

## Experimental Section

**Compound Preparation.** Analytical data for all compounds appear in Table I. Complexes with the condensation product of phenylenediamine with salicylaldehyde, that is  $\text{Cu}_2(\text{sal-}m\text{-pda})_2$ ,  $\text{Ni}_2(\text{sal-}m\text{-pda})_2$ , and  $\text{Cu}_2(\text{sal-}p\text{-pda})_2$ , were prepared according to the procedure reported by Bear et al.<sup>7</sup>

**Samples of  $\text{Cu}_2(\text{sal-tabp})$ ,  $\text{Ni}_2(\text{sal-tabp})\cdot\text{H}_2\text{O}$ , and  $\text{Co}_2(\text{sal-tabp})\cdot\frac{1}{2}\text{H}_2\text{O}$**  were prepared by the following procedure. One millimole of ligand, prepared by the condensation of salicylaldehyde with 2,2',6,6'-tetraaminobiphenyl,<sup>24</sup> was dissolved in ca. 30 mL of warm absolute methanol. A methanol solution (ca. 25 mL) of 1 mmol of the appropriate  $\text{M}(\text{OAc})_2\cdot n\text{H}_2\text{O}$  salt was added to the ligand solution and the resulting solution was refluxed for 0.5 h and then allowed to cool to room temperature. At this stage of the preparation, a solid had formed in all cases. The solid was collected by filtration and washed with methanol and then diethyl ether. The solids were recrystallized from  $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$  (1:1 by volume). All solids were dried in vacuo over  $\text{P}_4\text{O}_{10}$  at room temperature for 12 h.

**Physical Measurements.** EPR and variable-temperature magnetic susceptibility measurements were carried out as described in a previous paper.<sup>25</sup> All EPR samples were loaded into quartz tubes and sealed under vacuum (ca. 10  $\mu$ ); solutions were degassed prior to sealing the tubes under vacuum. Polarographic measurements were carried out with a Princeton Applied Research Model 174 polarograph. Background corrections were made on all runs and all measurements were made at 25 °C. All solutions were thoroughly bubbled with nitrogen gas before the runs.

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**Registry No.**  $\text{Cu}_2(\text{sal-}m\text{-pda})_2$ , 38651-40-0;  $\text{Cu}_2(\text{sal-}p\text{-pda})_2$ , 66172-41-6;  $\text{Cu}_2(\text{sal-tabp})$ , 56132-49-1;  $\text{Ni}_2(\text{sal-}m\text{-pda})_2$ , 66213-50-1;  $\text{Ni}_2(\text{sal-tabp})$ , 66172-42-7;  $\text{Co}_2(\text{sal-tabp})$ , 66172-43-8.

**Supplementary Material Available:** Tables II, IV, V, and VI, observed and theoretically calculated variable-temperature magnetic susceptibility data for  $\text{Cu}_2(\text{sal-}p\text{-pda})_2$ ,  $\text{Ni}_2(\text{sal-}m\text{-pda})_2\cdot 3\text{H}_2\text{O}$ ,  $\text{Ni}_2(\text{sal-tabp})\cdot\text{H}_2\text{O}$ , and  $\text{Co}_2(\text{sal-tabp})\cdot\frac{1}{2}\text{H}_2\text{O}$  (4 pages). Ordering information is given on any current masthead page.

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Contribution from the School of Chemical Sciences and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

## EPR and Magnetic Susceptibility Studies of the Trinuclear Complex Cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)], the Binuclear Complex Uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)], and Related Compounds

BENJAMIN F. FIESELMANN,<sup>1</sup> DAVID N. HENDRICKSON,\*<sup>2</sup> and GALEN D. STUCKY\*<sup>1</sup>

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The first reported paramagnetic titanium(III) trinuclear compounds, cyanuratotris[bis( $\eta^5$ -cyclopentadienyl)titanium(III)] (3) and cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] (4), were prepared. The structurally related mononuclear compound bis( $\eta^5$ -cyclopentadienyl)(2-hydroxypyridinato)titanium(III) (1) and binuclear compound uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] (2) were also synthesized in order to investigate the magnetic exchange interaction between the paramagnetic metal centers. All the compounds are thermally stable and melt without decomposition at over 100 °C. They are also air sensitive. The susceptibility of cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] shows the presence of an antiferromagnetic interaction at temperatures below 10 K with a  $J$  value of  $-0.93\text{ cm}^{-1}$ . The EPR spectrum of this trinuclear species in a glass at 77 K is that expected for thermal population of both the quartet ( $S = 3/2$ ) and the two doublet ( $S = 1/2$ ) states. The two Ti(III) ions in the dimer, uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)], are weakly antiferromagnetically coupled with a  $J$  value of  $-2.25\text{ cm}^{-1}$ . The EPR spectrum of the dimer in a glass at 77 K is that of a triplet system ( $S = 1$ ) with zero field splitting. The six  $\Delta M_s = 1$  resonances can be fit to the theoretical equations to give  $|D| = 0.0117(4)\text{ cm}^{-1}$  and  $|E| = 0.0018(4)\text{ cm}^{-1}$ . The similarity in  $J$  values for the binuclear and trinuclear molecules suggests that related magnetic exchange pathways are operative.

## Introduction

Magnetic exchange interactions have been reported for trinuclear paramagnetic complexes of Cr(III),<sup>3</sup> Fe(III),<sup>4</sup> Ni(II),<sup>5</sup> and Cu(II).<sup>6</sup> Because most of these trinuclear complexes are either insoluble or dissociate in solution, the characterization has been limited largely to magnetic studies on polycrystalline powders. The EPR spectra for these

powders generally provide little information due to poor resolution. One exception is the trinuclear vanadyl pyrophosphate complex,  $\text{Na}_6(\text{VOP}_2\text{O}_7)_3\cdot 12\text{H}_2\text{O}$ , which exhibits a 22-line hyperfine spectrum in aqueous solution.<sup>7</sup> On the other hand, several organic triradicals have been studied with EPR. The organic triradicals, of course, also display magnetic exchange interactions, but the magnitude of the exchange

parameter (i.e.,  $J$  in the spin Hamiltonian  $-2JS_1S_2$ ) is generally poorly characterized. Exceptions are the triradical mesitylene derivatives of the general formula (1,3,5-R)benzene, where R is (biphenyl)<sub>2</sub>C<sup>-</sup> or some other radical, which give characteristic quartet state EPR spectra in solution.<sup>8,9</sup> These unique spectra have been interpreted theoretically and have been successfully computer simulated. In the case where R is a nitrogen radical (1,5-diphenyl-3-verdazyl), the solution EPR spectrum showed signals for both the quartet and doublet states expected from the exchange interaction of three  $S = 1/2$  centers.<sup>10</sup>

