

Table IX. Comparison of Metal-Phosphorus Geometries in MH_2P_4 Structures

| Complex | M-P, Å | M(II) radius, ^a Å | Cis P-P, Å | Δ_{oct} , ^b deg | Δ_{tet} , deg |
|--|--|------------------------------|---------------------|-----------------------------------|----------------------|
| <i>trans</i> - $RuH_2[(C_6H_5)_2P(OC_2H_5)_2]_4$ | 2.272 (4) | 1.33 | 3.253 (3.244-3.261) | 26 | 82 |
| <i>cis</i> - $FeH_2[(C_6H_5)_2P(OC_2H_5)_2]_4$ | 2.122 (2) _{ax} 2.150 (2) _{eq} | 1.23 | 3.355 (3.222-3.481) | 53 | 32 |

^a Reference 17. ^b Δ represents the rms deviation from idealized angles.

tion is less in *trans*- RuH_2P_4 than *cis*- FeH_2P_4 . At least two reasons for this seem pertinent. First, the Ru(II) radius is larger than the Fe(II) radius, a fact which is reflected in the corresponding M-P distances. Second, the idealized *cis* geometry has five angles of 90° (P-M-P) whereas the *trans* geometry has only four. Thus, for these bulky ligands the expected net distortion for *cis* geometry might be larger than for *trans* geometry. The P-P contacts are comparable in both structures, but this is of questionable significance since the interligand steric effects arise from many contacts.

We have been attempting to assess further the influence of steric effects on structures of this type by comparing these two structures with that of *trans*- FeH_2P_4 . However, we have not been able as yet to obtain suitable single crystals of the *trans* isomer for X-ray studies. Based on the data for *trans*- RuH_2P_4 and *cis*- FeH_2P_4 we would predict that the *trans*- FeH_2P_4 structure is significantly distorted from octahedral symmetry (more distorted than in *trans*- RuH_2P_4), but closer to octahedral than tetrahedral symmetry.

Although the interligand steric contacts between the phosphine ligands seem to be structure determining with respect to molecular symmetry, the intramolecular contacts involving the hydride hydrogen cannot be discounted entirely. Some of the short contacts are given in Table IV. The steric effect

of the hydride hydrogen is perhaps more obvious from the angles in Table V where it is seen that angles involving O(2) and O(3) differ from those involving O(1) and O(4); *i.e.*, Ru-P-O(2) is $123.5(2)^\circ$ whereas Ru-P-O(1) is $111.8(5)^\circ$. The O(2) and O(3) atoms are pushed away from the hydride hydrogen by the contacts between the hydride hydrogen and the methylene hydrogen atoms of the O(2) and O(3) ethoxy groups.

Finally, we have seen how the solid-state distortions in MH_2P_4 structures of this type are naturally away from octahedral symmetry toward tetrahedral MP_4 environments. These distortions are relevant to the nature of the solution behavior in these complexes as seen at the nmr time scale. Further discussion on the interpretation of the nmr spectra and possible rearrangement mechanisms is found elsewhere.⁴ The preferred rearrangement mechanism for these complexes is through a tetrahedral MP_4 environment. If this mechanism is correct, in view of the distortions observed here, the expected barrier to rearrangement for *trans*- RuH_2P_4 should be significantly larger than for *cis*- FeH_2P_4 . This is, in fact, what is found from the nmr data.

Registry No. $RuH_2[(C_6H_5)_2P(OC_2H_5)_2]_4$, 38619-44-2.

Contribution from the Chemistry Department,
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Crystal Structures of Bis(2,4-pentanedionato)bis(2,6-diisopropylphenoxo)titanium(IV), Bis(8-quinolinolato)bis(2,6-diisopropylphenoxo)titanium(IV), and Bis(2-methyl-8-quinolinolato)bis(2,6-diisopropylphenoxo)titanium(IV)

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The crystal and molecular structures of three bis-chelate complexes of bis(2,6-diisopropylphenoxo)titanium(IV) have been determined by single-crystal X-ray diffraction techniques. The chelating ligands were 2,4-pentanedionate (acetylacetonate), 8-quinolinolato (oxinate), and 2-methyl-8-quinolinolato (quinaldinate). The unit cell data for the three compounds are as follows: for the acetylacetonate $(C_5H_7O_2)_2(C_{12}H_{17}O)_2Ti$, space group $C2/c$ (No. 15), $Z = 4$, $a = 18.90(1)$, $b = 8.871(6)$, $c = 21.04(1)$ Å, $\beta = 106.92(4)^\circ$, $V = 3374$ Å³; for the oxinate $(C_9H_8NO)_2(C_{12}H_{17}O)_2Ti$, space group $C2/c$ (No. 15), $Z = 4$, $a = 19.51(1)$, $b = 9.193(6)$, $c = 21.84(1)$ Å, $\beta = 105.57(4)^\circ$, $V = 3774$ Å³; for the quinaldinate $(C_{10}H_8NO)_2(C_{12}H_{17}O)_2Ti$, space group $P1$ (No. 2), $Z = 2$, $a = 16.047(5)$, $b = 12.383(4)$, $c = 12.997(4)$ Å, $\alpha = 96.37(1)$, $\beta = 127.58(1)$, $\gamma = 77.97(1)^\circ$, $V = 2001.4$ Å³. Diffractometer data were collected using a θ - 2θ scan technique and final unweighted R values after anisotropic full-matrix refinement were 6.6, 7.7, and 6.3% for the acetylacetonate, oxinate, and quinaldinate, respectively. All three compounds are monomeric with a distorted octahedral coordination of the titanium. All molecules have twofold symmetry, which is crystallographically required for the acetylacetonate and oxinate complexes and approximate for the quinaldinate. The phenoxy ligands are found *cis*, as are the nitrogen atoms of the oxinate and quinaldinate groups. In the acetylacetonate and oxinate the phenyl rings are directed away from one another, whereas in the quinaldinate they are more nearly parallel. In all three molecules the isopropyl groups are positioned with their hydrogen atoms directed toward the titanium.

Introduction

Among the extensive studies of configurational rearrangement phenomena in complexes with chelating ligands,¹

certain bis(alkoxy)bis(chelate)titanium(IV) and bis(aryloxy)-

(1) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, **17**, 391 (1972).

bis(chelate)titanium(IV) complexes have recently been subjected to further studies.^{2,3} The original purpose behind the preparation of the 2,6-diisopropylphenoxy complexes whose crystal structures are described here was an attempt to prepare less accessible trans aryloxy compounds by using a bulky ligand. While this was not achieved, the complexes are nevertheless of interest since the nmr signals of the diisopropyl methyl protons are potentially a sensitive probe for the rearrangement processes of the chelating ligands. The interpretation of the nmr results has been hampered by uncertainties about the precise molecular geometry of these complexes. In particular, it has proved difficult to predict the steric restrictions on intramolecular bond rotations using conventional models without foreknowledge of the probable ranges for bond lengths and angles. The object of the three structure determinations reported here was largely to provide these missing molecular parameters before the nmr results² are published in more detail.

Experimental Section

Samples of the bis(2,6-diisopropylphenoxy)bis(chelate)titanium(IV) complexes where the chelating ligands were acetylacetonate, oxinate, and quinaldinate were kindly supplied by Mr. K. Taylor of McGill University. All three compounds were recrystallized by slowly cooling saturated solutions in a 1:5 mixture of ether and pentane. The first two crystallized as parallelepipeds with no particularly well-developed direction, and the third formed short needles. Crystals suitable for X-ray diffraction studies were sealed in Lindemann capillaries, partly because of a tendency to dissolve in glue and also because of the danger of decomposition by atmospheric moisture, although this latter process proved extremely slow.

