

## Configurational Correlations of *cis*-Bis(2,2'-bipyridine) and of *cis*-Bis(1,10-phenanthroline) Complexes of Trivalent Metals by Means of X-Ray Powder Photographs

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Series of *cis*-bis(2,2'-bipyridine) and of *cis*-bis(1,10-phenanthroline) complexes of trivalent metals have been investigated by X-ray powder photograph techniques and the compounds within each series are in this way shown to be isomorphous. The series investigated are [Mphen<sub>2</sub>Cl<sub>2</sub>]Cl.aq (two series), [Mphen<sub>2</sub>C<sub>2</sub>O<sub>4</sub>]Cl.4H<sub>2</sub>O, [Mphen<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](NO<sub>3</sub>)<sub>3</sub>.2H<sub>2</sub>O, [Mbipy<sub>2</sub>Cl<sub>2</sub>]Cl.2H<sub>2</sub>O, [Mbipy<sub>2</sub>Cl<sub>2</sub>]Cl.HCl.2H<sub>2</sub>O, and [Mbipy<sub>2</sub>OH(H<sub>2</sub>O)](ClO<sub>4</sub>)<sub>2</sub> (phen = 1,10-phenanthroline, bipy = 2,2'-bipyridine, and M = Cr, Co, Rh, Os, and Ir, or some of these metals). Observed *d*-spacings are given for all the compounds. Some of the photographs have been indexed and here also the calculated *d*-spacings and the unit cell dimensions are given.

It is concluded that the stereochemical configuration of the cations is the same within each series, *i.e.* a correlation of the Cr(III), Co(III), Rh(III), Os(III), and Ir(III) complexes, and on the basis of the preparations and of the chemical and the spectral similarities of the compounds it is concluded that all the complexes investigated have the same stereochemical configuration. Other workers, including those from this laboratory, have shown that this configuration is *cis*.

In some recent papers from this laboratory<sup>1,2</sup> it was stated that series of compounds containing the ions [M(III)bipy<sub>2</sub>X<sub>2</sub>]<sup>n+</sup> and [M(III)phen<sub>2</sub>X<sub>2</sub>]<sup>n+</sup> were all *cis*-octahedral complexes (M = Cr, Co, Rh, and Ir; X = Cl, F, and H<sub>2</sub>O; bipy = 2,2'-bipyridine and phen = 1,10-phenanthroline). This statement was based upon comparisons of ligand field spectra within the chromium(III) and cobalt(III) series, and upon extensive chemical evidence within the chromium(III) series. This evidence can be summarized by the following key properties: their parentage correlation to the oxalatobis(N-N) complexes and di- $\mu$ -hydroxo-bis[bis(N-N)chromium(III)] complexes (the diols), their chiral properties, and their chemical interconvertibility coupled with the apparent existence of only one isomer in each case where a *cis* and a *trans* isomer could be expected. Further, comparisons of X-ray powder photographs on some



Table 3. X-Ray powder data of crystal series III - V.

