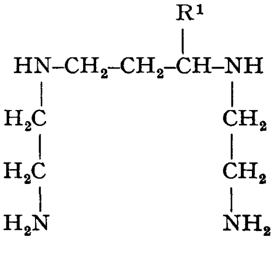
Correlations between Chirality and Circular Dichroism among *trans*-Diacidotetra-amines of Cobalt(III)

By LOUIS J. DEHAYES, MICHAEL PARRIS, and DARYLE H. BUSCH*
(*Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio* 43210)

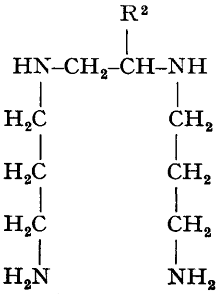
Summary. A series of optically active linear tetradentate ligands, which form six-, as well as five-membered chelate rings, has been stereospecifically synthesized and used to prepare the complexes *trans*-$Co(N_4)Cl_2^+$ in an attempt to correlate the signs of the Cotton effects with the known chiralities of the new compounds.

SARGESON and his co-workers have described the stereochemistry and absolute configurations of the cobalt(III) complexes of triethylenetetramine in great detail.[1] Other workers[2] have described the synthesis of analogues of triethylenetetramine containing central or terminal six-membered chelate rings, 2,3,2-tet (Ia) and 3,2,3-tet (Ic), respectively. There is at present no comparatively complete study of the chiralities of the complexes of these ligands. We believe that these systems may provide a general test for certain correlations between absolute configuration and optical activity.[3,4] Accordingly, we report the preparation of derivatives of the 2,3,2-tet and 3,2,3-tet ligands of known absolute configuration with methyl substituents on the central chelate ring.

5-*R*-Methyl-1,10-diamino-4,7-diazadecane, *R*-3,2′,3 (Id), was prepared from acrylonitrile and *R*-propylenediamine according to the route outlined by Israel *et al.*[5]



(Ia) $R^1 = H$
(Ib) $R^1 = Me$



(Ic) $R^2 = H$
(Id) $R^2 = Me$

trans-SS-$[Co(R\text{-}3,2',3)Cl_2]^+$ (II) was prepared and its c.d. spectrum recorded. The c.d. and ordinary absorption spectra of the compounds are shown in Figures 1 and 2.

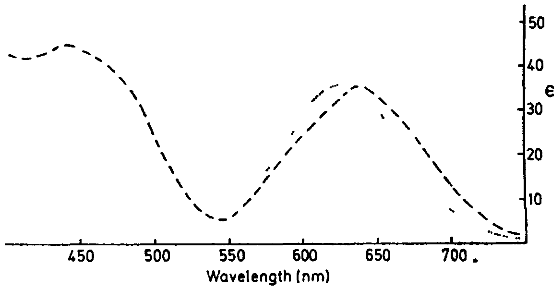


FIGURE 1. *Electronic spectra of complex* (II) (– –) *and complex* (III) (· · · ·).

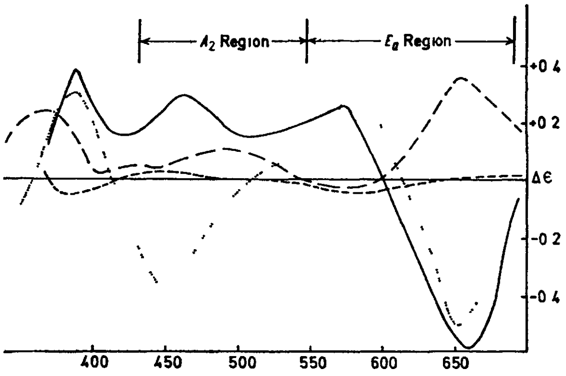
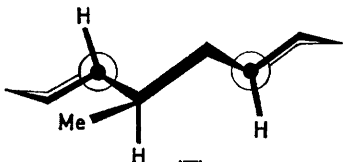
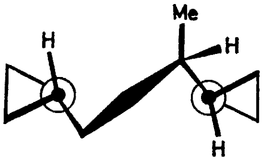


FIGURE 2. —*c.d. of complex* (V) (½ × scale), -·-*c.d. of complex* (IV) (2 × scale), · · · · *c.d. of complex* (III), – – *c.d. of complex* (II).

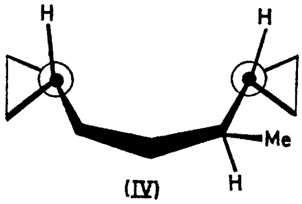
The absorption spectra are readily interpretable on the basis of approximate local D_{4h} symmetry. Using the proposed hexadecant rule[3] for D_{4h} we predict that this complex will show a positive c.d. band corresponding to the $A_1 \rightarrow A_2$ transition and a negative c.d. band due to the $A_1 \rightarrow E_a$ transition.



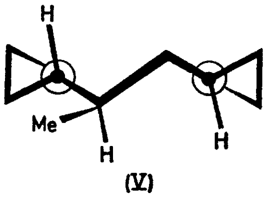
(II)



(III)



(IV)



(V)

The band at *ca.* 480 nm (Figure 2) is assigned to the $A_1 \rightarrow A_2$ transition. There are, however, two components of opposite sign associated with the $A_1 \rightarrow E_a$ transition. This ambiguity in the region of the E_a transition makes any assignment of chirality based on the transition to E_a impossible.

