SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY
SOUTH. BRAZ. J. CHEM., Vol. 9 , N° 10, 2001

NEW Cr(III) COMPOUNDS IN ANALYTICAL CHEMISTRY. BI(III) CONDUCTOMETRIC DETERMINATION

Olimpia Rusu, Maria Pleniceanu, Mihaela Mureseanu, Al. Popescu and Ioana Mitrache

Faculty of Chemistry, University of Craiova, Calea Bucuresti, BB 165, Craiova, 1100, Romania

ABSTRACT

This study presents the synthesis and characterization of the complex $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$. The new complex was analyzed by thermogravimetric, oxidation, infra red and other spectrometric techniques and was used for the determination of bismuth in drugs. The dosage of Bi(III) in Ulcerotrat was done by conductometric titration with rhodanine and complex anions of Cr(III), respectively.

RESUMO:

Este estudo trata da síntese e caracterização do complexo $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$. O novo complexo foi analisado através de vários métodos, incluindo termogravimetria, oxidação, infravermelho e outros e foi usado para quantificar Bi(III) em medicamentos. A dosagem de Bi(III) no Ulcerotrat foi obtida attravés de titulação conductimétrica com rodanina e ânions complexos de Cr(III), respectivamente.

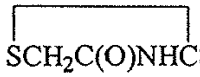
KEYWORDS: Cr(III) Complexes, Rhodanine, Bismuth Determination, Conductometric Titrations

DOI: 10.48141/SBJCHEM.v9.n10.2001.65_2001.pdf

INTRODUCTION

Bismuth based drugs are used as dressings in the treatment of gastro-duodenal affections.

The determination of bismuth in drugs by classic laborious methods implies a previous destruction of the organic compound. A direct approach to avoid these operations is based on complexometric titration with EDTA. For bismuth dosage in Dermatol and Airol drugs pirocathehine violet it is used as indicator[1], and its dosage from Gastrosedol and Ulcerotrat is made in the presence of taron[2].

Because at the equivalence point the color change is not very clear and cannot be easily observed, we propose the determination of Bi(III) from Ulcerotrat by conductometric titration with Rhodanine and with complex anions of Cr(III) with which bismuth forms stable complex combinations. Rhodanine is (2-thio-4-keto-thiazolidine),  .

EXPERIMENTAL

The synthesis and characterization of $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$ complex. A sample of 100 mL Bi(III) (pH=1.8) solution was treated with 1 % Rhodanine alcoholic solution in excess. A yellow complex compound $[Bi(Rhodanine)_3]^{3+}$ which remained stable with time and also at high temperatures was formed. We studied the structure of this complex and also the influence of various factors on its stability.[3]

The sample was brought to a constant volume of 25 mL with distilled water followed by the precipitation with complex anions of Cr(III), 3% aqueou-alcoholic solution.

A red-orange precipitate was obtained which was filtered with a filtering crucible G_4, it was washed tow or three times with distilled water, subsequently it was dried for 1 hour at 105 °C.

The complex salt obtained, $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$, was analyzed termogravimetrically, oxidimetrically and by spectrometric methods.[4]

The I.R. analysis of the complex was performed with a Perkin-Elmer 1600 spectrometer and the results are presented in Table 1.

RESULTS AND DISCUSSION

The I.R. spectral studies of the complex anions of $[Cr(NCS)_4(Aniline)_2]_3$ type[5-8] show that the vibration frequencies $\nu_{C=N}$ of the NSC group appears at 2110-2140 cm^{-1}, and the vibration frequencies ν_{C-S} at 760-810 cm^{-1}, respectively, which proves the covalent nature of the Cr(III)-NCS bond. The bond between Cr(III) and SCN is through the N atom and not the S atom[9].

The very intense absorption maximum at the vibration frequency of 2079 cm^{-1} is assigned to the SCN group.

The data mentioned in the literature[10-12] confirm that the coordination effect has an insignificant influence on the line of the complexes of $NH_4[Cr(NCS)_4(Aniline)_2]$ type. The $\nu_{C=N}$ and ν_{C-S} bands do not shift if there are aliphatic or aromatic amines in the internal sphere of coordination.

In the case of combinations with aniline in the internal sphere of coordination the vibration frequencies of the N-H bond are around 3100-3200 cm^{-1} (the shift being

insignificant (120-200 cm^{-1}) in comparison with free uncoordinated amines). This confirms that the Cr-N bond (with amines) had a strong covalent character.

Table 1. The I.R. absorbtion maximum for $[Bi(Rhodanine)_3][Cr(NCS)_4(Aniline)_2]_3$.

