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Binuclear Bis(η^5-methylcyclopentadienyl)titanium(III) Complexes Bridged by the Dianion of 2,4-Dithiopyrimidine and Related Dianions: Preparation of Complexes and Molecular Structure of (2,4-Dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]

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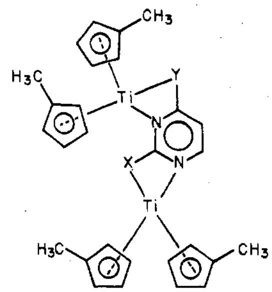
The preparation of six binuclear titanium(III) metallocenes of the composition $[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2B$, where bridge B is variously the dianion of 2,4-dithiopyrimidine, 2,4-diselenopyrimidine, 2-thiouracil, 4-thiouracil, 4,6-dihydroxypyrimidine, or 4,6-dithiopyrimidine, is reported. The preparations of an analogous trinuclear titanium(III) complex with the trianion of trithiocyanuric acid as a bridge and the mononuclear titanium(III) complex with the anion of 2-mercaptopyridine are also given. Analytical, mass spectral, and, in the following paper, magnetic susceptibility and EPR data are presented to establish the binuclear (trinuclear) structure of these complexes. The crystal and molecular structure of (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)], $C_4H_2N_2S_2[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2$, has been determined by using direct X-ray methods for 1444 reflections measured on a computer-automated four-circle diffractometer. The complex crystallizes as dark green plates belonging to the space group *Pbca* with eight molecules in a unit cell with a = 16.91 (2) Å, b = 22.22 (2) Å, c = 13.93 (1) Å, ρ_{obsd} = 1.37 (1) g/cm^3, and ρ_{calcd} = 1.41 g/cm^3. The structure was refined to final discrepancy indices of R_1 = 0.085 and R_2 = 0.056. The compound $C_4H_2N_2S_2[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2$ consists of asymmetric binuclear titanium(III) complexes, each with the dianion of 2,4-dithiopyrimidine acting as a bis-bidentate bridge between two (η^5-$CH_3C_5H_4$)$_2$Ti moieties. The 2,4-dithiopyrimidine dianionic bridge interacts with each titanium ion by means of one nitrogen and one sulfur atom [average distances of Ti–N = 2.21 ± 0.01 Å and Ti–S = 2.594 ± 0.04 Å]. A comparison of bond angles in the bridging group with those found for the uncoordinated 2,4-dithiopyrimidine confirms that both the sulfur and nitrogen atoms are coordinated to the titanium ion. The bridging dianion is essentially planar with the two titanium ions lying close to the plane (metal ion distances from the least-squares plane of 0.033 and 0.109 Å). The Ti–Ti distance in the binuclear complex is 6.075 (2) Å.

Introduction

The interactions of metal ions with nucleic acid constituents such as pyrimidine have been of recent interest.[4,5] At present, there is no reported compound where either cytosine, thymine, or uracil has been established to chelate to a first-row transition-metal ion. The only reported example where a pyrimidine type molecule was shown to function as a bidentate ligand is the second-row transition-metal complex bis(pyrimidine-2-thiolato)bis(triphenylphosphine)ruthenium(II).[6] Cytosine[7] and the thymine anion[8] have been shown to coordinate to copper(II) with a single nitrogen atom. In a recent paper[9] we reported the preparation of a compound which was indicated by mass spectral, EPR, and magnetic susceptibility data to be a binuclear titanium(III) complex with the dianion of uracil functioning as a bridge between two (η^5-$CH_3C_5H_4$)$_2$Ti$^+$ moieties. It was suggested that the uracil dianion is chelating the two titanium ions in the binuclear complex.

In the present study, new analogous binuclear titanium(III) metallocenes have been prepared and characterized. In this first paper, the preparation of binuclear titanium(III) complexes bridged by the dianions of six different pyrimidines are described and the results of an X-ray crystal structure are presented for one of the binuclear complexes. The six binuclear complexes are illustrated together with one new trinuclear complex and one new mononuclear complex: see structures **1**–**8**. In the following paper, variable-temperature magnetic susceptibility and EPR data are given for these complexes. Some of the results were very recently communicated.[10]



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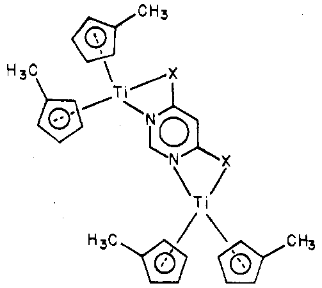
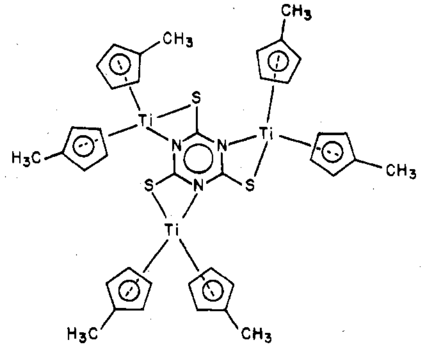
2, X = Y = Se
3, X = S, Y = O
4, X = O, Y = S



5, X = O
6, X = S



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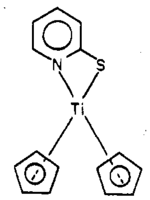

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Experimental Section

Compound Preparation. Most synthetic work was performed in a Vacuum Atmospheres Corp. inert-atmosphere glovebox under helium. Dithiouracil (2,4-dithiopyrimidine), 4,6-dihydroxypyrimidine, 2-mercaptopyridine, and trithiocyanuric acid were purchased from Aldrich and used without further purification. 2-Thiouracil was purchased from Pfaltz and Bauer. 4-Thiouracil,[11] 4,6-dithiopyrimidine,[11] $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$,[12] $[(\eta^5\text{-}CH_3C_5H_4)_2TiCl]_2$,[12] and $(\eta^5\text{-}CH_3C_5H_4)_2TiCl_2$[13] were prepared by literature methods. $(\eta^5\text{-}C_5H_5)_2TiCl_2$ was purchased from Alfa. Solvents were distilled from sodium and benzophenone under a nitrogen atmosphere. Elemental analyses were performed by the Microanalytical Laboratory of the University of Illinois School of Chemical Sciences. Mass spectra were obtained on a MAT-Varian CH-5 spectrometer. Computer calculations were performed on a DEC-20 computer at the Materials Research Laboratory.

