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Complexes of Zn(II), Pd(II), Hg(II), Pb(II), Cu(I), Ag(I) and Tl(I) With 4-Amino-5-Mercapto-3-(o- Tolyloxymethyl)-1,2,4-Triazole

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The synthesis and characterization of complexes of Zn(II), Pd(II), Cd(II), Hg(II), Pb(II), Cu(I), Ag(I), and Tl(I) with 4-amino-5-mercapto-3-(o-tolyloxymethyl)-1,2,4-triazole are described. Based on analytical results, electronic and infrared spectral data and magnetic susceptibility measurements suitable structures have been proposed.

Introduction

3-Substituted-4-amino-5-mercapto-1,2,4-triazoles are sulphur and nitrogen donor ligands and are potentially multidentate. The potential coordinating sites are (i) sulphur of thiol group (ii), nitrogen of the primary amino group and (iii) two nitrogen atoms at positions 1 and 2 in triazole ring systems. Thus these ligands can be polydentate. It has been shown and experimentally verified that bidentate or multidentate ligands in general form more stable complexes than monodentate ligands¹. Since metal ions of class 'a' have a preference for coordination with hard nitrogen and class 'b' metal ions have a preference for coordination with soft sulphur, it would be interesting to investigate this aspect using both types of metal ions, as these ligands contain both hard nitrogen and soft sulphur as donor atoms.

There has been considerable interest in the study of organic ligands containing two or more different donor atoms because such ligands throw light on the nature of metal-ligand bonding. Many quantitative studies have confirmed that metal chelates are more stable than those of related unidentate ligands. Furthermore, five- or six-membered chelates are by far the most common and are in general the most stable^{2,3}. If coordination through thiol sulphur and amino group nitrogen occurs as expected, it results in the formation of a favoured five-membered stable chelate.

In this paper the preparation and characterization of Zn(II), Pd(II), Cd(II), Hg(II), Pd(II), Cu(II), Ag(I) and Tl(I) complexes with 4-amino-5-mercapto-3-(o-tolyloxymethyl)-1,2,4-triazole (AMT) are described.

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Experimental

The chemicals used were all of Analar or chemically pure grade, and the ligands used were prepared following the reported procedure⁴. Alcoholic solution of AMT was used for the preparation of the metal complexes.

Preparation of Metal Complexes

Bis[1,2,4-Triazole-3-(o-tolyoxymethyl)-4-amino-5- thiolato]-zinc(II)

To a solution of $ZnSO_4 \cdot 7H_2O$ (2 mmol) in 50 ml of water containing 1 g of NH_4Cl and enough ammonia to render the solution ammoniacal, a warm solution of AMT (4 mmol) in 50 ml alcohol was added. The product was digested in a water bath for about 3-4 hours. Thereafter, a white crystalline complex slowly separated. The complex was filtered by suction and washed repeatedly with hot alcohol and finally with ether. The complex was finally dried at 100-110 C.

Bis[1,2,4-triazole-3-(o-tolyoxymethyl)-4-amino-5- thiolato]-cadmium(II)

To a solution of $CdCl_2 \cdot 2H_2O$ (2 mmol) in 50 ml of hot alcohol, a hot solution of AMT (4 mmol) in 50 ml of alcohol was added. On cooling, a white crystalline compound separated. The product was washed and dried as described above.

Bis[1,2,4-Triazole-3-(o-tolyoxymethyl)-4-amino-5- thiolato]-mercury(II)

The complex was prepared according to the above procedure using $HgCl_2$ in place of $CdCl_2 \cdot 2H_2O$. The dried complex was white and crystalline in nature.

Bis[1,2,4-Triazole-3-(o-tolyoxymethyl)-4-amino-5- thiolato]-palladium(II)

The complex was prepared by the above procedure by using $PdCl_2$ in place of $CdCl_2 \cdot 2H_2O$. On cooling, an orange yellow complex was separated. The complex was washed and dried.

[1,2,4-triazole-3-(o-tolyoxymethyl)-4-amino-5- thiolato]-copper(I)

To a solution of $CuSO_4 \cdot 5H_2O$ (8 mmol) in 100 ml of water, rendered strongly ammoniacal and heated nearly to boiling, a hot solution of AMT (8 mmol) in 100 ml of alcohol was added. The dark green complex first formed changed rapidly to light yellow and finally turned almost white on being heated over a water bath. The complex was digested in a water bath for 3 hours. The product was dried.

[1,2,4-Triazole-3-(o-tolyoxymethyl)-4-amino-5- thiolato]-silver(I)

To a hot solution of AMT (4 mmol) in 30 ml of alcohol was added a hot ammoniacal solution of $AgNO_3$ (4 mmol) in 100 ml of water, a white complex separated readily. It was digested in a water bath for 1 h and filtered, washed and dried.

