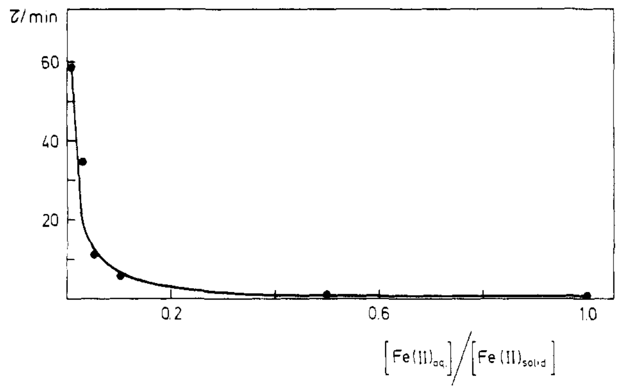

Figure 3. Induction period τ as a function of $\mathrm{Fe^{II}(aq)}$ concentration, expressed as its ratio respective to the concentration of Fe(II) originated by total dissolution of the solid. All experiments were performed at pH 4.1 and T = 30 °C.

processes may account for the induction period. This possibility was explored by preconditioning the solid in oxalate solutions at pH 8 for up to 7 days. The reaction profiles obtained were quite similar to the one shown in Figure 2 with an induction period corresponding to zero time of preconditioning. Furthermore, in another experiment, a partially reacted slurry was filtered off and the solid thoroughly rinsed. Upon resuspension of the solid in a solution of the same composition as the original, the induction time was observed again.

The influence of Fe(II) and Fe(III) concentration in solution was then explored. In the same Figure 2 we compare the kinetics of two similar runs, in one of which a ferrous salt had been added beforehand (solid circles); it can be seen that the induction period practically disappears. The same situation, with the induction period decreasing in a rather erratic fashion, is observed when ferric salt is added and the system is kept for some time in the light, in which case Fe(II) species are generated by photolysis of $\mathrm{Fe(C_2O_4)_3^{3-}}$,[20] while if light is rigorously excluded, the induction period is not suppressed by addition of Fe(III). This indicates that the species involved in the autoacceleration of the dissolution reaction is the Fe(II) ion transfered from the solid to the solution.

Figure 3 shows the dependence of the induction period on $\mathrm{Fe^{II}(aq)}$ concentration; the plot shows that an initial ratio $\mathrm{Fe^{II}(aq)/Fe^{II}(s)} = 0.2$ is enough to reduce the induction period to practically zero.

On the basis of all this evidence we propose the following mechanism for the dissolution of magnetite by oxalic acid solutions. As already mentioned, the first step must be the replacement of surface –OH groups by oxalate (eq 1; $-\mathrm{Fe^{III}}$–R indicates that this species is part of the solid).

$$-\mathrm{Fe^{III}{-}OH} + {}^{-}\mathrm{OOC{-}COOH} \rightleftharpoons -\mathrm{Fe^{III}(C_2O_4)} + \mathrm{H_2O} \tag{1}$$

An analogous equilibrium can in principle be written for Fe(II) of the solid; however, because of the relative strengths of Fe–O bonds, Fe(II) is expected to be released quickly as compared to Fe(III), and the dissolution rate is probably governed by Fe(III) phase transfer. During the induction period, Fe(III) complexed by oxalate must be dissolved according to eq 2. This must be a slow process, and this accounts for the induction period.

$$-\mathrm{Fe^{III}(C_2O_4)} \rightleftharpoons \mathrm{Fe(C_2O_4)^+(adsorbed)} \rightleftharpoons \mathrm{Fe(C_2O_4)^+(bulk)} \tag{2}$$

During the induction period, when (2) is rate determining, Fe(II) builds slowly into solution. However, once a critical amount is reached, a new pathway gives rise to fast dissolution. This is the reductive dissolution through reactions 3 and 4.

