

Acknowledgment. We thank D. Heijdenrijk for collecting the X-ray data, R. Fokkens for recording the mass spectra, and J. M. Ernsting for recording the 250-MHz NMR spectra. We thank the Netherlands Foundation for Chemical Research (S.O.N.) and The Netherlands Organization for Pure Research (Z.W.O.) for their financial support.

Registry No. Ru(CO)₃(R-DAB) (R = *i*-Pr), 94249-99-7; Ru(CO)₃(R-DAB) (R = *c*-Hx), 94250-00-7; Ru(CO)₃(R-DAB) (R = *i*-Bu), 94250-01-8; Ru(CO)₃(R-DAB) (R = *neo*-Pent), 94250-02-9; Ru(CO)₃(R-DAB) (R = *p*-Tol), 94250-03-0; Ru₂(CO)₆(R-DAB) (R = *i*-Pr), 94278-61-2; Ru₂(CO)₆(R-DAB) (R = *c*-Hx), 94250-04-1; Ru₂(CO)₅(R-DAB) (R = *i*-Bu), 94250-05-2; Ru₂(CO)₅(R-DAB) (R = *neo*-Pent), 94250-06-3; Ru₂(CO)₄(R-DAB)₂ (R = *p*-Tol), 94250-07-4; Ru₂(CO)₄(R-DAB)₂ (R = *i*-Bu), 94250-08-5; Ru₂(CO)₄(R-DAB)₂ (R = *neo*-Pent), 94294-07-2; Ru₃(CO)₉(R-DAB) (R = *neo*-Pent), 94278-62-3; Ru₃(CO)₉(R-DAB) (R = *i*-Bu), 94250-09-6; Ru₃(CO)₈(R-DAB) (R = *neo*-Pent), 94250-11-0; Ru₃(CO)₈(R-DAB) (R = *i*-Bu), 94250-12-1; Ru₃(CO)₉(R-DAB) (R = *c*-Hx), 94250-10-9; Ru₃(CO)₁₂, 15243-33-1.

Supplementary Material Available: Listings of analytical data and anisotropic thermal parameters, Figure 4 showing IR spectra, and listings of observed and calculated structure factors and bond distances (24 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

A Novel d¹⁰-d³-d¹⁰ Trinuclear Bimetallic Linear Complex of Zinc and Vanadium

F. ALBERT COTTON,*^{1a} STAN A. DURAJ,^{1a} WIESLAW J. ROTH,^{1a} and C. DAVID SCHMULBACH*^{1b}

Received May 31, 1984

The reaction of [V₂(μ-Cl)₃(THF)₆]₂[Zn₂Cl₆] with triphenylphosphine in benzene furnishes [V₂(μ-Cl)₃(THF)₅(PPh₃)₂][Zn₂Cl₆], which in turn gives (PPh₃)₂(Cl)Zn(μ-Cl)₂(THF)V(THF)(μ-Cl)₂Zn(Cl)(PPh₃) upon treatment with dichloromethane. The mono(triphenylphosphine) derivative was characterized by elemental analysis and X-ray fluorescence measurements. The V-[Zn(Cl)₃(THF)(PPh₃)₂·2CH₂Cl₂] molecule was fully characterized by single-crystal X-ray studies. The data are as follows: triclinic space group, P $\bar{1}$, *a* = 11.922 (3) Å, *b* = 14.189 (2) Å, *c* = 8.991 (3) Å, α = 107.47 (1)°, β = 108.03 (2)°, γ = 86.16 (1)°, *V* = 1379 (1) Å³, *Z* = 1. The principal structural features of interest are as follows: Zn-V distance of 3.289 (1) Å; Zn-P distance of 2.392 (1) Å; Zn-Cl distances of 2.324 (1) and 2.293 (1) Å for Zn-Cl(2)_b and Zn-Cl(3)_b, respectively, and of 2.197 (1) Å for Zn-Cl(1)_a.