Space Group and Unit Cell Parameter Determination

Preliminary Weissenberg and precession photographs were taken with filtered Mo K α radiation. These were used to check that the chosen crystals were free from defects other than a normal mosaic structure, and to determine the probable space groups. Subsequently, accurate cell dimensions were obtained on a Picker FACS-1 fully automated diffractometer, equipped with a graphite monochromator. The wavelength of the Mo K α radiation used was taken as 0.71069 Å. Other instrument parameters have been described in detail previously.⁴ In each case accurate values of 2θ , ω , χ , and ϕ obtained for 12 Bragg reflections, centered at both positive and negative 2θ values and appropriately averaged, were used in a least-squares refinement of the unit cell parameters and the crystal orientation matrix. (The α_1 - α_2 doublet was not resolved during this process.) The programs supplied by the Picker-Nuclear Co. were used for this procedure.⁴

Data Collection and Reduction

Intensity data were collected on the diffractometer using a θ - 2θ scan (2θ scanned at 1°/min) with a base width of 2° increasing with 2θ to allow for α_1 - α_2 dispersion. For the acetylacetonate and oxinate complexes, backgrounds were estimated from a carefully measured curve, but those for the quinaldinate complex were individually measured for 40 sec before and after the scan, since the former procedure was judged less satisfactory. In all cases an asymmetric unit of data was collected within angular limits chosen to include all reasonably strong reflections. Instrument stability was monitored by re-measuring the intensity of a standard reflection every 30 measurement cycles and also by measuring the intensity of reciprocal axis reflections with both positive and negative indices before and after data collections. Only a random variation of less than 5% was detected; thus the data were judged of acceptable quality.

Data reductions were performed using a locally written program which also determined an approximate scale factor and overall isotropic thermal parameter from reflection statistics.⁵ Reflection intensities I were computed as $[N - Bt_s/t_b]$ and the standard deviation $\sigma(I) = [N + B(t_s/t_b)^2 + (0.02N)^2]^{1/2}$, where N and B are the total counts accumulated during the scan period t_s and total background counting time t_b , respectively. Data for which $I < 3\sigma(I)$ were dis-

carded entirely and the remaining data were corrected for Lorentz and polarization effects, $(Lp)^{-1} = \sin 2\theta_m (\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$, where $2\theta_m$ and $2\theta_s$ are diffraction angles at the monochromator and sample crystal, respectively. No corrections for absorption were applied, since the absorption coefficients, ranging from 2.70 (for the quinaldinate) to 3.09 (for the acetylacetonate), are low enough to produce little variation in the transmission factors (90-95%).

Structure Solution and Refinement

The Sir George Williams University CDC 3300 and 6400 computers were used for all computing.⁶ All three structures were solved from Patterson syntheses based on "sharpened" data,⁷ which revealed the titanium atom positions. Subsequent structure factor calculations followed by Fourier syntheses revealed the remaining atoms. In least-squares refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(F_o)]^{-2}$. The discrepancy indices referred to below are $R = [\sum (|F_o| - |F_c|)] / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2] / \sum w|F_o|^2$. The error in an observation of unit weight (the "goodness of fit") is defined by $[\sum w(|F_o| - |F_c|)^2 / (n - m)]^{1/2}$ where n and m are the numbers of observations and parameters varied, respectively. The scattering factors for neutral atoms were obtained from the compilation of Ibers.⁸ Hydrogen atoms included in structure factor calculations were placed 1.08 Å from the appropriate carbon atom at positions which were recalculated every two cycles of refinement and after convergence.

Bis(2,4-pentanedionato)bis(2,6-diisopropylphenoxy)titanium(IV). The crystal chosen was a parallelepiped *ca.* 0.30 × 0.30 × 0.40 mm. It was mounted to rotate about its longest dimension. Weissenberg photographs of the $h0l$, $h1l$, $0kl$, and $1kl$ indicated the space groups Cc (No. 9) or $C2/c$ (No. 15). The unit cell dimensions obtained on the diffractometer were $a = 18.90$ (1), $b = 8.871$ (6), $c = 21.04$ (1) Å, $\beta = 106.92$ (4)°, $V = 3374$ Å³. The observed density of 1.21 (1) g cm⁻³ obtained by flotation in aqueous zinc iodide solution agrees with the value 1.188 g cm⁻³ calculated on the basis of 4 molecules in the unit cell. Collection of intensity data in the region 4° < 2θ < 45° yielded 2794 reflections of which 1381 remained after data reduction. Successful solution of the structure led to final assignment of $C2/c$ as the appropriate space group, with the molecules lying on the crystallographic twofold axis.

After three cycles of full-matrix refinement using isotropic thermal parameters, the reliability factors were $R = 13.6\%$ and $R_w = 14.2\%$. At this point, all hydrogen atoms not on methyl groups were observed on a difference Fourier map (0.4-0.8 e Å⁻³), together with the usual peaks attributable to anisotropic vibration of the nonhydrogen atoms. Further full-matrix refinement using anisotropic thermal parameters and including the hydrogen atoms in the structure factor calculations led to convergence with $R = 6.6\%$, $R_w = 7.3\%$, and the "goodness of fit" 3.46 after five cycles. (The rather high value here and for the oxinate suggests that the standard deviations in the data have been underestimated or that the conventional anisotropic model is inadequate to fit the data well.) The final atomic parameters are shown in Table IA.⁹

Bis(8-quinolinolato)bis(2,6-diisopropylphenoxy)titanium(IV). Procedures for this structure determination were essentially identical with those detailed above for the acetylacetonate. The dimensions of the crystal were 0.15 × 0.20 × 0.40 mm. The unit cell data are space group $C2/c$ (No. 15), $a = 19.51$ (1), $b = 9.193$ (6), $c = 21.84$ (1) Å, $\beta = 105.57$ (4)°, $V = 3774$ Å³, $\rho_{\text{obsd}} = 1.20$ (1) and $\rho_{\text{calcd}} = 1.215$ g cm⁻³ for $Z = 4$. Of 3260 diffraction intensities measured in the range 4 < 2θ < 45°, 1481 were retained after data processing. The isotropic phase of refinement (five cycles) converged with $R = 11.7\%$ and $R_w = 13.1\%$. During the anisotropic phase of refinement, computer memory limitations required that the parameters be divided

(6) Fourier and Patterson calculations were performed using FORADP by A. Zalkin. Structure factor and least-squares calculations were obtained using SFLS-5 by C. T. Prewitt. Both programs have been highly modified for the CDC computers. All other crystallographic computing involved locally written programs.

(7) R. A. Jacobson, J. A. Wunderlich, and W. N. Lipscomb, *Acta Crystallogr.*, **14**, 598 (1961).

(8) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 202.

(9) A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1322.

(2) J. F. Harrod and K. Taylor, *Chem. Commun.*, 696 (1971).

(3) D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 282 (1969).

(4) A. D. Adley, P. H. Bird, A. R. Fraser, and M. Onyszchuk, *Inorg. Chem.*, **11**, 1402 (1972).

(5) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

Table I. Final Positions^a and Thermal Parameters^b with Estimated Standard Deviations^c