4-*S*-Methyl-1,9-diamino-3,7-diazanonane, *S*-2,3′,2 (Ib) was prepared from *S*-1,3-butylenediamine *via* the corresponding *NN*′-disubstituted 1,3-diazine. Two *trans*-[Co(*S*-2,3′,2)Cl$_2$]$^+$ isomers have been isolated[6] and assigned the structures *trans-RR*-[Co(*S*-2,3′,2)Cl$_2$]$^+$ (III) and *trans-SR*-[Co(*S*-2,3′,2)Cl$_2$]$^+$ (IV). For complex (III) the hexadecadal rule predicts a positive A_2 band and a negative E_a band. The long-wavelength component of the E_a band is indeed negative, but so is the A_2 transition.

All the sources of optical activity in the pseudo-*meso*-complex (IV) except the asymmetric methyl group cancel; *i.e.*, chelate ring conformations are $\delta\gamma\lambda$ and the nitrogen configurations are *R* and *S*. The intensity of the c.d. bands for this compound are expected to be very low. It is seen from Figure 1 that while the c.d. spectra of (III) and (IV) are qualitatively similar the intensity of the spectrum of (III) is an order of magnitude greater than that of (IV). The asymmetric methyl group lies in a sector of the XYZ $(X^2 - Y^2)$ pseudo-scalar function which should give a positive A_2 and a negative E_a transition. We do observe a positive A_2 band but again the E_a region is ambiguous.

It appears[4] that there are difficulties in making a general use of the D_{4h} hexadecant rule for all complexes of the type [Co(N$_4$)Cl$_2$]$^+$. S. F. Mason has recently suggested[4] that it is necessary to consider an octahedral contribution, XYZ $(X^2 - Y^2)(Z^2 - X^2)(Y^2 - Z^2)$, as well as the tetragonal perturbation for these complexes. However, no data have previously been used on the contributions of δ or λ six-membered chelate rings. Using available data on the tris-complexes of 2,4-diaminopentane[7] and the proposed pseudoscalars, we have derived the appropriate octahedral and tetragonal contributions for six-membered rings of the twist conformation. We find that the sum of the octahedral and tetragonal contributions will correctly correlate the sign of the *A* band with the chirality of the complex for (III) and (V) but not for (II), where the only apparent contribution comes from a five-membered chelate ring of λ-chirality.

For this class of linear tetradentate ligands there appear to be two main difficulties with the correlations presented up to now, namely:

(i) The ambiguity in the E_a region arising from the fact that the effective symmetry seen by the chromophore is less than D_{4h}.

(ii) The fact that the sign of the A_2 transition does not always correlate with that predicted by the sector rules.

We are currently investigating several alternative possibilities. The first is a simplistic empirical approach. We have observed a correlation between the long-wavelength portion of the c.d. effect in the E_a region and the net chirality of the chelate rings in the various complexes. The c.d. spectrum of *trans-SS*-[Co(*R*-2,2′,2)Cl$_2$]$^+$ (V) (chelate ring conformations $\delta\lambda\delta$, net $= \delta$) contains an intense negative component in the long-wavelength region of the E_a band. Complex (II) (chelate ring conformations $\gamma\lambda\gamma$, net λ) has a positive band in this region. The complex (III) (chelate ring conformation $\delta\ \lambda\ \delta$, net δ) has a negative band while complex (IV) (chelate ring conformations $\delta\gamma\lambda$, net 0) has almost no optical activity in this region.

On the other hand, we find that the sign of the $A_1 \rightarrow A_2$ transition can be correlated with the chirality of the asymmetric secondary nitrogens. The 2,2′,2 complex (V) and 3,2′,3 complex (II) have secondary nitrogens of *S*-configuration and have positive A_2 bands. The *RR*-2,3′,2 complex (III) has nitrogen configurations of the opposite chirality and has a negative A_2 band, while the *SR*-2,3′,2 complex (IV) with one nitrogen of each chirality has relatively no optical activity in the A_2 region.

Another possibility is a further descent in symmetry to either D_{2h} or D_2. This would remove the ambiguity in the *E* region and allow the introduction of an additional pseudoscalar.

Richardson[8] has approached the theoretical problem along a rather different route by deriving the one-electron rotatory strength for each transition and examining the symmetry dependence of these functions in D_2 symmetry. We are currently attempting to apply the latter two possibilities to the linear tetradentate complexes.

(*Received, July 9th*, 1971; *Com.* 1171.)

---

[1] D. A. Buckingham, P. A. Marzilli, and A. M. Sargeson, *Inorg. Chem.*, 1967, **6**, 1032 and refs cited therein.
[2] M. D. Alexander and H. G. Hamilton, *Inorg. Chem.*, 1969, **8**, 2131.
[3] S. F. Mason, *Chem. Comm.*, 1969, 856.
[4] S. F. Mason, *J. Chem. Soc.* (*A*), 1971, 667.
[5] M. Israel, J. S. Rosenfield, and E. J. Modest, *J. Medicinal Chem.*, 1964, **7**, 710.
[6] E. H. Hung, Ph.D. Thesis, The Ohio State University, 1971.
[7] F. Mizukami, H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Japan*, 1970, **43**, 3973.
[8] F. S. Richardson, *J. Chem. Phys.*, 1971, **54**, 2453.