Introduction

[V₂(μ-Cl)₃(THF)₆]₂[Zn₂(μ-Cl)₂Cl₄]₂,² previously known in the literature as VCl₂(THF)₂, represents an interesting starting material for entry into the nonaqueous chemistry of lower valent vanadium complexes. Under certain conditions it leads to compounds that contain vanadium only, e.g., V₃(μ₃-O)(CF₃CO₂)₆(THF)₃³ or [VCl(dppm)BH₄]₂,⁴ but it can also give rise to unusual vanadium- and zinc-containing metal complexes such as [VZnO(C₆H₅CO₂)₃(THF)]₄·2THF⁵ or [VZnH₂(BH₄)(PMePh₂)₂]₂.⁶ In this paper we report another example of a bimetallic compound, with some unusual features of interest, that was obtained from [V₂Cl₃(THF)₆]₂[Zn₂Cl₆], albeit by a two-step procedure. This novel linear complex, (PPh₃)₂(Cl)Zn(μ-Cl)₂(THF)V(THF)(μ-Cl)₂Zn(Cl)(PPh₃)·2CH₂Cl₂ provides a rare example of a zinc complex containing phosphine ligands.

Experimental Section

All operations were performed under an atmosphere of argon by using standard Schlenk techniques and a double-manifold vacuum line. Solutions and solvents were transferred via stainless cannulae and/or syringes. Dichloromethane was freshly distilled from P₂O₅, and benzene and hexane were distilled from benzophenone ketyl prior to use. Triphenylphosphine was deaerated under vacuum at room temperature. [V₂(μ-Cl)₃(THF)₆]₂[Zn₂Cl₆] was prepared according to the published procedure.² Elemental analyses were performed by Galbraith Microanalytical Laboratories. Source-excited X-ray fluorescence analysis was done with a 100-mCi ²⁴¹Am excitation source. X-rays emitted from the sample were detected and analyzed on a KEVEX lithium-drifted silicon detector [Si(Li)]. Detector output pulses were digitized and evaluated with a Nuclear Data ND66 pulse height analyzer. We thank Professor

Table I. Summary of Crystallographic Data

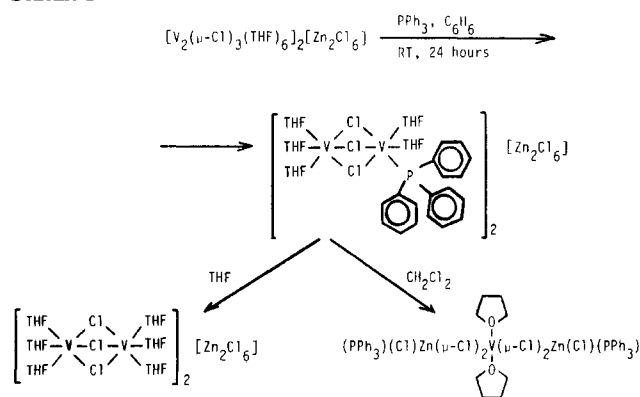
| | |
|--|---|
| formula | Zn ₂ VCl ₁₀ P ₂ O ₂ C ₄₆ H ₅₀ |
| fw | 1233.07 |
| space group | P $\bar{1}$ |
| <i>a</i> , Å | 11.922 (3) |
| <i>b</i> , Å | 14.189 (2) |
| <i>c</i> , Å | 8.991 (3) |
| α, deg | 107.47 (1) |
| β, deg | 108.03 (2) |
| γ, deg | 86.16 (1) |
| <i>V</i> , Å ³ | 1379 (1) |
| <i>Z</i> | 1 |
| <i>d</i> _{calcd} , g/cm ³ | 1.485 |
| cryst size, mm | 0.3 × 0.6 × 0.6 |
| μ(Mo Kα), cm ⁻¹ | 16.261 |
| data colln instrum | Syntax P $\bar{1}$ |
| radiation (monochromated in incident beam) | Mo Kα (λ = 0.710 73 Å) |
| orientation reflns: no.; range (2θ), deg | 15; 18.14 ≤ 2θ ≤ 31.18 |
| temp, °C | 20 |
| scan method | ω-2θ |
| data collecn range (2θ), deg | 4 ≤ 2θ ≤ 50 (+h, ±k, ±l) |
| no. of unique data; total with <i>F</i> _o ² > 3σ(<i>F</i> _o ²) | 3770; 3094 |
| no. of parameters refined | 283 |
| transmissn factors: max, min | 0.999, 0.8840 |
| <i>R</i> ^a | 0.0545 |
| <i>R</i> _w ^b | 0.0820 |
| quality-of-fit indicator ^c | 1.796 |
| largest shift/esd, final cycle | 0.061 |
| largest peak, e/Å ³ | 1.161 ^d |

