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Stability and Electronic Spectra of the Copper(II) Chloro Complexes in Aqueous Solutions

M. A. KHAN and M. J. SCHWING-WEILL*

The stability constants and the electronic spectra of the chlorocuprates $CuCl_j^{(j-2)-}$ (with $j \leq 4$) in aqueous solutions of constant 5 M ionic strength have been calculated from spectrophotometric data at 12 wavelengths ranging from 240 to 780 nm. The calculated spectra are compared to those of solid chlorocuprates and solutions in molten salts or organic solvents, in order to get eventual structural information.

Introduction

Aqueous solutions of copper(II) chloro complexes, which absorb in the uv and in the visible regions ($\lambda_{max} \sim 250$ and 800 nm), have mainly been investigated by spectrophotometric methods;[1-14] potentiometric studies are not feasible in Cu(II)–Cl⁻ media.[15,16]

The main studies at constant ionic strength by uv spectrophotometry are those of McConnel and Davidson,[8] Kruh,[9] Lister and Rosenblum,[1] Wendling et al.,[10] and Libus.[14] The values found for the stability constant β_1 of $CuCl^+$ range from 1 to 3.5, except Kruh's value $\beta_1 = 0.27$ which has been contested by the author himself.

The overall apparent stability constant β_2 of $CuCl_2$ (according to the equation $Cu^{2+} + 2Cl^- \rightleftharpoons CuCl_2$) has only been determined by McConnel and Davidson who found $\beta_2 = 0.30 \pm 0.20$ at ionic strength $\mu = 1$. The overall stability constants β_3 and β_4 have not been determined at all, as the studied media were too poor in chloride ions for any appreciable formation of the $CuCl_3^-$ and $CuCl_4^{2-}$ ions.

One of us (M.J.S.) has recently published the results of the spectrophotometric investigation, at 25 °C, of copper(II) chloro complexes in aqueous solutions of constant ionic strength 5 M containing $NaClO_4$–$NaCl$ mixtures.[17] This high ionic strength was especially chosen in order to promote formation of the most chlorinated complexes. Eventual formation of polynuclear complexes was avoided by always keeping the copper analytical concentration γ lower than the chloride analytical concentration C. Copper hydrolysis was prevented by adjusting the pH of all studied solutions to 2, with perchloric acid.

The optical densities of 37 different solutions with C ranging from 0.005 to 4.9 and γ equal to 6×10^{-4} (up to $C = 0.2$ M) and 6×10^{-3} (for $0.2 < C \leq 4.9$) were measured at six different wavelengths, i.e., 230, 250, 280, 360, 380, and 756 nm.

The matrix rank treatment of Hugus and El-Awady,[18] applied to the measured optical densities, showed unambiguously that a minimum of four chloro complexes have to be taken into account in order to interpret the whole set of data.

Under the chosen experimental conditions, only mononuclear complexes $CuCl_j^{(j-2)-}$ have been considered, e.g., $CuCl^+$, $CuCl_2$, $CuCl_3^-$ and $CuCl_4^{2-}$.

The simultaneous least-squares treatment of the 152 data obtained at 250, 280, 360, 380, and 756 nm leads to the following values of the 95% probability ranges of the overall apparent stability constants $\beta_j = [CuCl_j^{(j-2)-}]/[Cu^{2+}][Cl^-]^j$: β_1 is 3.1–4.9; β_2 is 3.7–5.7; β_3 is 1.26–1.94; β_4 is 0.14–0.17.

The given ranges correspond to four times the standard deviations. The central values of the constants, $\beta_1 = 4.0$, $\beta_2 = 4.7$, $\beta_3 = 1.60$, and $\beta_4 = 0.17$, allowed the recalculation within 1% of all the measured optical densities.

We report here the results of our extension of the previous study, made in order to determine the electronic spectra of the four chloro complexes in aqueous solutions. We have measured the optical densities at seven more wavelengths, e.g., 240, 260, 300, 340, 400, 720, and 780 nm, under the same experimental conditions as in the previous work.[17] The stability constants have been refined with the complete set of all experimental data, including those of the previous study (324 experimental data in all, excluding those at 230 nm), and the specific extinction coefficients of each chloro complex at the various wavelengths have been adjusted.