General Preparation of the Binuclear Bis(η^5-methylcyclopentadienyl)titanium(III) Complexes. In approximately 90 mL of THF,

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Table I. Analytical Data

		% C		% H		% N		% S		% Ti		mass spectrum	
no.	complex	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
1	(2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]	60.65	60.43	5.45	5.67	5.05	5.10	11.57	11.52	17.28	16.95	554	554
2	(2,4-diselenopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)][a]	51.88	51.25	4.66	4.74	4.32	4.06			14.78	14.75	648	648
3	(2-thiouracilato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]	62.46	62.56	5.62	5.70	5.20	5.15	5.96	6.14	17.79	17.31	538	538
4	(4-thiouracilato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]	62.46		5.62		5.20		5.96		17.79		538	538
5	(4,6-dihydroxypyrimidinato)bisbis(η^5-methylcyclopentadienyl)titanium(III)]	64.38	64.46	5.79	5.74	5.36	5.33			18.34	18.14	522	522
6	(4,6-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]	60.65	60.16	5.45	5.66	5.05	4.98	11.57	10.99	17.28	17.11	554	
7	(trithiocyanurato)tris[bis(η^5-methylcyclopentadienyl)titanium(III)]	59.09	58.96	5.34	5.33	5.30	5.43	12.14	11.63	18.12	18.08	793	793
8	(2-mercaptopyridinato)[bis(η^5-cyclopentadienyl)titanium(III)]	62.50	61.08	4.90	4.76	4.86	4.76	11.12	11.62	16.62	16.11	288	288

[a] % Se = 24.34 (calcd 24.36).

the pyrimidine (2.0 mmol) and sodium sand (4.3 mmol) were mixed. $[(\eta^5\text{-}CH_3C_5H_4)_2TiCl]_2$ (2.1 mmol) was then added. The mixture was stirred and heated slightly. After 3–4 days, the solvent was removed under reduced pressure. The product was extracted by using refluxing hexane, heptane, or toluene. The filtrate was reheated to reflux and allowed to cool slightly. After several days, crystals were formed. The elemental analyses and mass spectral results for these complexes are found in Table I.

(2-Mercaptopyridinato)bis(η^5-cyclopentadienyl)titanium(III). In approximately 40 mL of THF, 2-mercaptopyridine (0.22 g, 2.0 mmol) and sodium sand (0.05 g, 2.2 mmol) were mixed. This mixture was refluxed for 20 min with stirring and then filtered to remove the excess sodium. Bis[bis(η^5-cyclopentadienyl)titanium(III) chloride] (0.43 g, 1.0 mmol) was added. After the solution was stirred overnight with slight heating, the solvent was removed under reduced pressure. The product was extracted with refluxing hexanes and filtered. The filtrate was reheated and allowed to cool slowly. After about 1 day dark green crystals were collected. Analytical and mass spectral data are found in Table I.

(Trithiocyanurato)tris[bis(η^5-methylcyclopentadienyl)titanium(III)]. In 30 mL of THF, trithiocyanuric acid (0.55 g, 3.1 mmol) and sodium sand (0.22 g, 9.6 mmol) were mixed. The mixture was stirred for 1.5 h without heating. Bis[bis(methylcyclopentadienyl)titanium(III) chloride] (2.27 g, 4.7 mmol) and 60 mL of THF were then added. The solution was stirred with moderate heating for 5–7 days. The solvent was removed under reduced pressure. The resulting gray powder was washed with cold heptane, removing a brown impurity. The crude product was then dissolved in refluxing toluene and filtered while hot through a glass frit. After the filtrate was reheated to relux, the solution was allowed to cool slowly. After several days, 1.32 g of dark crystals was collected for a 35% yield. Analytical and mass spectral data are found in Table I.

Structure Determination and Refinement for (2,4-Dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]. Several crystals were mounted in thin-walled glass capillaries in the inert-atmosphere box and sealed off. Precession and Weissenberg photographs showed orthorhombic symmetry and systematic absences $0kl$, $k = 2n + 1$, $h0l$, $l = 2n + 1$, and $hk0$, $h = 2n + 1$, indicating the space group *Pbca*. Two crystals were used for data collection. Both were cleaved from larger platelike crystals. The first had the dimensions 0.20 × 0.44 × 0.75 mm and the second 0.28 × 0.34 × 0.64 mm. Eighteen reflections were centered on the diffractometer and cell parameters refined by least squares to the values a = 16.92 (1), b = 22.21 (2), c = 13.93 (1) Å and a = 16.91 (2), b = 22.22 (2), c = 13.93 (1) Å for the first and second crystals, respectively. The density was found to be 1.37 (1) g/cm^3 by flotation in carbon tetrachloride–octane. This compared favorably with 1.41 g/cm^3 calculated for 8 molecules/unit cell.

