CHEMISTRY LETTERS, pp. 1143-1146, 1972. Published by the Chemical Society of Japan

ABSORPTION AND CIRCULAR DICHROISM SPECTRA OF COBALT(III) COMPLEXES CONTAINING N_3^- OR NCS^- IN THEIR "SPECIFIC ABSORPTION BAND" REGION

Kiyoshi YAMASAKI, Jinsai HIDAKA, and Yoichi SHIMURA
Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka

Circular dichroism spectra of *cis*-$[Co(en)_2(NH_3)(X)]^{2+}$ and *cis*-$[Co(en)_2(X)_2]^+$ type complexes with a pseudohalogeno ligand X (N_3^- or NCS^-) were measured in 15–45 kK region. So-called specific absorption bands of these complexes were analyzed on the basis of CD patterns, which were also discussed in relation to the absolute configurations.

It is well known that transition metal complexes with some particular ligands, such as NO_2^-, N_3^-, NCS^-, or SO_3^{2-}, show characteristic intense absorption bands, so-called "specific absorption bands", in the ultraviolet or near-ultraviolet region. These absorption bands have been considerably investigated hitherto;[1-10] nevertheless, the problem of their origins is still unsettled. That is, alternative characterizations have been assigned, the one attributes the bands to intraligand transitions[2, 7] and the other to ligand-to-metal charge transfer transitions.[4,6,9,10] The present letter is concerned with the circular dichroism (CD) and absorption spectra of *cis*-$[Co(en)_2(NH_3)(X)]^{2+}$ and *cis*-$[Co(en)_2(X)_2]^+$ (X = N_3^- and NCS^-), and the CD behaviors are considered in relation to the origins of the specific absorption bands and absolute configurations of the complex ions.

$[Co(en)_2(NH_3)(N_3)]Cl_2$ was derived by a new process from *cis*-$[Co(en)_2(NH_3)(Cl)]Cl_2$. $[Co(en)_2(N_3)_2]NO_3$,[11] $[Co(en)_2(NH_3)(NCS)](SCN)_2$,[12] and $[Co(en)_2(NCS)_2]Cl \cdot H_2O$[13] were prepared by the methods described in literature. The optically active ammine-isothiocyanato complex, $(-)_{589}$-$[Co(en)_2(NH_3)(NCS)]^{2+}$, was obtained as the bromide salt by treating $(+)_{589}$-$[Co(en)_2(Cl)(NCS)]^+$ with liquid ammonia and removing the less soluble inactive bromide salt. $[Co(en)_2(NCS)_2]^+$,[14] $[Co(en)_2(NH_3)(N_3)]^{2+}$,[15] and $[Co(en)_2(N_3)_2]^+$ [11] were resolved by the reported methods. CD spectra were recorded with a JASCO Model ORD/UV-5 or J-20 spectrophotometer.

The azido and isothiocyanato complexes show very similar absorption curves (Figs. 1 and 2). The absorption behaviors in the marked region are complicated because of the overlap of the second spin-allowed d-d absorption bands. However, the CD curves in the corresponding region reveal the positions of the second d-d absorption bands; namely the CD bands at 26.2 kK for the monoazido complex, at 25.8 kK for the diazido one, at 27.7 kK for the monoisothiocyanato one, and at 25.3 and 27.3 kK for the diisothiocyanato one, correspond to the second d-d absorption bands. Such location of the second d-d absorption bands agrees with those evaluated[16] (shown by arrows in Figs. 1 and 2) from the first d-d absorption band positions.