Series III		Series IV		Series V	
h k l	[Cr pheng <sub>4</sub> ] Cl <sub>1</sub> -2R <sub>0</sub> 0	[Co pheng <sub>4</sub> ] <sub>1</sub> Cl <sub>1</sub> -2R <sub>0</sub> 0	[Cr/Co pheng <sub>4</sub> ] <sub>1</sub> Cl <sub>1</sub> -2R <sub>0</sub> 0	[Co pheng <sub>4</sub> ] <sub>2</sub> Cl <sub>1</sub> -2R <sub>0</sub> 0	[Cr/Co pheng <sub>4</sub> ] <sub>2</sub> Cl <sub>1</sub> -2R <sub>0</sub> 0
	I <sub>obs</sub> d <sub>obs</sub> (Å) d <sub>calc</sub> (Å)	I <sub>obs</sub> d <sub>obs</sub> (Å) d <sub>calc</sub> (Å)	I <sub>obs</sub> d <sub>obs</sub> (Å) d <sub>calc</sub> (Å)	I <sub>obs</sub> d <sub>obs</sub> (Å) d <sub>calc</sub> (Å)	I <sub>obs</sub> d <sub>obs</sub> (Å) d <sub>calc</sub> (Å)
0 2 0	11.648	11.652	11.825	9.162	9.181
1 0 0	11.174	11.174	11.825	8.723	8.723
1 0 2	8.246	8.237	8.112	8.195	8.172
1 1 0	7.626	7.614	7.659	7.186	7.192
0 2 2	6.926	6.917	6.855	6.951	6.945
1 1 1	6.722	6.720	6.959	6.214	6.216
1 1 2	6.494	6.496	6.572	6.222	6.238
2 2 0	5.765	5.757	5.730	4.721	4.734
0 4 1 0	5.779	5.588	5.585	4.626	4.634
1 2 0	5.482	5.480	5.585	4.156	4.154
2 0 2	5.274	5.287	5.085	4.052	4.051
1 4 1	5.025	5.030	5.085	3.821	3.823
1 1 3	4.894	4.890	5.087	3.726	3.807
1 2 0	4.565	4.565	4.591	3.657	3.727
2 1 3	4.225	4.222	4.225	3.547	3.652
2 1 5	4.095	4.094	4.225	3.475	3.555
0 6 0 0	3.874	3.874	3.940	3.471	3.550
1 2 4	3.727	3.726	3.668	3.337	3.420
2 5 1	3.615	3.616	3.666	3.342	3.380
1 6 1	3.456	3.459	3.499	3.264	3.267
2 0 4	3.426	3.421	3.421	3.219	3.219
2 1 5	3.322	3.325	3.298	3.215	3.219
2 2 2				3.184	3.180
				2.932	2.927
				2.926	2.901
				2.902	
				3.205	
				3.456	
				3.368	
				3.281	
				3.267	
				3.554	
				3.514	
				3.526	
				3.488	
				3.956	
				4.047	
				4.085	
				3.584	
				3.584	
				4.675	
				4.560	
				4.521	
				4.357	
				4.371	
				4.348	
				4.136	
				4.047	
				4.085	
				3.584	
				3.584	
				3.554	
				3.514	
				3.526	
				3.488	
				3.205	
				3.267	
				3.281	
				3.368	
				3.456	

the diffraction lines were measured and their intensities estimated. For four of the series (I–IV) the diffraction lines were indexed and the unit cell dimensions were calculated (Table 5).

### EXPERIMENTAL

X-Ray powder photographs were all taken with  $\text{CuK}\alpha$  radiation using a focussing camera of the Guinier type calibrated with silicon at 25°C.

The methods of preparation, analyses and spectra of the Rh, Os, and Ir complexes referred to in Ref. 1 and in this publication will shortly appear as part of another publication.<sup>4</sup> Methods of preparation and analyses of the investigated Cr and Co complexes can be found elsewhere.<sup>3</sup>

Table 4. X-Ray powder data of crystal series VI and VII.

[Cr bipy <sub>2</sub> Cl <sub>2</sub> ]Cl·HCl·2H <sub>2</sub> O		[Rh bipy <sub>2</sub> Cl <sub>2</sub> ]Cl·HCl·2H <sub>2</sub> O		[Cr/Rh bipy <sub>2</sub> Cl <sub>2</sub> ]Cl·HCl·2H <sub>2</sub> O		[Cr bipy <sub>2</sub> OH(H <sub>2</sub> O)](ClO <sub>4</sub> ) <sub>2</sub>		[Co bipy <sub>2</sub> OH(H <sub>2</sub> O)](ClO <sub>4</sub> ) <sub>2</sub>	
I <sub>obs</sub>	d <sub>obs</sub> (Å)	I <sub>obs</sub>	d <sub>obs</sub> (Å)	I <sub>obs</sub>	d <sub>obs</sub> (Å)	I <sub>obs</sub>	d <sub>obs</sub> (Å)	I <sub>obs</sub>	d <sub>obs</sub> (Å)
ms	9.123	ms	9.168	a	9.130	mw	8.391	n	8.357
a	7.502	a	7.516	va	7.516	a	7.775	n	7.721
ms	7.061	a	7.073	a	7.049	vw	6.871	w	6.790
n	6.735	n	6.745	ms	6.735	vw	5.937	w	5.864
vw	6.007	vw	6.001	v	6.046	vw	4.964	vwv	5.068
vw	5.708	vw	5.699	v	5.997	v	4.834	vw	4.942
vw	5.173	vw	5.175	v	5.716	v	4.585	w	4.753
n	4.880	mw	4.877	v	5.181	v	4.275	w	4.549
mw	4.467	v	4.470	mw	4.464	vw	4.250	mw	4.232
n	4.384	n	4.381	n	4.384	vw	4.208	mw	4.182
ms	4.157	n	4.159	n	4.157	v	4.167	mw	4.143
v	3.852	n	3.850	vw	3.850	v	4.077	w	4.055
mw	3.561	mw	3.563	n	3.561	vw(br)	3.950	vw(br)	3.900
ms	3.374	mw	3.374	ms	3.372	n	3.630	n	3.584
va	3.298	n	3.293	va	3.292				
v	3.202			vw	3.199				

Table 5. Unit cell dimensions for the crystal series I–IV. The specific densities have been measured (by flotation in pentachloroethane and 1-bromonaphthalene mixtures) for some of the compounds.

