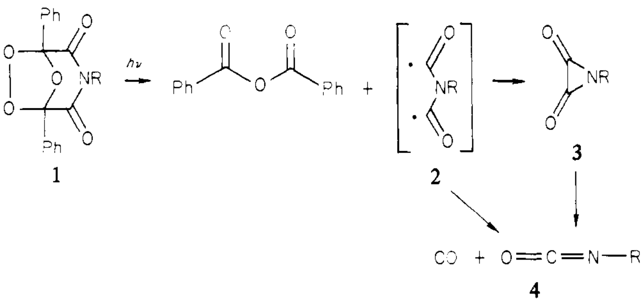
Scheme I



a, R = H
b, R = CH_3
c, R = $CH(CH_3)_2$
d, R = CH_2CH_2Ph

Table I. IR Spectra of Products in the Photolysis of Diphenylmaleylimide Ozonides[a]

reactant	aziridine-2,3-diones	iso-cyanates	carbon monoxide	benzoic anhydride
1a	1954	2260	2130	1785 1720
1b	1940 1750	2270 2245		
1c	1930 1753	2260		
1d	1933 1742	2265		

[a] Units, cm^{-1}; in KBr at 77 K.

followed by IR spectroscopy.[10] The spectrum showed two strong absorptions at 1940 and 1750 cm^{-1}, in addition to the absorptions of methyl isocyanate (2270 and 2245 cm^{-1}), carbon monoxide (2130 cm^{-1}), and benzoic anhydride (1785 and 1720 cm^{-1}). The spectrum did not change when the photolysate in KBr was allowed to stand for 1 h at 77 K after irradiation. However, shortly after liquid nitrogen had been evaporated, the two absorptions rapidly decreased, *with increase of the absorptions of methyl isocyanate and carbon monoxide*, while that of benzoic anhydride remained unchanged. This fact shows that the elusive species decomposes to these two compounds, and strongly indicates that it is *N*-methylaziridine-2,3-dione (**3b**). Thermal decarbonylation of three-membered ring carbonyl compounds is not exceptional. Diaziridinones undergo decarbonylation spontaneously at room temperature.[11]

Imides show two carbonyl absorptions (symmetric and antisymmetric modes).[12] The positions of $\nu_{C=O}$ at 1940 and 1750 cm^{-1} are quite reasonable for the structure of **3b** in comparison with those of other cyclic imides: a *N*-methylmalonimide derivative (1820 and 1710 cm^{-1} in KBr),[13] *N*-methylsuccinimide (1760 and 1690 cm^{-1} in KBr),[14] *N*-methylglutarimide (1718 and 1670 cm^{-1} in KBr).[14] The ring size effects in the carbonyl absorptions of these cyclic imides (3–6-membered rings) are quite analogous to those of other cyclic carbonyl compounds such as lactams and lactones.[2a] The large splitting of the two carbonyl absorptions of **3b** (190 cm^{-1}) is also reasonable for the structure, because the two carbonyls are directly bonded and should be completely coplanar.[12]

The low-temperature photolysis of other ozonides gave similar results (Table I). In the case of **1a**, the absorption of aziridine-2,3-dione was weak, and the lower carbonyl absorption was not clear. It is presumably hidden in the strong absorptions of benzoic anhydride. The isocyanates and carbon monoxide formed in the low-temperature photolysis are presumed to be produced by cleavage of the biradical (**2**) rather than decomposition of **3**, because (a) the absorptions of **3**, **4**, carbon monoxide, and benzoic anhydride increase in parallel during irradiation, and (b) the aziridine-2,3-diones are stable at 77 K. Since the aziridine-2,3-diones (**3a**–**3d**) were not detected when the ozonides (**1a**–**1d**) in KBr pellets were photolyzed at −78 °C, they are presumed to decompose rapidly at that temperature. An attempt to trap **3b** with ethanol at low temperature was unsuccessful.[15]

In summary, the ozonides of diphenylmaleylimides (**1a**–**1d**) are photolyzed according to Scheme I in which oxygen–oxygen bond homolysis is followed by a double β scission, as in the case of most ozonides, to produce benzoic anhydride and the 1,3-biradical (**2**). The IR spectra of the photolysates at 77 K revealed the presence of unstable compounds which decompose to carbon monoxide and the isocyanates. The spectral characteristics of the compounds are in full accord with those expected for three-membered cyclic imides. These results permit the assignment of structure **3**, aziridine-2,3-diones, to the elusive species.

Acknowledgment. We thank Associate Professor Takahiro Tezuka and Professor Wataru Ando for making the apparatus for low-temperature IR spectroscopy available for our present study.

---

(10) The apparatus used in the present study consists of a pellet holder, a vacuum shroud, dewar, and two CaF_2 windows. Irradiation and the measurement of IR spectra were carried out through the windows. IR spectra were recorded with a JASCO IRA-1 spectrophotometer. A 300-W high-pressure mercury lamp (Eikosha) was used as an irradiation source.

(11) Renner, C. A.; Green, F. D. *J. Org. Chem.* **1976**, *41*, 2813.