One goal of the present study was to prepare a paramagnetic trinuclear transition metal complex which could be characterized not only by magnetic susceptibility studies on the powder but also by EPR studies of frozen glass solutions of the complex. Three observations led to the synthesis of the present complexes. First, with the complex bis(cyclopentadienyl)titanium-bipyridyl, we have recently demonstrated extensive delocalization of electron density onto the aromatic ligand from the Ti(II) metal ion.<sup>11</sup> Second, a large number of transition-metal cations form multimetallic adducts with cyanuric acid and numerous other chelating triazine derivatives.<sup>12,23</sup> Third, a few related Ti(III) compounds of the composition  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{NN})]\text{Cl}$  have been synthesized where the bidentate ligand NN is either bipyridine, phenanthroline, 2-picolyamine, or phenylenediamine.<sup>13,14</sup> Thus, we undertook to complex three bis(cyclopentadienyl)titanium(III)  $d^1$  moieties to the trianion of cyanuric acid. The synthesis and characterization of two such trinuclear Ti(III) complexes are reported in this paper. In addition, the analogous binuclear Ti(III) complex uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] and mononuclear Ti(III) complex bis( $\eta^5$ -cyclopentadienyl)(2-hydroxypyridinato)titanium(III) are reported. It is relevant to note that structural and magnetic studies of several binuclear exchange-interacting titanium(III) metallocenes have been reported from these laboratories.<sup>15</sup> In fact, magnetic exchange interactions between  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}^{\text{III}}$  moieties have been detected for bridging units that are as extended as the cyanurato trianion and dianion of uracil, e.g.,  $[(\eta^2\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{ZnCl}_4$  and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{BeCl}_4$ .<sup>16</sup>

## Experimental Section

All synthetic work was carried out in a Vacuum Atmospheres drybox with a helium atmosphere. Solvents were distilled from sodium and benzophenone under a nitrogen atmosphere. Cyanuric acid, uracil, and 2-hydroxypyridine were purchased from Aldrich and used with no further purification. Bis(cyclopentadienyl)titanium monochloride and bis(methylcyclopentadienyl)titanium monochloride were prepared by literature methods.<sup>16,17</sup> Bis(cyclopentadienyl)titanium dichloride was purchased from Alfa, and bis(methylcyclopentadienyl)titanium dichloride was prepared by the method of Reynold and Wilkinson.<sup>18</sup> Elemental analyses were performed at the University of Illinois School of Chemical Sciences' Microanalytical Laboratory. Computer calculations were done either on an IBM 360-75 at the University of Illinois or on a Sigma 5 computer at the Materials Research Laboratory.

**Physical Measurements.** EPR spectra were run on samples sealed in quartz tubes using a Varian E-9 X-band spectrometer fitted with a Varian temperature controller. Q-Band spectra were run on a Varian spectrometer employing a E-110 bridge and a E266 cavity. Powdered DPPH was used as a reference. Solution and glass spectra were run in a 4:1 toluene-benzene solution. The glass spectra of dimeric compounds were computer fit by an iterative procedure.<sup>19</sup>

Magnetic susceptibilities were measured using a PAR Model 150A vibrating-sample magnetometer calibrated with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Data collection was carried out as previously described.<sup>20</sup> Diamagnetic corrections were taken from published sources.<sup>21</sup> The data were computer fit to a form of the Van Vleck equation<sup>21</sup> appropriate for the number of equivalent paramagnetic metal atoms of spin  $1/2$  by an iterative procedure<sup>19</sup> (see Results and Discussion).

The mass spectra of samples were run on a MAT-Varian CH-5

spectrometer. The experimental isotropic peaks for the parent ions were compared to the calculated spectra using the program MASSPEC.<sup>22</sup>

**Compound Preparation. Bis( $\eta^5$ -cyclopentadienyl)(2-hydroxypyridinato)titanium (1).** In a drybox, 0.21 g (2.2 mmol) of 2-hydroxypyridine in 45 mL of THF was reacted with 0.05 g (2.2 mmol) of sodium sand and refluxed for 15 min with stirring until most of the sodium reacted. After filtering to remove excess sodium, 0.44 g (2.1 mmol) of bis( $\eta^5$ -cyclopentadienyl)titanium monochloride was added with vigorous stirring. The solution turned blue-green immediately and, after stirring at 45–55 °C for 30 min, the solvent was removed at reduced pressure. The green powder was extracted with 20 mL of refluxing heptane and filtered through a glass frit while hot. On slow cooling, 0.26 g of dark green, air-sensitive crystals were recovered for a yield of 46%. Anal. Calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2\text{Ti}$ : C, 66.19; H, 5.18; N, 5.15; Ti, 17.60. Found: C, 65.58; H, 5.03; N, 5.20; Ti, 17.28. In a sealed capillary, the compound melted at 125–129 °C without decomposition. Mass spectrum: calcd 272, found 272.

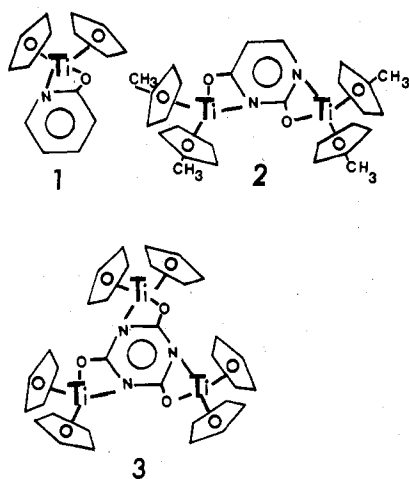
**Uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium] (2).** In 90 mL of THF, 0.10 g (4.3 mmol) of sodium sand and 0.23 g (2.1 mmol) of uracil were mixed. One gram (4.1 mmol) of bis(methylcyclopentadienyl)titanium(III) monochloride was added and the mixture was stirred and heated in a drybox at 45–55 °C for 3 days. The brown solution gradually turned blue. The solvent was removed under vacuum to yield a dark blue-black tar. The tar was extracted with 15 mL of boiling hexane and the solution was filtered while hot through a glass frit. The filtrate was reheated to dissolve all the material and, on slow cooling to room temperature, 0.26 g of air-sensitive, dark blue-green prisms was formed. After reducing the volume of the solution to 5 mL and then permitting most of the remaining solvent to evaporate, 0.21 g more of the crystals was recovered for a total yield of 0.47 g or 43%. In a sealed capillary, the compound melted without decomposition at 112–114 °C. Anal. Calcd for  $((\text{CH}_3)_2\text{C}_5\text{H}_4)_2\text{Ti}_2(\text{C}_4\text{H}_2\text{N}_2\text{O}_2)_2$ : C, 64.38; H, 5.79; N, 5.36; Ti, 18.34. Found: C, 64.30; H, 5.65; N, 5.54; Ti, 18.44. Mass spectrum: calcd 522, found 522.

