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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

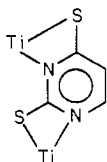
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Variable-temperature (4.2–244 K) magnetic susceptibility and EPR data are presented for five binuclear titanium(III) metallocenes bridged by the dianions of 2,4-dithiopyrimidine, 2,4-diselenopyrimidine, 2-thiouracil, 4,6-dihydropyrimidine, and 4,6-dithiopyrimidine 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-diselenopyrimidine) 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 complex 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, CuSO₄·5H₂O 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 ($\mu_{\text{eff}}/\text{Ti ion}$) 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 equation⁷ for an isotropic exchange interaction ($\hat{H} = -2JS_1 \cdot S_2$) 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-

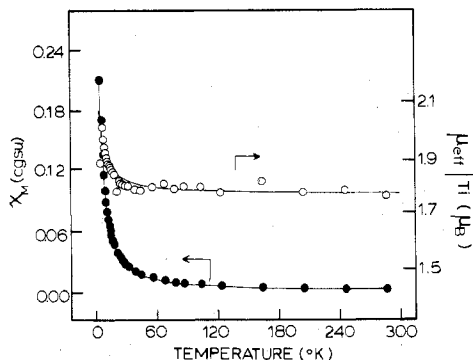


Figure 1. Molar paramagnetic susceptibility and $\mu_{\text{eff}}/\text{Ti}$ vs. temperature curves for 2,4-dithiopyrimidinate-bridged compound **1**. The solid lines represent least-squares fits of the data to the theoretical equations.

Table VIII. Magnetic Susceptibility Least-Squares Fitting Parameters^a

compd ^b	bridge	J, cm^{-1}	g	$\Theta, ^\circ\text{K}$
1	2,4-dithiopyrimidinate(2-) (dithiouracilate(2-))	+2.0	2.04	+0.45
2	2,4-diselenopyrimidinate(2-) uracilate(2-)	+2.5 -1.3	2.10 1.99	-0.90
3	2-thiouracilate(2-)	-1.9	1.95	
5	4,6-dihydroxypyrimidinate(2-)	-1.4	1.96	
6	4,6-dithiopyrimidinate(2-)	-1.6	2.00	
7	trithiocyanurate(3-)	sample a sample b	+3.2 +3.1	-0.77 -1.0
	cyanurate(3-)	-0.93	2.08	-0.21

^a In fitting of the data for all of the compounds, the temperature-independent paramagnetism was taken as zero. The parameters for the uracilate(2-) and cyanurate(3-) complexes were taken from ref 5, except that the susceptibility data for the uracilate(2-) complex were refit under the conditions that $\Theta = 0 \text{ K}$. ^b See preceding paper for molecular structures that correspond to the numbers. ^c Only if the polynuclear complex has a paramagnetic ground state, is it appropriate to use a Curie-Weiss constant, Θ , to gauge intermolecular exchange interactions; see ref 8.

parameters are g , the exchange parameter J , and Θ the Curie-Weiss constant which gauges the intermolecular interaction between the triplet-state molecules.⁸ As summarized in Table VIII, the J values for these two complexes are ca. 2 cm^{-1} . The observation of a ferromagnetic interaction for compounds **1** and **2** is interesting in view of the fact that the analogous oxygen-containing complex bridged by the dianion of uracil was reported⁵ to have an antiferromagnetic interaction.

It is unusual to find a ferromagnetic exchange interaction for a binuclear complex possessing an extended bridging unit. Only a few examples have been reported.⁹ Several facts indicate that the ferromagnetic interactions observed for compounds **1** and **2** are, however, intramolecular and not intermolecular. First of all, the unit-cell packing diagram for compound **1**, which is given in the preceding paper, shows that there is no viable intermolecular pathway available for an exchange interaction. Two additional types of magnetic susceptibility measurements were carried out to substantiate this.

Variable-temperature (4.2–224 K) magnetic susceptibility data were collected for the 2,4-dithiopyrimidine complex **1** at three other magnetic fields in addition to the data illustrated in Figure 1 for 13.5 kG. Data sets obtained at either 18.5, 27.0, or 35.0 kG gave the same μ_{eff} vs. temperature curves within experimental error as found at 13.5 kG. In each case, $\mu_{\text{eff}}/\text{Ti}$ ion remained relatively constant as the temperature was decreased until ca. 20 K whereupon $\mu_{\text{eff}}/\text{Ti}$ increased by ca. $0.3 \mu_{\text{B}}$. In another experiment, a sample of compound **1** was maintained at 4.2 K and the relative magnetization of the

