

**264.** *Absolute Configurations of some  $d^6$  Complex Ions of Cobalt, Rhodium, Iridium, and Platinum, and of Complex Ions of Chromium(III).*

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Corey and Bailar's principles for the assignment of absolute configurations in octahedral complexes, which involve the stereospecific inducement of configuration at the metal atom by optically active ligands and a comparison of Cotton-effect curves for a given spectroscopic transition, are applied to a number of  $d^6$  complex ions of cobalt, rhodium, iridium, and platinum. An extension is made to some octahedral chromium(III) complexes.

THERE has been much work on the theory of optical rotation in complex ions of transition metals whose electronic spectra lend themselves to interpretation.<sup>1</sup> However, as a check and to supplement the mathematical theories of the origin of rotatory power, it is desirable to have correlations of configuration among octahedral complex ions.

Corey and Bailar<sup>2</sup> carried out conformational analysis of chelate rings for diamines in trisdiamine-metal complexes and showed that there is a most favoured isomer, which in their notation is termed *kkk*. For the *cis*-bisdiamine series of complexes, the favoured isomer is *kk* and this leads to the fact that, when the diamine itself is optically active, one configuration at the metal atom is preferentially induced. Thus (+)-propylenediamine\*

\* Signs of rotations both for the central metal atom and for the ligands refer throughout to the  $\text{Na}_D$  line, unless some other wavelength is specified. When the absolute configuration of either the metal or a ligand is known, this is given according to convention, as in  $\text{D-(+)-[Co en}_3\text{]}^{3+}$ . Abbreviations used throughout for ligands are: bn, butylenediamine; chxn, *trans*-cyclohexane-1,2-diamine; cptn, *trans*-cyclopentane-1,2-diamine; en, ethylenediamine; ibn, "isobutylenediamine" (2-methylpropane-1,2-diamine); pent, pentanediamine; pn, propylenediamine; tn, trimethylenediamine; trien, triethylenetetramine.

<sup>1</sup> Mason, *Quart. Rev.*, 1963, **17**, 20.

<sup>2</sup> Corey and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

gives the favoured isomers (+)-[Co(+pn)<sub>3</sub>] and (+)-[Co(+pn)<sub>2</sub>X<sub>2</sub>]<sup>n+</sup>, and these have the same configuration at the metal atom.<sup>3</sup> Corey and Bailar further applied their stereochemical analysis to the determination of the absolute configuration for asymmetrically substituted metal ions, pointing out that a knowledge is required only of (i) the relative orientation of various groups in the complex, and (ii) the absolute configuration of one of the ligand groups. They were then able to deduce the absolute configuration for D-[Co(+pn)<sub>3</sub>]<sup>3+</sup>, and noted that, since the optical rotatory dispersion (o.r.d.) curves for this compound and for D-[Co en<sub>3</sub>]<sup>3+</sup> correspond, the latter has the same absolute configuration, in agreement with the X-ray determination.<sup>4</sup> The configuration which is derived from this standard, by opening up one chelate ring, must also give the D-configuration for the bisdiamine chelates [ML<sub>2</sub>X<sub>2</sub>] (C<sub>2</sub> symmetry). Since the energy levels for trisdiamine-[CoL<sub>3</sub>] complexes are all extremely similar, and the Cotton effects in the various complexes arise from corresponding transitions, it seems that a comparison of configuration on the basis of the shapes of Cotton-effect curves is quite legitimate. This principle has been widely used in deducing absolute configurations of organic molecules,<sup>5</sup> and Corey and Bailar's method would appear to be of equally wide application. Spectroscopic assignments are not required in deducing the absolute configuration by such comparisons, and we do not make them. Although there is a large quantity of data available on trisoxalato-metallates(III), [M<sup>III</sup>ox<sub>3</sub>]<sup>3-</sup>, we omit such complexes because there is some doubt concerning the true nature of the species in solution. Thus kinetic evidence<sup>6</sup> suggests that one chelate ring may be open and a water molecule bound to the metal atom; it also appears<sup>7</sup> that, in the solid state, not all the complex anions possess D<sub>3</sub> symmetry.

