(d) The silver cyanate was freshly prepared as commercially available material was shown to be unreactive.

Diisocyanatotetramethyldisilane.—To a solution of 5 g (0.0267 mole) of *sym*-dichlorotetramethyldisilane (bp 147.5–149.5°) in 35 ml of anhydrous diethyl ether, contained in a 100-ml three-necked flask, to which was attached a reflux condenser, thermometer, and solid addition flask, was added silver cyanate (9.3 g, 0.0621 mole, a slight excess). The addition of the solid silver cyanate, at room temperature and over a 30-min period, was accompanied with a very slight rise in temperature. The reaction mixture was stirred for 10–12 hr at room temperature under a deoxygenated anhydrous nitrogen atmosphere and then filtered. The precipitate (8.7 g) was washed with several small portions of anhydrous ether. The filtrate and the washings were combined and the ether was removed by distillation (under nitrogen). The product was obtained by distillation under reduced pressure giving the desired *sym*-diisocyanatotetramethyldisilane (bp 105.5–106.5° (30 mm)); yield: 2.19 g, 54%.

Anal. Calcd for $C_6H_{12}N_2O_2Si_2$: N, 13.98; Si, 28.1; hydrogen value for one Si–Si bond per molecule, 111.8. Found: N, 13.9; Si, 27.7; hydrogen value, 112.5.

The infrared spectrum was compatible with the assigned structure. A strong band at 2280 cm^{-1} was attributed to the isocyanate grouping.

Diisocyanatotetraphenyldisilane.—Using a procedure similar to that described for the preparation of diisocyanatotetramethyldisilane, a solution of *sym*-dichlorotetraphenyldisilane (4.0 g, 0.0092 mole) in 75 ml of anhydrous diethyl ether was treated with silver cyanate (2.8 g, 0.0183 mole, a slight excess). The precipitate (3.2 g) obtained by filtration was washed with several small portions of anhydrous diethyl ether and the washings were combined with the filtrate. The ether was removed by distillation under nitrogen, leaving a white solid which was recrystallized once from a 1:1 benzene–petroleum ether (bp range 30–60°) mixture, giving 3.5 g (84%) of the desired material (mp 123–124°).

Anal. Calcd for $C_{26}H_{20}N_2O_2Si_2$: N, 6.25; Si, 12.5; hydrogen value for one Si–Si bond per molecule, 50.1. Found: N, 5.93; Si, 12.7; hydrogen value, 53.8.

The infrared spectrum of this material was compatible with the assigned structure. The strong NCO band appeared at 2280 cm^{-1}.

Hydrolysis of *sym*-Diisocyanatotetramethyldisilane.—In a 50-ml flask connected to a condenser was placed 0.5 g (0.0025 mole) of 1,2-diisocyanatotetramethyldisilane, and 10 ml of a 10% water–piperidine solution was added. The resulting solution was then heated at reflux temperature for a period of 24 hr. The cooled solution was then diluted with 25 ml of water and extracted with three 20-ml portions of ether. The water phase was then concentrated to dryness under reduced pressure giving a white solid which was recrystallized from benzene–petroleum ether (1:1). Piperidine carboxamide (0.15 g) was isolated having an infrared spectrum identical with that isolated from the hydrolysis of 1,2-diisocyanatotetraphenyldisilane.

Anal. Calcd for $C_6H_{12}ON_2$: N, 21.85. Found: N, 21.60.

Hydrolysis of *sym*-Diisocyanatotetraphenyldisilane.—The products remaining in the moist piperidine solution from three runs in the determination of the hydrogen value of *sym*-diisocyanatotetraphenyldisilane were combined and treated as described above for the hydrolysis of the tetramethyl derivative. The isolated material, piperidine carboxamide, melted at 105–106° (lit.[8] 105–106°). The infrared spectrum was compatible with the assignment.