$$\mathrm{Fe^{II}(C_2O_4)(adsorbed)} + -\mathrm{Fe^{III}(C_2O_4)} \rightleftharpoons \mathrm{Fe^{III}(C_2O_4)^+(adsorbed)} + -\mathrm{Fe^{II}(C_2O_4)} \tag{3}$$

$$-\mathrm{Fe^{II}(C_2O_4)} \rightleftharpoons \mathrm{Fe(C_2O_4)(adsorbed)} \rightleftharpoons \mathrm{Fe(C_2O_4)(bulk)} \tag{4}$$

Either (3) or (4) may be rate determining. The reductive process may take place if the Fe(III) complex is stabilized in relation to the Fe(II) complex. Thus, ligands that stabilize Fe(II) are not effective in bringing about dissolution; this has been demonstrated with $\mathrm{Fe^{II}{-}CN^-}$ complexes.[21]

In the presence of added Fe(II), the induction period disappears because reaction 3 takes place directly; a certain minimum amount of Fe(II) is required because competition for adsorbed oxalate must take place between $\mathrm{Fe^{II,III}(s)}$, $\mathrm{H^+}$, and added Fe(II).

Oxalate plays an unique role among complexing carboxylic ligands in the dissolution of magnetite; it not only facilitates the electron-transfer reaction (3) but also mediates in a relatively fast dissolution during the initial induction period (the induction period is much shorter than in the case of the dissolution of magnetite by ethylenediaminetetraacetic[22a] or nitrilotriacetic acid.[22b] This unique role has been used in the development of a very efficient scale removal formulation used in the decontamination of nuclear power plants.[23]

No direct evidence is provided by the present study as to whether (3) is an outer-sphere or inner-sphere electron transfer. Oxalate is known to be a very efficient bridging ligand in electron-exchange reactions involving Cr(III)/Cr(II),[24] Co(III)/Cr(II),[25,26] and Co(III)/Fe(II)[27,28] couples, and the activated state in the electron-transfer reaction (3) probably involves Fe(III) as the solid, Fe(II) in solution, and a bridging oxalate ion. It should be noted however that oxalic acid is in large excess in our system, and an outer-sphere transfer from $\mathrm{Fe(C_2O_4)_2^{2-}(aq)}$ to a surface $-\mathrm{Fe^{III}(C_2O_4)}$ group cannot be ruled out.

Registry No. Magnetite, 1309-38-2; iron oxide ($\mathrm{Fe_3O_4}$), 1317-61-9; iron, 7439-89-6; oxalic acid, 144-62-7.

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Received January 20, 1983

$[\mathrm{PtCl(PEt_3)(CH(PPh_2S)_2)}]$, a Novel C,S-Bonded Chelate with Dynamic Stereochemistry Controlled by a Metal–Ligand Pivot

Sir:

The monoanions (**1**) derived from acetylacetone and its dithio analogue have been extensively studied as ligands in inorganic chemistry. By contrast the analogous phosphorus-containing species (**2**) have been essentially ignored,[1] even

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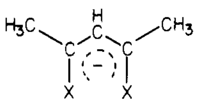
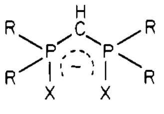


1



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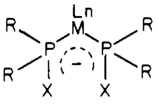
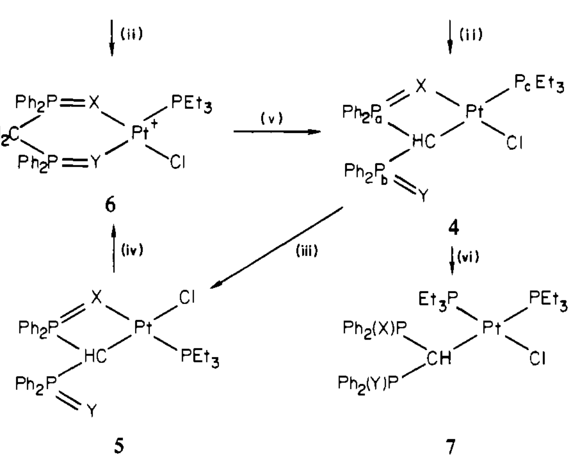