*Applications to d<sup>6</sup> Complexes of Cobalt, Rhodium, Iridium, and Platinum.*—(1) *Trisdiaminecobalt(III) ions.* Positive Cotton effects, due to the absorption band at ca. 470 mμ, are observed in rotatory dispersion for the complex ions (a) D-(+)-[Co en<sub>3</sub>]<sup>3+</sup>,<sup>8</sup> (b) (+)-[Co(+pn)<sub>3</sub>]<sup>3+</sup>,<sup>9</sup> (c) (-)-[Co(+chxn)<sub>3</sub>]<sup>3+</sup>,<sup>10</sup> (d) (+)-[Co(-tn)<sub>3</sub>]<sup>3+</sup>,<sup>11</sup> (e) (+)-[Co(m-2,3-bn)<sub>3</sub>]<sup>3+</sup>,<sup>11</sup> (f) (+)-[Co(-cptn)<sub>3</sub>]<sup>3+</sup>,<sup>12</sup> and (g) (+)-[Co en<sub>2</sub>ibn]<sup>3+</sup>.<sup>11</sup> A negative Cotton effect is shown by (h) (-)-[Co(-2,3-bn)<sub>3</sub>]<sup>3+</sup>.<sup>11</sup> Complexes (a) and (b) also show parallel circular dichroism<sup>9</sup> for the 470 mμ absorption band (a positive circular dichroism band corresponds to a positive Cotton wave in optical rotatory dispersion). Hence, since D-(+)-[Co en<sub>3</sub>]<sup>3+</sup> has a known configuration, the complex ions (a)—(g), inclusive, have the D-configuration, as has the antipode of (h).

Corey and Bailar deduced the absolute configuration of (-)-*trans*-cyclopentane-1,2-diamine from the relation of (b) and (f) above. Similarly, from the relation of (b) and (c), (+)-pn ≡ (+)-chxn; since the absolute configuration of +pn is known<sup>13</sup> from its relation to L-alanine, the absolute configuration of (+)-chxn is hence as in (I).

(2) *Relationships in the bisdiamine series.* The stable isomer<sup>14</sup> of *cis*-[Co(+pn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> is dextrorotatory; because of the steric requirement of the ligand, it has the D-configuration. It is D-(+)-[Co(+pn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>; the o.r.d. curves of (+)-[Co en<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> and D-(+)-*cis* [Co(+pn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> are extremely similar,<sup>15</sup> so that (+)-[Co en<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> may be assigned to the D-series. (+)-cptn induces the L-configuration at the cobalt in L-(-)-[Co(+cptn)<sub>3</sub>]<sup>3+</sup>;

<sup>3</sup> Dwyer, MacDermott, and Sargeson, *J. Amer. Chem. Soc.*, 1963, **85**, 661.

<sup>4</sup> Saito, Nakatsu, Shiro, and Kuroya, *Acta Cryst.*, 1955, **8**, 729.

<sup>5</sup> Klyne, "Stereochemical Correlations," R.I.C. Monograph, No. 4, 1962; Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, 1960.

<sup>6</sup> Barton and Harris, *Inorg. Chem.*, 1962, **1**, 251.

<sup>7</sup> Porte, Gutowsky, and Harris, *J. Chem. Phys.*, 1961, **34**, 66; Gillard, *J.*, 1963, 2092.

<sup>8</sup> Drouard and Mathieu, *Compt. rend.*, 1953, **236**, 2395.

<sup>9</sup> Mathieu, *Ann. Physique*, 1944, **19**, 335.

<sup>10</sup> Jaeger and Bijkerk, *Z. anorg. Chem.*, 1937, **233**, 97.

<sup>11</sup> Woldbye, "Optical Rotatory Dispersion of Transition Metal Complexes," Tech. U.S. Army Report DA-91-508-EOC-246, 1959.

<sup>12</sup> Jaeger and Blumendal, *Z. anorg. Chem.*, 1928, **175**, 161.

<sup>13</sup> Reihlen, Weinbrenner, and Hessling, *Annalen*, 1932, **494**, 143.

<sup>14</sup> Smirnov, *Helv. Chim. Acta*, 1920, **3**, 195.