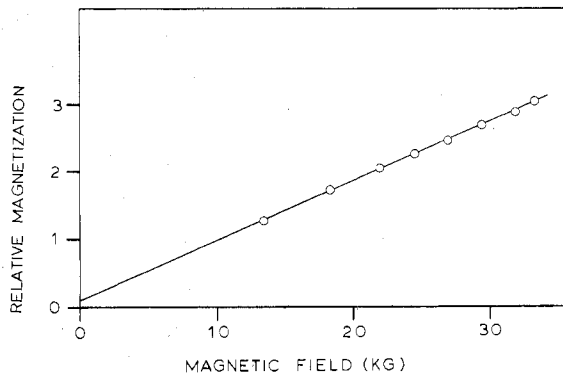


Figure 2. Relative magnetization vs. magnetic field strength curve for 2,4-dithiopyrimidinate-bridged compound **1** at 4.2 K.

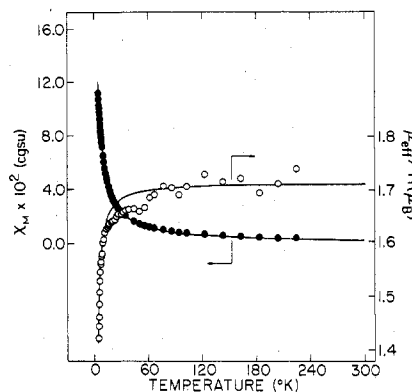


Figure 3. Molar paramagnetic susceptibility and $\mu_{\text{eff}}/\text{Ti}$ vs. temperature curves for 4,6-dithiopyrimidinate-bridged compound **6**. The solid lines represent least-squares fits of the data to the theoretical equations.

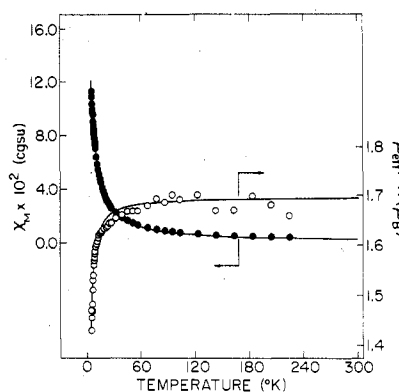


Figure 4. Molar paramagnetic susceptibility and $\mu_{\text{eff}}/\text{Ti}$ vs. temperature curves for 4,6-dihydroxypyrimidinate-bridged compound **5**. The solid lines represent the least-squares fits of the data to the theoretical equations.

sample was measured as the magnetic field was increased from 13.5 to 35.0 kG. Figure 2 shows that the magnetization increases linearly with the magnetic field. If the ferromagnetic exchange interaction observed for compound **1** was due to an extended interaction throughout the lattice, i.e., an intermolecular interaction, then the magnetization of the compound would not be linear with magnetic field.¹⁰ Thus, it is clear that the observed ferromagnetic interaction is intramolecular.

Antiferromagnetic exchange interactions were detected for the binuclear $[\eta^5\text{-CH}_3\text{C}_5\text{H}_4]_2\text{Ti}(\text{bridge})$ complexes, where the bridge is the dianion of either 4,6-dithiopyrimidine, 4,6-dihydroxypyrimidine, or 2-thiouracil. These are compounds numbered **6**, **5**, and **3**, respectively, in the preceding paper. Least-squares fitting the data gave the solid line curves

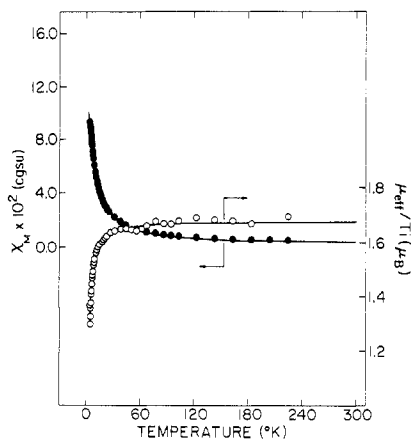


Figure 5. Molar paramagnetic susceptibility and $\mu_{\text{eff}}/\text{Ti}$ vs. temperature curves for 2-thiouracilate-bridged compound **3**. The solid lines represent the least-squares fits of the data to the Bleaney-Bowers equation.

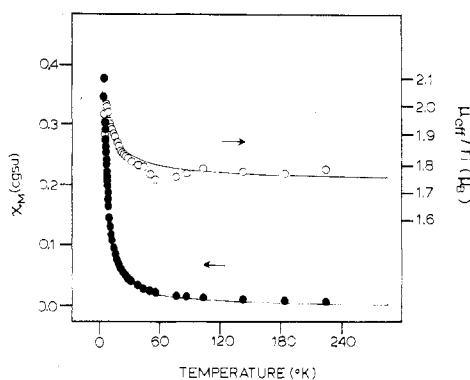


Figure 6. Molar paramagnetic susceptibility and $\mu_{\text{eff}}/\text{Ti}$ vs. temperature curves for trithiocyanurate-bridged compound **7**. The solid lines represent the least-squares fits of the data to the theoretical equation given in the text.

represented in Figures 3–5 and the parameters given in Table VIII. It is not appropriate to use a Curie-Weiss constant in fitting the data for binuclear complexes involved in an antiferromagnetic interaction. Only two parameters were used: g and J . The weak antiferromagnetic interactions in these three complexes are characterized by J values in the range of -1.4 to -1.9 cm^{-1} .

