On a New Type of Cyclododecatriene - Silver Nitrate Complex

By Shunsuke KURIBAYASHI, Noritake YASUOKA, Toshiko MITSUI, Hiroshi TAKAHASHI and Muneaki YAMAGUCHI

(Received June 19, 1964)

In the course of X-ray work on the cyclododecatriene - silver nitrate complex, we have found a new type of complex.

Zakharkin and Korneva reported[1] that *trans, trans, cis*-cyclododecatriene-1, 5, 9 (abbreviated *t, t, c*-CDT) forms a complex with silver nitrate and gave it the formula $(C_{12}H_{18})AgNO_3$ (m. p. 166~167°C). This complex crystallizes as a platelet. In the course of a structure analysis by X-ray diffraction, we found a few needle-like crystals among them. These needles gave X-ray diffraction patterns different from those of platelets. We cite below the former (needles) as the β-type and the latter (platelets) as the α-type. The β-type crystal melts at 149°C and was found by elementary analyses to be of the formula $(C_{12}H_{18})_2AgNO_3$. (Found: C, 58.37, 58.67; H, 7.33, 7.27; Calcd. C, 58.30; H, 7.34%.) Crystallographic data of both complexes are shown in Table I.

The infrared absorption spectra of *t, t, c*-CDT and of both complexes are shown in Fig. 1. The absorption maximum at 970 cm^{-1}, which is assigned to an out-of-plane bending of the CH bond related to the trans C=C bond, is shifted to 990 cm^{-1} in the case of the α-type.

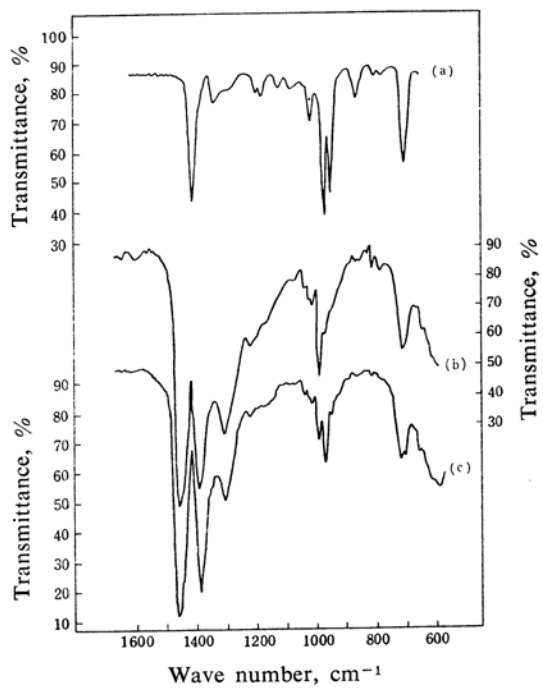

Fig. 1. Infrared spectra of
(a) *trans, trans, cis*-Cyclododecatriene,
(b) α-Type complex in Nujol and
(c) β-Type complex in Nujol.

1) L. I. Zakharkin and V. V. Korneva, *Doklady Akad. Nauk. S.S.S.R.*, **132**, 1078 (1960).

TABLE I. CRYSTALLOGRAPHIC DATA OF *trans, trans, cis*-CYCLODODECATRIENE-SILVER NITRATE

	Crystal system	a (A)	b (A)	c (A)	Probable space groups from missing reflections
α-Type	Orthorhombic	15.72	17.62	9.66	$Cmc2_1$, $Cmcm$, $C2cm$
β-Type	Orthorhombic	5.35	15.34	29.80	$Pbcn$

On the other hand, in the case of β-type crystals, the absorption band at 970 cm^{-1} still remains, and that at 990 cm^{-1} is also observed. The absorption at 720 cm^{-1}, assigned to an out-of-plane bending of the CH bond related to the cis C=C bond, remains unchanged in both cases.

These facts suggest that both of the two trans C=C bonds of the α-type coordinate to the Ag^+ ion, but that only one of them does in the case of the β-type and that the cis C=C bond remains free in both cases.

Preliminary X-ray work supports these conclusions. Details of the results of our X-ray crystal structure analysis will be reported in the near future.

Government Industrial Research Institute, Osaka
Oyodo-ku, Osaka