

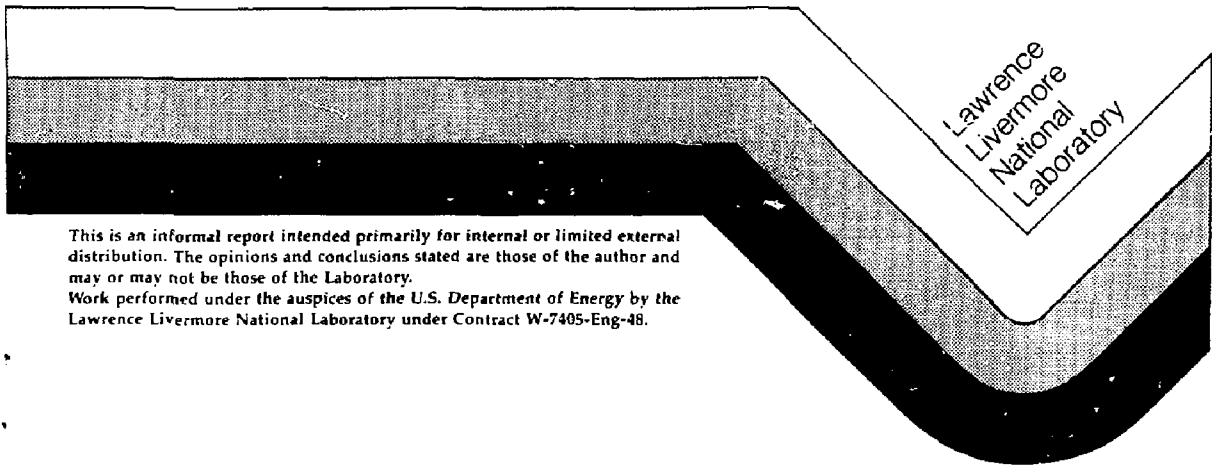
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X-RAY DIFFRACTION PATTERNS OF  
METAL AUROCYANIDES

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and  
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## X-Ray Diffraction Patterns of Metal Aurocyanides

Walter S. Selig, Gordon S. Smith, Kerstin K. Harding, and Leslie J. Summers

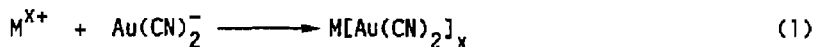
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### ABSTRACT

Aurocyanides of the following metal cations have been prepared: Ag, Hg(II), Ga, Fe(III), Tl(I), Bi, Pb, Mn(II), Ni, Zn, Cu(II), Cd, In, and Co(II). Most of the aurocyanides are of the type  $M[Au(CN)_2]_x$  where M is the metal cation and x its valence. However, under some conditions mixed aurocyanides containing K may be formed, such as  $KCo[Au(CN)_2]_3$ . Only Ag and Hg(II) form aurocyanides which are sufficiently insoluble for the potentiometric determination of the aurocyanide anion. The diffraction patterns of the various aurocyanides are reported.

### INTRODUCTION

We have previously reported new analytical methods for the determination of aurocyanide ion,  $Au(CN)_2^-$ , by potentiometric titration with silver ions (1) or with mercuric ions (2), according to the equation



where M is the metal cation and x its valence.

Very little information is available on metal aurocyanides (3, 4). We have therefore prepared several metal aurocyanides and report their X-ray diffraction patterns here.

### EXPERIMENTAL

Potassium aurocyanide, from Engelhard, had a nominal gold content of 68%. The metal salts, with the exception of mercuric acetate, were nitrates. Their

nominal degree of hydration is shown in Table 1. Unmodified aqueous solutions of the materials were prepared at a concentration of 0.25 M. The solution of mercuric acetate was acidified to pH 1.25 with 1 M nitric acid, and bismuth nitrate was prepared in 1 M nitric acid.

The metal aurocyanides were prepared by adding a 100% excess of the metal salt solution to 10 mL of 0.25 M aurocyanide solution, heating on a hot-plate to near boiling, and cooling to ambient temperature. The resulting precipitates were filtered on No. 541 Whatman paper, washed thoroughly with deionized water, and air-dried at ambient temperature for at least 48 hrs.

X-ray diffraction patterns were obtained with  $\text{CuK}\alpha$  radiation,  $\lambda=1.54050 \text{ \AA}$ .