Intensity data were collected by a θ–2θ scan method using Mo Kα radiation on a Picker four-circle diffractometer equipped with a graphite monochromator. Several ω scans showed typical peak widths at half-height to be 0.13°. Data were collected by using a scan rate of 2°/min and a takeoff angle of 1.7°. A scan width of 1.6° was used for the first crystal and 1.4° for the second. The 10-s stationary-background counts were measured before and after each reflection. Three standards were measured every 50 reflections and showed no systematic variations in intensity for either crystal. Measurements were made to 2θ = 45° for the first crystal, giving a total of 3822 reflections of which 1432 were rejected as being systematically absent. It was subsequently determined that a transistor in the counting circuitry of the diffractometer was giving intermittent problems which showed up primarily in the background measurements. These data were used only to solve the structure. For the second crystal, data were collected to 2θ = 55° for a total of 6643 unique reflections of which 2249 were rejected as being systematically absent or geometrically inaccessible. With the criteria $F_o^2 > 3\sigma(F_o^2)$, where $F_o^2 = [N_T - K(N_{B1} + N_{B2})]/Lp$ and $\sigma(F_o^2) = [N_T + K^2(N_{B1} + N_{B2}) + (pI)^2]^{1/2}/Lp$ and where N_T, N_{B1}, and N_{B2} are the total peak count and the two background counts, K is the ratio of the peak scan time to the total background scan time, $p = 0$, $I = (N^2 - 2)/(N_{B1} + N_{B2})$, and Lp is the Lorentz–polarization factor, 1444 reflections were considered observed. A total of 4394 unique reflections were used in the refinement of the structure. No absorption corrections (μ = 7.26 cm^{-1}) were made as the maximum variation in the transition factors which were calculated for all reflections was from 0.78 to 0.82. The maximum deviation introduced into the intensities was thus estimated to be 5%.

The structure was solved by using direct methods in the SHELX program package.[14] The function minimized during least squares was $w(|F_o| - |F_c|)^2$ where w was taken as $1/\sigma^2(F_o)$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$. With the use of the intensity data from the first crystal, all atom positions were found. Refinement of these positional parameters, using anisotropic temperature factors for Ti(1), Ti(2), S(1), S(2), N(1), and N(2), gave R_2 (defined as $(\sum w(F_o - F_c)^2/\sum wF_o^2)^{1/2}$) = 0.14. Further attempts at refinement were unsuccessful. At this point, the instrument problem noted above was found and data were collected on the second crystal. Least-squares refinement of these data with anisotropic thermal parameters for Ti(1), Ti(2), S(1), N(1), N(2), C(1), and C(2) and with all the cyclopentadienyl rings treated as regular pentagons, R_2, converged at 0.220. During further refinement, one of the methylcyclopentadienyl rings was determined to be disordered. A model was devised for the disorder as follows. The

Table II. Positional Parameters for Nonhydrogen Atoms in (2,4-Dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)-titanium(III)]

atom	x/a^a	y/b	z/c
Ti(1)	0.4617 (1)	−0.0363 (1)	0.1981 (1)
Ti(2)	0.2719 (1)	0.1872 (1)	0.0980 (1)
S(1)	0.4266 (1)	0.0540 (1)	0.0884 (2)
S(2)	0.2049 (2)	0.1783 (1)	0.2652 (2)
N(1)	0.3780 (4)	0.0273 (3)	0.2593 (5)
N(2)	0.3160 (4)	0.1130 (3)	0.1926 (5)
C(1)	0.3672 (5)	0.0668 (4)	0.1863 (7)
C(2)	0.2693 (5)	0.1203 (4)	0.2720 (7)
C(3)	0.2809 (6)	0.0779 (5)	0.3496 (6)
C(4)	0.3333 (6)	0.0349 (5)	0.3385 (7)
C(5)	0.5476 (8)	−0.0550 (6)	0.3425 (11)
C(6)	0.5398 (7)	0.0055 (7)	0.3231 (9)
C(7)	0.5715 (7)	0.0242 (5)	0.2311 (10)
C(8)	0.5955 (6)	−0.0258 (6)	0.1847 (7)
C(9)	0.5867 (7)	−0.0714 (5)	0.2514 (11)
C(10)	0.5292 (8)	−0.0891 (5)	0.4264 (7)
C(11)	0.3945 (8)	−0.0910 (5)	0.0741 (8)
C(12)	0.3306 (8)	−0.0776 (5)	0.1387 (8)
C(13)	0.3609 (8)	−0.1094 (5)	0.2266 (9)
C(14)	0.4361 (9)	−0.1397 (5)	0.2069 (10)
C(15)	0.4556 (7)	−0.1263 (5)	0.1118 (9)
C(16)	0.2575 (5)	−0.0460 (5)	0.1221 (9)
C(17)	0.1801 (14)	0.2018 (7)	−0.0318 (13)
C(18)	0.2451 (11)	0.1620 (9)	−0.0644 (10)
C(19)	0.2438 (8)	0.1093 (5)	−0.0130 (9)
C(20)	0.1785 (8)	0.1145 (6)	0.0485 (7)
C(21)	0.1421 (9)	0.1759 (7)	0.0398 (12)
C(22)	0.0667 (7)	0.1967 (7)	0.0685 (10)
C(23)	0.3840 (7)	0.2379 (6)	0.1679 (8)
C(24)	0.3177 (7)	0.2769 (6)	0.1742 (8)
C(25)	0.2934 (7)	0.2913 (6)	0.0794 (8)
C(26)	0.3447 (7)	0.2613 (6)	0.0145 (8)
C(27)	0.4008 (7)	0.2283 (6)	0.0692 (8)
C(28)	0.4428 (7)	0.2078 (6)	0.2369 (8)
C(23)′	0.3511 (8)	0.2564 (6)	0.1894 (10)
C(24)′	0.2944 (8)	0.2884 (6)	0.1343 (10)
C(25)′	0.3115 (8)	0.2788 (6)	0.0358 (10)
C(26)′	0.3789 (8)	0.2409 (6)	0.0299 (10)
C(27)′	0.4034 (8)	0.2270 (6)	0.1248 (10)
C(28)′	0.4735 (8)	0.2035 (6)	0.1735 (10)
C(28A)′	0.3978 (8)	0.2316 (6)	0.2739 (10)