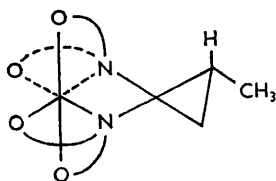
<sup>15</sup> Bailar and McReynolds, *J. Amer. Chem. Soc.*, 1939, **61**, 3199.

the stable isomer of the dichlorobisdiaminecobalt(III) cation is therefore L-(−)-[Co(+ cptn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>. The enantiomorphous D-(+)-[Co(− cptn)<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> has an o.r.d. curve<sup>12</sup> very similar to that of (+)-[Co en<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, which is again assigned to the D-series.

The stable isomer of the carbonatobis-(−)-propylenediaminecobalt(III) cation is (−)-[Co(− pn)<sub>2</sub>CO<sub>3</sub>]<sup>+</sup>. The o.r.d. curve shows a negative Cotton effect,<sup>15</sup> the opposite of that for (+)-[Co en<sub>2</sub>CO<sub>3</sub>]<sup>+</sup>, leading to the configuration D-(+)-[Co en<sub>2</sub>CO<sub>3</sub>]<sup>+</sup>. The more stable isomer<sup>3</sup> of the oxalatobis-(+)-propylenediaminecobalt(III) cation has an o.r.d. curve parallel to that of (+)-[Co en<sub>2</sub>ox]<sup>+</sup>, which is therefore D-(+)-[Co en<sub>2</sub>ox]<sup>+</sup>. (+)-[Co en<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup> has circular dichroism and o.r.d. curves virtually identical<sup>9</sup> with those of D-(+)-*cis*-[Co(+ pn)<sub>2</sub>(NO<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, and the circular dichroism and o.r.d. curves of (+)-[Co en<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> and D-(+)-*cis*-[Co(+ pn)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>3+</sup> are extremely similar.<sup>9</sup>

D-(+)-[Co en<sub>3</sub>]<sup>3+</sup> and (+)-[Co en<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]<sup>3+</sup>, with almost identical electronic spectra, have positive Cotton effects in the region of the longest wavelength absorption band. Archer and Bailar<sup>16</sup> pointed out the similarity of their o.r.d. curves when assigning them to the same configuration.

(3) *Compounds of cobalt with EDTA.* As noted above, the absolute configuration of (+)-propylenediamine is known from its relationship<sup>13</sup> to L-alanine. We have shown that both (+)-propylenediamine and (+)-H<sub>4</sub>PDTA (the tetra-acetic acid derived from it by condensation with chloroacetic acid) have plain positive o.r.d. curves. The absolute



(II)  
Configuration of  
L-(−)<sub>546.1</sub>[Co(+PDTA)]<sup>−</sup>

configuration of (+)-PDTA is thus known, and only one complex with cobalt(III) can be formed with the methyl group equatorial, as shown in (II). Since the asymmetry derives from the two N-O chelate rings, which are out of the plane containing the nitrogen atoms and the cobalt, this is effectively a complex of the bis-series with the L-configuration. This configuration was also assigned on different grounds by Im and Busch.<sup>17</sup>

The o.r.d. curves of (−)<sub>546.1</sub>[Co(EDTA)]<sup>−</sup><sup>18</sup> and L-(−)<sub>546.1</sub>[Co(+PDTA)]<sup>−</sup> are very similar; the circular dichroism curves<sup>19</sup> are also closely similar. Our conclusion that the absolute configuration is L-(−)<sub>546.1</sub>[Co(EDTA)]<sup>−</sup> is supported by some kinetic evidence.<sup>20</sup> The interconversions between L-(−)<sub>546.1</sub>[Co(EDTA)]<sup>−</sup>, (−)<sub>546.1</sub>[Co(HEDTA)Cl]<sup>−</sup>, and (+)<sub>546.1</sub>[Co(HEDTA)Br]<sup>−</sup> are configuration-retaining.<sup>20,21</sup> A check on this is provided by the very similar rotatory powers of (−)<sub>546.1</sub>[Co(−HPDTC)Cl]<sup>−</sup>, which has the D-configuration for steric reasons, and (−)<sub>546.1</sub>[Co(HEDTA)Cl]<sup>2−</sup>.

(4) *Rhodium(III).* Only one isomer of (−)<sub>546.1</sub>[Rh(+ HPDTC)(H<sub>2</sub>O)] exists,<sup>21</sup> which is remarkably similar to (−)<sub>546.1</sub>[Rh(HEDTA)(H<sub>2</sub>O)]. On the basis of the stereospecific requirement of (+)-PDTA, we assign them both to the L-series. Retention of configuration was demonstrated in interconversions of L-(−)-[Rh(HEDTA)(H<sub>2</sub>O)], (−)-[Rh(H<sub>2</sub>EDTA)Cl<sub>2</sub>]<sup>−</sup>, and (−)-[Rh(H<sub>2</sub>EDTA)Br<sub>2</sub>]<sup>−</sup>.

