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# CONFIGURATIONS OF 1,2-DIAMINES

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**Abstract**—By comparisons of Cotton effects for the visible transitions of certain classes of metal complexes containing optically active diamines, the relative configurations of several diamines are established, and, using the known absolute configuration of (+)1,2-diaminopropane, absolute configurations are postulated.

In recent work[1] on the stereospecific induction of optical configuration at a metal by a number of optically active diamines, the absolute configurations of the diamines have been required. Comparison of the optical configurations of molecules containing the carbonyl group by means of the Cotton effect associated with the $n \rightarrow \pi^*$ transition at about 300 m$\mu$ has been widely practised.[2] However, the optically active transitions of other classes of compounds such as amino acids or diamines are not so accessible. (From Drude plots of rotatory dispersion data[3] it appears that the absorption band of diamines at ca. 230 m$\mu$ is optically inactive.) Cotton effects are, therefore, not observed in the accessible spectral region. This difficulty may be overcome by allowing the organic molecule to form a chelate ring with a transition metal, when the *d–d* transitions of the metal in the visible spectrum become optically active by asymmetric induction from the ligand. A large amount of data is available on several classes of metal complex compounds with optically active diamines, and it is the purpose of this paper to use these data in elucidating configurations of the diamine ligands.

Comparisons of configurations of organic molecules by means of metal complexes have been made previously for amino acids. Karrer *et al.*,[4] using rotatory dispersion, employed the Cotton effect of the *d–d* band of complexes of copper (II) with amino acids to establish the *L* configuration of some natural amino acids, relative to one another. A similar relationship may be derived[5] from complexes of the formula $[Co(NH_3)_4$ (L-amino-acidate)$]^{2+}$, using circular dichroism to establish the signs of the rotational strengths of the *d–d* bands of the cobalt (III) atom, which become optically active by induced asymmetry from the ligand. The rationale of configurational comparison by this means is that similar ligands with related configurations, when they form similar complexes, will induce rotational strengths of the same sign in corresponding transitions of the metal ion.

The several classes of complexes which can be used to give configurational relationships among ligands are treated separately. Since most of the diamines appear as

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[1a] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.* 1368 (1964); [b] J. H. Dunlop, R. D. Gillard and G. Wilkinson, *ibid.*, 3160 (1964); [c] J. H. Dunlop and R. D. Gillard, *J. Inorg. Nuclear Chem.* In press.

[2] C. Djerassi, *Optical Rotatory Dispersion.* McGraw-Hill, New York (1959).

[3] T. D. O'Brien and R. C. Toole, *J. Amer. Chem. Soc.* 77, 6368 (1955).

[4] P. Pfeiffer, *Ber. Dtsch. Chem. Ges.* 57, 44 (1944) and Refs. therein.

[5] J. H. Dunlop and R. D. Gillard, *J. Chem. Soc.* 2822 (1964).

ligands in more than one of the classes, a number of internal checks are available. Abbreviations for the diamines are as follows: pn, 1,2-diaminopropane; bn, 2,3-diaminobutane; cptn, *trans*-1,2-diaminocyclopentane; chxn, *trans*-1,2-diaminocyclohexane; phenen, phenylethylenediamine; stien, 1,2-diamino-1,2-diphenylethane (stilbenediamine). The symbol AA is used to indicate any diamine.

### (a) trans-*Dichlorobisdiamine cobalt* (III) *cations*

The rotatory dispersion curves of (−)*trans*$[Co(-cptn)_2Cl_2]^+$, (−)*trans*$[Co(-pn)_2Cl_2]^+$, and (−)*trans*$[Co(-phenen)_2Cl_2]^+$ are exactly similar, showing a strong positive Cotton effect for the *d-d* transition ($'E_g + 'A_{2g} \leftarrow {}^1A_{1g}$, using the notation for $D_{4h}$ symmetry) at ca. 600 mμ, as shown in Table 1. The rotatory dispersion curve for (+)*trans*$[Co(-stien)_2Cl_2]^+$ is enantiomorphous with the others; it is, therefore, clear that (−)pn ≡ (−)cptn ≡ (−)phenen ≡ (+)stien.