[1,2,4-Triazole-3-(o-tolyoxymethyl)-4-amino-5- thiolato]-thallium(I)

A hot ammoniacal solution of $TlNO_3$ (3 mmol) in 50 ml of water was added to a hot solution of AMT (3mmol) in 30 ml of alcohol. On cooling the mixture, shining white crystals of the complex separated out. The crystals were filtered, washed and dried.

Bis[1,2,4-Triazole-3-(o-tolyoxymethyl)-4-amino-5- thiolato]-lead(II)

To a hot solution of $Pb(CH_3COO)_2 \cdot 3H_2O$ (2 mmol) in 50 ml of alcohol, a hot solution of AMT (4 mmol) in 50 ml alcohol was added. White crystals of the complex separated on cooling. The crystals were suction filtered, and washed thoroughly with hot alcohol and with ether. The complex was dried over anhydrous $CaCl_2$ in a vacuum desiccator.

Analytical, Magnetic and Spectral Data

Sulphur analysis was carried out by fusing in a nickel crucible a known amount of the ligand/complex with a mixture of potassium hydroxide pellets and potassium nitrate crystals (8:1 w/w). The cooled melt

was extracted with distilled water, acidified with an appropriate mineral acid, and the sulphate in the extract was estimated as $BaSO_4$.

The analysis of the metal ions in the complex were carried out by disintegrating a known amount of each complex using concentrated nitric acid followed by evaporation to dryness, extraction with distilled water and estimation of the metal ions by standard methods⁵.

Carbon, hydrogen and nitrogen were analysed by the Regional Sophisticated Instrumentation Centre of the CDRI Lucknow. The results of the analyses are given in Table 1.

Table 1. Analytical Data of Tamt Complexs

Compound	Calc. (Found) %				
	C	H	N	S	M
$Cu(C_{10}H_{11}N_4OS)$	40.19 (39.98)	3.68 (3.73)	18.76 (18.52)	10.72 (10.91)	21.29 (12.40)
$Ag(C_{10}H_{11}N_4OS)$	35.00 (35.07)	3.21 (3.31)	16.33 (16.54)	9.33 (9.52)	31.46 (31.71)
$Tl(C_{10}H_{11}N_4OS)$	27.31 (27.62)	2.50 (2.48)	12.75 (12.92)	7.28 (7.39)	46.51 (46.44)
$Zn(C_{10}H_{11}N_4OS)_2$	44.83 (44.98)	4.11 (4.19)	20.92 (21.03)	11.95 (12.08)	12.21 (12.41)
$Cd(C_{10}H_{11}N_4OS)_2$	41.21 (41.08)	3.78 (3.83)	19.23 (19.51)	10.99 (10.73)	19.30 (19.53)
$Hg(C_{10}H_{11}N_4OS)_2$	35.79 (35.66)	3.28 (3.16)	16.70 (16.83)	9.54 (9.64)	29.91 (29.76)
$Pd(C_{10}H_{11}N_4OS)_2$	41.64 (41.73)	3.82 (3.94)	19.43 (19.26)	11.10 (11.30)	18.46 (18.40)
$Hg(C_{10}H_{11}N_4OS)_2$	35.44 (35.49)	3.25 (3.26)	16.54 (16.79)	9.45 (9.62)	30.60 (30.48)

(i) Visible and Ultraviolet Spectra

The absorption spectra of the Pd(II) complex was recorded in acetone on a Beckman DU-6 uv-vis spectrophotometer in the range of 200-900 nm.

(ii) Infrared

The infrared spectra of the ligand and of the metal complexes in Csl phase were recorded on a Perkin-Elmer infrared spectrophotometer model 1330 in the range of 4000-200 cm^{-1} . The major IR bands and their probable assignments are given in Table 3.

Magnetic Susceptibility Measurement

Magnetic susceptibilities of all the complexes were determined at room temperature with a Gouy balance. All the complexes reported in this paper were found to be diamagnetic.

Results and Discussion

The analytical results show that Cu(I), Ag(I), Tl(I) form ML type complexes while Zn(II), Cd(II), Hg(II), Pd(II) and Pb(II) form ML_2 type complexes.

Electronic Spectra: The bands actually observed and their assignments are given in Table 2.

Infrared Spectra

The infrared spectra of the ligand and the complexes are expected to be too complex to allow unambiguous assignments and identification of bands. This is because in the $-CH_2-O$ -group, the phenyl ring and the thioamide bands have modes very close to one another, so semiquantitative studies in infrared spectral analysis are needed to determine the gain or loss in intensity of the bands so as to deduce shifts in positions of some of the bands due to complexation of the ligand unit with the metal ion.

