I. As expected, the Cr–F stretching force constant f_r decreases from CrF_6^- to CrF_6^{2-} due to a bond weakening caused by the increased $Cr^{\delta+}-F^{\delta-}$ polarity of the bonds in CrF_6^{2-}.

Conclusion. Chromium pentafluoride is a moderately strong Lewis acid capable of forming stable CrF_6^- salts with NF_4^+ and NO^+. The NF_4^+ salt is of particular interest as an oxidizer because in it an oxidizing anion is combined with a strongly oxidizing cation. Contrary to previous reports,[4] no evidence was found for CrF_5 forming a distinct, predominantly ionic $CrF_4Sb_2F_{11}$ adduct with SbF_5. The oxidizing power of CrF_5 is greatly enhanced by strong Lewis acids but does not match that of PtF_6. Chromium(V) salts can selectively be reduced to Cr(IV) salts with NO. In this manner the new Cr(IV) salts $(NO)_2CrF_6$ and $NOCrF_5$ can be prepared. Similarly, CrF_5 can be reduced to mainly CrF_4 with either Cl_2 or $CFCl_3$. Reaction of CrF_5 with stoichiometric amounts of H_2O in HF produces an unstable oxonium salt that decomposes on HF removal to CrF_3O, thus providing a convenient new synthesis for this compound.


Contribution from Division of Physical Chemistry 1, Chemical Center, University of Lund, S-221 00 Lund, Sweden

Kinetics and Mechanism for Oxidation of Tetracyanoplatinate(II) by Chlorine and Hypochlorous Acid and for Hydrolysis of Chlorine in Aqueous Solution[†]

LISE DROUGGE and LARS I. ELDING*

Oxidation of $Pt(CN)_4^{2-}$ in aqueous solutions of chlorine has been followed by stopped-flow spectrophotometry. For pH $< \sim 7$, the reaction takes place by two parallel paths with Cl_2 and HOCl as oxidants according to the rate law rate = $(k_{Cl_2}[Cl_2] + k_{HOCl}[HOCl])[Pt(CN)_4^{2-}]$. In unbuffered solutions of chlorine in aqueous $NaClO_4$, the slow HOCl path is predominant, whereas in weakly acidic solutions buffered with HCl, oxidation takes place via the 10^5 times faster Cl_2 path. For certain conditions, the displacement of the hydrolysis equilibrium of chlorine

$$Cl_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + Cl^- + H^+$$
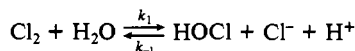
becomes rate-determining for the oxidation of $Pt(CN)_4^{2-}$ by Cl_2, which then appears to be zero order in complex. Such experiments give k_1 and k_{-1}. Rate constants at 25 °C for a 1.00 M perchlorate medium are $k_{Cl_2} = (1.08 \pm 0.10) \times 10^7$ M^{-1} s^{-1}, $k_{HOCl} = 97.9 \pm 1.1$ M^{-1} s^{-1}, $k_1 = 8.7 \pm 0.2$ s^{-1}, and $k_{-1} = (2.66 \pm 0.03) \times 10^4$ M^{-2} s^{-1}. The equilibrium constant for the chlorine hydrolysis is obtained from the kinetics as $(3.27 \pm 0.11) \times 10^{-4}$ M^2. The primary reaction product for oxidation of $Pt(CN)_4^{2-}$ by an excess of Cl_2 in acidic solution is *trans*-$Pt(CN)_4Cl(H_2O)^-$, which slowly reacts with a second chloride to give *trans*-$Pt(CN)_4Cl_2^{2-}$. Oxidation by HOCl gives primarily *trans*-$Pt(CN)_4(OH)_2^{2-}$, which rapidly reacts with a second molecule of HOCl to form a stable hypochlorite complex, *trans*-$Pt(CN)_4(OCl)(OH)^{2-}$. In weakly alkaline solution (pH 11), oxidation of $Pt(CN)_4^{2-}$ with ClO^- gives *trans*-$Pt(CN)_4(OH)_2^{2-}$ as the reaction product. Oxidation with HOCl and ClO^- is an inner-sphere two-electron transfer with the oxygen of the hypochlorite as the bridging atom. Chloride anation of *trans*-$Pt(CN)_4(OCl)(H_2O)^-$ is a rapid second-order reaction with rate constant 26.5 ± 0.2 M^{-1} s^{-1}.

Introduction

Oxidation of square-planar complexes of platinum(II) by chlorine or bromine in aqueous solution gives a *trans*-dihalo complex of platinum(IV) as the final reaction product. This is a classical method to prepare such platinum(IV) complexes.[1] It was shown already in 1954, in a study of the chlorination of $PtCl_4^{2-}$, that aqua complexes appear as intermediates in this reaction.[2] The two-step mechanism of eq 1 has been suggested[2-7]

$$PtL_4 + X_2 \xrightarrow{\text{fast}} X\text{-}PtL_4\text{-}OH_2 \xrightarrow{+X^-} X\text{-}PtL_4\text{-}X \quad (1)$$
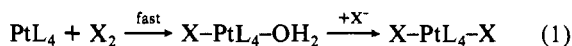
(X = halide). The first and very rapid reaction has been described as an oxidative addition of dihalogen to the platinum(II) complex.[3-7] This reaction is very fast in most cases, and there are very few reports on its kinetics so far. From stopped-flow measurements of the oxidation of $PtCl_4^{2-}$ by chlorine, it was concluded that the rate was independent of the concentration of one or both reactants.[5] That conclusion was later rebutted, and the oxidation was shown to be first order in both chlorine and complex.[7] Such a rate law was also found for the oxidation of $PdCl_4^{2-}$ by chlorine.[8] Oxidation of $Pt(CN)_4^{2-}$ by iodine has been studied by use of stopped-flow spectrophotometry, and those results are also compatible with a mechanism involving reaction between an iodine molecule and the complex.[7]

The subsequent reaction of eq 1 is much slower, and it has been the subject of several kinetic studies. It is a substitution of the water ligand of the intermediate aqua complex by halide. This reaction is accelerated by platinum(II) complexes[5-7] and by free halide.[3,4,7,9]

Aqueous solutions of chlorine contain Cl_2 and HOCl in equilibrium with each other according to eq 2.[10] Both these molecules

$$Cl_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HOCl + H^+ + Cl^- \quad (2)$$
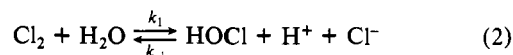
oxidize platinum(II) complexes quantitatively.[11] The possibility

