

The Zn(II), Cd(II), Pd(II) and $\text{UO}_2(\text{II})$ -complexes also display 1 : 1 metal-ligand stoichiometry besides having a water or pyridine molecule. All these compounds were found to be diamagnetic. Based on these data a tetrahedral structure is assigned to Zn(II) and Cd(II) complexes and an octahedral structure to $\text{UO}_2(\text{II})$ -complex.

The Pd(II) complex indicates three absorption bands with their peaks at 22400, 26300 and 30400 cm^{-1} assignable to the transitions, $^1A_{1g} \rightarrow ^1B_{1g}$, $^1A_{1g} \rightarrow ^1E_{1g}$ and $^1A_{1g} \rightarrow ^1A_{2g}$. Thus the Pd(II) complex displays a squareplanar configuration. These results are also in agreement with an earlier finding⁷.

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Modified Synthesis of Tris(Biguanide) Cobalt (III) Base and its Salts

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THE title compounds have been the subject of many investigations : asymmetric transformation of the second order during resolution¹, intramolecular twist mechanism of racemisation², inner sphere formation constant³, aquation kinetics⁴, outer sphere association constants⁵, filter paper and thin layer chromatography⁶. Original synthesis⁷ involved an over-cautious, somewhat cumbersome and lengthy air

oxidation of the insoluble bis(biguanide) cobalt(II) base in presence of alkaline biguanide. We have been successfully using for many years now a quicker H_2O_2 oxidation procedure. A recent report by Krishnamurthy⁸ describing the efficacy of H_2O_2 in radically reducing the time of synthesis of trans- $[\text{CoCl}_2(\text{en})_2] = \text{Cl}(\text{en} = \text{ethylenediamine})$ prompts us to describe our own on $[\text{Co}(\text{BigH})_3](\text{OH})_3$ and its salts.

Biguanide acid sulfate⁹ (8.5 g) was dissolved in water (75 ml) containing NaOH (6.0 g). To this was added with stirring a solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (2.5 g) in water (5.0 ml) H_2O_2 (5.0 ml, 20 vol.) was added and the mixture heated on a steam bath for 30 min with stirring. The solution along with the red crystals of $[\text{Co}(\text{BigH})_3](\text{OH})_3$ were cooled in ice for 1 hr, filtered and the crystals washed with ice cold ethanol (25 ml.). The base was then triturated with ice cold HCl (1 : 3) to a pH \sim 6.0. The orange red coloured tris(biguanide) cobalt(III) chloride was filtered with the aid of ethanol (10 ml) and was finally recrystallised from hot water (70 ml.). Yield 2.6 g. Found : Cl, 22.74; Co, 12.80; Eq.wt. 156. Calcd.: Cl, 22.88; Co, 12.68; Eq.wt. 156.

The compound gave the two usual transitions ; $^1A_{1g} \rightarrow ^1T_{1g}$ 21.1 kK; $^1A_{1g} \rightarrow ^1T_{2g}$ 28.4 kK.

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Estimation of Ba^{2+} , Ag^+ and Tl^+ as chromates by A.C. Amperometry

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KOLTHOFF and Gregor^{1,2} estimated barium with chromate ion in aqueous and aqueous-ethanol mixtures by conventional amperometric titration which yielded results that were 2 to 5% low. Many

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others^{3,4} have also studied the precipitation of Ba²⁺ as chromate. Kalvoda and Zyka⁵ estimated Tl⁺ in the concentration range 10⁻³ to 10⁻²M in 0.3M KNO₃ containing 10% acetone using dichromate ion. This investigation, however, gives the results obtained in the estimation of Ba²⁺, Ag⁺ and Tl⁺ as chromates in aqueous-ethanol mixtures by a.c. amperometry and the comparison of the results by d.c. amperometry.