Table 2. Electronic Spectral Bands and Their Probable Assignments

Complex	band	Position	Assignments
	nm	cm ⁻¹	
Pd(TAMT) ₂	W ₁	556	1A _{1g} → 1A _{2g}
	W ₂	486	1A _{1g} → 1B _{1g}
	W ₃	378	1A _{1g} → 1E _g

Table 3. Major Infrared Band Positions (cm⁻¹) and Their Probable Assignments of TAMT and the Complexes

Ligand	Complexes	Assignments
3300-3140 B (Split bands)	3160-3040 (Split bands)	$\nu(N-H)$
2940 MB	2930±20 MB	$\nu(C-H)$
2560	-	$\nu(CS-H)$
1610 m	1600 ± 10 M	$\nu(C=N)$
1995 S	1595 M	Aromatic ring
1520 M	1500±10 M	Thioamide Band I*
1480 VS	1470 M	$\delta(CH_2)$
1450 M	1460±5 M	$\delta(C-CH_3)$
1330 S	1350±10 M	Thioamide Band II*
1040 M	1020±10 M	Thioamide Band III*
760 S	-	Thioamide Band IV* and phenyl group
-	750± 5 M Phenyl group with adj. H atoms	
690 M	-	Aromatic ring
-	680±10 VS	Thioamide band IV* and aromatic ring
-	420±10 W	$\nu(M-N)$
-	370±10 W	$\nu(M-S)$

M=Medium; B=Broad; S=Strong; W=Weak; V=Very

The IR spectrum of the ligand has bands in regions (a) 3300-3140 cm⁻¹ and (b) 2560 cm⁻¹. This can readily be assigned to $\nu(N-H)$ and $\nu(S-H)$, respectively. This establishes the coexistence of tautomeric forms of the ligand. This is not surprising in any way. It is reasonable to expect deprotonation of the ligand molecules before complexation, especially in an ammoniacal medium. The complete disappearance of the band due to $\nu(S-H)$ in the spectra of the complexes unambiguously supports this view.

After deprotonation, the ligand unit can link with the metal ion at either the N or the S end of the thioamide group. Bonding at the S end is more favourable because such a thing would result in a stable

five-membered chelate. Further support to this view comes from the nature of the metal ions, which, being 'b' class or border line acids, might prefer to bond with a 'b' class base such as sulphur.

The bonding scheme as explained above would result in localization of the charge between C and N of the thioamide group, as shown in Figure 1(b). As a result, shifts in the positions of thioamide bands could be observed in the spectra of the metal complexes.

Thioamide band I, expected to be around 1520 cm^{-1} , has major contribution from $\delta(N-H)$ and so may not show much of a shift. But thioamide band II, expected to be around 1330 cm^{-1} , which has major contribution from $\nu(C=N)$, could show a considerable shift towards a higher wave number side if the double bond is localized between C and N. Similarly, the thioamide band IV around 760 cm^{-1} in the spectrum of the ligand, which is exclusively because of $\nu(C=S)$, is expected to show considerable shift towards a lower wave number side^{6,7}, if the bond turns into a single bond.

New bands should also appear in the region $350\text{-}420\text{ cm}^{-1}$ in the spectra of the complexes because of $\nu(M-N)$ and $\nu(M-S)$.

In the spectrum of the ligand, a strong and sharp band is observed around 1595 cm^{-1} . This may be assigned to aromatic $\nu(C=C)$. There is also a strong band at 1480 cm^{-1} in the spectrum of the ligand. This band could be due to $\nu(CH_2)$. Furthermore the very strong band at 760 cm^{-1} in the spectrum of the ligand could be due to a mixing up of thioamide band IV and the band characteristic of phenyl ring with adjacent hydrogens. A band around 750 cm^{-1} , though less intense than the one in the spectrum of the ligand, is also seen in the spectra of the complexes. This only confirms the presence of the phenyl ring in the ligand and the complexes. As against a medium intensity band at 690 cm^{-1} in the spectrum of the ligand assignable to an aromatic ring, there is a very strong band around 680 cm^{-1} in the spectra of the complexes. This increased intensity could be due to considerable red shift of thioamide band IV and to the mixing of this band with the frequencies of the aromatic ring.

The $\nu(N-H)$ band, expected to be around 3300 cm^{-1} in the spectrum of the ligand, is considerably split. The splitting of this band is slightly reduced in the spectra of the complexes because of deprotonation and consequent reduction in the interaction between the stretching frequencies of the triazole N-H and the amino N-H. As a result, the band position is slightly shifted towards lower wave number side in the spectra of the complexes. This indicates diversion of the electron cloud from the N of the NH_2 group, thus resulting in a lowering of the N-H frequency. This suggests that the N of the amino group is linked with the metal ion, though feebly. This doubtlessly results in the formation of a stable five-membered chelate.

In addition, new weak bands observed in the region of $350\text{-}420\text{ cm}^{-1}$ in the spectra of the complexes can be assigned to $\nu(M-N)$ and $\nu(M-S)$ coupled with other lower modes of vibrations of the ligand molecules.