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(1) "Gmelins Handbuch der Anorganischen Chemie", 8th ed.; Verlag Chemie: Weinheim, West Germany, 1940, 1957; Platinum, Parts C and D (for instance: Part C, pp 206, 292; Part D, pp 490, 509).
(2) Rich, R. L.; Taube, H. *J. Am. Chem. Soc.* **1954**, *76*, 2608.
(3) Skinner, C. E.; Jones, M. M. *J. Am. Chem. Soc.* **1969**, *91*, 4405.
(4) Mason, W. R. *Inorg. Chem.* **1971**, *10*, 1914.
(5) Jones, M. M.; Morgan, K. A. *J. Inorg. Nucl. Chem.* **1972**, *34*, 259.
(6) Morgan, K. A.; Jones, M. M. *J. Inorg. Nucl. Chem.* **1972**, *34*, 275.
(7) Elding, L. I.; Gustafson, L. *Inorg. Chim. Acta* **1976**, *19*, 165.
(8) Mureinik, R. J.; Pross, E. *J. Coord. Chem.* **1978**, *8*, 127.
(9) Vuik, C. P. J.; Poë, A. *Inorg. Chim. Acta* **1979**, *34*, 129.
(10) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 54.
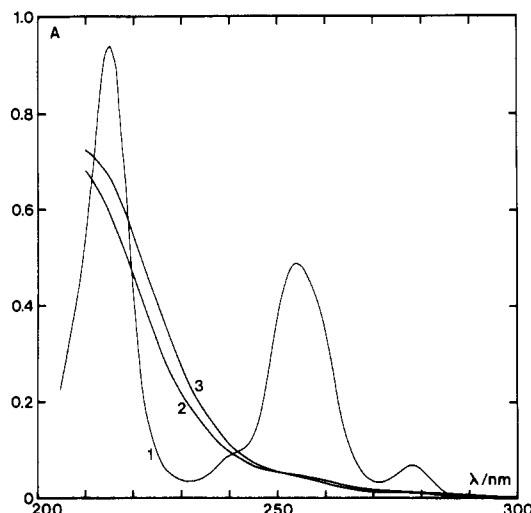
Figure 1. Spectral changes for oxidation of a 4.0×10^{-5} M solution of Pt(CN)$_4^{2-}$ by 6×10^{-5} M Cl$_2$ in 0.02 M HCl + 0.98 M HClO$_4$ (1.00-cm cell): (1) spectrum of 4.0×10^{-5} M Pt(CN)$_4^{2-}$; (2) spectrum of reaction mixture 5 min after mixing, representing complete conversion to *trans*-Pt(CN)$_4$Cl(H$_2$O)$^-$; (3) spectrum of reaction mixture after 24 h, showing a subsequent chloride anation to *trans*-Pt(CN)$_4$Cl$_2^{2-}$.

of oxidation by HOCl has not been considered in the two previous studies of the oxidative-addition step,[5,7] in spite of the fact that HOCl was the predominant species in the solutions used.

We report here an investigation of the kinetics and mechanism of oxidation of Pt(CN)$_4^{2-}$ by aqueous solutions of chlorine. For pH <7, both Cl$_2$ and hypochlorous acid (HOCl) are efficient as oxidants in two parallel reactions, according to the scheme of eq 3. Oxidation by Cl$_2$ is ca. 10^5 times faster than that by HOCl,

$$\text{Cl}_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{HOCl}$$

$$+\text{Pt(CN)}_4^{2-} \Big\downarrow k_{\text{Cl}_2} \qquad k_{\text{HOCl}} \Big\downarrow +\text{Pt(CN)}_4^{2-} \qquad (3)$$
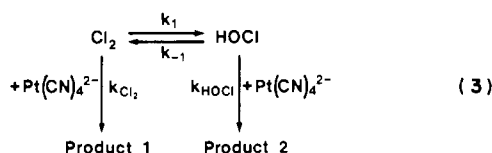
$$\text{Product 1} \qquad\qquad \text{Product 2}$$

but for carefully controlled experimental conditions, each reaction can be followed by use of the stopped-flow method. The two parallel reactions give different products.

Hypochlorite ion (OCl$^-$) also oxidizes Pt(CN)$_4^{2-}$. This reaction can be observed in weakly alkaline solution. The product is the same as with HOCl as oxidant, but the reaction is slower. For pH <7, reaction with OCl$^-$ is negligible.
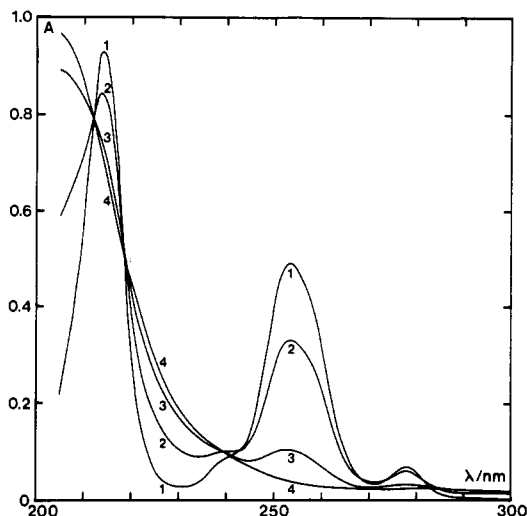
In some cases, the displacement of the hydrolysis equilibrium of eq 2 between Cl$_2$ and HOCl becomes rate determining for the oxidation of the complex by chlorine. The redox reaction then appears to be zero order with respect to the platinum complex. The kinetics of the reversible hydrolysis of eq 2 have been studied at 20 °C and 0.1 M ionic strength by use of temperature-jump relaxation.[12] A reexamination of the kinetics for the present experimental conditions by use of stopped-flow spectrophotometry is also included here.

Stoichiometry and Rate Expressions

Stoichiometry. Oxidation with an excess of Cl$_2$ gives *trans*-Pt(CN)$_4$Cl(H$_2$O)$^-$ or the corresponding hydroxo complex as the primary reaction product in a two-electron-transfer reaction according to eq 4. There are isosbestic points at 211, 218, and 242

$$\text{Pt(CN)}_4^{2-} + \text{Cl}_2 + \text{H}_2\text{O} \rightarrow \textit{trans-}\text{Pt(CN)}_4\text{Cl(H}_2\text{O)}^- + \text{Cl}^-$$

$$(4)$$
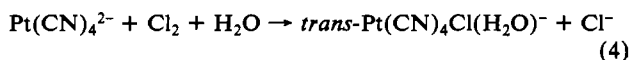
nm for this reaction in 1.00 M HClO$_4$, as shown by Figure 1. In the absence of Pt(CN)$_4^{2-}$ or large concentrations of chloride,

(11) (a) Milazzo, G.; Caroli, S. "Tables of Standard Electrode Potentials"; Wiley-Interscience: New York, 1978; pp 279, 377. (b) Reference 10, p 208.

(12) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.