Experimental

Pure recrystallised samples of barium chloride, silver nitrate, thallos sulphate, potassium chromate and indifferent electrolytes (BDH, AR) were used. Methanol, ethanol and acetone were AnalaR grade which were redistilled in an all-glass fractionating column and the middle one third of the distillate was used for experiments. The apparatus employed for d.c.⁶ and a.c.⁷ amperometry was the same as described earlier. Potentials were referred to SCE. The constants of the DME were: $m = 2.931$ mg/s, $t = 3.05$ s in 0.54M KCl (open circuit) and $h = 40$ cm (uncorrected for back pressure) for d.c. and $m = 4.564$ mg/s, $t = 1.8$ s in 0.1M KCl (open circuit) for a.c. polarographic work. Temperature was maintained at 30° ± 0.1° with a Townson and Mercer unit. Mercury used for the DME was first purified chemically and subsequently distilled under reduced pressure. Nitrogen gas was used for deoxygenation of the solution in d.c. polarographic work. pH measurements were made with Beckman (Model H2) pH meter.

Ba²⁺ and Ag⁺ do not give a.c. peaks. Chromate ion provides two a.c. peaks around -0.2V and -1.3V in aqueous-methanol or aqueous-ethanol using 0.1M KCl or 0.1M KNO₃ as supporting electrolytes. In the case of acetone-water mixtures the peak potentials shifted towards more cathodic side and the magnitude of the current decreased with increasing acetone concentration. The second peak was chosen for carrying out titrations as it was more pronounced than the first one. However, Tl⁺ gave pronounced a.c. peak around -0.47V.

A known excess of K₂CrO₄ was added to barium test solution of suitable strength containing appropriate amount of alcohol or acetone and the excess of chromate was back titrated with standard barium chloride solution. The back titration was found more suitable for the estimation of Ba²⁺; Ag⁺ and Tl⁺ were, however, estimated by direct a.c. amperometric titrations. The DME was maintained at -1.4V in d.c. amperometry (which lies on the plateau of the current-voltage curves of chromate) and the titrations were carried out at pH 6.8.

Results and Discussions

It was found that 0.1M or 0.2M KCl gave best results in the case of Ba²⁺. The optimum pH range was found to be 5.5 to 7.0 for Ba²⁺ and 6.0 to 7.0 for Ag⁺ and Tl⁺. It was observed that solutions containing 10% methanol, 20% ethanol or 5%

acetone gave fairly good results in the case of Ba²⁺. In the case of Ag⁺, solutions containing 20% ethanol were found most suitable. In the case of Tl⁺, best results were obtained in solutions containing 10% methanol when titrated at the peak potential of Tl⁺, and in solutions containing 20% ethanol when titrated at the peak potential of chromate ion.

Table 1 gives the comparative results obtained using d.c. and a.c. amperometric methods. In general it can be seen that a.c. amperometric method is more efficient than the d.c. method. Further it can be observed that concentration of Ba²⁺ as low as 2.5 × 10⁻⁴M can be estimated by back titration method with good accuracy. However, the accuracy in the case of Ag⁺ decreased considerably below the concentration of 8.0 × 10⁻³M. The estimation of Tl⁺ upto 1.0 × 10⁻³M could be done with fairly accurate results although at lower concentrations of Tl⁺ ion, the error increased. The error in most cases is within 1.3% in a.c. amperometric titrations.

TABLE 1—COMPARISON OF THE RESULTS OBTAINED BY D.C. AND A.C. AMPEROMETRIC METHODS IN THE ESTIMATION OF Ba²⁺, Ag⁺ AND Tl⁺ WITH POTASSIUM CHROMATE

Concentration of the test solution mM/liter	Titrant and its concentration mM/liter	Error%	
		A.C. Amperometry	D.C. Amperometry
<i>Back titration: Excess CrO₄⁻² = 0.50 mM</i>			
20% ethanol; pH = 6.8; E _p = -1.32V; E _{a.c.} = -1.4V; 0.1M KCl			
1.00 Ba ²⁺	BaCr ₂ , 10.00	-0.8	-2.0
0.50 Ba ²⁺	"	-0.8	-3.2
0.250 Ba ²⁺	"	-1.6	-3.6
<i>Direct titrations</i>			
20% ethanol; pH = 6.8; E _p = -1.32V; E _{a.c.} = -1.4V; 0.1M KNO ₃			
10.00 Ag ⁺	K ₂ CrO ₄ , 100.0	-1.2	-1.5
8.00 Ag ⁺	"	-1.5	-2.0
5.00 Ag ⁺	"	-3.2	-3.2
2.00 Tl ⁺	"	-1.0	-1.5
1.00 Tl ⁺	"	-1.2	-1.5
0.60 Tl ⁺	"	-2.7	-3.0

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