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> or β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} | |
|--|-------------|---------------|-------------|--------------------------|--------------|--------------|--------------|--------------|--------------|--|
| (A) C ₃₄ H ₄₈ O ₆ Ti | | | | | | | | | | |
| Ti | 0 | 0.10804 (23) | 0.25 | 29.6 (8) | 129.8 (32) | 17.2 (5) | 0 | 10.4 (5) | 0 | |
| O1 | 0.0762 (3) | -0.0286 (5) | 0.2734 (2) | 26 (2) | 124 (8) | 18 (1) | 3 (3) | 8 (1) | -4 (3) | |
| Cp1 | 0.1429 (4) | -0.0934 (8) | 0.2842 (3) | 19 (2) | 79 (10) | 17 (2) | 4 (5) | 5 (2) | 2 (4) | |
| Cp2 | 0.1913 (4) | -0.0883 (8) | 0.3490 (3) | 31 (3) | 92 (11) | 21 (2) | -5 (5) | 11 (2) | 3 (4) | |
| Cp3 | 0.2611 (4) | -0.1549 (9) | 0.3597 (4) | 31 (3) | 164 (15) | 26 (2) | -2 (6) | 11 (2) | -1 (5) | |
| Cp4 | 0.2788 (4) | -0.2296 (10) | 0.3093 (4) | 32 (3) | 215 (17) | 30 (3) | 12 (6) | 13 (3) | 3 (6) | |
| Cp5 | 0.2296 (5) | -0.2346 (10) | 0.2470 (4) | 38 (4) | 174 (15) | 27 (3) | 6 (7) | 15 (3) | -14 (5) | |
| Cp6 | 0.1598 (4) | -0.1697 (8) | 0.2330 (4) | 34 (3) | 120 (13) | 23 (2) | 3 (5) | 14 (2) | -1 (4) | |
| Cp7 | 0.1041 (5) | -0.1804 (10) | 0.1636 (4) | 44 (3) | 167 (15) | 18 (2) | 9 (6) | 7 (2) | -17 (5) | |
| Cp8 | 0.1411 (5) | -0.1407 (15) | 0.1096 (4) | 65 (5) | 443 (30) | 19 (2) | -21 (10) | 13 (3) | -2 (7) | |
| Cp9 | 0.0695 (6) | -0.3355 (12) | 0.1538 (5) | 81 (6) | 230 (23) | 44 (4) | -62 (9) | -11 (4) | -8 (7) | |
| Cp10 | 0.1684 (4) | -0.0149 (9) | 0.4056 (3) | 47 (4) | 122 (12) | 16 (2) | 14 (6) | 9 (2) | -3 (4) | |
| Cp11 | 0.2342 (6) | -0.0474 (13) | 0.4617 (5) | 83 (6) | 322 (25) | 34 (3) | -52 (9) | 21 (4) | -57 (7) | |
| Cp12 | 0.1234 (6) | -0.1272 (12) | 0.4324 (5) | 91 (6) | 248 (20) | 52 (4) | -46 (9) | 54 (4) | -25 (8) | |
| Hp3 | 0.3014 | -0.1475 | 0.4081 | 5.0 | | | | | | |
| Hp4 | 0.3319 | -0.2846 | 0.3190 | 5.0 | | | | | | |
| Hp5 | 0.2452 | -0.2911 | 0.2077 | 5.0 | | | | | | |
| Hp7 | 0.0603 | -0.0994 | 0.1592 | 5.0 | | | | | | |
| Hp10 | 0.1348 | 0.0822 | 0.3853 | 5.0 | | | | | | |
| O2 | -0.0131 (3) | 0.1437 (5) | 0.3390 (2) | 32 (2) | 152 (9) | 16 (1) | -5 (3) | 10 (1) | -4 (3) | |
| O3 | 0.0745 (3) | 0.2807 (6) | 0.2782 (3) | 32 (2) | 136 (9) | 28 (2) | -14 (4) | 13 (2) | -9 (3) | |
| Cac1 | -0.0253 (5) | 0.2397 (11) | 0.4406 (4) | 50 (4) | 314 (20) | 18 (2) | 7 (8) | 16 (3) | -14 (6) | |
| Cac2 | 0.0076 (4) | 0.2477 (9) | 0.3824 (3) | 29 (3) | 158 (14) | 13 (2) | 8 (6) | 4 (2) | -7 (5) | |
| Cac3 | 0.0585 (5) | 0.3568 (9) | 0.3801 (4) | 41 (4) | 135 (15) | 25 (2) | 9 (6) | 9 (3) | -11 (5) | |
| Cac4 | 0.0913 (4) | 0.3692 (9) | 0.3285 (4) | 32 (3) | 103 (13) | 26 (2) | 7 (5) | 4 (2) | -8 (5) | |
| Cac5 | 0.1478 (4) | 0.4908 (10) | 0.3291 (5) | 37 (4) | 123 (14) | 50 (3) | -31 (6) | 9 (3) | -7 (6) | |
| Hac6 | 0.0742 | 0.4375 | 0.4204 | 5.0 | | | | | | |
| (B) C ₄₂ H ₄₆ N ₂ O ₄ Ti | | | | | | | | | | |
| Ti | 0 | -0.03633 (25) | -0.25 | 29.5 (8) | 137.4 (36) | 18.4 (6) | 0 | 1.8 (6) | 0 | |
| O1 | 0.0722 (2) | 0.0890 (5) | -0.2158 (2) | 26 (2) | 140 (9) | 19 (2) | -8 (3) | -2 (2) | -3 (3) | |
| Cp1 | 0.1372 (4) | 0.1512 (10) | -0.2027 (4) | 24 (3) | 123 (15) | 22 (3) | 3 (5) | 3 (2) | -10 (5) | |
| Cp2 | 0.1567 (5) | 0.2289 (10) | -0.2499 (5) | 29 (4) | 126 (15) | 28 (3) | -5 (6) | 0 (3) | -5 (6) | |
| Cp3 | 0.2240 (4) | 0.2930 (10) | -0.2349 (4) | 27 (4) | 190 (18) | 30 (3) | 2 (6) | 6 (3) | -15 (6) | |
| Cp4 | 0.2703 (5) | 0.2771 (12) | -0.1738 (5) | 22 (3) | 222 (20) | 40 (4) | -2 (6) | 7 (3) | -24 (7) | |
| Cp5 | 0.2496 (5) | 0.1994 (11) | -0.1281 (4) | 31 (4) | 209 (20) | 22 (3) | 6 (7) | 0 (3) | -12 (6) | |
| Cp6 | 0.1836 (5) | 0.1336 (10) | -0.1418 (4) | 29 (3) | 143 (15) | 22 (3) | 4 (6) | 1 (3) | -13 (5) | |
| Cp7 | 0.1563 (5) | 0.0531 (10) | -0.0896 (4) | 52 (4) | 179 (17) | 19 (3) | -26 (7) | -3 (3) | 1 (6) | |
| Cp8 | 0.2186 (6) | -0.0198 (15) | -0.0398 (5) | 77 (5) | 340 (28) | 40 (4) | 21 (11) | -14 (4) | 58 (9) | |
| Cp9 | 0.1114 (6) | -0.1525 (14) | -0.0606 (5) | 92 (7) | 296 (25) | 42 (4) | 23 (10) | 46 (4) | -12 (8) | |
| Cp10 | 0.1058 (5) | 0.2509 (11) | -0.3165 (5) | 35 (4) | 180 (19) | 33 (3) | -25 (7) | -13 (3) | 15 (6) | |
| Cp11 | 0.1449 (7) | 0.2154 (20) | -0.3718 (6) | 87 (8) | 724 (52) | 21 (4) | 34 (16) | 14 (4) | 7 (11) | |
| Cp12 | 0.0733 (7) | 0.3998 (14) | -0.3232 (7) | 115 (8) | 208 (24) | 79 (6) | 68 (11) | -66 (6) | -26 (10) | |
| Hp3 | 0.2405 | 0.3553 | -0.2704 | 5.0 | | | | | | |
| Hp4 | 0.3225 | 0.3261 | -0.1628 | 5.0 | | | | | | |
| Hp5 | 0.2851 | 0.1897 | -0.0810 | 5.0 | | | | | | |
| Hp7 | 0.1214 | -0.0340 | -0.1120 | 5.0 | | | | | | |
| Hp10 | 0.0626 | 0.1740 | -0.3223 | 5.0 | | | | | | |
| O2 | 0.0385 (3) | -0.0815 (6) | -0.3216 (2) | 40 (2) | 172 (10) | 13 (2) | -15 (4) | 8 (2) | -8 (3) | |
| N | -0.0664 (4) | -0.2205 (7) | -0.2984 (3) | 38 (3) | 98 (11) | 18 (2) | -11 (4) | 1 (2) | 6 (4) | |
| Cq1 | -0.1195 (4) | -0.2874 (10) | -0.2850 (4) | 35 (3) | 150 (16) | 26 (3) | -21 (6) | 5 (3) | 4 (5) | |
| Cq2 | -0.1614 (5) | -0.3952 (11) | -0.3252 (6) | 37 (4) | 182 (18) | 40 (4) | -25 (6) | 5 (3) | 15 (7) | |
| Cq3 | -0.1428 (6) | -0.4334 (10) | -0.3798 (5) | 48 (5) | 120 (16) | 32 (3) | -6 (7) | -1 (3) | -13 (6) | |
| Cq4 | -0.0651 (6) | -0.3918 (12) | -0.4527 (6) | 50 (5) | 180 (21) | 29 (4) | 14 (7) | -2 (4) | -23 (7) | |
| Cq5 | -0.0110 (7) | -0.3132 (13) | -0.4633 (5) | 71 (6) | 216 (23) | 19 (3) | 18 (9) | 0 (4) | -16 (7) | |
| Cq6 | 0.0276 (5) | -0.2090 (11) | -0.4196 (4) | 45 (4) | 214 (19) | 19 (3) | 4 (7) | 5 (3) | 3 (6) | |
| Cq7 | 0.0073 (5) | -0.1790 (10) | -0.3649 (4) | 36 (4) | 176 (16) | 12 (2) | 12 (6) | 5 (3) | 2 (5) | |
| Cq8 | -0.0488 (4) | -0.2596 (10) | -0.3532 (4) | 24 (3) | 130 (15) | 20 (3) | -1 (5) | 1 (3) | -1 (5) | |
| Cq9 | -0.0870 (6) | -0.3623 (10) | -0.3967 (5) | 38 (4) | 120 (16) | 26 (3) | 7 (6) | 1 (3) | -2 (6) | |
| Hq1 | -0.1580 | -0.2424 | -0.2626 | 5.0 | | | | | | |
| Hq2 | -0.2063 | -0.4454 | -0.3132 | 5.0 | | | | | | |
| Hq3 | -0.1716 | -0.5189 | -0.4098 | 5.0 | | | | | | |
| Hq4 | -0.0912 | -0.4749 | -0.4857 | 5.0 | | | | | | |
| Hq5 | 0.0036 | -0.3305 | -0.5071 | 5.0 | | | | | | |
| Hq6 | 0.0725 | -0.1534 | -0.4289 | 5.0 | | | | | | |

