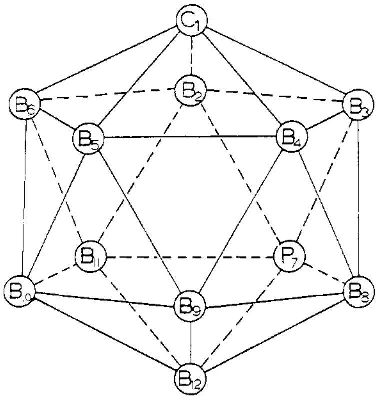

Figure 1. A proposed structure for 1,7-$B_{10}H_{10}CHP$.

The evolution of hydrogen bromide in this reaction and the broad doublet at τ 5.6 (CH) in the ^1H nmr spectrum indicate that halogen substitution occurs on the boron atoms. Bromination of *o*-carborane gave similar results.[11]

Reaction of $B_{11}H_{13}^{2-}$ with phenylphosphorus dichloride gave after repeated sublimation of the reaction products $B_{11}H_{11}PC_6H_5$ (III), mp 157–159°, in low yield. *Anal.* Calcd for $B_{11}H_{11}PC_6H_5$: C, 30.28; H, 6.78; P, 13.01. Found: C, 30.76, H, 6.62; P, 12.66. The mass spectrum of III at low electron voltage (13 ev) cuts off at *m/e* 241 corresponding to the $^{13}C_1{}^{12}C_5{}^1H_{16}{}^{11}B_{11}{}^{31}P_1{}^+$ ion. The ^1H nmr spectrum has a complex multiplet at τ 2.2 indicating the presence of a phenyl group. The ^{11}B nmr spectrum of III (32 Mc) contains three overlapping doublets with 1:5:5 relative areas at 3, 8.4, and 15 ppm, respectively [$BF_3 \cdot (C_2H_5)_2O$ = 0 ppm]. This spectrum is consistent with an icosahedral cage structure for this phosphaborane. Relative to trivalent phosphines (*i.e.*, R_3P), I appears to be a weak Lewis base since it does not react with methyl iodide. The unknown $B_{11}H_{11}P^-$ ion isoelectronic with III also contains a formally trivalent phosphorus atom. This ion should be more susceptible to attack by alkyl halides to form $B_{11}H_{11}PR$. This and other aspects of phosphaborane chemistry are under active investigation.

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Some Kinetic Evidence Pertaining to the Structure of the Cobalt(II)–Ethylenediaminetetraacetate (EDTA) Complex in Aqueous Solution

Sir:

The nature and number of bonding sites in multidentate ligands is one of the most interesting and important aspects of present-day coordination chemistry. In this context the investigations of the structures of metal–EDTA complexes in the solid state by Hoard and his colleagues[1] have produced some answers, but the structures of the species in aqueous solution are less settled. The question has been carefully considered by Higginson,[2] who concluded that a substantial number of EDTA complexes of bivalent metals contained quinquedentate ligand, *i.e.*, could be represented by $M(EDTA)(H_2O)^{2-}$ with one uncoordinated carboxylate group. Support for this idea comes from the observation of a common $pK \sim 3$ for these complexes[3] which is related to protonation of the free carboxylate group rather than involving any breakage of a metal–carboxylate bond. Offsetting this argument is the fact,[4] which we have confirmed, that definite spectral changes in the visible accompany the protonation of the copper(II) and cobalt(II) complexes, and this is more easily rationalized in terms of at least some six-coordinated EDTA present.

Our approach to the problem has been to treat the cobalt(II)–EDTA complex at various acidities with a variety of rapidly reacting oxidants and to examine the spectra of the resultant cobalt(III) complex soon after it is formed. The various forms of the latter, $Co(EDTA)^-$, $Co(EDTAH)(H_2O)$, $Co(EDTA)(H_2O)^-$, and $Co(EDTA)(OH)^{2-}$ are well characterized.[5] The three five-coordinate EDTA complexes revert to $Co(EDTA)^-$, the hydroxo species particularly slowly[5] so that solutions were adjusted to pH ~10 after reaction completion to prevent changes subsequent to the oxidation. As additional, necessary information the second-order rate constants have been determined. The results are shown in Table I.