Method of Calculation

At the wavelength λ, the apparent molar extinction coefficient ϵ of a solution of copper(II) analytical concentration γ and chloride analytical concentration C is given by

$$\epsilon - \epsilon_0 = \epsilon' = \frac{\sum\limits_{j=1}^{n} \epsilon_j' c^j \beta_j}{1 + \sum\limits_{j=1}^{n} c^j \beta_j} \tag{1}$$

where: ϵ_0 is the specific extinction coefficient of the Cu^{2+} ion at wavelength λ; $\epsilon_j' = \epsilon_j - \epsilon_0$; ϵ_j is the specific extinction coefficient of the $CuCl_j^{(j-2)-}$ ion at wavelength λ; c is the free chloride ion concentration; and n is the number of chloro complexes taken into account ($n = 4$).

The unknowns in eq 1 are the β_j, c, and ϵ_j' values (ϵ_0 has been determined experimentally).

The c values for each solution have been calculated by an iterative process, which was stopped either when the difference between the results of two successive iterations was smaller than 10^{-6}, or when the total number of successive iterations exceeded five.[19,20]

For a given set $|\beta_j\rangle$ of β_j values, the sum S^λ of the squares of the relative errors on ϵ at wavelength λ has been optimized by a least-squares treatment leading to the best ϵ_j' values for the given $|\beta_j\rangle$ set and to the corresponding $S^\lambda(|\beta_j\rangle)$. The total sum $S(|\beta\rangle) = \sum_\lambda S^\lambda(|\beta_j\rangle)$ has then been computed, as well as the standard deviation $\sigma^\lambda(|\beta_j\rangle)$ at wavelength λ

$$\sigma^\lambda(|\beta_j\rangle) = \sqrt{S^\lambda/(N - n)} \tag{2}$$

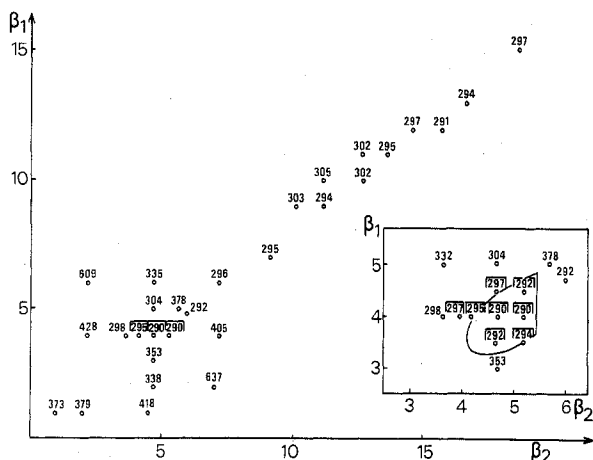N being the number of solutions investigated at wavelength

Figure 1. $10^4 S_m = f(\beta_1, \beta_2)$. (The framed values correspond to positive ϵ_j values).

Table I. Numerical Interpretation of the Experimental Data with the Refined Values of the Stability Constants: $\beta_1 = 4$; $\beta_2 = 4.7$; $\beta_3 = 1.96$; $\beta_4 = 0.23$

λ	ϵ_1	ϵ_2	ϵ_3	ϵ_4	S^λ	σ^λ	N
230^a	655	1074	1586	2146	0.018 96	0.0356	19
240	867	2321	1860	3272	0.000 532 6	0.005	25
250	1042	2424	2227	2885	0.001 129	0.0065	31
260	846	2349	2847	3633	0.000 586	0.0053	25
280	213	906	2708	2578	0.002 274	0.0086	35
300	13.3	440	1128	1864	0.005 019	0.0155	25
340	3.03	32.6	156	396	0.002 533	0.0119	22
360	0.45	17.8	90.7	290	0.006 632	0.0174	26
380	0.36	4.39	54.5	276	0.003 238	0.0119	27
400	0.24	0.02	25.6	216	0.002 044	0.0099	25
720	12.8	18.9	26.2	19.9	0.001 658	0.0083	28
756	16.3	24.2	34.4	34.8	0.001 229	0.0073	27
780	17.8	27.4	38.8	37.9	0.002 177	0.0095	28

^{a} Data relative to this wavelength have not been taken into account for the refinement of the stability constants.

