Figure 2. Experimental (●) and calculated (–) half-widths of α-methyl resonance as function of ρ, the $[Eu]_{total}/[M]_{total}$ ratio: (a) I with M = Ni; (b) I with M = Pt.

those of the nickel(II) compound.

The spectral data observed for these nickel(II) and platinum(II) compounds on formation of lanthanide shift reagent adducts provide classic examples of the nondilute case of two-site fast-exchange NMR line broadening. In each case the appreciable concentrations of both the diamagnetic substrate and its paramagnetic LSR adduct contribute to the last term in eq 1. This term is negligible in the more commonly encountered dilute case typified by the Swift and Connick[7] experiment in which the paramagnetic metal species is present in much lower concentration than the diamagnetic ligand. Differentiation of eq 1 leads to the prediction that, for an infinite formation constant (K), maximum broadening will occur at $\rho = {}^1/_3$—a condition closely approximated by the present systems (Figure 2).

For each complex, broadening of the ⁻CH⁻ ligand proton is also observed. It is clear from the spectra that these proton resonances also reach their maximum broadness near $\rho = {}^1/_3$, but the magnitude of the broadening is small and this, together with the relatively small lanthanide induced shifts, results in these resonances being of little use for calculation of rate data.

A duplicate set of experiments was also performed using Eu(fod)₃ and CDCl₃ as supplied (without further drying). The results illustrate that the presence of water has a marked effect on the lifetimes of the respective adducts. Under these conditions a lifetime for the nickel adduct of $\sim 5.8 \times 10^{-6}$ s was obtained whereas the value for the corresponding platinum adduct was $\sim 7.0 \times 10^{-6}$ s. Although for a given value of ρ the observed broadening was considerably smaller than for the corresponding anhydrous system, the overall broadening pattern was similar with the observed maximum broadening near to $\rho = {}^1/_3$ in each case.

The magnitude of the observed broadening depends on the mean lifetime of the adduct and on the square of the difference in the chemical shift between the adduct and the free metal complex. In contrast to previous work,[8,9] the dramatic effects found in the present work are a consequence of the longer lifetimes[10] which presumably reflect chelation of the substrate to the LSR as previously discussed.[2]

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(10) In the present study, the observed lifetimes are longer than the $\sim 10^{-7}$-s lifetimes found for other LSR-organic substrate adducts in which the organic substrate has only one site available for attachment to the LSR. See ref 9 and references therein.

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The Cr²⁺ Reduction of Titanium(IV). Comparisons with the Cr²⁺ Reduction of VO²⁺ and Evidence for a TiO²⁺ Structure in Aqueous Solutions, pH ≤1

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An important consideration when discussing reactions of Ti(IV) in acidic aqueous solutions is the question of the structure of Ti(IV) in such solutions and in particular whether monomeric TiO^{2+} or $Ti(OH)_2^{2+}$ (or some other form) is present. As a part of this study on the kinetics and mechanism of the Cr²⁺ reduction of Ti(IV), further attempts have been made to settle this controversial question.[1] A comparison of percentage yields of $CrCl^{2+}$ for the Cr²⁺ reductions of Ti(IV) and V(IV), as well as lack of an [H⁺] dependence for the Cr²⁺ reduction of Ti(IV) over the range [H⁺] = 0.1–1.9 M investigated, provides evidence for a TiO^{2+} structure similar to VO²⁺.

Experimental Section

Reactants. Solutions of Ti(IV) (ca. 0.04 M), V(IV) (ca. 0.20 M), Cr²⁺ (ca. 0.50 M) in dilute perchloric acid (ca. 1 M), and LiClO₄ were prepared by procedures as used in other work from these laboratories.[2] Solutions of HClO₄ and HCl were obtained by dilution of concentrated Analar acids. Air-free techniques (N₂ gas), Atlas nylon syringes, rubber serum caps, and stainless steel needles were used.