among two matrices. In order to preserve some correlation between them, atoms were moved randomly between matrices after each cycle. At convergence after six cycles, $R = 7.7\%$, $R_w = 8.7\%$, and the "goodness of fit" was 3.43. Final parameters appear in Table IB.⁹

Bis(2-methyl-8-quinolinolato)bis(2,6-diisopropylphenoxy)-titanium(IV). A fragment of an acicular crystal, $0.15 \times 0.15 \times 0.30$ mm, was mounted to rotate about its needle axis. With the crystal in this orientation, zero- and first-level Weissenberg and precession photographs showed the crystal to belong to the triclinic system, but in a nonstandard setting characterized by the systematic absence $2h +$

$k + 3l = 6n$. Before beginning diffractometry, a primitive cell was chosen by reindexing such that $h' = (2h + k)/3$, $k' = (k - h)/3$, and $l' = (2l - 2h - k)/6$. The refined cell parameters are $a = 16.047$ (5), $b = 12.383$ (4), $c = 12.997$ (4) Å, $\alpha = 96.37$ (1), $\beta = 127.58$ (1), $\gamma = 77.97$ (1)°, $V = 2001.4$ Å³, and $Z = 2$ where $\rho_{\text{obsd}} = 1.19$ (1) and $\rho_{\text{calcd}} = 1.198$ g cm⁻³. The centrosymmetric space group $P\bar{1}$ (No. 2) was assigned following successful solution of the structure. Within the angular limits $4 < 2\theta < 40^\circ$, 3998 intensities were measured, and 2368 were retained for the solution and refinement of the structure. Discrepancy indices after isotropic refinement (six cycles, two

Table I. (Continued)

