Investigations on Some Amino Complexes of Cobalt(II)phthalimide. I

Preparation and Preliminary Investigations

By G. NARAIN, P. SHUKLA and L. N. SRIVASTAVA

Abstract

Co-ordination complexes between cobalt(II)phthalimide, ammonia and a flew diamines have been prepared. The molecular formulae on the basis of percentages of constituent elements are $Co(Phthalimide)_2(amine)_2$ or 1. Conductivity measurements in nitrobenzene indicate the complexes to be non-electrolytes and hence it is suggested that phthalimide ion is also co-ordinated. Molecular weight measurements in the same solvent confirm this.

Introduction

A survey of the literature shows that a large number of amine complexes of Co(II) have been prepared with almost all possible inorganic anions. There are also a number of evidences to suggest that the nature of the anion is a contributing factor towards stability[1]), cordination number[2]) and colour of the complexes[3]). It is surprising that very little work of this type has been done with the organic salts of cobalt(II)[4–7]).

We have undertaken the study of a number of complexes of cobalt(II)-phthalimide with some amines with a view to find out:

I. The effect of phthalimide ion on the stability and colour of the complexes and

II. Whether phthalimide ion besides neutralizing the charge of the metal is also co-ordinated to it through its nitrogen, or through the oxygen of the carbonyl group.

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In the present paper, the synthesis and some of preliminary investigations as regards analysis molecular weight and conductivity measurements are reported. The complexes have been prepared with ammonia, ethylenediamine, 2,2′-dipyridyl and 1,10-phenanthroline.

Experimental

A. Synthesis

1.+Cobalt(II)phthalimide

The starting material of all these preparations is cobalt(II)phthalimide which has been obtained by treating calculated quantities of cobalt(II) chloride hexahydrate with potassium phthalimide. The blue precipiate after being washed several times with water was dried over P_2O_5 and analysed (Found Co = 17.02%, C = 55.01%, H = 2.80%, N = 7.46%; $C_{16}H_8O_4N_4$. Co requires Co = 16.8%, C = 54.71%, H = 2.28%, N = 7.98%).

2. Biphthalimido biamino, cobalt(II)

500 mgm of cobalt(II)phthalimide was suspended in acetone and treated with calculated quantity of 0.888 ammonia solution. Pink complex was formed, left overnight for crystallisation, washed several times and dried (Found Co = 15.02%, C = 49.01%, H = 3.8%, N = 14.15%; $C_{16}H_{14}O_4N_4$. Co requires Co = 15.32%, C = 49,9%, H = 3.63%, N = 14.55%).

3. Biphthalimido, ethylenediamine cobalt(II)

500 mgm of cobalt(II)phthalimide, calculated quantity of anhydrous amine and 15 c.c. of acetone were shaken for four hours. The brown complex was formed, left overnight, recrystallized with acetone and ether and dried (Found Co = 14.05%, C = 52.9%, H = 4.00%, N = 13.46%; $C_{18}H_{16}O_4N_4$. Co requires Co = 14.35%, C = 52.57%, H = 3.89%, N = 13.63%).

4. Biphthalimido, 2,2′-dipyridyl cobalt(II)

500 mgm of cobalt(II)phthalimide was suspended in 10 c.c. of acetone. A little more than the calculated quantity of amine was added and solution was refluxed for 6 hours. The resulting orange complex was kept overnight, filtered, washed and dried (Found Co = 11.26%, C = 61.03%, H = 3.32%, N = 11.15%; $C_{26}H_{16}O_4N_4$. Co requires Co = 11.62%, C = 61.54%, H = 3.15%, N = 11.05%).

5. Biphthalimido o-phenanthroline cobalt(II)

Prepared by the same method as (4). Complex is light brown in colour (Found Co = 11.20%, C = 63.32%, H = 3.06%, N = 10.35%, $C_{28}H_{16}O_4N_4$. Co requires Co = 11.1%, C = 63.29%, H = 3.01%, N = 10.55%).

B. Molecular weight measurements

Molecular weights were determined by the method of freezing point depression, using nitrobenzene as the solvent. As the complexes dissolve only to a limited extent, a BECKMANN thermometer with a scale of only 1 °C was used. The thermometer was extremely sensitive

to supercooling and hence a modified apparatus was constructed. A glass vessel containing the freezing point tube was placed in a copper cylinder filled with water maintained at 0.5 °C and being constantly stirred by a mechanical stirrer. This cylinder was surrounded by another well lagged copper cylinder containing ice.

C. Conductivity measurements

Measurements were done in nitrobenzene at a concentration of 10^{-3} M. The cell used had a cell constant of 0.0295.

D. Acetone and ether used were of A. R. grade. Nitrobenzene was purified by steam distillation followed by distillation over reduced pressure.

Results

The percentages of constituent elements have been given along with their synthesis. The results of molecular weight and conductivity measurements are tabulated below.

Table

No	Formulae	Molecular weight measurements			Calculated Mol.-wt.	Molar Conductance of 10^{-3} M sol.
		wt. of solute per 50 gm of solvent	Depression	Observed Mol.-wt.		
1.	$Co(Phth)_2$	Insoluble in nitrobenzene				
2.	$[Co(Phth)_2(NH_3)_2]°$	0.01925 gm	0.007°	367.3	384.94	0.52 mhos.
3.	$[Co(Phth)_2en]°$	0.02055 gm	0.0066°	419.0	410.94	0.62 mhos.
4.	$[Co(Phth)_2$ 2,2′dipy$]°$	0.02535 gm	0.007°	487.2	506.94	0.90 mhos.
5.	$[Co(Phth)_2$ o-phen$]°$	0.02655 gm	0.007°	510.1	530.94	0.82 mhos.

In the above Table

(I) Phth represents phthalimide

(II) en represents ethylenediamine

(III) 2,2′dipy represents 2,2′-dipyridyl

(IV) o-phen represents o-phenanthroline.

Discussion

On the basis of the percentages of metal, carbon, hydrogen and nitrogen, the molecular firmulae turn out to be Co(Phthalimide)$_2$(amine)$_2$ or 1. These complexes possess abnormal colours as they are pink, brown or orange. They do not melt, but if heated or warmed with acid or alkali, they decompose and become black in colour. Their solubility is extremely low and they are soluble in acetone nitrobenzene and alcohol.

The compounds dissolve in nitrobenzene to give very dilute solutions (10^{-3} M) and the measurements of molor conductance in these solutions give

a value of 0.56 to 0.9 mhos. These values indicate the compounds to be non-electrolytes[8]).

The freezing point determination in nitrobenzene give the normal absolute value of molecular weight. The results suggest that phthalimide ion is inside the co-ordination sphere along with the amine. The formulae must be written as $[Co(Phth)_2(am)\ 2\ or\ 1]^{\circ}$ and not as $[Co(am)\ 2\ or\ 1]^{+2}(Phth)_2$.

The structure of compounds is under investigation. The infra-red, magnetic susceptibility and visible absorption spectrophotometric measurements are being conducted and it is hoped that these results will help in elucidating the structure of these compounds and the site of attachment of phthalimide ion to the cobalt(II) atom.

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Lucknow (India), Department of Chemistry, Lucknow University.

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