Figure 2. Spectral changes for oxidation of a 2.0×10^{-5} M solution of Pt(CN)$_4^{2-}$ by 4×10^{-5} M HOCl in 1.00 M NaClO$_4$ (2.00-cm cell): (1) spectrum of 2.0×10^{-5} M Pt(CN)$_4^{2-}$; (2) spectrum of reaction mixture 2 min after mixing; (3) spectrum of reaction mixture 14 min after mixing; (4) spectrum of reaction mixture 2 h and 24 h after mixing. The equilibrium spectrum (curve 4) represents *trans*-Pt(CN)$_4$(OCl)(OH)$^{2-}$. Isosbestic points for the Pt(CN)$_4^{2-}$–HOCl reaction are at 212, 218, 241, and 284 nm.
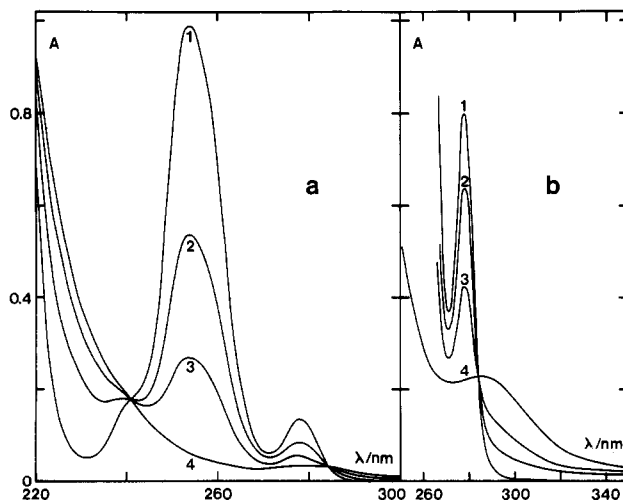
Figure 3. Spectra of equilibrated solutions of Pt(CN)$_4^{2-}$ in 1.00 M NaClO$_4$ with various concentrations of HOCl, showing the stoichiometry HOCl:Pt = 2:1 of reaction 5 (1.00-cm cell). Spectrum 4 is obtained for concentration ratios ≥ 2 (complete oxidation) and represents *trans*-Pt(CN)$_4$(OCl)(OH)$^{2-}$; spectrum 1 is for Pt(CN)$_4^{2-}$. There are isosbestic points at 241 and 284 nm. [Pt(CN)$_4^{2-}$]/mM was (a) 0.082 and (b) 0.50, and C_{Cl_2}/mM was (1) 0, (2) 0.077, (3) 0.14, and (4) 0.18 for part a and (1) 0, (2) 0.27, (3) 0.60, and (4) 1.1 for part b.

trans-Pt(CN)$_4$Cl(H$_2$O)$^-$ reacts extremely slowly with a second chloride to yield the final product *trans*-Pt(CN)$_4$Cl$_2^{2-}$.

The stoichiometry for the oxidation with HOCl is hypochlorous acid:platinum 2:1 according to eq 5. This is a two-step reaction,

$$\text{Pt(CN)}_4^{2-} + 2\text{HOCl} \rightarrow$$

$$\textit{trans-}\text{Pt(CN)}_4(\text{OCl})\text{OH}^{2-} + \text{H}^+ + \text{Cl}^- \quad (5)$$
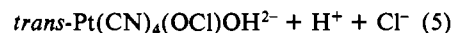
and a dihydroxo complex of platinum(IV) is the primary reaction product (vide infra). The absorbance changes and stoichiometry of the overall reaction are shown by the spectra in Figures 2 and 3. There are isosbestic points at 212, 218, 241, and 284 nm for this reaction in 1.00 M NaClO$_4$.

Aqueous Solutions of Chlorine: Determination of k_1. Both the equilibrium[10,13,14] and kinetics[12,15] of the reversible hydrolysis

(13) Connick, R. E.; Chia, Y. *J. Am. Chem. Soc.* **1959**, *81*, 1280 and references therein.

(disproportionation) reaction of eq 2 have been studied previously for various experimental conditions. The equilibrium constant (eq 6) is 3.94×10^{-4} M^2 at 25 °C for a pure aqueous medium[13]

$$K = [HOCl][H^+][Cl^-]/[Cl_2] = k_1/k_{-1} \qquad (6)$$

and 3.27×10^{-4} M^2 for the 1.00 M perchlorate medium used here (vide infra). Protolysis of hypochlorous acid,[16] as well as formation of Cl_3^-,[14,17] is negligible for the acid solutions and low chloride concentrations used here, so the total concentration of chlorine can be expressed as eq 7. Dilution of an aqueous solution of

$$C_{Cl_2} = [Cl_2] + [HOCl] \qquad (7)$$

chlorine will displace equilibrium 2 to the right. For constant concentrations of acid and chloride, the rate constant for equilibrium displacement is defined by eq 8. Since the equilibrium

$$k_{exptl} = k_1 + k_{-1}[H^+][Cl^-] \qquad [H^+], [Cl^-] = constant \qquad (8)$$

constant of eq 6 is so small, the second term on the right hand side of eq 8 becomes negligible for $[H^+][Cl^-] << 3 \times 10^{-4}$ M^2. This condition is fulfilled for dilute aqueous solutions of chlorine without extra chloride or acid added, when $C_{Cl_2} < \sim 1 \times 10^{-3}$ M. For those solutions, the rate constant for equilibrium displacement is simply

$$k_{exptl} = k_1 \qquad (9)$$

k_1 can thus be obtained from experiments in which ca. 2–3 mM solutions of chlorine are diluted with pure ionic medium.

Equilibrium Displacement of Eq 2 Rate Determining for Oxidation of Pt(CN)$_4^{2-}$: Determination of k_{-1}. In a sodium perchlorate medium with 0.01 M hydrochloric acid added and with $C_{Cl_2} << 0.01$ M, 77% of the chlorine is present as HOCl. If such a solution is mixed with an excess of Pt(CN)$_4^{2-}$, the hypochlorous acid will disappear via the two parallel reaction paths denoted by k_{HOCl} and k_{-1} in the scheme shown in eq 3. The reaction via the k_{HOCl} path will be negligibly slow for the condition of eq 10,

$$k_{HOCl}[Pt(CN)_4^{2-}] << k_{-1}[H^+][Cl^-] \qquad (10)$$

i.e. for platinum concentrations much smaller than ca. 30 mM, when $[H^+][Cl^-] = 10^{-4}$ M^2.[18] All HOCl will then disappear via the two consecutive reactions denoted k_{-1} and k_{Cl_2} of eq 3. The k_{-1} path becomes rate determining when the condition of eq 11

$$k_{Cl_2}[Pt(CN)_4^{2-}] >> k_{-1}[H^+][Cl^-] \qquad (11)$$

is fulfilled, i.e. for platinum concentrations much larger than 3 $\times 10^{-7}$ M.[19] Thus, in the concentration interval 3×10^{-7} M $<<$ [Pt(CN)$_4^{2-}$] $<< 3 \times 10^{-2}$ M, and for $[H^+] = [Cl^-] = 10^{-2}$ M, the reaction HOCl → Cl$_2$ becomes rate determining for the oxidation of Pt(CN)$_4^{2-}$ by chlorine, and, simultaneously, the direct oxidation of the platinum complex by HOCl is negligibly slow. [Cl$_2$] decreases rapidly to its steady-state concentration. Pt(CN)$_4^{2-}$ serves as a scavenger for the Cl$_2$ formed in the displacement of equilibrium 2, so the reverse reaction (k_1) is suppressed. Under these conditions, the oxidation of Pt(CN)$_4^{2-}$ by an aqueous solution of chlorine appears to be zero order with respect to platinum with a rate constant according to eq 12.