λ; and the standard deviation $\sigma(|\beta_j\rangle)$ which defines the precision with which the whole set of N' measurements (here $N' = 324$) performed at L different wavelengths (here $L = 12$) is interpreted

$$\sigma(|\beta_j\rangle) = \sqrt{S/(N' - P)} \qquad (3)$$

with $P = n(L + 1)$ (here $P = 52$).

The calculations have been performed with a UNIVAC 1108 computer by systematic tabulation of $S(|\beta_j\rangle)$, the (nL) values of $\epsilon_j'(|\beta_j\rangle)$, the L values of $S^\lambda(|\beta_j\rangle)$ and $\sigma^\lambda(|\beta_j\rangle)$, as well as $S(|\beta_j\rangle)$ and $\sigma(|\beta_j\rangle)$.

For each couple $|\beta_1, \beta_2\rangle$, the best values of β_3 and β_4, i.e., those which minimize the sum $S = \sum_\lambda S^\lambda$, have been determined, as well as the corresponding minimum value $S_m(\beta_1, \beta_2)$ of S.

Results and Discussion

Figure 1, which gives the values of $S_m(\beta_1, \beta_2)$ vs. β_1 and β_2, provides evidence that S_m remains small ($0.0290 \leq S_m \leq 0.0300$) along a "valley"; nevertheless, any point in this valley cannot be suitable because of the necessity for all ϵ_j to be positive. Only the framed values on Figure 1 correspond to a complete set of 48 positive values of the ϵ_j and thus the zone of the possible β_1 and β_2 values, enlarged in the inset of Figure 1, is considerably restricted. It may be seen also that near its minimum, the surface $S_m(\beta_1, \beta_2)$ is not a paraboloid but a hyperboloid.

The dispersion zone for β_1 and β_2 corresponding to 95% confidence is drawn on the inset of Figure 1. It has been defined by both conditions: (i) $S_m(\beta_1, \beta_2) \leq 0.0290 + 4\sigma^2$ with $\sigma = 0.01$; and (ii) all $\epsilon_j \geq 0$.

The best values of β_1 and β_2 thus obtained range from 3.3 to 4.7 for β_1 and from 4.1 to 5.3 for β_2. The corresponding best values of β_3 and β_4 have been found ranging from 1.71 to 2.21 for β_3 and 0.18 to 0.28 for β_4. The uncertainties given on β_3 and β_4 are defined by the intersection of the paraboloid approximating $S(\beta_3, \beta_4)$ near its minimum with the plane of ordinate $S_m(\beta_3, \beta_4) + 4\sigma^2$.

The value of σ, corresponding to the central values $\beta_1 = 4.0$, $\beta_2 = 4.7$, $\beta_3 = 1.96$, and $\beta_4 = 0.23$, is equal to 0.0103, which means that the 324 experimental data collected at 12 wavelengths can be recalculated within 1.03%.

The optimized values of the specific extinction coefficients of the four chloro complexes at 13 wavelengths are given in Table I, together with the S^λ and σ^λ. Figure 2 shows the calculated electronic spectra of the four complexes and Figure 3 gives their formation curves.

Figure 2 shows that the first three complexes $CuCl^+$, $CuCl_2$, and $CuCl_3^-$ have only one absorption band in the uv region,
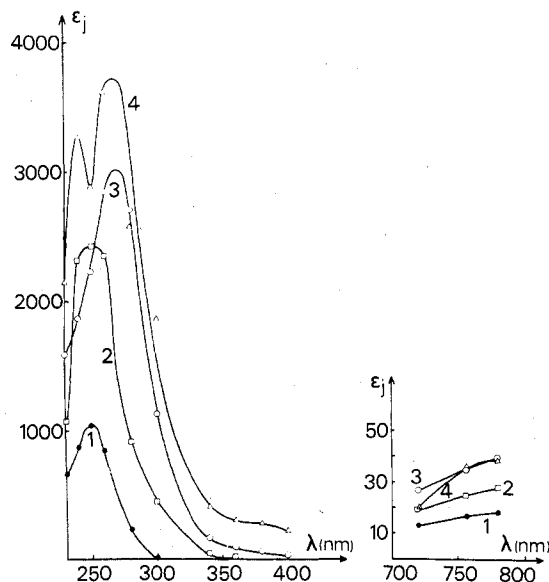

