Northwestern, Professor Fred Basolo and Dr. John Macdonald, for the original sample of Mo(phen)-$(PPh_3)_2(CO)_2$, and Professor Sighart Fischer for suggesting the use of eq 5 and for helpful discussions. We also thank Professor David Brown of University College, Dublin, for supplying matrix elements from his molecular orbital calculation. This research was supported by the National Science Foundation through a Science Faculty Fellowship to Sr. Agnes Alich and a research grant to D. F. Shriver.

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Crystal and Molecular Structures of Di-μ-oxo-bis(diacetylacetonatotitanium(IV))-Bisdioxane, $(TiO(C_5H_7O_2)_2)_2 \cdot 2C_4H_8O_2$, and Di-μ-oxo-bis(diacetylacetonatotitanium(IV)), $(TiO(C_5H_7O_2)_2)_2$

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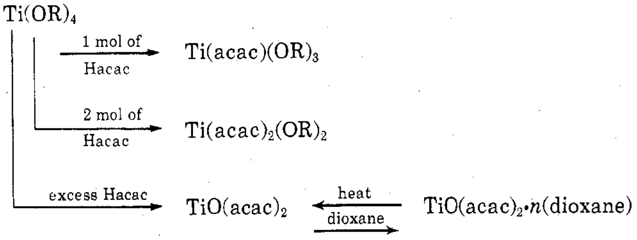
Received March 9, 1972

The structures of two crystals of di-μ-oxo-bis(diacetylacetonatotitanium(IV)), $(TiO(C_5H_7O_2)_2)_2$, have been determined by X-ray single-crystal methods, using data collected by counter methods. Crystal I, crystallizing with 2 molecules of dioxane, belonged to space group $P\bar{1}$, a = 12.08 (2) Å, b = 12.81 (1) Å, c = 9.98 (2) Å, α = 123.3 (1)°, β = 96.3 (1)°, γ = 124.0 (1)°, and Z = 1 for the Delaunay-reduced cell. Crystal II, with no molecules of solvent, belonged to space group $P2_1/c$, a = 9.270 (3) Å, b = 14.019 (3) Å, c = 9.644 (3) Å, β = 105.14 (2)°, and Z = 2. Crystal I refined to an R of 9.7% for 963 observed reflections while crystal II refined to an R of 5.0% for 1549 observed reflections. The structures consisted of a cyclic dimer with the titanium atom linked through oxygen atoms. The di-μ-oxo-dititanium ring is planar and slightly distorted from a square, with angles at oxygen being 97° and at titanium 83°. The acetylacetonate rings are very nearly planar. Some bond distances in the acetylacetone ring are C–O, 1.27 (1) Å; C–CH, 1.38 (1) Å; and C–CH_3, 1.52 (1) Å. The octahedral coordination around titanium is somewhat distorted; angles expected to be 90° vary from 83 to 100° while those expected to be 180° differ from this by as much as 20°. The solvent in crystal I is very loosely bound with little or no chemical bonding and is located in approximately spherically shaped holes between dimer units. The dioxane molecules in these sites show considerable disorder.

Introduction

The reaction of titanium alkoxides with acetylacetone and acetoacetate has been studied by Yamamoto and Kambara[1] and Puri, Pande, and Mehrotra.[2] Several products were reported by Mehrotra, *et al.*, depending on the quantity of acetylacetone used.



Yamamoto and Kambara prepared $TiO(acac)_2$ by hydrolysis of $Ti(acac)_2(OR)_2$[1] and proposed a cyclic dimeric structure based on molecular weight measurements and the ir spectrum.

The structure of at least one Ti(IV)–acetylacetonato complex has been studied by X-ray analysis.[3] Hollaway and Bradley[4] studied in detail the nmr spectra as well as some other aspects of metal complexes containing acetylacetone and discussed various factors influencing metal ligand interaction as well as the effects on the acetylacetone group of various ligands coordinated to the metal.

We report here the structure of $\{TiO(acac)_2\}_2$. Two crystals were studied, one containing no solvent and the other crystallizing with two molecules of dioxane; the dioxane shows no chemical bonding to the $\{TiO(acac)_2\}_2$.

Experimental Section

Preparation of this compound followed the procedure of Mehrotra, *et al.*[2] An excess of acetylactone was added to a solution of $Ti(OC_4H_7)_4$ in benzene. After refluxing for several hours, dioxane was added to the mixture and excess solvent distilled. Upon standing, brown crystals formed from the remaining mixture. These were the crystals containing dioxane, *i.e.*, $\{TiO(acac)_2\} \cdot 2C_4H_8O_2$, crystal I. This material was also recrystallized from a mixture of benzene and pyridine, producing crystal II, $(TiO(acac)_2)_2$. Experimental densities were not taken on either crystal due to the instability and solubility in organic solvents.

