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Determination of Cobalt in Cobalt(III) Complexes — A Comparative Study

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Cobalt in cobalt(III) complexes was determined by a gravimetric method, weighing cobalt as cobalt(II) sulfate after heating the complexes with concentrated sulfuric acid; by a spectrophotometric method, measuring the color of cobalt(II)-thiocyanate complex in water-acetone mixture after reducing cobalt(III) to cobalt(II) with chromium(II), and by atomic absorption. The three methods were compared for accuracy of results and for convenience in routine analysis.

INDEX DESCRIPTORS: Cobalt, cobalt(III) complexes

Many methods for the analysis of cobalt are known, but there is no fast and convenient method for the routine analysis of cobalt(III) complexes. The difficulty is that these complexes are inert and do not react readily with analytical reagents. In most publications on cobalt(III) complexes during the last twenty years the analysis of cobalt was either not reported or reported without any indication of the method used.¹

Jørgensen²⁻³ and Werner,⁴ in their classical work, both used a gravimetric method, weighting cobalt as CoSO_4 after heating the complexes with concentrated sulfuric acid. However, difficulties may be encountered with this method if the ligands contain carbon because the carbonaceous material must be burned off first, and the resulting residue is not pure CoSO_4 . Jørgensen² heated these latter complexes first with sodium carbonate, producing Co_6O_7 , then converted the oxide into CoSO_4 . Tobe⁵ and Chan⁶ used an iodometric titration method⁷ after first converting cobalt(III) to cobalt(II), the former by precipitating the sulfide and the latter by pyrolysis with sulfuric acid; but Chan⁸ reported that an explosion had occurred during pyrolysis when nitrate was present. Gould and Taube⁹ analyzed cobalt(III) complexes by measuring the color of cobalt(II) in hydrochloric acid solution, after first precipitating $\text{Co}(\text{OH})_2$ and dissolving the hydroxide in HCl ; but this method is sensitive to the exact concentration of HCl used. There are several spectrophotometric methods developed specifically for cobalt(III),¹⁰⁻¹⁵ but these methods are not suitable for routine analysis because of lack of sensitivity due to low molar absorptivity,^{10, 14} need of extraction into non-aqueous solvents,¹¹⁻¹² need of buffering the solution,¹³ and a broad absorption peak.¹⁵ With the availability of commercial atomic absorption spectrometers, AA has become a possible method for fast and routine analysis. In this paper we report the results of the analyses of 8 cobalt(III) complexes by 3 methods — the gravimetric method of Jørgensen and Werner, the cobalt(II)-thiocyanate method¹⁶ after reducing cobalt(III) to cobalt(II) with chromium(II), and the atomic absorption method.

EXPERIMENTAL

Cobalt(III) complexes

Published methods were used to prepare the cobalt(III) complexes: potassium tris(oxalato)cobaltate(III) 3-hydrate,¹⁷ pentaamminechlorocobalt(III) chloride,¹⁸ pentamminebromocobalt(III) bromide,¹⁹ pentamminecarbonatocobalt(III) nitrate 0.5-hydrate,²⁰ tetraamminecarbonatocobalt(III) nitrate 0.5-hydrate,²¹ *cis*-dichlorobis(ethylenediamine) cobalt(III) chloride 1-hydrate,²² *trans*-dichlorobis(ethylenediamine) cobalt(III) chloride,²³ and *cis*-aquachlorobis(ethylenediamine) cobalt(III) sulfate 2-hydrate.²³ Microanalyses of carbon, nitrogen, and hydrogen were obtained to show the correctness of their formulas (Table 1).

Chemicals

Standard cobalt solution in 0.1 F HNO_3 was prepared by dissolving cobalt metal (Ventron Corporation, Alfa Products, m2N7) in 6.3 ml of concentrated HNO_3 and diluting with water to 1 liter in a volumetric flask. Three standard solutions were prepared.

Standard cobalt solution in 0.1 F HClO_4 was prepared by first dissolving cobalt metal in 1 ml of concentrated HNO_3 . After evaporating the solution to dryness, the residue was treated 3 times with 2 ml of concentrated HClO_4 , evaporating the solution to dryness each time. The final residue was dissolved in 0.1 F HClO_4 and made up to volume in a volumetric flask. Three standard solutions were prepared.