TABLE 1. COTTON EFFECTS FOR *trans*$[Co(-AA)_2Cl_2]^+$

| AA | $\lambda_1$ | $[\phi]_1$ | $\lambda_0$ | $\lambda_2$ | $[\phi]_2$ | $\lambda_0$ | $\lambda_3$ | $[\phi]_3$ | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| (−)pn | 648 | +2000 | 600 | 565 | −1600 | 495 | – | | 1*a* |
| (−)cptn | 656 | +1950 | 600 | 575 | −1050 | 510 | 430 | +860 | 6 |
| (−)phenen | 640 | +1800 | 593 | 560 | −800 | 520 | | | 7 |
| (−)stien | 650 | −3000 | 590 | 570 | +400 | 540 | 470 | −3000 | 8 |

[a] $\lambda_1$ is the wavelength (in mμ) of the first turning point, going from long to short wavelength; $[\phi]$ is the molecular rotation at that point; subscripts 2 and 3 denote subsequent turning points. $\lambda_0$ denotes wavelengths where $[\phi] = 0$.

Similar results may be derived by considering the Lifschitz' salts of nickel (II). These have the formula $Ni(AA)_2X_2$ where X is an anion, and may be either blue and paramagnetic, or yellow and diamagnetic. The change may sometimes be produced in a given compound by a change of solvent. In water, the blue cation $[Ni(+pn)_2]^{2+}$ gives[9] a negative Cotton effect (in circular dichroism) at 600 mμ, and the blue cation $[Ni(-stien)_2]^{2+}$ gives[8a] a negative Cotton effect (in rotatory dispersion) centred about 600 mμ. Hence, (+)pn ≡ (−)stein. Both these cations give yellow solutions in certain organic solvents, and yellow $[Ni(+pn)_2]^{2+}$ shows[9] a negative Cotton effect ($\varepsilon_1 - \varepsilon_d = -0{\cdot}15$) in circular dichroism at 460 mμ, in nitromethane, while yellow $[Ni(-stien)_2]$ shows[8] a negative Cotton effect in rotatory dispersion, with a deep minimum at 490 mμ ($[\phi] = -2200°$). Again (+)pn ≡ (−)stein.

Similarly, the rotatory dispersion curve[8b] of bis(−)propylene-diaminecopper (II) is extremely similar to that[8c] of bis(−)cyclohexane-diaminecopper (II), so that (−)chxn ≡ (−)pn.

### (b) *Trisdiamine cobalt* (III) *cations*

It is well known[1,10] that three molecules of an optically active diamine combining with a metal dictate one of the two possible optical configurations about the metal. This stable isomer shows Cotton effects in the metal bands due to the asymmetry

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[6] F. M. Jaeger and H. B. Blumendal, *Z. Anorg. Chem.* **175**, 161 (1928).

[7] I. Lifschitz and K. M. Dijkema, *Proc. Kon. Akad., Amsterdam* **43**, 874 (1964).

[8a] I. Lifschitz and J. G. Bos, *Rec. Trav. Chim.* **59**, 407 (1940); [b] R. D. Gillard, *J. Inorg. Nuclear Chem.* **26**, 1455 (1964); [c] F. M. Jaeger, *Bull. Soc. chim. Fr.* **4**, 1201 (1937).

[9] J. H. Dunlop and R. D. Gillard, *J. Inorg. Nuclear Chem.* in press.

[10] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.* **81**, 2620 (1959).

induced by the diamine. Table 2 shows the available rotatory dispersion data for Band I ($^1A_2 + {}^1E_a \leftarrow {}^1A_1$), occurring at ca. 470 mμ, for tris diamine complexes of cobalt (III). It is clear that (−)pn ≡ (−)bn ≡ (−)chxn ≡ (−)phenen ≡ (+)stien.

TABLE 2. ROTATORY DISPERSION DATA FOR THE STABLE ISOMERS OF $[Co(AA)_3]^{3+}$

| AA | C.E.[a] | $\lambda_1$ | $[\phi]_1$ | $\lambda_0$ | $\lambda_2$ | $[\phi]_2$ | Ref |
|---|---|---|---|---|---|---|---|
| −pn | −ve | 523 | −2000 | 506 | 480 | +5100 | 1*a* |
| −chxn | −ve | 520 | −1300 | 511 | 480 | +8200 | 11 |
| −bn | −ve | 521 | −310[b] | 488 | . . | — | 12 |
| −phenen | −ve | 525 | −2850 | 501 | — | +6000 | 7 |
| −stien | +ve | 520 | +3500 | 500 | 485 | −10,000 | 8 |

[a] C.E. denotes the sign of the Cotton effect; other notation, e.g. $\lambda_1$, as in Table 1.