[a] Estimated standard deviations in the least significant figures are given in parentheses in this and all subsequent tables.

cyclopentadienyl ring (Cp 4: C(23)–C(27)) was treated as a rigid, regular pentagon (carbon–carbon distance of 1.42 Å and bond angles of 108°) with a site occupation factor (SOF) of 0.5. A second rigid cyclopentadienyl ring (C(23)′–C(27)′), also treated as a regular pentagon, was included as staggered to the first. Again, the rigid pentagon was given an SOF of 0.5. Later in the refinement the methyl carbon atoms were added. At this point, the first ring was treated as a rigid six-membered group with the methyl carbon atom given an SOF of 0.5 and the staggered ring was treated as a rigid seven-membered group with the methyl carbon atoms given site occupation factors of 0.25. The site occupancy factors of 0.5 and 0.25 were chosen on the basis of the assumption that the three configurations of the methylcyclopentadienyl ring were equally probable. Refinement of the site occupation factors showed this assumption to be valid. It should be pointed out that the model obtained, while adequate, still results in relatively large thermal displacements of the cyclopentadienyl carbon atoms. This is not unexpected since this group commonly exhibits large vibrational motions in the solid state.

Further refinement with this model, with anisotropic thermal parameters on all nonhydrogen atoms except for the disordered ring, with inclusion of hydrogen atoms at calculated positions, using a bond length of 0.98 Å, except on the disordered ring and methyl groups, and with statistical weights led to the final R factors. At convergence, R_1, which is defined as $\sum||F_o| - |F_c||/\sum|F_o|$ for $F_o^2 > 3\sigma(F_o^2)$, was found to be 0.085 and $R_2 = 0.056$ for the complete data set. The "goodness of fit" defined by $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$ was 1.99, where the number of reflections, NO, was 4394 and the total number of parameters refined, NV, was 278; the ratio NO/NV = 15.81. A final difference Fourier had a highest peak of 1.13 e/Å^3. The final positional and thermal parameters are found in Tables II and III, respectively.

Results and Discussion

A general reaction scheme has been established to prepare binuclear titanium(III) metallocenes bridged by the dianion of various substituted pyrimidines such as uracil or dithiouracil. The dianion of the substituted pyrimidine, which is formed in THF with a sodium sand, is reacted with $[(\eta^5\text{-}CH_3C_5H_4)_2TiCl]_2$ under an inert atmosphere. Extraction with hot hexane or toluene, followed by recrystallization, gives the binuclear complex. Analogous mononuclear and trinuclear complexes have been prepared in the same manner.

In a previous paper[9] we suggested that the anions of 2-hydroxypyridine, uracil, and cyanuric acid chelate the Ti(III) ions of the $(\eta^5\text{-}C_5H_5)_2Ti^+$ and $(\eta^5\text{-}CH_3C_5H_4)_2Ti^+$ moieties. The evidence consisted of relatively intense mass spectral peaks corresponding to the $(\eta^5\text{-}CH_3C_5H_4)_2Ti(NCO)^+$ or $(\eta^5\text{-}C_5H_5)_2Ti(NCO)^+$ fragment ions. Also, in the case of the binuclear uracil and trinuclear cyanuric acid complexes, antiferromagnetic exchange interactions were present which led to the observation of zero-field splittings in the EPR spectrum for each complex. It was assumed that the zero-field interaction was totally dipolar in nature, and, as such, the magnitude of the observed splitting was found to be consistent with a Ti–Ti distance, supporting the suggestion that the anions of uracil and cyanuric acid are chelating the titanium(III) ions.

In the present study similar evidence was found for the chelation of the anions of other substituted pyrimidines to the titanium(III) ion of the $(\eta^5\text{-}CH_3C_5H_4)_2Ti^+$ moieties. Six new binuclear complexes, compounds **1**–**6**, one new trinuclear complex (**7**) with the trithiocyanurate trianion, and a mononuclear complex (**8**) with the 2-mercaptopyridinate anion were prepared. In order to firmly establish the chelating nature of the substituted pyrimidine anions in these complexes, it was decided to determine the structure of compound **1**.

The single-crystal X-ray structure of (2,4-dithiopyrimidinato)bis[bis(η^8-methylcyclopentadienyl)titanium(III)], compound **1**, was solved. Interatomic bond distances are given in Tables IV and V, while bond angles are summarized in Table VI.