(12) Bellamy, L. J. "Advances in Infrared Group Frequencies", Methuen: New Fetter Lane, Great Britain, 1968; pp 127–132.

(13) Maruyama, K.; Ishitoku, T.; Kubo, Y. *J. Am. Chem. Soc.* **1979**, *101*, 3670.

(14) Dolphin, D.; Wick, A. "Tabulation of Infrared Spectral Data", Wiley-Interscience: New York, 1977.

(15) The ozonide in ethanol–ether–toluene glass (2:1:1) was photolyzed at 77 K, and the resulting reaction mixture was allowed to melt (−130 to ∼−120 °C) and eventually warmed up to room temperature gradually. Examination of the mixture by VPC indicated the absence of *N*-methyloxamic acid ethyl ester which would be formed by addition of ethanol to **3b**.

Hiromu Aoyama,* Masami Sakamoto, Yoshimori Omote

Department of Chemistry, The University of Tsukuba
Sakuramura, Ibaraki, 305 Japan

Received May 23, 1980

Isolation of an Entire Set of the Three Possible Isomers of *trans*-Diammine(triethylenetetraamine)cobalt(III) Ion

Sir:

Triethylenetetraamine ($NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$) is one of the most familiar ligands, and the stereochemistry of its complexes has been studied extensively. In 1967, Buckingham et al.[1] isolated, for the first time, one of the trans catoptromers; i.e., they obtained optically active *trans*-[$CoCl_2$(trien)]ClO_4 by isomerization of Λ,β-*S*,*S*-[$CoCl_2$(trien)]ClO_4. However, no reports have been found on the direct resolution of the racemic isomer of *trans*-[CoX_2(trien)]$^{n+}$. On the other hand, the trans "envelope" (meso) structure, the possible existence of which was also pointed out by Buckingham et al.,[1] has been known only for the trans-dicyano complex.[2] Now we have succeeded in isolating all of the three possible *trans*-[$Co(NH_3)_2$(trien)]$^{3+}$ isomers, the preliminary study of which will be described.

The trans-diammine complex was prepared by the oxidation of *trans*-[$Co(NCS)_2$(trien)]$^+$ with KIO_3 according to the method

---

(1) Buckingham, D. A.; Marzilli, P. A.; Sargeson, A. M. *Inorg. Chem.* **1967**, *6*, 1032.

(2) Spatola, E. A. *Diss. Abstr. Int. B* **1971**, *32*, 808. (b) Wismer, R. K.; Jacobson, R. A. *Inorg. Chim. Acta* **1973**, *7*, 477.

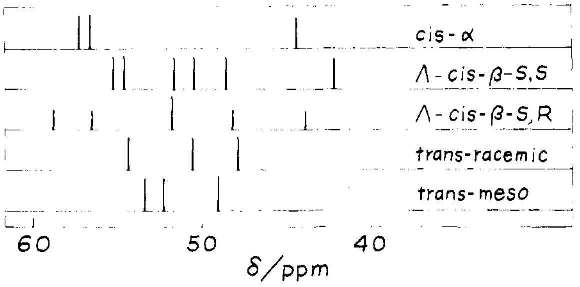


Figure 1. Diagrammatic representation of the ^{13}C NMR spectra of $[Co(NH_3)_2(trien)]^{3+}$ isomers in dilute HCl solutions. The ambient temperature was 30 °C. Tetramethylsilane was used as an external standard. Each of the two cis-β isomers was identified by the difference CD curve of both isomers. See: Utsuno, S.; Hayashi, A.; Kondo, S.; Utsumi, M. *Chem. Lett.* **1979**, 351.

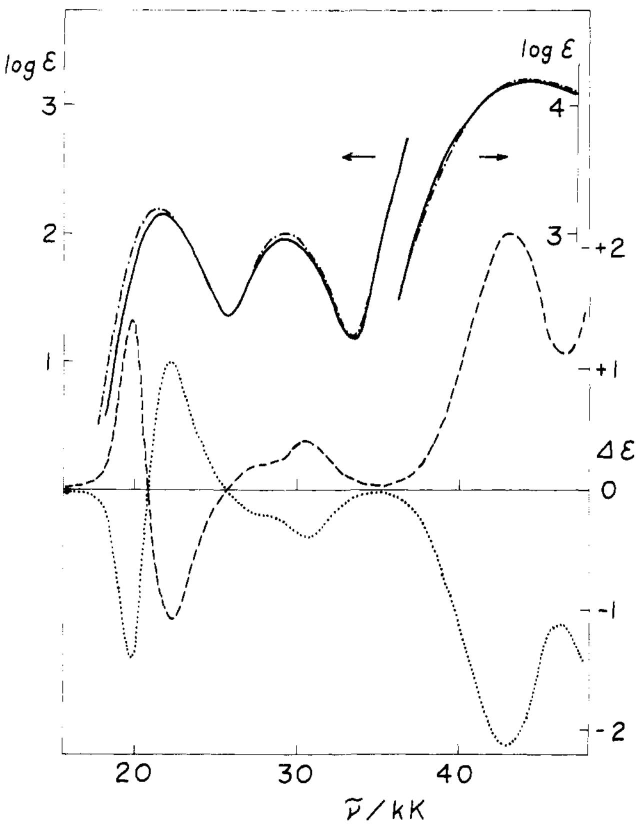


Figure 2. Electronic absorption spectra of the meso (—) and racemic (-·-·-·-) isomers of *trans*-$[Co(NH_3)_2(trien)]^{3+}$, and CD spectra of (+)-*trans*-$[Co(NH_3)_2(trien)]^{3+}$ (- - -) and (−)-*trans*-$[Co(NH_3)_2(trien)]^{3+}$ (···).