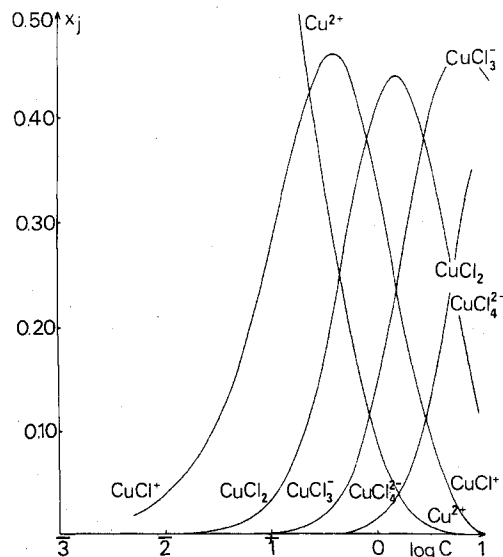**Figure 2.** Electronic spectra of the four chloro complexes.

Figure 3. Formation curves of the chloro complexes: $x_j = \beta_j c^j / [1 + \sum_{j=1}^{4} \beta_j c^j]$.

respectively situated at 250 nm (40 000 cm^{-1}) for $CuCl^+$ and $CuCl_2$, and at 270 nm (37 000 cm^{-1}) for $CuCl_3^-$. $CuCl_4{}^{2-}$ has three peaks at 240 nm (41 700 cm^{-1}), 265–270 nm

$(37\,800\text{--}37\,000\ cm^{-1})$, and 370–380 nm $(27\,000\text{--}26\,300\ cm^{-1})$.

It has already been reported in the previous paper[17] that when the analytical chloride concentration is progressively increased: (i) the absorption peak observed at 250 nm for C values inferior to 1 M is progressively shifted toward 265 nm; and (ii) a shoulder appears in the spectra around 380 nm for $C > 2.5$ M. Our present results, summarized on Figures 2 and 3, explain these two observations: (i) the shift of the uv band is due to the successive formation of $CuCl_3^-$ and $CuCl_4^{2-}$ which maxima are situated at higher wavelengths (270 nm) than $CuCl^+$ and $CuCl_2$ (250 nm); and (ii) the shoulder at 380 nm corresponds to the formation of $CuCl_4^{2-}$ which is not appreciable for C values inferior to 2 M.

Stability of the Complexes. The central values of β_1 and β_2 calculated in the present work are strictly identical with those determined in our previous work from measurements at five wavelengths, but the confidence interval $\pm 2\sigma$ is now found smaller. The central values of β_3 and β_4 are slightly different, but the new values are enclosed in the confidence interval given in the previous work.

The value of β_1, ranging from 3.3 to 4.7, is about four times higher than the values calculated by McConnel and Davidson (1.3 for $\mu = 1$), Lister and Rosenblum (1.1–1.3 for $\mu = 2$), and Libus (1.63 for $\mu = 0$) from measurements in the uv region, with low chloride concentrations, and $\lambda > c$ in order to minimize the formation of $CuCl_2$.

Two reasons may account for this difference: (i) As already pointed out by Lister and Rosenblum, the experimental conditions chosen by these authors may be favorable to the formation of polynuclear complexes such as Cu_2Cl^{3+}, the presence of which could explain the abnormal variation of β_1 with temperature observed by Lister and the abnormal variation of ϵ_1 with ionic strength reported by Libus. (ii) These authors have based their interpretation on the assumption that $CuCl^+$ is the only chloro complex present in solution. Their main argumentation is the linearity of the graph γ/d vs. $1/C$ (d = optical density). In fact, Schwing has shown that, at 230, 250, 280, and 756 nm, it is possible to interpret the data up to $C = 0.5$ M with an excellent precision by assuming the presence of $CuCl^+$ exclusively, but the values of β_1 thus calculated vary with the wavelength.[17] The linearity of the graph γ/d vs. $1/C$ is in most cases a sign of the presence of one complex only, but it may happen that such a linearity is observed although more than one complex is present, provided that the β_j and ϵ_j values satisfy specific conditions.[9]

One may question our not taking into account the variation of the different ions activity factors when ClO_4^- ions are progressively replaced by Cl^- ions. This question has already been raised and discussed in our previous paper, in connection with the recent similar studies of the lead chloro complexes performed in our laboratory.[19,20]

