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On the Oxidation State of Titanium in the Complex $Ti(bpy)_3$

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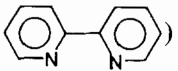
The formal oxidation state of titanium in $Ti(bpy)_3$ can vary from 0 to +4, because bipyridine (bpy = ) is a non-innocent ligand.

$Ti(bpy)_3$ is a well known compound, first prepared by Herzog many years ago [1]; it has been studied by several authors in connection with the problem of the metal oxidation state. Unfortunately, the results are conflicting and confusing. Thus, on the basis of solution electronic spectra, Herzog concludes that the bpy ligand in $Ti(bpy)_3$ has the character of bpy^- ion [2], while Kaizu and coworkers [3], starting from the same data, formulate $Ti(bpy)_3$ as a complex of Ti(0) bonded to the neutral bpy ligand. On the other hand, Nakamoto [4], interpreting IR spectral data, reaches the apparently correct conclusion that the Ti–N bond is essentially ionic; nevertheless the bipyridine complex is still classified as a Ti(0) complex [5].

In the course of a research project on the use of coordination compounds for organic syntheses, we have chosen $Ti(bpy)_3$ as the starting material, and we report here our considerations about which formal oxidation state of the metal best explains its chemical behaviour. In a recent paper in this journal [6], it was reported that the non-ambiguous Ti(0) complex, $K_4Ti(CN)_4$, reduces bipyridine to the radical anion $(bpy)^{\dot{-}}$; therefore, the zero oxidation state for the metal can no longer be proposed with confidence. We are convinced that $Ti(bpy)_3$ is best considered as a chelate complex of Ti^{3+} and bipyridyl anion for the reasons explained below.

^{1}H NMR Data (Fig. 1)

The resonances of coordinated bipyridine in the $Ti(bpy)_3$ complex are shifted upfield of *ca.* 1.5 ppm relative to the free ligand, and the same relationship is observed for free and bound 4,4′-dimethyl-bipyridine. The large screening effect observed upon complexation suggests the presence of a considerable negative charge on the bonded ligand. We do not attribute the negative charge to a M → (π*) mechanism active in the complex, since bpy is a poor π-acceptor. Indeed, when it is coordinated as a neutral

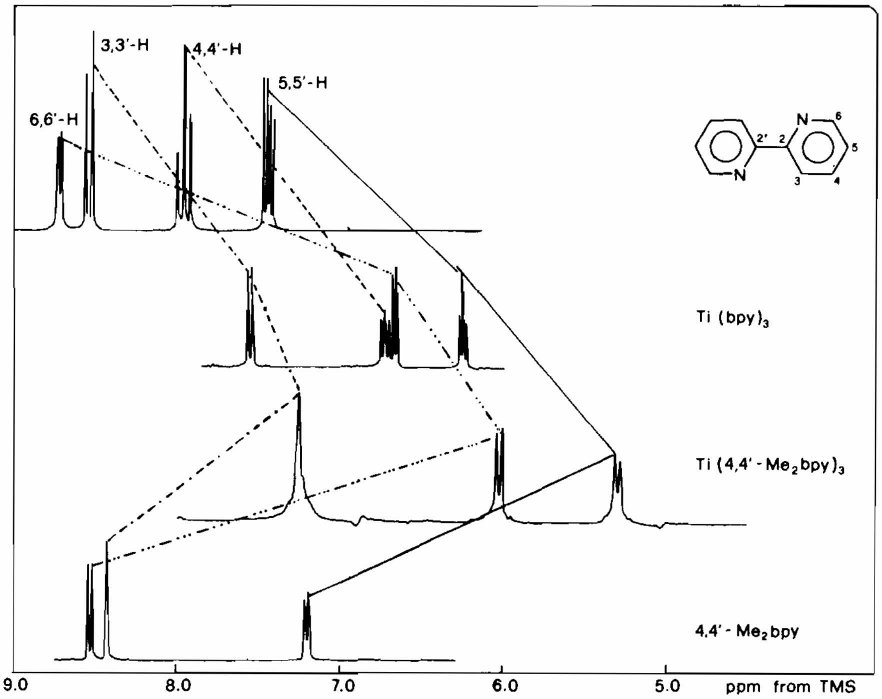


Fig. 1. 200 MHz ^{1}H NMR spectra of $Ti(bpy)_3$, $Ti(4,4'\text{-}Me_2bpy)_3$ and the free ligands in $[^2H]_8$-THF at 300 K.

