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Preparation and Physical Properties of Binuclear Bis(η^5-cyclopentadienyl)titanium(III) Complexes Bridged by the Dianions of Thymine, 3,6-Dihydroxypyridazine, 2,3-Dihydroxyquinoxaline, and Related Molecules

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The preparation and characterization of 10 new binuclear titanium(III) metallocenes are reported. One mole of a heterocycle is oxidatively added to 2 mol of (η^5-C_5H_5)$_2$Ti(CO)$_2$ to give binuclear (η^5-C_5H_5)$_2$Ti-bridge-Ti(η^5-C_5H_5)$_2$ complexes where the bridging species is the dianion of thymine, 3,6-dihydroxypyridazine, 2,3-dihydroxyquinoxaline, or related heterocycles. The binuclear nature of the complexes is established with mass spectral and EPR data. Each bridging species is bis bidentate and chelates each metal ion in a four-membered ring. A weak antiferromagnetic exchange interaction is found for each of the complexes. Triplet-state EPR spectra establish the *intra*molecular nature of the interaction and allow a determination of the Ti–Ti distance in each complex. Substitution of the 2,4-pyrimidinedianate (uracil dianion) bridge does not appreciably affect the magnitude of the exchange interaction where the range of exchange parameters is $J = -1.3$ to -2.2 cm^{-1}. The 3,6-dihydroxypyridazinate- and 2,3-dithioquinoxalinate-bridged complexes exhibit the strongest exchange interactions with $J = -6.9$ and -7.3 cm^{-1}, respectively.

Introduction

Recent results[4] from these laboratories have shown that bis(η^5-cyclopentadienyl)titanium 2,2′-bipyridyl has a thermally accessible triplet state. This triplet corresponds to a state in which one unpaired electron formally occupies a molecular orbital which is localized on the (η^5-C_5H_5)$_2$Ti moiety, while the second unpaired electron resides in the lowest π^* orbital of the chelating bipyridyl group. It was the observation of this transfer of an electron from the metal to a ligand that led us to further investigate magnetic exchange and electron transfer in binuclear complexes in which (η^5-C_5H_5)$_2$Ti moieties are bridged by anions of organic species such as pyrazole,[5] biimidazole,[5] and various substituted pyrimidines and related compounds.[6-9] These complexes were generally prepared by the reaction over several days of the sodium salt of the ligand with [(η^5-C_5H_5)$_2$TiCl]$_2$.

Floriani and co-workers[10-15] have found dicarbonylbis(η^5-cyclopentadienyl)titanium(II) to be a useful reagent in a number of reactions with organic molecules, including those with active protons. In this paper, we report a novel procedure using (η^5-C_5H_5)$_2$Ti(CO)$_2$ for the synthesis of 10 new binuclear titanium(III) complexes bridged by the dianions of thymine (5-methyl-2,4-pyrimidinedione) 3,6-dihydroxypyridazine, 2,3-dihydroxyquinoxaline, and related heterocycles. The 10 new complexes are illustrated in Figure 1. Variable-temperature magnetic susceptibility and EPR data are presented to characterize the complexes.

Experimental Section

Physical Measurements. EPR studies were performed primarily on a Varian E-9 X-band spectrometer operating in the range of 9.1–9.5 GHz. Several spectra were also obtained with use of a Varian E-15 Q-band spectrometer operating at 35 GHz. The X-band microwave frequency was determined with a Hewlett-Packard Model 5240A 12.4-GHz digital frequency meter while the Q-band frequency was calibrated with DPPH ($g = 2.0036$). Solution samples were run in a toluene/benzene solution (4:1) with use of sealed sample tubes. The quartz tubes were loaded in an inert-atmosphere box and then degassed and sealed on a vacuum line.

Variable-temperature (4.2–270 K) magnetic susceptibility measurements were made with a Princeton Applied Research Model 150A vibrating-sample magnetometer that was operated at 13.5 kG with $CuSO_4 \cdot 5H_2O$ as the standard. The compounds were loaded into press-fit Kel-F sample cells in the inert-atmosphere box.

Computer calculations were performed on an IBM-360 at the University of Illinois and on a DEC-20 computer at the Materials Research Laboratory. The qualitative gas chromatographic data were obtained on a system equipped with a 2–3-ft column containing 13X molecular sieves and a thermal conductivity detector.

Compound Preparation. Most of the synthetic work was performed in a Vacuum Atmosphere inert-atmosphere box employing a helium atmosphere. 2,3-Quinoxalinedithiol was purchased from Eastman Organics. All other ligands were obtained from Aldrich. Bis(η^5-cyclopentadienyl)titanium dichloride was purchased from Alfa and Pressure Chemicals. Dicarbonylbis(η^5-cyclopentadienyl)titanium(II) was prepared by literature methods.[16] Solvents were distilled from sodium and benzophenone under a nitrogen atmosphere. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences at the University of Illinois. Mass spectra were obtained on a MAT-Varian CH-5 spectrometer.

