

2-MERCAPTO- AND 2-METHYL-BENZIMIDAZOLES AS REAGENTS FOR SILVER

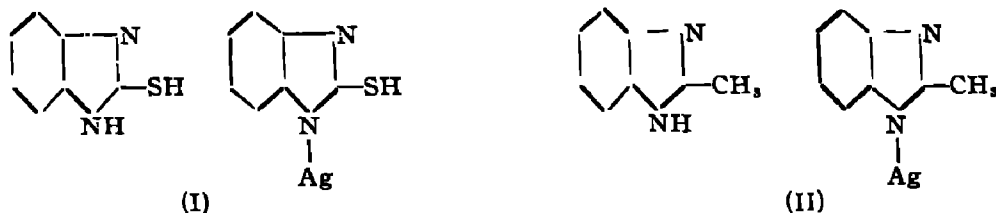
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2-Mercapto- and 2-methyl-benzimidazoles have been found to be useful reagents for gravimetric estimation of silver in ammoniacal medium in the presence of other metals by masking them with appropriate reagents. The silver salts of these reagents are stable towards light, and heat, and determination can be made rapidly

In an earlier communication (Dutta, this *Journal*, 1956, 33, 389) the use of benzimidazole as a reagent for the gravimetric determination of silver was reported. In the present paper are recorded the results of a study with 2-mercapto- and 2-methyl-benzimidazoles.

2-Mercaptobenzimidazole (I) was first studied by Kuras as a precipitating agent (*Chem. Abst.*, 1939, 33, 941, 7233, 9200). He has described procedures for gravimetric estimation of copper, cadmium and lead, but has made only qualitative observations on the precipitation of silver, mercury and gold. This reagent has also been used for the detection and spectrophotometric estimation of palladium (Steigmann, *Chem. Abst.*, 1943, 37, 3689; Xavier, *Proc. Ind. Sci. Congress*, 1956, Part III, p. 63).

Feigl and Gleich (*Monatsh.*, 1928, 49, 385) have reported the silver salt of 2-methyl-benzimidazole (II), but the reagent has not been utilised for the gravimetric estimation of silver.



These two substituted benzimidazoles precipitate silver quantitatively in ammoniacal medium and the precipitates being extremely granular, filtration becomes an easy proposition. The precipitates are insoluble in hot water, dilute ammonia but soluble in sodium thiosulphate and sodium cyanide. After drying at 120°, the silver salt of 2-methylbenzimidazole and of 2-mercaptobenzimidazole conform to the composition C₇H₅N₂ Ag and C₇H₅N₂S Ag, and the gravimetric factors therefore become 0.4513 and 0.41961 respectively. The interfering effects due to copper, nickel, cobalt, manganese, zinc, cadmium, lead, bismuth and thallium have been eliminated by masking them with EDTA. But mercury interferes. Sodium potassium tartrate has been used to keep metals like aluminium, beryllium, uranium in solution. In presence of appreciable amounts of ammonium salts, 2-methylbenzimidazole gives slightly low values, whereas 2-mercaptobenzimidazole still gives quantitative values.

E X P E R I M E N T A L

2-Methylbenzimidazole was prepared according to Phillips (*J. Chem. Soc.*, 1928, 172). Van Allan and Deacon ("Org. Synthesis", 30, p. 56) have described the preparation of 2-mercaptobenzimidazole. ** Preparation of silver nitrate solution and EDTA has been described in the earlier communication (Dutta, *loc. cit.*).

Effect of p_H on the Precipitation of Silver.—Precipitation in neutral or ammoniacal medium afforded a highly granular product. Precipitation in acid range resulted in a slimy product. In Table I some of the results showing the effect of p_H are described.

TABLE I

	With 2-mercaptobenzimidazole.				With 2-methylbenzimidazole.			
	Ag taken = 0.0473 g. (determined as chloride)				Ag taken = 0.0440 g.			
p_H (of the filtrate)	6.9	8.1	8.8	10.1	7.5	8.2	9.7	10.56
Ag found (in g.)	0.0474	0.0475	0.0474	0.0475	0.0439	0.0440	0.0440	0.04395

Procedure.— p_H of the silver nitrate solution was adjusted to within the range 8-10. The solution was warmed on the water bath, treated with an excess of the hot reagent solution with constant stirring and the mixture was then digested on the water-bath for 15-30 minutes. The precipitate formed was filtered through a Gooch crucible, washed with hot water, dried at 120° and weighed as $C_7H_7N_2SAg$ (for 2-mercaptobenzimidazole) or as $C_8H_7N_2Ag$ (for 2-methylbenzimidazole). Some of these results are recorded in Table II.