Crystal I: $(TiO(acac)_2)_2 \cdot 2C_4H_8O_2$.—These crystals were stable in equilibrium with the solution from which they were crystallized but lost their crystallinity upon removal from solution, a fact also noted by Yamamoto, *et al.*[1] The crystal used for collection of X-ray data, approximately 0.2 × 0.4 × 1.0 mm, was sealed in a Lindemann glass capillary along with a drop of solvent, and was stable throughout the data collection.

Preliminary Weissenberg photographs indicated a triclinic space group. Lattice parameters shown in Table I were determined on a GE XRD-5 diffractometer by least-squares refinement of 16 independent 2θ measurements using Mo Kα radiation. All intensities below a 2θ of 45° were measured by counting peak intensities for a fixed time, peaking up each reflection before the measurement. Poor quality of the crystal and slight movement in the capillary resulted in relatively unprecise measurements, precluding the inherently better accuracy of the θ–2θ method. The background was estimated as a function of 2θ over the whole range and an average background count for each 2θ was subtracted from the total peak count. Of the 1871 reflections

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[1] A. Yamamoto and S. Kambara, *J. Amer. Chem. Soc.*, **79**, 4344 (1957).

[2] C. M. Puri, K. C. Pande, and R. C. Mehrotra, *J. Less-Common Metals*, 4393 (1962).

[3] K. Watenpaugh and C. N. Caughlan, *Inorg. Chem.*, **6**, 963 (1967).

[4] D. C. Bradley and C. E. Hollaway, *J. Chem. Soc. A*, 1969, 282.

TABLE I

CRYSTAL DATA FOR CRYSTALS I AND II

$(TiO(acac)_2)_2 \cdot 2C_4H_8O_2$ (space group $P\bar{1}$)	$(TiO(acac)_2)_2$ (space group $P2_1/c$)
$a = 12.08\ (2)$ Å	$a = 9.270\ (3)$ Å
$b = 12.81\ (1)$ Å	$b = 14.019\ (3)$ Å
$c = 9.98\ (2)$ Å	$c = 9.644\ (3)$ Å
$\alpha = 123.3\ (1)°$	
$\beta = 96.3\ (1)°$	$\beta = 105.14\ (2)°$
$\gamma = 124.0\ (1)°$	
$Z = 1$	$Z = 2$
$D_{\text{calcd}} = 1.359$ g cm^{-3}	$D_{\text{calcd}} = 1.439$ g cm^{-3}
μ(abs), Mo Kα = 5.5 cm^{-1}	μ(abs), Mo Kα = 7.4 cm^{-1}

measured, 963 were considered observed on the basis of the estimated fluctuation of the background and the reproducibility of the measurements. Only the relatively intense reflections remained. Neither absorption nor extinction corrections were made and anomalous terms of the form factors were not used.

Crystal II: $(TiO(acac)_2)_2$.—Crystals were sealed in Lindemann glass capillaries along with a drop of solvent. Preliminary Weissenberg photographs showed the crystal to be in monoclinic space group $P2_1/c$. Lattice parameters shown in Table I were determined on a GE XRD-5 diffractometer by least-squares refinement of 20 independent 2θ measurements using Mo Kα radiation. The crystal used for both determination of lattice parameters and intensity data was mounted along the c axis and bounded by $\{100\}$, $\{010\}$, $\{011\}$, and $\{111\}$. Its approximate dimensions were 0.4 × 0.4 × 0.4 mm.

The θ–2θ scan technique was used on this crystal for collection of all data below a 2θ of 50°, using 2° scans in 2θ and counting backgrounds for 30 sec on each side of the peak. A total of 2108 reflections were scanned, of which 1549 were considered to be observed based upon the criteria $I_{\text{obsd}} \geq 2\sigma I_{\text{obsd}}$. Weights used in refinement for each reflection were calculated by the method described by Stout and Jensen.[5] Neither absorption nor extinction corrections were applied; however, both real and imaginary terms were used for the form factor of titanium.

The data for both crystal I and crystal II were corrected in the usual manner for Lorentz and polarization factors.[6] Form factors were taken from the International Tables for X-ray Crystallography.[7]

Structure Determination and Refinement

The structure of both crystals was solved from the Patterson function which showed clearly the titanium positions, and in the case of crystal I the oxygen positions, near the center of symmetry. Several series of Fourier synthesis showed the rest of the $(TiO(acac)_2)_2$ structure.