Table 1. Nominal degree of hydration of metal salts used

Cation	Number of water molecules <sup>a</sup>
Mn	51% solution
Fe(III)	9
Co(II)	6
Ni	6
Cu	2.5
Zn	6
Ga	9
Rh	3
Pd(II)	2
Ag	0
Cd	4
In	5
Hg(II)	0
Tl(I)	0
Pb	0
Bi	5

<sup>a</sup> according to supplier

## RESULTS AND DISCUSSION

Titrimetric methods for the determination of gold in plating solutions and in potassium aurocyanide usually require oxidation of gold from the monovalent to the trivalent state. After this conversion, various redox methods (5) are available for the determination. Another technique, controlled-potential coulometry, has been used at LLNL for many years as the primary assay technique for plating solutions (6, 7). This technique also requires that gold be in the trivalent state. This conversion requires treatment with aqua regia. Monovalent gold as aurocyanide can be determined without such treatment, using silver (1) or mercuric (2) ions as titrants, according to equation (1). The methods can be applied on the microscale, with  $10^{-3}$  M solutions, using a 0.01 M titrant.

According to an ancient reference (8) potassium aurocyanide yields precipitates with Fe(II), Cu(II), Zn, Ag, Hg(II), and Pb ions. This prompted us to attempt using these cations as possible titrants for aurocyanide. We found that only Ag and Hg(II) ions yielded precipitates in very dilute solutions. The other cations, as well as those listed in Table 1, yielded precipitates only in more concentrated solutions, as outlined in the experimental section. This indicates that except for silver and mercuric aurocyanide, the aurocyanides have appreciable solubility in water. Fe(II) did not yield a precipitate even from 0.25 M solution.

To the best of our knowledge only the aurocyanides of Ag (4), Tl(I) (9), and Co(II) (10) have been reported in the literature. Only for the cobalt compound have X-ray powder patterns been reported (patterns nos. 31-420 and 31-565 in reference 11). This work was done by Eisenmann who reported the compound  $\text{KCo}[\text{Au}(\text{CN})_2]_3$ , formed by using an excess of potassium aurocyanide, according to the equation



We confirmed the formation of this compound and have listed its diffraction pattern in Table 15. The pattern is similar, though not identical, with that presented in reference 11. The presence of potassium was confirmed by X-ray fluorescence spectroscopy (>1% found vs a theoretical 4.6%). Eisenmann found that recrystallization of  $\text{KCo}[\text{Au}(\text{CN})_2]_3$  from water

resulted in a compound yielding a different diffraction pattern, which contained no potassium and had a Au:Co ratio of 2:1,  $\text{CoAu}[\text{CN}]_2$ . The diffraction pattern of the decahydrate of this compound is listed as no. 31-420 in reference 11. We obtained a similar, though not identical, diffraction pattern by using an excess of potassium aurocyanide in the formation of this compound as shown in Table 16. This compound, as well as the others listed in the tables, were formed according to equation (1). Further work needs to be done to determine whether equation (2) applies in every case where an excess of the heavy metal nitrate is used.

Rh(III) yielded an amorphous material with potassium aurocyanide, while Pd(II) produced a weakly crystalline material.

We have previously found that the powder pattern of silver aurocyanide is isomorphous with that of AuCN (12). The diffraction patterns of the aurocyanides of Bi, Pb, Ni, Cu, Cd, and Co (Tables 7, 8, 10, 12, 13, and 16) also appear to be isomorphous.

#### ACKNOWLEDGMENT

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Table 2. X-ray diffraction pattern of  $\text{Ag}[\text{Au}(\text{CN})_2]$

d(Å)	height	d(Å)	height
5.12	64	1.615	8
2.953	100	1.600	4
2.570	61	1.511	3
1.712	22	1.481	14
1.705	17	1.105	1

Table 3. X-ray diffraction pattern of  $\text{Hg}[\text{Au}(\text{CN})_2]_2$ 

d(Å)	height	d(Å)	height
8.91	17	1.795	21
7.44	<1	1.677	11
4.73	11	1.648	10
4.47	78	1.627	17
4.18	72	1.600	23
3.349	3	1.581	21
3.253	8	1.557	28
3.136	100	1.540	29
2.992	67	1.528	18
2.840	77	1.500	8
2.525	24	1.494	14
2.490	39	1.478	4
2.368	19	1.462	6
2.231	44	1.429	12
2.117	50	1.429	10
2.094	24	1.423	8
2.025	4	1.398	15
1.916	41	1.338	9
1.859	3	1.317	9
1.820	2	1.302	7