3

though work on the metalloanions (**3**) has suggested a potentially rich chemistry for this type of system.[2,3] There has, moreover, been intense recent interest in phosphorus and sulfur ylides[4] and related species such as phosphorus dithiolates,[5] including a very recent suggestion that the lability of the metal–sulfur bond may occasion unusual chemistry.[6] Thus the derivatives **2** (X = S) are of special interest. We now report a novel coordination mode in which metal binding to the methine carbon and to one sulfur atom creates a four-membered chelate ring and in which the metal–sulfur bond is sufficiently labile to allow dynamic solution interchange with the other sulfur. The process is unusual in involving essentially a "bimolecular" reaction controlled by a pivotal motion about a strong metal–ligand bond, rather than the more common simple exchange of coordination sites in a "dangling" ligand.

Our principal results are summarized in Scheme I. Reaction of Li(CH(PPh$_2$S)$_2$) with [Pt$_2$Cl$_4$(PEt$_3$)$_2$] in tetrahydrofuran solution gave a high initial yield of **4** (X = Y = S), but during workup and recrystallization procedures this product gradually isomerized to **5** (X = Y = S). An X-ray diffraction study of **5** confirmed the proposed formulation (Figure 1) and allowed the related structures shown in Scheme I to be assigned with confidence on the basis of ^{31}P{^{1}H} NMR results. Scheme I has been fully characterized for X = Y = S, and **4** and **6** have also been obtained for X = S, Y = O. When X = Y = Se, complexes **4**–**6** are accessible but are much less stable than their sulfur analogues.

Scheme I. Coordination Chemistry of [CH(PPh$_2$X)(PPh$_2$Y)]$^-$ [a]



[a] Legend: (i) Li-*n*-Bu; (ii) Pt$_2$Cl$_4$(PEt$_3$)$_2$; (iii) THF, 25 °C; (iv) HCl(aq); (v) 1,8-bis(dimethylamino)naphthalene; (vi) PEt$_3$.

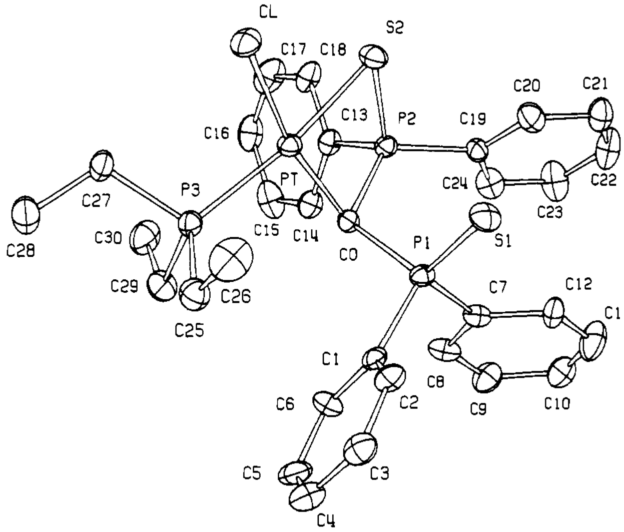


Figure 1. Molecular structure of [PtCl(PEt$_3$)(CH(PPh$_2$S)$_2$)]. Some important parameters are as follows: Pt–Cl 2.372 (3), Pt–P(3) 2.245 (4), Pt–S(2) 2.390 (4), Pt–C(0) 2.101 (12), P(1)–S(1) 1.936 (4), P(1)–C(0) 1.838 (11), C(0)–P(2) 1.821 (12), P(2)–S(2) 2.014 (5) Å; S(2)–P(2)–C(0) 100.9 (4), Cl–Pt–S(2) 89.3 (1), S(2)–Pt–C(0) 82.2 (3), C(0)–Pt–P(3) 97.5 (3), P(3)–Pt–Cl 92.8 (1)°.