General Preparation of the Binuclear Bis(η^5-cyclopentadienyl)titanium(III) Complexes. Dicarbonylbis(η^5-cyclcopentadienyl)titanium(II) (2.0 mmol) was added to a solution of the ligand (1.0 mmol) in approximately 75 mL of THF. The mixture was heated to reflux for 10–15 min with stirring. Stirring was continued overnight. The solvent was removed under reduced pressure. The product was then extracted with refluxing hexanes, heptane, or toluene. The filtrate was heated to reflux and allowed to cool. After several days, crystals

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Table I. Analytical Data

complex	% C		% H		% N		% Ti		mass spectrum	
	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
I (5-methyl-2,4-pyrimidinedionato)bis-[bis(η^5-cyclopentadienyl)titanium(III)]	62.52	62.54	5.04	5.15	5.83	5.79	19.95	19.95	480	480
II (6-methyl-2,4-pyrimidinedionato)bis-[bis(η^5-cyclopentadienyl)titanium(III)]	62.52	62.01	5.04	4.88	5.83	6.16	19.95	19.08	480	480
III (5,6-dimethyl-2,4-pyrimidinedionato)-bis[bis(η^5-cyclopentadienyl)titanium(III)]	63.18	63.76	5.30	5.27	5.67	5.84	19.38	19.19	494	494
IV (4,6-dihydroxy-2-methylpyrimidinato)-bis[bis(η^5-cyclopentadienyl)titanium(III)]	62.52	62.68	5.04	4.91	5.83	5.94	19.95	19.87	480	480
V (5-fluoro-2,4-pyrimidinedionato)bis[bis-(η^5-cyclopentadienyl)titanium(III)][a]	59.53	59.53	4.37	4.41	5.78	6.46	19.78	≥19.00	484	484
VI (2,4-quinazolinedionato)bis[bis(η^5-cyclopentadienyl)titanium(III)]	65.14	65.22	4.69	4.54	5.43	5.22	18.55	18.41	516	516
VII (1,4-phthalazinedionato)bis[bis(η^5-cyclopentadienyl)titanium(III)]	65.14	65.12	4.69	4.71	5.43	5.29	18.55	18.30	516	516
VIII (3,6-dihydroxypyridazinato)bis[bis(η^5-cyclopentadienyl)titanium(III)]	61.83	62.33	4.76	4.78	6.01	5.98	20.55	20.27	466	466
IX (2,3-dihydroxyquinoxalinato)bis[bis(η^5-cyclopentadienyl)titanium(III)]	65.14	66.16	4.69	5.01	5.43	4.87	18.55	17.34	516	516
X (2,3-dithioquinoxalinato)bis[bis(η^5-cyclopentadienyl)titanium(III)][b]	6.32	61.72	4.41	4.31	5.11	5.29	17.47	16.94	548	548

[a] % F: calcd, 3.92; found, 4.08. [b] % S: calcd, 11.69; found, 11.65.

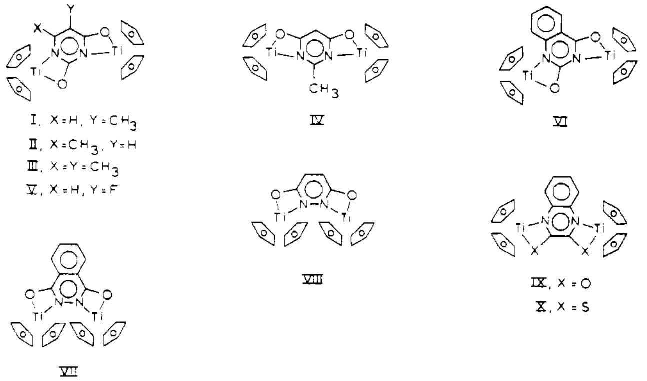
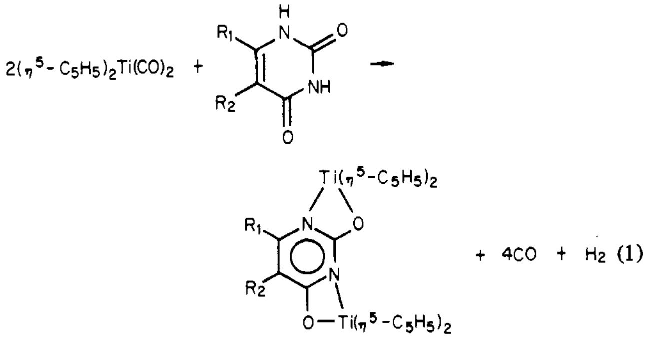


Figure 1. Molecular structures for the binuclear complexes I–X.

formed in most cases. The elemental analyses and mass spectral results for these complexes are found in Table I.