Electronic Spectra and Structure of the Copper(II) Chloro Complexes. (1) $CuCl^+$, $CuCl_2$, and $CuCl_3^-$. It is not possible to compare the calculated spectra of mono-, di-, and trichlorocuprates in aqueous solutions to those of analogous solid compounds, as there is no solid chlorocuprate consisting of well-defined units made of one copper atom surrounded by one, two, or three chlorine atoms. In solid $CuCl_2$, each copper atom has a deformed octahedral environment consisting either of six chlorine atoms in the case of anhydrous $CuCl_2$[21] or of four chlorine atoms and two oxygen atoms in the case of $CuCl_2 \cdot 2H_2O$.[22] The spectrum of the latter exhibits one single maximum in the uv region at 280 nm.

It has generally been admitted up to now that the monochlorocuprate charge transfer band is centered on 250–255 nm. Our results confirm this assumption.

Wendling[10] has assigned this band to the less energetic charge transfer transition $t_{2u} \rightarrow e_g$ of a pseudo-octahedral ion

$[Cu(H_2O)_5Cl]^+$, and has calculated the corresponding absorption wavelength λ 256 nm, which is in excellent agreement with our experimental value.

It is probable that for $CuCl_2$ in aqueous solutions the copper environment is pseudooctahedral too, four water molecules being coordinated to each copper atom, the two chlorine atoms occupying both axial positions in order to minimize their mutual electrostatic repulsion.

(2) $CuCl_4^{2-}$. The molecular structure of $CuCl_4^{2-}$ has been extensively studied, as well in the solid state[23–32] as in molten salts solutions[33,34] or in organic solvents such as acetonitrile or nitromethane.[35–37]

Its structure in the solid state depends on the nature of the cation which is associated with the $CuCl_4^{2-}$ anion: x-ray structural studies have shown that in Cs_2CuCl_4[23,32] and $[N(CH_3)_4]_2CuCl_4$,[32] the copper atom is at the center of a flattened tetrahedron (D_{2d} symmetry) while in $(NH_4)_2CuCl_4$,[30] $[Pt(NH_3)_4]CuCl_4$,[24] $(C_2H_5NH_3)_2CuCl_4$,[30,31] and $(CH_3NH_3)_2CuCl_4$,[31] the chlorine atoms form a tetragonally distorted octahedral environment around each copper atom, with two axial bonds so long (2.8 Å) that it is commonly admitted that in fact the copper atoms are in a square-planar environment (D_{4h} symmetry).

The previous works show two main differences between the spectra of the D_{2d} and D_{4h} configurations: (i) the presence of a band between 435 and 455 nm for the D_{2d} form;[25] and (ii) the absence of any d–d transition band below 1100 nm for the D_{2d} configuration, whereas the configuration D_{4h} presents two bands at lower wavelengths, between 700 and 800 nm, and between 900 and 950 nm. The structure of $CuCl_4^{2-}$ in aqueous solution is a controversial problem. On the basis of the similarity between the spectra of solid Cs_2CuCl_4 and a Cs_2CuCl_4 aqueous solution (in the presence of a large excess of chloride), Helmholz and Kruth conclude in favor of an identity of structures, although the positions of the bands as well as their relative intensities are slightly different.[23] On the other hand, for Eswein and co-workers, $CuCl_4^{2-}$ in aqueous solution would rather have a square-planar structure because the characteristic absorption band at 450 nm of the D_{2d} configuration has never been observed in highly donor solvents such as water, alcohols, or molten chlorides;[38] this band is visible in a mixed acetic anhydride–acetic acid solvent, but disappears by addition of chloride or water. Eswein therefore suggests that there is an equilibrium in solution between the D_{2d} and D_{4h} configurations which can be strongly displaced by medium effects such as water or chloride concentrations. We think that this statement is plausible because of the small energy difference between both configurations: recent *ab initio* LCAO–MO–SCF calculations show that the T_d configuration is about 18 kcal/mol more stable than the D_{4h} one, and that the intermediate D_{2d} configuration is about 2 kcal/mol more stable than the T_d one.[39] Thus the calculated energy differences between D_{4h} and D_{2d} configurations are sufficiently small to account for an appreciable influence of the surrounding medium upon the geometry of the $CuCl_4^{2-}$ anion.