^a *R* = Σ||*F*_o|| - ||*F*_c|| / Σ||*F*_o||. ^b *R*_w = [Σw(|*F*_o|| - ||*F*_c||)² / Σw||*F*_o||²]^{1/2}; w = 1/σ²(||*F*_o||). ^c Quality of fit = [Σw(|*F*_o|| - ||*F*_c||)² / (N_{observns} - N_{parameters})]^{1/2}. ^d Located in the vicinity of the disordered CH₂Cl₂ molecule; the second largest peak with intensity 0.725 e/Å³.

E. Schweikert of this department for the X-ray fluorescence analysis. [V₂(μ-Cl)₃(THF)₅PPh₃]₂[Zn₂Cl₆]. To a slurry of [V₂Cl₃(THF)₆]₂[Zn₂Cl₆] (2.5 g, 1.5 mmol) in 20 mL of benzene, prepared in a 100-mL

- (1) (a) Texas A&M University. (b) Southern Illinois University
- (2) Cotton, F. A.; Duraj, S. A.; Extine, M. W.; Lewis, G. E.; Roth, W. J.; Schmulbach, C. D.; Schwotzer, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1377.
- (3) Cotton, F. A.; Lewis, G. E.; Mott, G. N. *Inorg. Chem.* **1982**, *21*, 3316.
- (4) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 4113.
- (5) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Inorg. Chem.* **1984**, *23*, 4042.
- (6) Bansemer, R. L.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 6163.

Scheme I



Schlenk tube equipped with a magnetic stirrer and a pressure-equalized funnel, was added a solution of triphenylphosphine (5.4 g, 20 mmol) in 10 mL of benzene dropwise. Stirring of the reaction mixture was continued at room temperature for 8 h, after which a light green precipitate was formed. The precipitate was filtered off and washed three times with 10 mL of fresh hexane (reproducible yields 1.6 g, 52%). The compound decomposes immediately when exposed to air.

Anal. Calcd for $\text{C}_{76}\text{H}_{105}\text{Cl}_{12}\text{O}_{10}\text{P}_2\text{V}_4\text{Zn}_2$: C, 45.65; H, 5.29; Cl, 21.26. Found: C, 46.09; H, 4.80; Cl, 22.71.

X-ray fluorescence for a 2:1 atom ratio of V to Zn: calcd, 1.56; found, 1.44.

$V(\text{THF})_2(\mu\text{-Cl})_2\text{ZnClPPH}_3]_2$. A solution of $[V_2\text{Cl}_3(\text{THF})_5(\text{PPh}_3)]_2[\text{Zn}_2\text{Cl}_6]$ (1.00 g, 0.5 mmol) in 20 mL of dichloromethane in a 50-mL Schlenk tube was carefully covered with 20 mL of freshly distilled hexane. The Schlenk tube was allowed to stand undisturbed for several days after which a homogeneous crop of air-sensitive green crystals (0.13 g, 22% yield) was formed. One of these crystals was sealed in a capillary, in mineral oil, and used for X-ray data collection.

X-ray Crystallography. General procedures have been described previously.⁷ The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Polarization, Lorentz, and absorption corrections were applied to the intensity data.

The structure was solved in space group $P\bar{1}$ from the Patterson function. The position of atoms in the coordination sphere was determined from a difference Fourier map. Development of the rest of the structure and refinement were continued in the centrosymmetric space group $P\bar{1}$. The solvent molecule present in the lattice was disordered, giving rise to a cluster of residual peaks in a difference Fourier map. With use of a trial and error approach, the following assignment of fractional occupancy was made: 0.8 and 0.2 for two pairs of chlorine atoms; 0.6 and 0.4 for carbon atoms. Four molecules of CH_2Cl_2 with overall occupancy equal to one can be derived from this set. The disorder problem could not be resolved completely, and some residual electron density (ca. $1.2 \text{ e}/\text{\AA}^3$) remained in the region.