Results and Discussion

Synthesis. A new and novel reaction using dicarbonylbis(η^5-cyclopentadienyl)titanium(II) has been established for the preparation of binuclear titanium(III) metallocenes bridged by the dianions of various substituted uracils and related heterocycles containing N–H, O–H, or S–H bonds. The bridging ligand and $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ are stirred for approximately 12 h in THF. Extraction, followed by recrystallization, gives the binuclear complex (see eq 1).



Recent studies of the reactivity of $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ have shown it to be a useful reagent in such reactions as the deoxygenation and disproportionation of CO_2,[15] the reductive coupling of carbonyl or imine functional groups,[13,14] and the disproportionation of phenyl isocyanate.[13] It is also known that $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ reacts with excess acetic acid to give the titanium(IV) complex, $(\eta^5\text{-}C_5H_5)_2Ti(O_2CCH_3)_2$, CO, and H_2.[10] For qualitative verification of the evolution of H_2 and CO in the reaction scheme reported in this work, the gas above a reaction mixture was injected into a gas chromatograph. The resulting separation clearly showed the evolution of H_2 and CO.

It has also been found that this new procedure is cleaner and faster than that used previously for similar complexes.[5-9] The new complexes reported here are the first examples of titanium(III) complexes prepared by reaction $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$ and ligands containing "active" protons.

As can be seen in Table I, mass spectral data for all 10 of the new complexes establish the binuclear nature of the complexes. Relatively intense parent ion peaks are seen. As before,[6-9] relatively intense peaks are also seen for the $(\eta^5\text{-}C_5H_5)_2Ti(NCO)^+$ or $(\eta^5\text{-}C_5H_5)_2Ti(NCS)^+$ fragment ions. This can be taken as evidence of the presence of four-membered ring chelation in the binuclear complexes (see Figure 1). It is likely, thus, that the 10 new complexes are binuclear by virtue of the dianion of the heterocycle bridging between the two $(\eta^5\text{-}C_5H_5)_2Ti^+$ moieties in a bis-bidentate fashion. This is the mode of bridging that we found[8] recently in the X-ray structure of (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)].

Electron Paramagnetic Resonance Studies. X-Band EPR spectra were obtained from liquid-nitrogen-temperature toluene/benzene (4:1) glasses of the 10 compounds illustrated in Figure 1. All of the complexes with the exception of compound IX gave typical rhombic zero-field split triple-state ($S = 1$) spectra, which establishes the binuclear nature of the complexes. Typical spectra are given in Figure 2 for compounds I–III and V. Six $\Delta M_s = 1$ features are seen in each spectrum, in addition to the formally forbidden $\Delta M_s = 2$ signal at half-field (not shown in Figure 2). On occasion there are some low-intensity features in the middle of the $\Delta M_s = 1$ region, and these are attributable to a doublet ($S = {}^1/_2$) signal from a monomeric Ti(III) species. This monomeric species is probably caused by dissociation of some of the binuclear complex upon dissolution of the binuclear complex.

The triplet state spectra can be described by the spin Hamiltonian expression

$$\hat{H} = \beta\hat{S}\cdot\hat{g}\cdot\hat{H} + D(\hat{S}_z^2 - {}^1\!/_3S^2 - {}^1\!/_3) + E(\hat{S}_x^2 - \hat{S}_y^2) \quad (2)$$