Variable-temperature magnetic susceptibility data were collected for two samples of the trinuclear trithiocyanurate complex, compound **7**. The data are found in Tables III and IV.⁶ As can be seen in Figure 6, $\mu_{\text{eff}}/\text{Ti}$ is relatively constant as the temperature is decreased and increases somewhat at low temperatures. Both samples showed the same behavior. A ferromagnetic interaction is present in this trinuclear complex.

The magnetic exchange interaction in an equilateral triangular arrangement of three $S = 1/2$ ions can be handled with one exchange parameter, J , which gauges the intramolecular interaction of any two of the ions. Three electronic states result from the exchange interaction in the triangular array, one is a quartet state with total spin, S' , of $3/2$ and the other two are doublet states, each with $S' = 1/2$. In the case of a ferromagnetic interaction, J is positive and the quartet state is the ground state. The two doublet states both have the same energy, which is $3J$ above the ground state.

The data for the trinuclear trithiocyanurate complex were least-squares fit to the appropriate theoretical susceptibility expression which was given previously.⁵ Fitting the data for the two different samples gave J values of 3.2 and 3.1 cm^{-1} (see Table VIII). In previous work,⁵ the oxygen-containing



Figure 7. EPR spectra at ca. 77 K for a toluene/benzene (4:1) glass of trithiocyanurate-bridged compound **7** (top) and for the cyanurate-bridged compound (bottom).

analogue of compound **6**, i.e., the trinuclear cyanurate complex, was found to exhibit an antiferromagnetic interaction with $J = -0.93$ cm^{-1} .

Magnetic exchange interactions have been reported for trinuclear complexes of Cr(III),¹¹ Fe(III),¹² Ni(II),¹³ and Cu(II).¹⁴ These complexes have largely only been characterized by magnetic studies on powdered samples. One trinuclear vanadyl pyrophosphate complex, $\text{Na}_6(\text{VOP}_2\text{O}_7)_3 \cdot 12\text{H}_2\text{O}$, was studied with EPR.¹⁵ Coutts and Wailes¹⁶ reported the isolation of compounds with the composition $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CN})]_3$ and $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{NCS})]_3$. The $\mu_{\text{eff}}/\text{Ti}$ for each compound was found to be ca. $1.0 \mu_{\text{B}}$, which is indicative of a strong antiferromagnetic interaction. On the basis of magnetic susceptibility, mass spectral, and infrared data, they proposed that the complexes are trinuclear and have a triangular structure.

Electron Paramagnetic Resonance Studies. X-Band EPR spectra were run for liquid-nitrogen temperature toluene/benzene (4:1) glasses of all seven of the polynuclear titanium(III) complexes prepared in this study. It was also deemed important to prepare and study with EPR one analogous sulfur-containing mononuclear complex. A sample of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}](\text{Spy})$ was prepared, where Spy^- is the anion of 2-mercaptopyridine. The Spy^- ligand is supposedly chelating the titanium(III) ion with the S and N atoms. The EPR spectrum of a glass of this compound shows three signals characteristic of a rhombic spectrum with g values of 2.00, 1.99, and 1.96. This spectrum is almost identical with that reported⁵ for $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}](\text{Opy})$, where Opy^- is the anion of 2-hydroxypyridine. The line widths (ca. 10 G) of the three signals in the spectrum of each of these two mononuclear complexes are relatively small.

The ferromagnetically coupled trinuclear compound **7** has three EPR active states: a quartet ground state and two doublet states that are ca. 9.7 cm^{-1} higher in energy. As we indicated previously,⁵ the two doublet states will probably give rhombic signals that are superimposed and that are very similar to the signal seen for a mononuclear complex. Computer simulations have been reported for the quartet state of organic triradicals.^{17,18} If axial symmetry is assumed, then the quartet state can be described by the spin Hamiltonian

$$\mathcal{H} = g\beta\hat{H}\cdot\hat{S} + D(\hat{S}_z^2 - \frac{1}{3}\hat{S}^2) \quad (1)$$