Table 4. X-ray diffraction pattern of  $\text{Ga}[\text{Au}(\text{CN})_2]_3$

d(Å)	height	d(Å)	height
15.45	5	2.579	35
10.27	51	2.395	2
7.76	2	2.312	31
5.15	94	2.063	4
3.851	2	1.988	33
3.434	17	2.802	10
3.118	100	1.776	7
2.988	64	1.720	17
2.846	3	1.701	8
2.671	49	1.595	3
2.631	49	1.562	3

Table 5. X-ray diffraction pattern of  $\text{Fe}[\text{Au}(\text{CN})_2]_3$

d(Å)	height	d(Å)	height
10.22	52	2.067	7
5.15	100	1.983	35
2.440	22	1.792	8
3.093	70	1.763	7
2.961	47	1.723	21
2.653	43	1.691	8
2.582	46	1.590	4
2.301	29		

Table 6. X-ray diffraction pattern of  $Tl[Au(CN)_2]$ 

d(Å)	height	d(Å)	height
7.51	3	2.235	14
6.87	5	2.218	8
5.76	7	2.189	10
4.87	3	2.151	37
4.59	15	2.104	100
4.49	27	2.080	9
4.41	25	1.999	2
4.10	10	1.960	13
3.903	9	1.958	6
3.792	12	1.936	10
3.717	38	1.919	11
3.587	3	1.891	12
3.424	2	1.879	5
3.206	97	1.865	6
3.140	71	1.838	1
3.056	11	1.796	4
2.989	83	1.771	11
2.919	5	1.755	5
2.879	6	1.727	10
2.798	21	1.699	4
2.764	4	1.675	22
2.696	8	1.659	3
2.629	2	1.643	7
2.590	26	1.635	10
2.531	22	1.616	5
2.383	4	1.607	14
2.354	17	1.583	18
2.306	9	1.548	12
2.283	12		

Table 7. X-ray diffraction pattern of  $\text{Bi}[\text{Au}(\text{CN})_2]_3$ 

d(Å)	height	d(Å)	height
11.86	2	2.442	70
9.13	40	2.283	45
5.97	16	2.250	16
5.49	2	2.212	2
4.88	56	2.126	20
4.56	100	2.096	10
3.965	5	2.049	2
3.870	9	2.006	2
3.509	7	1.888	7
3.243	22	1.825	5
3.136	26	1.792	41
3.093	5	1.775	15
3.044	16	1.741	23
3.004	3	1.670	8
2.930	30	1.642	4
2.758	18	1.629	6
2.731	11	1.601	7
2.693	33	1.581	7
2.635	12	1.568	15

Table 8. X-ray diffraction pattern of  $\text{Pb[Au(CN)}_2\text{]}_2$ 

d(Å)	height	d(Å)	height
9.73	12	2.229	36
6.54	7	2.198	40
6.08	1	2.167	13
5.44	7	2.142	2
5.15	1	2.087	5
4.88	100	2.044	1
4.75	22	1.999	12
4.27	13	1.983	9
3.924	4	1.967	6
3.804	1	1.924	6
3.699	7	1.910	5
3.440	20	1.881	3
3.408	21	1.852	12
3.329	5	1.817	5
3.290	16	1.814	5
3.261	10	1.784	2
3.149	25	1.758	3
3.118	44	1.732	14
3.047	17	1.705	7
2.912	80	1.686	12
2.839	51	1.667	3
2.811	14	1.651	17
2.732	5	1.635	33
2.706	8	1.625	13
2.611	6	1.612	5
2.591	8	1.603	11
2.451	62	1.588	14
2.371	4	1.567	7
2.319	26		

Table 9. X-ray diffraction pattern of  $\text{Mn}[\text{Au}(\text{CN})_2]_2$ 

d(Å)	height	d(Å)	height
15.41	13	2.242	6
8.01	80	2.216	1
7.72	5	2.159	16
5.92	10	2.108	14
5.16	26	2.005	34
4.75	69	1.984	36
4.01	59	1.957	8
3.876	3	1.920	11
3.424	7	1.898	4
3.319	14	1.801	2
3.149	45	1.789	2
3.101	4	1.774	3
3.036	17	1.726	5
2.964	69	1.713	19
2.829	3	1.675	14
2.781	100	1.660	24
2.699	6	1.611	6
2.675	40	1.603	6
2.617	10	1.590	9
2.588	11	1.575	23
2.435	15	1.548	8
2.383	88		