$$k_{exptl} = k_{-1}[H^+][Cl^-] \qquad (12)$$

Parallel Oxidation of Pt(CN)$_4^{2-}$ by Cl$_2$ and HOCl: Determination of k_{Cl_2}. Dilute solutions of chlorine in a 1.00 M sodium perchlorate medium without extra chloride added contain almost
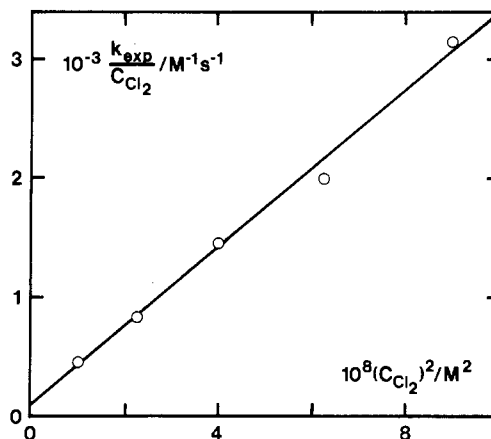

Figure 4. Plot according to eq 17 of the oxidation of 2.0×10^{-6} M Pt(CN)$_4^{2-}$ by excess chlorine in 1.00 M NaClO$_4$.

all the chlorine as HOCl (99.7% for $C_{Cl_2} = 10^{-3}$ M). If Pt(CN)$_4^{2-}$ is added in a very low concentration (ca. 10^{-6} M) to dilute solutions of chlorine (0.1–0.3 mM), the platinum(II) will be oxidized via the two parallel paths of the scheme of eq 3 and the rate of displacement of the equilibrium of eq 2 will be rapid compared to the observed kinetics. There will be a constant concentration ratio between Cl$_2$ and HOCl during the course of the reaction. The rate of disappearance of the platinum complex is then described by eq 13, where the observed rate constant is given by eq 14 and [HOCl] and [Cl$_2$] are constant. Equations 6 and 7 give

$$-d[Pt(CN)_4^{2-}]/dt = (k_{HOCl}[HOCl] + k_{Cl_2}[Cl_2])[Pt(CN)_4^{2-}] \qquad (13)$$

$$k_{exptl} = k_{HOCl}[HOCl] + k_{Cl_2}[Cl_2] \qquad (14)$$

eq 15, which can be simplified to eq 16, since [HOCl] $\approx$ [H$^+$]

$$k_{exptl}/C_{Cl_2} = (Kk_{HOCl} + k_{Cl_2}[H^+][Cl^-])/(K + [H^+][Cl^-]) \qquad (15)$$

$$k_{exptl}/C_{Cl_2} = (Kk_{HOCl} + k_{Cl_2}C_{Cl_2}^2)/(K + C_{Cl_2}^2) \qquad (16)$$

$\approx$ [Cl$^-$] $\approx C_{Cl_2}$ is valid with good approximation for the conditions used. $C_{Cl_2}^2$ is on the order of 10^{-7} M^2 and can be neglected compared to K, so eq 16 transforms into eq 17. Plots of k_{exptl}/C_{Cl_2}

$$k_{exptl}/C_{Cl_2} = k_{HOCl} + (k_{Cl_2}/K)C_{Cl_2}^2 \qquad (17)$$

vs. $C_{Cl_2}^2$ should be linear with slope k_{Cl_2}/K and intercept k_{HOCl}. The rate constant k_{Cl_2} can be accurately determined from such experiments.

Direct Oxidation of Pt(CN)$_4^{2-}$ by HOCl: Determination of k_{HOCl}. Hypochlorous acid is predominant in dilute solutions ($<5 \times 10^{-4}$ M) of chlorine in 1.00 M sodium perchlorate. If large concentrations of Pt(CN)$_4^{2-}$ are added to such solutions in at least a 10-fold excess, the rate of displacement of reaction 2 to the left is slow compared to the rate of oxidation of Pt(CN)$_4^{2-}$ by HOCl ($k_{-1}[H^+][Cl^-] << k_{HOCl}$[complex] for $[H^+] = [Cl^-] \leq 5 \times 10^{-4}$ M). Since the concentration of Cl$_2$ is very small, the very rapid and parallel oxidation by Cl$_2$ does not disturb the observed kinetics. The rate of the redox reaction is simply

$$rate = k_{exptl}[HOCl] \qquad (18)$$

with the observed first-order rate constant

$$k_{exptl} = k_{HOCl}[Pt(CN)_4^{2-}] \qquad (19)$$

Experimental Section

Chemicals and Solutions. K$_2$Pt(CN)$_4$·3H$_2$O (Johnson Matthey), NaCl (Merck p.a.), HClO$_4$ (Baker p.a.), and HCl (Merck p.a.) were used directly. NaClO$_4$ (Baker p.a.) was recrystallized once, and water was doubly distilled from a quartz apparatus. Ca. 70–80 mM stock solutions of chlorine were prepared by reaction between HCl and KMnO$_4$ (Merck p.a.) and by bubbling the resulting gas through water for 10–15 min. These solutions were analyzed for chlorine by addition of an excess of

(14) Zimmermann, G.; Strong, C. F. *J. Am. Chem. Soc.* **1957**, *79*, 2063.
(15) Lifschnitz, A.; Perlmutter-Haymann, B. *J. Phys. Chem.* **1960**, *64*, 1663.
(16) Reference 10, p 55.
(17) Dodgen, H. W.; Jordan, A. D.; Jordan, R. B. *J. Phys. Chem.* **1973**, *77*, 2149.
(18) Calculated from eq 10 and the values of k_{HOCl} and k_{-1}.
(19) Calculated from eq 11 and the values of k_{-1} and k_{Cl_2}.