Table IX. EPR Parameters^a

Compd ^b	bridge	g_x, g_y, g_z	$ D , \text{cm}^{-1}$	$ E , \text{cm}^{-1}$
1	2,4-dithiopyrimidinate(2-) (dithiouracilate(2-))	2.00	0.0530	0.0058
		1.99		
		1.96		
2	2,4-diselenopyrimidinate(2-)	1.98	0.0524	0.0061
		1.97		
		1.95		
[(η^5 -CH ₃ C ₃ H ₄) ₂ Ti] ₂ (uracilate)	uracilate(2-)	1.99	0.0117	0.0018
		1.98		
		1.97		
3	2-thiouracilate(2-)	1.96	0.0449	0.0052
		1.95		
		1.95		
4	4,6-dihydroxypyrimidinate(2-)	1.97	0.0077	0.0018
		1.98		
		1.98		
5	4,6-dithiopyrimidinate(2-)	1.97	0.0084	0.0015
		1.98		
		1.99		
6	trithiocyanurate(3-)	1.97	0.0324	
		1.96		
		1.95		
[(η^5 -CH ₃ C ₃ H ₄) ₂ Ti] ₃ (cyanurate)	cyanurate(3-)	2.01	0.0095	
		1.98		
		1.96		

^a Parameters are taken from X-band EPR spectra of toluene/benzene (4:1) glasses at liquid-nitrogen temperature. ^b See preceding paper for the molecular structures that correspond to the various compound numbers.

where D is the axial zero-field splitting parameter.

The X-band glass spectrum of compound 7 is illustrated in Figure 7 (upper). In the lower tracing of this same figure is shown, for comparison purposes, the X-band spectrum for the analogous oxygen-containing trinuclear cyanurate complex from a previous study. The two spectra are similar in appearance, and the same assignment of signals can be made for the spectrum of compound 7 as was made previously for the cyanurate complex.⁵ The three intense signals at 2872, 3245, and 3566 G are assigned to the quartet ground state, whereas the other three signals are attributed to the two doublet states. The spacing between either of the outer signals in the quartet pattern and the central and most intense signal at 3245 G gives the absolute value of the zero-field splitting in the quartet state, which is evaluated from the spectrum to be $|D| = 0.0324 \text{ cm}^{-1}$. From the comparison of spectra in Figure 7 it can be readily seen that the trinuclear cyanurate complex has a zero-field splitting ($|D| = 0.0095 \text{ cm}^{-1}$) which is more than 3 times smaller than that for trinuclear trithiocyanurate complex.

The relatively large zero-field splitting present in the trithiocyanurate complex leads to the appearance of intense formally forbidden $\Delta M_s = 2$ and $\Delta M_s = 3$ transitions. These signals are not present for the trinuclear cyanurate complex. The low-field region of the spectrum of the trithiocyanurate complex is shown in Figure 8. There are five signals observed at 1075, 1350, 1460, 1760, and 1965 G. The sharp signal at 1075 G is assignable to the " $\Delta M_s = 3$ " transition, whereas the other four are " $\Delta M_s = 2$ " transitions. The $\Delta M_s = 3$ transition appears at $H_0/3$, where $H_0 = h\nu/g\beta = 3245 \text{ G}$ and g is the average g value of the quartet state. The calculated resonance value is 1082 G, which compares favorably with the observed value of 1075 G.

The four $\Delta M_s = 2$ transitions are expected^{17,18} at fields of $1/2 H_0 \pm 1/2 D$ and $1/2 H_0 \pm D$, which with $H_0 = 3245 \text{ G}$ give calculated fields of 1281, 1452, 1794, and 1965 G. These calculated resonance fields are in reasonable agreement with the observed signals in Figure 8.

The six binuclear titanium(III) metallocenes studied in this work give typical zero-field-split rhombic X-band spectra for glasses maintained at liquid-nitrogen temperatures. The EPR signal that is observed for each of these complexes arises from the triplet state for each complex. The zero-field interaction

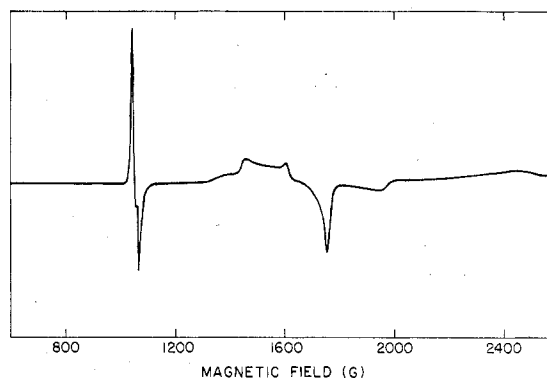


Figure 8. EPR spectrum at ca. 77 K of trithiocyanurate-bridged compound 7, showing the $\Delta M_s = 2$ and $\Delta M_s = 3$ signals.

in the triplet state leads to six $\Delta M_s = 1$ signals for a binuclear complex with a rhombic g tensor. A typical spectrum is shown in Figure 9, which is an illustration of the $\Delta M_s = 1$ region in the glass spectrum for the binuclear complex bridged by the dianion of 2,4-diselenopyrimidine, i.e., compound 2. Six signals are seen in this spectrum in addition to a signal centered at ca. 3300 G (g values of 1.95, 1.97, and 1.98) which is due to some mononuclear complex resulting from a partial dissociation of the binuclear complex upon dissolution.