| Atom | x | y | z | B or β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|----------------------------|-------------|--------------|--------------|-------------------|--------------|--------------|--------------|--------------|--------------|
| (C) $C_{44}H_{50}N_2O_4Ti$ | | | | | | | | | |
| Ti | 0.2329 (1) | -0.2393 (1) | -0.0459 (2) | 56 (1) | 57 (1) | 78 (2) | -3 (1) | 40 (1) | 9 (1) |
| O1 | 0.2213 (4) | -0.1733 (4) | 0.0781 (5) | 76 (5) | 75 (6) | 88 (7) | -12 (4) | 52 (5) | 2 (5) |
| Cp1 | 0.2515 (6) | -0.1505 (7) | 0.2028 (7) | 37 (7) | 96 (9) | 47 (10) | 12 (6) | 27 (7) | -5 (7) |
| Cp2 | 0.2326 (6) | -0.2266 (7) | 0.2569 (8) | 64 (7) | 83 (9) | 101 (12) | 25 (6) | 67 (8) | 41 (8) |
| Cp3 | 0.2669 (7) | -0.2041 (7) | 0.3840 (8) | 80 (9) | 101 (10) | 94 (13) | -4 (8) | 57 (9) | 18 (9) |
| Cp4 | 0.3141 (7) | -0.1132 (8) | 0.4464 (8) | 82 (9) | 139 (12) | 73 (12) | -4 (8) | 43 (9) | 1 (9) |
| Cp5 | 0.3274 (7) | -0.0404 (7) | 0.3860 (8) | 82 (9) | 109 (10) | 91 (12) | -18 (8) | 41 (9) | -25 (9) |
| Cp6 | 0.2961 (6) | -0.0566 (7) | 0.2597 (8) | 65 (8) | 76 (9) | 107 (13) | -15 (7) | 40 (9) | -28 (8) |
| Cp7 | 0.3062 (8) | 0.0215 (7) | 0.1866 (9) | 167 (12) | 67 (10) | 147 (15) | -47 (8) | 108 (11) | -14 (9) |
| Cp8 | 0.2249 (10) | 0.1222 (11) | 0.1441 (18) | 152 (16) | 214 (18) | 674 (43) | 96 (13) | 234 (23) | 295 (23) |
| Cp9 | 0.4178 (8) | 0.0492 (10) | 0.2629 (12) | 98 (11) | 200 (16) | 326 (25) | -44 (11) | 100 (14) | 67 (16) |
| Cp10 | 0.1745 (7) | -0.3223 (7) | 0.1810 (8) | 97 (7) | 65 (9) | 128 (14) | -26 (7) | 77 (10) | -12 (8) |
| Cp11 | 0.0521 (7) | -0.2813 (9) | 0.0932 (10) | 36 (8) | 150 (13) | 196 (17) | -21 (8) | 36 (10) | -6 (11) |
| Cp12 | 0.2125 (9) | -0.4237 (7) | 0.2712 (10) | 196 (13) | 77 (10) | 162 (16) | -22 (9) | 131 (13) | 35 (10) |
| Hp3 | 0.2564 | -0.2582 | 0.4334 | 5.0 | | | | | |
| Hp4 | 0.3414 | -0.0985 | 0.5451 | 5.0 | | | | | |
| Hp5 | 0.3629 | 0.0308 | 0.4379 | 5.0 | | | | | |
| Hp7 | 0.2925 | -0.0219 | 0.1022 | 5.0 | | | | | |
| Hp10 | 0.1957 | -0.3533 | 0.1173 | 5.0 | | | | | |
| O1' | 0.3264 (4) | -0.3637 (4) | 0.0443 (5) | 62 (5) | 54 (5) | 82 (7) | 3 (4) | 37 (5) | 24 (5) |
| Cp1' | 0.3795 (6) | -0.4435 (6) | 0.1421 (7) | 46 (7) | 72 (8) | 77 (11) | 17 (6) | 41 (8) | 29 (7) |
| Cp2' | 0.4643 (6) | -0.4149 (6) | 0.2672 (7) | 45 (7) | 79 (9) | 70 (10) | 24 (6) | 38 (7) | 28 (7) |
| Cp3' | 0.5110 (7) | -0.4958 (8) | 0.3637 (8) | 70 (9) | 103 (11) | 54 (12) | -7 (8) | 35 (9) | 1 (9) |
| Cp4' | 0.4904 (8) | -0.5976 (9) | 0.3663 (9) | 85 (10) | 95 (11) | 108 (14) | 6 (7) | 65 (10) | 35 (10) |
| Cp5' | 0.3988 (7) | -0.6209 (7) | 0.2110 (9) | 97 (9) | 72 (9) | 132 (14) | -7 (7) | 69 (10) | 38 (9) |
| Cp6' | 0.3453 (7) | -0.5448 (7) | 0.1063 (9) | 78 (8) | 43 (8) | 147 (14) | -17 (7) | 77 (10) | 3 (9) |
| Cp7' | 0.2580 (7) | -0.5703 (7) | -0.0333 (8) | 93 (9) | 75 (10) | 72 (12) | -40 (7) | 21 (9) | -9 (8) |
| Cp8' | 0.3002 (9) | -0.6821 (11) | -0.0735 (11) | 125 (12) | 242 (17) | 207 (19) | -19 (12) | 90 (14) | -130 (15) |
| Cp9' | 0.1556 (7) | -0.5784 (10) | -0.0539 (10) | 56 (8) | 229 (16) | 189 (17) | -70 (9) | 52 (10) | -52 (13) |
| Cp10' | 0.5042 (6) | -0.3069 (6) | 0.2909 (8) | 67 (8) | 50 (8) | 110 (12) | -19 (6) | 33 (8) | -8 (8) |
| Cp11' | 0.5728 (7) | -0.3149 (7) | 0.2414 (9) | 88 (9) | 124 (11) | 149 (14) | -44 (8) | 89 (10) | -21 (10) |
| Cp12' | 0.5668 (8) | -0.2733 (9) | 0.4352 (9) | 147 (12) | 139 (12) | 82 (14) | -74 (10) | 49 (11) | -71 (10) |
| Hp3' | 0.5731 | -0.4780 | 0.4628 | 5.0 | | | | | |
| Hp4' | 0.5203 | -0.6589 | 0.4146 | 5.0 | | | | | |
| Hp5' | 0.3749 | -0.7005 | 0.1921 | 5.0 | | | | | |
| Hp7' | 0.2390 | -0.5027 | -0.0942 | 5.0 | | | | | |
| Hp10' | 0.4352 | -0.2424 | 0.2364 | 5.0 | | | | | |
| O2 | 0.0961 (4) | -0.2842 (4) | -0.1462 (5) | 50 (5) | 84 (6) | 96 (8) | -14 (4) | 44 (5) | -1 (5) |
| N | 0.2091 (5) | -0.3191 (5) | -0.2327 (6) | 63 (6) | 60 (6) | 58 (8) | -4 (5) | 38 (6) | 1 (6) |
| Cq1 | 0.2755 (7) | -0.3492 (6) | -0.2645 (8) | 122 (10) | 41 (8) | 128 (13) | -4 (7) | 106 (10) | 1 (8) |
| Cq2 | 0.2296 (9) | -0.3771 (8) | -0.3978 (10) | 111 (11) | 79 (11) | 129 (15) | -7 (9) | 84 (11) | -4 (10) |
| Cq3 | 0.1253 (10) | -0.3803 (8) | -0.4855 (10) | 95 (12) | 97 (11) | 101 (16) | -3 (10) | 52 (13) | -2 (10) |
| Cq4 | -0.0519 (9) | -0.3627 (8) | -0.5323 (9) | 102 (11) | 101 (11) | 93 (14) | -18 (9) | 31 (11) | -13 (10) |
| Cq5 | -0.1096 (7) | -0.3435 (8) | -0.4855 (9) | 61 (9) | 106 (11) | 138 (15) | -36 (8) | 6 (10) | -12 (10) |
| Cq6 | -0.0636 (6) | -0.3170 (8) | -0.3550 (9) | 58 (8) | 106 (11) | 141 (15) | -33 (7) | 45 (9) | -14 (10) |
| Cq7 | 0.0421 (6) | -0.3082 (7) | -0.2726 (8) | 56 (8) | 66 (8) | 104 (12) | -10 (6) | 41 (8) | 5 (8) |
| Cq8 | 0.1017 (6) | -0.3254 (6) | -0.3239 (8) | 54 (7) | 56 (8) | 98 (12) | -7 (6) | 36 (8) | 11 (8) |
| Cq9 | 0.0553 (9) | -0.3543 (8) | -0.4521 (9) | 61 (10) | 82 (10) | 70 (13) | -8 (8) | 11 (10) | 12 (9) |
| Cq10 | 0.3939 (7) | -0.3555 (7) | -0.1632 (9) | 20 (8) | 124 (11) | 104 (13) | -17 (7) | 17 (9) | -20 (9) |
| Hq2 | 0.2807 | -0.3961 | -0.4277 | 5.0 | | | | | |
| Hq3 | 0.0944 | -0.4032 | -0.5839 | 5.0 | | | | | |
| Hq4 | -0.0898 | -0.3845 | -0.6326 | 5.0 | | | | | |
| Hq5 | -0.1934 | -0.3489 | -0.5506 | 5.0 | | | | | |
| Hq6 | -0.1113 | -0.3038 | -0.3202 | 5.0 | | | | | |
| O2' | 0.3362 (4) | -0.1714 (5) | -0.0312 (5) | 54 (5) | 67 (6) | 91 (8) | -9 (4) | 38 (5) | 6 (5) |
| N' | 0.1350 (5) | -0.0784 (5) | -0.1778 (6) | 72 (6) | 68 (7) | 93 (9) | -3 (5) | 56 (7) | 8 (6) |
| Cq1' | 0.0340 (7) | -0.0260 (7) | -0.2392 (8) | 65 (8) | 64 (9) | 125 (13) | 33 (7) | 45 (9) | 23 (8) |
| Cq2' | -0.0050 (8) | 0.0565 (7) | -0.3376 (9) | 105 (10) | 76 (10) | 150 (15) | 32 (8) | 65 (11) | 35 (10) |
| Cq3' | 0.0591 (8) | 0.0862 (8) | -0.3613 (10) | 142 (11) | 98 (11) | 184 (17) | 10 (9) | 113 (12) | 54 (11) |
| Cq4' | 0.2410 (8) | 0.0653 (8) | -0.3010 (10) | 167 (12) | 88 (10) | 199 (17) | -16 (9) | 143 (13) | 23 (11) |
| Cq5' | 0.3453 (8) | 0.0161 (8) | -0.2202 (10) | 145 (11) | 87 (10) | 227 (18) | -28 (9) | 149 (13) | 2 (11) |
| Cq6' | 0.3831 (7) | -0.0646 (7) | -0.1255 (9) | 94 (9) | 82 (9) | 164 (15) | -31 (7) | 84 (10) | 10 (9) |
| Cq7' | 0.3101 (7) | -0.0956 (7) | -0.1168 (8) | 84 (8) | 60 (9) | 111 (13) | -11 (7) | 63 (9) | 12 (8) |
| Cq8' | 0.2021 (6) | -0.0445 (6) | -0.1978 (8) | 73 (8) | 55 (8) | 91 (11) | 1 (7) | 50 (8) | 5 (8) |
| Cq9' | 0.1660 (7) | 0.0365 (7) | -0.2895 (9) | 106 (9) | 88 (10) | 142 (14) | 12 (8) | 87 (10) | 35 (9) |
| Cq10' | -0.0338 (7) | -0.0522 (8) | -0.2042 (10) | 79 (9) | 105 (11) | 218 (17) | 9 (8) | 107 (11) | 26 (10) |
| Hq2' | -0.0880 | 0.0957 | -0.3942 | 5.0 | | | | | |
| Hq3' | 0.0270 | 0.1478 | -0.4353 | 5.0 | | | | | |
| Hq4' | 0.2156 | 0.1257 | -0.3731 | 5.0 | | | | | |
| Hq5' | 0.4017 | 0.0398 | -0.2290 | 5.0 | | | | | |
| Hq6' | 0.4668 | -0.1010 | -0.0618 | 5.0 | | | | | |

^a Hydrogen atoms are placed 1.08 Å from the carbon atom to which they are bonded. ^b Anisotropic thermal parameters which have been multiplied by 10^4 were applied in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. ^c Esd's are shown in parentheses. They are right justified to the least significant digit of the preceding number.

matrices) were $R = 11.4\%$ and $R_w = 10.5\%$, and after anisotropic refinement (five cycles, five matrices) they were $R = 6.3\%$ and $R_w = 6.1\%$ with a "goodness of fit" of 2.20. The final atomic parameters appear in Table IC.⁹ In view of the close approximation to twofold symmetry displayed by the quinaldinate and the confusingly non-standard cell originally selected, it is reassuring to note that the reduced cell¹⁰ ($a_x = 18.112$, $b_x = 12.383$, $c_x = 13.117$ Å, $\alpha_x = 98.45^\circ$, $\beta_x = 116.79^\circ$, $\gamma_x = 120.02^\circ$) cannot be interpreted as a C-face-centered mono-

clinic cell similar to the other two structures! The reduced cell is derived from the cell actually used by $\vec{a}_x = \vec{a} + \vec{b}$, $\vec{b}_x = \vec{b}$, and $\vec{c}_x = \vec{a} + \vec{c}$.