Complete tables of anisotropic thermal parameters and structure factor data are available as supplementary material.

Results and Discussion

The reaction of $[V_2(\mu\text{-Cl})_3(\text{THF})_6]_2[\text{Zn}_2\text{Cl}_6]$ with triphenylphosphine in benzene yields a light green precipitate, which we postulate to correspond to the following chemical formula: $[V_2(\mu\text{-Cl})_3(\text{THF})_5(\text{PPh}_3)]_2[\text{Zn}_2\text{Cl}_6]$. We support this conclusion by elemental analysis for C, H, and Cl and also by direct analyses for both V and Zn via X-ray fluorescence. In contrast to the starting material, the mono(triphenylphosphine) derivative is easily soluble in THF. This solubility feature was crucial in establishing the structure of $[V_2\text{Cl}_3(\text{THF})_6]_2[\text{Zn}_2\text{Cl}_6]$ ² since excellent quality single crystals are formed when a THF solution of $[V_2\text{Cl}_3(\text{THF})_5(\text{PPh}_3)]_2[\text{Zn}_2\text{Cl}_6]$ is carefully layered with hexane. Under these conditions the PPh_3 ligand is slowly displaced by THF. However, when $[V_2(\mu\text{-Cl})_3(\text{THF})_5(\text{PPh}_3)]_2[\text{Zn}_2\text{Cl}_6]$ was dissolved in dichloromethane and carefully covered with hexane, in another effort to grow single crystals of it, we obtained instead green single crystals of $V[\text{ZnCl}_3(\text{THF})(\text{PPh}_3)]_2\cdot 2\text{CH}_2\text{Cl}_2$. We do not at present have any explanation for this result. The overall reaction pattern is depicted in Scheme I.

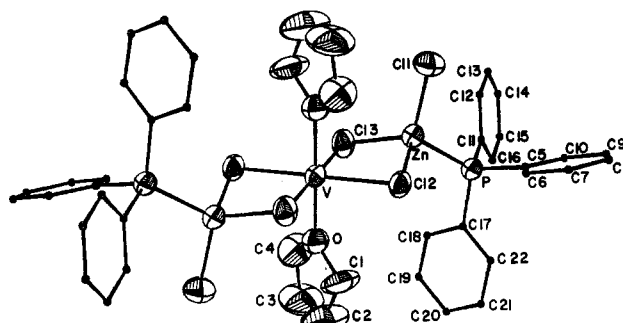


Figure 1. ORTEP drawing of $V(\text{THF})_2(\mu\text{-Cl})_2\text{ZnCl}_2\text{PPh}_3$. Atoms are represented by ellipsoids of thermal vibrations enclosing 40% probability. Phenyl carbon atoms were assigned arbitrarily small thermal parameters for the sake of clarity.

Table II. Positional and Isotropic Equivalent Thermal Parameters for $V\text{Zn}_2\text{Cl}_6(\text{PPh}_3)_2(\text{THF})_2\cdot 2\text{CH}_2\text{Cl}_2^a$