TABLE II

With 2-mercaptobenzimidazole.			With 2-methylbenzimidazole.		
Ag taken.	Ag salt.	Ag found.	Ag taken.	Ag salt.	Ag found.
0.09460 g.	0.2262 g.	0.0949 g.	0.0880 g.	0.1947 g.	0.0880 g.
0.07568	0.1800	0.0755	0.0704	0.1560	0.0701
0.04730	0.1130	0.04774	0.0440	0.09715	0.0438
0.02838	0.0679	0.02837	† 0.0440	0.09715	0.0438
0.00946	0.0225	0.00944	* 0.0440	0.09735	0.0440
* 0.04730	0.1130	0.04740			
† 0.04730	0.1130	0.04740			

† In presence of EDTA.

* In presence of NaK-tartrate.

Effect of Ammonium Salts.—The effect of ammonium salts on the precipitation of silver with these two reagents is shown in Table III.

TABLE III

With 2-methylbenzimidazole.			With 2-mercaptobenzimidazole.		
Ag taken.	Amm. salt added.	Ag found.	Ag taken.	Amm. salt added.	Ag found.
0.0880 g.	NH_4Cl 0.5 g.	0.0858 g.	0.0473 g.	NH_4NO_3 2 g.	0.0474 g.
	" 1.0	0.0836		" 5	0.04745
	NH_4NO_3 2.0	0.0882		NH_4Cl 1	0.04740
			" 2	0.04740	

** 1% Solutions of 2-methyl- and 2-mercapto-benzimidazole were made in hot water and hot aq. alcohol respectively.

Determination of Silver in presence of Cu, Ni, Co, Mn, Pb, Zn, Cd, Bi, Hg, Tl etc.—To the silver solution having any of these interfering metals was added with stirring 20 c.c. of the ammoniacal EDTA solution; the mixture was warmed on the water-bath and silver precipitated with excess of any of the reagents.

Determination in presence of Be, Al, U, Th etc.—To the slightly acid solution of silver and these metals was added sodium potassium tartrate (5 g.) and the mixture then treated with ammonia solution. If a precipitate of the hydroxide formed, some more tartrate was added and the mixture heated to get a clear solution. Afterwards silver was precipitated as usual.

In Table IV are recorded some typical results of estimation of silver in presence of some interfering ions.

TABLE IV

Ions.	Amount added.	* Ag found with		Ions.	Amount added.	* Ag found with	
		2-Mercapto-B	2-Methyl-B.			2-Merc pto-B.	2-Methyl-B.
Cu ²⁺	63.5 mg.	0.0474 g.	0.0440 g.	Pb ²⁺	207.2 mg.	0.04735 g.	0.04387 g.
Ni ²⁺	58.7	0.0474	0.04389	Tl ⁺	204.0	0.04745	0.04398
Co ²⁺	59.0	0.04745	0.04392	Bi ³⁺	209.0	0.04740	0.04410
Mn ²⁺	54.9	0.04745	...	Be ²⁺	36.0	0.04745	0.0440
Mg ²⁺	48.0	0.0473	...	Al ³⁺	52.0	0.04740	0.0441
Hg ²⁺	2000	Interferes	0.0440	Th ⁴⁺	232.0	0.04730	0.04415
Zn ²⁺	65.3	0.04745	...	UO ₂ ²⁺	135.0	0.04725	0.04410
Cd ²⁺	112.4	0.0474	0.0439				

Ag present in case with 2-mercapto B was 0.0473 g. and with 2-methyl-B was 0.044 g.
B denotes benzimidazole.

Composition of the Precipitates.—The dried silver salts were ignited to metallic silver, and nitrogen was determined by combustion.

(1) *Silver salt of 2-mercaptobenzimidazole:* (Found: Ag, 42.30; N, 11.12. C₇H₅N₂S requires Ag, 41.96; N, 10.90 %).

(2) *Silver salt of 2-methylbenzimidazole:* (Found: Ag, 45.00; N, 11.61. C₈H₇N₂, Ag requires Ag, 45.13; N, 11.72 %).

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