All these shifts and new bands are given in Table 3. Wherever the ligand has IR bands in regions where band shifts are expected, the intensity of the band is found to have considerably increased. All these observations help to provide a fairly satisfactory insight into the bonding scheme. Thus, these results establish that the ligand chelates with metal ions through the deprotonated sulphur of the thiol (thione) group and the nitrogen of the primary amino group, as shown in Figure 1(b).

These confirm unambiguously the bonding scheme proposed, keeping in view the preferences of the metal ions. Tetrahedral structures are proposed for Zn(II), Cd(II), Hg(II) and Pb(II) complexes (Figure 1. (c)). The Ag(I), Tl(I) and Cu(I) complexes could also be tetrahedral polymers, although linear polymeric structure cannot be ruled out altogether (Figure 1 (d)). but the Pd(II) complex however, is square planar (Figure 1 (e)).

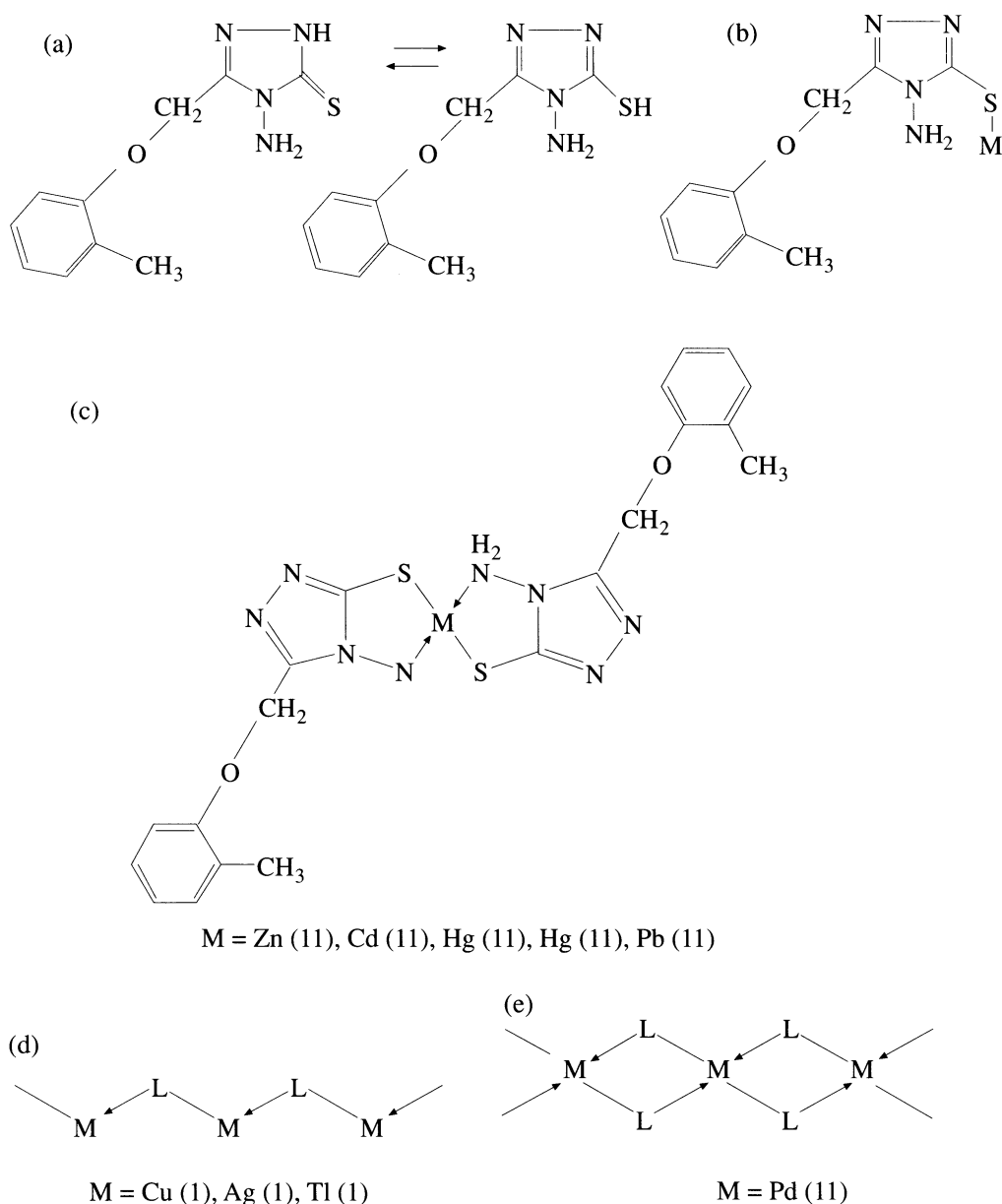


Figure 1.

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