Reactions of Cobalt (II) Oxalate with Primary Aliphatic Amines

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Summary

Some molecular addition compounds of cobalt (II) oxalate with primary aliphatic amines have been prepared. The general molecular formula on the basis of analysis of constituent elements turn out to be $CoC_2O_4 \cdot RNH_2$. The formation of compounds is independent of the excess amine concentration. The compounds behave as electrolytes. The molecular weight measurements and Van't Hoff factor "i" also confirm this fact.

A survey of the literature shows that a large number of amine compounds of Cobalt (II) with different anions have been prepared[1–4]. Recently few of the amine complexes of cobalt (III) oxalate have been studied[5][6]. However, no work has been reported on the molecular addition compounds of cobalt (II) oxalate.

The present investigation has been carried out with a view to study the formation, molar conductance, molecular weight and general properties of the compounds of cobalt (II) oxalate with primary aliphatic amines. The compounds were prepared with ammonia, methyl, ethyl, iso and n-propyl, iso and n-butyl and iso and n-amylamines.

Experimental Section

Synthesis. All the complexes were prepared by the following general method.

500 mg of cobalt (II) oxalate were suspended in 15 ml of 95% alcohol and then the calculated quantity of amine was added. The reaction mixture was shaked for six hours. The resulting compound was kept over night, filtered next morning, washed several times with alcohol and acetone and dried first over calcium chloride then over phosphorus (V) oxide.

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[1] J. R. Allan, D. H. Brown, R. H. Nuttol and D. W. A. Sharp, J. Inorg. Nucl. Chem. **26** (11), 1895 (1964).

[2] H. C. A. King, E. Koros and S. M. Nelson, J. chem. Soc. London 4832 (1964).

[3] W. E. Hatfield and J. T. Yoke, Inorg. Chem. **1**, 463 (1962).

[4] A. V. Babawa and I. B. Baranovskii, Zhur. Neorg. Khim., **5**, 749 (1960).

[5] V. A. Golovnefa, L. A. Kokh and S. K. Sokol, Zhur. Neorg. Khim. **6**, 1552 (1961).

[6] Wei-Tao Liu and Fan-Siyien, Hua Hseuh Hsiich Pao **24**, 445 (1958).

If an excess of amine was added i.e. cobalt (II) oxalate and amine ratio 1:2, 1:3, 1:4, 1:5 and 1:6; the formation of only 1:1 adduct resulted.

Analysis: Metal was estimated as α-nitroso-β-naphthol complex, oxalate as calcium oxalate monohydrate and nitrogen by KJELDAHL method [7]). The analytical results are given below:

1. Ammonia adduct

The compound is violet pink in colour, soluble in water nitrobenzene and formamide. Found Co = 35.65%, C_2O_4 = 53.46%, N = 8.44%; $CoC_2O_4 \cdot NH_3$ requires Co = 35.93%, C_2O_4 = 53.69%, N = 8.54%.

2. Methylamine adduct

The compound is maroon in colour, soluble in water, formamide, dimethylformamide and nitrobenzene. Found Co = 32.98%, C_2O_4 = 49.36%, N = 7.77%; $CoC_2O_4 \cdot CH_3NH_2$ requires Co = 33.11%, C_2O_4 = 49.47%, N = 7.869%.

3. Ethylamine adduct

The compound is pink in colour, soluble in water, chloroform, nitrobenzene and formamide. Found Co = 30.97%, C_2O_4 = 45.76%, N = 7.40%; $CoC_2O_4 \cdot C_2H_5NH_2$ requires Co = 30.70%, C_2O_4 = 45.86%, N = 7.296%.

4. iso-Propylamine adduct

The compound is whitish pink in colour, well crystalline and soluble in water, nitrobenzene and formamide. Found Co = 28.33%, C_2O_4 = 42.48%, N = 6.77%; $CoC_2O_4 \cdot C_3H_7NH_2$ requires Co = 28.60%, C_2O_4 = 42.74%, N = 6.80%.

5. n-Propylamine adduct

The compound is pink in colour, amorphous and soluble in water, chloroform, formamide and nitrobenzene. Found Co = 28.8%, C_2O_4 = 42.66%, N = 6.45%; $CoC_2O_4 \cdot C_3H_7NH_2$ requires Co = 28.6%, C_2O_4 = 42.74%, N = 6.8%.

6. iso-Butylamine adduct

The compound is pink in colour, amorphous and soluble in water, nitrobenzene and formamide. Found Co = 26.43%, C_2O_4 = 40.32%, N = 6.28%; $CoC_2O_4 \cdot C_4H_9NH_2$ requires Co = 26.78%, C_2O_4 = 40.02%, N = 6.36%.

7. n-Butylamine adduct

The compound is almost similar to the isobutylamine adduct in colour and solubility. Found Co = 26.98%, C_2O_4 = 40.42%, N = 6.50%; $CoC_2O_4 \cdot C_4H_9NH_2$ requires Co = 26.78%, C_2O_4 = 40.02%, N = 6.36%.