Table 10. X-ray diffraction pattern of  $\text{Ni}[\text{Au}(\text{CN})_2]_2$ 

d(Å)	height	d(Å)	height
10.13	3	2.559	16
7.62	51	2.340	91
5.87	9	2.231	7
5.10	4	2.144	16
4.67	66	2.047	14
3.830	39	1.935	38
3.403	7	1.907	10
3.216	16	1.828	3
3.110	43	1.752	2
3.036	3	1.706	12
2.949	68	1.684	11
2.819	2	1.666	14
2.754	100	1.641	1
2.699	1	1.611	29
		1.560	29

Table 11. X-ray diffraction pattern of  $\text{Zn}[\text{Au}(\text{CN})_2]_2$ 

d(Å)	height	d(Å)	height
6.78	41	2.106	19
4.98	5	2.014	47
4.11	100	1.952	3
4.12	15	1.683	27
3.593	69	1.821	13
3.257	12	1.773	4
3.220	13	1.718	7
2.976	64	1.672	37
2.731	61	1.631	3
2.433	65	1.595	34
2.294	82	1.552	32
2.199	1		

Table 12. X-ray diffraction pattern of  $\text{Cu}[\text{Au}(\text{CN})_2]_2$ 

d(Å)	height	d(Å)	height
10.12	93	2.319	15
6.01	6	2.283	13
5.10	100	2.261	9
3.409	28	2.142	3
3.335	10	2.047	6
3.162	40	1.991	13
3.068	30	1.967	15
3.019	66	1.954	15
2.938	22	1.820	6
2.897	17	1.787	6
2.687	20	1.708	20
2.628	18	1.646	3
2.602	21	1.584	3
2.559	40	1.562	1

Table 13. X-ray diffraction pattern of  $\text{Cd}[\text{Au}(\text{CN})_2]_2$

d(Å)	height	d(Å)	height
8.09	72	2.132	9
5.89	1	2.047	53
4.76	18	2.008	11
4.07	100	1.963	1
3.409	1	1.935	1
3.358	3	1.919	5
3.149	13	1.732	6
2.957	17	1.712	3
2.777	16	1.686	20
2.725	35	1.675	2
2.477	14	1.640	4
2.397	25	1.612	3
2.240	1	1.602	3
2.159	6	1.580	12



Table 14. X-ray diffraction pattern of  $\text{In}[\text{Au}(\text{CN})_2]_3$ 

d(Å)	height	d(Å)	height
7.97	33	1.657	16
5.70	1	1.647	43
4.66	78	1.624	13
4.01	34	1.607	3
3.309	5	1.559	12
3.060	40	1.548	8
2.868	74	1.533	26
2.699	61	1.447	6
2.674	13	1.437	10
2.556	1	1.411	11
2.428	21	1.404	11
2.335	100	1.370	6
2.169	2	1.352	14
2.094	29	1.341	4
2.083	21	1.300	5
2.009	13	1.293	7
1.959	23	1.280	14
1.909	1	1.267	6
1.862	11	1.239	4
1.729	1	1.232	2
1.686	18	1.215	14

Table 15. X-ray diffraction pattern of  $\text{KCo[Au(CN)}_2\text{]}_3$ 

d(Å)	height	d(Å)	height
7.751	100	2.147	11
5.901	7	2.067	12
4.706	43	1.951	46
3.897	55	1.910	8
3.408	4	1.852	4
3.252	12	1.758	2
3.123	27	1.707	13
2.953	42	1.696	10
2.761	61	1.667	10
2.599	28	1.628	31
2.381	14	1.605	5
2.354	63	1.563	22
2.235	5		

Table 16. X-ray diffraction pattern of  $\text{Co[Au(CN)}_2\text{]}_2$   
(or decahydrate)

d(Å)	d(Å) height	height	
10.040	8	2.051	3
5.093	15	1.996	10
3.409	5	1.941	19
3.184	55	1.800	30
3.040	42	1.772	17
2.972	100	1.699	23
2.853	54	1.685	25
2.706	18	1.663	8
2.564	43	1.597	27
2.328	12	1.578	9
2.241	19		