As illustrated in Figure 1, compound **1** consists of asymmetric binuclear titanium(III) complexes with an intramolecular Ti–Ti distance of 6.075 (2) Å. The bond distances and angles in the binuclear complex clearly show that the dianion of 2,4-dithiopyrimidine acts as a bis-bidentate bridge between the two $(\eta^5\text{-}CH_3C_5H_4)_2Ti^+$ moieties. A comparison of the bond angles in the bridging dianion with those found[15] for uncoordinated 2,4-dithiopyrimidine confirms that both the sulfur and nitrogen atoms are coordinated to the titanium atom. For example, the N(1)–C(1)–S(1) and N(2)–C(2)–S(2) angles in the uncoordinated ligand are 125.9 (5) and 119.3 (4)°, while in the bridging dianion these angles are 114.6 (8) and 114.2 (8)°, respectively. In addition, the C(1)–N(1)–Ti(1) and C(2)–N(2)–Ti(2) angles in the binuclear complex are less than the 120° expected for sp^2-hybridized atoms of the heterocyclic ring.

It is interesting to note that the C(1)–S(1) and C(2)–S(2) distances in uncoordinated 2,4-dithiopyrimidine are 1.645 (6) and 1.684 (6) Å, respectively.[15] The difference in these two distances could be accounted for by assuming that the S(2) atom is in the zwitterionic configuration, i. e., $-NH^+{=}C{-}S^-$, to a greater extent than the S(1) atom. In the bridging dianion of the complex, the opposite situation is observed. The C(1)–S(1) bond is longer (1.718 (9) Å) than the C(2)–S(2) bond (1.689 (10) Å).

Table III. Thermal Parameters for Nonhydrogen Atoms in (2,4-Dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]

atom	U_{11}[a]	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti(1)	0.0586 (12)	0.0487 (11)	0.0534 (12)	−0.0016 (11)	0.0022 (12)	0.0007 (13)
Ti(2)	0.0666 (13)	0.0434 (11)	0.0660 (13)	−0.0010 (12)	0.0062 (12)	0.0042 (12)
S(1)	0.0551 (17)	0.0566 (18)	0.0448 (15)	−0.0007 (15)	0.0136 (15)	0.0071 (15)
S(2)	0.0708 (21)	0.0686 (19)	0.0750 (22)	−0.0145 (19)	0.0170 (18)	0.0120 (20)
N(1)	0.0474 (52)	0.0364 (49)	0.0456 (50)	0.0076 (47)	−0.0148 (46)	−0.0054 (46)
N(2)	0.0472 (55)	0.0693 (62)	0.0376 (49)	−0.0230 (51)	0.0154 (47)	0.0083 (51)
C(1)	0.0467 (70)	0.0506 (67)	0.0496 (68)	−0.0006 (63)	−0.0087 (61)	0.0106 (60)
C(2)	0.0382 (62)	0.0732 (75)	0.0538 (70)	−0.0249 (62)	0.0154 (58)	−0.0282 (62)
C(3)	0.0610 (79)	0.1032 (98)	0.0241 (54)	−0.0007 (61)	0.0087 (59)	0.0071 (79)
C(4)	0.0445 (71)	0.0870 (87)	0.0469 (68)	−0.0166 (69)	0.0229 (57)	0.0141 (70)
C(5)	0.0696 (95)	0.078 (10)	0.170 (16)	−0.048 (11)	−0.044 (10)	0.0255 (90)
C(6)	0.0406 (74)	0.156 (13)	0.0557 (86)	−0.0452 (93)	−0.0048 (70)	−0.0104 (99)
C(7)	0.0641 (91)	0.0812 (94)	0.089 (11)	0.0027 (88)	−0.0244 (78)	−0.0176 (84)
C(8)	0.0545 (74)	0.0885 (96)	0.0656 (83)	−0.0250 (82)	−0.0126 (66)	0.0350 (81)
C(9)	0.0772 (94)	0.0745 (96)	0.112 (11)	0.0075 (96)	−0.0590 (89)	0.0043 (87)
C(10)	0.143 (12)	0.200 (13)	0.0589 (73)	0.0663 (72)	0.0094 (82)	−0.029 (12)
C(11)	0.098 (10)	0.0525 (84)	0.087 (10)	0.0030 (75)	−0.0148 (89)	−0.0145 (81)
C(12)	0.147 (12)	0.0787 (97)	0.0481 (76)	−0.0185 (72)	0.0644 (88)	−0.0619 (93)
C(13)	0.109 (11)	0.0524 (84)	0.080 (10)	−0.0157 (78)	0.0348 (93)	−0.0319 (84)
C(14)	0.150 (15)	0.0476 (76)	0.085 (11)	−0.0110 (79)	−0.015 (11)	−0.0241 (91)
C(15)	0.100 (10)	0.0741 (93)	0.0705 (95)	−0.0369 (81)	0.0029 (97)	−0.0154 (88)
C(16)	0.0266 (64)	0.131 (11)	0.183 (12)	−0.0661 (96)	0.0033 (83)	0.0234 (77)
C(17)	0.260 (28)	0.088 (15)	0.132 (16)	0.026 (12)	−0.121 (17)	−0.069 (16)
C(18)	0.176 (19)	0.174 (19)	0.0397 (91)	0.030 (12)	−0.014 (12)	−0.074 (16)
C(19)	0.0651 (92)	0.0802 (94)	0.0570 (80)	−0.0293 (75)	−0.0052 (76)	0.0067 (84)
C(20)	0.0809 (91)	0.0832 (96)	0.0460 (75)	0.0095 (72)	−0.0129 (71)	−0.0442 (82)
C(21)	0.157 (13)	0.092 (11)	0.168 (14)	0.048 (10)	−0.127 (12)	−0.060 (11)
C(22)	0.1180 (77)	0.406 (13)	0.306 (15)	−0.1579 (88)	−0.1344 (93)	0.1352 (64)

atom	U, Å^2	atom	U, Å^2	atom	U, Å^2
C(23)	0.0554 (60)	C(28)	0.0888 (80)	C(26)′	0.0735 (72)
C(24)	0.0650 (65)	C(23)′	0.1051 (89)	C(27)′	0.1078 (91)
C(25)	0.0612 (64)	C(24)′	0.0888 (80)	C(28)′	0.048 (11)
C(26)	0.0704 (71)	C(25)′	0.0859 (80)	C(28A)′	0.042 (12)
C(27)	0.0764 (78)				

[a] The form of the anisotropic thermal ellipsoid is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$.