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TABLE I. ^{1}H-NMR Data of 2,2'-Bipyridine Complexes

Compound	δ (ppm from TMS)				Solvent
	H_3	H_4	H_5	H_6	
2,2'-bipyridine	8.45	7.83	7.32	8.67	$C^2H_2Cl_2$
4,4'-Me_2bpy	8.42		7.19	8.52	$[^2H]_8$-THF
Ti(bpy)$_3$	7.54	6.28	5.56	6.19	$[^2H]_8$-THF
Ti(4,4'-Me_2bpy)$_3$	7.25		5.30	6.02	$[^2H]_8$-THF
cis-$[Pt(bpy)_2]^{+2}$ [a]	8.5	8.5	7.9	8.9	^2H_2O
$[Pt(bpy)(OH)_2]$ [b]	7.79	7.98	7.41	8.45	^2H_2O
cis-$[Rh(bpy)_2(OH)_2]^{+3}$ [c]	8.90, 8.71	8.76, 8.38	8.30, 7.62	9.41, 7.75	^2H_2O
cis-$[Rh(bpy)_2(OH)_2]^{+}$ [c]	8.70, 8.54	8.52, 8.18	8.09, 7.43	9.27, 7.71	^2H_2O
$[Ru(bpy)_3]^{+2}$ [d]	8.97	8.23	7.56	7.74	$[^2H]_6$-DMSO
cis-$[Mo(CO)_4bpy]$ [e]	8.16	7.95	7.39	9.12	$C^2H_2Cl_2$
cis-$[Mo(bpy)_2(CO)_2]$ [e]	8.39	7.91	7.41	8.68	$[^2H]_6$-DMSO
$[Cu(bpy)(CO)_2]^+$ [f]	8.67	8.35	7.89	9.13	$[^2H]_6$-acetone
cis-$[Ir(bpy)_2Cl_2]^+$ [g]	8.91, 8.82	8.50, 8.20	8.15, 7.51	9.65, 7.85	$[^2H]_6$-DMSO
$[Fe(bpy)(CO)_3]$ [h]	8.48	7.84	7.39	9.41	$[^2H]_6$-acetone

[a] Ref. 7 [b] Ref. 8. [c] Ref. 9. [d] Ref. 10. [e] Ref. 11. [f] Ref. 12. [g] Ref. 13. [h] Ref. 14.

molecule, it remains negative, irrespective of the metal and of its oxidation state, even when the M → (π^*) mechanism is certainly operating (e.g. Mo(bpy)$_2$(CO)$_2$, Fe(bpy)(CO)$_3$); from the NMR point of view, this behaviour is clearly demonstrated by the data reported in Table I.

Chemical Evidence

The reaction of Ti-complexes with benzophenone can be considered a test reaction for the oxidation state of the metal: Ti(III) complexes reduce benzophenone to pinacol [15]; Ti(II) complexes reduce it further to tetraphenylethylene [16]; and Ti(0) complexes reduce it even further to tetraphenylethane, abstracting hydrogen from the protic solvent [16]. There is little doubt that Ti(bpy)$_3$ should be formulated as a Ti(III) complex on the basis of chemical evidence, since, by reacting it with benzophenone, we have obtained a Ti(IV) complex (1) containing the pinacol dianion $[(\phi_2CO)_2]^=$, together with a negligible amount of tetraphenylethylene, according to the stoichiometry:

$$Ti(bpy)_3 + 4\phi_2CO \longrightarrow Ti(bpy)[(\phi_2CO)_2]_2 + 2bpy$$

Analogies with the Ti(III) Complex: [$Ti^{+3}Cp_2(bpy^{-1})$] [17]

Ti(bpy)$_3$ and the analogous Ti(III) complex, [$TiCp_2bpy$] (Cp = $C_5H_5^-$), react in a similar way with tetracyanoethylene, reducing it to the dianion; then two molecules of the dianion condense, via a metal promoted mechanism, to give, by elimination of HCN, a new heterocycle whode formula is $C_{11}N_7H_2^-$ [18]. Obviously the titanium is in the same oxidation state in the two complexes.

In conclusion, Ti(bpy)$_3$ should be formulated as [$Ti^{3+}(bpy^{-1})_3$], with a singlet ground state far below the first excited triplet state which is not thermally accessible, since Ti(bpy)$_3$ is diamagnetic and does not give any EPR signal even on heating.

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