| atom | x | y | z | $B, \text{\AA}^2$ |
|--------|-------------|-------------|--------------|-------------------|
| V | 0.000 | 0.000 | 0.000 | 3.54 (3) |
| Zn | 0.11752 (6) | 0.20189 (5) | -0.00472 (8) | 3.85 (2) |
| Cl(1) | 0.0515 (2) | 0.3413 (1) | 0.1225 (2) | 5.70 (5) |
| Cl(2) | 0.1908 (1) | 0.0953 (1) | 0.1529 (2) | 4.34 (4) |
| Cl(3) | -0.0321 (2) | 0.0993 (1) | -0.1998 (2) | 4.64 (4) |
| P | 0.2729 (1) | 0.2334 (1) | -0.1011 (2) | 3.54 (4) |
| O | -0.0823 (4) | 0.1089 (3) | 0.1482 (6) | 5.1 (1) |
| C(1) | -0.2028 (7) | 0.1429 (7) | 0.089 (1) | 8.5 (3) |
| C(2) | -0.214 (1) | 0.2266 (9) | 0.227 (1) | 11.6 (4) |
| C(3) | -0.119 (1) | 0.2287 (8) | 0.371 (1) | 11.8 (4) |
| C(4) | -0.0329 (8) | 0.1528 (8) | 0.326 (1) | 8.0 (3) |
| C(5) | 0.3921 (5) | 0.3037 (4) | 0.0713 (7) | 3.8 (1) |
| C(6) | 0.4169 (6) | 0.2840 (6) | 0.2191 (8) | 5.3 (2) |
| C(7) | 0.5044 (7) | 0.3388 (7) | 0.3550 (9) | 6.6 (2) |
| C(8) | 0.5654 (7) | 0.4142 (6) | 0.344 (1) | 5.8 (2) |
| C(9) | 0.5424 (8) | 0.4336 (6) | 0.197 (1) | 7.7 (3) |
| C(10) | 0.4547 (7) | 0.3771 (6) | 0.059 (1) | 6.4 (2) |
| C(11) | 0.2277 (5) | 0.3094 (4) | -0.2397 (7) | 3.8 (1) |
| C(12) | 0.1529 (6) | 0.3857 (5) | -0.2026 (8) | 5.0 (2) |
| C(13) | 0.1191 (7) | 0.4497 (5) | -0.3013 (9) | 5.6 (2) |
| C(14) | 0.1603 (7) | 0.4347 (5) | -0.4348 (9) | 5.4 (2) |
| C(15) | 0.2349 (7) | 0.3589 (5) | -0.4699 (8) | 5.4 (2) |
| C(16) | 0.2708 (6) | 0.2964 (5) | -0.3722 (8) | 4.6 (2) |
| C(17) | 0.3380 (5) | 0.1240 (4) | -0.2065 (7) | 3.9 (1) |
| C(18) | 0.2660 (7) | 0.0608 (6) | -0.3506 (9) | 5.8 (2) |
| C(19) | 0.3095 (8) | -0.0234 (6) | -0.435 (1) | 6.7 (2) |
| C(20) | 0.4282 (7) | -0.0457 (6) | -0.377 (1) | 6.8 (2) |
| C(21) | 0.4981 (7) | 0.0141 (7) | -0.233 (1) | 7.8 (3) |
| C(22) | 0.4541 (6) | 0.1010 (6) | -0.145 (1) | 6.0 (2) |
| C(23) | 0.245 (2) | 0.638 (2) | 0.130 (3) | 11.9 (6)* |
| C(23A) | 0.218 (2) | 0.691 (2) | 0.222 (3) | 7.7 (6)* |
| Cl(4) | 0.3584 (4) | 0.7290 (3) | 0.2311 (5) | 10.7 (1)* |
| Cl(4A) | 0.363 (1) | 0.672 (1) | 0.167 (2) | 8.3 (3)* |
| Cl(5) | 0.2158 (4) | 0.5694 (3) | 0.2368 (5) | 11.5 (1)* |
| Cl(5A) | 0.184 (2) | 0.631 (1) | 0.297 (2) | 10.9 (4)* |

^a Starred values were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Molecular Structure of $V(\text{THF})_2(\mu\text{-Cl})_2\text{ZnClPPH}_3]_2\cdot 2\text{CH}_2\text{Cl}_2$. An ORTEP drawing of the entire molecular unit is shown in Figure 1, which also defines the numbering scheme. Important interatomic dimensions are given in Table III. Less important bond distances and bond angles are available as supplementary material. The positional parameters are listed in Table II.

Crystals of this complex consist of an ordered array of discrete molecules that have vanadium occupying the central position and residing on a crystallographic inversion center. Two zinc atoms in their tetrahedral coordination of three chlorine atoms and one triphenylphosphine molecule are connected to the vanadium center via two chlorine bridges each. Two molecules of tetrahydrofuran complete the octahedral coordination sphere of the vanadium atom.

