Synthesis, Characterization and Fungitoxicity of the Complexes of Hg(II), Cd(II), Cu(II) and Ag(I) with 3-0-Tolyloxymethyl-4-aryl-5-mercapto-1,2,4-triazole

S. C. BAHEL, B. L. DUBEY, N. NATH and JANMEJAI K. SRIVASTAVA

Department of Chemistry, Gorakhpur University, Gorakhpur 273001, India

Received September 27, 1983

Triazoles have been reported to be biologically versatile compounds, having bactericidal [1, 2] fungicidal [3, 4] insecticidal [5, 6] and pesticidal [7, 8] properties. The toxicological importance of the –N–C–S– moiety has been well established in many fungicides. Several metal chelates are also known to possess bactericidal [9] fungicidal [10] and antiviral [11] activities. In several cases the metal chelates have been found to be more fungitoxic than the chelating agents themselves [12]. With this in view the preparation and characterization of the complexes are reported.

Experimental

All chemicals used were of AR grade or equivalent quality.

Preparation of 3-0-tolyloxymethyl-4-aryl-5-mercapto-1,2,4-triazole

A mixture of 0-tolyloxyacetyl hydrazine (0.01 *M*) and phenylisothiocyanate (0.012 *M*) was refluxed in 8% NaOH solution for 5 to 6 hours when a clear solution resulted. It was cooled, poured into water and filtered. The filtrate on acidification gave a precipitate which was filtered, washed and recrystallised [13].

Preparation of Metal Complexes

The complexes were precipitated by refluxing a methanolic solution of 3-0-tolyloxymethyl-4-aryl-5-mercapto-1,2,4-triazole (0.01 *M*) with an aqueous solution of metal salts (0.03 *M*) for 2 to 4 hours. The precipitate was filtered, washed successively with a large excess of water, hot methanol and ether and dried *in vaccuo.* The analytical results are given in Table I.

Physical Measurements

The complexes were analysed for their metal content after destroying the organic residue with a mixture of concentrated hydrochloric and nitric acids. Standard methods were used for the purpose [14].

The water content of the complexes was determined by heating them at temperatures of 150–300 °C and determining the loss in weight.

The magnetic susceptibility of the complexes was determined by the Faraday method using ferrous ammonium sulphate as calibrant. Experimental magnetic susceptibilities were corrected for diamagnetism [15]. The magnetic moments of the complexes at room temperature are given in Table I.

The IR spectra of the complexes and the ligands were recorded on a Beckman infrared spectrophotometer in the KBr phase in the 4000-600 cm^{-1} range.

The thermogravimetry of the complexes was carried out with the help of TG-750. Stanton Red Croft (U.K.) thermogracimetric analyser at a heating rate of 10 °C min^{-1} in air with chart speed 300 mm/hr. The results are recorded in Table II.

Fungitoxicity was evaluated against *A.niger* and *A.flavus* by the agar plate method [16] at three different concentrations. The average percentage inhibition by various compounds is recorded in Table III.

$$\text{Percentage Inhibition} = \frac{(C - T)100}{C}$$

where,

C = diameter of the fungus colony in the control plate after 96 hours

T = diameter of the fungus colony in treated plates after 96 hours.

TABLE I. Analytical Data and General Behaviour of the Complexes.

Complexes	Metal %		Nitrogen %		Sulphur %		$\mu_{eff.}$(B.M.)
	Obs.	Cal.	Obs.	Cal.	Obs.	Cal.	
$HgL_2(Ac)_2$ [a]	21.8	22.01	9.27	9.30	7.10	7.00	Dia.
$Cd \cdot L_3 \cdot SO_4$	10.15	10.19	11.56	11.46	11.73	11.64	Dia.
$CuL_4 \cdot SO_4$	4.59	4.74	12.50	12.46	11.79	11.86	1.98
$Ag \cdot L \cdot (NO_3)$	23.00	23.12	9.15	8.99	7.01	6.85	Dia.

[a] L = Ligand; Ac = CH_3COO.

0020-1693/84/$3.00

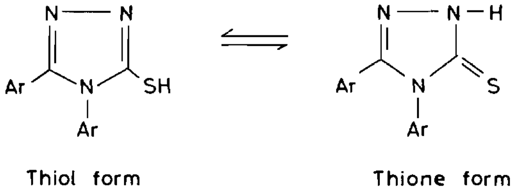
TABLE II. TG Data for Metal Complexes.

Stable phase or thermal decomposition	Temperature range (°C)	% Weight Loss	
		Found	Calc.
Hg·L_2·$(Ac)_2$	80–258	30.62	32.53
Hg·L·(Ac)	258–430	67.81	65.06
Hg·$(Ac)_2$	430–544	75.54	76.23
HgO			
Cd·L_3SO_4	100–300	27.85	27.02
Cd·L_2·SO_4	300–400	81.39	81.07
Cd·SO_4	400–548	87.89	88.35
CdO			
Cu·L_4·SO_4	60–140	44.72	44.06
Cu·L_2·SO_4	140–290	86.73	88.13
Cu·SO_4	290–494	90.32	89.31
Cu_2O			
Ag·L·(NO_3)	140–325	2.35	2.00
Ag·L·(NO_3)	325–548	65.05	63.59
Ag·NO_3			

Results and Discussion

The Hg(II), Cd(II) and Ag(I) complexes, as expected for d^{10} electronic configurations, are diamagnetic. The structure proposed for the complexes is also in accordance with the diamagnetic behaviour. The magnetic moment value for the Cu(II) sulphate complex is found to be 1.98, which is in accordance with the expected tetrahedral geometry of the complex.