**Cyanuratotris[bis( $\eta^5$ -cyclopentadienyl)titanium]-Toluene (3).** In a solution of 45 mL of THF and 10 mL of toluene, 0.40 g (3.1 mmol) of cyanuric acid and 0.22 g (9.6 mmol) of sodium sand were mixed. After a day of stirring, 2.0 g (9.4 mmol) of bis(cyclopentadienyl)titanium monochloride was added and the temperature was maintained at 45–50 °C while the heterogeneous mixture was vigorously stirred. After 2 days, a sky blue powder formed. After a week of stirring, the light blue product was filtered and dried to give approximately 0.5 g of a very air-sensitive product with a very slight solubility in refluxing toluene and tetrahydrofuran. Attempts to sublime the product at 250 °C were unsuccessful; however, a remarkably small amount of decomposition occurred at the elevated temperature. The product was purified by Soxhlet extraction with toluene and filtered as a slightly darker blue powder from the solvent. The elemental analysis showed that the product was not pure, but the mass spectrum did allow identification of the compound. Anal. Calcd for  $((\text{C}_5\text{H}_5)_2\text{Ti})_3(\text{C}_3\text{H}_3\text{O}_3) \cdot \text{C}_7\text{H}_8$ : C, 63.85; H, 5.09; N, 5.58; Ti, 19.09. Found: C, 63.86; H, 5.58; N, 5.33; Ti, 16.31.

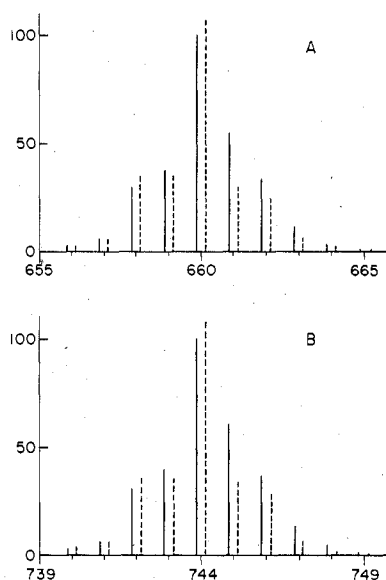
**Cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium]-Toluene (4).** Cyanuric acid (0.40 g, 3.1 mmol) and sodium sand (0.22 g, 9.6 mmol) were mixed in 30 mL of THF. This mixture was stirred for 2 h and then 2.27 g (9.4 mmol) of bis(methylcyclopentadienyl)titanium monochloride was added and the solution immediately turned blue-green. After 5 days of stirring at 45–50 °C, the solvent was removed under reduced pressure to give a blue-green powder. The powder was washed with cold heptane to remove a green impurity and this gave a sky blue powder that was very air sensitive, soluble in THF and toluene, and slightly soluble in heptane. The product was dissolved in refluxing toluene and filtered while hot through a glass frit and, after 2 days, large dark blue crystals formed. Upon drying, the surface of some of the crystals turned light blue, possibly due to the loss of the toluene molecule of solvation. A total of 0.69 g of product or 27% was recovered. Anal. Calcd for  $((\text{CH}_3)_2\text{C}_5\text{H}_4)_2\text{Ti}_3(\text{C}_3\text{N}_3\text{O}_3) \cdot \text{C}_7\text{H}_8$ : C, 66.04; H, 6.02; N, 5.02; Ti, 17.18. Found: C, 65.83; H, 5.82; N, 4.81; Ti, 16.60. In a sealed capillary tube, compound 4 melted without decomposition at 266–268 °C. Mass spectrum: calcd 744, found 744 (see Figure 2).

## Results and Discussion

**Compound Synthesis and Structure.** The reaction of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}]_2$ , or the methylated derivative, with the

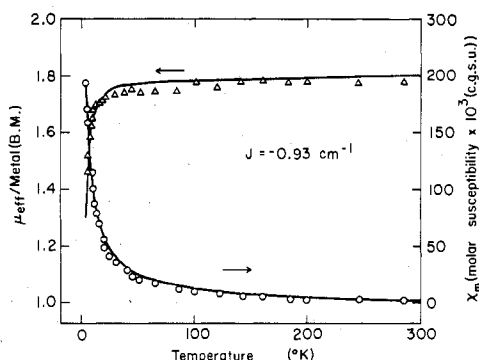


**Figure 1.** Structures of the mononuclear compound (1) bis( $\eta^5$ -cyclopentadienyl)(2-hydroxypyridinato)titanium(III), the binuclear compound (2) uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)], and the trinuclear compound (3) cyanuratotris[bis( $\eta^5$ -cyclopentadienyl)titanium(III)].



**Figure 2.** Mass spectral parent ion peaks for (A) cyanuratotris[bis( $\eta^5$ -cyclopentadienyl)titanium(III)] and (B) cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] where the solid lines (—) are the experimental and the dashed lines (---) are the calculated peak intensities.

sodium salt derived from 2-hydroxypyridine, uracil, or cyanuric acid was used to prepare the compounds bis( $\eta^5$ -cyclopentadienyl)(2-hydroxypyridinato)titanium(III) (1), uracilatobis[bis( $\eta^5$ -cyclopentadienyl)titanium(III)] (2), and cyanuratotris[bis( $\eta^5$ -cyclopentadienyl)titanium(III)] (3), respectively. The presumed molecular structures of these three compounds are sketched in Figure 1. Compound 4, the methyl derivative of 3, was also prepared. All four compounds are air sensitive. Substantiation for the presence of discrete, not polymeric, molecular units was readily obtained with mass spectral data. In each case, the spectrum showed an intense pattern of peaks assignable to the parent ionization peak. Figure 2 illustrates the parent peaks observed in the mass spectra of compounds 3 and 4. In the case of compound 3, the most intense peak occurs at  $m/e$  ratio of 660, which is in accord with a molecular weight of 660. The parent peak is observed at  $m/e$  744 for compound 4 and this also agrees with a molecular weight of 744 for this molecule. Furthermore, as indicated in Figure 2, the patterns of peaks observed in each



**Figure 3.** The temperature dependence of the magnetic susceptibility  $\chi_m$  and the magnetic moment  $\mu_{\text{eff}}$  per Ti(III) ion for the trimetallic compound cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)]. The circles and triangles are experimental points and the solid lines are the theoretical fit with  $J = -0.93 \text{ cm}^{-1}$ ,  $g = 2.08$ , and  $\theta = -0.21 \text{ }^\circ\text{C}$ .

case can be simulated by a computer program to calculate the relative abundances of different isotopes present in the parent ions.

It also seems very reasonable to suggest that the anions of 2-hydroxypyridine, uracil, and cyanuric acid do chelate the Ti(III) ions of the  $(\text{cp})_2\text{Ti}^+$  moieties, as indicated in Figure 1. There are various pieces of evidence to support this suggestion. As noted in the Experimental Section, compounds 3 and 4 do not decompose appreciably at temperatures up to  $200 \text{ }^\circ\text{C}$ . Also, the parent peaks are the second most intense peaks in the mass spectra. The thermal stability of compounds 1, 2, 3, and 4 probably results from the chelate effect. Additional evidence for a chelate is that compounds 3 and 4 exhibit relatively intense mass spectral signals attributable to the ions  $(\text{cp})_2\text{Ti}(\text{NCO})^+$  and  $(\text{Mecp})_2\text{Ti}(\text{NCO})^+$ , respectively. This suggests that the four-member rings stay intact while a fragmentation of the cyanurate molecule occurs.