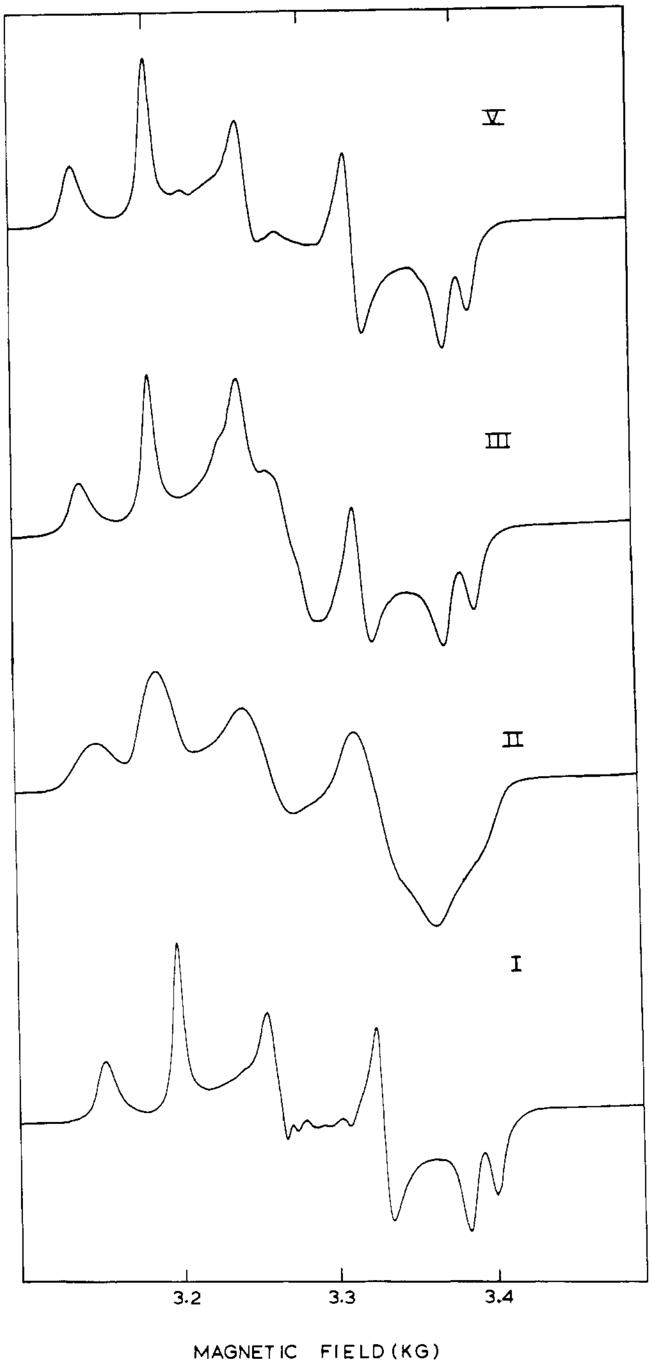


Figure 2. X-Band EPR spectra for liquid-nitrogen-temperature glasses (toluene/benzene, 4:1) of complexes I–III and V.

where D and E are the axial and nonaxial zero-field splitting parameters. Wassermann[17] derived six equations for the resonance field of the six $\Delta M_s = 1$ transitions in terms of the magnetic field expected for a free electron and the zero-field parameters D and E. As we indicated previously,[6] an interative least-squares computer program is employed to fit a spectrum to give values of $|D|$, $|E|$, g_x, g_y, and g_z for the particular complex. The Wassermann equations strictly apply only when the binuclear complex has a center of inversion. If there is no pseudo dipolar zero-field interaction present in the compounds I–X (which seems reasonable), then the magnitude of the axial zero-field splitting is inversely related to the *intra*molecular Ti–Ti distance (R) in a complex. If the direction of the z component of the g tensor is collinear with the Ti–Ti vector, the dipolar axial zero-field splitting, D_{dd}, which is apparent as a splitting of the g_z signal, is given as eq 3.

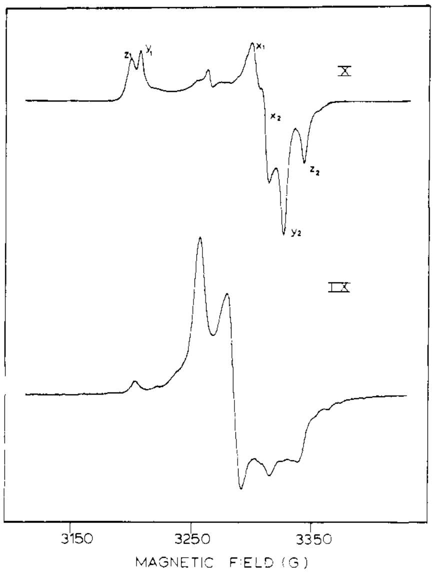


Figure 3. X-Band EPR spectra for liquid-nitrogen-temperature glasses (toluene/benzene, 4:1) of complexes IX and X.

$$D_{dd} = 0.650g_z^2/R^3 \qquad (3)$$

Examination of Figure 1 shows that, in terms of *intra*molecular Ti–Ti distances, there are four types of complexes. The quinoxalinate complexes IX and X have similar Ti–Ti distances. A second type of complex with a relatively long Ti–Ti distance is the 4,6-dihydroxy-2-methylpyrimidinate-bridged complex IV. The series of 2,4-pyrimidinedionate complexes I–III, V, and VI form a third type of complex with an intermediate Ti–Ti distance. The shortest Ti–Ti distance is clearly present in complexes VII and VIII.

As expected, it is found that the X-band EPR spectra reflect the Ti–Ti distances in these complexes. It can be seen in Figure 2 that the EPR signals seen for complexes I–III and V are similar and encompass the same magnetic field range, which indicates that the zero-field splittings are the same for these four complexes. The six magnetic field resonance positions for each compound were least-squares fit to Wassermann's equations[17] to give the parameters in Table II. The axial zero-field splitting parameter, $|D|$, ranges from 0.0110 to 0.0119 cm^{-1}. With an average g value of 1.98, this corresponds to a Ti–Ti distance of 6.0 Å. This calculated distance is close to the 5.6–5.8-Å value obtained from models for the binuclear 2,4-pyrimidinedionate complexes.[6] This agreement is partially fortuitous, because it is clear that the complexes I–III, V, and VI are not centrosymmetric. The principle axis of the zero-field splitting tensor is most likely not collinear with the principle axis of the molecular g tensor. It is of interest to note that, in the series of complexes I–III, V, and VI, there seems to be no appreciable effect of the ring substituent. Only in the case of 6-methyl substitution do the spectral features seem broadened. The g_x, g_y, and g_z values obtained by fitting to Wasserman's equations (see Table II) are not close to those (2.00, 1.98, and 1.96) found[6] for the analogous mononuclear complex bis(η^5-cyclopentadienyl)(2-hydroxypyridinato)titanium(III).