Stoichiometry. Spectra of reactant solutions (a) [Cr²⁺] = 0.05 M, [Ti(IV)] = 0.10 M and (b) [Cr²⁺] = 0.136 M, [Ti(IV)] = 0.013 M, both with [H⁺] = 0.50 M, were measured at 350–750 nm after ca. 1 min reaction time. Analysis of these indicated a reaction as in (1), with a stoichiometry 1.00 ± 0.02. No evidence was obtained for

$$Cr(II) + Ti(IV) \rightarrow Cr(III) + Ti(III) \tag{1}$$

absorbing species other than monomers in (1), peak positions for Cr²⁺ (λ 715 nm, ϵ 4.8 M⁻¹ cm⁻¹), Ti³⁺ (λ 502, ϵ 3.97), and Cr³⁺ (λ 408, ϵ 15.5; λ 571, ϵ 13.2). Slower subsequent reactions occur due to the Ti(III) reduction of perchlorate[3] and, if Cr²⁺ is present in excess, reduction of the Ti(IV) which is regenerated.

Kinetics. Formation of Cr³⁺ was monitored on a Durrum-Gibson stopped-flow spectrophotometer at λ 408 nm. At this Cr³⁺ peak position ϵ 0.8 M⁻¹ cm⁻¹ for Ti³⁺. Runs monitored at 502 and 575 nm were in good agreement with those at 408 nm. The Cr²⁺ reactant was generally in tenfold excess. First-order plots of absorbance (A) readings log ($A_\infty - A_t$) against time (where A_∞ is the observed final

Table I. The Dependence of Second-Order Rate Constants k for the Cr^{2+} Reduction of Titanium(IV) on Hydrogen-Ion Concentration and Temperature[a]

Temp, °C	$[H^+]$, M	$10^{-3}k$, M^{-1} s^{-1}
3.0	0.50	2.93
	1.00	3.17
	1.50	2.94
10.0	0.10	4.14
	0.13	4.23
	0.20	3.89
	0.50	4.01
	1.00	4.06
	1.50	4.26
	1.90	4.04
17.5	0.50	5.53
	1.00	5.73
	1.50	5.39
25.0	0.50	7.73
	0.98	7.35[b]
	1.00	7.44
	1.96	7.40[b]
	1.50	7.75

[a] $[Cr^{2+}] = (1.00 \pm 0.02) \times 10^{-2}$ M, $[Ti(IV)] = 10^{-3}$ M, $I = 2.00$ M $(LiClO_4)$, λ 408 nm. [b] $[Cr^{2+}] = 8.4 \times 10^{-4}$ M, $[Ti(IV)] = 6.7 \times 10^{-3}$ M.

absorbance) were linear to >80% completion. Rate constants were evaluated from the slopes ($\times 2.303$). The ionic strength was adjusted to $I = 2.00$ M using $LiClO_4$.

Product Analysis for Reactions in the Presence of Cl^-. Separation of products was carried out using a Dowex 50W-X2 100–200 mesh resin (column 18 cm long, 2.5 cm diameter) in the H^+ form. Twenty minutes was allowed for the reaction to proceed to completion, after which solutions were diluted to ionic strength 0.2 M. Two Cr(III) bands were obtained. A 2+ complex, identified as $CrCl^{2+}$ (peaks λ 428 nm, ϵ 22 M^{-1} cm^{-1}; λ 608 nm, ϵ 17.4 M^{-1} cm^{-1}),[4] was eluted with 0.8 M $HClO_4$, and a 3+ complex, identified as Cr^{3+} (details of the spectrum as above), was eluted with 2 M $HClO_4$. There is no induced aquation of $CrCl^{2+}$ on the ion-exchange column during the time required for separation. The Cr was determined as chromate(VI) (λ 372, ϵ 4.82 $\times$ 10^3) by oxidation with alkaline hydrogen peroxide. Retrieval of the Cr was >98%. It was demonstrated using solutions of known composition that vanadium and titanium do not interfere with the Cr determination.