The specific absorption band at 33.0 kK of *cis*-$[Co(en)_2(N_3)_2]^+$ is 1.23 times as broad (and 1.45 times as intense) as that of *cis*-$[Co(en)_2(NH_3)(N_3)]^{2+}$ (Fig. 1). The same is also realized for the isothiocyanato complexes, that is, the specific absorption band at 32.7 kK of *cis*-$[Co(en)_2(NCS)_2]^+$ is 1.23 times as broad (and 1.70 times as intense) as that of *cis*-$[Co(en)_2(NH_3)(NCS)]^{2+}$. These absorption behaviors concerning the band breadth are quite in contrast to that of the corresponding nitro complexes, where the dinitro complex shows very similar specific absorption band in breadth to the mononitro one. The band broadening in the diazido and diisothiocyanato complexes suggests a band splitting such as that was pointed out by Linhard *et al.*[4)] for complexes of ammine-azido series.
This suggestion is confirmed from the CD spectra; in fact, the diazido complex shows two CD bands of opposite signs across a zero line at ∿33 kK, while the monoazido complex shows a single CD band at ∿33 kK. Similarly, the diisothiocyanato complex shows two CD bands of opposite signs across a zero line at ∿33 kK, while the monoisothiocyanato complex shows a single CD band at ∿34 kK. The similarity of the azido and isothiocyanato complexes in CD and absorption spectra may be related to the fact that both the ligands, N_3^- and NCS^-, are linear triatomic pseudohalide ions having sixteen valence electrons.[17)]

In the case of halogeno-ammine cobalt(III) complexes, Nakamoto *et al.* showed by an MO treatment that a single $\pi\to$(lower d_γ) transition is expected for $[Co(NH_3)_5(X)]^{2+}$ (C_{4v}) and four $\pi\to$(lower d_γ) transitions for *cis*-$[Co(NH_3)_4(X)_2]^+$

