Configurational Correlations of *cis*-Bis(2,2′-bipyridine) and *cis*-Bis(1,10-phenanthroline) Complexes of Trivalent Metals

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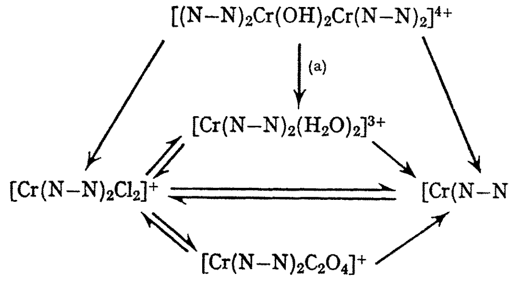
THE new compounds[1] *cis*-[Cr bipy$_2$ F$_2$]ClO$_4$ and *cis*-[Cr phen$_2$ F$_2$]ClO$_4$, together with the known compounds *cis*-[Cr(N–N)$_2$ Cl$_2$]Cl,aq and *cis*-[Cr(N–N)$_2$(H$_2$O)$_2$](NO$_3$)$_3$,aq {(N–N) = bipy or phen}, have been prepared[2] from the corresponding di-μ-hydroxo-bis[bis(N–N)] compounds (the diol compounds) and, in the presence of the appropriate reagents, are interconvertible in satisfactory yield according to equation 1. [(a) refers also to similar work with optically active complexes[3]].



This constitutes a classical proof for the *cis*-configuration of all the chromium(III) bis(N–N) complexes. Each compound was characterized by chemical analysis, and identified by comparison of absorption spectral properties of authentic samples; in all cases only one cation of each stoicheiometry was observed. [Cr phen$_2$ Cl$_2$]Cl,2H$_2$O, formerly thought to be *trans* because of its green colour,[4] was also found to be identical with our *cis*-salt of equation 1. A tetrahydrate (see below) and a hydrochloride also exist, both red in colour. The hydrochloride of the corresponding bipyridine complex has according to Guinier diagram evidence a structure similar to its rhodium analogue.

The empirical rule[5] that complexes of *trans*-configuration have the privilege of forming acid salts is therefore not valid.

All of the compounds referred to in equation 1 have a single absorption band in the visible region ($\epsilon < 100$ l./mol Cr.cm.) which we identify as the ligand field band having essentially the octahedral parentage $^4A_{2g}(O_h) \rightarrow {}^4T_{2g}(O_h)$. The common stereochemical configuration of the bipyridine and phenanthroline complexes is in agreement with the fact that their corresponding ligand field bands practically fall at the same wavenumber and in no case vary more than 1%.

The Guinier diagrams are very similar within each of the following series and have all been indexed in the monoclinic (I) and the triclinic (II) systems.

Series I:

[Cr phen$_2$ Cl$_2$]NO$_3$,3$\frac{1}{2}$H$_2$O, [Co phen$_2$ Cl$_2$]NO$_3$,3H$_2$O, [Rh phen$_2$ Cl$_2$]NO$_3$,3H$_2$O, [Ir phen$_2$ Cl$_2$]NO$_3$,3H$_2$O, [Cr phen$_2$ Cl$_2$]Cl,4H$_2$O, and [Co phen$_2$ Cl$_2$]Cl,3H$_2$O

Series II:

[M bipy$_2$ Cl$_2$]Cl,2H$_2$O (M = Cr, Co, Rh, and Ir).

On the basis of the *cis*-configuration of the chromium(III) compounds together with the results of the *X*-ray powder diagrams we conclude that the compounds of the other metals also have the *cis*-configuration. It is remarkable that chloride and nitrate can apparently replace one another without essentially changing the crystal structure and that the number of water molecules of crystallization may vary. This fact must be connected with the size and rigidity of the cation.

A single crystal *X*-ray analysis[6] of *cis*-[Co phen$_2$ Cl$_2$]Cl, 3H$_2$O (R = 21% on 1000 reflections) supports our conclusions; this violet salt is a member of crystal series I.

The cobalt(III) complexes were prepared according to ref. 7. In those cases where *trans*-complexes have earlier been thought to have been prepared, this possibility has been excluded.[8]

The rhodium(III) and iridium(III) complexes were shown by chemical analysis, together with their i.r., visible, and u.v. spectra to be identical with those reported,[9] just as for the Cr$^{\text{III}}$ and Co$^{\text{III}}$ compounds only one cation of each stoicheiometry was found.

Although we have confined this report to complexes of trivalent metals, we have been unable to find evidence for the existence of any octahedral *trans*-bis(bipyridine) and *trans*-bis(phenanthroline) complexes. This should be seen in the light of the fact that tetra-co-ordinated Pd in the [Pd phen$_2$]$^{2+}$ ion, in addition to being quite unstable, has been reported to have a distorted square planar configuration.[10]

A considerable distortion would, for steric reasons, also be expected or *trans*-octahedral complexes—if they exist.

We thank Dr. H. Buchwald for his very accurate chromium analyses.

Note added in proof. Three papers of relevance to this problem have recently appeared: R. D. Gillard and B. T. Heaton, *J. Chem. Soc.* (*A*), 1969, 451; J. D, Miller and R. H. Prince, *ibid.*, p. 519, G. C. Kulasingam, W. R. McWhinnie and J. D. Miller, *ibid.*, p. 521.

(*Received, December 9th*, 1968; *Com.* 1683.)

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