Results and Discussion

First-order rate constants were dependent on $[Cr^{2+}]$, which is consistent with a rate law

$$\text{rate} = k[Cr^{2+}][Ti(IV)] \qquad (2)$$

Second-order rate constants k were independent of reactant concentrations, $10^2[Cr^{2+}] = 0.30–3.84$ M, $10^3[Ti(IV)] = 0.30–1.00$ M, where 12 runs at 10 °C, $[H^+] = 1.0$ M, $I = 2.00$ M $(LiClO_4)$, gave k values in the range $(4.03 \pm 0.15) \times 10^{-3}$ M^{-1} s^{-1}. Rate constants were also independent of $[H^+] = 0.10–1.90$ M, Table I. At 25 °C, $k = 7.5 \times 10^3$ M^{-1} s^{-1}, and from a nonlinear least-squares program,[5] weighting factor $1/k^2$, activation parameters are $\Delta H^\ddagger = 6.26 \pm 0.15$ kcal mol^{-1}, $\Delta S^\ddagger = -19.8 \pm 0.5$ cal K^{-1} mol^{-1}, $I = 2.00$ M $(LiClO_4)$.

The rate law 2 is of the same form as for the V^{2+} reductions of VO^{2+} [6] and Ti(IV),[2] with no dependence on $[H^+]$. From the kinetic data both reactions are believed to be in part at least V^{2+}-substitution controlled, and this is substantiated in the V^{2+} reduction of VO^{2+} by the detection of an intermediate, formulated as VOV^{4+}. A small portion of the Cr^{2+} reduction of VO^{2+} is known to proceed by way of a Cr–V binuclear intermediate.[7] No binuclear intermediate was detected in the present study, which is possibly due to the greater lability of Ti^{3+} as compared to V^{3+}, where rate constants (25 °C) for water exchange are 10^5 [8] and 1.6×10^3 s^{-1},[9] respectively.

The lack of an $[H^+]$ dependence for the Cr^{2+} and V^{2+} reductions of Ti(IV) suggests that the latter has a structure

Table II. Chromium(III) Products for the Cr^{2+} Reduction of Titanium(IV) and Vanadium(IV) in the Presence of Cl^- 25 °C, $I = 2.00$ M $(LiClO_4)$, as Determined Following Ion-Exchange Separation

| $[H^+]$, M	$[Cl^-]$, M	10^2-$[Cr^{2+}]$, M	10^2-[Oxidant], M	% $CrCl^{2+}$ yield[a] from reaction with Ti(IV)	% $CrCl^{2+}$ yield[a] from reaction with V(IV)
1.95	0.04	0.7	1.0	0	0
1.89	0.10	1.46	2.0	1.5	2
1.89	0.15	1.46	2.0	2	4
1.89	0.20	1.46	2.0	3	4
0.61	0.50	0.67	1.0	9	8
0.61	1.00	0.67	1.0	17	
1.94	1.42	0.72	1.0		22

[a] Expressed relative to Cr^{2+} present initially.

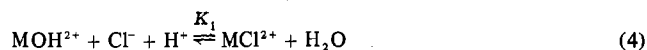**Table III.** Literature Values of K_a and K_{Cl} and Estimated Values for K_1 (eq 3)

	K_a, M	K_{Cl}, M^{-1}	K_1, M^{-2}
Fe^{3+}	1.6×10^{-3} [a]	4.57 [b]	2.86×10^3
Ti^{3+}	1.68×10^{-3} [c]	0.07–0.2 [d]	42–120
Co^{3+}	2×10^{-3} [e]	30 [f]	1.5×10^4

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TiO^{2+}, similar to VO^{2+}, and is not a hydroxo species $Ti-(OH)_n^{(4-n)+}$. Further experiments were carried out in order to substantiate this. The aim was to determine the Cr(III) products for the Cr^{2+} reduction of Ti(IV) in the presence of Cl^- and make comparisons with the product pattern for the Cr^{2+} reduction of VO^{2+} under identical conditions, Table II. If Ti(IV) is present as a hydroxo species, most probably $Ti(OH)_2^{2+}$, then complexing with Cl^- by displacement of OH^- would be expected.