of Garbett and Gillard.[3] The trans structure is expected to be retained, because none of the coordination bonds were broken during the reaction. Column chromatography of the yellow product with SP-Sephadex (C-25) and acidic 0.15 M Na_2SO_4 (pH 3.0) gave two bands. The first band was found to consist of the meso isomer and the second the racemic mixture of catoptromers. The latter was resolved completely by SP-Sephadex column chromatography by using 0.15 M $Na_2[Sb_2(tart)_2]$ as eluant. The three isomers were isolated as chloride or perchlorate. The optically active isomers readily isomerize and lose their activities in a neutral solution, which can distinguish these trans catoptromers from the cis ones.[4] *meso-trans*-$[Co(NH_3)_2(trien)]Cl_3{\cdot}H_2O$: Anal. C, H, N; Co calcd, 16.21; found, 16.03. (−)-*trans*-$[Co(NH_3)_2(trien)](ClO_4)_3{\cdot}H_2O$: Anal. C, H, N; Co calcd, 10.61; found, 10.46; $[\alpha]_{546} = -358°$ (0.27% 0.01 M $HClO_4$). (+)-*trans*-$[Co(NH_3)_2(trien)](ClO_4)_3{\cdot}H_2O$: Anal. C, H, N; Co calcd, 10.61; found, 10.60; $[\alpha]_{546} = +360°$ (0.27% 0.01 M $HClO_4$).

Table I. Final Energy Terms (kJ mol^{-1}) for the *trans*-$[Co(NH_3)_2(trien)]^{3+}$ Isomers

terms	catoptromer	meso isomer
bond strain	5.75	5.95
nonbonded interaction	26.62	27.27
valence angle deformation	32.64	21.02
torsional interaction	18.95	26.28
total strain energy	83.96	80.47

Figure 1 shows the diagrammatic representation of the ^{13}C NMR spectra of the present isomers in dilute HCl solutions together with those of the cis isomers. The spectra and the above chromatographic findings show that *meso*-$[Co(NH_3)_2(trien)]^{3+}$ has undoubtedly been obtained.

Figure 2 shows the CD spectra of (+)- and (−)-*trans*-$[Co(NH_3)_2(trien)]^{3+}$. The trans isomers contain no skew chelate pairs. Thus, like the optically active *mer*-$[Co(dien)_2]^{3+}$ isomer without skew chelate pairs,[5] they show small $\Delta\epsilon$ values in the CT band region, almost one order of magnitude smaller than those of the cis-α and cis-β isomers. On the other hand, the $\Delta\epsilon$ values in the first-band region are considerably larger in comparison with those of the cis isomers. A similar tendency was found for (+)-*trans*-$[CoCl_2(trien)]^+$ and the corresponding complex containing methyl-substituted triethylenetetraamine.[6]

These trans isomers underwent isomerization in a solution buffered with 2,6-lutidine–HCl. Standing the solution of the racemic trans isomer for 30 min at pH 5.8 gave a 4:5 meso/racemic mixture, which was estimated by ^{13}C NMR. The same mixture was also obtained from the meso-trans isomer by isomerization under the same conditions.

For these trans isomers, the strain energy minimized calculations were carried out by using a modification of the computer program of Boyd.[7] The final energy terms are given in Table I. Significant angular and torsional strains are found in the catoptromer and the meso isomer, respectively; however, their total energies differ only slightly from each other. With the consideration that more or less arbitrary parameters are contained in the calculations, the calculated energy difference is consistent with the experimental formation ratio of 4:5 for meso to a pair of catoptromers.

Acknowledgment. The CD spectra were recorded on a Jasco J-40C instrument of the Institute for Molecular Science, Japan.

Shunji Utsuno,* Yukio Sakai

Department of Chemistry, Shizuoka University
Oya, Shizuoka 422, Japan

Yuzo Yoshikawa, Hideo Yamatera

Department of Chemistry, Nagoya University
Chikusa-ku, Nagoya 464, Japan

Received June 2, 1980

---

(3) Garbett, K.; Gillard, R. D. *J. Chem. Soc.* **1965**, 6084. Preparation and separation of possible isomers of isothiocyanato complex are now in progress in one of the authors' (S.U.) laboratory.

(4) Their stereochemistry will be published elsewhere.

(5) Yoshikawa, Y.; Yamasaki, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 179.

(6) Goto, M.; Matsushita, H.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1973**, *12*, 1498.

(7) Boyd, R. H. *J. Chem. Phys.* **1968**, *49*, 2574. (b) Yoshikawa, Y. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 159.