It is clear from the X-ray data concerning V-Zn distance of $3.289 (1) \text{ \AA}$ that there is no significant bonding between these

Table III. Important Interatomic Dimensions for $VZn_2Cl_6(PPH_3)_2(THF)_2 \cdot 2CH_2Cl_2^a$

| A. Bond Distances (Å) | | | |
|-----------------------|------------|----------------|------------|
| V-Zn | 3.289 (1) | Zn-Cl(1) | 2.197 (1) |
| -Cl(2) | 2.501 (1) | -Cl(2) | 2.324 (1) |
| -Cl(3) | 2.526 (1) | -Cl(3) | 2.293 (1) |
| -O | 2.120 (3) | -P | 2.392 (1) |
| B. Bond Angles (deg) | | | |
| Cl(2)-V-Cl(2)' | 180.00 | Cl(2)-Zn-Cl(3) | 97.22 (5) |
| -Cl(3) | 87.08 (4) | -P | 106.81 (5) |
| -O | 88.5 (1) | Cl(3)-Zn-P | 114.64 (5) |
| Cl(3)-V-Cl(3)' | 180.00 | V-Cl(2)-Zn | 85.87 (4) |
| -O | 91.0 (1) | V-Cl(3)-Zn | 85.94 (4) |
| Cl(1)-Zn-Cl(2) | 114.88 (6) | | |
| -Cl(3) | 112.10 (6) | | |
| -P | 110.58 (6) | | |

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

two metals as expected for a Zn d¹⁰ configuration.

The dimensions of the tetrahedral ZnCl₃PPh₃ unit are reasonable when compared with those of the structurally characterized ZnBr₃PPh₃ anion,⁸ which, to the best of our knowledge, provides the only close analogue to the zinc(II) portion of our trimer. The distortions from an ideal tetrahedron for these two zinc atoms are

(8) DeSimone, R. E.; Stucky, G. D. *Inorg. Chem.* 1971, 10, 1808.

comparable. All angles around the zinc atom for the ZnCl₃PPh₃ unit range from 97.22 (5) to 114.88 (6)° as compared to the range of 101.2 (4)–115.9 (3)° for ZnBr₃PPh₃⁻. The Zn-P distance in our vanadium compound is 2.392 (1) Å, a slightly shorter value than that for Zn-P, 2.425 (9) Å, in ZnBr₃PPh₃. The difference may be attributed to the larger bromine atoms that tend to force the PPh₃ away from the metal atom.

The Zn-Cl distances in V(THF)₂[(μ-Cl)₂ZnClPPh₃]₂ are as expected: longer for the bridging chlorine atoms, Zn-Cl(2) = 2.324 (1) Å and Zn-Cl(3) = 2.293 (1) Å, and shorter for the terminal chlorine, Zn-Cl(1) = 2.197 (1) Å.

The coordination sphere of vanadium is also distorted. Whereas the Cl(2)-V-Cl(2)' and Cl(3)-V-Cl(3)' angles are of course ideal, 180.00° each, by symmetry, the other angles show the expected effects of the long V...Zn distances, with Cl(2)-V-Cl(3) smaller and Cl(2)-V-Cl(3)' larger than 90°. The two V-Cl distances are very close; V-Cl(2) = 2.501 (1) Å and V-Cl(3) = 2.526 (1) Å.

Acknowledgment. We are grateful to the Robert A. Welch Foundation for support under Grant No. A-494.

Registry No. [V₂(μ-Cl)₃(THF)₃PPh₃]₂[Zn₂Cl₆], 94090-06-9; V-(THF)₂[(μ-Cl)₂ZnClPPh₃]₂, 94090-08-1; [V₂Cl₃(THF)₆]₂[Zn₂Cl₆], 89172-48-5.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal vibration parameters, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Stereochemistry and Relative Stability of Isomers of *trans*-Dichlorocobalt(III) Complexes with Chirally Substituted 3,7-Diazanonane-1,9-diamine