$$Ti(OH)_2{}^{2+} + Cl^- + H^+ \overset{K_1}{\rightleftharpoons} Ti(OH)Cl^{2+} + H_2O \qquad (3)$$
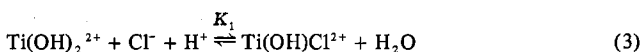
Equilibrium constants, K_1, for

$$MOH^{2+} + Cl^- + H^+ \overset{K_1}{\rightleftharpoons} MCl^{2+} + H_2O \qquad (4)$$

can be obtained for Fe(III), Ti(III), and Co(III) aquo ions from available acid dissociation constants (K_a) and chloride formation constants (K_{Cl}), Table III. On this basis a reasonable estimate for K_1 in (3) is >10 M^{-2}, and at $[H^+] = 2.0$ M, $[Cl^-] = 0.5$ M, the ratio $[Ti(OH)Cl^{2+}]/[Ti(OH)_2^{2+}]$ is >10. The constant for complexing of chloride to VO^{2+} is believed to be 0.24 ± 0.10 M^{-1}.[10] For a given $[Cl^-]$ the % $CrCl^{2+}$ is practically the same for the Cr^{2+} reduction of Ti(IV) and VO^{2+}. There is no information as to whether Cl^- is brought into the activated complex by the oxidant or reductant in either case. However, if $Ti(OH)_2^{2+}$ were present, and (3) effective, then it would be most unusual if $Ti(OH)Cl^{2+}$ were not involved in an inner-sphere chloride-bridged reaction pathway yielding $CrCl^{2+}$. We conclude that there is no evidence for enhanced complexing of Cl^- with Ti(IV) as compared to VO^{2+} and believe this to be strong supporting evidence for a TiO^{2+} species.

An x-ray study of $(NEt_4)_2[TiOCl_4]$ has shown that this complex contains discrete Ti–O bonds.[11] However, the majority of Ti(IV) compounds containing Ti–O bonds have polymeric –Ti–O–Ti–O chains, for example, $TiOX_2$ (X = F, Cl, Br, I) and $[TiO(SO_4)_2]^{2-}$. In one case at least, that of

$[TiO(C_2O_4)_2]^{2-}$,[12-14] a ring structure is formed. Ion-exchange behavior of Ti(IV) in aqueous perchloric acid solutions, in particular the similar elution rate to VO^{2+}, has previously indicated a mononuclear 2+ species.[2]

Registry No. Ti(IV), 16043-45-1; Cr^{2+}, 22541-79-3; VO^{2+}, 20644-97-7; $CrCl^{2+}$, 14931-91-0; Cl^-, 16887-00-6; TiO^{2+}, 12192-25-5.

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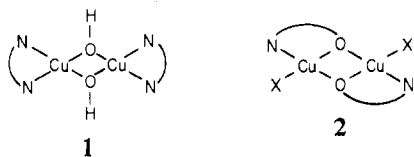University of North Carolina, Chapel Hill,
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Structural and Magnetic Properties of Binuclear Copper(II) Complexes

Derek J. Hodgson

The structural and magnetic properties of binuclear copper(II) complexes of the types **1** and **2** have been the subjects of considerable recent research.[1-13] This large body of data

clearly suggests that the geometry of the four-membered Cu–O–Cu–O ring is the dominant feature in determining the magnitude and the sign of the magnetic exchange parameter J, which is defined by the exchange Hamiltonian

$$H_{ex} = -2J(\mathbf{S_1 \cdot S_2})$$

There is, however, some apparent difference of interpretation concerning the precise structural feature (or parameter) which dominates the magnetic exchange. Hatfield and Hodgson[7,10,11,14,15] have demonstrated an experimental correlation for complexes of type **1** between J and the Cu–O–Cu bridging angle, ϕ, and this relationship has been placed on a sound theoretical basis through the application of molecular orbital theory;[11,16,17] Sinn and his co-workers,[3,8] however, have noted that for a variety of complexes of type **2** which demonstrate large antiferromagnetic interactions the magnitude of J is influenced by the deviation from planarity at the copper atom and is relatively insensitive to changes in ϕ. In this communication the apparent distinction between these two sets of observations will be explained.