The Crystal and Molecular Structures

Table II contains intramolecular bonding and nonbonding (10) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962, p 530.

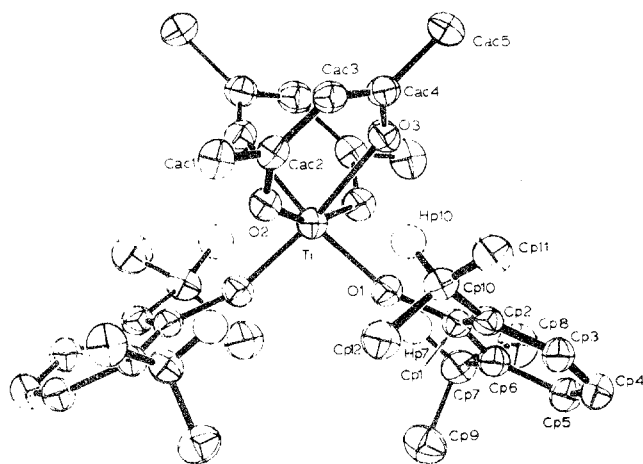


Figure 1. Molecular structure of $C_{34}H_{48}O_6Ti$ (the acetylacetonate) showing 68% probability ellipsoids, projected down [001].

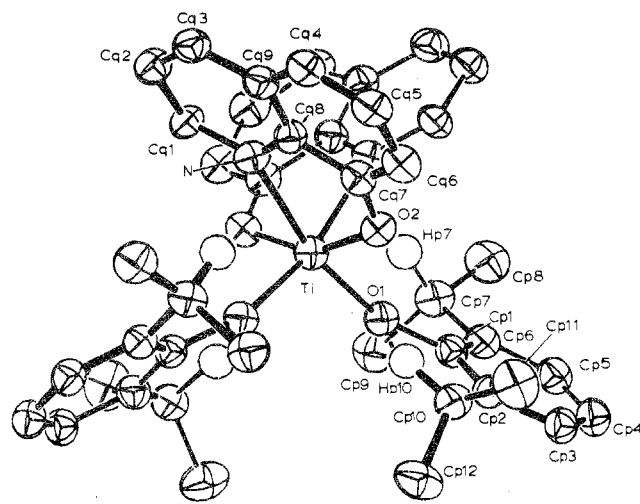


Figure 2. Molecular structure of $C_{42}H_{46}N_2O_4Ti$ (the oxinate) projected down [001].

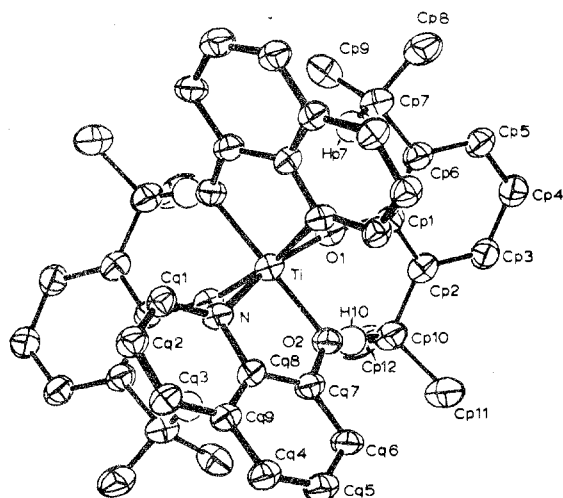


Figure 3. Molecular structure of $C_{44}H_{50}N_2O_4Ti$ (the oxinate) projected down [010].

distances and angles. In Figures 1-4 various views of the molecules and the method of labeling atoms are shown. Figures 5 and 6 show the molecular packing. The three molecules are monomeric, with no intermolecular distances that could be considered close on the basis of van der Waals radii.¹¹ A distorted octahedral coordination is observed

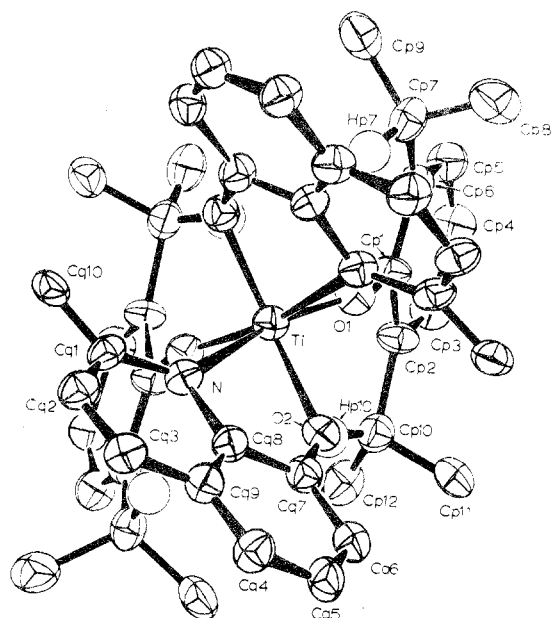


Figure 4. Molecular structure of $C_{44}H_{50}N_2O_4Ti$ (the quinaldinate) projected down the pseudo twofold axis of the molecule. Throughout this paper, atoms related by either a real or pseudo axis of symmetry to those labeled are designated by a prime.

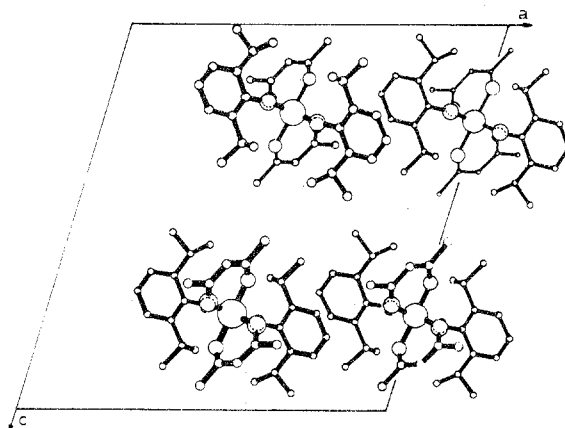


Figure 5. Crystal packing of $C_{34}H_{48}O_6Ti$ (the acetylacetonate) projected down [010]. The packing of the oxinate is essentially the same.

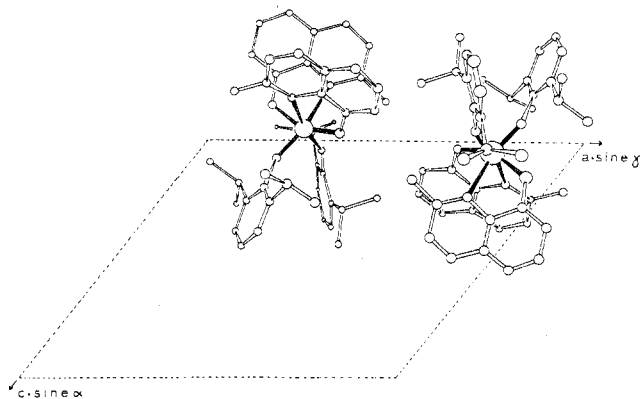


Figure 6. Crystal packing of $C_{44}H_{50}N_2O_4Ti$ projected down [010]. about the titanium atoms with bond angles ranging from 74.5° (between the nitrogen and oxygen atoms of the quinaldinate ligand) to 104.0° (between a quinaldinate ligand oxygen atom and a phenoxy group oxygen).

(11) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1945, p 187.