***sym*-Dipiperidinecarboxamidyltetramethyldisilane.**—In a 100-ml flask attached to a condenser and under a nitrogen atmosphere was placed piperidine (0.52 g, 0.006 mole) in 5 ml of benzene. To this was added dropwise 1,2-diisocyanatotetramethyldisilane (0.59 g, 0.0029 mole) dissolved in 2 ml of benzene. A clear solution resulted. It was warmed to 50° and maintained at that temperature for 1 hr. On cooling, long slender needles formed. Petroleum ether (10 ml) was added to the mixture and the contents of the flask allowed to stand overnight at 10°. Filtration under suction to remove the crystalline solid gave 0.75 g of a material melting at 108–112°. The material recrystallized from a benzene–petroleum ether mixture (3:1) melted at 109–111°.

Anal. Calcd for $C_{16}H_{34}O_2N_4Si_2$: N, 15.11; Si–Si, 60.6 ml/g; Si, 15.17. Found: N, 15.28; Si–Si, 60.7 ml/g; Si, 14.81.

The assigned structure was compatible with the infrared spectrum of the material.

***sym*-Dipiperidinecarboxamidyltetraphenyldisilane.**—In a 100-ml flask attached to a reflux condenser and under an atmosphere of nitrogen was placed piperidine (0.18 g, 0.002 mole) dissolved in 8.0 ml of benzene. To this was added 1,2-diisocyanatotetraphenyldisilane (0.45 g, 0.001 mole) dissolved in 5.0 ml of benzene. The resulting solution was heated at 60° for a period of 4 hr. To the cooled solution was added 15 ml of *n*-hexane and the solution was allowed to stand at 10° overnight. The white crystalline solid (0.43 g) removed by filtration melted at 134–136° after drying.

Anal. Calcd for $C_{36}H_{42}N_4O_2Si_2$: N, 9.05; Si, 9.06. Found: N, 8.75; Si, 9.14.

The assigned structure was compatible with the infrared spectrum of the compound.

---

[8] W. Seibert, *Chem. Ber.*, **80**, 494 (1947).

CONTRIBUTION FROM THE DEPARTMENT OF
SYNTHETIC CHEMISTRY, FACULTY OF ENGINEERING,
THE UNIVERSITY OF TOKYO, TOKYO, JAPAN

Stereochemical Studies of Metal Chelates. I. Cobalt(III) Complexes Containing an Optically Active Tetramine

BY SADAO YOSHIKAWA, TAKESHI SEKIHARA,
AND MASAFUMI GOTO

Received July 5, 1966

Remarkable progress has been recently made in stereochemical studies of triethylenetetramine–cobalt(III) complexes,[1–3] which were prepared by Basolo for the first time.[4] Recently, Asperger and Liu[5] have synthesized a new optically active ligand, 2,9-dimethyltriethylenetetramine, a C-substituted derivative of trien, and prepared its cobalt(III) complexes. They conclude that nmr spectra could be used in distinguishing the three geometrical isomers and that the complexes having the absolute configuration D(+)-α, and L(−)-β predominate for the *l* ligand by the stereospecific coordination.

Independently we also synthesized two other new optically active derivatives of trien, 5-methyltriethylenetetramine (5-Metrien) and 3,8-dimethyltriethylenetetramine (3,8-Dimetrien), and some novel observations in the stereochemistry of their cobalt(III) complexes are briefly reported here.

The ligand 5-Metrien was synthesized as follows

---

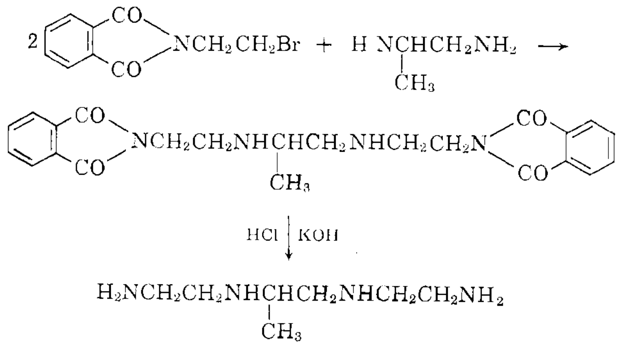
[1] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **4**, 45 (1965).