Table I. Experiments To Determine k_{-1}^a

$10^4[\text{Pt(CN)}_4^{2-}]/\text{M}$	$10^5 C_{\text{Cl}_2}/\text{M}$	$10^2[\text{H}^+]/\text{M}$	$10^2[\text{Cl}^-]/\text{M}$	λ/nm	$k_{\text{exptl}}/\text{s}^{-1}$	$10^{-4}k_{-1}/\text{M}^{-2}\,\text{s}^{-1}$
1.0	1.0	1.0	1.0	253	2.79	2.79
1.0	5.0	1.0	1.0	253	2.72	2.72
1.0	1.0	2.0	2.0	253	10.8	2.70
2.0	2.0	2.0	2.0	253	11.0	2.75
2.0	2.0	1.0	1.0	230	2.47	2.47
4.0	4.0	1.0	1.0	230	2.44	2.44
4.0	4.0	10.0	0.10	230	2.59	2.59
5.0	5.0	1.0	1.0	253	2.70	2.70
5.0	5.0	10.0	0.10	230	2.72	2.72
7.0	7.0	1.0	1.0	230	2.67	2.67
10.0	7.0	1.0	1.0	230	2.65	2.65

mean 2.66 ± 0.03

^{a} The displacement of the hydrolysis equilibrium (eq 2) with rate constant according to eq 12 is rate determining for the redox reaction.
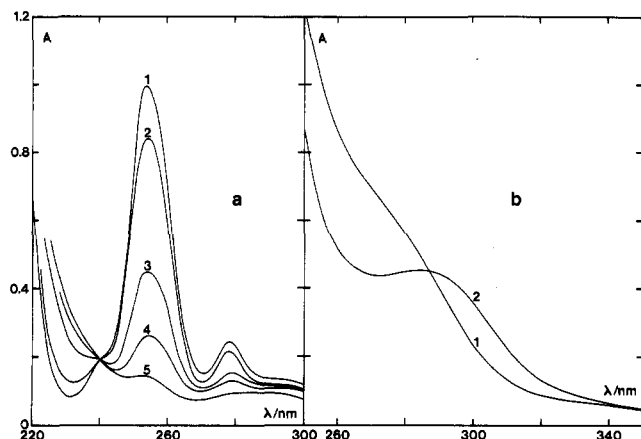
Figure 5. (a) Spectral changes for oxidation of Pt(CN)$_4^{2-}$ by hypochlorite ion in weakly alkaline solution (pH 11) according to eq 22. 0.16 mM Pt(CN)$_4^{2-}$ in water was mixed with an equal volume of 0.50 mM chlorine in 2.0 mM NaOH. Spectra were recorded (1) 25 min, (2) 5 h, (3) 25 h, (4) 45 h, and (5) 100 h after mixing. Equilibrium was not attained after 100 h. The isosbestic point is at 241 nm (1.00-cm cell; reference water). (b) Spectral changes resulting from the formation of the hypochlorite complex according to eq 21: Spectrum 1 is for 1.0 mM *trans*-Pt(CN)$_4$(OH)$_2^{2-}$ recorded 2 days after mixing of 2.0 mM Pt-(CN)$_4^{2-}$ in water with 2.2 mM chlorine in 4.0 mM NaOH (1.00-cm cell). After recording of spectrum 1, the solution was further mixed with an equal volume of 6.0 mM chlorine in water, and spectrum 2 was immediately recorded (2.00-cm cell; reference chlorine and hydroxide in water). Spectrum 2 is identical with spectrum 4 of Figure 3 and shows that the hypochlorite complex *trans*-Pt(CN)$_4$(OCl)(OH)$^{2-}$ has been formed on addition of excess chlorine according to eq 21.

KI (Merck p.a.) to diluted samples (1:5000) and spectrophotometric measurement on the oxidation product I$_3^-$ at 353 nm, where $\epsilon_{\text{I}_3^-} = 26\,400$ cm^{-1} M^{-1}.[20,21] Stock solutions of chlorine for the kinetics were mixed from freshly prepared aqueous chlorine stock solution and 1.00 or 2.00 M stock solutions of HCl, HClO$_4$, NaCl, and NaClO$_4$ to give an ionic strength of 1.00 M and the desired concentrations of acid and chloride. Chlorine solutions were carefully stoppered and protected from illumination.

Spectra. Absorption spectra were recorded by use of a Beckman 25 spectrophotometer. Spectra of aqueous solutions of chlorine and hypochlorous acid are given in the literature.[14] Figure 1 shows spectral changes for the oxidation of Pt(CN)$_4^{2-}$ by an aqueous solution of chlorine in 1.00 M perchloric acid, where the reaction with Cl$_2$ is predominant and the oxidation is extremely rapid. Figures 2 and 5 show the much slower spectral changes for the reaction in 1.00 M sodium perchlorate, where the HOCl path is predominant, and for the reaction in alkaline solutions, where OCl$^-$ is the oxidant.

Kinetics. A modified Durrum-Gibson stopped-flow instrument described elsewhere[22] was used for the kinetics. Rate constants were calculated directly from the transmittance vs. time curves by use of a least-squares program. The values given represent means of at least three repetitive runs. The temperature was 25.0 ± 0.1 °C, and the ionic

Table II. Experiments To Determine k_{HOCl}^a

$10^3[\text{Pt(CN)}_4^{2-}]/\text{M}$	$10^4[\text{HOCl}]/\text{M}$	$k_{\text{exptl}}/\text{s}^{-1}$
0.50	0.5	0.056
1.00	0.5	0.089
2.00	0.5	0.182
3.00	1.0	0.287
4.00	1.0	0.39
5.00	1.0	0.49
8.00	5.0	0.78

^{a} At 290 nm and 1.00 M NaClO$_4$.

strength was 1.00 M with sodium perchlorate as the supporting electrolyte.

Dilution Experiments to Determine k_1. Solutions of chlorine (2.0 or 3.0 mM) in 1.00 M sodium perchlorate medium were mixed with equal volumes of 1.00 M sodium perchlorate directly in the stopped-flow apparatus. The decrease of transmittance vs. time was followed at 240 nm, where $\epsilon_{\text{HOCl}} = 100$ cm^{-1} M^{-1} and $\epsilon_{\text{Cl}_2} = 15$ cm^{-1} M^{-1}.[14] The series of dilution experiments gave the following values of $k_{\text{exptl}}/\text{s}^{-1}$: 7.7, 9.9, 10.9, 9.3, 7.9, 9.0, 10.0, 9.4, 8.8, 8.3, 8.1, 8.0, 8.7, 8.4, 7.3, 8.7, 8.6, 7.3, and 9.9. This gives $k_1 = 8.7 \pm 0.2$ s^{-1} according to eq 9.

Determination of k_{-1}. Solutions of chlorine (2 × 10^{-5} to 1.4 × 10^{-4} M) were mixed with equal volumes of platinum complex solution (2 × 10^{-4} to 2 × 10^{-3} M) directly in the stopped-flow instrument. Both reactants were dissolved in a sodium perchlorate medium with added hydrochloric and perchloric acid to give suitable concentrations of acid and chloride. Pt(CN)$_4^{2-}$ was used in at least 10-fold excess. Since the reaction between Cl$_2$ and the platinum complex is extremely rapid, the Cl$_2$ present at the time of mixing rapidly decreases to its steady-state concentration, whereafter the equilibrium displacement with a rate constant defined by eq 12 can be observed as an increase of transmittance vs. time at 253 nm, where the formed platinum(IV) product has a much smaller molar absorptivity (1250 cm^{-1} M^{-1}) than Pt(CN)$_4^{2-}$ (12 500 cm^{-1} M^{-1}); cf. Figure 1. Alternatively, the reaction was followed as a decrease of transmittance at 230 nm, where the product has a molar absorptivity of 5500 cm^{-1} M^{-1} and that of Pt(CN)$_4^{2-}$ is only 400 cm^{-1} M^{-1}. Table I reviews these experiments.

