

Investigations on some Amino Complexes of Copper (II) Benzoate

Preparation, Preliminary Investigations and Absorption Spectra

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Abstract

Co-ordination complexes between Copper (II) benzoate and ammonia, some diphenyl and aromatic amines and a few diamines have been prepared. The molecular formulae on the basis of percentages of constituent elements are $\text{Cu}(\text{benzoate})_2(\text{amines})_2$ and $\text{Cu}(\text{benzoate})_2(\text{amine})$. Conductivity measurements in formamide, nitrobenzene and water indicate the complexes to be non-electrolytes and hence it is suggested that the benzoate ions are also co-ordinated. Molecular weight measurements in the same solvents confirm this. Visible absorption measurements show a single band in the 600–900 μ region of the spectrum.

Introduction

A survey of the literature shows that a large number of copper complexes with ammonia and various amines have been studied. However, only a few solid complexes, have been prepared with aliphatic amines as ligands¹⁾²⁾. There are also a number of evidences to suggest that the nature of the anion is a contributing factor towards stability³⁾, co-ordination number⁴⁾ and colour⁵⁾ of the complexes. Although an extensive series of investigations with inorganic salts of copper are reported, comparatively very little work of this type has been done with the organic salts⁶⁻⁹⁾.

1) M. STRAUMANIS and A. CIRCLUS, *Z. anorg. allg. Chem.* **230**, 65 (1936).

2) S. PRASAD and P. D. SHARMA, *J. Proc. Inst. Chem.* **30**, 245 (1958).

3) T. MOELLER, *Inorganic chemistry*, Ist Indian Printing (Asia Publishing House) p. 237 (1962).

4) J. C. BAILOR, *Chemistry of Coordination Compounds*. II. Printing (Rheinhold Publishing Corporation, New York) p. 142 (1956).

5) R. S. NYHOLM, *Chem. Rev.* **53**, 278 (1953).

6) L. TSCHUGAEFF, *Ber. dtsh. chem. Ges.* **38**, 2899 (1905).

7) A. R. BURKIN, *J. chem. Soc. London* 122 (1950).

8) H. GROSSMAUN and G. JAGER, *Z. anorg. Chem.* **73**, 48 (1912).

9) G. SPACU and P. VOICHESCU, *Z. anorg. allg. Chem.* **226**, 273 (1936).

The author has undertaken the study of a series of complexes prepared with copper benzoate and a number of amines, with a view to find out:

- (I) the effect of benzoate ion on the stability and colour of the complexes;
- (II) the possible changes this ion could bring about in the co-ordination number of copper and
- (III) whether benzoate ion besides neutralizing the charge of the metal, is also co-ordinated to it.

Experimental

A. Synthesis

The complexes were prepared by following two general methods.

(I) 500 mg of copper benzoate (A.R./BDH) were suspended in 15 cm³ of acetone and then a little more than the calculated quantity of amine was added. The solution was shaken for four hours and the resulting complex was filtered, dried and analysed.

(II) 1 g of copper benzoate in 15 cm³ of acetone was refluxed with a little more than the calculated quantity of amine for five hours. The resulting complex was kept overnight, filtered next morning and dried and analysed.

1. Bi-benzoato, bi (ammine) copper (II). Prepared by method (I) and is blue in colour (Found Cu = 18.51, N = 8.02%; C₁₄H₁₆O₄N₂Cu requires Cu = 18.71, N = 8.25).

2. Bi-benzoato, bi (methylamino) copper (II). Prepared by method (I) and is bluish green in colour (Found Cu = 17.40%, N = 7.46%; C₁₆H₂₀O₄N₂Cu requires Cu = 17.28, N = 7.62%).

3. Bi-benzoato, bi (ethylamino) copper (II). Prepared by method (I) and is blue in colour (Found Cu = 15.88%, N = 6.98%; C₁₈H₂₄O₄N₂Cu requires Cu = 16.06%, N = 7.08%).

4. Bi-benzoato, bi (n-propylamino) copper (II). Prepared by method (I) and is blue in colour (Found Cu = 14.86%, N = 6.42%; C₂₀H₂₈O₄N₂Cu requires Cu = 15.00%, N = 6.61%).

5. Bi-benzoato, bi (iso-propylamino) copper (II). Prepared by method (I) and is blue in colour (Found Cu = 14.80%, N = 6.50%; C₂₀H₂₈O₄N₂Cu requires Cu = 15.00%, N = 6.61%).

6. Bi-benzoato, bi (n-butylamino) copper (II). Prepared by method (I) and is blue in colour (Found Cu = 14.20%, N = 6.06%; C₂₂H₃₂O₄N₂Cu requires Cu = 14.07%, N = 6.20%).

7. Bi-benzoato, bi (iso-butylamino) copper (II). Prepared by method (I) and is blue in colour (Found Cu = 14.26%, N = 6.1%; C₂₂H₃₂O₄N₂Cu requires Cu = 14.07%, N = 6.20%).

8. Bi-benzoato, bi (Di-isopropylamino) copper (II). Prepared by method (I) and is blue in colour (Found Cu = 12.23%, N = 5.30%; C₂₆H₄₀O₄N₂Cu requires Cu = 12.51%, N = 5.52%).

9. Bi-benzoato, bi (pyridino) copper (II). Prepared by method (II). First the complex crystallizes with shining blue colour which changes to green colour after few hours (Found Cu = 13.58%, N = 5.88%; C₂₄H₂₀O₄O₂Cu requires Cu = 13.70%, N = 6.04%).

10. Bi-benzoato, bi (piperidino) copper (II). Prepared by both the methods and is blue in colour (Found Cu = 13.50%, N = 5.67%, C₂₄H₃₂O₄N₂Cu requires Cu = 13.35%, N = 5.89%).