[2] E. Kyuno, L. J. Boucher, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **87**, 4458 (1965).

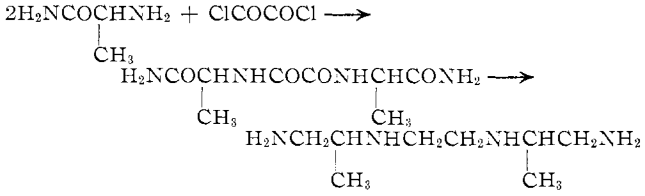
[3] D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

[4] F. Basolo, *J. Am. Chem. Soc.*, **70**, 2634 (1948).

[5] R. G. Asperger and C. F. Liu, *Inorg. Chem.*, **4**, 1395 (1965).



3,8-Dimetrien was synthesized as follows



$$2H_2NCOCH(CH_3)NH_2 + ClCOCOCl \longrightarrow H_2NCOCH(CH_3)NHCOCONHCH(CH_3)CONH_2 \longrightarrow H_2NCH_2CH(CH_3)NHCH_2CH_2NHCH(CH_3)CH_2NH_2$$

Experimental Section

(1) **Synthesis of 5-Methyltriethylenetetramine.**—β-Bromoethylphthalimide was prepared from ethanolamine, phthalic acid anhydride, and phosphorus tribromide according to the literature.[6] Commercially available propylenediamine was distilled before use.

β-Bromoethylphthalimide (152 g, 0.60 mole) was measured into a 500-ml four-necked flask equipped with a stirrer, dropping funnel, reflux condenser, and thermometer. It was then heated in an oil bath and melted completely. The distilled propylenediamine was added to it over a period of about 5 hr at 130–140°. After the addition, stirring and heating were continued, and the reaction mixture became dark brown and viscous. After about 35-hr heating, the reaction mixture was hydrolyzed with 550 ml of concentrated HCl at 130–140°. After cooling to room temperature overnight, the precipitate was filtered and washed with water. The filtrate and washings were combined and concentrated under reduced pressure until the dark brown viscous product resulted. The oily layer, formed by the addition of 400 g of NaOH in 300 ml of water to the residue, was separated from the aqueous layer, and then the aqueous solution was extracted with benzene several times. This benzene extract and oily matter were combined and distilled to remove benzene and water. The residue was then treated with metallic sodium to remove traces of water and distilled under reduced pressure [121° (5 mm)]. The yield is 6–8 g.

(2) **Synthesis of 3,8-Dimethyltriethylenetetramine.**—L(+)-Alanineamide was obtained by usual method.[7] Oxalyl chloride was synthesized according to the directions by Staudinger.[8] A solution of 30.8 g (0.35 mole) of L(+)-alanineamide and 28 g of anhydrous sodium carbonate in 200 ml of water and a solution of 22.2 g (0.18 mole) of oxalyl chloride in 150 ml of benzene were placed in a household blender jar and stirred vigorously at room temperature.

The reaction was exothermic and accompanied by the separation of a white precipitate and the evolution of gas. After continuous stirring for 1 hr (a few minutes might be enough to complete the reaction), the precipitate was filtered, washed sufficiently with water and ether, and dried *in vacuo*. The yield was 22.7 g (55% of the theoretical amount).

L(+)-Tetramide thus obtained did not dissolve in common organic solvents except dimethylformamide. *Anal.* Calcd for $C_8H_{14}N_4O_4$: C, 41.74; H, 6.13; N, 24.34. Found: C, 41.29; H, 6.41; N, 24.07. The optical rotation in dimethylformamide was $[\alpha]_D$ +77.1° (*c* 0.106).