The spin Hamiltonian for the triplet state of the binuclear complexes is written as

$$\mathcal{H} = \beta \hat{S} \cdot \hat{g} \cdot \hat{H} + D(\hat{S}_z^2 - 1/3 S^2 - 1/3) + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (2)$$

In this expression, D and E are the axial and nonaxial (rhombic) zero-field splitting parameters. Wasserman¹⁹ derived the equations for the six resonance fields corresponding to the $\Delta M_s = 1$ transitions for randomly oriented triplet-state molecules. As indicated in our previous paper,⁵ a least-squares computer program is used to fit the observed resonance fields to the six equations and this procedure gives the parameters D , E , g_x , g_y , and g_z for the particular complex. Table IX summarizes the parameters obtained in this manner for the five binuclear complexes. Table X lists the calculated and observed resonance fields for the complexes.

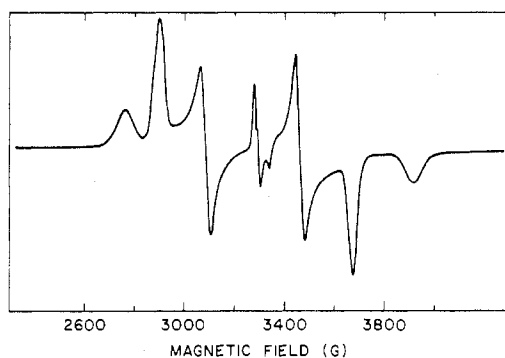


Figure 9. EPR spectrum at ca. 77 K for a glass (toluene/benzene, 4:1) of 2,4-diselenopyrimidinate-bridged compound **2**.

Table X. Observed and Calculated X-Band EPR Resonance Fields for Binuclear Titanium Metallocenes^a

compd	peak assignt	field obsd, G	field calcd, G
1	Z1	2733	2740
	Y1	2876	2873
	X1	3051	3050
	X2	3435	3440
	Y2	3636	3640
	Z2	3891	3890
2	$\Delta M_s = 2$	1604	1580
	Z1	2761	2763
	Y1	2906	2902
	X1	3091	3088
	X2	3464	3460
	Y2	3676	3673
3	Z2	3913	3920
	$\Delta M_s = 2$	1621	1670
	Z1	2970	2843
	Y1	2970	2996
	X1	3110	3147
	X2	3490	3467
4	Y2	3700	3662
	Z2	3900	3828
	Z1	3197	3196
	Y1	3222	3223
	X1	3286	3287
	X2	3310	3310
5	Y2	3366	3365
	Z2	3364	3365
	$\Delta M_s = 2$	1645	1644
	Z1	3182	3183
	Y1	3222	3221
	X1	3282	3282
6	X2	3326	3327
	Y2	3361	3363
	Z2	3363	3363
	$\Delta M_s = 2$	1644	1638

^a Toluene/benzene glasses (4:1) at liquid-nitrogen temperature.

An analysis of parameters given in Table IX and those previously reported⁵ for the binuclear titanium(III) metallocene bridged by the dianion of uracil and for the trinuclear cyanurate complex reveals some very interesting facts. Compounds **1** and **2**, which are bridged by the 2,4-dithiopyrimidine and 2,4-diselenopyrimidine anions, respectively, have D values that are approximately 4 times larger than the D value reported for the oxygen-containing analogue, the uracilate-bridged complex. This is easily seen from a comparison of the spectra, for the $\Delta M_s = 1$ regions of the spectra for compounds **1** and **2** span field ranges that are approximately 4 times the range found in the spectrum of the uracilate-bridged complex. This is interesting in view of the fact that compounds **1** and **2** are involved in ferromagnetic exchange interactions, whereas the uracilate-bridged complex is antiferromagnetic. In keeping with the observation of large zero-field splitting for compounds **1** and **2** is the fact that these two show $\Delta M_s = 2$ signals that are considerably more intense

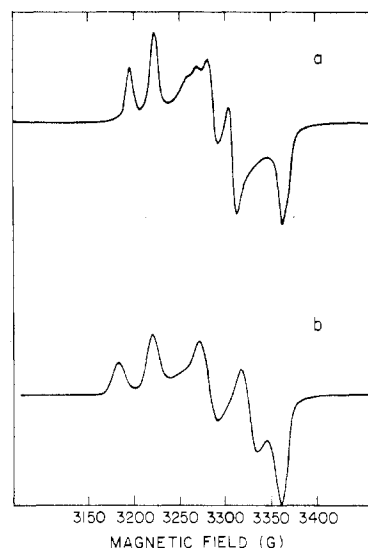


Figure 10. EPR spectra of glasses (toluene/benzene, 4:1) at 77 K for compound **5** (top) and compound **6** (bottom).

