AN X-RAY STUDY ON BIVALENT SILVER AND COPPER NICOTINATE COMPOUNDS*

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ABSTRACT. The X-ray diffraction data on bivalent silver and copper nicotinate compounds are given and the results are discussed in full details.

1. INTRODUCTION

The argentic compound of picolinic acid, an isomer of nicotinic acid, was prepared by Barbieri (1934). This compound along with the copper picolinate was studied by the X-ray diffraction method by Cox, Wardlaw and Webster (1936). The X-ray data for both the compounds were analyzed in detail, and it was concluded that the bivalent silver and copper compounds of picolinic acid were isomorphous.

Here in this communication we are extending our work to bivalent silver and copper nicotinates ($Ag[C_6H_4O_2N]_2$ and $Cu[C_6H_4O_2N]_2$) in order to obtain complete preliminary X-ray diffraction data, and then to analyze the data to see how the compounds are interlinked in their structural aggregation.

2. PREPARATION OF COMPOUNDS

To prepare copper nicotinate the aqueous solution of potassium nicotinate (7.0 gm in 20 c.c.) was added to a hot aqueous copper acetate solution (4.0 gm in 60 c.c.) with constant stirring. On cooling, the precepitate of copper nicotinate separated, which was filtered, and dried at 110°C. The cupric nicotinate was obtained as bluish white powder. The amount of copper estimated was 20.6% which agrees well with the theoretically calculated value, namely 20.66%. Argentic nicotinate has been prepared by Banerjee and Roy (1955) by a special process and it is brick red in colour and microcrystalline in nature.

The bivalent compounds of silver and copper are paramagnetic. The magnetic behaviour of these two substances were also studied and were found out to be paramagnetic. The μ_B values for argentic and cupric nicotinates were 1.74 and 1.89 respectively.

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3. X-RAY DIFFRACTION RESULTS

The X-ray pictures were taken in copper radiation at 35 kv. and 15 mA. in a cylindrical camera of radius 4.13 cm., the radius being standardised with the help of known spacings of aluminium lines. The glancing angles θ's of the X-ray pictures of silver and copper nicotinates were calculated in the usual way and the spacings 'd' were obtained from the Bragg equation. The 'd' values are given in kX units (1 kX unit = 1.002Å). The data are tabulated in Tables I and II, and θ, d and visually estimated intensities of the lines are given side by side. As far as possible the spacing for Cuβ lines are eliminated.

TABLE I

Argentic nicotinate (Ag[C$_6$H$_4$O$_2$N]$_2$)

No. of lines	θ	d in kX units	Intensity
1	6°.330	6.982	v.s.
2	8°.932	4.958	v.s.
3	10°.49	4.233	s.
4	11°.45	3.879	m.s.
5	12°.75	3.489	m.s.
6	14°.05	3.172	m.
7	14°.83	3.007	s.
8	16°.82	2.662	m.
9	17°.86	2.505	m.
10	19°.51	2.305	m.w.
11	20°.46	2.203	v.s.
12	21°.43	2.108	w.
13	22°.28	2.032	m.
14	23°.13	1.960	s.
15	23°.93	1.898	v.w.
16	24°.62	1.848	w.
17	25°.66	1.778	m.w.
18	26°.91	1.701	w.
19	28°.62	1.608	m.
20	29°.31	1.573	m.w.
21	30°.09	1.536	w.
22	32°.51	1.433	w.

TABLE I (*contd.*)

No. of lines	θ	d in kX units	Intensity
23	33°.3	1.403	w.
24	34°.68	1.353	w.
25	35°.46	1.327	w.
26	36°.76	1.286	w.
27	37°.71	1.259	w.
28	39°.96	1.199	v.w.
29	42°.32	1.144	v.w.
30	43°.18	1.126	v.w.
31	45°.44	1.081	v.w.
32	46°.13	1.068	v.w.
33	47°.17	1.050	v.w.
34	47°.68	1.041	v.w.
35	48°.64	1.026	w.
36	50°.46	.9986	m.w.

TABLE II

Cupric nicotinate ($Cu[C_6H_4O_2N]_2$)

No. of lines	θ	d in kX unit	Intensity
1	6°.501	6.801	v.s.
2	7°.803	5.671	m.s.
3	8°.670	5.110	m.s.
4	10°.06	4.411	s(broad)
5	11°.36	3.823	m.s.
6	12°.48	3.563	v.s.
7	13°.53	3.291	m.s.
8	14°.85	2.997	s.
9	16°.99	2.636	m.s.(broad)
10	19°.04	2.361	v.s.
11	21°.76	2.077	m.
12	22°.72	1.1994	m.s.(broad)
13	25°.49	1.789	m.
14	32°.60	1.429	w.

4. DISCUSSION OF RESULTS

From Tables I and II it appears that the silver salt of nicotinic acid is a bett er crystalline substance than copper nicotinate. Also there are certain X-ray lines in copper nicotinate which are broad and are likely to be due to disorder in lattices. If the d values are compared, it will be seen that certain spacings of both the tables are similar. The similar spacings are tabulated in Table III.

TABLE III

d in kx unit (Silver nicotinate)	d in kx unit (Copper nicotinate)
6.98	6.80
4.96	5.11
3.88	3.82
3.49	3.56
3.17	3.29
3.01	3.00
2.66	2.64
2.31	2.36
3.01	3.00
2.66	2.64
2.03	2.08
1.96	1.99
1.78	1.79
1.43	1.43

This similarity of spacings of both the substances suggests that copper and silver nicotinates may be isomorphous. Practically line to line spacings of copper compound have similarity with those of silver compound. The extra lines appearing in both the pictures, particularly the argentic nicotinate, are either due to better degree of crystallinity in certain direction or in whole of the aggregates. This type of isomorphism is quite likely. In fact in the paper of Cox, Wardlaw and Webster (1936) certain extra lines appeared in both copper and silver salts (more lines in silver salt) of picolinic acid, an isomer of nicotinic acid, but their general X-ray patterns, as in our case, agreed quite well.

Due to different atomic scattering factors of copper and silver, the intensities of all the similar lines are not identical.

Further X-ray studies are being undertaken by one of the authors (D. M. C.) and a detailed interpretation of the lines from the lattice structure will be published later.

REFERENCES

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