Crystal series	a (Å)	b (Å)	c (Å)	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	Volume of unit cell (Å <sup>3</sup> )	Spec. density obs. (g/ml)	Spec. density calc. (g/ml)	
I	Cr phen <sub>2</sub> Cl <sub>2</sub> Cl · 4H <sub>2</sub> O <sup>a</sup>	12.48	13.60	15.68	90.0	100.3	90.0	2619		
	Co phen <sub>2</sub> Cl <sub>2</sub> Cl · 3.5H <sub>2</sub> O <sup>b</sup>	12.27	13.50	15.33	90.0	99.4	90.0	2505		
	Cr phen <sub>2</sub> Cl <sub>2</sub> NO <sub>2</sub> · 3.5H <sub>2</sub> O	12.77	13.48	15.45	90.0	100.0	90.0	2620		
	Co phen <sub>2</sub> Cl <sub>2</sub> NO <sub>2</sub> · 3H <sub>2</sub> O	12.41	13.49	15.28	90.0	98.8	90.0	2528		
	Rh phen <sub>2</sub> Cl <sub>2</sub> NO <sub>2</sub> · 3H <sub>2</sub> O	12.66	13.41	15.53	90.0	98.9	90.0	2606	1.670	1.657
	Ir phen <sub>2</sub> Cl <sub>2</sub> NO <sub>2</sub> · 3H <sub>2</sub> O	12.85	13.40	15.55	90.0	99.1	90.0	2640		
II	Cr bipy <sub>2</sub> Cl <sub>2</sub> Cl · 2H <sub>2</sub> O	7.040	12.38	13.03	90.8	93.5	100.0	1117	1.507	1.507
	Co bipy <sub>2</sub> Cl <sub>2</sub> Cl · 2H <sub>2</sub> O	7.005	12.26	12.89	91.6	93.3	100.1	1088	1.560	1.568
	Rh bipy <sub>2</sub> Cl <sub>2</sub> Cl · 2H <sub>2</sub> O	7.018	12.40	13.00	90.8	93.4	100.1	1111		
	Ir bipy <sub>2</sub> Cl <sub>2</sub> Cl · 2H <sub>2</sub> O	7.048	12.43	13.03	90.0	93.5	100.5	1121		
III	Cr phen <sub>2</sub> Cl <sub>2</sub> Cl · 2H <sub>2</sub> O <sup>c</sup>	12.74	23.24	16.47	90.0	90.0	90.0	4879		
	Cr/Co phen <sub>2</sub> Cl <sub>2</sub> Cl · 2H <sub>2</sub> O	12.74	23.24	16.32	90.0	90.0	90.0	4835		
	Co phen <sub>2</sub> Cl <sub>2</sub> [CoCl <sub>2</sub> ] · 2H <sub>2</sub> O <sup>d</sup>	12.67	23.64	16.25	90.0	90.0	90.0	4871	1.645	1.659
IV	Cr phen <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [(NO <sub>2</sub> ) <sub>2</sub> · 2H <sub>2</sub> O] <sup>e</sup>	9.540	32.78	9.032	90.0	90.0	90.0	2824		
	Cr/Co phen <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [(NO <sub>2</sub> ) <sub>2</sub> · 2H <sub>2</sub> O]	9.569	32.71	9.029	90.0	90.0	90.0	2826	1.592	1.584

<sup>a</sup> Ref. 7 finds  $a=15.7$  Å,  $b=13.6$  Å,  $c=12.5$  Å;  $\beta=100.5^\circ$ .

<sup>b</sup> Ref. 8 finds  $a=15.46$  Å,  $b=13.50$  Å,  $c=12.28$  Å;  $\beta=90.2^\circ$  (99<sup>88</sup>).

<sup>c</sup> Ref. 7 finds  $a=12.8$  Å,  $b=23.3$  Å,  $c=16.4$  Å; spec. dens. (exp.): 1.50; (calc.): 1.51.