Vibration attribution	Frequency (cm^{-1})
ν_{C-H}	3396 v.w.
$\nu_{NH_2} + \nu_{C=S-NH_2}$	3190 m.
$\nu^{as}_{CH_2-S}$	3114 m.
ν_{CH_2OR}	2920 v.w.
ν_{SCN}	2079 v.i.
$\nu_{C=O}$	1601 w.
δ_{NH}	1576 m.
$\delta_{NH} + \delta_{CN}$	1526 m.
δ_{CH_2}	1492 m.
$\delta_{CN} + \nu_{NH}$	1283 m.
$\nu_{C=S}$	1130 i.
	1026 w.
$\nu_{C=N}$	693 w. and 481 m.

w. - weak; m - medium; i - intense; v.w. - very weak; v.i. - very intense; as - antisymmetric; s - symmetric; ν - valence vibration; δ - deformation vibration

The Bi(III) dosage from Ulcerotrat by conductometric titration with Rhodanine. Ulcerotrat is a drug used as a dressing in gastric injuries. It appears in the form of tablets (1.1022 g/tablet).

To 1 g Ulcerotrat 20 mL of concentrated HNO_3 is added and then the solution is diluted with distilled water is up to 1L. A sample of 100 mL of the solution obtained is titrated under magnetic stirring with 1% Rhodanine alcoholic solution. The results obtained are presented in Figure 1. From the graphic representation the volume at the equivalence point, V_e = 3.2 mL was determined in perfect concordance with the calculated value (V_e = 3.215 mL).

The experiments was repeated 5 times using sample with the same content of Bi(III) and the experimental data were statistically interpreted. The results are presented in Table 2.

Table 2. Statistic interpretation of the experimental data for Bi(III) dosage from Ulcerotrat by conductometric titration with Rhodanine.

No.	V Rhodanine (mL)	X Bi(III) found (mg)	$X-X_i$	$(X-X_i)^2$	
1	3.15	16.4819	0.2093	0.0438	$S^2 = 0.0222$
2	3.20	16.7435	-0.0523	0.0027	$S = 0.1490$
3	3.175	16.6127	0.0785	0.0062	$S_x = 0.06$
4	3.20	16.7435	-0.0523	0.0027	$t = 4.616$
5	3.225	16.8743	-0.1831	0.0335	
		$\bar{x} = 16.691$			

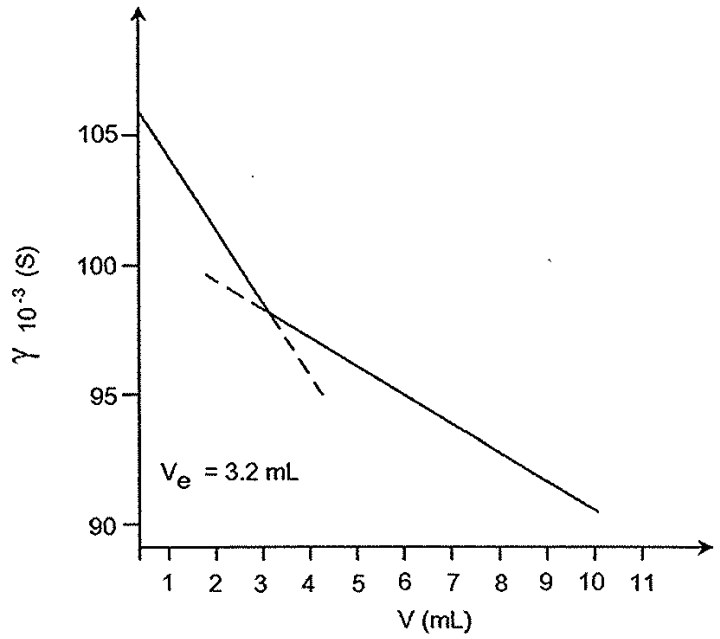


Fig. 1. The Bi(III) conductometric titration from Ulcerotrat using Rhodanine.

The Bi(III) dosage from Ulcerotrat after complexation with Rhodanine by conductometric titration with $[Cr(NCS)_4(Aniline)_2]^-$.

To 100 mL Ulcerotrat solution, prepared as above, 10 mL Rhodanine (in excess) is added and it is titrated under magnetic stirring with 3% alcoholic solution $NH_4[Cr(NCS)_4(Aniline)_2]\ H_2O$. The experimental results are presented in Figure 2.

In this case, too, the V_e = 5.6 mL obtained by experimental methods is in agreement with the one determined by calculations (V_e = 5.65 mL).

The data obtained by repeating the titration five times using samples with the same content of Bi(III) were statistically interpreted. The results are presented in Table 3.

