by the Yatsimirskii method[21] by measuring the absorptions of the mixtures of Cu(II) (in solutions of OH^- and lactic acid) and PTS at 250 nm and 30 °C. There is evidence for a complex of Cu(II) and CAT too, but no such complexation is indicated kinetically. Some of the results are given in Figure 2.

Discussion

Various Species Participating in the System. There are three main reactants, CAT, lactic acid, and copper(II). The form of their species may depend on the concentration of OH^- and/or the interaction among themselves to form complexes. Lactic acid would be present as the acetate ion. CAT ionizes in solution into $RNCl^-$ and Na^+, and thus the predominant species of CAT in alkaline solutions would be $RNCl^-$. The concentration of RNHCl would be insignificant in alkaline solutions since the protonation constant[7,22] is only 4.2×10^2 and hence subsequent hydrolytic and disproportionation reactions would also be insignificant. The hydroxide ion dependence should be connected with copper(II). Margerum and co-workers[23] have reported two species, $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$, in alkaline solutions of Cu(II), and the formation constant for the equilibrium (3) is reported to be about 16.

$$Cu(OH)_3^- + OH^- \overset{K_3}{\rightleftharpoons} Cu(OH)_4^{2-} \tag{3}$$

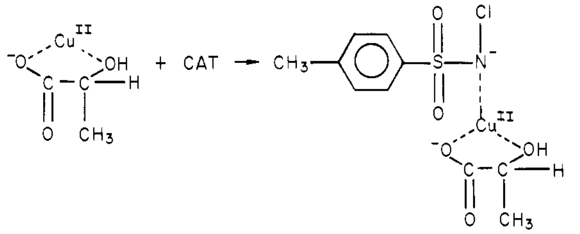
Our kinetic results indicate a lower value (<0.1) so that $[Cu(OH)_3^-] \gg [Cu(OH)_4^{2-}]$. Alternatively K_3 may be much larger than 16 and an equilibrium (eq 4) with a small value

$$Cu(OH)_4^{2-} + OH^- \overset{K_4}{\rightleftharpoons} Cu(OH)_5^{3-} \tag{4}$$

for K_4 may exist in the system. In any case the two copper(II) species in the present investigation are undefined, but they differ by one OH^- in an equilibrium of the type

$$Cu(OH)_n^{(n-2)-} + OH^- \rightleftharpoons Cu(OH)_{n+1}^{(n-1)-} \tag{5}$$

The hydroxy species of copper(II) form a complex with the lactate ion, and this further complexes with CAT at the nitrogen site as shown, yielding a ternary complex:



Such a configuration for the intermediate and then activated complex is facile for the electron transfer, and such ternary reactive complexes have been reported also in the oxidations with peroxydisulfate[24] and hydrogen peroxide.[25]

Visual observations on systems containing CAT, copper(II), and OH^- have indicated a transient yellow species, which is likely to be Cu^{III}. However, in the presence of lactic acid, it either is not formed or disappears quickly. Lister[26] and Margerum[27] have reported the formation of $Cu(OH)_4^-$ in the copper(II)-catalyzed decomposition of hypochlorite. There are other copper(II)-catalyzed reactions[28] in which copper(III) is said to be formed. It is therefore very likely that Cu^{III} is formed in the present investigation too. In general, copper(II) catalysis in an acid medium operates through a more reactive coordination complex with oxidant or reductant, and in alkaline solutions, it operates through the Cu^{II}/Cu^{III} cycle. The latter is more probable if some coordinating oxidant ligand is present,[29] and since the oxidant CAT can serve as a ligand in the present case, the formation of transient Cu^{III} is possible.