Determination of k_{Cl_2}. Solutions of chlorine (0.2–0.6 mM) in 1.00 M sodium perchlorate were mixed with equal volumes of 4 × 10^{-6} M Pt-(CN)$_4^{2-}$ in 1.00 M sodium perchlorate directly in the stopped-flow apparatus. The increase of transmittance was followed at the 253-nm maximum of Pt(CN)$_4^{2-}$; cf. Figure 1. Since oxidation by Cl$_2$ is very rapid, it was necessary to use very low concentrations of this species. After the solutions were mixed, C_{Cl_2} was ≤3 × 10^{-4} M, and less than 0.02% of the chlorine is in the Cl$_2$ form. The following values of $10^4 C_{\text{Cl}_2}/\text{M}$, $k_{\text{exptl}}/\text{s}^{-1}$ were obtained: 1.00, 0.046; 1.50, 0.126; 2.00, 0.292; 2.50, 0.50; 3.00, 0.95. A plot is shown in Figure 4.

When equal volumes of the reactant solutions are mixed in the stopped-flow apparatus, the reactants are diluted and the hydrolysis equilibrium of eq 2 is displaced to the right. The rate constant for that equilibrium displacement is ≥$k_1 = 8.7$ s^{-1}, which is much larger than the observed rate constants. The condition of a rapid establishment of the hydrolysis equilibrium after dilution is fulfilled.

Determination of k_{HOCl}. Solutions of chlorine (0.1–1.0 mM) in 1.00 M sodium perchlorate were mixed with equal volumes of Pt(CN)$_4^{2-}$ solution (1.0–16 mM) in 1.00 M sodium perchlorate directly in the stopped-flow instrument. The decrease of transmittance was followed vs. time at 290 nm, where Pt(CN)$_4^{2-}$ is practically transparent and the platinum(IV) product has a molar absorptivity of ca. 500 cm^{-1} M^{-1}; cf. Figure 3b. Table II reviews these experiments.

(20) Awtrey, A.; Connick, R. E. *J. Am. Chem. Soc.* **1951**, *73*, 1842.
(21) Allen, T. L.; Keefer, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2957.
(22) Elding, L. I. *Inorg. Chim. Acta* **1972**, *6*, 683.

Table III. Parameters for the Hydrolysis of Chlorine (eq 2)

| k_1/s^{-1}	$10^{-4}k_{-1}/$ $M^{-2}\,s^{-1}$	$10^4K/M^2$	$t/°C$	I/M	ref
5.60			9.5	0	15[a]
11.0	1.80	6.0	20	0.1	12[b]
		3.94	25	0	13[c]
8.7 ± 0.2	2.66 ± 0.03	3.27 ± 0.11	25	1.0	this paper

[a] Continuous flow. [b] T jump. [c] Equilibrium conductivity.
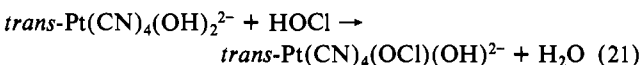
Results and Discussion

Hydrolysis of Chlorine. The observed kinetics are compatible with the stoichiometric mechanism of eq 2. The present measurements allow rather accurate determinations of both k_1 and especially k_{-1}. The rate constants obtained agree satisfactorily with those calculated previously from temperature-jump[12] and continuous-flow[15] experiments; cf. Table III. The equilibrium constant calculated from the kinetics as k_1/k_{-1} is also in good agreement with previous constants obtained by use of various equilibrium methods.[13]

Rate Constants for Oxidation of Pt(CN)$_4$$^{2-}$. Figure 4 shows a plot according to eq 17, which has the slope $(3.3 \pm 0.2) \times 10^{10}$ $M^{-3}\,s^{-1}$. Since $K = (3.27 \pm 0.11) \times 10^{-4}\,M^2$, we get $k_{Cl_2} = (1.08 \pm 0.10) \times 10^7\,M^{-1}\,s^{-1}$. According to eq 17, the intercept of the plot gives a value of k_{HOCl} of approximately $100 \pm 80\,M^{-1}\,s^{-1}$. This is compatible with the quantitative determination of this rate constant by use of eq 19. A plot of k_{exptl} from Table II vs. [Pt(CN)$_4$$^{2-}$] is linear with slope $k_{HOCl} = 97.9 \pm 1.1\,M^{-1}\,s^{-1}$.

Mechanism for Oxidation with HOCl and OCl$^-$. The reaction of eq 5 is first order in HOCl (Table II) and has a stoichiometry of 2:1. This is compatible with a two-step process, with an initial and rate-determining redox reaction in which hypochlorous acid acts a two-electron oxidant according to eq 20. Here the oxygen

$$Pt(CN)_4{}^{2-} + HOCl + H_2O \rightarrow$$
$$\textit{trans-}Pt(CN)_4(OH)_2{}^{2-} + H^+ + Cl^- \quad (20)$$
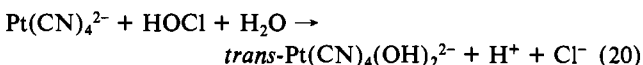
of the HOCl molecule acts as the bridging atom for electron transfer.[23] The primary product $\textit{trans-}$Pt(CN)$_4$(OH)$_2$$^{2-}$ is an intermediate that cannot be detected in the neutral solutions used, as indicated by the spectra. The rate-determining reaction (20) must then be followed by a rapid reaction between the hydroxide complex and a second molecule of HOCl, forming a hypochlorite complex according to eq 21. The two-step process can be visu-

$$\textit{trans-}Pt(CN)_4(OH)_2{}^{2-} + HOCl \rightarrow$$
$$\textit{trans-}Pt(CN)_4(OCl)(OH)^{2-} + H_2O \quad (21)$$

alized, if the redox reaction is followed in weakly alkaline solution, where reaction 21 does not take place. In the experiment of Figure 5a with pH 11, all the chlorine is present as hypochlorite ion ($pK_a = 7.5$ for HOCl[12]) and the spectral changes are due to the slow (compare time scales of Figures 1, 2, and 5a) oxidation of Pt-(CN)$_4$$^{2-}$ by hypochlorite according to eq 22. Addition of an excess

$$Pt(CN)_4{}^{2-} + OCl^- + H_2O \rightarrow \textit{trans-}Pt(CN)_4(OH)_2{}^{2-} + Cl^-$$
$$(22)$$
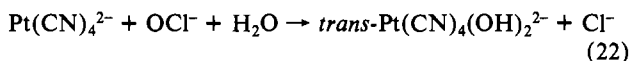
of HOCl to the product solution of this reaction immediately results in the formation of the hypochlorite complex according to eq 21.[24] This is shown by the experiment of Figure 5b. Spectrum 2 of this figure is identical with spectrum 4 of Figure 3 and represents $\textit{trans-}$Pt(CN)$_4$(OCl)OH^{2-}.