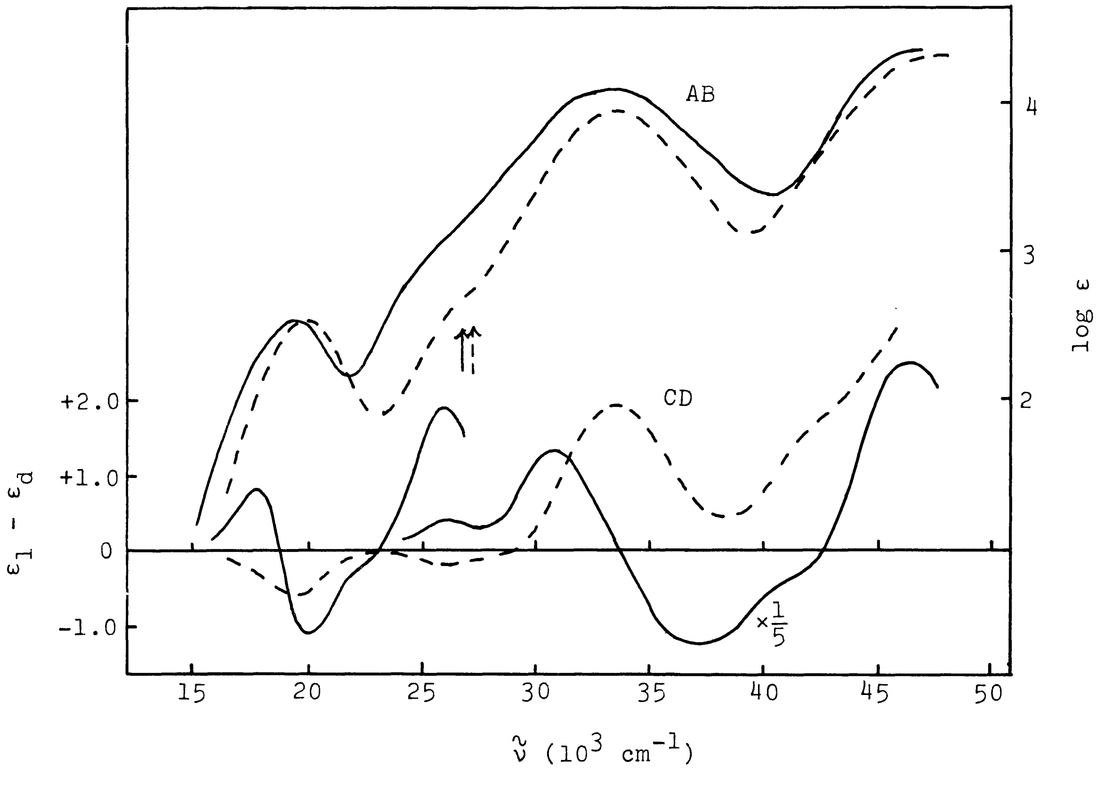

Fig. 1. Absorption (AB) and CD curves of $(+)_{589}$-$[Co(en)_2(N_3)_2]ClO_4$ (———) and $(-)_{589}$-$[Co(en)_2(NH_3)(N_3)]Cl_2\cdot0.5H_2O$ (-----).

(C_{2v}) and that two transitions of the latter four have approximately the same energy and the remaining two another same energy.[18] If it is presumed that the ring effect of the ethylenediamine chelate is negligible and the ligand field due to the amine and the ammine is quite the same, the symmetry of *cis*-$[Co(en)_2(NH_3)(X)]^{2+}$ is approximated to C_{4v} and that of *cis*-$[Co(en)_2(X)_2]^+$ to C_{2v}. Then, taking into consideration the fact that the specific absorption bands of the present diazido and diisothiocyanato complexes are shifted to lower energy than those of the corresponding ammine-azido and ammine-isothiocyanato complexes in parallel with the first spin-allowed d-d absorption bands, the splitting of the specific absorption bands in the diacido complexes can be reasonsbly explained by the theory that the specific absorption bands are due to charge transfer transitions from π orbitals of the pseudohalogeno ligand to the lower empty d_γ orbital of central cobalt(III) ion.

$(-)_{589}$-$[Co(en)_2(NH_3)(N_3)]^{2+}$, which shows a positive CD band in the specific absorption band region, is assigned to Δ configuration from the CD pattern in the first absorption band region,[19] and $(+)_{589}$-$[Co(en)_2(N_3)_2]^+$, which shows a positive and a negative CD bands (listing from the lower energy side) in the specific absorption band region, is also assigned to Δ configuration on the same basis. Similarly, $(-)_{589}$-$[Co(en)_2(NH_3)(NCS)]^{2+}$ having a positive CD band in the region is assigned to Δ and $(-)_{589}$-$[Co(en)_2(NCS)_2]^+$ having a negative and a positive CD bands to Λ. The CD patterns in the specific absorption band region are systematically related with the absolute configurations expected on the basis of the CD in the first d-d absorption band region and this suggests that the absolute configuration of this