Crystal I: $(TiO(acac)_2)_2 \cdot 2C_4H_8O_2$.—The R factor was reduced to 12% following several cycles of full-matrix least-squares refinement, treating the vibration of the titanium, oxygen, and acetylacetonate groups anisotropically. Much difficulty was encountered in locating the solvent molecules. Calculation of a difference map showed a number of broad peaks forming chemically reasonable six-membered rings around two other centers of symmetry. One of these rings was very definitely nonplanar while the other ring was very nearly planar. On the basis of interatomic distances, two of the atoms in the nonplanar ring were designated as oxygens and the second ring was considered to be a benzene molecule because of its planarity. However, refinement of these two rings produced unreasonable shifts in both the positional and thermal parameters. Refinement of the two rings with oxygens in any of the atomic sites again produced unreasonable shifts. After consideration of the general structure and noting the looseness with which the solvent was held, it seemed reasonable to assume that the solvent molecules were disordered by partial occupancy of oxygen atoms in the six atomic sites of the ring. Accordingly, each atom in the dioxane molecule was assumed to be one-third oxygen and two-thirds carbon. The occupation factors for these atoms were then refined along with the parameters for the other atoms until all shifts were less than the standard deviations. The final R factor was 9.7%. Unit weights were assigned to all observed reflections in the refinement for crystal I. Final positional and thermal parameters along with standard deviations are listed in Table II.[8]

Crystal II: $(TiO(acac)_2)_2$.—Initial full-matrix least-squares refinement of the positional and isotropic thermal parameters for the 16 atoms produced an R factor of 9.6%. Further refinement, using anisotropic thermal parameters for all atoms, continued until the shifts for all atoms were much less than the standard deviations. The resulting R factor was 5.0% (weighted R, 6.4%).

A difference map calculated at this point showed all methyl hydrogens to be nearly uniformly distributed around the carbon atoms. Because of this disorder in the methyl groups, no hydrogen atoms were included in the final structure factor calculations. Final positional and thermal parameters are listed in Table III.[8]

Discussion of the Structure

Figure 1 is an ORTEP drawing of the metal complex while Table IV lists the bond distances and angles corresponding to this figure for both determinations. Since the structure of the metal complex is essentially the same in both determinations, the discussion will be limited to the results from crystal II since it is the better determination.

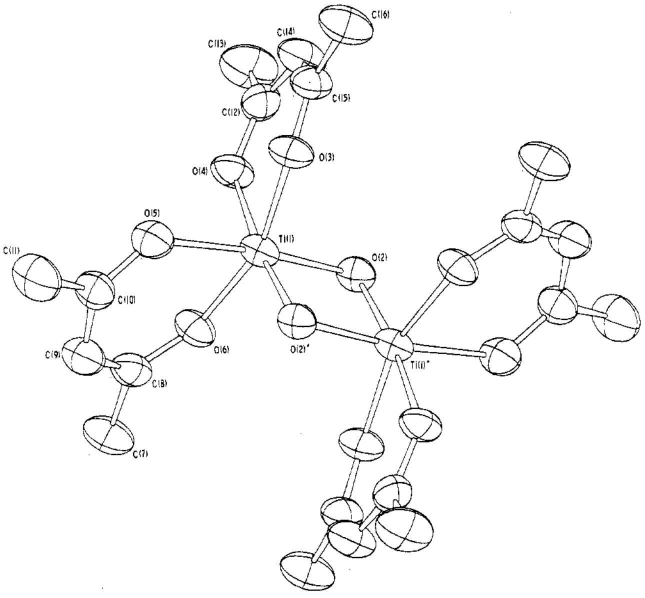

Figure 1.—ORTEP drawing of $(TiO(acac)_2)_2$.

As can be seen from Figure 1, the structure consists of a cyclic dimer placed around a center of symmetry, with the titanium atoms linked through oxygen atoms 2 and 2′. The di-μ-oxo-dititanium ring is planar and slightly distorted from a square, the angles at oxygen being 96.6 (2)° and at titanium 83.4 (2)°, the sides dif-

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[5] $\sigma(F) = (k/2\sqrt{Lp})[(N_{\text{T}} + N_{\text{bg}_1} + N_{\text{bg}_2} + (0.01N_{\text{pk}})^2)/(N_{\text{T}} - N_{\text{bg}_1} - N_{\text{bg}_2})]^{1/2}$: G. H. Stout and L. H. Jensen, "X-ray Structure Determination," Macmillan, New York, N. Y., p 457.

[6] The computer programs used were the following: NRC-2, data reduction program, written by F. R. Ahmed and C. P. Sanderson; NRC-8, Fourier program, written by F. R. Ahmed, National Research Council, Ottawa, Ontario, Canada; the full-matrix least-squares program is ORFLS, that of W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Oak Ridge, Tenn. These have been adapted for the XDS Sigma-7 computer. The rest of the programs were written by C. N. Caughlan, G. D. Smith, and E. L. Enwall, Montana State University, Bozeman, Mont. In full matrix least squares, the function minimized was $\Sigma w \cdot (|F_{\text{o}}| - |F_{\text{c}}|)^2$.