With oxidants 1–4, outer-sphere oxidation occurs. The overwhelming product is $Co(EDTA)^-$, and, were the rate constants for oxidation of five- and six-coordinated EDTA–cobalt(II) complexes identical, this would show that $Co(EDTA)^{2-}$ is present to the extent of 97% or more. However, pH-dependence studies show that $Co(EDTAH)(H_2O)^-$, which predominates at pH <3 and in which EDTA must be acting as a five-coordinate ligand, reacts by a factor of some 5–12 slower than the unprotonated complex. This is not merely an electrostatic effect since this behavior persists even when the noncharged oxidant $Fe(phen\text{-}5\text{-}SO_3)_3$ is used. It appears reasonable therefore to assume that $Co(EDTA)(H_2O)^{2-}$ will also react slightly slower than $Co(EDTA)^{2-}$, and this must be allowed for in the analysis of the product distribution.[6]

For the oxidation by $Fe(phen)_3{}^{3+}$, $k_{Co(EDTA)^{2-}}[Co(EDTA)^{2-}]/k_{Co(EDTA)(H_2O)^{2-}}[Co(EDTA)(H_2O)^{2-}] \gtrsim 33$ and at pH 5.0, $k_1[Co(EDTA)^{2-} + Co(EDTA)(H_2O)^{2-}] = k_{Co(EDTA)^{2-}}[Co(EDTA)^{2-}] + k_{Co(EDTA)(H_2O)^{2-}}[Co(EDTA)(H_2O)^{2-}]$ so that with $k_1 = 9.1 \times 10^4$ (see Table I) and $k_{Co(EDTA)(H_2O)^{2-}} \sim k_{Co(EDTAH)(H_2O)^-} \sim 1.6 \times 10^4$, this leads to a value of $\geqslant 80\%$ of $Co(EDTA)^{2-}$

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[6] The reduced reactivity of $Co(EDTAH)(H_2O)^-$ probably resides in its having a slightly more negative oxidation potential than $Co(EDTA)^{2-}$, $E° = -0.38$ v. That a five-coordinated EDTA species, however, would react inordinately slow and thus vitiate our reasoning is improbable when $Co(A)(H_2O)^-$ (A = hydroxyethylethylenediaminetriacetate) reacts with $Fe(bipy)_3{}^{3+}$ with a second-order rate constant (3.5×10^4 M^{-1} sec^{-1} at 25°) and gives $CoA(H_2O)^0$, in which both Co(II) and Co(III) contain a five-coordinated ligand.

Table I. Products and Rate Constants for Oxidation of Cobalt(II)–Ethylenediaminetetraacetate Complex at 25° (I = 0.5)

No.	Oxidant	pH	% product[a] of Co(EDTA)$^-$	k_1,[b] M^{-1} sec^{-1}	k_2,[c] M^{-1} sec^{-1}
1	Fe(bipy)$_3^{3+}$	5.0	$\geqslant$95[d]	3.3 × 10^4	2.8 × 10^3
		2.5	86[d]		
2	Fe(phen)$_3^{3+}$	4.4	$\geqslant$97[d]	9.1 × 10^4	1.6 × 10^4
3	Fe(phen-5-SO$_3$)$_3^0$	...	...	4.6 × 10^4	1.0 × 10^4
4	Ru(bipy)$_3^{3+}$	2.5	73[d]	7.9 × 10^5 [e]	7.3 × 10^4 [e]
5	Co(py)$_4$Cl$_2^+$	5.0	Co(EDTA)Cl^{2-}	48	48
		2.7	Co(EDTA)Cl^{2-}		
6	Mn(EDTA)(H$_2$O)$^-$	5.0	17	1.6[f]	
		4.3	37		
7	Mn(CyDTA)(H$_2$O)$^-$	5.5	62		
		4.5	80		

