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Silver Complexes of Substituted Triazinone Thiones and Their Gravimetric Applications

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Silver complexes of 4-amino-3-thio-1,2,4-triazin(4H)-5-one(ATT) and 4-amino-3-thio-6-phenyl-1,2,4-triazin(4H)-5-one (ATPT) are prepared and characterized by elemental analysis and infrared spectral data. The complexation being quantitative in ammoniacal tartrate medium and the complexes being thermally stable, non-hygroscopic and non-photosensitive in nature, their probable use as gravimetric reagents for the determination of miligram quantities of silver in complexes and alloys is proposed.

INTRODUCTION

Silver(I) ion being a soft acid favours complexation with sulphur-containing ligands. Several sulphur-containing reagents like 4-(2-mercaptopropionamido) benzoic acid[1], 2-mercaptopyridine-N-oxide[2], 2-mercaptomethylbenzimidazole[3], *p*-phenylene-bis-(1-tetrazoline-5-thione)[4], 4-amino-3-methyl-5-mercapto-1,2,4-triazole[5], 2-thioorotic acid[6] etc., have been proposed as gravimetric reagents for silver. The determinations were carried out in acid medium in case of 4-(2-mercaptopropionamido) benzoic acid and *p*-phenylene-bis-(1-tetrazoline-5-thione); in the latter case drying of the silver complex under vacuum is necessary before weighing. 2-Thioorotic acid suffered from serious interference by other base metal ions. In the present work, silver complexes of 4-amino-3-thio-1,2,4-triazin(4H)-5-one (ATT) and 4-amino-3-thio-6-phenyl-1,2,4-triazin(4H)-5-one (ATPT) were prepared.

EXPERIMENTAL

The reagents were prepared by the methods reported in literature.[7,8] Twice-recrystallised samples of the reagents were used for preparing 1% aqueous solutions. In the case of the ATPT, a few drops of aqueous ammonia were required to be added for obtaining a clear solution.

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A stock solution of silver(I) was prepared by dissolving a known amount of silver nitrate in doubly distilled water containing a few ml. of conc. nitric acid. The solution was standardized by the chloride method[9].

Recommended Procedure

To an aliquot of the stock solution of silver ions, diluted to about 100 ml., about 1 gm of tartaric acid and 1 : 1 ammonia solution were added till the solution was distinctly ammoniacal. To the hot ammoniacal solution, a slight excess of 1% aq. solution of the reagent was added. The precipitate formed was digested over a steam bath for an hour and filtered through a G_4 sintered glass crucible. The precipitate was repeatedly washed with distilled water containing a few drops of ammonia, followed by ethanol and finally ether. The precipitate was dried to a constant weight at 120°C. The precipitates can be weighed as $(C_3H_3N_4OS)Ag$ and $(C_9H_7N_4OS)Ag$ respectively for the two reagents.

RESULTS AND DISCUSSION

The ligands may exist in thione as well as thiol forms and can coordinate as ambidentate neutral or monoanionic forms using either N–O or N–S atoms. It has been reported that in basic medium the ligand is deprotonated and forms neutral complexes[10]. In the ammoniacal tartrate medium employed for the present study, the deprotonated form of the ligands form 1 : 1 neutral complexes with silver(I) as is evidenced by the analytical data. The light yellow and yellow coloured complexes formed are insoluble in water and common organic solvents like methanol, ethanol, benzene, etc., but the complexes are slightly soluble in DMF. The very low electrical conductivity values of 5–6 $\Omega\ cm^2\ mol^{-1}$ in DMF solutions at room temperature indicate the non-ionic nature of the complexes.

The IR spectra of the ligands show NH stretch at around 3290 cm^{-1} which disappears in the complexes. The medium split bands in the region 3050–3250 cm^{-1} in the ligands are assigned to symmetric and asymmetric NH_2 stretches. These bands are shifted to lower frequencies by 20–30 cm^{-1} in the complexes indicating involvement of NH_2 nitrogen in coordination[11]. The absence of ν_{SH} around 2550 cm^{-1} in the ligands indicates that the free ligands exist in thione form in the solid state. The ν_{CO} of the ligands around 1640 cm^{-1} is slightly shifted to higher frequency side in the complexes indicating that the CO oxygen is not involved in bonding. The thioamide bands I (1520–1530 cm^{-1}), II (around 1375 cm^{-1}) and III (around 1240 cm^{-1}) of the free ligands are shifted to higher wave number side in the complexes. The thioamide band IV seen in the region 740–750 cm^{-1} indicates coordination of thioamide sulphur by deprotonation of the thiol form[12]

Effect of diverse ions

Various metal ions were added to study the potential interference in the quantitative precipitation of silver by the proposed method. To aliquots containing about 50 mg of silver, known amounts of foreign ions were added and the silver contents estimated by the proposed method.