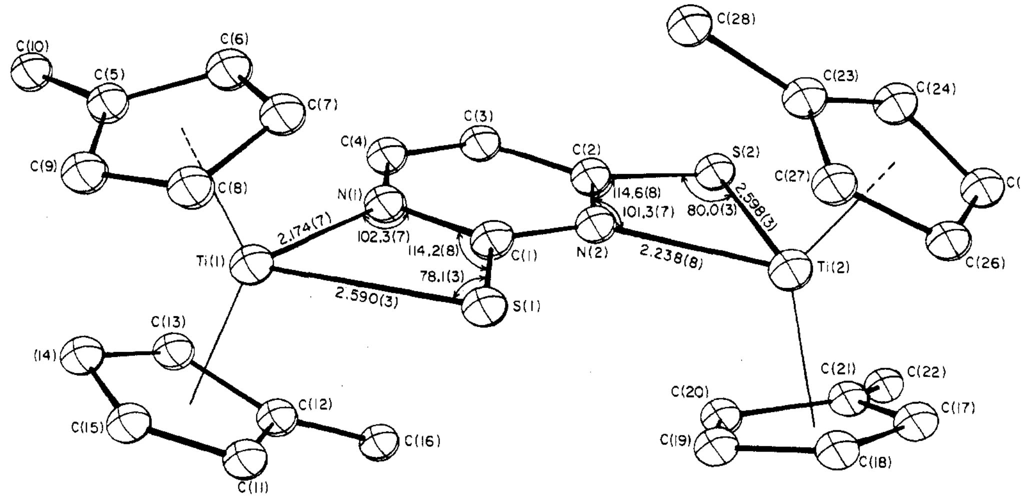

Figure 1. Molecular structure of (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)] showing nonhydrogen atoms.

In each binuclear complex the two Ti–N bond distances [2.174 (7) and 2.238 (8) Å] are comparable to those found for the (η^5-C_5H_5)Ti^{IV} complex (η^5-C_5H_5)TiCl(8-quinolinol)$_2$ with Ti–N = 2.224 (7) and 2.270 (10) Å[16] and the (η^5-C_5H_5)$_2$Ti^{III} compound μ-pyrazole-bis(η^5-cyclopentadienyl)-titanium(III) with Ti–N = 2.206 (5) and 2.183 (5) Å.[17] On the other hand, the two Ti–S bonds in the binuclear complex [2.590 (3) and 2.598 (3) Å] are somewhat longer than those reported for complexes such as (η^5-C_5H_5)$_2$Ti(SC$_6$H$_5$)$_2$ with Ti–S = 2.395 (8) and 2.424 (8) Å[18] and (η^5-C_5H_5)$_2$TiS$_5$ with Ti–S = 2.443 (2) and 2.438 (3) Å.[19] The titanium–cyclopentadiene ring carbon distances [2.28 (1)–2.54(1) Å] and the dihedral angle (133°) between the rings on one titanium atom of the binuclear complex are also comparable to values observed for other (η^5-C_5H_5)$_2$TiX$_2$[20] and [(η^5-C_5H_5)$_2$TiCl]$_2$MX$_2$ complexes.[21,22]

The bridging 2,4-dithiopyrimidine dianion is essentially planar, and, as summarized in Table VII, a least-squares plane including the bridging dianion and the two titanium ions shows that the two metal ions are close to being in the plane of the bridging dianion. The importance of the arrangement of binuclear complexes in the solid state will be apparent in the

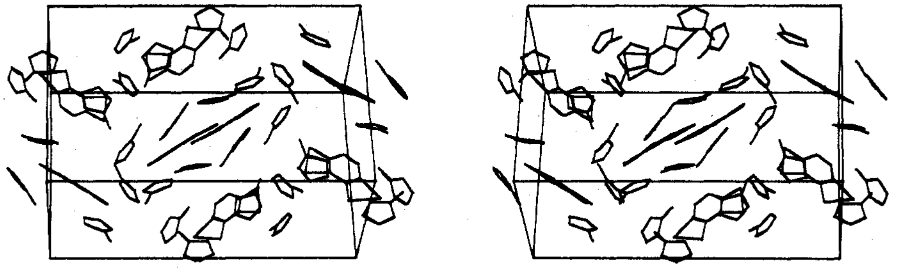

Figure 2. Stereoscopic view of the molecular packing in the unit cell of (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)] omitting hydrogen atoms. The view is down the *c* axis with the *b* axis horizontal and the *a* axis vertical.