The frozen toluene/benzene glass X-band spectra of the two quinoxalinate-bridged complexes IX and X are illustrated in Figure 3. The sulfur-containing compound X gives a typical spectrum, the resonance fields in which can be fit to give $|D|$ = 0.0063 cm^{-1}. This corresponds to a Ti–Ti distance of 7.4 Å which is reasonable for complex X. Several preparations

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Table II. EPR Parameters[a]

compd	bridge	g_x, g_y, g_z	$\|D\|$, cm^{-1}	$\|E\|$, cm^{-1}
I	5-methyl-2,4-pyrimidinedianate(2–) (thyminate(2–))	1.97, 1.98, 1.98	0.0110	0.0012
II	6-methyl-2,4-pyrimidinedionate(2–)	1.97, 1.98, 1.99	0.0114	0.0017
III	5,6-dimethyl-2,4-pyrimidinedionate(2–)	1.98, 1.98, 1.99	0.0118	0.0019
IV	4,6-dihydroxy-2-methyl-pyrimidinate(2–)	1.99, 1.99, 1.99	0.0078	0.00098
V	5-fluoro-2,4-pyrimidinedionate(2–)	1.97, 1.98, 1.99	0.0119	0.0021
VI	2,4-quinazolinedionate(2–)	1.98, 1.98, 1.99	0.0119	0.0019
VII	1,4-phthalazinedionate(2–)	1.97, 1.98, 2.00	0.0205	0.0015
VIII	3,6-dihydroxypyridazinate(2–)	1.96, 1.99, 2.01	0.0206	0.0020
X	2,3-dithioquinoxalinate(2–)	1.96, 2.00, 1.99	0.0063	0.0016
$[(\eta^5\text{-}(CH_3C_5H_4)_2Ti]_2$(uracilate)[b]	2,4-pyrimidinedionate(2–)(uracilate(2–))	1.99, 1.98, 1.97	0.0117	0.0018
$[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2$(4,6-dihydroxypyrimidinate)[c]	4,6-dihydroxypyrimidinate(2–)	1.97, 1.98, 1.98	0.0077	0.0018

[a] Parameters are taken from X-band EPR spectra of toluene/benzene (4:1) glasses at liquid-nitrogen temperature. [b] Reference 6. [c] Reference 9.

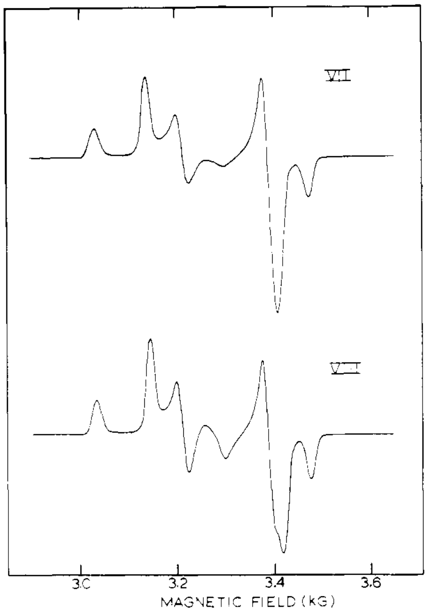

Figure 4. X-Band EPR spectra for liquid-nitrogen-temperature glasses (toluene/benzene, 4:1) of complexes VII and VIII.

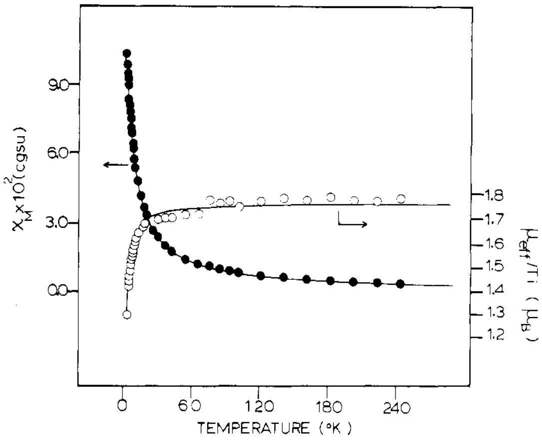

Figure 5. Molar paramagnetic susceptibility and μ_{eff}/Ti vs. temperature curves of complex I. The solid lines represent least-squares fits of the data to the theoretical equations.