[7] International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, England, 1962.

[8] A listing of calculated and observed structure factors for both structures will appear following these pages in the microfilm edition of this journal. Single copies may be obtained from the Business Operations Office, Books and Journal Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036, by referring to code number INORG-72-2989. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE II

ATOMIC POSITIONS AND ANISOTROPIC THERMAL PARAMETERS OF CRYSTAL I

Symbol	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ti(1)	0.064 (1)	0.005 (1)	0.628 (1)	0.014 (1)	0.019 (1)	0.020 (1)	0.011 (1)	0.010 (1)	0.014 (1)
O(2)	−0.093 (1)	−0.165 (1)	0.363 (2)	0.017 (2)	0.016 (3)	0.022 (5)	0.012 (2)	0.013 (2)	0.013 (3)
O(3)	−0.076 (1)	−0.018 (2)	0.722 (2)	0.016 (2)	0.024 (3)	0.027 (5)	0.015 (2)	0.012 (3)	0.019 (3)
O(4)	0.010 (1)	−0.186 (2)	0.610 (2)	0.025 (3)	0.028 (3)	0.031 (5)	0.020 (3)	0.017 (3)	0.024 (4)
O(5)	0.262 (1)	0.223 (2)	0.929 (2)	0.017 (2)	0.029 (3)	0.024 (5)	0.013 (2)	0.010 (3)	0.020 (4)
O(6)	0.235 (1)	0.041 (2)	0.595 (2)	0.014 (2)	0.030 (3)	0.026 (5)	0.015 (2)	0.011 (3)	0.021 (4)
C(7)	0.476 (2)	0.157 (3)	0.609 (4)	0.027 (5)	0.049 (7)	0.039 (3)	0.029 (5)	0.028 (6)	0.027 (9)
C(8)	0.390 (3)	0.172 (3)	0.708 (4)	0.023 (5)	0.030 (6)	0.039 (10)	0.022 (5)	0.018 (6)	0.026 (7)
C(9)	0.488 (2)	0.327 (3)	0.916 (4)	0.017 (4)	0.030 (6)	0.034 (9)	0.019 (4)	0.016 (5)	0.028 (7)
C(10)	0.422 (2)	0.340 (3)	1.021 (3)	0.016 (4)	0.031 (6)	0.037 (9)	0.016 (4)	0.014 (5)	0.027 (7)
C(11)	0.530 (2)	0.495 (3)	1.246 (3)	0.019 (4)	0.030 (5)	0.032 (9)	0.012 (4)	0.008 (5)	0.024 (6)
C(12)	−0.067 (2)	−0.259 (3)	0.658 (3)	0.015 (4)	0.023 (5)	0.023 (9)	0.012 (4)	0.011 (5)	0.016 (6)
C(13)	−0.082 (2)	−0.401 (3)	0.619 (3)	0.031 (5)	0.031 (6)	0.054 (9)	0.024 (5)	0.020 (6)	0.033 (7)
C(14)	−0.148 (2)	−0.232 (3)	0.725 (3)	0.020 (4)	0.027 (6)	0.037 (8)	0.015 (4)	0.014 (5)	0.028 (6)
C(15)	−0.147 (2)	−0.106 (2)	0.763 (3)	0.016 (3)	0.024 (5)	0.022 (8)	0.013 (3)	0.014 (4)	0.018 (6)
C(16)	−0.243 (2)	−0.082 (3)	0.827 (3)	0.020 (4)	0.040 (6)	0.034 (10)	0.019 (4)	0.019 (5)	0.029 (7)

Solvent atoms[b]	x	y	z	β_{iso}	Occupation factor
C(17)	0.579 (4)	0.047 (5)	0.159 (5)	13.9 (8)	0.62 (6)
C(18)	0.582 (5)	0.126 (5)	0.006 (6)	16.6 (10)	0.66 (6)
C(19)	0.674 (3)	0.151 (3)	0.118 (4)	9.8 (6)	0.72 (6)
C(20)	−0.104 (3)	0.372 (4)	−0.008 (5)	11.8 (7)	0.76 (6)
C(21)	0.003 (3)	0.376 (4)	−0.073 (5)	14.0 (8)	0.68 (6)
C(22)	−0.014 (3)	0.430 (4)	−0.174 (5)	12.4 (7)	0.56 (6)

[a] The form of the anisotropic temperature expression is $\exp(\Sigma_{i=1}{}^3\Sigma_{j=1}{}^3\beta_{ij}h_ih_j)$. [b] Due to the disorder of the dioxane molecules, there is an oxygen atom associated with each carbon atom. The occupation factor of each oxygen is equal to one minus the occupation factor of the corresponding carbon atom.