Crystals of **5** (X = Y = S) suitable for study by X-ray diffraction were obtained by crystallization from a tetrahydrofuran/diethyl ether solvent mixture.[7] As is illustrated by Figure 1, the molecular structure contains approximately square-planar platinum but with a significant twist (16.1°) between the planes defined by P(3)–Pt–Cl and C(0)–Pt–S(2). The novel chelate system subtends a rather small angle (82.3 (3)°) at platinum and is folded by 23.06° about the C(0)–S(2) axis. The P(2)–C(0) bond, 1.821 (12) Å, is apparently a normal single bond similar in length to those of the phosphorus–phenyl bonds, which average 1.805 Å. To our knowledge, the only comparable system is a very recently reported nickel complex of the [Ph$_2$P(S)CH$_2$]$^-$ ion.[6] This differs in that the four-membered ring is essentially planar, being folded by only 1.7° about the S–C axis. Also, the metal coordination is more closely planar in the Ni complex and the P–C bond, 1.776 (8) Å, is shorter, suggesting some ylide character.[6] Our complex has the additional feature of the noncoordinated sulfur atom, Pt–S(1) = 3.70 Å. Moreover, the Pt–S(2) bond, 2.390 (4) Å, is one of the longest reported for Pt^{II} and is similar to those in Pt^0/SO$_2$ complexes, which lose SO$_2$ at about 110 °C.[8] The noncoordinated sulfur requires only a small relative motion to assume the transition state for substitution of S(2) by S(1). Thus, the solid-state structure of **5** clearly foreshadows the lability observed in solution.

Ambient-temperature ^{31}P{^{1}H} NMR spectra[9] of **5** (X = Y = S) in tetrahydrofuran show a triplet, ^3J(P–P) = 5.7 Hz, due

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(7) The pale yellow crystals of **4** (X = Y = S), C$_{31}$H$_{36}$ClP$_3$PtS$_2$, are monoclinic, space group $P2_1/n$, with a = 34.679 (5) Å, b = 8.360 (1) Å, c = 11.980 (2) Å, β = 93.92 (2)°, V = 3465 (1) Å^3, Z = 4, and ρ_{calcd} = 1.526 g cm^{-3} (Mo Kα = 0.71069 Å). The structure was solved and refined with use of 4378 independent reflections ($I > 0$) measured on a Picker four-circle diffractometer automated with a PDP-11/10 computer. The measurements were for two octants in the range 2θ = 0–50°. The platinum atoms were located by direct methods, and the structure was then developed and refined by Fourier difference maps and the method of least squares, anisotropic thermal corrections being applied to all non-hydrogen atoms. The crystal structure is molecular. Convergence (maximum shift/esd = 0.32) was attained at R = 0.0617, R_w = 0.0889. The final difference map had no interpretable peaks (maximum 1.99 e Å^{-3} near Pt).

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(9) ^{31}P{^{1}H} NMR spectra were recorded at 24.3 MHz. Chemical shifts were measured relative to external P(OMe$_3$)$_3$ and are reported relative to 85% H$_3$PO$_4$ with a conversion factor of +141 ppm. Positive values are downfield of the reference.

to PEt$_3$ at +4.1 ppm and a doublet at +40.3 ppm due to P(1,2). Each resonance has satellites due to coupling to ^{195}Pt (^1J(Pt–P) = 3906 Hz, ^2J(Pt–P) = 301 Hz). When the temperature is reduced, the low-field resonance broadens and at about −55 °C splits into two resonances assignable to the P(1) and P(2) atoms of the solid-state structure. Clearly, at higher temperatures a rapid dynamic interchange occurs between the coordinated and noncoordinated sulfur atoms, which in turn renders the phosphorus atoms equivalent on the NMR time scale. The unusual pivotal nature of the process has been pointed out above, and it is also noteworthy that the complex is chiral at C(0) and the dynamic interchange inverts the configuration. This occurs by interchange of the roles of the two sulfur atoms despite the fact that the actual motion is simply a rotation about the Pt–C(0) bond.