Three other facts point to the chelated structures. Because the bis(cyclopentadienyl)titanium(III) cation is an electron-deficient center, two other ligands are found to be attached to the metal ion to form a pseudotetrahedral structure in the vast majority of compounds.<sup>15,16</sup> In the case of the 2-hydroxypyridinato anion and other similar ligands, the formation of a chelate results in an 17-electron metal system of greater stability than that expected for a nonchelated 15-electron structure. The strong Ti-O bond (ca. 167 kcal/mol) is a significant factor in the formation of the chelate. Finally, recent studies with bidentate ligands of the form X-Y and X-X, where X and Y are O, N, S, or As, reacting with titanium tetrachloride indicate that heteroatom type X-Y ligands are more tightly bound.<sup>36</sup> Thus, the heteroatomic chelating feature of cyanuric acid anion could optimize the polar and covalent component to the titanium chelate bond and contribute to its strength.

This work provides another example<sup>15,16</sup> where the use of the (methylcyclopentadienyl)titanium species instead of simply the cyclopentadienyltitanium species led to the isolation of highly pure and crystalline products. Cyanuratotris[bis( $\eta^5$ -cyclopentadienyl)titanium(III)] was found to be very slightly soluble in toluene and not at all soluble in hexane, while the methylcyclopentadienyl analogue, compound 4, was found to be soluble in hexane and conveniently recrystallized from toluene. In addition to their ability to increase solubility, (methylcyclopentadienyl)titanium species are of greater utility for X-ray crystallography studies because the methyl group tends to "lock in" the position of the cyclopentadienyl rings, preventing thermal disorder.<sup>30</sup>

**Magnetic Susceptibility of  $[(\eta^5\text{-C}_3\text{H}_4\text{CH}_3)_2\text{Ti}]_3(\text{C}_3\text{H}_3\text{N}_3\text{O}_3)$ .** Variable-temperature (4.2–285.5 K) magnetic susceptibility

**Table I.** Magnetic Susceptibility Data for Cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)]-Toluene<sup>a</sup>

T, K	$10^3 \chi_m$ , cgsu		$\mu_{\text{eff}}/\text{Ti}$ , $\mu_B$	
	Obsd	Calcd	Obsd	Calcd
285.5	4.168	4.361	1.78	1.82
244.6	4.836	5.066	1.78	1.82
203.7	5.824	6.052	1.78	1.81
183.3	6.474	6.708	1.78	1.81
162.8	7.306	7.528	1.78	1.81
143.5	8.266	8.513	1.78	1.80
122.5	9.468	9.934	1.76	1.80
102.8	11.42	11.79	1.77	1.80
86.1	12.98	14.01	1.73	1.79
65.7	16.73	18.22	1.71	1.79
52.0	21.27	22.84	1.72	1.78
45.5	24.68	25.97	1.73	1.77
38.6	29.40	30.40	1.74	1.77
31.4	35.77	36.99	1.73	1.76
23.1	48.11	49.33	1.72	1.74
19.4	56.84	57.94	1.71	1.73
15.9	69.73	69.37	1.71	1.71
14.0	77.19	77.67	1.70	1.70
12.3	86.27	86.95	1.68	1.69
10.5	100.7	99.49	1.68	1.67
8.8	115.8	115.1	1.65	1.64
7.7	127.6	127.9	1.62	1.62
6.8	143.4	140.6	1.61	1.60
5.8	161.9	157.7	1.58	1.56
5.1	170.9	172.1	1.52	1.53
4.2	191.6	194.3	1.46	1.48

<sup>a</sup> Diamagnetic correction:  $-548 \times 10^{-6}$  cgsu/mol.  $J = -0.93 \text{ cm}^{-1}$ ,  $g = 2.08$ ,  $\Theta = -0.21 \text{ K}$ , TIP = 0.

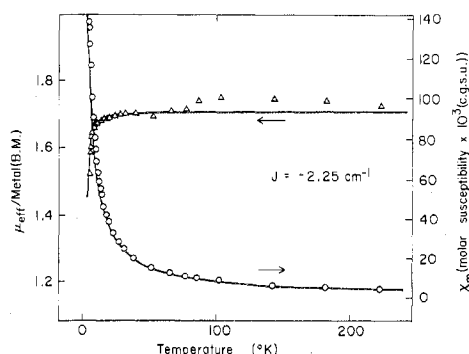
data were collected for a powdered sample of the only analytically pure trinuclear complex, compound **4**. The data are summarized in Table I and are illustrated in Figure 3. The value of  $\mu_{\text{eff}}/\text{Ti}$  varies from  $1.78 \mu_B$  at 285.5 K to  $1.46 \mu_B$  at 4.2 K. As can be seen in Figure 3, most of the decrease in  $\mu_{\text{eff}}/\text{Ti}$  occurs at low temperature. There is clearly an antiferromagnetic exchange interaction present in this trinuclear complex.

The magnetic exchange interaction in an equilateral triangular arrangement of three  $S = 1/2$  ions can be treated with one exchange parameter. Thus, for compound **4** there is one  $J$  value which gauges the interaction of any one of the Ti(III) ions with its neighbor. The interaction of the three  $S = 1/2$  ions leads to three electronic states for the trinuclear molecule. One molecular state is a spin quartet with a total spin,  $S'$ , of  $3/2$ . There are also two doublet states, each with  $S' = 1/2$ . Within this simple model of an isotropic exchange interaction, both of the doublet states have the same energy, which we will take as zero. The quartet state is found at an energy of  $-3J$ . Thus, when there is an antiferromagnetic interaction,  $J$  is negative and the quartet state is at higher energy than the two degenerate doublet states. The molar paramagnetic susceptibility for such a trinuclear system can be written as<sup>24</sup>

$$\chi_M = \frac{Ng^2\beta^2}{4k(T-\Theta)} \left[ \frac{1 + 5 \exp(3J/kT)}{1 + \exp(3J/kT)} \right] + N\alpha \quad (1)$$

where  $N$  is Avogadro's number,  $g$  is the average electronic  $g$  factor,  $\beta$  is the Bohr magneton,  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\Theta$  is the Weiss constant, and  $N\alpha$  is the TIP correction.

The data for compound **4** were least-squares fit to eq 1 to give  $J = -0.93 \text{ cm}^{-1}$ ,  $g = 2.08$ , and  $\Theta = -0.21 \text{ }^\circ\text{C}$  so that the quartet state is  $2.79 \text{ cm}^{-1}$  at higher energy than the two doublets. In Figure 3, the least-squares fit is represented by solid lines and it can be seen that the fit to the data is reasonable. The quartet state is populated even at 4.2 K. If only



**Figure 4.** The temperature dependence of the magnetic susceptibility  $\chi_m$  and the magnetic moment  $\mu_{\text{eff}}$  per Ti(III) ion for the bimetallic compound uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)]. The circles and triangles are experimental points and the solid lines are the theoretical fit with  $J = -2.25 \text{ cm}^{-1}$ ,  $g = 1.97$ , and  $\Theta = 1.5 \text{ K}$ .

the doublet states were populated at 4.2 K, the  $\mu_{\text{eff}}/\text{Ti}$  should be  $1.00 \mu_B$ , whereas the observed value is  $1.46 \mu_B$ . It was found that a reasonable variation of TIP had little effect on the  $J$  value obtained. This was of concern, because there are no accurate values of TIP for trinuclear Ti(III) complexes. The fit given in Figure 3 assumes that  $N\alpha = 0$ . No attempt was made to obtain magnetic susceptibility data for cyanuratotris[bis( $\eta^5$ -cyclopentadienyl)titanium(III)], because the compound could not be prepared sufficiently pure.