Discussion

As has been noted elsewhere,[11,16] the Cu_2O_2 bridging fragment has approximate D_{2h} symmetry since in virtually all of the complexes studied this moiety is planar and the Cu–O bond lengths are all equal. In complexes of type **1**, it is also found that the entire $Cu_2O_2N_4$ system is approximately planar.[18] Thus, if one examines the σ-bonding framework of the bridge (neglecting oxygen 2s orbitals) the eight σ orbitals transform[11] as 2 A_g + 2 B_{1g} + 2 B_{2u} + 2 B_{3u}. At $\phi = 90°$ (again neglecting 2s orbitals) the highest occupied molecular orbitals (HOMO) are the accidentally degenerate B_{1g}^* and B_{2u}^* orbitals, each of which is singly occupied. Hence, under these conditions, the ground state is the triplet and, therefore, $J > 0$. Any appreciable change in ϕ from this value raises the degeneracy of these two orbitals and eventually leads to a singlet ground state ($J < 0$).[17,21] If the contribution of the oxygen 2s orbitals is included, this view is not qualitatively changed, i.e., there is some ϕ_0 (near 90°) at which B_{1g}^* and B_{2u}^* are degenerate, and at angles of $\phi_0 + \Delta\phi$ this degeneracy is lifted.[9] Experimentally, it is observed that at $\phi > 97.6°$ the value of J is negative, i.e., that the ground state is the singlet.[15]

The effect of distorting the geometry at the copper atom can be understood within this molecular orbital framework. Sinn and co-workers[8] have defined the angle τ (**3**) as the angle between the bridging Cu_2O_2 plane and the $Cu_2N_2X_2$ (in **2**) or Cu_2N_4 (in **1**) plane; this angle, which is zero for square-planar geometry at copper and would be 90° for tetrahedral geometry, gives an excellent measure of the distortion toward tetrahedral geometry which is often observed[8] in complexes of type **2**.

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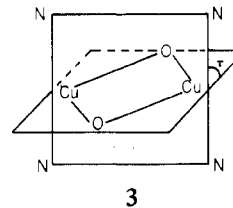
All of the complexes of type **2** which have been studied in detail have $\phi \gg 97.6°$, which means (vide supra) that the ground state is the singlet and that $J < 0$. In these cases, the effect of increasing τ from zero is to attenuate the overlap between the Cu (d_{xy} and $d_{x^2-y^2}$) and the oxygen (p_x and p_y) σ orbitals, since these orbitals are coplanar at $\tau = 0$ and become progressively less aligned as τ increases. Since the magnetic exchange depends on this orbital overlap, the principal magnetic effect of the geometric distortion is to reduce the magnitude of J without affecting its sign. Thus, for example, a progressive increase of τ from 33.1 to 39.3° leads to a decrease in $|J|$ from 240 to 146 cm^{-1} [8] for a series of complexes whose ϕ values are all close to 103°. It is to be expected that, at large values of ϕ, the magnitude of J is more sensitive to changes in τ than to changes in ϕ since (at $\phi \gg \phi_0$) the degree of orbital overlap varies more rapidly with τ. Our experience with chromium(III) dimers parallels this conclusion that the magnitude of J is largely determined by the degree of orbital overlap; the overlap between the Cr(III) (t_{2g}) orbitals containing the unpaired spin and the oxygen p orbitals is much less than is the case for copper(II), and hence the magnitude of J observed in Cr(III) complexes analogous to **1** is much less than that for the Cu(II) systems.[22] It remains true that the sign of J is determined largely by ϕ.

It is also noteworthy that at $\phi = \phi_0$, the effect of a small increase from zero in τ must also lead to a lifting of the degeneracy of the B_{1g}^* and B_{2u}^* orbitals. Unfortunately the available data do not allow an examination of this effect since complexes of type **1** have $\tau \approx 0°$ and complexes of type **2** have $\phi \gg \phi_0$.