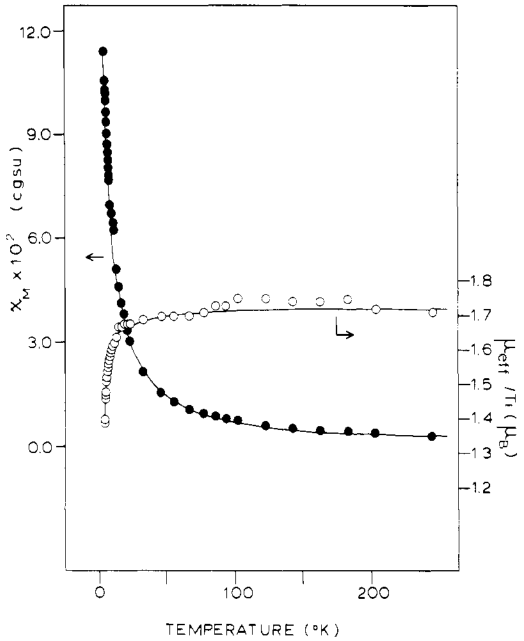

Figure 6. Molar paramagnetic susceptibility and μ_{eff}/Ti vs. temperature curves for complex V. The solid lines represent least-squares fits of the data to the theoretical equations.

of complex IX were examined, and in all cases the frozen glass spectrum was dominated by a three-feature doublet signal. This quinoxalinate complex apparently dissociates appreciably upon dissolution.

The frozen-glass spectra of complexes VII and VIII, illustrated in Figure 4, are very similar. They encompass the largest magnetic field range, in keeping with the fact that the Ti–Ti distance is the shortest in all of the complexes studied. The spectrum for complex VIII was fit to give $|D| = 0.0206$ cm^{-1}, which corresponds to a Ti–Ti distance of 5.0 Å.

Magnetic Susceptibility. In a previous study[6] it was found that the uracilate(2–) ion (dianion of 2,4-pyrimidinedione) propagated an antiferromagnetic exchange interaction of $J = -1.3$ cm^{-1} in a binuclear $[(\eta^5\text{-}C_5H_5)_2Ti^{III}]^+$ complex.[18] In the present study it was of interest to examine what effect substituents on the uracilate(2–) bridge would have on the exchange interaction. It was also of interest to determine how much the magnetic exchange interaction changed in this type of binuclear complex as the bridging unit is changed from uracilate(2–) to quinoxalinate(2–) and pyridazinate(2–).

Variable-temperature magnetic susceptibility data were obtained for compounds I, V, VIII, IX, and X; the data are given in Tables IV–VIII.[19] As can be seen in Figure 5–8 for compounds I, V, VIII, and X, respectively, the compounds all exhibit weak antiferromagnetic exchange interactions.

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(18) The data were taken from ref 6 and refit to the theoretical equation under the conditions that $\theta = 0$, as is used in ref 9.

(19) Supplementary material.

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

compd	peak assignt	field, G obsd	field, G calcd
I	Z1	3150	3169
	Y1	3198	3204
	X1	3262	3267
	X2	3330	3347
	Y2	3346	3363
	Z2	3404	3409
	$\Delta M_s = 2$	1790	1646
II	Z1	3148	3149
	Y1	3189	3190
	X1	3264	3265
	X2	3334	3335
	Y2	3366	3367
	Z2	3393	3394
	$\Delta M_s = 2$	1648	1640
III	Z1	3142	3144
	Y1	3188	3188
	X1	3260	3260
	X2	3324	3325
	Y2	3376	3378
	Z2	3397	3397
	$\Delta M_s = 2$	1648	1639
IV	Z1	3191	3191
	Y1	3216	3216
	X1	3249	3249
	X2	3301	3301
	Y2	3331	3332
	Z2	3359	3359
	$\Delta M_s = 2$	1637	1637
V	Z1	3148	3145
	Y1	3188	3189
	X1	3263	3264
	X2	3327	3325
	Y2	3389	3386
	Z2	3401	3402
	$\Delta M_s = 2$	1635	1641
VI	Z1	3140	3141
	Y1	3188	3189
	X1	3257	3258
	X2	3323	3324
	Y2	3380	3381
	Z2	3396	3397
	$\Delta M_s = 2$	1648	1639
VII	Z1	3032	3036
	Y1	3138	3141
	X1	3215	3218
	X2	3390	3393
	Y2	3408	3411
	Z2	3474	3476
	$\Delta M_s = 2$	1672	1635
VIII[a]	Z1	3034 (12 298)	3031 (12 302)
	Y1	3146 (12 455)	3128 (12 460)
	X1	3213 (12 691)	3229 (12 677)
	X2	3388 (12 827)	3389 (12 836)
	Y2	3420 (12 743)	3412 (12 745)
	Z2	3478 (12 743)	3470 (12 742)
	$\Delta M_s = 2$	1649	1634
X[a]	Z1	3200 (12 614)	3209 (12 610)
	Y1	3208 (12 544)	3299 (12 543)
	X1	3301 (12 818)	3306 (12 817)
	X2	3311 (12 838)	3324 (12 834)
	Y2	3326 (12 656)	3317 (12 661)
	Z2	3344 (12 746)	3345 (12 746)
	$\Delta M_s = 2$	1635	1641

[a] Observed and calculated Q-band EPR resonance fields are given in parentheses.