The infrared spectrum of the ligand, 3-0-tolyloxymethyl-4-aryl-5-mercapto-1,2,4-triazole shows a band at 3500, 3040 cm^{-1} which may be assigned to ν_{assy} N–H and ν_{sym} N–H vibrations. A weak band in the region 2550–2600 cm^{-1} in the spectrum of the ligand may be assigned as a ν_{S-H} stretching vibration. The band observed at 1120 cm^{-1} in the spectrum of the ligand is due to >C=S stretch. The ligand spectrum shows a band due to conjugated >C=N and the o-disubstituted benzene ring at 1735–1740 and 960–1040 cm^{-1} respectively. It may be concluded from these that the ligand exists in the following tautomeric form:



An analysis of the spectra of the complexes and their respective ligands shows that the ν_{S-H} band in the region 2550–2600 cm^{-1} is absent in the spectra of the complexes whereas the ν_{N-H} band is present. Further, there is a strong negative shift in the $\nu_{C=S}$ band in the 1050–1200 cm^{-1} region. These clearly indicate that the thione form is favoured for complexation and coordination takes place through the S atom of the thione and the ligand acts as monodentate.

The asymmetric and symmetric >C=O stretching frequencies of the free acetate ion reported at 1578 and 1425 cm^{-1} respectively in the mercury(II) acetate complex show that the acetato group behaves as a unidentate ligand in the above complex [17].

The presence of one strong band in the region 1105–1140 cm^{-1} and a very weak band in the 960–980 cm^{-1} region in the spectra of sulphato complexes and their absence in the spectrum of the ligand indicates the presence of an ionic sulphato group in the complexes [18].

In the case of the Ag(I) nitrate complex the presence of two bands at 1520 and 1285 cm^{-1} due to the ν_3 of nitrato group, indicates that the nitrate ion behaves as a monodentate ligand [19].

On the basis of thermoanalytical data, the mechanism of decomposition of the complexes has been reported to take place as shown in Table II. The decomposition products of all the complexes were analysed. The end products were found to be the respective metal oxides except for the silver nitrate complex. From TG data it is clear that the mass loss starts at about 80 °C. The mass loss at a low rate right from the start may be due to desorption of absorbed gases or moisture.

TABLE III. Fungicidal Screening Data.

Compound serial as in Table I	Average Percentage inhibition					
	Organism-*A.niger*			Organism-*A.flavus*		
	10 ppm	100 ppm	1000 ppm	10 ppm	100 ppm	1000 ppm
1	45.2	45.5	48.5	40.1	42.9	43.4
2	30.5	38.2	39.0	36.5	41.6	53.3
3	35.5	39.2	43.4	34.5	38.6	48.4
4	40.5	42.0	48.7	38.8	39.2	39.8
Ligand	23.3	32.3	38.9	28:5	35.6	36.6

Fungicidal screening data (Table III) clearly indicate that the complexes are more fungitoxic than the free ligand.

Acknowledgements

The authors are thankful to Prof. R. P. Rastogi, Head, Department of Chemistry, Gorakhpur University, for facilities and to the P. and D. Division, F.C.I., Sindri for TG analysis.

References

1 S. C. Bennur, V. B. Jigajinni and V. V. Badiger, *Rev. Roum. Chim., 21,* 757 (1976); *Chem. Abstr., 84,* 94306j (1976).
2 I. Chiyomara, E. Yoshinaga and G. Dotike, *Jap. Pat., 460,* 7339 (1973); *Chem. Abstr., 81,* 73392m (1974).
3 S. A. Greenfield, C. S. Michael and W. C. Von Meyer, *Ger. Offen., 1,* 806,966 (1974); *Chem. Abstr., 82,* 150485.
4 W. Kraemer, K. H. Buechel, W. Brandes and P. E. Prohbergee, *Ger. Offen.,* 352, 2,334 (1975); *Chem. Abstr., 82,* 170967f (1975).
5 G. Tanaka, *Japan Kokai, 973,* 7495 (1974); *Chem.Abstr., 82,* 15632Oh (1975).
6 T. I. Wakins and D. M. Weighton, *Ger. Offen., 287,* 2, 530, 287 (1976); *Chem. Abstr., 89,* 135677f (1976).
7 B. Boehner, W. Meyer and D. Dowes, *Swiss, 206,* 573 (1976); *Chem. Abstr., 84,* 135677f (1976).
8 L. Gsell and W. Meyer, *Ger. Offen., 084,* 2739 (1978); *Chem. Abstr., 88,* 190844r (1978).
9 K. K. Chaturvedi and R. Kaushal, *Indian J. Pharm., 37,* 85 (1975).
10 C. L. Mason, *Phytophol., 38,* 740 (1948).
11 F. P. Dwyer and D. P. Mellor, 'Chelating agents and metal chelates', Academic Press, London (1964).
12 D. R. Williams, *Chem. Rev., 203,* 72 (1972).
13 S. C. Bahel, B. L. Dubey, N. Nath, A. Tripathi and J. K. Srivastava, *J. Indian Chem. Soc.,* Vol. LIX, Oct. 82.
14 A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", ELBS, 1973.
15 B. N. Figgis and J. Lewis, "Modern Coordination Chemistry" (Eds) J. Lewis and R. G. Willikins, Interscience Publishers, Inc., N.Y., p. 400 (1960).
16 J. G. Horsfall, *Bot. Rev., 11,* 357 (1954).
17 K. Nakamoto, J. Fujta and S. Tanaka, *J. Am. Chem. Soc., 79,* 4904 (1957).
18 K. Nakamoto, 'Infrared spectra of Inorganic and Coordination Compounds', 2nd Ed. Wiley Interscience, N.Y., pp. 173, 212 (1970).
19 B. M. Gatehouse, S. E. Livingstone and R. S. Nyholm, *J. Chem. Soc.,* 4222 (1975); *J. Inorg. Nuclear Chem., 8,* 75 (1958).