Our calculated spectrum of $CuCl_4^{2-}$ is consistent with the spectra generally admitted for $CuCl_4^{2-}$ in aqueous solutions.[23,42–44]

It would be very hazardous to draw any structural conclusion from the positions of these bands, especially as the differences between the D_{2d} and the D_{2h} configurations are most obvious in the d–d transition region which we unfortunately could not explore beyond 800 nm because of the lack of an appropriate spectrophotometer. The absence of any band at 450 nm as well as the shape of the spectrum between 700 and 800 nm could be considered as arguments in favor of a square-planar structure, but could by no means be taken as a proof. Moreover, it is not out of question that $CuCl_4^{2-}$ in

aqueous solutions may have the geometry of a tetragonally distorted octahedron, with two water molecules coordinated to copper. Similar structures have been found in the solid state for $CuCl_2 \cdot 2H_2O$ made of $[CuCl_4(H_2O)_2]^{2-}$ units[22] (λ_{max} 280 nm[40]) and for $LiCuCl_3 \cdot 2H_2O$ made of $[CuCl_5(H_2O)]^{3-}$ units (λ_{max} 270, 380, 485 nm[40]).

Registry No. $CuCl^+$, 15697-17-3; $CuCl_2$, 7447-39-4; $CuCl_3^-$, 15697-18-4; $CuCl_4^{2-}$, 15489-36-8.

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Studies on Metal Carboxylates. 12.[1] Reactions of Molybdenum(II), Rhodium(II), and Rhenium(III) Acetates with Gaseous Hydrogen Chloride and Hydrogen Bromide

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Molybdenum(II) acetate ($Mo_2(O_2CCH_3)_4$) reacts with gaseous hydrogen chloride and hydrogen bromide at 300 °C to afford the phases β-MoX_2, where X = Cl or Br. Reaction of these halides with pyridine and monodentate tertiary phosphines to produce metal–metal bonded dimers of the type $Mo_2X_4L_4$ suggests that they are best formulated as $[Mo_2X_4]_n$ and are accordingly the parent halides of haloanions $Mo_2X_8^{4-}$. In contrast to this behavior, the rhenium(III) acetates, $Re_2(O_2CCH_3)_4X_2$, where X = Cl or Br, react with HCl and HBr to yield the trinuclear halides Re_3X_9. This is the first instance where a dinuclear rhenium halide containing a quadruple metal–metal bond has been converted to a trinuclear cluster. The related reaction of dinuclear rhodium(II) acetate with HCl and HBr differs from those involving $Mo_2(O_2CCH_3)_4$ and $Re_2(O_2CCH_3)_4X_2$ in that disproportionation to RhX_3 and rhodium metal occurs.

During a study of the x-ray photoelectron spectra of transition metal chloride clusters,[2] we showed that the β form of molybdenum(II) chloride[3-5] is not structurally related to the α form, in which a hexanuclear cluster of molybdenum atoms is known to be present[6] and which may, using Schäfer's notation,[6] be written as $[Mo_6Cl_8]Cl_{4/2}Cl_2$. In view of the absence of any detailed information concerning the structure of β-$MoCl_2$ and the paucity of studies dealing with its chemical reactivity, we decided to explore its chemistry in more detail. In particular, since this phase is prepared by the reaction of molybdenum(II) acetate with hydrogen chloride, we were interested in establishing whether metal–metal bonded Mo_2 units, as present in $Mo_2(O_2CCH_3)_4$,[7] are preserved in this phase. During the course of this work we extended the

preparative procedure which has been used[3,4] to prepare β-$MoCl_2$ to include the reactions of $Mo_2(O_2CCH_3)_4$, $Rh_2(O_2CCH_3)_4$, and $Re_2(O_2CCH_3)_4Cl_2$ with both hydrogen chloride and hydrogen bromide. The results of these studies are now reported in detail.[8]

Experimental Section

Starting Materials. Molybdenum hexacarbonyl, hydrated rhodium(III) chloride, potassium perrhenate, tertiary phosphines and pyridine, together with all reagent-grade solvents and gases, were obtained from commercial sources. All solvents were deoxygenated by purging with nitrogen gas for at least 1 h prior to use.

The following compounds were prepared by standard literature procedures: $Mo_2(O_2CCH_3)_4$,[3] $K_4Mo_2Cl_8$,[9] $Cs_3Mo_2Br_8H$,[10,11] Rh_2-