Some calculations and comparisons may be worthwhile to make. The calculated value of $k_1 + k_2[OH^-]$ with an average value of $k_1 = 2.7 \times 10^{-5}$ s^{-1} and that of $k_2 = 3.4 \times 10^{-5}$ M^{-1} s^{-1} is 4.4×10^{-5} s^{-1} at $[OH^-] = 0.5$ M. The extrapolated value from the plot of k_0 vs. [Cu(II)] was found to be 4.3×10^{-5} s^{-1}. Similarly the calculated value of $k_3 + k_4[OH^-]$ with an average value of $k_3 = 0.11$ M^{-1} s^{-1} and that of $k_4 = 0.95$ M^{-2} s^{-1} is 0.585 M^{-1} s^{-1} at $[OH^-] = 0.5$ M. The extrapolated value (Figure 1) from the plot of (slope)$^{-1}$ vs. [PTS] was found to be 0.77 M^{-1} s^{-1}. The agreement in the calculated and extrapolated values should be considered satisfactory in view of the complexity of the system.

Registry No. Lactic acid, 50-21-5; chloramine T, 127-65-1; copper ion (2+), 15158-11-9.

Supplementary Material Available: Listings of pseudo-first-order rate constants and absorptions for mixtures of copper(II), OH^-, and lactic acid (2 pages). Ordering information is given on any current masthead page.

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An Easy Preparation with Full Characterization of Pd_6Cl_{12}: A Form of Palladium Chloride Soluble in Aromatic Solvents

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Palladium chloride is reported to exist in two forms called α and β.[1,2] An usual method of preparation involves the direct chlorination of metallic palladium or its reaction with HCl in the presence of an oxidant (e.g., HNO_3 or NO_2). When the preparation is carried out at temperatures below 550 °C, the resulting $PdCl_2$ is claimed to be the β-form.[1-3]

The structural nature of this form was investigated by Shäfer et al.[4] Its isomorphism with β-$PtCl_2$[5] together with the determination of the molecular mass by mass spectroscopy supported the conclusion that the β-form contains discrete molecular clusters of formula Pd_6Cl_{12}. This proposed structure is quite different from that of the α-form, which is known to be a polymeric chain of $PdCl_2$ units, bridged by chlorine atoms.[6]

Unfortunately Shäfer et al. did not report the experimental method of preparation of the β-form that they have investigated. Only later was it claimed[1-3] that the β-form corresponded to ordinary commercial $PdCl_2$.

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Table I. X-ray Powder Spectrum of Pd_6Cl_{12}[a]

hkl	*d*,[b,d] Å	*d*,[c] Å	*hkl*	*d*,[b,d] Å	*d*,[c] Å
101	6.857	6.845	220	3.257	3.261
110	6.510	6.523	122	3.034	3.030
021	4.727	4.722	131	2.942	2.944
012	4.029	4.020	113	2.621	2.625
300	3.763	3.766	312	2.536	2.533

[a] Radiation at 1.541 78 Å. [b] Obtained with our form of $PdCl_2$. [c] Calculated from the X-ray data of β-$PtCl_2$.[5] [d] The observed pattern also contains the following peaks of low intensity at 2θ: 11.27, 11.93, 12.20, 15.71, 20.86, 24.15, 28.00, 32.80, and 33.46, which do not correspond to those calculated for α-$PdCl_2$ or observed for commercial $PdCl_2$. They can be related to another known form of $PdCl_2$.[9] These peaks have relative intensities that vary with preparation.

Table II. Mass Spectrum of Pd_6Cl_{12}[a]

m/e	intens, %	assignt
1062	100	$Pd_6Cl_{12}^+$
1027	46	$Pd_6Cl_{11}^+$
992	62	$Pd_6Cl_{10}^+$
920	15	$Pd_6Cl_8^+$
885	22	$Pd_5Cl_{10}^+$ (or $Pd_6Cl_7^+$)
848	12	$Pd_5Cl_9^+$ (or $Pd_6Cl_6^+$)
814	40	$Pd_5Cl_8^+$ (or $Pd_6Cl_5^+$)
708	30	$Pd_4Cl_8^+$ (or $Pd_5Cl_5^+$ or $Pd_6Cl_2^+$)
672	15	$Pd_4Cl_7^+$ (or $Pd_5Cl_4^+$ or Pd_6Cl^+)
601	7	$Pd_4Cl_5^+$ (or $Pd_5Cl_2^+$)
566	40	$Pd_4Cl_4^+$ (or Pd_5Cl^+)
530	40	$Pd_3Cl_6^+$ (or $Pd_4Cl_3^+$)
495	30	$Pd_3Cl_5^+$ (or $Pd_4Cl_2^+$)
427	75	$Pd_3Cl_3^+$