Properties of the Hypochlorite Complex. Spectra of $\textit{trans-}$Pt(CN)$_4$(OCl)(OH)$^{2-}$ in aqueous 1.00 M NaClO$_4$ solution (spectrum 4 of Figure 3) are stable for several months. They do not change on addition of chloride or mercury(II). Thus, the complex does not react with chloride, as expected for a hydroxo

(23) If chloride was the bridging ligand, the same platinum(IV) complex as for the Cl$_2$ oxidation should have been obtained. This is not the case according to the spectra.

(24) On the other hand, addition of an excess of perchloric acid results in the well-known spectrum of $\textit{trans-}$Pt(CN)$_4$(H$_2$O)$_2$. This helps to identify the dihydroxo complex of reaction 22.

Table IV. Chloride Anation of $\textit{trans-}$Pt(CN)$_4$(OCl)(H$_2$O)$^-$ Followed at 285 nm, 25 °C, and 1.00 M Ionic Strength[a] at Two Different pHs

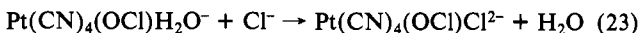| 10^3[Pt(CN)$_4$- (OCl)(OH)$^{2-}$]/ M	[Cl$^-$]/M	k_{exptl}/s^{-1}	
0.50	0.020	0.62[b]	0.54[c]
0.50	0.040	1.04	1.11
0.50	0.050	1.32	1.36
0.50	0.100	2.49	2.76
1.00	0.300		7.9
1.00	0.500		13.3

[a] The platinum solution was prepared by oxidation of 2.0 mM Pt-(CN)$_4$$^{2-}$ with 4.2 mM chlorine in 1.00 M NaClO$_4$. The kinetics were started by mixing this solution directly in the stopped-flow instrument with HCl/HClO$_4$/NaClO$_4$ solutions of appropriate concentrations. [b] 0.20 M H$^+$. [c] 0.50 M H$^+$.

Table V. Rate Constants for Oxidative Addition to Square-Planar Complexes at 25 °C

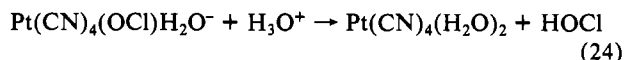| reactants	$k/M^{-1}\,s^{-1}$	I/M	ref
PtCl$_4$$^{2-}$ + HOCl	$(4.5 \pm 0.5) \times 10^5$	0.50	7
Pt(CN)$_4$$^{2-}$ + HOCl	97.9 ± 1.1	1.00	this work, eq 19
Pt(CN)$_4$$^{2-}$ + OCl$^-$	~10	water	this work, Figure 5a
Pt(CN)$_4$$^{2-}$ + Cl$_2$	$(1.08 \pm 0.10) \times 10^7$	1.00	this work, eq 17

complex. Nor is it possible to remove chloride from the complex; the chlorine of the hypochlorite ligand has the oxidation state of 1+.

Addition of perchloric acid gives a rapid change of the spectrum due to formation of the corresponding aqua complex, $\textit{trans-}$Pt-(CN)$_4$(OCl)H$_2$O$^-$. The aqua form reacts readily with chloride in a first-order process. Table IV summarizes some stopped-flow experiments performed to determine the rate constant for the chloride anation of eq 23. A plot of the observed rate constants

$$Pt(CN)_4(OCl)H_2O^- + Cl^- \rightarrow Pt(CN)_4(OCl)Cl^{2-} + H_2O \quad (23)$$

vs. excess chloride is linear with a slope of $26.5 \pm 0.2\,M^{-1}\,s^{-1}$. Thus, the aqua form of the hypochlorite complex reacts several orders of magnitude faster with chloride than $\textit{trans-}$Pt-(CN)$_4$ClH$_2$O$^-$, in which the spontaneous chloride anation is extremely slow.[25]

In acidic solution, the complexes $\textit{trans-}$Pt(CN)$_4$(OCl)H$_2$O$^-$ and $\textit{trans-}$Pt(CN)$_4$(OCl)Cl^{2-} slowly form $\textit{trans-}$Pt(CN)$_4$(H$_2$O)$_2$ and $\textit{trans-}$Pt(CN)$_4$ClH$_2$O$^-$, respectively, for instance according to eq 24. This reaction is accelerated, if the acidic solutions are flushed

$$Pt(CN)_4(OCl)H_2O^- + H_3O^+ \rightarrow Pt(CN)_4(H_2O)_2 + HOCl$$
$$(24)$$

with nitrogen to evaporate chlorine.

Rate Comparisons. Table V contains the rate constants for the oxidative-addition step of eq 1 determined so far. An approximate estimation of the rate constant for oxidation of Pt(CN)$_4$$^{2-}$ by hypochlorite ion based on the spectra of Figure 5 has also been included.

In the previous study[7] of the oxidation of PtCl$_4$$^{2-}$ by aqueous solutions of chlorine, HOCl was the predominant form of chlorine in the solutions used. The observed rate constants (18–106 s^{-1}) were much larger than the rate constant of eq 8 for the equilibrium displacement HOCl $\rightarrow$ Cl$_2$, which is <10 s^{-1} for the experimental conditions used. This means that the reaction observed in ref 7 was *not* the oxidation by Cl$_2$ as believed, but instead the reaction between HOCl and PtCl$_4$$^{2-}$.

It appears from Table V that oxidation of Pt(CN)$_4$$^{2-}$ by HOCl is ca. 10^5 times slower than by Cl$_2$. One obvious reason for this large difference in rate is that the oxygen of the HOCl molecule is a less efficient bridging ligand for electron transfer than chloride. Differences in the energy of the d$_{z^2}$ orbitals of the two complexes

(25) Elding, L. I.; Gustafson, L. *Inorg. Chim. Acta* **1976**, *18*, L35.

$PtCl_4^{2-}$ and $Pt(CN)_4^{2-}$ might cause the factor of 5×10^3 in rate for oxidation of those complexes by HOCl.

Acknowledgment. Thanks are due to I. Lind and B. Jönsson for experimental assistance and to the Swedish Natural Science

Research Council for financial support.