Table IV. Interatomic Bond Distances (Å) for (2,4-Dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]

Ti(1)–N(1)	2.174 (7)	Ti(1)–C(13)	2.388 (10)
Ti(1)–S(1)	2.590 (3)	Ti(1)–C(14)	2.341 (10)
S(1)–C(1)	1.718 (9)	Ti(1)–C(15)	2.337 (10)
Ti(2)–N(2)	2.238 (8)	Ti(2)–C(17)	2.406 (17)
Ti(2)–S(2)	2.598 (3)	Ti(2)–C(18)	2.375 (14)
S(2)–C(2)	1.689 (10)	Ti(2)–C(19)	2.369 (10)
N(1)–C(1)	1.356 (10)	Ti(2)–C(20)	2.362 (10)
C(1)–N(2)	1.347 (10)	Ti(2)–C(21)	2.354 (14)
N(2)–C(2)	1.369 (9)	Ti(2)–C(23)	2.411 (12)
C(2)–C(3)	1.448 (11)	Ti(2)–C(24)	2.386 (13)
C(3)–C(4)	1.312 (12)	Ti(2)–C(25)	2.356 (13)
C(4)–N(1)	1.348 (9)	Ti(2)–C(26)	2.362 (13)
Ti(1)–C(5)	2.516 (14)	Ti(2)–C(27)	2.397 (13)
Ti(1)–C(6)	2.376 (10)	Ti(2)–C(23)′	2.404 (15)
Ti(1)–C(7)	2.336 (10)	Ti(2)–C(24)′	2.337 (15)
Ti(1)–C(8)	2.282 (11)	Ti(2)–C(25)′	2.312 (16)
Ti(1)–C(9)	2.373 (11)	Ti(2)–C(26)′	2.365 (16)
Ti(1)–C(11)	2.399 (11)	Ti(2)–C(27)′	2.422 (15)
Ti(1)–C(12)	2.538 (12)		

Table V. Interatomic Bond Distances (Å) for Methylcyclopentadienyl Rings of (2,4-Dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]

	Cp 1		
C(5)–C(6)	1.38 (2)	C(8)–C(9)	1.38 (1)
C(6)–C(7)	1.45 (1)	C(9)–C(5)	1.48 (2)
C(7)–C(8)	1.35 (1)	C(5)–C(10)	1.43 (2)
	Cp 2		
C(11)–C(12)	1.44 (1)	C(14)–C(15)	1.40 (1)
C(12)–C(13)	1.50 (1)	C(15)–C(11)	1.40 (1)
C(13)–C(14)	1.46 (1)	C(12)–C(16)	1.44 (1)
	Cp 3		
C(17)–C(18)	1.48 (2)	C(20)–C(21)	1.50 (2)
C(18)–C(19)	1.37 (2)	C(21)–C(17)	1.32 (2)
C(19)–C(20)	1.40 (1)	C(21)–C(22)	1.41 (2)

Table VI. Bond Angles (deg) for Nonhydrogen Atoms in (2,4-Dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]

Ti(1)–S(1)–C(1)	78.1 (3)	C(6)–C(5)–C(10)	131.0 (16)
Ti(1)–N(1)–C(1)	102.3 (7)	C(6)–C(7)–C(8)	107.5 (11)
Ti(1)–N(1)–C(4)	140.2 (7)	C(7)–C(8)–C(9)	104.4 (11)
Ti(2)–S(2)–C(2)	80.0 (3)	C(9)–C(5)–C(10)	132.1 (14)
Ti(2)–N(2)–C(2)	101.3 (7)	C(11)–C(12)–C(13)	99.1 (11)
S(1)–Ti(1)–N(1)	65.2 (2)	C(11)–C(12)–C(16)	130.2 (13)
S(1)–C(1)–N(1)	114.2 (8)	C(11)–C(15)–C(14)	107.6 (12)
S(2)–Ti(2)–N(2)	65.0 (2)	C(12)–C(11)–C(15)	115.8 (12)
S(2)–C(2)–N(2)	114.6 (8)	C(12)–C(13)–C(14)	111.0 (11)
N(1)–C(1)–N(2)	122.1 (9)	C(13)–C(12)–C(16)	130.7 (12)
N(1)–C(4)–C(3)	124.5 (10)	C(13)–C(14)–C(15)	106.6 (12)
N(2)–C(2)–C(3)	116.6 (9)	C(17)–C(18)–C(19)	109.7 (16)
C(1)–N(1)–C(4)	117.2 (9)	C(17)–C(21)–C(20)	104.9 (17)
C(1)–N(2)–C(2)	120.9 (9)	C(17)–C(21)–C(22)	120.7 (21)
C(2)–C(3)–C(4)	118.6 (9)	C(18)–C(17)–C(21)	109.5 (19)
C(5)–C(6)–C(7)	114.6 (13)	C(18)–C(17)–C(20)	105.1 (13)
C(5)–C(9)–C(8)	116.4 (7)	C(19)–C(20)–C(21)	110.5 (12)
C(6)–C(5)–C(9)	96.7 (13)	C(20)–C(21)–C(22)	130.1 (16)

Table VII. Deviation from Planarity of Rings in (2,4-Dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)]

atom	dist, Å	atom	dist, Å
Ti(1)	0.109	C(17)	−0.026
Ti(2)	0.033	C(18)	0.046
S(1)	−0.051	C(19)	0.030
S(2)	0.056	C(20)	−0.010
N(1)	−0.037	C(21)	−0.141
N(2)	−0.045	C(22)	−0.100
C(1)	−0.028	C(23)	−0.048
C(2)	−0.008	C(24)	0.029
C(3)	−0.010	C(25)	0.064
C(4)	−0.023	C(26)	0.008
C(5)	0.025	C(27)	−0.061
C(6)	0.021	C(28)	−0.038
C(7)	−0.039	C(23)′	−0.025
C(8)	0.030	C(24)′	0.019
C(9)	−0.022	C(25)′	0.009
C(10)	−0.015	C(26)′	−0.040
C(11)	−0.016	C(27)′	−0.062
C(12)	−0.024	C(28)′	0.178
C(13)	−0.025	C(28A)′	−0.034
C(14)	0.026		
C(15)	0.009		
C(16)	0.030		

following paper. Figure 2 illustrates the unit cell packing for (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)].