Reduction of L(+)-tetramide to L(+)-tetramine was carried out as follows: Into a 2-l. four-necked round-bottomed flask equipped with a mechanical stirrer, thermometer, and reflux condenser protected by a calcium chloride tube was placed a solution of 12.1 g (0.32 mole) of $LiAlH_4$ in 300 ml of completely dehyrated tetrahydrofuran. To it was gradually added 10.5 g (0.046 mole) of L(+)-tetramide suspended in 100 ml of completely dehydrated tetrahydrofuran over a period of 30 min with vigorous stirring. On addition of the suspension, the reaction mixture became yellowish with the evolution of H_2 gas. Then it was refluxed for 4 hr on a water bath. The reaction mixture again turned colorless when allowed to stand to room temperature with stirring. A stoichiometric amount of water was added slowly to decompose $LiAlH_4$ present in the reaction mixture. The precipitate was filtered and washed repeatedly with tetrahydrofuran until no amine was detected by an aqueous solution of $CuSO_4$. The filtrate and washings were combined and tetrahydrofuran was removed under reduced pressure, yielding a pale yellow liquid. This residue was distilled under reduced pressure after addition of metallic sodium. The yield is 2.2 g (25% of the theoretical amount) of product boiling at 104° (2 mm) or 117° (3.5 mm). The optical rotation for L(+)-3,8-dimethyltrien was measured in dry benzene; $[\alpha]^{20}_D$ +101.8° (*c* 0.42).

(3) **Preparation of Dichlorocobalt(III) Complexes.**—A solution of 8.7 g (0.050 mole) of the tetramine in 130 ml of water was added to 50 ml of an aqueous solution of 16.1 g (0.068 mole) of cobaltous chloride hexahydrate. The solution was aerated for 24 hr with CO_2-free air. After 35 ml of concentrated hydrochloric acid was added, the solution was evaporated on a steam bath until a precipitate began to separate. On standing overnight in a refrigerator, the resulting crystalline product was collected on a filter and washed with acetone followed by alcohol and ether. The salt was dried at 110°. A purple salt was obtained for the ligand, *dl*-5-Metrien. *Anal.* Calcd for $[CoCl_2(dl\text{-}C_7H_{20}N_4)]Cl \cdot 0.5H_2O$: C, 25.12; H, 6.33; N, 16.74. Found: C, 25.24; H, 6.17; N, 16.57. A green salt was obtained for the ligand L(+)-3,8-Dimetrien. *Anal.* Calcd for $[CoCl_2(d,d\text{-}C_8H_{22}N_4)]Cl \cdot HCl \cdot 1.5H_2O$: C, 23.8; H, 6.5; N, 13.9; Cl, 35.2. Found: C, 24.0; H, 5.5; N, 13.9; Cl, 35.2.

Results and Discussion

The free amines were purified by distillation and identified by nmr and infrared spectra.

It is very interesting that a green salt, not a purple salt, was obtained for the ligand *d,d*-3,8-Dimetrien, in contrast to the purple salt which was the main product for the ligand trien. The electronic absorption spectra and circular dichroism of this complex in methanol are shown in Figure 1.

The color of the complex salt, the absorption spectra, and the chemical behavior in aqueous solution make it possible to assign this complex as the *trans* isomer in comparison with the corresponding dichlorobis(ethylenediamine)cobalt(III) complex.

Since the *trans* isomer is not intrinsically optically active such optical activity observed in the circular dichroism of *trans*-$[Co(d,d\text{-}3,8\text{-}Dimetrien)Cl_2]Cl$ must be attributed to the vicinal effect of the optically active ligand.

The transition at about 21,200 cm^{-1} of circular dichroism can be assigned to the electronic transition ${}^1A_{1g} \rightarrow {}^1A_{2g}$, in good agreement with the results obtained for dichlorobis(*l*-propylenediamine)cobalt(III) ion by Wentworth and Piper.[9] It is quite remarkable that *trans*-$[Co(d,d\text{-}3,8\text{-}Dimetrien)Cl_2]Cl$ has two dis-

---

[6] *Org. Syn.*, **32**, 18 (1952).