Contribution from the Istituto di Chimica Generale e Inorganica, Università di Sassari, 07100 Sassari, Italy, and Dipartimento di Chimica Inorganica e Metallorganica and Centro CNR, Università di Milano, 20133 Milan, Italy

Synthesis, Spectral Properties, and Crystal and Molecular Structure of Tetrakis(μ-2,6-dimethoxybenzoato)diaquadicopper(II) and of Bis(μ-2,6-dimethoxybenzoato)bis(μ-acetato)diaquadicopper(II), a Case of a Dimeric Copper(II) Carboxylate Complex with Mixed Bridges[1]

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The title complexes have been prepared, investigated by single-crystal X-ray analysis, and characterized through magnetic susceptibility and spectroscopic measurements. The tetrakis(μ-2,6-dimethoxybenzoato)diaquadicopper(II) complex (**1**) crystallizes in the orthorhombic space group *Cmca* (No. 64) with cell constants $a = 27.890$ (7) Å, $b = 7.098$ (3) Å, $c = 19.691$ (5) Å, and $Z = 4$. Least-squares refinement based on 959 significant counter data led to a final conventional R factor of 0.047. The bis(μ-2,6-dimethoxybenzoato)bis(μ-acetato)diaquadicopper(II) complex (**2**) gives monoclinic crystals, space group $P2_1/a$ (No. 14), with $a = 7.898$ (2) Å, $b = 20.334$ (6) Å, $c = 8.148$ (3) Å, $\beta = 101.31$ (3)°, and $Z = 2$. The structure refinement, on the basis of 1479 significant reflections, led to a final conventional R factor of 0.025. The dinuclear compounds have the usual carboxylate quadruply bridged structure, and in complex **2** the groups of the same type act as bridging ligands in mutually trans positions. The copper-copper distance of **2** (2.597 (1) Å) is shorter than that in **1** (2.619 (1) Å) and also shorter than that in copper(II) acetate monohydrate. This fact and the pattern of the other bonding parameters indicate that the molecular framework is rather flexible and can undergo small rearrangements in response to the bonding requirements of the carboxylato ligands or to packing factors. The spectroscopic and magnetic properties of the complexes are interpreted on the basis of the crystal structures. In particular, the complexes exhibit significantly different exchange integrals, $-2J$ (325 and 250 cm⁻¹ for **1** and **2**, respectively). The structural and magnetic results are compared with those for a series of related dimers.

Introduction

In the course of an investigation on the interaction of metal ions with humic acid like molecules, we have already described the monomeric complexes formed by 2,6-dihydroxybenzoic acid.[3,4] In order to ascertain the effects of methoxy substitution of the phenolic groups on the coordination behavior of the above salicylic acid like ligand, we have examined the copper(II) complexes of 2,6-dimethoxybenzoic acid (HDMB). Here we describe the structural and spectroscopic properties of two copper(II) acetate like complexes, one of which represents the first recorded example of a dimeric copper(II) carboxylate with mixed bridges.

Experimental Section

Materials. All chemicals were reagent grade. 2,6-Dimethoxybenzoic acid (Merck) was twice recrystallized from water.

Preparation of Complexes. Tetrakis(μ-2,6-dimethoxybenzoato)diaquadicopper(II). Copper(II) nitrate trihydrate (1.6 mmol) and 2,6-dimethoxybenzoic acid (3.2 mmol) were dissolved in ca. 50 mL of water at pH 4. When the solution was allowed to stand at 50 °C, green crystals separated. Anal. Calcd for $C_{18}H_{20}CuO_9$: C, 48.70; H, 4.54; H_2O, 4.06. Found: C, 48.50; H, 4.44; H_2O, 4.0.

When evaporated at room temperature, the solution yielded a green powderlike precipitate that was analyzed as $Cu(DMB)_2 \cdot 1.5H_2O$. Anal. Calcd for $C_{18}H_{21}CuO_{9.5}$: C, 47.73; H, 4.67; H_2O, 5.96. Found: C, 47.60; H, 4.73; H_2O, 6.0.

Bis(μ-2,6-dimethoxybenzoato)bis(μ-acetato)diaquadicopper(II). Copper(II) acetate hydrate (1.6 mmol) and 2,6-dimethoxybenzoic acid (3.2 or 1.6 mmol) were dissolved in 50 mL of water. After slow evaporation at room temperature, the solution yielded a blue powderlike precipitate, which was analyzed as $Cu(DMB)(CH_3COO) \cdot 1.5H_2O$. Anal. Calcd for $C_{11}H_{15}CuO_{7.5}$: C, 39.94; H, 4.57; H_2O, 8.17. Found: C, 39.75;

(1) Part 4 of the series Interaction of Metal Ions with Humic Acid Like Models. Part 3: Micera, G.; Piu, P.; Strinna Erre, L.; Cariati, F.; Pusino, A. *Thermochim. Acta* **1984**, *77*, 67.
(2) (a) Università di Sassari. (b) Università di Milano.
(3) Cariati, F.; Erre, L.; Micera, G.; Panzanelli, A.; Ciani, G.; Sironi, A. *Inorg. Chim. Acta* **1983**, *80*, 57.
(4) Cariati, F.; Erre, L.; Micera, G.; Panzanelli, A.; Piu, P. *Thermochim. Acta* **1983**, *66*, 1.

Table I. Crystallographic Data

	[Cu(DMB)₂(H₂O)]₂ (1)	[Cu(DMB)(CH₃COO)(H₂O)]₂ (2)
formula	$C_{36}H_{40}Cu_2O_{18}$	$C_{22}H_{28}Cu_2O_{14}$
fw	887.8	643.5
cryst syst	orthorhombic	monoclinic
space group	*Cmca* (No. 64)	$P2_1/a$ [nonstd setting of $P2_1/c$ (No. 14)]
a, Å	27.890 (7)	7.898 (2)
b, Å	7.098 (3)	20.334 (6)
c, Å	19.691 (5)	8.148 (3)
α, deg	90.0	90.0
β, deg	90.0	101.31 (3)
γ, deg	90.0	90.0
V, Å³	3898.1	1283.1
ρ_{calcd}, g cm⁻³	1.513	1.666
Z	4	2
F(000)	1832	660
cryst dimens, mm	0.11 × 0.21 × 0.40	0.12 × 0.15 × 0.24
μ(Mo Kα), cm⁻¹	11.67	17.29
ϑ range, deg	3–24	3–24
reflcns measd	$+h,+k,+l$ ($h + k = 2n$)	$\pm h,+k,+l$
no. of reflcns measd	1754	2010
no. of indep reflcns used in struct anal. [$I > 3\sigma(I)$]	958	1479
no. of variable parameters	130	228
weighting *p* factor[a]	0.04	0.03
R	0.047	0.025
R_w	0.063	0.032
GOF[b]	1.885	1.180

[a] See text. [b] $\text{GOF} = [\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{var})]^{1/2}$.

H, 4.47; H_2O, 8.0. By recrystallization from water suitable crystals of the monohydrate complex separated. Anal. Calcd for $C_{11}H_{14}CuO_7$: C, 41.06; H, 4.38; H_2O, 5.59. Found: C, 40.98; H, 4.39; H_2O, 6.0.

Analytical and Physical Measurements. Analyses for C and H were performed on a Perkin-Elmer 240 B elemental analyzer. Thermo-