[a] Error depends on measurement of optical density ±0.02 unit representing *ca.* ±5% Co(EDTA)$^-$. [b] Oxidation of unprotonated Co–EDTA^{2-} complex. [c] Oxidation of protonated Co–EDTA complex, Co(EDTAH)(H$_2$O)$^-$. [d] Estimated spectrally after removal of the iron(II) or ruthenium(II) complex on a cation-exchange resin. [e] At 5.0° and I = 1.0 M. [f] Second-order rate constant at pH ~5. The dependence on pH is complex since several paths contribute, and we have not investigated the system thoroughly.

in the cobalt(II) solution. For the other oxidants, Fe(bipy)$_3^{3+}$ and Ru(bipy)$_3^{3+}$, our experiments show also that a preponderance of the six-coordinated complex exists in nonprotonated solutions.

The use of the other oxidants 5–7 has been less fruitful in shedding light on the structure of cobalt(II)–EDTA. The oxidation by Co(py)$_4$Cl$_2^+$ is unambiguously inner-sphere since Co(EDTA)Cl^{2-} is the sole product at all pH's. An inner-sphere reaction has been previously observed in the oxidation[7] by Fe(CN)$_6^{3-}$ and has been postulated[8] to occur with IrCl$_6^{2-}$. Such behavior of course is compatible with either formulation of the cobalt(II) complex since the carboxylate is easily ruptured from the metal.

The reactions with the strong oxidants Mn(EDTA)(H$_2$O)$^-$ and Mn(CyDTA)(H$_2$O)$^-$ (CyDTA = *trans*-1,2-diaminocyclohexanetetraacetate) are best understood also in terms of an inner-sphere process. The large amount of five-coordinate product produced by Mn(EDTA)(H$_2$O)$^-$ arises we feel because an effective hydroxo-bridged path can operate with the substantial amount of Mn(EDTA)(OH)$^{2-}$, pK = 5.1,[9] present in the oxidation solution. A five-coordinate product then results by addition of a proton to the cobalt(III)–hydroxo species formed after collapse of the bridge. This viewpoint is supported by the fact that increasing amounts of six-coordinate product arise (a) as the acidity increases and (b) when Mn(CyDTA)(H$_2$O)$^-$ with a much higher pK value (8.1)[10] is used as oxidant.

Summarizing, our work using outer-sphere oxidants indicates that some 80% or more of the six-coordinate species is present in the Co(II)–EDTA solutions at pH $\gtrsim$4.5, and there is no reason to doubt that large amounts of six-coordinate EDTA also may be present in other EDTA–metal complexes. Indeed, the manganese(II) complex contains seven-coordinate manganese, Mn(EDTA)(H$_2$O)$^{2-}$, in the solid state[1] and, it has been suggested, in solution also.[11,12]

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(12) Professor W. C. E. Higginson has informed us that the results of measurements of the association constant of the protonated and nonprotonated cobalt(II)–EDTA complex as well as the hydroxyethylethylenediaminetriacetate complex with a variety of unidentate ligands lead him now to believe that there is a predominance of the six-coordinated EDTA in the cobalt(II) complex (provisional results 77 ± 3%). We thank him for this information prior to publication.

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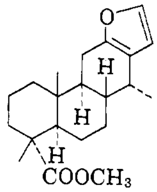
Total Synthesis of Racemic Methyl Vinhaticoate

Sir:

We wish to report the stereoselective total synthesis of the racemic form of the tetracyclic furanoid diterpene methyl vinhaticoate.[1] On the the basis of this synthesis, the previously undefined configuration of the secondary methyl group of the natural product can be assigned as shown in complete structure **1**.



1

In an improved synthesis of a suitable bicyclic intermediate,[2] reductive carbomethoxylation[3] of **2**[4] afforded 68% of **3**.[5] Methylation of **3** (NaH, CH$_3$OCH$_2$CH$_2$OCH$_3$, CH$_3$I), followed by methanolysis of the protecting group, yielded 62% of **4**, mp 123–124°. Preparation of the ethylene dithioketal derivative and Raney nickel reduction afforded **5**, mp 95–96° (90%), which was oxidized to **6**, mp 82–83° (97%).

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