TABLE III

ATOMIC POSITIONS AND ANISOTROPIC THERMAL PARAMETERS OF CRYSTAL II

Symbol	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{28}
Ti(1)	0.8846 (1)	0.0246 (1)	0.0581 (1)	0.0108 (1)	0.0031 (1)	0.0070 (1)	−0.0005 (1)	0.0006 (1)	−0.0003 (1)
O(2)	0.9870 (4)	−0.0830 (2)	0.0311 (4)	0.0113 (5)	0.0026 (2)	0.0088 (5)	−0.0004 (3)	0.0022 (4)	0.0005 (3)
O(3)	0.7174 (4)	0.0149 (3)	−0.1182 (4)	0.0111 (5)	0.0043 (2)	0.0076 (5)	−0.0012 (3)	−0.0005 (4)	0.0005 (3)
O(4)	0.7453 (4)	−0.0586 (3)	0.1443 (4)	0.0131 (6)	0.0045 (2)	0.0082 (5)	−0.0017 (3)	0.0028 (5)	0.0002 (3)
O(5)	0.7921 (4)	0.1550 (3)	0.0823 (4)	0.0115 (6)	0.0035 (2)	0.0110 (5)	0.0006 (3)	0.0005 (5)	−0.0015 (3)
O(6)	0.9955 (4)	0.0460 (3)	0.2598 (4)	0.0143 (6)	0.0042 (2)	0.0065 (4)	−0.0002 (3)	−0.0001 (4)	−0.0007 (2)
C(7)	1.1380 (8)	0.1112 (5)	0.4832 (6)	0.0193 (13)	0.0081 (5)	0.0087 (8)	−0.0007 (6)	−0.0030 (8)	−0.0012 (5)
C(8)	1.0244 (7)	0.1226 (5)	0.3340 (6)	0.0115 (10)	0.0063 (4)	0.0074 (7)	−0.0015 (5)	0.0015 (7)	−0.0012 (5)
C(9)	0.9611 (7)	0.2103 (5)	0.2934 (7)	0.0149 (11)	0.0051 (4)	0.0115 (9)	0.0001 (5)	−0.0005 (8)	−0.0017 (5)
C(10)	0.8447 (7)	0.2217 (4)	0.1695 (7)	0.0129 (10)	0.0041 (4)	0.0131 (9)	−0.0005 (5)	0.0056 (8)	−0.0016 (5)
C(11)	0.7739 (8)	0.3201 (4)	0.1356 (7)	0.0204 (13)	0.0036 (4)	0.0177 (11)	0.0033 (6)	0.0015 (9)	−0.0009 (5)
C(12)	0.6433 (7)	−0.1160 (4)	0.0808 (6)	0.0118 (9)	0.0034 (3)	0.0121 (9)	−0.0004 (5)	0.0035 (7)	−0.0004 (4)
C(13)	0.5917 (8)	−0.1893 (5)	0.1736 (7)	0.0220 (13)	0.0060 (5)	0.0132 (10)	−0.0052 (6)	0.0062 (9)	0.0008 (5)
C(14)	0.5778 (7)	−0.1157 (4)	−0.0664 (6)	0.0155 (11)	0.0044 (4)	0.0092 (8)	−0.0020 (5)	0.0024 (7)	−0.0004 (4)
C(15)	0.6120 (6)	−0.0472 (4)	−0.1565 (6)	0.0099 (8)	0.0041 (4)	0.0095 (7)	0.0012 (4)	0.0004 (6)	−0.0016 (4)
C(16)	0.5210 (7)	−0.0412 (5)	−0.3126 (6)	0.0160 (10)	0.0064 (5)	0.0084 (7)	−0.0005 (6)	−0.0026 (7)	−0.0005 (5)

[a] The form of the anisotropic temperature expression is $\exp(\Sigma_i\Sigma_j\beta_{ij}h_ih_j)$.

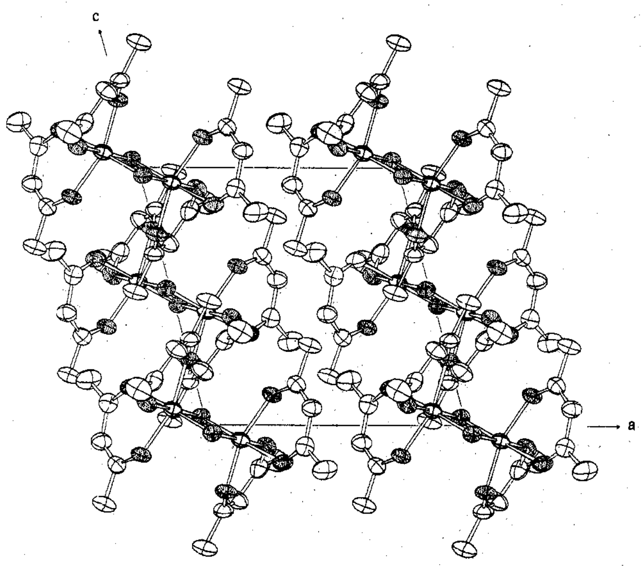

Figure 2.—Packing diagram for $(TiO(acac)_2)_2$, projected onto (010).