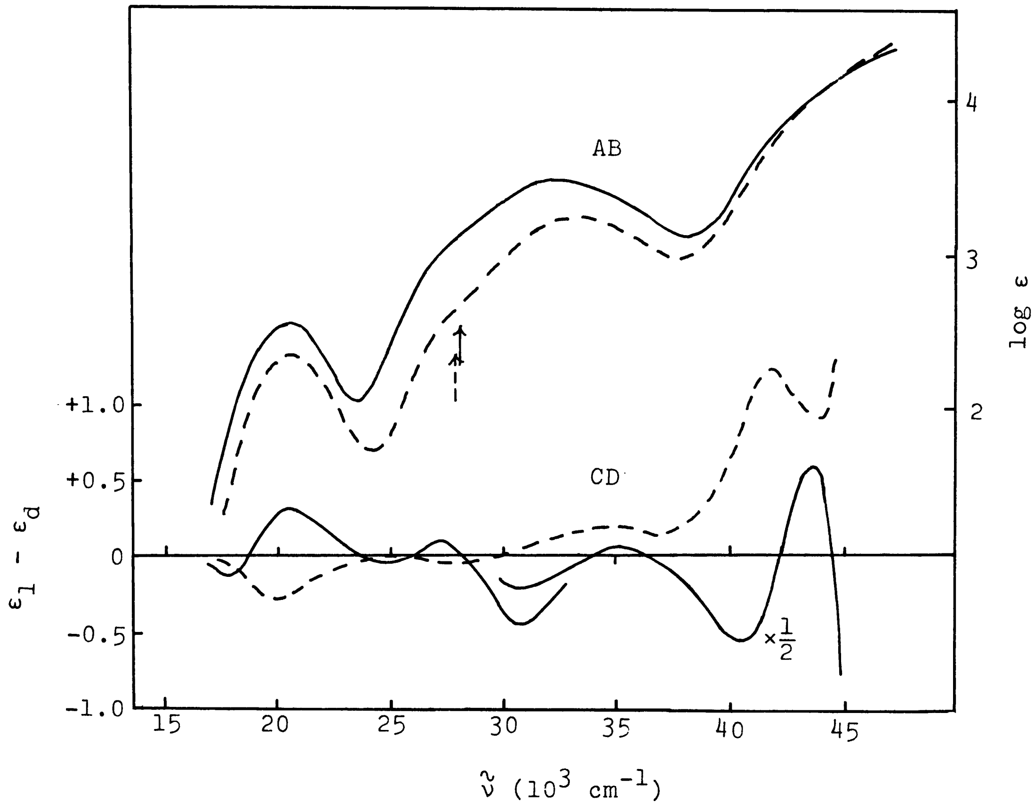

Fig. 2. Absorption (AB) and CD curves of $(-)_{589}$-$[Co(en)_2(NCS)_2]Cl$ (———) and $(-)_{589}$-$[Co(en)_2(NH_3)(NCS)]Br_2 \cdot 0.5H_2O$ (-----).

kind of complex is also assignable from the CD in the specific absorption band region.

References

1) Y. Shibata, *J. Chem. Soc. Japan*, 35, 807 (1914); R. Tsuchida, *ibid.*, 59, 586 (1938); Y. Uzumasa, H. Okuno, and K. Doi, *ibid.*, 59, 655 (1938).
2) R. Tsuchida and M. Kobayashi, *Bull. Chem. Soc. Japan*, 13, 471 (1938); H. Kuroya and R. Tsuchida, *J. Chem. Soc. Japan*, 59, 1142 (1938).
3) A. v. Kiss and D. v. Czeglédy, *Z. Anorg. Chem.*, 235, 407 (1938).
4) M. Linhard and M. Weigel, *Z. Anorg. Chem.*, 267, 113, 121 (1951).
5) M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Chem.*, 278, 287 (1955).
6) J. Fujita, Thesis, Osaka University, 1958.
7) C. K. Jϕrgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, (1962), p.196; H.-H. Schmidtke, *Z. Physik. Chem. N. F.*, 40, 96 (1964).
8) J. C. Barnes and P. Day, *J. Chem. Soc.*, 1964, 3886.
9) H.-H. Schmidtke, *Ber. Bunsenges. Physik. Chem.*, 71, 1138 (1967); H.-H. Schmidtke and D. Garthoff, *J. Am. Chem. Soc.*, 89, 1417 (1967).
10) D. F. Gutterman and H. B. Gray, *J. Am. Chem. Soc.*, 93, 3364 (1971).
11) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 1960, 4812.
12) A. Werner, *Ann.*, 386, 1 (1912).
13) A. Werner and F. Bräunlich, *Z. Anorg. Chem.*, 22, 125 (1900).
14) K. Garbett and R. D. Gillard, *J. Chem. Soc.*, 1965, 6084; R. D. Gillard and R. Maskill, *ibid.*, 1971, 1813.
15) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, 90, 6654 (1968).
16) K. Sone, *J. Chem. Soc. Japan*, 71, 270 (1950); J. Fujita and Y. Shimura, *Bull. Chem. Soc. Japan*, 36, 1281 (1963).
17) R. S. Mulliken, *J. Chem. Phys.*, 3, 720 (1935); R. S. Mulliken, *Rev. Mod. Phys.*, 14, 204 (1942).
18) K. Nakamoto, J. Fujita, M. Kobayashi, and R. Tsuchida, *J. Chem. Phys.*, 27, 439 (1957).
19) A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 1965, 5094.

(Received October 4, 1972)