Table 3. Statistic interpretation of the experimental data for Bi(III) dosage from Ulcerotrat after complexation with Rhodanine by conductometric titration with $[Cr(NCS)_4(Aniline)_2]^-$.

No.	V Rhodanilate (mL)	X Bi(III) found (mg)	$X-X_i$	$(X-X_i)^2$	
1	5.650	16.7487	0.03854	0.001485	$S^2 = 1.27582 \times 10^{-3}$
2	5.670	16.8080	-0.0208	0.000433	S = 0.03572
3	5.650	16.7487	-0.03854	0.001485	$S_x = 0.01597$
4	5.670	16.7487	-0.0208	0.00433	t = 4.616
5	5.675	16.8228	-0.0356	0.001267	
		$\bar{x} = 16.787$			

Comparing the experimental data from both cases presented one can observe that the better result was with the titration with Rhodanine. This may be explained by a more reduced mobility of the complex salt obtained following the titration, in the second case.

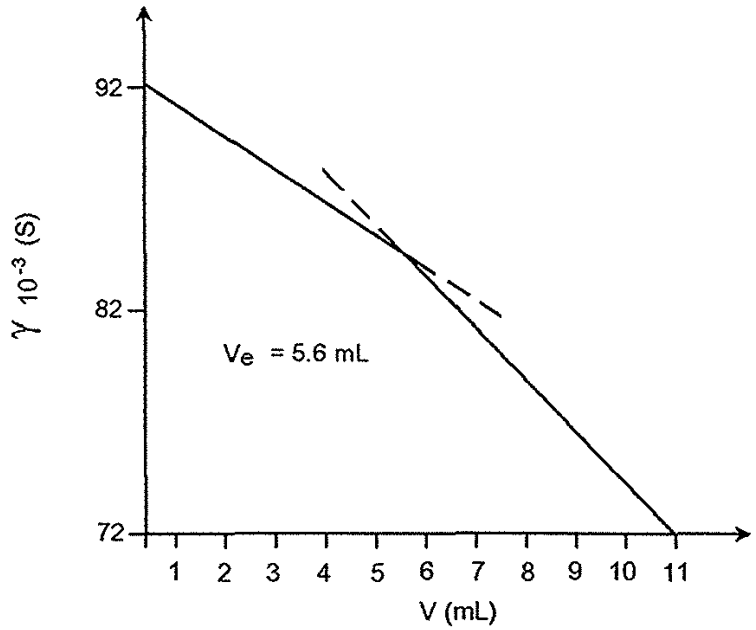


Fig. 2. . The Bi(III) conductometric titration from Ulcerotrat as $[Bi(Rhodanine)_3]^{3+}$ using $NH_4[Cr(NCS)_4(Aniline)_2]\,H_2O$.

The suggested method for the determination of Bi(III) in drugs (Ulcerotrat) is, rapid, particularly, sensitive and accurate.

The method used for determination the Bi(III) could be used also in the presence of other ions[4].

REFERENCES

1. R. Vasiliev, E. Sisman, I. Chialda, M. Jecu, *Rev. Chim.*, 11, 42 (1960).
2. A. Arnflet, J. Edmmudson, *Talanta*, 8, 135 (1961).
3. I. Ganescu, M. Pleniceanu, O. Rusu, M. Mureseanu, *Anal. Univ. Craiova, Seria Chimie*, XXIV, 88 (1997).
4. O. Rusu, M. Pleniceanu, M. Mureseanu, *Anal. Univ. Craiova, Seria Chimie*, XXIV, 104 (1997).
5. M. Chamberlain, J. C. Bailer, *J. Am. Chem. Soc.*, 81, 6412 (1959).
6. V. Fujita, K. Natamoto, *J. Am. Chem. Soc.*, 78, 3295 (1956).
7. E. Wasiliewska, *Inorg. Chem. Acta*, 1, 122 (1986).
8. C. Calu, N. Branzan, *Rev. Roum. Chem.*, 31, 1074 (1986).
9. S. K. Singh, *Acta Chim. Sinica*, 31, 40 (1987).
10. S. C. Shome, S. Nandy, *Mikrochim. Acta*, 2, 243 (1979).
11. F. R. Dans, Y. Goassens, L. Moens, *Mikrochim. Acta*, 119, 277 (1995).
12. H. Y. Lewellyn, *Uspekhi Khim*, 24, 688 (1995).

The SOUTHERN BRAZILIAN JOURNAL OF CHEMISTRY (ISSN: 2674-6891; 0104-5431) is an open-access journal since 1993. Journal DOI: 10.48141/SBJCHEM.
http://www.sbjchem.com.
This text was introduced in this file in 2021 for compliance reasons.