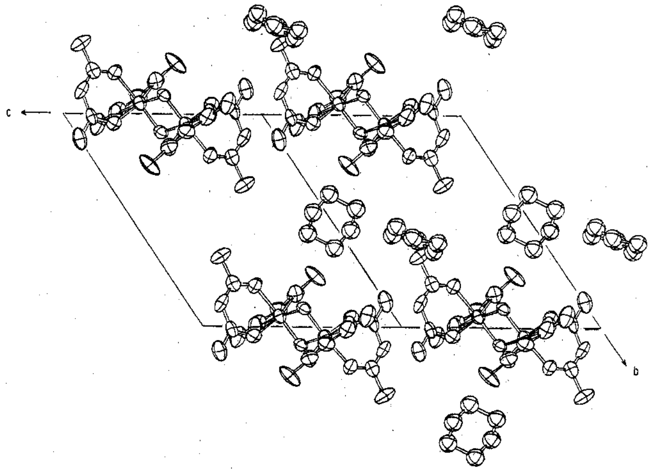

Figure 3.—Packing diagram for $(TiO(acac)_2)_2 \cdot 2C_4H_8O_2$, viewed down the a^* axis.

fering by about two standard deviations. The Ti–Ti distance is 2.729 (1) Å while the O–O distance is 2.430 (4) Å.

TABLE IV

BOND DISTANCES Å AND ANGLES (DEG) FOR CRYSTALS I AND II

	Crystal I	Crystal II		Crystal I	Crystal II
Ti(1)–O(2)	1.81 (2)	1.831 (3)	Ti(1)–O(2)′	1.82 (2)	1.824 (4)
Ti(1)–O(3)	1.98 (2)	1.974 (4)	Ti(1)–O(6)	1.96 (2)	1.968 (4)
Ti(1)–O(4)	2.04 (3)	2.059 (4)	Ti(1)–O(5)	2.07 (2)	2.054 (4)
O(3)–C(15)	1.30 (4)	1.28 (1)	O(6)–C(8)	1.24 (4)	1.28 (1)
O(4)–C(12)	1.26 (4)	1.26 (1)	O(5)–C(10)	1.30 (4)	1.27 (1)
C(12)–C(14)	1.34 (4)	1.39 (1)	C(9)–C(10)	1.38 (5)	1.39 (1)
C(14)–C(15)	1.43 (5)	1.38 (1)	C(8)–C(9)	1.40 (4)	1.37 (1)
C(12)–C(13)	1.53 (5)	1.52 (1)	C(7)–C(8)	1.53 (5)	1.55 (1)
C(15)–C(16)	1.48 (4)	1.52 (1)	C(10)–C(11)	1.50 (3)	1.52 (1)
C(17)–C(18)′	1.37 (7)		C(20)–C(21)	1.50 (7)	
C(18)–C(19)	1.23 (7)		C(21)–C(22)	1.55 (7)	
C(17)–C(19)	1.50 (8)		C(20)–C(22)′	1.45 (6)	
O(2)–Ti(1)–O(2)′	82.4 (8)	83.4 (2)	O(2)′–Ti(1)–O(5)	91.7 (9)	89.5 (2)
O(3)–Ti(1)–O(4)	82.9 (9)	83.4 (2)	O(2)–Ti(1)–O(5)	172.5 (10)	172.6 (2)
O(5)–Ti(1)–O(6)	82.2 (9)	82.8 (2)	O(2)′–Ti(1)–O(4)	174.7 (10)	171.9 (2)
O(2)–Ti(1)–O(3)	99.7 (9)	97.6 (2)	O(3)–Ti(1)–O(6)	163.8 (11)	161.1 (2)
O(2)–Ti(1)–O(4)	95.3 (9)	89.2 (2)	O(3)–Ti(1)–O(5)	85.2 (9)	84.7 (2)
O(2)–Ti(1)–O(6)	93.9 (9)	96.6 (2)	O(4)–Ti(1)–O(5)	90.9 (9)	98.1 (2)
O(3)–Ti(1)–O(2)′	92.8 (9)	94.4 (2)	O(4)–Ti(1)–O(6)	87.2 (9)	84.4 (2)
Ti(1)–O(3)–C(15)	134 (2)	130.7 (4)	O(6)–Ti(1)–O(2)′	97.7 (9)	99.6 (2)
Ti(1)–O(4)–C(12)	133 (2)	128.6 (4)	Ti(1)–O(5)–C(10)	132 (2)	129.5 (4)
O(3)–C(15)–C(14)	122 (2)	124.6 (5)	Ti(1)–O(6)–C(8)	134 (2)	131.2 (4)
C(12)–C(14)–C(15)	123 (3)	122.3 (5)	O(6)–C(8)–C(9)	125 (3)	125.6 (6)
O(4)–C(12)–C(14)	124 (3)	124.1 (5)	C(8)–C(9)–C(10)	123 (3)	121.4 (6)
O(3)–C(15)–C(16)	113 (2)	115.2 (5)	O(5)–C(10)–C(9)	121 (3)	124.1 (6)
C(14)–C(15)–C(16)	124 (3)	120.2 (5)	O(6)–C(8)–C(7)	116 (3)	115.1 (5)
O(4)–C(12)–C(13)	118 (3)	116.8 (5)	C(7)–C(8)–C(9)	119 (3)	119.3 (6)
C(13)–C(12)–C(14)	118 (3)	119.1 (5)	O(5)–C(10)–C(11)	116 (3)	117.3 (5)
C(17)′–C(18)–C(19)	122 (6)		C(9)–C(10)–C(11)	122 (3)	118.6 (6)
C(18)–C(19)–C(17)	110 (4)		C(20)–C(21)–C(22)	98 (4)	
C(18)–C(17)–C(19)′	113 (5)		C(21)–C(20)–C(22)	100 (4)	
			C(21)–C(22)–C(20)′	97 (4)	