(as large as $\Delta M_s = 1$ signals) than the same signal seen for the uracil complex.

A similar correlation can be made between the parameters for the trinuclear trithiocyanurate complex, compound **7**, and the parameters for the oxygen-containing analogue, the cyanurate-bridged complex. The D value for compound **7** is ca. 3.4 times larger than the D value reported⁵ for the cyanurate-bridged complex. Compound **7** is ferromagnetic and the oxygen analogues are antiferromagnetic.

It is interesting to note that, on the other hand, the third pair of analogous complexes, compounds **5** and **6**, have very comparable D values. This can be readily seen in Figure 10, which shows that the $\Delta M_s = 1$ regions of the two X-band spectra encompass comparable field ranges. Compounds **5** and **6** are also both antiferromagnetic. Relatively weak $\Delta M_s = 2$ signals are seen in the EPR spectra of these two complexes, which is in keeping with the relatively small D values.

The zero-field splitting parameter D can be comprised of both dipolar (D_{dd}) and pseudodipolar (D_{ls}) contributions. D_{dd} and D_{ls} are of opposite sign. The dipolar contribution arises, of course, from a simple through-space dipole-dipole interaction and is related²⁰ to the titanium-titanium distance, R , by

$$R = (0.65g_{\parallel}^2/D_{dd})^{1/3} \quad (3)$$

The uracilate-bridged binuclear complex, the cyanurate-bridged trinuclear complex, and compounds **5** and **6** have D values that are almost totally dipolar in nature. This was verified by taking the Ti-Ti distances from models for the various complexes and the crystal structure reported in the preceding paper and using these distances to estimate the D_{dd} values with eq 3. For example, the D value obtained for compound **5** gives a calculated Ti-Ti distance of 6.88 Å, which is in good agreement with a value of 6.8 ± 0.2 Å estimated from a model.

The observed D values for compounds **1**, **2**, and **7** must be dominated then by appreciable pseudodipolar zero-field interactions, particularly since D_{ls} is of opposite sign to D_{dd} . Pseudodipolar zero-field splitting in the triplet state is due to a spin-orbit interaction of the triplet state with an excited state, where the excited state is involved in an exchange interaction.²¹ Generally, excited-state exchange parameters are an order of magnitude smaller than the J value for the ground state.²² A few instances of appreciable pseudodipolar zero-field interactions have been noted for complexes with weak magnetic exchange interactions present in the ground state. The ex-

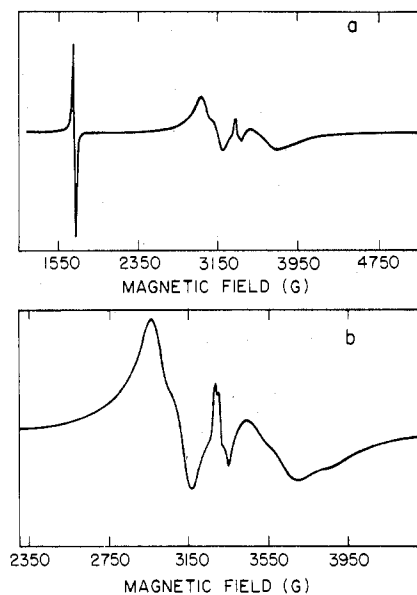


Figure 11. EPR spectra of 2-thiouracilate-bridged compound **3** as a glass (toluene/benzene, 4:1) at ca. 77 K; $\Delta M_s = 2$ region illustrated in tracing a.

amples include $(\text{Ph}_4\text{As})_2\text{Cu}_2\text{Cl}_2$ ²³ and $[\text{Cu}_2(\text{"dien"})_2(\text{N}_3)_2]$ - $(\text{BPh}_4)_2$ ²⁴ where "dien" is a triamine ligand. Comments pertaining to why compounds **1**, **2**, and **7** apparently have appreciable excited-state exchange interactions are deferred to the next section.