Table II. Intermolecular Bond Distances and Selected Angles^a

| Atom 1-atom 2 | Distances and esd's, ^b Å | | | Atom 1-atom 2-atom 3 | Angles at atom 2 and esd's, deg | | |
|---------------|---|--|---|------------------------|---|--|--|
| | C ₃₄ H ₄₈ O ₆ Ti | C ₄₂ H ₄₆ N ₂ O ₄ Ti | C ₄₄ H ₅₀ N ₂ O ₄ Ti ^c | | C ₃₄ H ₄₈ O ₆ Ti | C ₄₂ H ₄₆ N ₂ O ₄ Ti | C ₄₄ H ₅₀ N ₂ O ₄ Ti |
| Ti-O1 | 1.834 (5) | 1.818 (5) | 1.819 (7), 1.813 (6) | O1-Ti-O1' ^d | 97.3 (2) | 101.4 (3) | 98.8 (3) |
| Ti-O2 | 1.985 (5) | 1.953 (6) | 1.920 (6), 1.911 (6) | O1-Ti-O2 | 99.2 (2) | 92.4 (2) | 94.5 (3), 94.8 (3) |
| Ti-N | | 2.220 (7) | 2.347 (8), 2.355 (7) | O1-Ti-O2' | 92.9 (2) | 103.2 (2) | 104.0 (3), 103.7 (3) |
| Ti-O3 | 2.046 (5) | | | O1-Ti-N | | 165.4 (2) | 168.1 (3), 167.4 (3) |
| O1-Cp1 | 1.34 (1) | 1.35 (1) | 1.39 (1), 1.39 (1) | O1-Ti-N' | | 89.9 (2) | 90.5 (3), 88.3 (3) |
| Cp1-Cp2 | 1.40 (1) | 1.39 (1) | 1.42 (1), 1.41 (1) | O2-Ti-O2' | 161.7 (3) | 155.5 (3) | 151.6 (3) |
| Cp2-Cp3 | 1.40 (1) | 1.39 (1) | 1.40 (1), 1.40 (1) | O2-Ti-N | | 75.9 (2) | 74.5 (3), 74.6 (3) |
| Cp3-Cp4 | 1.37 (1) | 1.41 (1) | 1.38 (1), 1.38 (1) | O2-Ti-N' | | 85.4 (2) | 83.9 (3), 84.8 (3) |
| Cp4-Cp5 | 1.37 (1) | 1.37 (1) | 1.38 (1), 1.38 (2) | N-Ti-N' | | 80.6 (2) | 84.0 (3) |
| Cp5-Cp6 | 1.39 (1) | 1.38 (1) | 1.40 (1), 1.41 (1) | O1-Ti-O3 | 89.9 (2) | | |
| Cp6-Cp1 | 1.38 (1) | 1.40 (1) | 1.39 (1), 1.39 (1) | O1-Ti-O3' | 172.1 (2) | | |
| Cp2-Cp10 | 1.53 (1) | 1.54 (1) | 1.52 (1), 1.52 (1) | O2-Ti-O3 | 82.8 (2) | | |
| Cp6-Cp7 | 1.53 (1) | 1.57 (1) | 1.52 (1), 1.52 (1) | O2-Ti-O3' | 83.5 (2) | | |
| Cp7-Cp8 | 1.54 (1) | 1.55 (2) | 1.47 (2), 1.59 (2) | O3-Ti-O3' | 83.1 (2) | | |
| Cp7-Cp9 | 1.51 (1) | 1.52 (2) | 1.52 (2), 1.52 (2) | Ti-O1-Cp1 | 162.2 (4) | 159.5 (5) | 157.2 (6), 155.0 (6) |
| Cp10-Cp11 | 1.54 (1) | 1.62 (2) | 1.55 (2), 1.56 (2) | O1-Cp1-Cp2 | 117.5 (6) | 119.2 (8) | 115.6 (7), 116.9 (7) |
| Cp10-Cp12 | 1.52 (1) | 1.50 (2) | 1.57 (1), 1.55 (2) | O1-Cp1-Cp6 | 119.8 (6) | 118.9 (8) | 117.0 (8), 116.6 (7) |
| O2-Cq7 | | 1.33 (1) | 1.34 (1), 1.34 (1) | Cp2-Cp1-Cp6 | 122.6 (6) | 121.8 (8) | 127.4 (9), 126.5 (8) |
| N-Cq1 | | 1.30 (1) | 1.34 (1), 1.34 (1) | Cp1-Cp2-Cp3 | 117.1 (6) | 118.0 (9) | 114.6 (8), 114.6 (8) |
| Cq1-Cq2 | | 1.43 (1) | 1.44 (2), 1.46 (1) | Cp5-Cp6-Cp1 | 117.4 (7) | 118.8 (8) | 114.0 (8), 114.0 (9) |
| Cq2-Cq3 | | 1.38 (2) | 1.34 (2), 1.36 (2) | Cp1-Cp2-Cp10 | 121.2 (6) | 122.2 (8) | 122.8 (9), 121.6 (8) |
| Cq3-Cq9 | | 1.40 (2) | 1.40 (2), 1.39 (2) | Cp3-Cp2-Cp10 | 121.7 (6) | 119.7 (8) | 122.5 (8), 123.7 (8) |
| Cq9-Cq4 | | 1.42 (2) | 1.38 (2), 1.42 (2) | Cp5-Cp6-Cp7 | 121.0 (7) | 121.8 (8) | 124.4 (8), 123.5 (8) |
| Cq4-Cq5 | | 1.35 (2) | 1.36 (2), 1.36 (2) | Cp1-Cp6-Cp7 | 121.6 (7) | 119.1 (8) | 121.6 (9), 122.5 (9) |
| Cq5-Cq6 | | 1.42 (2) | 1.41 (2), 1.41 (1) | Ti-O2-Cac2 | 133.9 (5) | | |
| Cq6-Cq7 | | 1.38 (1) | 1.37 (1), 1.38 (1) | Ti-O3-Cac4 | 132.8 (5) | | |
| Cq7-Cq8 | | 1.40 (1) | 1.44 (1), 1.40 (1) | O2-Cac2-Cac1 | 115.4 (7) | | |
| Cq8-N | | 1.38 (1) | 1.39 (1), 1.40 (1) | O2-Cac2-Cac3 | 123.6 (7) | | |
| Cq8-Cq9 | | 1.40 (1) | 1.39 (2), 1.39 (1) | Cac1-Cac2-Cac3 | 120.9 (7) | | |
| Cq1-Cq10 | | | 1.50 (2), 1.51 (2) | O3-Cac4-Cac5 | 116.4 (7) | | |
| O2-Cac2 | 1.28 (1) | | | O3-Cac4-Cac3 | 122.3 (7) | | |
| O3-Cac4 | 1.28 (1) | | | Cac3-Cac4-Cac5 | 121.3 (7) | | |
| Cac1-Cac2 | 1.53 (1) | | | Cac2-Cac3-Cac4 | 123.6 (7) | | |
| Cac2-Cac3 | 1.38 (1) | | | Ti-O2-Cq7 | | 120.8 (5) | 123.2 (6), 122.9 (6) |
| Cac3-Cac4 | 1.41 (1) | | | Ti-N-Cq1 | | 130.5 (6) | 132.3 (6), 133.4 (6) |
| Cac4-Cac5 | 1.52 (1) | | | Ti-N-Cq8 | | 111.4 (5) | 107.8 (6), 106.1 (6) |
| | | | | Cq1-N-Cq8 | | 118.0 (7) | 119.7 (8), 120.2 (7) |
| | | | | O2-Cq7-Cq8 | | 117.3 (8) | 116.3 (8), 116.5 (9) |
| | | | | O2-Cq7-Cq6 | | 124.6 (8) | 125.4 (9), 123.4 (9) |
| | | | | Cq6-Cq7-Cq8 | | 118.1 (8) | 118.3 (9), 120.0 (9) |
| | | | | Cq7-Cq8-N | | 114.1 (8) | 114.4 (8), 115.7 (8) |
| | | | | Cq7-Cq8-Cq9 | | 122.1 (9) | 121.4 (9), 121.5 (9) |
| | | | | N-Cq8-Cq9 | | 123.6 (8) | 124.0 (9), 122.8 (9) |

^a The angles included in the table have been limited to those at titanium and those in the ligands close to titanium. ^b The estimated standard deviations shown in parentheses are computed from the diagonal elements of the inverted least-squares matrices and do not include contributions from the cell constant errors. ^c Where two figures are given in this column, the second applies to the bond length or angle generated by the pseudo twofold axis. ^d Atom labels marked with a prime indicate an atom derived by real or pseudo twofold symmetry.