[7] P. S. Yang and M. R. Rising, *J. Am. Chem. Soc.*, **53**, 3183 (1931).

[8] H. Staudinger, *Chem. Ber.*, **41**, 3563 (1908).

[9] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 202 (1965).

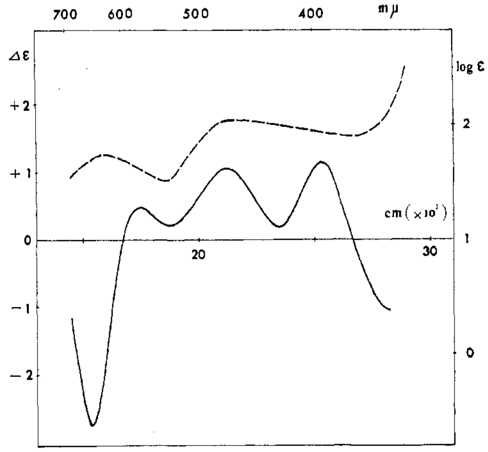


Figure 1.—Absorption spectrum (— — —) and circular dichroism (———) of [$CoCl_2$(*d,d*-3,8-Dimetrien)]Cl.

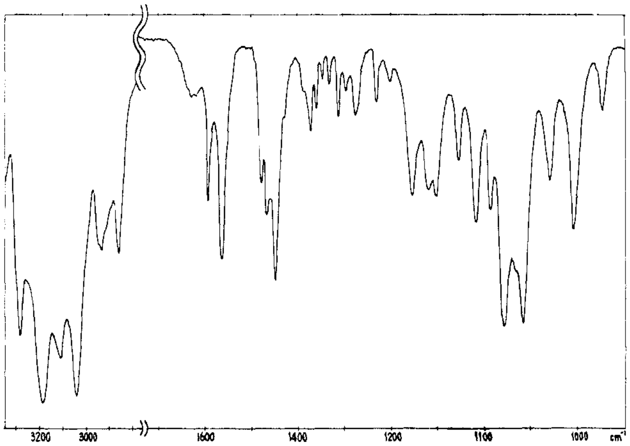


Figure 2.—Infrared spectrum of [$CoCl_2$(*dl*-5-Metrien)]Cl.

tinct circular dichroism bands with opposite sign in the 15,000–18,000 cm^{-1} region which is usually assigned to the electronic transition of $^1A_{1g} \rightarrow {}^1E_a$. For *trans*-[Co(*l*-pn)$_2$Cl$_2$]Cl, only a single transition (16,400 cm^{-1}) was observed.[9] Assuming C_2 or D_2 symmetry, the ^1E_a energy level for D_{4h} symmetry degrades to ^1A and ^1B intrinsically. In *trans*-[Co(*l*-pn)$_2$Cl$_2$]$^+$,[9] the energy levels are so close that only one circular dichroism band appears at 16,400 cm^{-1}. But in *trans*-[Co(*d,d*-3,8-Dimetrien)Cl$_2$]$^+$, the great distortion causes the energy levels to be further apart as two circular dichroism bands of opposite sign are observed.

As is shown in Figure 2, the infrared spectrum of the purple salt, [$CoCl_2$(*dl*-5-Metrien)]Cl, has four strong absorptions in the 3300–3000 cm^{-1} (N–H stretching) region, two medium absorptions near 1600 cm^{-1} (N–H antisymmetric deformation), and two strong and two medium absorptions at 1090–990 cm^{-1}. Buckingham and Jones[8] identified the three geometrical isomers of the dichlorotrien–cobalt(III) complex according to their infrared spectra. On the basis of these assignments, it may be possible to assign the purple salt as the so-called *cis*-β isomer. This assignment is supported by the absorption spectrum.