[a] Below *m/e* 400 numerous peaks were observed that could not be assigned to some definite species.

However we have found that $PdCl_2$, available commercially to us, is a solid completely insoluble in noncomplexing organic solvents including aromatic hydrocarbons, with an X-ray powder spectrum different from that calculated for both the known structure of the polymeric α-form[6] and the possible crystal structure, containing Pd_6Cl_{12}, isomorphous with β-$PtCl_2$.[5]

The pattern of the X-ray powder spectrum of our commercial $PdCl_2$ is quite comparable to that reported for a third unknown form, obtained at low temperatures.[6] It follows that the so-called β-form of $PtCl_2$ still deserves a well-defined method of preparation together with a better characterization of its properties.

Results and Discussion

In the course of our investigation on palladium-catalyzed carbonylations, we found that when $Pd_3(CH_3COO)_6$[7] is reacted with CO in glacial acetic acid containing $HClO_4$ (about 0.5–0.8 M), a solid separates, which is quite soluble in aromatic solvents and which is analyzed to be $PdCl_2$. The chloride ions obviously originate in the palladium-catalyzed reduction of ClO_4^- by CO.[7] The same material was obtained when we added to $Pd_3(CH_3COO)_6$, dissolved in glacial acetic acid, 2 equiv of concentrated HCl. The yields are quantitative.

The $PdCl_2$ so obtained is soluble in aromatic solvents, but it is insoluble in other nondonor organic solvents such as saturated hydrocarbons or halogenated solvents or even acetic acid. This observation is in agreement with the conclusions of Schäfer et al.,[4] who suggested that Pd_6Cl_{12}, as Pt_6Cl_{12}, must bind to electron donors such as aromatic solvents.

In order to confirm that the $PdCl_2$, isolated with our preparative methods, was the β-form described by Schäfer et al.,[4] we have carried out both an X-ray powder and a mass spectroscopic investigation. The X-ray powder data, which are reported in Table I, show the presence of all the expected peaks calculated on the basis of the isomorphism of β-$PdCl_2$ with β-$PtCl_2$, the structures of which correspond to an octahedral Pt_6 cluster with a symmetrical arrangement of bridging chloride ligands.[5]

Other rather weak peaks are present which can not be attributed to the presence of small amounts of either the polymeric α-$PdCl_2$ or the so-called commercial $PdCl_2$ (see Table I). This observation would suggest that in our preparation β-$PdCl_2$ is contamined by a small amount of an other unknown modification of $PdCl_2$ which is also soluble in aromatic hydrocarbons.

The mass spectrum (Table II) of our $PdCl_2$ is completely consistent with its formulation as Pd_6Cl_{12}.

Strangely enough Schäfer et al.[4] reported that the mass spectrum of β-$PdCl_2$ did not show peaks corresponding to $(PdCl_2)_n^+$ ions with $n < 6$. We have observed peaks of low intensities at *m/e* ratios of 885, 708, and 530, which could theoretically correspond to $(PdCl_2)_n^+$ ions with $n = 5$, 4, and 3, respectively.