In all molecules the phenoxide ligands are cis, and the oxinate and quinaldinate groups coordinate with nitrogen atoms cis and oxygen atoms trans. The lengths of bonds from the titanium atoms to the phenoxy group oxygen atoms are 1.834 (5) Å in the acetylacetonate complex, 1.818 (5) Å in the oxinate, and 1.813 (6) and 1.819 (7) Å in the quinaldinate (which does not possess the rigorous twofold symmetry of the other two). The different value found in the acetylacetonate is readily rationalized if it is assumed that the trans bonds Ti-O3 and Ti-O3' (2.046 (5) Å) are stronger than the similarly positioned titanium-nitrogen bonds in the other two complexes (2.220 (7) Å in the oxinate and 2.347 (8) and 2.355 (7) Å in the quinaldinate). This seems reasonable since, as has been observed in other oxinate complexes,¹² the 0.2-0.3-Å difference between the two types of bond (Ti-O and Ti-N) is much greater than the difference between the covalent radii of nitrogen and oxygen. The remaining titanium-oxygen bond lengths (Ti-O2, Ti-O2') parallel the above trends, in that, from acetylacetonate (1.985 (5) Å) to oxinate (1.953 (6) Å) to quinaldinate (1.920 (6), 1.911 (6)

Å), the oxygen atom concerned must carry an increasing share of the coordinative burden and bonding to the other end of the ligand weakens.

This brings into question the origin of the bond length differences both within and between the two quinoline derivatives. The possibilities previously discussed are (1) an electronic trans effect arising out of stronger p_π-d_π bonding from the trans ligand,¹³ (2) differences in relative "hardness" between oxygen and nitrogen,¹⁴ and (3) distortions due to steric crowding.¹² In the structures described here, it appears that the steric factors may be of prime importance. Thus, if a carbon atom is inserted in a calculated position on each oxinate ligand, then it is but 2.4 Å from the oxygen atom of the other oxinate ligand. However, the true distance in the quinaldinate compound is 3.01 (1) Å, and the change in position of the chelating ligands manifests itself in two ways. First, there is a change in the angle between the planes of the two quinoline ring systems from 89.6° in the oxinate to 58.3° in the quinaldinate. This effect is visible in Figure 4.

(12) J. D. Matthews, N. Singer, and A. H. Swallow, *J. Chem. Soc. A*, 2545 (1970), and references therein.

(13) L. O. Alovmyan and Yu. A. Sokolova, *Chem. Commun.*, 649 (1969).

(14) E. O. Schlemper, *Inorg. Chem.*, 6, 2012 (1967).

Table III. Deviations from Least-Squares Planes,^a Å

| (A) 2,6-Diisopropylphenoxy Groups | | | |
|-----------------------------------|---|--|--|
| Atom | C ₃₄ H ₄₈ O ₆ Ti | C ₄₂ H ₄₆ N ₂ O ₄ Ti | C ₄₄ H ₅₀ N ₂ O ₄ Ti |
| (Ti) | 0.54 | 0.58 | -0.80, -0.87 |
| (O1) | 0.00 | -0.01 | -0.05, -0.07 |
| Cp1 | 0.02 | 0.00 | -0.01, -0.02 |
| Cp2 | -0.02 | 0.00 | 0.01, 0.02 |
| Cp3 | 0.01 | 0.00 | 0.00, -0.01 |
| Cp4 | -0.01 | 0.00 | -0.01, 0.00 |
| Cp5 | 0.00 | -0.01 | 0.01, 0.00 |
| Cp6 | -0.01 | 0.01 | 0.01, 0.01 |
| (Cp7) | -0.05 | -0.10 | 0.05, 0.06 |
| (Cp8) | 0.99 | 0.59 | 1.40, 1.28 |
| (Cp9) | -1.45 | -1.52 | -1.00, -1.23 |
| (Cp10) | -0.10 | -0.04 | 0.10, 0.17 |
| (Cp11) | 0.52 | 1.09 | 1.57, 1.64 |
| (Cp12) | -1.55 | -1.41 | -0.60, -0.30 |

| (B) Oxinate and Quinaldinate Groups | | |
|-------------------------------------|--|--|
| Atom | C ₄₂ H ₄₆ N ₂ O ₄ Ti | C ₄₄ H ₅₀ N ₂ O ₄ Ti |
| (Ti) | 0.18 | 0.49, 0.57 |
| (O2) | 0.01 | 0.00, 0.04 |
| (N) | 0.00 | 0.08, 0.08 |
| Cq1 | 0.01 | -0.04, -0.04 |
| Cq2 | 0.02 | -0.04, -0.03 |
| Cq3 | -0.02 | 0.00, 0.01 |
| Cq4 | -0.01 | 0.00, 0.01 |
| Cq5 | 0.03 | -0.03, -0.03 |
| Cq6 | 0.00 | -0.05, -0.04 |
| Cq7 | 0.01 | 0.01, 0.03 |
| Cq8 | -0.03 | 0.09, 0.06 |
| Cq9 | 0.00 | 0.06, 0.04 |
| Cq10 | | -0.20, -0.21 |

| (C) Acetylacetonate Group | | | |
|---------------------------|---|------|---|
| Atom | C ₃₄ H ₄₈ O ₆ Ti | Atom | C ₃₄ H ₄₈ O ₆ Ti |
| (Ti) | -0.16 | Cac2 | -0.01 |
| O2 | 0.04 | Cac3 | -0.01 |
| O3 | -0.03 | Cac4 | 0.00 |
| Cac1 | -0.01 | Cac5 | 0.02 |

^a Atoms in parentheses were given zero weight in the least-squares calculation. The remainder were given unit weight.

Second, the titanium atom is 0.18 Å out of the mean quinoline plane in the oxinate complex, but an average of 0.53 Å out of the quinoline planes in the quinaldinate. See Table III. This enforced change presumably reduces the strength of the titanium-nitrogen bond in the quinaldinate relative to the oxinate, while the titanium-oxygen bond, which is not subject to the same directional constraint, strengthens slightly.

A second major difference between the oxinate and quinal-

dinate structures lies in the relative positioning of the phenoxy rings. In the former compound, the angle between the rings is 112.2°, and the normals to the centers of the rings would almost intersect. In the latter compound, the angle between the rings is 33.8°, and an isopropyl substituent on one ring lies roughly over the center of the other. This second arrangement is reminiscent of that in bis(2,4,6-trichlorophenoxy)-*N,N,N',N'*-tetramethylethylenediamine-copper(II).¹⁵ Presumably the differences in the molecular geometry associated with the quinoline portions of the molecule are sufficient to make the triclinic space group with modified phenoxy ring positions the preferred packing mode: intermolecular rather than intramolecular forces lead to the change in ring orientation.

While the orientation of the phenoxy groups varies among the three compounds, certain parameters remain essentially constant. Thus the titanium-oxygen-carbon angle (Ti-O1-Cp1) is 162.2 (4)° in the acetylacetonate, 159.5 (5)° in the oxinate, and 157.2 (6) and 155.0 (6)° in the quinaldinate. By comparison, in the copper complex mentioned above the average angle is 122°, and in di- μ -phenoxy-bis[dichlorophenoxotitanium(IV)]¹⁶ the corresponding angle at a terminal phenoxy group is 165.9° while the titanium-oxygen distance in this latter complex is 1.74 (1) Å, rather shorter than those reported here. In all three structures the isopropyl groups are positioned with the hydrogen atom directed toward the titanium atom thereby minimizing interactions between the methyl groups and the rest of the molecule. It seems probable, from an examination of these solid-state structures, that even in solution there will be appreciable barriers to overcome before the phenoxy groups and isopropyl groups can rotate, but it is not immediately evident why this barrier should be so much lower in the case of the acetylacetonate.² The construction of mechanical or computer models may lead to clarification.

Registry No. (C₅H₇O₂)₂(C₁₂H₁₇O)₂Ti, 38781-11-2; (C₉H₆NO)₂(C₁₂H₁₇O)₂Ti, 38781-12-3; (C₁₀H₈NO)₂(C₁₂H₁₇O)₂Ti, 38781-13-4.

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(15) L. H. Vogt, S. La Placa, and A. Bednowitz, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., March-April 1968, No. M 123.

(16) K. Waterpugh and C. N. Caughlan, *Inorg. Chem.*, **5**, 1782 (1966).