While most of the cations did not interfere in ammoniacal tartrate medium, Cu(II), Co(II), Ni(II), Mn(II), Hg(II) and Cd(II) did interfere. But the interference could be avoided by using disodium salt of EDTA as masking agent. Among the anions, halides interfered most seriously (Table 1).

TABLE 1
DETERMINATION OF SILVER IN PRESENCE OF FOREIGN IONS
(Silver present in solution = 49.02 mg)

Foreign ion	Quantity added (mg)	†Error in the determination of silver (%)	
		Using ATT	Using ATPT
Pb(II)	100	–0.76	+0.10
Bi(III)	100	+0.60	+0.37
Cd(II)*	100	+0.31	+0.63
Cu(II)*	100	–0.25	–0.51
Hg(II)*	100	–0.54	+0.37
Al(III)	100	–0.54	–0.41
Fe(III)	100	+0.38	+0.24
Zn(II)*	100	–0.18	+0.98
Ni(II)*	100	–0.05	+0.16
Co(II)*	100	–0.61	–0.10
Mn(II)*	100	–0.68	+0.43
Mg(II)	100	–0.33	+0.37
Nitrate	1000	–0.18	+0.10
Sulphate	1000	+0.10	+0.16
Oxalate	1000	+0.31	+0.24
Tartrate	1000	+0.10	–0.04
Citrate	1000	+0.25	–0.10
EDTA	1000	+0.54	+0.04

*In presence of EDTA
†Average for 5 determinations

Accuracy and Precision of the Method

The silver contents of different solutions containing varying amounts of silver(I) in the range of 9.8 to 96.84 mg were determined by the proposed methods. The average errors of the methods were found to be ± 0.25% and ± 0.11% respectively for the two ligands ATT and ATPT.

To determine the accuracy and precision of the methods, five determinations were carried out at a fixed concentration of silver, chosen around the midpoint of the working range. The results show a relative mean error 0.06% and a standard deviation of 0.20 with ATT. The corresponding values for ATPT were 0.02% and

0.14 respectively. These figures clearly indicate that the proposed methods are quite precise and accurate.

The thermal analysis of the ATT-silver complex indicated that it did not lose weight up to 190°C beyond which decomposition commenced. For the ATPT-silver complex, the decomposition commenced beyond 226 °C. Thus both the complexes can be safely dried at 120°C.

The proposed method was also applied to determine the silver content of alloys and silver complexes. The results indicated the suitability of the method for routine analysis as the results obtained are reproducible and accurate. The reagents are selective for silver in ammoniacal tartrate medium and the silver complexes are neither hygroscopic nor photosensitive and hence no elaborate precautions need be taken during the course of the analysis unlike in the case of the halide method. Low conversion factors of 0.4315 and 0.330 for ATT and ATPT as compared to 0.75 of the chloride method are the added advantages.

REFERENCES

1. S.V. Muktibodh and K.S. Boparai, *J. Indian Chem. Soc.*, **54**, 623 (1977).
2. M. Edrissi, A. Massoumi and M. Rezazdeh, *Anal. Chim. Acta*, **71**, 215 (1974).
3. B.C. Betra and M.M. Chakrabarty, *Z. Anal. Chem.*, **223**, 1169 (1966).
4. G.S. Johar and U. Aggarwala, *Curr. Sci. (India)*, **38**, 139 (1969).
5. R.V. Gadag and M.R. Gajendragad, *Talanta*, **25**, 418 (1978).
6. M. Srivastava and G.S. Pandey, *Curr. Sci. (India)*, **53**, 143 (1984).
7. M.M. Fawzi, Fr. 1,547,854 (Cl Co 7d AO1N); *Chem. Abstr.* 91538 (1969).
8. A Dornow, H. Menzel and P. Marx, *Chem Ber.*, **97**, 2173 (1964).
9. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 4th Ed., Longman, London (1978).
10. P.D. Singh and L.K. Mishra, *J. Indian Chem. Soc.*, **65**, 21 (1988).
11. L.J. Bellamy, The Infrared Spectra of Complex Molecules, Wiley, New York, p. 249 (1957).
12. N.F. Curtis and Y.M. Curtis, *Inorg. Chem.*, **4**, 804 (1961).

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