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Registry No. **1**, 71359-26-7; **2**, 71359-27-8; **3**, 71360-24-2; **4**, 71360-25-3; **5**, 71360-26-4; **6**, 71360-27-5; **7**, 71486-14-1; **8**, 71360-28-6; $[(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)_2\text{TiCl}]_2$, 62415-22-9; $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}]_2$, 1271-18-7.

Supplementary Material Available: The final values of $|F_o|$ and $|F_c|$ for (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)] (25 pages). Ordering information is given on any current masthead page.

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Binuclear Bis(η^5-methylcyclopentadienyl)titanium(III) Complexes Bridged by the Dianion of 2,4-Dithiopyrimidine and Related Dianions: Magnetic and EPR Properties

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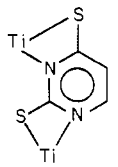
Variable-temperature (4.2–244 K) magnetic susceptibility and EPR data are presented for five binuclear titanium(III) metallocenes bridged by the dianions of 2,4-dithiopyrimidine, 2,4-diselenopyrimidine, 2-thiouracil, 4,6-dihydroxypyrimidine, and 4,6-dithiopyrimidine and one trinuclear titanium(III) metallocene bridged by the trianion of trithiocyanuric acid. The one trinuclear complex and two of the binuclear complexes (2,4-dithiopyrimidine and 2,4-diselenopyrimidne) exhibited weak ferromagnetic exchange interactions with $J = +2$ to $+3$ cm^{-1}. The other three binuclear complexes have susceptibility vs. temperature curves characteristic of weak antiferromagnetic interactions with J values in the range of -1.4 to -1.9 cm^{-1}. The liquid-nitrogen temperature X-band EPR spectrum for a toluene-benzene (4:1) glass of each of the binuclear complexes shows well-resolved zero-field splittings. The magnitude of the zero-field interaction observed for the 4,6-dithiopyrimidine-bridged complexes is shown to be in keeping with the presence of only dipolar through-space interactions. Appreciable pseudodipolar zero-field interactions, in addition to dipolar interactions, are seen for the other three binuclear complexes and the one trinuclear complex. Possible explanations are advanced for why some of these complexes are antiferromagnetic whereas others are ferromagnetic and also why some complexes exhibit appreciable pseudodipolar interactions in their EPR spectra.

Introduction

In the preceding paper the preparation of one trinuclear and five binuclear titanium(III) metallocenes bridged by the anions of various substituted pyrimidines was presented. The results of the crystal structure of (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)] were also given. The pyrimidine dianion functions as a bis-bidentate bridge in this binuclear complex, viz.



In this paper, variable-temperature magnetic susceptibility and EPR results are presented for the six new complexes. As we recently communicated,[4] it is shown that the binuclear 2,4-dithiopyrimidine (2,4-dithiouracil) and trinuclear trithiocyanuric acid complexes exhibit unusual magnetic properties compared to the oxygen-containing analogues reported previously.[5]

Experimental Section

The details of the preparations of the compounds are given in the preceding paper together with the analytical data.

Variable-temperature magnetic susceptibility data were measured with a PAR Model 150A vibrating-sample magnetometer. In this study, the superconducting magnet was operated variously at four field strengths, 13.5, 18.5, 27.0, and 35.0 kG. A calibrated GaAs diode is used for temperature determination, with due attention paid to the magnetic field dependence of such a diode at high fields and low temperatures. In all measurements, $CuSO_4{\cdot}5H_2O$ was used as a standard together with determinations on other compounds previously reported in the literature. The compounds were loaded into the press-fit Kel-F sample cells in the inert-atmosphere box.

EPR spectra of toluene/benzene (4:1) glasses were recorded at liquid-nitrogen temperature on a Varian E-9 X-band spectrometer operating in the range of 9.1–9.5 GHz. The X-band frequency was determined with a Hewlett-Packard Model 5240A 12.4-GHz digital frequency meter. All of the compounds in this study are air sensitive both as solids and in solution. The samples for the EPR investigations were loaded into quartz tubes in the helium-charged inert-atmosphere box. The tubes were then connected to a vacuum stopcock, removed from the box, and then degassed and sealed on a glass vacuum line.

Results and Discussion

Magnetic Susceptibility. Variable-temperature (generally 4.2–224 K) magnetic susceptibility data were measured for six of the new polynuclear titanium(III) metallocenes prepared in this study. The data, which were taken at 13.5 kG except where indicated, are given in Tables I–VII.[6] As illustrated in the Introduction of the preceding paper, most of these complexes are binuclear and one is trinuclear. The susceptibility data for the complexes indicate the presence of a weak magnetic exchange interaction in all six complexes.

Two of the five binuclear complexes exhibit ferromagnetic exchange interactions. Compounds **1** and **2**, which are bridged by the dianions of 2,4-dithiopyrimidine (otherwise known as dithiouracil) and 2,4-diselenopyrimidine, have effective magnetic moments (μ_{eff}/Ti ion) that increase somewhat at temperatures approaching 4.2 K. Figure 1 illustrates the data for the 2,4-dithiopyrimidine complex. The solid line in this figure results from a least-squares fit of the data to the Bleaney–Bowers equation[7] for an isotropic exchange interaction ($\hat{H} = -2J\hat{S}_1{\cdot}\hat{S}_2$) where $S_1 = S_2 = {}^1/_2$. In the case of a ferromagnetic interaction, the ground state of the binuclear complex is the triplet state and the least-squares fitting pa-

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