11. Bi-benzoato, mono (ethylenediamino) copper (II). Prepared by both the methods and is violet in colour (Found Cu = 17.48%, N = 7.46%; $C_{16}H_{18}O_4N_2Cu$ requires Cu = 17.37%, N = 7.66%).

12. Bi-benzoato, mono (propylenediamino) copper (II). Prepared by both the methods and is violet in colour (Found Cu = 16.60%, N = 7.20%; $C_{17}H_{20}O_4N_2Cu$ requires Cu = 16.73%, N = 7.38%).

B. Determination of total base and molecular weight

Estimation of amine content and molecular weight measurements were done using the methods as outlined by PADMAJA SHUKLA and others¹⁰.

C. Conductivity measurements

Measurements were done in formamide, nitrobenzene and water at a concentration of 10^{-3} M. The cell used had a cell constant of 0.0248.

D. Spectral measurements

Spectra were recorded on a Unicam S.P. 500 spectrophotometer.

Results

The percentages of constituent elements have been given along with the synthesis of the complexes. The results of the determination of percentages of total base, molecular weights, molar conductances and visible absorption spectra are tabulated below.

Table 1

No.	Formula	Percentage of base		Molecular weight		Molar conductance in mhos	Spectral measurement λ max in μ
		Calc.	Obs.	Calc.	Obs.		
1	$[Cu(C_6H_5COO)_2(NH_3)_2]^0$	10.02	10.23	339.5	319	0.35	642
2	$[Cu(C_6H_5COO)_2(CH_3NH_2)_2]^0$	16.87	16.47	367.5	348	0.61	630
3	$[Cu(C_6H_5COO)_2(C_2H_5NH_2)_2]^0$	22.75	22.31	395.5	371	0.56	635
4	$[Cu(C_6H_5COO)_2(pr)_2]^0$	22.87	27.50	423.5	438	0.63	640
5	$[Cu(C_6H_5COO)_2(bu)_2]^0$	32.34	32.90	451.5	430	0.42	635
6	$[Cu(C_6H_5COO)_2(py)_2]^0$	34.09	34.26	463.5	446	0.58	630
7	$[Cu(C_6H_5COO)_2(pipe)_2]^0$	35.74	35.06	475.5	489	0.91	630
8	$[Cu(C_6H_5COO)_2(di-iso-pr)_2]^0$	39.81	39.24	507.5	483	0.93	650
9	$[Cu(C_6H_5COO)_2(en)]^0$	16.42	16.06	365.5	347	0.80	660
10	$[Cu(C_6H_5COO)_2(pn)]^0$	19.5	19.30	379.5	364	0.86	665

In the above table pr represents iso- and n-propylamine; bu represents iso- and n-butylamine; py represents pyridine; pipe represents piperidine; di-iso-pr represents di-isopropylamine; en represents ethylenediamine; pn represents propylenediamine.

¹⁰) PADMAJA SHUKLA and others, J. prakt. Chem. 28, 21 (1965).

Discussion

On the basis of the percentage of metal, nitrogen and total bases, the molecular formulae turn out to be $\text{Cu}(\text{benzoate})_2(\text{amine})_2$ and $\text{Cu}(\text{benzoate})_2(\text{amine})$ showing that two molecules of unidentate and one molecule of bidentate amines are added per molecule of copper (II) benzoate. These complexes dissolve in formamide and the solution has typical ink blue colour characteristic of cupric amine complexes. The pyridine complex is soluble only in nitrobenzene.

The molar conductance of these solutions (concn. 10^{-3} M) gives a value varying from 0.35 to 0.93 mhos. This value being less than one indicates, that these complexes behave as non-electrolytes¹¹). When a voltage is applied to two platinum electrodes dipping in the complex solution in a tube, no migration of the blue colour towards the negative electrode was noticed, showing, thereby that the complexes do not ionize.

The freezing point determination give the normal absolute value of molecular weight. These results suggest that benzoate ion is inside the coordination sphere, along with the two or one amine ligands. The formulae of the complexes must therefore be written as $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{am})_2]^0$ and $[\text{Cu}(\text{C}_6\text{H}_5\text{COO})_2(\text{am})]^0$.

The complexes dissolve in formamide, with the exception of the pyridine complex (which is soluble in nitrobenzene) and the solution shows a single absorption band in the range of 600—900 $\text{m}\mu$. This particular band arises due to some d—d transitions taking place inside the metal atom.

Copper (II) ion is a d^9 ion and its d—d spectrum can be discussed on the basis of crystal field theory in the same way as that of a d^1 ion, due to the general idea of "hole formalism" according to which a d^{10-n} ion will have the same behaviour in the crystal field, except for certain changes in the signs of energy terms, as a d^n ion¹²). In case of this ion, the ground state is associated with configuration $(t_{2g})^6(\text{eg})^3$ and excited level with $(t_{2g})^5(\text{eg})^4$. In the ground state the positron thus occupies a t_{2g} level from where it is excited to eg level providing energy.

The position of this band depends on the intensity of ligand field around the metal. Thus for tetraquo copper (II) ion the band is observed at 800 $\text{m}\mu$ and for a tetramine copper (II) ion at 600 $\text{m}\mu$. This bathochromic effect is due to the stronger amine field which causes the band to move from far red to the middle of the red region of the spectrum.

¹¹) R. S. NYHOLM, J. chem. Soc. London 1714 (1957).

¹²) F. A. COTTON and R. I. WILKINSON, *Inorganic Chemistry* (Intersciences publishers) 1862, p. 562.

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