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[7]) A. I. VOGEL, A Text book of Quantitative inorganic analysis, (ELBS and Longmans Green & Co. Ltd.) 3rd. edition, p. 528, 578 and 256 (1961).

8. iso-Amylamine adduct

The compound is light pink in colour, amorphous solid and soluble in water and formamide. Found Co = 25.10%, C_2O_4 = 35.57%, N = 5.87%; $CoC_2O_4 \cdot C_5H_{11}NH_2$ requires Co = 25.17%, C_2O_4 = 37.62%, N = 5.984%.

9. n-Amylamine adduct

The compound is almost similar to the iso-amylamine adduct in colour and solubility. Found Co = 25.10%, C_2O_4 = 37.49%, N = 5.78%; $CoC_2O_4 \cdot C_5H_{11}NH_2$ requires Co = 25.17%, C_2O_4 = 37.76%, N = 5.98%.

Molar conductance and molecular weight measurements

The conductance measurements were done in conductivity water at a concentration of 10^{-3} M. The cell used had a cell constant of 0.0245. The molecular weight measurements were also done in conductivity water. A modified apparatus was used as outlined by the author[8]) to avoid supercooling.

Results

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

Table 1
Molar conductance and molecular weight

No.	Formula	Molar conductance 10^{-3} M solution	Molecular weight		
			Observed	Calculated	Van't Hoff factor "i"
1	$CoC_2O_4 \cdot NH_3$	80.8 mhos	80 ± 10	163.94	2.0375
2	$CoC_2O_4 \cdot CH_3NH_2$	103 mhos	101 ± 15	177.94	1.7623
3	$CoC_2H_4 \cdot C_2H_5NH_2$	95.6 mhos	108 ± 10	191.94	1.7685
4	$CoC_2O_4 \cdot$ iso-$C_3H_7NH_2$	107 mhos	100 ± 20	205.94	2.0300
5	$CoC_2O_4 \cdot$ n-$C_3H_7NH_2$	140 mhos	100 ± 20	205.94	2.0300
6	$CoC_2O_4 \cdot$ iso-$C_4H_9NH_2$	165 mhos	115 ± 25	219.94	1.9130
7	$CoC_2O_4 \cdot$ n-$C_4H_9NH_2$	70.5 mhos	115 ± 25	219.94	1.9130
8	$CoC_2O_4 \cdot$ iso-$C_5H_{11}NH_2$	120.2 mhos	108 ± 15	233.94	2.1666
9	$CoC_2O_4 \cdot$ n-$C_5H_{11}NH_2$	133 mhos	108 ± 15	233.94	2.1666

Discussion

On the basis of percentages of constituent element, i.e. cobalt, oxalate and nitrogen, the general molecular formula turn out to be $CoC_2O_4 \cdot RNH_2$ (where R = H, CH_3, C_2H_5, C_3H_7, C_4H_9 and C_5H_{11}). It has been pointed out

[8]) Gopal Narain, P. Shukla and L. N. Srivastava, J. prakt. Chem. [4] **31**, 123 (1966).

that irrespective of the quantity of amine added, the ratio of cobalt (II) oxalate to amine is always 1:1 in all the compounds. This shows the weak affinity of cobalt (II) oxalate to primary aliphatic amines in this particular case. Attempts to prepare true co-ordination compounds (4 or 6 co-ordinate) have been unsuccessful.

These molecular addition compounds possess typical pink colour, all are amorphous solids except the isopropylamine compound, which is well crystalline. They are neither hygroscopic nor decompose when they come into contact with moisture. Their solubility is extremely high in water and most of the organic solvents, such as formamide, dimethylformamide, nitrobenzene and chloroform. Their solublity is low in acetone, alcohol and carbontetrachloride.

The value of molar conductance (10^{-3} M solution in conductivity water) of the compounds ranges from 70 to 170 mhos. These values indicate the compounds to be electrolytes[9]).

For compounds, which dissociate into two or three ions, the coefficient "i" is never greater then two or three. An estimation of the VAN'T HOFF factor (the ratio of the calculated molecular weight to the observed molecular weight) should give us some idea of the degree of dissociation, if any[10]). If the value of "i" is greater than one it denotes dissociation. The observed molecular weight and VAN'T HOFF factor "i" of the individual compounds indicate that they are dissociated.

The structure of these compounds is under investigation. Infrared, magnetic susceptibility and visible spectrophotometric measurements are being conducted and it is hoped that these results will help in elucidating the structure of these addition compounds.

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[9]) H. J. EMELEUS and J. S. ANDERSON, Modern aspects of Inorganic Chemistry (Routledge & Kegan Paul Ltd.) Second edition, p. 127 (1962).

[10]) GROSCHIUFF, Z. anorg. Chem. **47**, 331 and 347 (1905).

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