TABLE V

	$(TiCl(acac)_2)_2\cdot CHCl_3$	$(TiO(acac)_2)_2\cdot 2C_4H_8O_2$	$(TiO(acac)_2)_2$
C–O	1.33 (5) Å	1.28 (4) Å	1.27 (1) Å
C–CH	1.37 (7) Å	1.39 (5) Å	1.38 (1) Å
$C–CH_3$	1.51 (6) Å	1.51 (5) Å	1.52 (1) Å

TABLE VI

LEAST-SQUARES PLANES[a]

	Crystal I					Crystal II				
	A	*B*	*C*	*D*	Σ[b]	*A*	*B*	*C*	*D*	Σ[b]
Ti, O(5), O(6), C(7), C(8), C(9), C(10), C(11)	−0.436	0.900	−0.026	−4.34	0.054	0.6816	0.2322	−0.6938	5.21	0.0509
Ti, O(3), O(4), C(12), C(13), C(14), C(15), C(16)	0.319	0.001	0.948	4.16	0.092	−0.5922	0.6176	0.5175	−4.25	0.0743
Ti, O(2), O(2)′, O(4), O(5)	0.894	0.396	−0.210	2.64	0.023	0.5314	0.1415	0.8352	4.88	0.0101
Ti, O(2), O(3), O(5), O(6)	−0.388	0.915	0.105	−3.78	0.071	0.6200	0.4072	−0.6706	4.86	0.0833
Ti, O(2)′, O(3), O(4), O(6)	0.214	0.048	0.976	3.94	0.072	−0.4760	0.7951	0.3756	−3.41	0.114
Ring 1: C(17), C(18), C(19), C(17)′, C(18)′, C(19)′	0.804	−0.161	−0.572	4.86	0.140					
Ring 2: C(20), C(21), C(22), C(20)′, C(21)′, C(22)′	0.734	0.078	0.675	−2.22	0.786					

[a] The equation for the least-squares plane is $AX + BY + CZ - D = 0$ where *A*, *B*, and *C* are direction cosines and *D* is the perpendicular distance from the plane to the origin. The orthogonal coordinate system from which these values are calculated is defined by *X* along the *a* axis, *Y* in the *ab* plane, and *Z* along the c^* axis. [b] Σ is the sum of the squares of the deviations of the atoms from the least-square plane.

Examination of Table V shows that the acetylacetonate rings are very nearly planar. Comparison of similar bond lengths in the acetylacetone rings of both structures with $(TiCl(acac)_2)_2\cdot CHCl_3$[3] shows that the average values for C–CH, $C–CH_3$, and C–O bond lengths probably agree within standard deviations of the measurements.

The octahedral coordination around titanium is somewhat, although not severely, distorted. The titanium atom is near the center of the octahedron and nearly coplanar with O(2), O(2′), O(4), O(5); O(2), O(3), O(5), O(6); and O(2′), O(3), O(4), O(6). Angles expected to be 90° in a perfect octahedron vary from 83 to 100° while those expected to be 180° differ from this by as much as 20°. The equations of the least-square planes are listed in Table VI. The dihedral angles between the various planes in the octahedron vary from 78.6 to 80°.