This work represents the first study of paramagnetic trinuclear titanium compounds and the only comparison possible is with the data on various Cu(II) trimers. A trimeric complex was proposed<sup>24</sup> for *N*-[2-(2-hydroxyethylthio)phenyl]-4-toluenesulfonamidatocopper(II) based on the fit of susceptibility data to eq 1 and on the observed molecular weight in chloroform. The  $\mu_{\text{eff}}/\text{Cu}$  for this compound was found to be  $1.26 \mu_B$  at  $25 \text{ }^\circ\text{C}$ . The proposed structure involved alkoxide oxygen atoms bridging between the copper ions set in an equilateral triangular arrangement. The  $J$  value was obtained by fitting the data and it was reported as  $-114 \text{ cm}^{-1}$ .

Hatfield and Bunger<sup>25</sup> reported a trimeric Schiff base copper(II) complex where  $\mu_{\text{eff}}/\text{Cu}$  varied from  $1.3 \mu_B$  at room temperature to  $1.0 \mu_B$  at  $77 \text{ K}$ . Again, the proposed structure was one of an equilateral triangular arrangement of Cu(II) ions with phenoxy oxygen atoms bridging between the metal ions. No attempt was made to evaluate  $J$ . The most thoroughly characterized trinuclear copper(II) complexes are compounds of the composition  $\text{Cu}_3\text{L}_3(\text{OH})$ , where L is pyridine-2-carboxaldehyde oxime.<sup>6</sup> A crystal structure analysis has confirmed that the copper ions and the hydroxide ion are in a "tripod" arrangement such that all three copper ions are bonded to the single hydroxide ion at the apex. It is not surprising that the antiferromagnetic interaction is so strong that from 105 to 401 K the observed  $\mu_{\text{eff}}/\text{Cu}$  is constant at  $1.0 \mu_B$ . The exchange parameter cannot be evaluated in this case because it is so large. In summary, all the trinuclear Cu(II) systems which have been studied have significantly greater antiferromagnetic interactions than we observed for the one cyanurato trimer.

**Magnetic Susceptibility of  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{Ti}]_2(\text{C}_4\text{H}_4\text{O}_2\text{N}_2)$ .** In view of the weak antiferromagnetic interaction observed for the trinuclear titanium(III) cyanurato compound, it was anticipated that uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] would also exhibit a similar weak interaction. The susceptibility data for this compound are given in Table II and Figure 4. Even without fitting data it is clear from the decrease in  $\mu_{\text{eff}}/\text{Ti}$  at low temperature that this compound also displays a weak antiferromagnetic exchange interaction. The Bleaney-Bowers equation<sup>26</sup> given below

**Table II.** Magnetic Susceptibility Data for Uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)]<sup>a</sup>

T, K	10 <sup>3</sup> χ <sub>m</sub> , cgsu		μ <sub>eff</sub> /Ti, μ <sub>B</sub>	
	Obsd	Calcd	Obsd	Calcd
224.1	3.298	3.247	1.72	1.71
183.3	4.120	4.971	1.74	1.71
142.6	5.329	5.329	1.74	1.71
102.8	7.409	7.074	1.74	1.71
86.1	8.779	8.443	1.74	1.71
76.9	9.486	9.451	1.71	1.70
65.7	11.03	11.06	1.70	1.70
52.0	13.67	13.96	1.69	1.70
38.6	18.58	18.77	1.69	1.70
31.4	22.85	23.04	1.69	1.70
27.4	26.10	26.36	1.69	1.70
23.1	30.77	31.19	1.69	1.70
19.4	36.44	37.02	1.68	1.69
17.7	39.93	40.48	1.68	1.69
15.9	44.33	44.93	1.68	1.69
14.0	50.11	50.80	1.68	1.69
13.2	53.04	53.74	1.67	1.68
12.3	56.59	57.48	1.67	1.68
11.4	60.82	61.76	1.67	1.68
10.5	66.60	66.70	1.67	1.67
9.5	72.02	73.17	1.67	1.67
8.8	78.65	78.44	1.66	1.66
7.7	88.57	88.35	1.65	1.65
6.8	98.62	98.32	1.64	1.64
5.8	114.2	111.9	1.63	1.61
5.1	125.1	123.4	1.60	1.59
4.6	134.1	131.7	1.58	1.57
4.2	136.7	140.7	1.52	1.54

<sup>a</sup> Diamagnetic correction:  $-340 \times 10^{-6}$  cgsu/mol. Parameters used to get calculated values:  $J = -2.25$  cm<sup>-1</sup>,  $g = 1.97$ ,  $\Theta = 1.5$  K, and TIP = 0.

describes the molar paramagnetic susceptibility for such a dimer.

$$\chi_M = \frac{2Ng^2\beta^2}{3k(T - \Theta)} [1 + \frac{1}{3} \exp(-2J/kT)]^{-1} \quad (2)$$

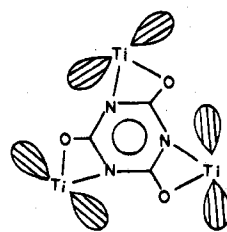
Least-squares fitting the data for compound **2** gives  $J = -2.25$  cm<sup>-1</sup>,  $g = 1.97$ , and  $\Theta = 1.5$  K. As before, the theoretical fit is represented by the solid lines in Figure 4. No correction for TIP was made.

The magnetic properties of several binuclear titanium(III) compounds with bridging halide ions have been studied in detail. The dimers  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}]_2$ ,  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)\text{TiCl}]_2$ , and  $[(\eta^5\text{-C}_5\text{H}_4\text{CH}_3)_2\text{TiBr}]_2$  have exchange parameters of -111, -160, and -138 cm<sup>-1</sup>, respectively.<sup>15</sup> For these molecules it was found that as the metal-metal distance decreases in the chloride-bridged dimers, the magnitude of antiferromagnetic interaction increases which was taken to be consistent with an exchange pathway involving an appreciable amount of direct overlap of metal orbitals.

Several other dibridged titanium(III) dimers have been synthesized which should have structures similar to those of the dihalide-bridged systems. The compounds  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2]_2$ ,<sup>27</sup>  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiPR}_2]_2$  (R = C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>4</sub>H<sub>9</sub>),<sup>28</sup> and  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiSPh}]_2$ <sup>29</sup> are reported to be diamagnetic while  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiOR}]_2$ , R = C<sub>2</sub>H<sub>5</sub> and C<sub>6</sub>H<sub>5</sub>,<sup>29</sup> are weakly paramagnetic at room temperature.