The most stable isomer of the tris-(−)-cyclohexanediaminerhodium(III) cation is the dextrorotatory isomer.<sup>10</sup> The absolute configuration of the diamine being known, the stable *kkk* form leads to the configuration L-(+)-[Rh(− chxn)<sub>3</sub>]<sup>3+</sup>. The same argument may be applied to give the configuration D-(+)-[Rh(− cptn)<sub>3</sub>]<sup>3+</sup>.

(5) *Iridium(III).* The most stable isomer of the tris-(−)-*trans*-cyclohexane-1,2-diamineiridium(III) cation will have the L-configuration; Jaeger and Bijkerk<sup>10</sup> found this L-(+)-[Ir(− chxn)<sub>3</sub>]<sup>3+</sup> to have a plain, positive o.r.d. curve; this is the opposite of that<sup>22</sup>

<sup>16</sup> Archer and Bailar, *J. Amer. Chem. Soc.*, 1961, **83**, 812.

<sup>17</sup> Im and Busch, *J. Amer. Chem. Soc.*, 1961, **83**, 3362.

<sup>18</sup> Albinak, Bhatnagar, Kirschner, and Sonnessa, *Canad. J. Chem.*, 1961, **39**, 2360.

<sup>19</sup> Gillard, *Nature*, 1963, **198**, 580.

<sup>20</sup> Busch, Swaminathan, and Cooke, *Inorg. Chem.*, 1962, **1**, 260.

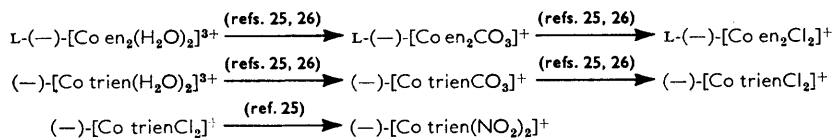
<sup>21</sup> Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1961, **83**, 2610.

<sup>22</sup> Werner and Smirnov, *Helv. Chim. Acta*, 1920, **3**, 483.

for  $(-)-[\text{Ir en}_3]^{3+}$ , which we therefore assign to the D-configuration.  $(-)-[\text{Ir en}_3]^{3+}$  shows <sup>22a</sup> a positive Cotton effect for the longest wavelength transition.

(6) *Platinum(IV)*. The more stable isomer <sup>23</sup> of the tris-(+)-propylenediamine-platinum(IV) cation is  $(-)-[\text{Pt}(+ \text{pn})_3]^{4+}$ . From the stereospecific requirement of the ligands, this has the D-configuration. Only two wavelengths were used for the determination of optical rotation, but the trend is exactly parallel to that in  $(-)-[\text{Pt en}_3]^{4+}$ , which we assign as D- $(-)-\text{Pt en}_3]^{4+}$ . This shows <sup>24</sup> a positive Cotton effect in both o.r.d. and circular dichroism in the region of the lowest energy absorption.

(7) *Triethylenetetramine complexes of cobalt(III)*. Complexes of formula *cis*- $[\text{Co en}_2\text{X}_2]^{n+}$  and *cis*- $[\text{Co trienX}_2]^{n+}$  have extremely similar electronic arrangements, as shown by their absorption spectra.<sup>25</sup> The following reactions occur (the starting compounds, made by asymmetric synthesis, were probably not optically pure):



On the basis of the similarities between the two series, we assign all the compounds of trien above to the L-configuration. The value,  $[\alpha]_D = -50^\circ$ , for  $\text{L-}(-)-[\text{Co trien}(\text{NO}_2)_2]^+$  suggests that essentially complete resolution has, in fact, been obtained, the corresponding value <sup>27</sup> for  $\text{L-}(-)-[\text{Co en}_2(\text{NO}_2)_2]^+$  being  $-44^\circ$ .  $(+)-[\text{Co en}_2(\text{NO}_2)(\text{ONO})]^+$  undergoes mutarotation to D- $(+)-[\text{Co en}_2(\text{NO}_2)_2]^+$ , *via* an intramolecular mechanism;<sup>28</sup> presumably, configuration is retained, so we assign the nitrito-complex to the D-configuration.

