Circular Dichroism Spectra of Some Trigonal-bipyramidal Complexes

By IZUMI ENDO, SOICHIRO HORIKOSHI, and SHUNJI UTSUNO*
(*Department of Chemistry, Shizuoka University, Oya, Shizuoka 422, Japan*)

Summary Some chiral five-co-ordinate complexes with the formula $[MX(S\text{-tan})](ClO_4)_n$ [$M = Cu^{II}$, Ni^{II}, or Co^{II}; $X = Br^-$ or NH_3; *S*-tan = (*S*)-2,4,8-trimethyl-5-(3-methyl-3-azabutyl)-2,5,8-triazanonane: $Me_2NCH_2CHMeN(CH_2CH_2NMe_2)_2$] exhibit c.d. spectra which can be interpreted assuming that each complex has C_{3v} symmetry.

ALTHOUGH extensive investigations have been carried out on the chiroptical nature of numerous octahedral complexes, there are few reports on that of five co-ordinate complexes.[1–3]

Recently, we prepared the chiral tripodal ligand *S*-tan [(*S*)-2,4,8-trimethyl-5-(3-methyl-3-azabutyl)-2,5,8-triazanonane: $Me_2NCH_2CHMeN(CH_2CH_2NMe_2)_2$], which formed five-co-ordinate complexes with Cu^{II}, Ni^{II}, and Co^{II} ions, as in the case of tris(2-dimethylaminoethyl)amine (tren-Me).[4] The c.d. spectra of the *S*-tan complexes have been interpreted assuming that they possess C_{3v} symmetry.

The ligand *S*-tan was prepared from (+)-alanine, which was converted into alanine-*N*,*N*-diacetic acid by the literature method.[5] In the presence of dicyclohexylcarbodiimide, the acid was converted into its tris-(*p*-nitrophenyl) ester, from which the tris(dimethylamide) was prepared.

Reduction of the amide with $LiAlH_4$ gave the tetra-amine, *S*-tan. Although it was contaminated with amino-alcohols, it could be purified through formation of metal complexes.

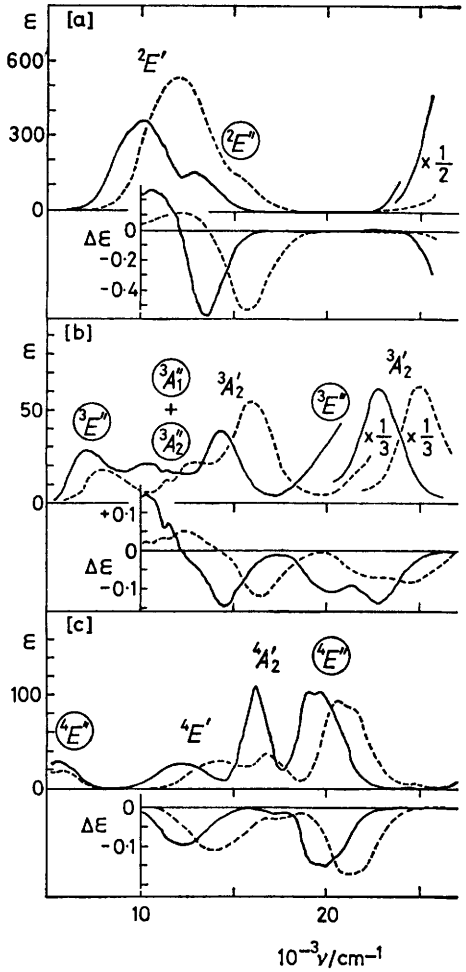

FIGURE. Electronic and c.d. spectra of [MBr(*S*-tan)]ClO_4 (————) and [M(NH_3)(*S*-tan)]$(ClO_4)_2$ (- - - - -) in nitromethane: (a) Cu, (b) Ni, and (c) Co complexes. The circles denote each magnetic dipole transition allowed under D_{3h} symmetry.

The complexes [MX(*S*-tan)]$(ClO_4)_n$ (M = Cu, Ni, or Co; X = Br^- or NH_3; n = 1 or 2), were prepared by adding LiBr or aqueous ammonia to a methanolic solution of [M(H_2O)(*S*-tan)]$(ClO_4)_2$. All the complexes gave satisfactory analyses (C, H, N, and M).

The Figure shows the electronic and c.d. spectra of the complexes. The absorption spectra of the ammine complexes are quite similar to those of the bromo complexes, and the latter are comparable with the spectra of the corresponding trenMe complexes.[4] Thus, trigonal-bipyramidal geometry would be expected for all the present complexes.[6]

The absorption bands were assigned on the basis of D_{3h} symmetry from the work of Ciampolini, *et al.*[7] The circled states in the Figure are the excited states to which magnetic dipole transitions are allowed from the ground state under D_{3h} symmetry. The observed c.d. spectra correspond fairly well with the expected transitions. However, some forbidden magnetic transitions are also observed, although their rotational strengths are comparatively small taking into account their large ϵ_{max} values. This is the case for the strongest absorptions of Cu^{2+} ($^2E' \leftarrow {}^2A_1'$) and Ni^{2+} ($^3A_2' \leftarrow {}^3E'$) complexes.

Lowering of the symmetry from D_{3h} to C_{3v} does not cause splitting of each doubly degenerate level, but causes changes in the selection rule for the magnetic dipole transitions. Thus, all transitions for the copper, nickel, and cobalt complexes are magnetically allowed under C_{3v} symmetry, except for the $^4A_2 \leftarrow {}^4A_2$ transition of the cobalt complexes. This is in satisfactory agreement with the observed c.d. spectra.

Even the most symmetrical ammine complexes possessing the MN_5 chromophore do not obey the selection rules under D_{3h} symmetry. The effective symmetry is expected to be lowered because of the influence of chelate rings and also the distortion of the trigonal-bipyramidal structure. Each metal ion in the present complexes must lie out of the plane formed by three dimethylamino-nitrogen atoms, which is analogous to the case for the trenMe complexes.[6]

The authors thank Dr. Sakurai of Shizuoka University for useful suggestions about the preparation of the ligand.

(*Received*, 9*th December* 1980; *Com.* 1313.)

---

[1] T. A. Kaden, B. Holmquist, and B. L. Vallee, *Inorg. Chem.*, 1974, **13**, 2585.

[2] D. Gatteschi and E. Krausz, *Chem. Phys. Lett.*, 1975, **34**, 348.

[3] Y. Ohtani and S. Utsuno, *Chem. Lett.*, 1980, 465.

[4] M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, **5**, 41.

[5] N. Koine, N. Sakota, J. Hidaka, and Y. Shimura, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1737.

[6] M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, 1967, **6**, 955; M. Di Vaira and P. L. Orioli, *Acta Crystallogr., Sect. B*, 1968, **24**, 595.

[7] M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, 1966, **1**, 222, and references therein.