Extended bridges propagate the exchange interaction between (cp)<sub>2</sub>(Ti<sup>III</sup>)<sup>+</sup> moieties in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}^{\text{III}}]_2\text{ZnX}_2$ , where X = Cl and Br.<sup>15</sup> The tetrahalozincate dianion bridges result in antiferromagnetic interactions with  $J$  values of -8.93 and -15.66 cm<sup>-1</sup>, respectively. In these two molecules, the weaker interaction is clearly of the superexchange type.

Without a crystal structure it is probably not possible to present a detailed description of the Ti(III)-Ti(III) exchange pathway present in cyanuratotris[bis( $\eta^5$ -methylcyclopenta-



**Figure 5.** Proposed locations according to the Alcock model for the unpaired electrons on nonbonding titanium orbitals in cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)]. The methylcyclopentadienyl rings have been removed for clarity.

**Table III.** Theoretical Fit of X-Band EPR Spectrum for a Toluene-Benzene Glass (4:1) at 77 K of Uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] to a  $D$  of 0.0117 (8) cm<sup>-1</sup> and an  $E$  of 0.018 (4) cm<sup>-1</sup>

Peak <sup>a</sup>	Field obsd, G	Field calcd, G
Z	3144	3144
Y	3190	3190
X	3258	3258
X	3326	3325
Y	3378	3377
Z	3397	3397
Half-field ( $\Delta M_s = \pm 2$ )	1633	1639

<sup>a</sup> Peaks are taken as labeled left to right (low field to high field) from Figure 6(2) except for the "forbidden" half-field peak which is not shown.

diene)titanium(III)] and uracilatobis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)]. From studies with molecular models and analysis of crystal structure determinations of metal-uracil compounds, it is possible to estimate a Ti-Ti distance of 5.6-5.8 Å in these compounds. It is interesting that the Ti-Ti distance in  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}]_2\text{ZnCl}_4$  is 6.84 Å and the interaction is of the same order of magnitude.<sup>16</sup> However, such interactions do not depend simply on the metal-metal distance but reflect the symmetries and energies of the bridging unit. Dahl et al.<sup>30</sup> have recently demonstrated by single-crystal EPR experiments and photoelectron spectroscopy that the unpaired electron in the  $d^1$  system,  $(\eta^5\text{-C}_5\text{H}_5)_2\text{VCl}_2$ , is primarily in a molecular orbital of a<sub>1</sub> symmetry (C<sub>2v</sub> point group). The unpaired electron density is primarily in a nonbonding metal orbital which is perpendicular to the twofold symmetry axis of the molecule and is in the plane of the VCl<sub>2</sub> group. Figure 5 illustrates the relative orientation of these three nonbonding metal orbitals for cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)]. The three metal orbitals are located in the plane of the cyanurate trianion. The trinuclear molecule probably has C<sub>3h</sub> symmetry, in which the three orbitals lead to a representation that is reduced to a' + e' in the C<sub>3h</sub> point group. The cyanurate trianion undoubtedly has molecular orbitals of a' and e' symmetry and it is these orbitals that propagate the superexchange interaction. The relatively close  $J$  values for the trinuclear cyanurate and binuclear uracilato compounds strongly suggest that there are similar exchange pathways in the two molecules.

**EPR Studies.** The room-temperature X-band EPR spectra of compounds **1**, **2**, and **4** as powdered solids exhibited nearly identical unstructured single-derivative peaks. There were no temperature dependencies observed down to ca. 123 K. The only observable difference between the spectra of the three solids was that the line width increased uniformly in the progression from the monomer to the trimer (120 G for **1**, 180 G for **2**, and 240 G for **4**). This trend could result from increased dipolar broadening with the addition of paramagnetic metal centers to the molecule. With DPPH as a standard, the powdered samples gave identical  $g$  values within the experimental error as is shown in Table III. The fact that all the

Table IV. EPR Parameters for the Titanium(III) Mononuclear, Binuclear, and Trinuclear Complexes

Compound	$g_{av}^a$	$g_x g_y g_z^b$	$ D ,^b \text{ cm}^{-1}$	$ E ,^b \text{ cm}^{-1}$	$A,^c \text{ G}$
1	1.978 (4) (120 G)	2.00 (1) 1.98 (1) 1.96 (1)			8.6 (2)
2	1.979 (4) (180 G)	1.99 (1) 1.98 (1) 1.97 (1)	0.0117 (4)	0.0018 (4)	
3	1.978 (4) (240 G)	X band <sup>d</sup> $\left\{ \begin{array}{l} 2.088 (5) \\ 2.056 (5) H_{xzy_1} \\ 1.997 (5) D_2 \\ 1.993 (5) H_{xzy_2} \\ 1.957 (5) D_3 \\ 1.931 (5) H_{xzy_2} \\ 1.831 (5) \end{array} \right.$ Q band $\left\{ \begin{array}{l} 2.012 (2) D_1 \\ 2.010 (2) H_{xzy_1} \\ 1.992 (2) H_{xzy_2} \\ 1.979 (2) D_2 \\ 1.976 (2) H_{xzy_2} \\ 1.956 (2) D_3 \end{array} \right.$	0.0095 (8)		

<sup>a</sup> Polycrystalline powder at 24 °C with DPPH ( $g = 2.0036$ ) as an internal standard. Number in parentheses is the line width. <sup>b</sup> Spectra taken as a glass at 77 K (toluene-benzene (4:1)). The values of  $D$  and  $E$  are absolute values. <sup>c</sup> Solution (toluene-benzene (4:1)) at 24 °C.  $A$  for  $^{47}\text{Ti}$  ( $I = 5/2$ ) equals  $A$  for  $^{49}\text{Ti}$  ( $I = 7/2$ ). <sup>d</sup> The  $g$  values for each peak in the X-band and Q-band spectra are given with labels used in Figure 7.

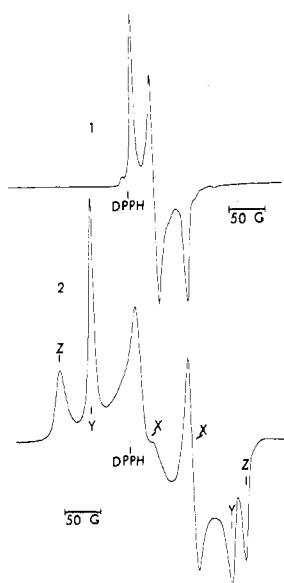


Figure 6. X-Band EPR spectra taken at 77 K in a toluene-benzene (4:1) glass of bis( $\eta^5$ -cyclopentadienyl)(2-hydroxypyridinato)titanium(III) (upper tracing) and uracilato[bis[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] (lower tracing).

$g$  values are near the free-electron value of 2.0023 is in accord with the fact that the metal ions are  $d^1$  species with little spin-orbit coupling.