The variation in magnetic susceptibility as a function of temperature for exchange-interacting binuclear Ti(III) systems should follow the Bleaney–Bowers equation (eq 4).[20] All of

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{2}{3 + \exp(-2J/kT)}\right] + \text{TIP} \qquad (4)$$

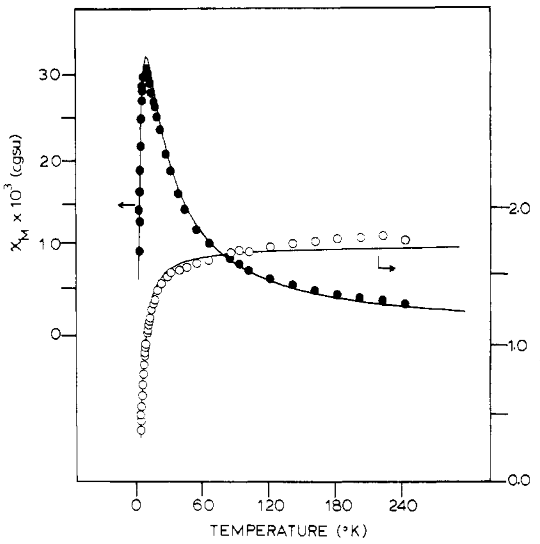

Figure 7. Molar paramagnetic susceptibility and μ_{eff}/Ti vs. temperature curves for complex VIII. The solid lines represent least-squares fits of the data to the theoretical equations.

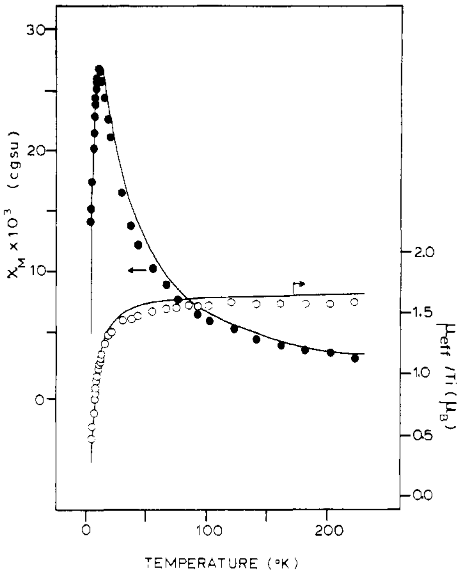

Figure 8. Molar paramagnetic susceptibility and μ_{eff}/Ti vs. temperature curves for complex X. The solid lines represent least-squares fits of the data to the theoretical equations.

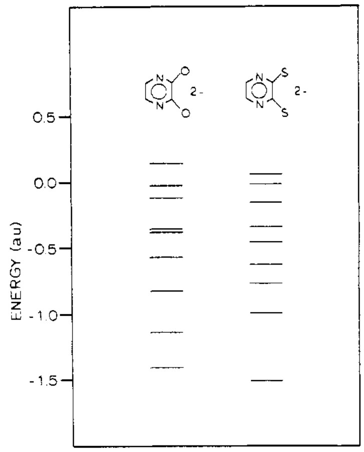

Figure 9. Eigenvalues for the antiferromagnetic exchange propagating molecular orbitals (a_1 symmetry) of modified forms of the dianions of 2,3-dihydroxyquinoxaline and 2,3-dithioquinoxaline.

Table IX. Magnetic Susceptibility Least-Squares Fitting Parameters[a]

compd	bridge	J, cm^{-1}	g
I	5-methyl-2,4-pyrimidinedionate(2−) (thyminate(2−))	−2.2	2.05
V	5-fluoro-2,4-pyrimidinedionate(2−)	−1.7	1.99
VIII	3,6-dihydroxypyridazinate(2−)	−6.9	2.05
IX	2,3-dihydroxyquinoxalinate(2−)	−1.7	1.96
X	2,3-dithioquinoxalinate(2−)	−7.3	1.94
$[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2$(uracilate)[b]	2,4-pyrimidinedionate(2−) (uracilate(2−))	−1.3	1.99
$[(\eta^5\text{-}CH_3C_5H_4)_2Ti]_2$(4,6-dihydroxypyrimidinate)[c]	4,6-dihydroxypyrimidinate(2−)	−1.4	1.96

[a] TIP was assumed to be zero. [b] Reference 6. [c] Reference 9.

the symbols have the usual meanings. The two parameters are g and the exchange parameter J, for we have elected to assume that the temperature-independent paramagnetism (TIP) is zero for a binuclear titanium(III) metallocene. The susceptibility data given in Tables IV–VIII[19] were least-squares fit to eq 4, and the resulting parameters are given in Table IX.

