The Absolute Configuration of some Bis-chelated Octahedral Cobalt(III) Complexes

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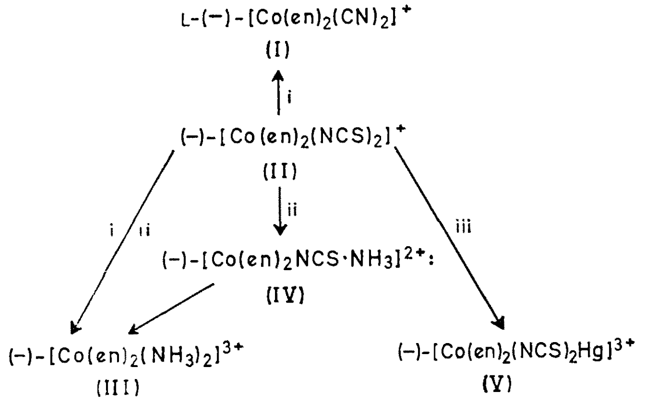
Summary The optical configurations of (—)-$[Co(en)_2(NCS)_2]^+$, L-(—)-$[Co(en)_2(CN)_2]^+$, and (—)-$[Co(en)_2(NH_3)_2]^{3+}$ have been correlated by chemical means (en = ethylenediamine).

MUCH work has been done on the absolute configurations of optically-active metal complexes,[1,2] particularly on the important class of complexes $[Co(en)_2XY]^{n+}$, where X and Y vary widely. However, the absolute configuration of only one complex within this class is known with certainty from the Bijvoet method of *X*-ray analysis,[3] that of D-(+)-$[Co(en)_2(CN)_2]^+$. The others are inferred, either from spectroscopic comparisons[1,4] or from chemical interconversions.[2]

We report here the first direct chemical correlation of L-(—)-$[Co(en)_2(CN)_2]^+$ with other complexes within the series, providing a vital confirmation of the spectroscopic methods used throughout the series. The interconversions achieved are shown in the Scheme.



SCHEME. (i) H_2O_2–H^+: this work. (ii) HIO_3: ref. 2. (iii) Hg^{2+}: ref. 2.

Following the recent discovery by Norris and Caldwell[5] that $[(NH_3)_5CoNCS]^{2+}$ (A) may be converted by oxidation into $[(Co(NH_3)_6]^{3+}$ (B) and $[(NH_3)_5CoCN]^{2+}$ (C), and accepting the suggestion[6] by Schug and his co-workers that the conversion of (A) into (C) is intramolecular, we applied the method described,[5] (the conditions are very critical, 10^{-3}M-complex, 0·5M-H^+, and 2M-H_2O_2) to the oxidation of (—)-*cis*-di-isothiocyanatobisethylenediaminecobalt(III) salts (recrystallised to optical constancy) in order to correlate optical configurations of factor and products.

By gradient elution of the products of the reaction (with 0·5—3M-KCl solution) down a Zeokarb 225 cation exchange column, and by subsequent Sephadex chromatography, L-(—)-$[Co(en)_2(CN)_2]^+$ (see Figure) was obtained optically pure.[1] A second product of this reaction has been obtained impure. It has a first *d–d* band at about 438nm, but it has proved very difficult to obtain chromatographically pure. This is probably the cyanoamino-complex, and work is at present in progress to isolate and characterise this product.

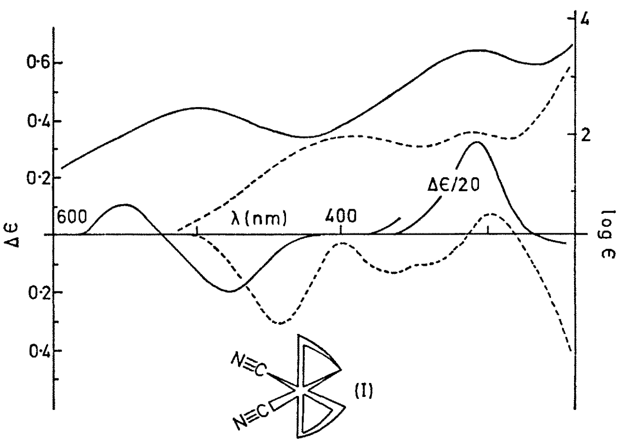


FIGURE. *The properties of* L-(—)-$[Co(en)_2(CN)_2]^+$ (I) (————) *and* (—)-$[Co(en)_2(NCS)_2]^+$ (II) (– – – – –): *the upper curves absorption spectra and the lower curves c.d. spectra. The absolute configuration of* L-(—)-$[Co(en)_2(CN)_2]^+$ *is also shown.* (*Each diagrammatic chelate ring represents* $H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$).

By varying the conditions of the oxidation, good yields of (—)-$[Co(en)_2(NH_3)_2]^{3+}$ have been obtained from the same starting material.

These observations therefore correlate the absolute configurations of (II), (III), (IV), and (V) with that of (I), L-(—)-$[Co(en)_2(CN)_2]^+$ shown, and lend support to the empirical spectroscopic rules used to interrelate bis-diamine complexes.

It is also relevant that the intuitive correlation[7] of the configuration of (+)-$[Co(en)_2(NH_3)_2]^{3+}$ with that of D-(+)-$[Co(en)_3]^{3+}$ on the basis of their qualitatively extremely similar Cotton effects is borne out by the present work.

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