One of the goals of this study was to prepare neutral polynuclear transition-metal complexes that would dissolve in various solvents and remain intact. This would permit solution EPR studies. The mass spectral observation of relatively intense parent peaks for compounds 2, 3, and 4 demonstrated the stability of these compounds.

Room-temperature solution X-band spectra of compounds 2 and 4 dissolved in a toluene-benzene (4:1) solvent showed single-derivative signals, each about 80 G wide. The mononuclear complex bis( $\eta^5$ -cyclopentadienyl)(2-hydroxypyridinato)titanium(III) also gave a single derivative under the same conditions; however, titanium hyperfine for  $^{47}\text{Ti}$  ( $I = 5/2$ , 7.75% abundance) and  $^{49}\text{Ti}$  ( $I = 7/2$ , 5.51%) could be observed. The observed splitting ( $A$  value) is 8.6 (2) G for both isotopes.

More informative EPR spectra were obtained for toluene-benzene (4:1) glasses at ca. 77 K. Figure 6, upper tracing, shows the X-band glass spectrum for mononuclear compound 1, a typical rhombic spectrum. The three  $g$  values are given in Table III and are reasonable for such a titanium(III) metallocene.

The glass spectrum of the binuclear uracilato compound (2) in Figure 6 is more complex than that of compound 1 and reflects the interaction of two metal centers. The spectrum of compound 2 is interpretable as a triplet state signal showing the effects of zero-field splitting. Similar triplet state spectra have been reported by several others,<sup>11,31-33</sup> and we have very recently observed triplet spectra from other Ti(III) dimers.<sup>34</sup> Excluding the isotropic magnetic exchange term ( $-2J\hat{S}_1\hat{S}_2$ ), the usual spin Hamiltonian for an  $S = 1$  system in a low-symmetry ligand field is

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

In this equation,  $D$  is the axial zero-field splitting parameter and  $E$  is the nonaxial (rhombic) zero-field splitting parameter. For randomly oriented triplet state molecules, Wasserman et al.<sup>31a</sup> used the above Hamiltonian to derive a set of equations for the resonance fields of the six  $\Delta M_s = 1$  transitions. These equations are

$$\begin{aligned} H_{x_1} &= \frac{2.0023}{g_x} [(H_0 - D + E)(H_0 + 2E)]^{1/2} \\ H_{y_1} &= \frac{2.0023}{g_y} [(H_0 - D - E)(H_0 - 2E)]^{1/2} \\ H_{z_1} &= \frac{2.0023}{g_z} [(H_0 - D)^2 - E^2]^{1/2} \\ H_{x_2} &= \frac{2.0023}{g_x} [(H_0 + D - E)(H_0 - 2E)]^{1/2} \\ H_{y_2} &= \frac{2.0023}{g_y} [(H_0 + D + E)(H_0 + 2E)]^{1/2} \\ H_{z_2} &= \frac{2.0023}{g_z} [(H_0 + D)^2 - E^2]^{1/2} \end{aligned} \quad (4)$$

In these equations,  $H_0$  stands for the magnetic field expected for a free electron (depends upon the microwave frequency used) and  $D$  and  $E$  are expressed in gauss. A least-squares fitting computer program was written that incorporated the above equations.

The six features in the spectrum of the uracilato compound (2), see Figure 6, were assigned to the various zero-field split transitions and the six resonance fields were least-squares fit to eq 4 to get two parameters,  $|D| = 0.0117$  (8)  $\text{cm}^{-1}$  and  $|E| = 0.0018$  (4)  $\text{cm}^{-1}$ . The sign of the zero-field splitting parameters cannot be determined by this procedure. In Table IV are listed the observed resonance fields and the resonance fields calculated with these two parameters. As can be seen, there is excellent agreement. Wasserman et al.,<sup>31a</sup> also give

an expression for the resonance field of the  $\Delta M_s = 2$  transition and this calculates to be 1639 G in this case, which compares very favorably with the position (1633 G) of the observed "half-field" resonance. It should be pointed out that the distortion of the expected line shape of the triplet spectrum just to the high-field side of the DPPH mark in Figure 6 (2) can be ascribed to the presence of a small amount of monomeric Ti(III) compound which may be present either as an impurity or as the result of an equilibrium setup upon dissolution that produces a small percent of a monomeric species in solution.

The  $D$  value for the uracilato compound has contributions from both dipole-dipole ( $D_{dd}$ ) interactions and pseudodipolar ( $D_b$ ) terms. The latter term results from spin-orbit admixture of excited states into the triplet state and it is usually assumed to be small when the ground-state exchange parameter is small. We will assume that the pseudodipolar term is small for the uracil compound. Chasteen and Belford<sup>35</sup> have shown that the dipolar term,  $D_{dd}$ , can be related to the metal-metal distance ( $R$ ) by the formula

$$R = (0.650g^2/D_{dd})^{1/3} \quad (5)$$

With this equation and the experimental values  $g = 1.979$  and  $D_{dd} = 0.0117 \text{ cm}^{-1}$ , the Ti-Ti distance in the uracilato compound is calculated to be 5.93 Å. This calculated distance is close to the 5.6–5.8 Å value obtained from molecular models.

The small singlet-triplet separation is 4.50  $\text{cm}^{-1}$  for the uracilato compound, 2, and thus even at 77 K both the singlet and triplet states are populated. Because the singlet state is EPR inactive, only a triplet state spectrum is observed. In contrast, the trinuclear cyanurato compound 4 has three EPR active states populated at 77 K as a result of the small doublet-quartet separation of 2.8  $\text{cm}^{-1}$ . The two doublet states have the same energy and could have very similar  $g$  values. Computer simulations of the quartet state spectrum for an axial organic triradical with no hyperfine contributions have been reported.<sup>8,10</sup> The spin Hamiltonian employed is

$$\mathcal{H} = \beta \hat{S}_z \hat{H} + D(\hat{S}_z^2 - 1/3S^2 - 1/3) \quad (6)$$

The 77 K X-band EPR spectrum of a toluene-benzene (4:1) glass of cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)], compound 4, is illustrated by the top tracing in Figure 7. Six signals are evident in this spectrum and the  $g$  values are summarized in Table III. The EPR spectrum expected for the quartet state of such a molecule has been shown to consist of five signals. If there is only axial zero-field splitting in the quartet state (i.e., eq 6), then the spacing between nearby signals in this pattern of five is  $D$ , the axial zero-field splitting parameter. As indicated in Figure 7 (top), there are three relatively intense features that are assignable to the quartet signal. The most intense feature at  $g = 1.993$  results from the  $m = -1/2$  to  $m = 1/2$  transition, whose intensity is independent of molecular orientation and always is the most intense feature in the quartet spectrum. This signal is identified as  $H_{xyz}$ . The other two signals at  $g = 1.931$  and 2.056, identified as  $H_{xy2}$  and  $H_{xy1}$ , respectively, are of medium intensity and originate as  $m = \pm 3/2$  to  $m = \pm 1/2$  transitions for molecules whose magnetic  $x, y$  plane is parallel to the magnetic field. Two much weaker signals are expected on either side of the three observed signals and these two signals are  $m = \pm 3/2$  to  $m = \pm 1/2$  transitions for molecules whose magnetic  $z$  plane is parallel to the magnetic field. At present, it is not known why these last two signals are not seen. Perhaps, the intensity of these two signals is dependent on the  $D$  value, which is relatively large in this case. Or, perhaps there is some nonaxial zero-field splitting which might account for their very low intensity. Nevertheless, the spacing between the three observed quartet signals gives  $|D| = 0.0095$  (3)  $\text{cm}^{-1}$ .