CONTRIBUTION FROM THE CHEMISTRY RESEARCH LABORATORY,
AEROSPACE RESEARCH LABORATORIES, WRIGHT-
PATTERSON AIR FORCE BASE, OHIO, AND THE DEPARTMENT
OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, SAN DIEGO,
LA JOLLA, CALIFORNIA

The Metal Ion Reduction of Tris(2,4-pentanedionato)cobalt(III)

BY R. G. LINCK[1] AND J. C. SULLIVAN[2]

Received August 8, 1966

Of the many reactions involving reduction of Co(III) complexes by Cr^{2+}(aq) that have been studied kinetically, only a few have been shown by product analysis to proceed by the outer-sphere mechanism. In each of the two outer-sphere cases where V^{2+}(aq) and Eu^{2+}(aq) have also served as reducing agents, it has been observed that the relative rates of reduction by Cr^{2+}(aq), V^{2+}(aq), and Eu^{2+}(aq) are nearly constant. During an investigation of the Cr(II) reduction of tris(2,4-pentanedionato)cobalt(III), Co(aa)$_3$, in aqueous ethanol,[3] it was observed that Co(aa)$_3$ has a sufficient solubility in aqueous acid to make feasible the determination of the reaction kinetics of Cr^{2+}(aq), V^{2+}(aq), and Eu^{2+}(aq) toward this neutral Co(III) oxidant. The results in this case, where the Co(III) complex has oxygen as donor atoms, can then be compared with the previously studied outer-sphere systems, where nitrogen atoms are the donor atoms.

The results of this study indicate that the reduction of Co(aa)$_3$ by Cr^{2+}(aq) proceeds at least partially by an inner-sphere mechanism; however, the agreement between the rates of reduction by V^{2+}(aq) and Eu^{2+}(aq), relative to Cr^{2+}(aq), for Co(aa)$_3$ and tris(ethylenediamine)cobaltic ion, Co(en)$_3^{3+}$, respectively, as oxidants suggests that the outer-sphere path may also be present.

Experimental Section

Tris(2,4-pentanedionato)cobalt(III) was prepared from $CoCO_3$ and acetylacetone, Haa, with PbO_2 as the oxidant. This mixture was shaken overnight and extracted with benzene, and the organic layer was evaporated to give crude Co(aa)$_3$. The compound was purified as described in the literature.[4] Several preparations gave identical kinetic results. *Anal.* Calcd: C, 50.58; H, 5.90; Co, 16.55. Found for two preparations, respectively: C, 50.72, 50.79; H, 5.83, 5.85; Co, 16.30, 16.62. That a true solution of the oxidant in aqueous acid existed was verified by obtaining data that fit Beer's law, over the concentration range used in this study, at 5967 A (ε 129) and 3240 A (ε 7760). Europous ion was prepared from perchloric acid and $EuCO_3$[5] and was stored in a CO_2 atmosphere. Vanadium pentoxide[6] and $Cr(ClO_4)_3 \cdot 6H_2O$[7] were reduced by amalgamated zinc in perchloric acid, and the solutions of the divalent ions were stored in a nitrogen atmosphere. Stock solutions of the reductants were standardized spectrophotometrically by reactions with excess

---

[1] Chemistry Department, University of California, San Diego, La Jolla, Calif.

[2] Chemistry Division, Argonne National Laboratory, Argonne, Ill.

[3] R. G. Linck and R. E. Sievers, to be submitted.

[4] B. E. Bryant and W. C. Fernelius, *Inorg. Syn.*, **5**, 188 (1957).

[5] R. A. Cooley and D. M. Yost, *ibid.*, **2**, 69 (1946).

[6] E. H. Appleman and J. C. Sullivan, *J. Phys. Chem.*, **66**, 442 (1962).

[7] C. Postmus and E. L. King, *ibid.*, **59**, 1208 (1955).