The magnetic susceptibility data for the thyminate-bridged complex I are illustrated in Figure 5. A weak antiferromagnetic exchange interaction is present, and μ_{eff}/Ti drops from a spin-only value to 1.30 μ_B at 4.2 K. The data were fit to give $J = -2.2$ cm^{-1}, which is not very different from the value of $J = -1.3$ cm^{-1} found[6] for the uracilate-bridged complex (thymine is a methyl-substituted uracil). Substitution of a fluorine atom on the uracilate bridge also does not dramatically affect the level of antiferromagnetic interaction. The data for complex V, which are illustrated in Figure 6, were fit to give $J = -1.7$ cm^{-1}. Substitution on the uracilate bridge apparently does not lead to pronounced changes in the antiferromagnetic interaction.

It must be admitted that the 3,6-dihydroxypyridazinate bridge present in complexe VIII was selected with the anticipation that, compared to the uracilate bridges, it would lead to a stronger magnetic exchange interaction. Figure 7 shows that this is indeed the case, for there is now a maximum seen in the χ_M vs. T curve at 11 K. The value of μ_{eff}/Ti drops to 0.40 μ_B at 4.2 K, and fitting the data gives $J = -6.9$ cm^{-1}.

Pyrazine (pyz) has recently attracted considerable interest as a bridge in various binuclear complexes. There has been controversy[21,22] about the viability of the pyrazine bridge for mediating electron transfer in the mixed-valence Creutz–Taube ion $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{6+}$. Hoffmann and co-workers[23] concluded from the results of extended Hückel molecular orbital calculations that pyrazine would be very effective in supporting antiferromagnetic interactions with a σ type of exchange pathway. Haddad et al.[24] demonstrated, however, that a binuclear copper(II) complex constructed so as to have a σ type of exchange interaction propagated by a pyrazine bridge does not, in fact, exhibit a very strong antiferromagnetic interaction. The magnetic susceptibility results for complexes IX and X are further support for the fact that pyrazine does not afford a very good bridge for magnetic exchange interactions. In the case of complex IX we only find an interaction with $J = -1.7$ cm^{-1}. It is somewhat of a puzzlement that the interaction ($J = -7.3$ cm^{-1}) observed for complex X is larger. The data for this complex are shown in Figure 8.

A possible explanation for the observation that the interaction in complex X is stronger than that in complex IX can be gleaned from molecular orbital calculations. Dahl et al.[24] have shown that the unpaired electron in the d^1 system $(\eta^5\text{-}C_5H_5)_2VCl_2$ resides primarily in a molecular orbital of a_1 symmetry (C_{2v} point group) which is σ bonding in the plane of the VCl_2 group. Similarly, each titanium(III) unpaired electron in our binuclear complexes is located in an orbital which is σ bonding in the plane of the bridge. CNDO/2 molecular orbital calculations[25] were carried out for the dianions 2,3-dihydroxyquinoxalinate(2−) and 2,3-dithioquinoxalinate(2−) in the modified forms shown in Figure 9. Interatomic bond distances were estimated with use of the structural results for (2,4-dithiopyrimidinato)bis[bis(η^5-methylcyclopentadienyl)titanium(III)].[8]

The energies of the highest occupied molecular orbitals with the correct symmetry to combine with a bonding combination of titanium a_1 orbitals are shown in Figure 9 for the bridging dianions of complexes IX and X. Both 2,3-dihydroxyquinoxalinate(2−) and its sulfur analogue have C_{2v} symmetry. Each of these dianions has nine filled a_1 orbitals which can serve as pathways for an antiferromagnetic exchange interaction. In Figure 9 it can be seen that replacing the oxygen atoms with sulfur atoms leads to a slight stabilization of the a_1 orbitals. This stabilization should lead to a reduction of the magnitude of the antiferromagnetic interaction, not the increased interaction that is observed.

If the substitution of the oxygen atom with a sulfur atom is assumed to be the origin of the stronger exchange interaction observed for the complex bridged by 2,3-dithioquinoxalinate(2−) compared to that bridged by 2,3-dihydroxyquinoxalinate(2−), it is necessary to examine the composition of the individual molecular orbitals to rationalize the change. The most striking difference noted for the highest occupied a_1 orbitals for these two dianions is found in the second highest orbital, where a very small contribution from the two ring carbon atoms between the oxygen and nitrogen atoms exists for the 2,3-dihydroxyquinoxalinate(2−) dianion. The corresponding molecular orbital for the 2,3-dithioquinoxalinate(2−) dianion has appreciable contributions from these same two ring carbon atoms as well as from the two sulfur atoms.

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Registry No. I, 77071-36-4; II, 77071-37-5; III, 77071-38-6; IV, 77071-39-7; V, 77071-40-0; VI, 77071-41-1; VII, 77071-42-2; VIII, 77071-43-3; IX, 77071-44-4; X, 77071-45-5; 2,3-dihydroxypyrazinate(2−), 77070-46-3; 2,3-dithiopyrazinate(2−), 77070-47-4; $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, 12129-51-0.

Supplementary Material Available: Tables IV–VIII (experimental and calculated magnetic susceptibility data) (9 pages). Ordering information is given on any current masthead page.

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