The major peaks correspond to the progressive loss of chlorine atoms: the first three most abundant peaks are those due to $Pd_6Cl_{12}^+$, $Pd_6Cl_{11}^+$, and $Pd_6Cl_{10}^+$ ions. The assignment of the other following peaks is not so unambiguous since it is not possible to distinguish between ions of approximately equal masses such as $Pd_nCl_m^+$ and $Pd_{n+1}Cl_{m-3}^+$ ions owing to the high complexity of the isotopic structure of each signal. For instance, the peak at about *m/e* 885 may correspond to $Pd_6Cl_7^+$ or $Pd_5Cl_{10}^+$ ions. The most intense fragmentation peak is that of the $Pd_3Cl_3^+$ ion (*m/e* 423), corresponding to the symmetrical rupture of the original Pd_6 cluster frame.

In conclusion from the mass spectrum it appears that the Pd_6 cage is quite stable, although some degradation to Pd_5, Pd_4, and Pd_3 may occur, in parallel with chlorine dissociation from the original parent ion, which is the major mechanism of degradation.

This is unexpected because the metal–metal bond in the Pd_6 cluster is supposed to be rather weak considering the reported structure of the Pt_6 cage of Pt_6Cl_{12}.[5]

We have examined the properties of Pd_6Cl_{12}: it dissolves in aromatic solvents (the solubility, which is about 5×10^{-3} M, increases with increasing the donor properties of the hydrocarbon), producing solutions with electronic absorption spectra quite different from the reflectance spectra of the solid. Molecular weight determinations in benzene show that cluster structure is mantained (the molecular weight determination is slightly lower than the calculated value of 1062). All the spectra show a broad charge-transfer band at about 360 nm, with intensity about 10^3 mol^{-1} cm^{-1}; a similar kind of spectrum with a charge-transfer band with intensity of about 10^3 mol^{-1} cm^{-1} is observed in benzene solutions of an other acido clusters such as $Pd_3(CH_3COO)_6$.[8]

These observations would support the unique solubility in aromatic solvents of Pd_6Cl_{12} being due to an acid–base interaction with the aromatic donor hydrocarbons.

It is also quite probable that the easy synthesis of Pd_6Cl_{12} from $Pd_3(CH_3COO)_6$ must be related to the facile aggregation of two Pd_3 units into a Pd_6 unit, since the structure of Pd_6Cl_{12} is formed by two symmetrical Pd_3Cl_3 units linked together by six chlorine bridges.[5] This correlation is substantiated by the high intensity of the $Pd_3Cl_3^+$ ion in the mass spectrum.

The aromatic solutions of β-$PdCl_2$ may find particular applications in catalytic synthesis, since it is expected that the

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catalytic properties of a Pd_6Cl_{12} cluster can be different from those of a $Pd_3(CH_3COO)_6$ cluster or those of mononuclear Pd^{2+} species. In this respect the different catalytic activity of low- and high-temperature forms of $PdCl_2$ in the isomerization of 1-hexene must be mentioned.[10]

Experimental Section

Palladium acetate was prepared by a literature method.[8] Electronic absorption spectra and reflectance spectra were recorded on a Beckman DK-2A spectrophotometer. The mass spectrum was recorded on a Varian Mat 112 mass spectrometer at 70 eV and 150 °C.

X-ray powder spectra were obtained with a Philips diffractometer equipped with a pulse discriminator and driven by a General Automation minicomputer. Internal calibration was made with silicon (ASTM). Molecular weight determinations in benzene have been carried out by F. Pascher Laboratory, Bonn, West Germany.

Preparation of Pd_6Cl_{12}. To a solution of $Pd_3(CH_3COO)_6$ in glacial acetic acid (about 0.05 M) was added the calculated quantity (2 equiv) of concentrated HCl at room temperature. The resulting brown fine precipitate was separated by centrifugation, washed with acetic acid, and dried in vacuo over NaOH. The yields of Pd_6Cl_{12} are nearly quantitative.

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Registry No. Pd_6Cl_{12}, 12268-04-1; $PdCl_2$, 7647-10-1; palladium diacetate, 3375-31-3.