Chromium(II) solution was prepared by the reduction of hydrated chromium(III) perchlorate (G.F. Smith Chemical Co.) in 1 F HClO_4 with zinc amalgam under purified nitrogen. It was found that *ca.* 50 g of the hygroscopic material in 100 ml of solution was *ca.* 1 M in chromium.

All other chemicals used were reagent grade, and the water used was distilled water passed through a mixed-bed cation-anion exchange resin.

Table 1. Analytical data for 8 cobalt (III) complexes.

Complex	Theoretical			Found		
	% C	% N	% H	% C	% N	% H
$\text{K}_3[(\text{Co}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$	14.58		1.22	14.59		1.04
$[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$		27.96	6.04		27.97	6.00
$[\text{CoBr}(\text{NH}_3)_5]\text{Br}_2$		18.25	3.94		17.49	4.06
$[\text{Co}(\text{CO}_3)(\text{NH}_3)_5]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$	4.37	30.55	5.86	4.19	29.61	6.01
$[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]\text{NO}_3 \cdot 0.5\text{H}_2\text{O}$	4.65	27.14	5.08	4.62	27.25	4.92
<i>cis</i> - $[\text{CoCl}_2(\text{en})_2]\text{Cl} \cdot \text{H}_2\text{O}$	15.83	18.46	5.31	15.94	18.22	5.84
<i>trans</i> - $[\text{CoCl}_2(\text{en})_2]\text{Cl}$	16.83	19.62	4.71	16.16	18.97	5.40
<i>cis</i> - $[\text{CoCl}(\text{H}_2\text{O})(\text{en})_2]\text{SO}_4 \cdot 2\text{H}_2\text{O}$	13.17	15.36	6.08	13.34	15.72	6.06

Table 2. Cobalt percentages found for 8 cobalt(III) complexes.^a

Complex	Theor.	Sulfate Method	Spectrophotometric Method		AA Method
			HNO ₃ soln.	HC10 ₄ Soln.	
K ₃ [Co(C ₂ O ₄) ₃]·3H ₂ O	11.92	----- ^b	12.23 ± 0.09	11.93 ± 0.09	12.95 ± 1.08
[CoCl(NH ₃) ₅]Cl ₂	23.53	29.09 ± 0.29	23.31 ± 0.14	22.28 ± 0.08	23.25 ± 0.40
[CoBr(NH ₃) ₅]Br ₂	15.35	14.90 ^c	15.74 ± 0.04	15.24 ± 0.01	17.43 ± 0.73
[Co(CO ₃)(NH ₃) ₅]NO ₃ ·0.5H ₂ O	21.42	20.90 ^c	21.52 ± 0.26	21.20 ^c	19.38 ± 1.27
[Co(CO ₃)(NH ₃) ₄]NO ₃ ·0.5H ₂ O	22.84	24.08 ^c	23.52 ± 0.19	23.01 ^c	25.87 ± 0.58
<i>cis</i> -[CoCl ₂ (en) ₂]Cl·H ₂ O	19.42	20.20 ± 0.33	19.37 ± 0.47	19.15 ± 0.05	20.48 ± 0.33
<i>trans</i> -[CoCl ₂ (en) ₂]Cl	20.64	21.65 ± 0.42	20.67 ± 0.03	20.27 ± 0.20	21.40 ± 1.55
<i>cis</i> -[CoCl(H ₂ O)(en) ₂]SO ₄ ·2H ₂ O	16.16	----- ^d	16.90 ± 0.25	16.76 ^c	18.69 ± 0.99

^aThe deviation listed is the deviation from the mean.

^bCannot be analyzed by this method.

^cSingle sample.

^dNot done.

Procedure

For the gravimetric method of analysis, the procedures of Jørgensen²⁻³ and Werner⁴ were followed.

In the spectrophotometric method, for constructing standard curves, duplicate or triplicate 2-, 3-, 4-, 5-, and 6-ml aliquots of the standard solutions were each placed in a 50-ml beaker; and 0.1 cm³ of *ca.* 1M Cr(II) solution was added into each solution by a syringe, which was purge with purified nitrogen before use. The solutions were each aerated for 5 minutes, and 5 g of solid ammonium thiocyanate was added to each solution. After most of the ammonium thiocyanate was dissolved, the contents of each beaker was transferred into a 50-ml volumetric flask containing 25 ml of acetone. Each beaker was rinsed 3 times with a little water, and the washings were combined into the flask. Finally, water was added to each flask to the mark. The solutions were mixed well, and the absorbance of each at 622.5 nm was measured by a Beckman DU-2 spectrophotometer in 1-cm cells, using a reagent blank, similarly prepared, as the reference. For the analysis of cobalt(III) complexes, duplicate sample solutions of *ca.* 3mM were prepared in either 0.1 F HNO₃ or 0.1 F HC10₄. Duplicate 5-ml aliquots of each sample solution were used to follow the procedure described above for the standards.