The lability of the Pt–S(2) bond in **5** (X = Y = S) may be attributed in part to the trans influence of the 4, PEt$_3$ ligand. It is thus interesting that isomer **4** (X = Y = S), in which the sulfur is trans to Cl, exhibits an ambient-temperature ^{31}P{^{1}H} NMR spectrum assignable to a static structure. The resonances of P$_a$ and P$_b$ at +61.9 and +39.9 ppm are both doublets, due to coupling to P$_c$ (^3J(P–P) = 11.4 and 9.5 Hz, respectively), with platinum satellites (^2J(Pt–P) = 451 and 84 Hz, respectively). The P$_c$ resonance at +5.4 ppm is an overlapping doublet of doublets with platinum satellites (^1J(Pt–P) = 2949 Hz). When the temperature is raised, isomerization to **5** begins but there is also evidence for dynamic interchange of the P$_a$ and P$_b$ atoms of **4**, with a coalescence temperature of about +50 °C.

Our research into the various coordination modes exemplified by Scheme I is continuing, and full details will be published at a later date.

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Registry No. **4** (X = Y = S), 85957-01-3; **4** (X = S, Y = O), 85957-02-4; **4** (X = Y = Se), 85957-03-5; **5** (X = Y = S), 85994-29-2; **5** (X = Y = Se), 85994-30-5; **6** (X = Y = S), 85957-04-6; **6** (X = S, Y = O), 85957-05-7; **6** (X = Y = Se), 85957-06-8; **7** (X = Y = S), 85976-64-3; CH$_2$(PPh$_2$S)(PPh$_2$S), 14633-92-2; Li(CH(PPh$_2$S)$_2$), 85976-65-4; Pt$_2$Cl$_4$(PEt$_3$)$_2$, 15692-96-3; PEt$_3$, 554-70-1.

Supplementary Material Available: Tables of fractional atomic coordinates, interatomic distances, bond angles, selected intermolecular distances, anisotropic temperature parameters, and structure factors (27 pages). Ordering information is given on any current masthead page.

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Articles

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Structural Nomenclature for Polyboron Hydrides and Related Compounds. 1. Closed and Capped Polyhedral Structures

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Received November 11, 1982

The method for uniquely describing closed, fully triangulated boron polyhedra developed previously is used for naming closed polyboron hydrides and their replacement analogues and derivatives. A descriptor system for uniquely describing capped closed polyboron polyhedra is proposed.

Introduction

Polyboron hydrides and their replacement analogues and derivatives have been described in the past by a stoichiometric nomenclature[2a–d,3a–c] that provides information only on the number and type of skeletal atoms and exopolyhedral hydrogen atoms, substituents, or ligands. Except for recognition of "closed" structures by the prefix *closo*-,[2b,e,3d,e,4] the specific polyhedral structure of a polyboron hydride was not provided by its name. A knowledge of boron hydride chemistry was necessary in order to know the structure. Even this has not been sufficient in an increasing number of cases, where structures could not be inferred from previous chemistry.[7] Recently, we reported a method for definitively describing structures of closed polyhedral compounds.[8] This report

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(1) (a) Chemical Abstracts Service. (b) The University of Chicago; Camille and Henry Dreyfus Teacher-Scholar. Present address: Department of Chemistry, University of California, Irvine, CA 92717.

(2) American Chemical Society. "The Nomenclature of Boron Compounds", *Inorg. Chem.* **1968**, *7* (10), 1945–1964: (a) Rules 1.3 and 1.4, pp 1946–1947; (b) Rule 4.1, pp 1950–1951; (c) Rules 7.3 and 7.4, p 1953; (d) Rule 7.5, p 1953; (e) Rule 1.6, p 1947, and Rule 7.4, p 1953; (f) Rule 1.6, Comment, p 1947; (g) Rule 2.3234, p 1949; (h) Rules 3.2–3.4, p 1950; (i) Rule 6, p 1952; (j) Rule 4.2, p 1951.

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