[b] This value is for [α], not [ϕ].

The correlation of (−)pn and (−)chxn given here may be confirmed by a different route. Both (−)chxn and (−)pn condense with chloroacetic acid forming analogues of ethylenediamine-N,N,N′N′-tetra-acetic acid, abbreviated (−)CDTA and (−)PDTA respectively. These combine stereospecifically with cobalt (III), forming only one of the two possible diastereoisomers, $(+)_{546\cdot1}[Co(-CDTA)]^-$, and $(+)_{546\cdot1}[Co(-PDTA)]^-$ respectively, which have[13] extremely similar rotatory dispersion curves, so that (−)CDTA ≡ (−)PDTA, and hence (−)chxn ≡ (−)pn.

### (c) *Other trisdiamine cations*

Although the greatest proportion of work on complexes using diamines as ligands has involved cobalt (III), rotational data on complexes of other metals are available. The rotatory dispersion curves[6,11] of the stable isomers of $[Cr(-cptn)_3]^{3+}$ and $[Cr(-chxn)_3]^{3+}$ are extremely similar, leading to (−)cptn ≡ (−)chxn. The only other metal complexes where rotatory dispersion studies have extended into regions of electronic absorption are those of nickel (II). The complicated rotatory dispersion curve[14] of $[Ni(+bn)_3]^{2+}$ is essentially enantiomorphous with that[12] of $[Ni(-pn)_3]^{2+}$ from 800 mμ to 300 mμ. The cations $[Ni(+bn)_3]^{2+}$ and $[Ni(-pn)_3]^{2+}$ are seen to have enantiomorphous configurations. Hence, (−)pn ≡ (−)bn.

### (d) *Conclusion*

The results from all the classes of complexes thus agree; the summarized relations may be given as

(+) pn ≡ (+) bn ≡ (+) cptn ≡ (+) chxn ≡ (+) phenen ≡ (−) stien.

It should perhaps be pointed out that the rotatory dispersion curves of several of these diamines have been measured[3] in the visible region; those of (+)pn, (+)cptn, (+)chxn and (+)phenen are parallel, being plain, positive curves. The rotatory dispersion curve of (−)stien in the same region is, however, a plain negative curve. Measurements of rotatory dispersion outside regions of electronic absorption (plain curves) are of limited value in comparing configurations.

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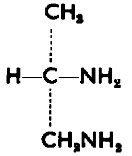
[11] F. M. Jaeger and L. Bijkerk, *Z. Anorg. Chem.* **233**, 97 (1937).

[12] F. Woldbye, Research Document DA-91-508-EUC-246, European Research Office, U.S. Army (1959).

[13] T. E. Macdermott and A. M. Sargeson, *Austr. J. Chem.* **16**, 334 (1963).

[14] F. Woldbye, *Proceedings of the 8th International Conference on Coord. Chem.* Vienna (1964).

The absolute configuration (I) of diaminopropane is known from three routes;



$$\begin{array}{c} CH_3 \\ \vdots \\ H—C—NH_2 \\ \vdots \\ CH_2NH_2 \end{array}$$

(+)pn is chemically related to L-alanine,[15] and X-ray determinations by the Bijvoet method have been carried out on $(-)trans[Co(-pn)_2Cl_2)Cl$,[16] and on $L[Co(-pn)_3]Br_3$.[17] The absolute configurations of the five other diamines collated here are therefore established as L, using L-alanine as a reference. The configuration L(+)-2,3-diaminobutane arrived at here is the same as that deduced[18] from chemical studies.

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[15] a S. Schnell and P. Karrer, *Helv. Chim. Acta* **38**, 2036 (1955); b H. Reihlen, E. Weinbrenner and G. V. Hessling, *Liebigs Ann.* **494**, 143 (1932).

[16] Y. Saito and H. Iwasaki, *Bull. Chem. Soc., Japan* **35**, 1131 (1962).

[17] Y. Saito, H. Iwasaki and H. Ota, *Bull. Chem. Soc., Japan* **36**, 1543 (1963).

[18] F. H. Dickey, W. Fickett and H. J. Lucas, *J. Amer. Chem. Soc.* **74**, 944 (1952).