Up to this point, we have not discussed in any detail the EPR and susceptibility data obtained for compound **3**, the binuclear complex bridged by the dianion of 2-thiouracil. As can be seen in Table VIII, the complex is antiferromagnetic with $J = -1.9 \text{ cm}^{-1}$. The X-band glass spectrum for this compound is illustrated in Figure 11, and in contrast to the spectra of the other complexes, it consists of relatively broad signals. Two characteristics of the spectrum point to a relatively large D value for this complex. First, there is a relatively intense $\Delta M_s = 2$ transition seen at 1710 G; the intensity is comparable to the intensity of the $\Delta M_s = 2$ transitions seen for compounds **1** and **2**. Second, in tracing b of Figure 11, it can be seen that the $\Delta M_s = 1$ signals in the spectrum span a relatively large field range of ca. 1400 G. The sharp signals centered around ca. 3300 G ($g = 1.98, 1.97, \text{ and } 1.94$) are due to a monomeric species.

Compound **3** is a unique complex in the series, for the two titanium(III) ions in the binuclear complex have different ligands; one ion is coordinated to the sulfur atom and the other to the oxygen.²⁵ The broadness observed in the spectrum might in some way reflect this inequivalency. There could be either an incomplete exchange averaging or an antisymmetric exchange interaction²⁶ present. Table X gives our assignment for the $\Delta M_s = 1$ signals in the spectrum. The zero-field splitting parameters were evaluated to be $|D| = 0.045 \text{ cm}^{-1}$ and $|E| = 0.005 \text{ cm}^{-1}$. It can be seen in Table X that this is the only binuclear complex for which the observed field positions of signals do not fit well to the theoretical equations. Irrespective of the exact assignment of the spectrum, it is clear that compound **3** does have a relatively large D value.

Magnetic Exchange Mechanisms. In this last section two questions will be addressed: Why are some of the complexes antiferromagnetic, while others are ferromagnetic? Why do some of the complexes exhibit appreciable pseudodipolar zero-field effects?

Three major factors determine the nature of the magnetic exchange interaction found for each of the polynuclear titanium(III) metallocenes. The magnitude of the interaction

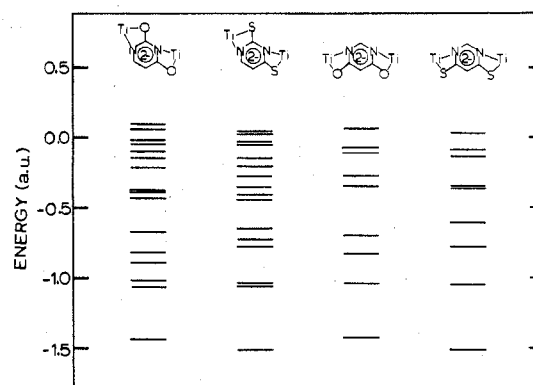


Figure 12. Energies for the antifermagnetic exchange-propagating molecular orbitals of 2,4-dithiopyrimidine(2-), uracil(2-), 4,6-dihydroxypyrimidine(2-), and 4,6-dithiopyrimidine(2-).

can be determined by two factors: the bond distances between the titanium(III) ion and the atoms of the bridge and the availability of bridge molecular orbitals with the correct symmetry to propagate an interaction between the two metal orbitals containing the unpaired electrons. As indicated previously,^{5,27} each titanium(III) unpaired electron is located in an orbital which is σ bonding in the plane of the bridge. The bond angles between each titanium(III) ion and the atoms of the bridge are the essence of the third major factor that will determine whether a given complex is antiferromagnetic or ferromagnetic.

CNDO/2 molecular orbital calculations²⁸ were carried out for 2,4-dithiopyrimidine(2-) (i.e., dithiouracil(2-)), uracil(2-), 4,6-dihydroxypyrimidine(2-), and its sulfur analogue. The molecular dimensions of the first dianion, as deduced from the X-ray structure of (2,4-dithiopyrimidinato)bis[bis(η^5 -methylcyclopentadienyl)titanium(III)] in the preceding paper, were used as a model for the assumed dimensions of the other three dianions.

Both 4,6-dihydroxypyrimidine(2-) and its sulfur analogue have C_{2v} symmetry. In this point group, the a_1 symmetry orbitals of the bridge will serve as pathways^{29,30} to propagate an antiferromagnetic exchange interaction. Each of these dianions have nine filled a_1 symmetry molecular orbitals. As can be seen in Figure 12, replacing the two oxygen atoms by sulfur atoms only serves to slightly stabilize the a_1 orbitals due partially to an admixture of a small amount of sulfur d orbitals. This slight stabilization of a_1 symmetry orbitals would only tend to reduce the magnitude of the antiferromagnetic interaction. That both of the binuclear complexes **5** and **6** exhibit comparable antiferromagnetic exchange interactions probably reflects a greater covalency between the titanium(III) ions and the sulfur atoms in complex **6** than between the titanium(III) ions and the oxygen atoms in complex **5**, taken together with the change in bridge orbitals.