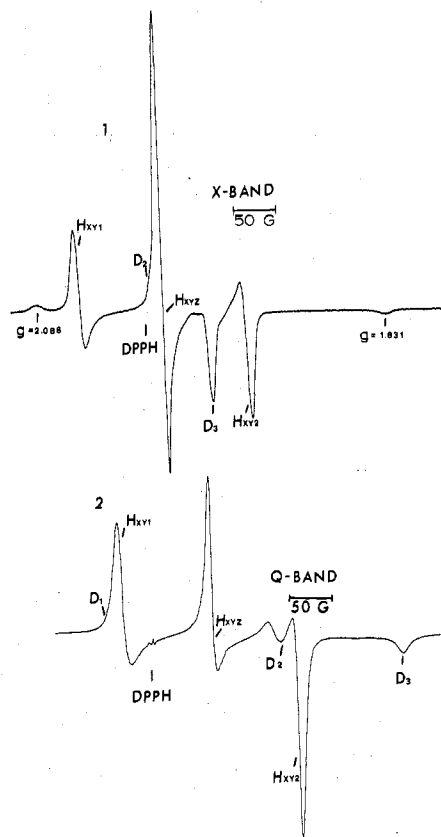


Figure 7. X-Band (1) and Q-band (2) EPR signal for a toluene-benzene (4:1) glass at 77 K of cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)].

Before we discuss the other signals observed in the X-band spectrum of cyanuratotris[bis( $\eta^5$ -methylcyclopentadienyl)titanium(III)] in Figure 7, it is best to examine additional evidence in support of the above assignment of quartet signals. The lower tracing in Figure 7 is the 77 K glass Q-band spectrum for the same compound. As can be seen, there are some changes. However, the grouping of three signals assigned to the quartet state is *unchanged* with respect to the magnetic field separations between the three. This is as it should be, because the spacing between the signals is equal to the zero-field splitting parameter. The zero-field interaction is independent of the magnetic field. This substantiates the assignment of these three features. It is also important to note that the  $|D|$  value observed for the cyanurato compound is quite close to that observed for the uracilato compound.

There are several additional signals to be assigned in the X- and Q-band spectra of the cyanurato compound in Figure 7. It seems reasonable to assume that the two doublet states which are at the same energy might have the same principal  $g$  values. Table III shows that the  $g$ -value pattern observed for the binuclear uracilato compound is essentially the same as the pattern observed for the analogous mononuclear complex. This same pattern would probably be expected for the doublet states. In the X-band spectrum of the cyanurato compound, there is a signal observed at  $g = 1.957$ . This is designated as  $D_3$  because it is probably the high-field signal for the doublet states. The same signal is also seen in the Q-band spectrum. The Q-band spectrum also shows a signal at  $g = 1.979$ , designated as  $D_2$ . This is probably the intermediate-field signal for the doublets. The low-field doublet state signal would be expected at a  $g$  value of ca. 2.00 and is obscured by the  $H_{xy1}$  resonance. Further and more detailed work is needed to be sure of these assignments. This is made even more evident by the appearance of two unexplained signals in the X-band spectrum. These are the weak signals

at  $g = 2.088$  and  $1.831$ . There was no very low-field signal at  $g = 2.088$  seen in the Q-band spectrum. In several spectra, however, a signal at  $g = 1.922$  was observed in the Q-band spectrum.

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Contribution from the School of Chemical Sciences and the Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

## Magnetic Exchange between Titanium(III) Centers in a Series of Linear Trimetallic Compounds and the Structural Properties of Bis[ $\mu$ -dichloro-bis(cyclopentadienyl)titanium(III)]manganese(II)-Bis(tetrahydrofuran), $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}]_2\text{MnCl}_2 \cdot 2\text{OC}_4\text{H}_8$

DENNIS SEKUTOWSKI, RUDOLPH JUNGST, and GALEN D. STUCKY\*

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The magnetic properties of a series of  $d^1$  titanium(III) complexes of general formula  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiX}]_2\text{MX}_2$  ( $X = \text{halide}$ ,  $M = \text{Zn, Be, Mn}$ ) have been determined. From variable-temperature magnetic susceptibility measurements, an intramolecular antiferromagnetic interaction between the  $d^1$  centers of those compounds containing a diamagnetic ( $d^0$  or  $d^{10}$ ) central metal atom has been observed. The triplet state has been found to be between  $31.4$  and  $13.8 \text{ cm}^{-1}$  above the singlet ground state. Although the magnitude of the exchange coupling constant is larger than one would expect for an intermolecular exchange interaction, it is much lower than what has previously been observed in titanium(III) halide dimers of general formula  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiX}]_2$ . Single-crystal X-ray diffraction methods have been employed to determine the molecular structure of  $[(\eta^5\text{-C}_5\text{H}_5)_2\text{TiCl}]_2\text{MnCl}_2 \cdot 2\text{OC}_4\text{H}_8$ . This material crystallizes in the monoclinic space group  $P2_1/c$  ( $C_{2h}^5$ ) with two dimers in a unit cell of dimensions  $a = 8.167$  (5) Å,  $b = 11.453$  (8) Å,  $c = 16.249$  (12) Å, and  $\beta = 91.64$  (3)°. Least-squares refinement of 2768 independent reflections has led to a final weighted  $R$  factor of 0.057. The structure consists of a linear trimetallic molecule with chlorine atoms bridging the metal atoms. The geometry around the central manganese atom is tetragonal as opposed to the pseudotetrahedral geometry of the central atom in the other members of the series. The tetrahydrofuran molecules are coordinated in a trans geometry to the manganese atom and the cyclopentadienyl rings on each titanium atom are eclipsed. Attempts have been made to simulate the magnetic susceptibility of this compound with theoretical equations including both terminal interactions  $\text{Ti}(d^1)\text{-Ti}(d^1)$  and nearest-neighbor interactions  $\text{Ti}(d^1)\text{-Mn}(d^1)$ . The fit was only sensitive to  $J_{1/2,5/2}$  and this was found to be  $-8 \text{ cm}^{-1}$ .

## Introduction

Interest in magnetic interactions has greatly expanded over the last few years. A number of recent reviews have indicated the success that workers in this field have had in correlating the magnitude of the magnetic coupling constant to both structural parameters and molecular orbital calculations for

dimeric metal complexes.<sup>1-3</sup> The results have been particularly useful in the understanding of exchange mechanisms. However, very few studies have been undertaken to examine the magnetic properties of trimetallic systems.

Three metals can be geometrically arranged in a triangular or linear configuration. Magnetic exchange in homonuclear