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Thermal and Photochemical Reactivity of Fe and Fe_2 toward CH_4 in Low-Temperature Matrices

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Diiron, but not iron atoms in their ground electronic states, has been reported to react with methane at cryogenic temperatures, to form species of the type CH_3Fe_2H, structure unknown.[1] This proposal was based on Mössbauer and infrared spectroscopic studies. Subsequently, the nonobservation of a resonance Raman spectrum for Fe_2 in solid CH_4 was considered to be consistent with the idea of a special kind of reactivity associated with the diiron moiety,[2] and analogies with the dissociative chemisorption of CH_4 on bulk iron,[3] involving at least two iron sites have been envisaged.[1] Reactivity patterns of a similar type have also been suspected for Fe/Fe_2 in solid N_2, as determined by Mössbauer, infrared,[4] and optical spectroscopy, $Fe_2(N_2)_n$ complexes being formed, with Fe atoms remaining unreactive.[2] Evidence for the coexistence of Fe atoms and Fe_2 molecules in solid rare gas matrices was originally established by Barrett et al.[5a] using Mössbauer spectroscopy and subsequently observed by De Vore et al.[5b] using optical spectroscopy.

Montano et al. have recently reported matrix EXAFS data for the $Fe/Fe_2/Ar$ system that shed considerable light on the local environment of Fe atoms as well as a value of 2.02 ± 0.13 Å for the bond length of Fe_2 entrapped in the fccub lattice of solid Ne.[6] On the basis of Mössbauer spectroscopy, Montano[7] has assigned a $^7\Sigma_g$ term for the ground electronic state of Fe_2 in solid Ar, with vibrational constant $\omega_e = 300.26$ cm^{-1} and dissociation energy $D_e = 1.2$ eV being obtained by DiLella et al.[2] from an analysis of the corresponding resonance Raman spectrum.

Reactions of a number of photoexcited metal atoms[8,9] and metal clusters[10] with methane and higher alkanes[11] under cryogenic conditions have recently been discovered. In particular, the infrared spectrum of Fe/CH_4 matrices subjected to either broad-band[8] or narrow-band[12] irradiation at $\lambda > 330$ nm and $\lambda = 300$ nm, respectively, showed the production of a new species assigned to CH_3FeH. The latter excitation corresponded to a ($3d^74p^1$, $^5D_4 \leftarrow 3d^64s^2$, $^5D_4$) resonance line of atomic iron.[13] Because of the open-shell electronic configurations of atomic[13] and diatomic[7] iron, the Fe/Fe_2 matrix system offers an opportunity for probing ground- and excited-state selectivity and reactivity patterns with CH and CC bonds of saturated hydrocarbons that are not readily accessible with Cu/Cu_2.[9,10]

In this note we wish to report that under the conditions of our experiments Fe_2 could be coisolated with Fe atoms in solid CH_4 at 10–12 K and was found to neither react thermally (10–50 K) nor react photochemically (400–580 nm) with CH_4, in contrast to the observations of earlier studies.[1] On the other hand, Fe atoms photoexcited at 300 nm are highly reactive toward CH_4 at 12 K, leading to the oxidative-addition product CH_3FeH.[8,12]

The optical spectra of matrix entrapped Fe atoms and Fe atoms coisolated with Fe_2 in solid Kr are illustrated in Figure 1B,C. Gas- to matrix-phase correlations for the observed Fe atomic resonance lines can be seen from an examination of Figure 1A,B. The gas-phase spectrum (only spin- and dipole-allowed transitions shown) is represented by sticks (Figure 1A), the wavelengths, heights, and notation of which are in accord with the energies, oscillator strengths, and Russell–Saunders electronic state assignments, respectively, suggested from earlier studies.[13] The three most prominant visible bands of Fe_2 in Kr occur at 418, 474, and 532 nm, close to the wavelengths observed for Fe_2 in solid Ar, 414.5, 474.0, and 544.8 nm in previous investigations.[2,5] Partially resolved vibronic structure is best seen on the 474-nm absorption of Fe_2

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