<sup>d</sup> Although the number of diffraction lines is rather low, this compound has been included as a member of series III, to show that it has been possible to index all the diffraction lines in correspondence with those of the chlorides, and to show the good agreement between the observed and the calculated specific densities (four formula units *per* unit cell in the tetrachlorocobaltate(II) in contrast to eight formula units in the chlorides).

<sup>e</sup> Ref. 13 finds  $a=9.49$  Å,  $b=32.2$  Å,  $c=9.03$  Å.

## RESULTS

The X-ray results are given in Tables 1 – 5. Here the complexes are divided into the series I – VII. Within each series the diffraction patterns of the X-ray powder photographs are almost identical as can be seen from the tables. On this basis we find it safe to conclude that the crystals within each series are closely related in structure and accordingly that the cations within each series have the same configuration of atoms. In this conclusion the composition of the complex molecules (the presence of the large phenanthroline or bipyridine molecules) has been taken into consideration – in contrast to the actual complexes it might be difficult, if not impossible, to distinguish in this way between, *e.g.*, *cis*- and *trans*- $[M(NH_3)_4(H_2O)_2]^{n+}$ . A discussion of the relation between similar powder photographs and the associated crystal structures can be found along with an X-ray powder investigation of tris-(diamine) complexes.<sup>5</sup>

It is remarkable that  $Cl^-$  and  $NO_3^-$  in series I can replace one another without changing the diffraction pattern very much and that the number of water molecules of crystallization may vary. This must be connected with the size and rigidity of the cation, and with the fact that the cation dominates the diffraction pattern (there is only one rather light anion and 2 – 4 water molecules of crystallization per cation). This isomorphous replacement of the anion in  $[Mphen_2Cl_2]^+$ -salts has been observed by others<sup>6,7</sup> – the anions including  $Cl^-$  and  $NO_3^-$  (series I),  $Br^-$ ,  $SCN^-$  and  $N_3^-$ .

Besides the correlation of the Cr, Co, Rh, Os, and Ir complexes through the series I and II, we have established the series III – VII, which correlate Cr and Co (in series VI also Cr and Rh) in other bis(2,2'-bipyridine) and bis(1,10-phenanthroline) complexes. Two metals appear in some of the compounds due to syncrystallization.

Two forms of the  $[Mphen_2Cl_2]Cl.aq$  crystals are found. The dichloro-complexes of series III correspond in diffraction pattern to those called  $\delta$ -*cis* in an investigation by Gibson and McKenzie,<sup>7</sup> whereas the dichloro-complexes of series I correspond to their  $\alpha$ -*cis*.<sup>7</sup> The crystal series II corresponds to their  $\alpha$ -*cis*-bis(2,2'-bipyridine) complexes.<sup>7</sup>

The unit cell volumes of the compounds of series I – IV are given in Table 5 together with some of the specific densities (observed and calculated). They are in good agreement with what was found from the investigation of some tris(diamine) complexes of Cr(III), Co(III), and Rh(III)<sup>5</sup> on the point that they indicate similar metal-ligand distances for Cr(III) and Rh(III) and somewhat shorter distances for Co(III). Here Os(III) and Ir(III) find their place in the neighbourhood of Cr(III) and Rh(III).

## CONCLUSIONS

On the basis of the results obtained through X-ray powder photographs, of the preparations, and of the chemical and the spectral similarities of the compounds, we find it safe to conclude that all the complexes investigated here have the same stereochemical configuration. The X-ray part of the work leads to this conclusion within each of the crystal series I – VII, *i.e.* correlates

Cr(III), Co(III), Rh(III), Os(III), and Ir(III); and the other properties of the compounds extend the conclusion to concern all the complexes involved.

The spectral results and interconversion reactions<sup>1,3</sup> mentioned above further show that the configuration is *cis*. This is in agreement with a single crystal X-ray analysis of  $[\text{Cophen}_2\text{Cl}_2]\text{Cl}\cdot 3\text{H}_2\text{O}$  by Ablov *et al.*,<sup>8</sup> who find it to have the *cis*-configuration; this violet salt is a member of our crystal series I.

While a lot of evidence for the existence of *cis*-bis(phenanthroline) and *cis*-bis(bipyridine) complexes now turns up<sup>7,9-12</sup> we have not been able to find any evidence of the corresponding *trans*-complexes.

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