Dithiouracil(2-) and uracil(2-) have C_s symmetry only, and this lower symmetry leads to a larger number of molecular orbitals that are of the correct symmetry (a') to propagate an antiferromagnetic interaction between two ($\eta^5\text{-CH}_3\text{C}_5\text{H}_4$)₂Ti⁺ moieties. As indicated in Figure 12, each of these dianions has 16 a' -symmetry molecular orbitals. As in the previous case, the replacement of the oxygen atoms by sulfur atoms leads to a slight stabilization of the a' orbitals. This would only reduce the magnitude of the antiferromagnetic exchange interaction. The explanation for why the uracilate-bridged complex exhibits an antiferromagnetic interaction whereas the dithiouracilate-bridged complex exhibits a net ferromagnetic interaction must stem from some other factor.

At this time, it can only be suggested that the net ferromagnetic interaction seen for the dithiouracilate-bridged complex **1** (and, for that matter, complex **2**) is the result of

the Ti-bridged bond angles. Reference to the preceding paper shows that in complex **1** the Ti-S-C angle is ca. 79°. This bond angle could be so situated as to produce an orthogonality at the sulfur atom. Similar observations have been reported before. For example, in a series of di- μ -hydroxo-bridged copper(II) dimers, it was found³¹ that when the Cu-O-Cu bridging angle is greater than 97.6°, the interaction between copper(II) ions is antiferromagnetic, whereas when the angle is less than 97.6°, there is a ferromagnetic interaction. The net ferromagnetic interaction results from the situation where the dominant pathway for exchange interaction involves an orthogonality at the bridging oxygen atom. The unpaired-electron orbitals of the two copper(II) ions are interacting with two different 2p orbitals of the oxygen atom. A similar observation has been made for dimeric nickel(II) complexes with *polyatomic* bridges. The NCX⁻ ions bridge in an end-to-end fashion in [Ni₂(tren)₂(NCX)₂](BPh₄)₂, where X = O, S, or Se and tren is N(CH₂CH₂NH₂)₃.³² The NCO⁻ complex is antiferromagnetic ($J = -4.4$ cm⁻¹), whereas the NCS⁻ ($J = +2.4$ cm⁻¹) and NCSe⁻ ($J = +1.6$ cm⁻¹) complexes are ferromagnetic. An orthogonal interaction develops at the S and Se atoms as a result of the acute Ni-X-C (X = S and Se) angles.

In short, it is suggested that changing from the oxygen to the sulfur analogues for the binuclear uracil complexes and for the trinuclear cyanurate complexes leads to an acute Ti-S-C angle and a net ferromagnetic interaction. In complexes **5** and **6** the two (η^5 -CH₃C₅H₄)₂Ti⁺ moieties are further apart, which leads to less steric interaction and perhaps a different value for the Ti-S-C angle. Additional X-ray structural work is needed to substantiate this qualitative explanation. This is particularly true in view of the fact that the 2-thiouracilate-bridged complex **3** exhibits a net antiferromagnetic interaction.

Binuclear complexes **1**, **2**, and **3** and the trinuclear complex **7** give EPR spectra reflecting the presence of appreciable pseudodipolar zero-field interactions. Pseudodipolar zero-field splitting of an electronic state results from a spin-orbit interaction with an excited state which is involved in an appreciable magnetic exchange interaction. The magnitude of the pseudodipolar interaction is of the order of $J_{\text{ex}}\lambda^2/\Delta^2$, where J_{ex} is the exchange parameter for the excited state, Δ is the energy difference between the two states, and λ is the spin-orbit coupling constant. A J_{ex} value of 30 cm⁻¹ would be needed to give a pseudodipolar interaction of the magnitude that is seen for complexes **1**, **2**, **3**, and **7**. Thus, the excited-state exchange interactions are considerably greater than those characterized for the ground states of these complexes.

It is difficult to identify which excited state(s) is (are) giving the relatively large pseudodipolar splittings observed for complexes **1**, **2**, **3**, and **7**. However, it is noted that in the series of eight polynuclear titanium(III) metallocenes, these four complexes are the only ones that have a -S-C-N- fragment interposed between the two metal ions.²⁵ The calculations of Dahl et al.²⁷ show that a low-lying excited state in these complexes would have an unpaired electron in a π -type orbital consisting of contributions from metal d_{xy} and d_{xz} as well as cyclopentadienide orbitals. A π type of interaction propagated by the -S-C-N- fragment could be responsible for the rel-

atively large excited-state exchange interactions.

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Supplementary Material Available: Tables I-VII (experimental and calculated magnetic susceptibility data) (12 pages). Ordering information is given on any current masthead page.

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