*Application to Complexes of Chromium(III) ( $d^3$ )*.—Because a reference compound  $\{\text{D-}(+)-[\text{Co en}_3]^{3+}\}$  of known absolute configuration was available for  $d^6$  complexes, it was unnecessary to utilize recent developments in the theory of optical activity. However, no reference compound is available for octahedral complexes of chromium(III), and the method using stereospecific induction of configuration at the metal by an optically active ligand cannot be applied, owing to lack of data. The absolute configurations of octahedral complexes have recently been considered <sup>29</sup> by applying Moffitt's argument <sup>30</sup> that the same sign for the rotational strengths of magnetic-dipole-allowed transitions in a cobalt(III) compound ( ${}^1T_{1g} \leftarrow {}^1A_{1g}$  in  $O_h$  symmetry) and the analogous chromium(III) compound ( ${}^4T_{2g} \leftarrow {}^4A_{2g}$  in  $O_h$  symmetry) indicate the same sign for the trigonal field, and hence the same absolute configuration.

The circular dichroisms <sup>31</sup> of the (+)-trisethylenediaminechromium(III) and D-(+)-trisethylenediaminecobalt(III) cations are similar, in that both show a dominant positive Cotton effect, so we assign the compound of chromium to the D-configuration. Few o.r.d. curves for compounds of chromium are available, although Woldbye <sup>11</sup> has shown that the curves of  $(-)-[\text{Cr}(\text{tn})_3]^{3+}$  and D-(+)- $[\text{Cr en}_3]^{3+}$  are parallel, giving D- $(-)-[\text{Cr}(\text{tn})_3]^{3+}$ . Several studies of the circular dichroism of tartratochromate(III) systems have been made, but we do not use these because the nature of the species present is not clear. The one complex of chromium(III) with an optically active ligand of known configuration is <sup>21</sup>  $(+)_546\text{-1-}[\text{Cr}(+\text{PDTA})(\text{H}_2\text{O})]^-$ , which, because of the steric requirements of the ligand, is  $\text{L-}(+)_546\text{-1-}[\text{Cr}(+\text{PDTA})(\text{H}_2\text{O})]^-$ .

<sup>22a</sup> Mathieu, *J. chim. phys.*, 1936, **33**, 78.

<sup>23</sup> Dwyer and Garvan, *J. Amer. Chem. Soc.*, 1959, **81**, 1042.

<sup>24</sup> Mathieu, *Bull. Soc. chim. France*, 1939, **6**, 1258.

<sup>25</sup> Gillard and Wilkinson, *J.*, 1963, 3193.

<sup>26</sup> Dassarma and Bailar, *J. Amer. Chem. Soc.*, 1955, **77**, 5480.

<sup>27</sup> Dwyer and Garvan, *Inorg. Synth.*, 1960, **6**, 192.

<sup>28</sup> Murmann, *J. Amer. Chem. Soc.*, 1955, **77**, 5190.

<sup>29</sup> Piper, *J. Amer. Chem. Soc.*, 1961, **83**, 3908.

<sup>30</sup> Moffitt, *J. Chem. Phys.*, 1956, **25**, 1189.

<sup>31</sup> Mathieu, Victor Henri Volume Commemoratif, Liège, 1947, p. 111.

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A complex of chromium(III) with  $O_h$  symmetry gives rise to the same number of spectroscopic transitions as a complex of cobalt(III) with the same symmetry. This is also true for complexes with  $D_3$  symmetry, like the trisdiamine complexes, and for complexes with  $C_2$  symmetry. We extend Moffitt's argument by postulating that the same signs for Cotton effects due to related transitions in complexes with  $C_2$  symmetry indicate the same signs for the asymmetric potentials, and hence the same configuration for the complexes. The circular dichroism of D-(+)-[Co en<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup> is parallel to that<sup>32</sup> of (+)-[Cr en<sub>2</sub>Cl<sub>2</sub>]<sup>+</sup>, to which we therefore assign the D-configuration.

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<sup>32</sup> Mathieu, *Bull. Soc. chim. France*, 1936, **3**, 476.

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