MASAHIKO SABURI,* YOUICHI ISHII, SHUSEI OBATA, MOTOWO YAMAGUCHI, and SADA O YOSHIKAWA*

Received May 30, 1984

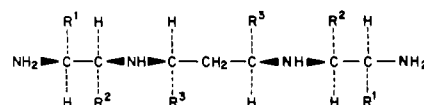
The stereochemistry of *trans*-dichlorocobalt(III) complexes with chiral derivatives of 3,7-diazanonane-1,9-diamine such as (2*S*,8*S*)-2,8-dimethyl-3,7-diazanonane-1,9-diamine (3,9-Me₂-2,3,2-tet), (3*S*,11*S*)-2,12-dimethyl-5,9-diazatridecane-3,11-diamine (2,10-*Ip*₂-2,3,2-tet), and (2*S*,10*S*)-1,11-diphenyl-4,8-diazaundecane-2,10-diamine (2,10-Bn₂-2,3,2-tet) was examined on the basis of ¹³C NMR and circular dichroism (CD) measurements. The *trans*-dichloro complexes obtained by treating the corresponding carbonato complexes with hydrochloric acid adopt specifically the *RR* configuration with respect to the coordinated secondary nitrogen centers. The *trans-RR* isomers of 3,9-Me₂- and 2,10-*Ip*₂-2,3,2-tet isomerized in methanol (63 °C) to give rise to equilibrated mixtures of *trans-RR* and *trans-RS* isomers. The isomer ratio [*RS*]/[*RR*] was estimated as 1.65 ± 0.05 and 2.4 ± 0.4, respectively, for 3,9-Me₂- and 2,10-*Ip*₂-2,3,2-tet complexes. The observed influences of position or bulkiness of substituents on the isomer distribution were discussed, taking the steric interactions involved in the *RS* isomer into consideration. Δ-β-(Oxalato)cobalt(III) complexes with 2,3,2-tet derivatives including (3*S*,9*S*)-3,9-bis(aminomethyl)-2,10-dimethyl-4,8-diazaundecane (3,9-*Ip*₂-2,3,2-tet) were also prepared to interpret the fact that 3,9-*Ip*₂-2,3,2-tet gave no *trans*-dichloro complex.

A number of chirally substituted linear tetraamines have been synthesized in order to provide chiral circumstances to control the stereoselectivity of epimerization of amino acidates¹⁻³ and of decarboxylation of α-alkyl-α-aminomalonates⁴⁻⁸ within cobalt(III) coordination sites. We have found that *trans*-dichlorocobalt(III) complexes with chirally substituted 3,7-diazanonane-1,9-diamine (2,3,2-tet) were most conveniently employed for preparing amino

Table I. Structures and Abbreviations of Chiral 2,3,2-tet Derivatives^a

| R ¹ | R ² | R ³ | abbrev |
|---|------------------------------------|-----------------|---|
| CH ₃ | H | H | 2,10-Me ₂ -2,3,2-tet |
| H | CH ₃ | H | 3,9-Me ₂ -2,3,2-tet |
| H | H | CH ₃ | 5,7-Me ₂ -2,3,2-tet |
| (CH ₃) ₂ CH | H | H | 2,10- <i>Ip</i> ₂ -2,3,2-tet |
| H | (CH ₃) ₂ CH | H | 3,9- <i>Ip</i> ₂ -2,3,2-tet |
| C ₆ H ₅ CH ₂ | H | H | 2,10-Bn ₂ -2,3,2-tet |

^a Positions of the substituents R¹, R², and R³ are as follows:



acidato¹⁻³ or α-alkyl-α-aminomalonato complexes.^{6,7} Concurrently, fundamental stereochemistry of these tetraamine complexes has attracted attention, particularly with regard to the restricted occurrence of stereoisomers due to substituent effects.⁹⁻¹⁴

- (1) Yamaguchi, M.; Yamamatsu, S.; Furusawa, T.; Yano, S.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* 1980, 19, 2010.
- (2) Yamaguchi, M.; Yano, S.; Saburi, M.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* 1980, 53, 691.
- (3) Yamaguchi, M.; Masui, Y.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* 1982, 21, 4138.
- (4) Asperger, R. G.; Liu, C. F. *Inorg. Chem.* 1967, 6, 796.
- (5) Job, R. C.; Bruce, T. C. *J. Am. Chem. Soc.* 1974, 96, 809.
- (6) Yamaguchi, M.; Yamamatsu, S.; Oikawa, H.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* 1981, 20, 3179.
- (7) Ajioka, M.; Yano, S.; Matsuda, K.; Yoshikawa, S. *J. Am. Chem. Soc.* 1981, 103, 2459.
- (8) Jun, M. J.; Yoon, N. M.; Liu, C. F. *J. Chem. Soc., Dalton Trans.* 1983, 999.