a mass loss of 87.62% (theoretical 87.53%).

The structures of the complexes are given in Schemes 1–3.
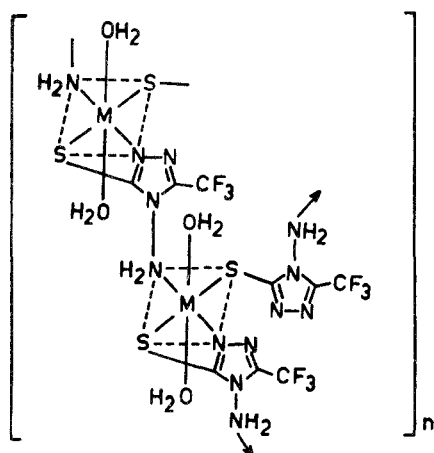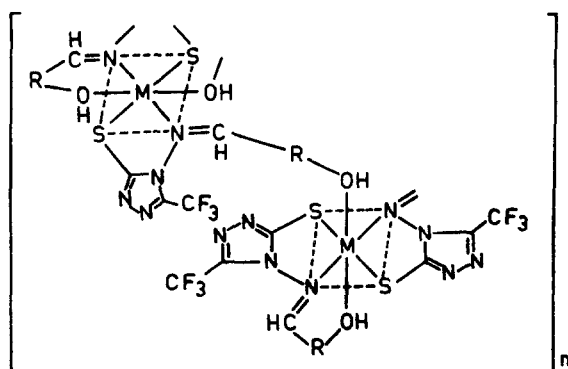

M = Co(II), Ni(II) or Cd(II)

Scheme 1

R = Phenyl

M = Co(II) or Ni(II)

Scheme 2

R = Phenyl

M = Cu(II) or Zn(II)

R = Phenyl

M = Co(II), Ni(II), Cu(II), Zn(II)
    or Cd(II)

Scheme 3

Acknowledgements

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