In the atomic absorption method, standard and sample solutions in the concentration range of 1 to 8 × 10⁻⁵ M were prepared in 0.1 F HNO₃. The measurements were made at 240.73 nm, using a Beckman 440 atomic absorption spectrometer and air-acetylene flame. The concentrations of cobalt in the sample solutions were found by interpolation of the standard curves.

RESULTS AND DISCUSSION

The results of the analyses of the 8 cobalt(III) complexes by the 3 methods are summarized in Table 2. We found that the gravimetric method is very time-consuming and unsuitable for routine analysis because it is difficult to run tens of samples at the same time. This method cannot be used if the cobalt(III) complex is an anion.

The spectrophotometric method and the atomic absorption method produced comparable results, but the mean deviation is lower for the spectrophotometric method. For the spectrophotometric method, results obtained by using 0.1 F HNO₃ solutions and by using 0.1 F HC10₄ solutions are comparable, provided that each set of data is calculated by

its own standard curve. Plots of absorbance vs. cobalt concentration for both sets of standard solutions are straight lines up to 4 × 10⁻⁴ M cobalt, but the standard curve for 0.1 F HNO₃ solutions did not pass through the origin. Thus the equation of the line A = (1820 ± 10) × [Co] - (0.021 ± 0.002) was used to calculate the cobalt concentration. For 0.1 F HC10₄ solutions, the molar absorptivity was found to be 1800 ± 20 M⁻¹ cm⁻¹. After these standard curves were constructed, there was no need for further standardization while running samples. For the atomic absorption method, on the other hand, due to the irreproducibility of the flame, a standard curve must be obtained each time samples are to be analyzed. This was judged to be an inconvenience.

From the above considerations, we have chosen the spectrophotometric method for routine analysis of cobalt in cobalt(III) complexes for the following reasons: (1) no solvent extraction is necessary, (2) no buffer solution is necessary, (3) the absorption peak is sharp, (4) the absorption peak is above 600 nm so that interference by organic material is minimized, (5) there is no need to obtain a new standard curve each time samples are analyzed, (6) the chemicals are readily available, (7) no specialized equipment is necessary, and (8) a large number of samples can be analyzed in a relatively short time. The methods of conversion of cobalt(III) to cobalt(II) found in the literature are not satisfactory. The method of Zvenigorodskaya²⁴ is long and tedious while the ultraviolet photo-reduction method of Hughes *et al.*²⁵ did not work very well for some complexes. Espenson²⁶ used chromium(II) to reduce cobalt(III), and it was found that this method is the most convenient. From the published data on the rates of reduction of various cobalt(III) complexes by chromium(II),²⁷⁻³⁰ it was estimated that most cobalt(III) complexes can be reduced in less than a minute, often in a matter of seconds, by 1 M chromium(II).

After the reduction of cobalt(III) to cobalt(II), the sample solutions were aerated in order to oxidize the excess chromium(II) to chromium(III). It was found that more consistent results were obtained if the chromium(II) was oxidized. Although it was reported that chromium does not interfere in the cobalt(II)-thiocyanate method,³¹ we found that the reagent blank solution gave a spectrum typical of chromium(III) complexes, showing two absorption peaks at 565 nm ($\epsilon = 50\text{M}^{-1}\text{cm}^{-1}$) and 423 nm ($\epsilon = 56\text{M}^{-1}\text{cm}^{-1}$). The molar absorptivity at 622.5 nm, where the cobalt(II)-thiocyanate complex was measured, is *ca.* 30 M⁻¹cm⁻¹; however, this low absorbance was already compensated for by using a reagent blank as the reference in the measurements. Also, the cobalt(II)-thiocyanate complex in water-acetone mixture did

not seem to be oxidized by air during the time required for the measurements since consistent absorbances were obtained by repeated measurements 30 to 60 minutes after the solutions were prepared.

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