There are three different Ti–O distances found in both of these structures, *i.e.*, those in the di-*μ*-oxo-dititanium ring that average 1.83 Å, and those bonding to each (acac) group which average 1.97 and 2.06 Å. An interesting aspect of these differences is the trans effect across the titanium atom. The longer Ti–O bond to each (acac) is found to be trans to the bridging oxygen in both structures. Since this effect is observed in both structures and since the difference in the bond distance is approximately 4 standard deviations in the case of $(TiO(acac)_2)_2 \cdot 2C_4H_8O_2$ and 20 standard deviations for $(TiO(acac)_2)_2$, it is felt that this trans effect is real. It should also be noted that a comparison of corresponding Ti–O bond distances in both structures shows that these distances agree to within 1 standard deviation.

The Ti–O bond distances of this study compare with 1.988 and 1.944 Å in rutile,[9] 1.79 and 1.81 Å in $(TiCl(acac)_2)_2 \cdot CHCl_3$,[3] and 1.91, 1.744, and 2.122 Å in $TiCl_2(OC_6H_5)_2$.[10] It is interesting that the short Ti–O bond length does not involve a large oxygen bond angle as it does in the other similar cases of TiO distances of the order of 1.8 Å.

One of the most interesting and still puzzling aspects of this structure is the presence of the solvent molecules in crystal I. Examination of the least-squares planes for the solvent (Table VI) shows that ring 1 is more nearly planar than is ring 2. This is apparently due to a different mechanism of disorder for each dioxane molecule since the occupation factors indicate that the oxygens are nearly equally spread out over the two molecules.

Since the shortest distance from a solvent atom to an atom in the dimer unit is 3.42 Å (C(19)–C(13)), we conclude that the solvent molecules are simply trapped in the spaces between dimer units with little or no chemical bonding. These holes occupied by the solvent molecules are approximately spherical and have a diameter of about 7 Å.

Acknowledgment.—We wish to acknowledge the National Science Foundation for a grant (GP-8301) for partial support of this research. We also wish to thank the Montana State University Computing Center for a grant of computing time.

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The Crystal and Molecular Structure of Chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) Perchlorate

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Received March 16, 1972

The crystal structure of chloro(bis{2-[(2-pyridylmethyl)amino]ethyl} disulfide)nickel(II) perchlorate, $Ni(C_{16}H_{22}N_4S_2)Cl(ClO_4)$, has been determined by single-crystal X-ray diffraction techniques and was refined by full-matrix least-squares methods to a final conventional R index of 0.058. The deep blue crystals form as rectangular prisms in space group *Pbca* with $a = 24.019$ (8), $b = 14.700$ (4), and $c = 12.439$ (6) Å. The nickel(II) ion is coordinated octahedrally by four nitrogen atoms, a chloride ion, and one sulfur atom of the disulfide group. The two pyridine rings are cis; the two amino groups are cis; and the chloride ion and the coordinating sulfur atom are cis. The octahedral angles are all within 10° of right angles, and the largest deviations can be explained by ring strain. The nickel(II)–sulfur distance, 2.472 (5) Å, is comparable with the sum of the corresponding Pauling covalent radii, 2.43 Å, indicating a strong interaction. Exploratory X-ray photographs and structure factor calculations indicate that $Ni(C_{16}H_{22}N_4S_2)I_2$ and $Ni(C_{16}H_{22}N_4S_2)Br(ClO_4)$ are isostructural with $Ni(C_{16}H_{22}N_4S_2)Cl(ClO_4)$.

Introduction

The breaking of aliphatic disulfide bonds is catalyzed by Ag(I),[1] Hg(II),[2] and Pd(II)[3] by a mechanism in which the –S–S– group first complexes the transition metal ion. An intermediate was isolated in the Pd(II) system which is expected to show disulfide–Pd(II) coordination. Disulfide formation[4,5] has also been postulated in ferredoxin activity, presumably through coordination involving delocalized orbitals.[6,7] A weak Cu(II) cystine complex was reported[8–11] on the basis of anomalous stability constants. The structures of (diethyl disulfide)copper(I) chloride,[12] of a dinuclear cobalt disulfide complex,[13] and of an iridium disulfide complex[14] have been determined crystallographically. Complexes of cystine with Cd, Ni, and Zn have also been postulated.[15]

In the preparation of the Ni(II) complexes, two ligands which differed only by one methylene group per half molecule showed very different behavior[16,17] in the presence of the metal ion. Where five-membered rings formed, the disulfide was stable. Where six-membered rings were expected, the disulfide bond proved to be unstable. The metal ion by itself, then, showed this great selectivity by the nature of the complex it formed with the ligand (substrate). Ample

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