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Nature of the Copper(I) Carbonyl Formed by Acid Cuprous Chloride in the Presence of Carbon Monoxide

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Acid solutions of cuprous chloride have long been used to absorb carbon monoxide,[1] but in spite of a history of over 125 years the exact nature of the copper complex or complexes formed *in solution*[2] when CO is absorbed has never been satisfactorily determined. Among the formulas proposed are a cation[3a] $Cu(CO)^+$, an anion[3b], a carbonyl halide[3c] Cu(CO)Cl, and the dimer[3d] $Cu_2(CO)Cl_2$.

During the investigation of methods for increasing the efficiency of the CO/O_2 fuel cell,[4] the interaction of CO with a series of solutions containing Cu(I) in hydrochloric acid was investigated by several electrochemical techniques. Some of the potentiometric measurements resulting from this study have been interpreted so as to define the most probable formula of the species formed in acid cuprous chloride when CO is absorbed.

Experimental Section

Copper(I) chloride was purchased as reagent grade (Mallinckrodt) and repurified according to standard procedures.[5] Nitrogen, carbon dioxide, and carbon monoxide (Matheson) were passed through a heated copper catalyst (BASF) at 120 °C (N_2 and CO_2) or 40 °C (CO) to remove traces of oxygen. Just prior to use, each gas was bubbled through aqueous HCl of the same concentration as the Cu(I) solution under study to saturate the gas with water vapor and HCl. All other chemicals were purchased as reagent grade and used as received.

The cell consisted of a three-necked, 500-mL, round-bottomed flask. A platinum wire indicator electrode and a Beckman saturated calomel reference electrode (SCE) were sealed into the cell through the two side necks. A gas inlet–outlet system, equipped with stopcocks and a fritted-glass bubbler, was sealed through the center neck.

Copper(I) solutions were prepared by the following procedure. Concentrated (37%) hydrochloric acid and distilled water were mixed in the cell. Oxygen was removed by freezing the solution with liquid nitrogen, evacuating the cell on a vacuum line, and then filling the cell with nitrogen gas. The desired amount of copper(I) chloride was then added to the solution under a positive pressure of nitrogen, the cell was resealed, and gases were again removed by vacuum pumping. Small amounts of oxygen were inevitably introduced during the addition of the copper(I) chloride but were found to be necessary in order to produce a small but sufficient Cu(II) concentration for stable potentiometric readings. The solution was stirred rapidly, and the potential of the cell was monitored using a Leeds and Northrup potentiometer until the readings became stable (30–60 min). These solutions are colorless or pale yellow if small amounts of Cu(II) are present. No solids were observed prior to or during the addition of carbon monoxide.

In a typical run nitrogen was first introduced into the cell to establish a baseline potential in the absence of carbon monoxide and check that the inlet system had been cleared of oxygen. Gases were then evacuated as before, and the background pressure (water vapor, residual nitrogen, and HCl vapor) was measured using a manometer attached to the gas outlet side of the cell. Carbon monoxide was introduced (2–5 Torr increase/min) until the desired reading on the manometer had been reached. The solution was stirred rapidly until no further drop in pressure or change in potential could be observed (typically 2–4 h). Final pressure and cell potential were noted, and more carbon monoxide was introduced.

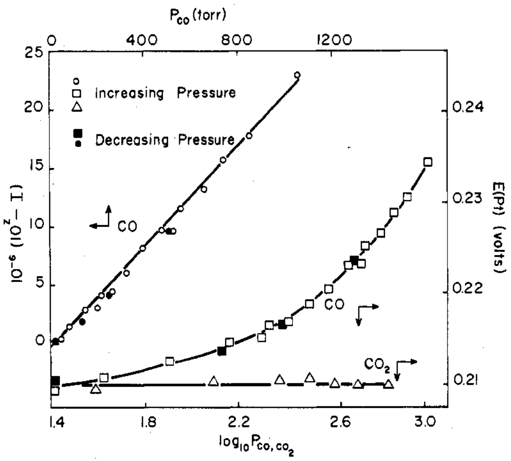

Figure 1. The nonlinear relationship between measured cell potential, *E*(Pt), and the logarithm of the equilibrium partial pressure of carbon monoxide, P_{CO}, contrasted with the linear relationship obtained from eq 11 assuming one carbonyl per complex. The potential of the cell is reversibly altered by the presence of carbon monoxide but is insensitive to the presence of carbon dioxide.

A baseline potential (no CO present) was also measured on a copper indicator electrode prior to the start of each run. The copper electrode was removed prior to the addition of carbon monoxide.

The introduction of oxygen into the cell during a run caused a large (100–200 mV) jump in the cell potential which was irreversible when the gas was removed from the cell. At the end of each run the CO pressure was reduced to determine whether the potential readings at low CO pressures could be reestablished.

Each solution was analyzed for total copper both by standard iodometric procedures[6] and by atomic absorption. Total chloride was determined by the Volhard method.[7]

Results and Discussion

Well-established potentiometric methods exist for obtaining metal:ligand ratios in reactions involving complex formation.[8] In this specific case the cell potential measured on the Pt indicator electrode, *E*(Pt), vs. a saturated calomel electrode will vary with the partial pressure of CO over the solution because the formation of a copper(I) carbonyl complex alters a_{Cu^+}, the Cu^+ ion activity, by an amount related to the magnitude of the stability constant for the carbonyl.

$$E(\mathrm{Pt}) = E^\circ_{Cu^{2+},Cu^+} - E(\mathrm{SCE}) + 0.059 \log (a_{Cu^{2+}}/a_{Cu^+}) \quad (1)$$

$E^\circ_{Cu^{2+},Cu^+}$, the standard electrode potential for the Cu^{2+},Cu^+ couple vs. the normal hydrogen electrode (NHE),[9] *E*(SCE), the saturated calomel reference potential vs. NHE,[10] and $a_{Cu^{2+}}$, the activity of the Cu^{2+} ion in solution, are constant. Numerical values for both a_{Cu^+} and $a_{Cu^{2+}}$ can be determined by combining eq 1 with eq 2 where *E*(Cu) is the cell potential

$$E(\mathrm{Cu}) = E^\circ_{Cu^+,Cu^0} - E(\mathrm{SCE}) + 0.059 \log a_{Cu^+} \quad (2)$$

measured on a copper indicator electrode and $E^\circ_{Cu^+,Cu^0}$ is the standard electrode potential of the Cu^+,Cu^0 couple vs. NHE.[11]

Any valid potentiometric treatment is expected to yield a Cu:CO ratio of 1:1 for the complex or complexes in question because a limit of one CO molecule per Cu atom is approached but never exceeded during gas absorption.[1,12] If only *one* single carbonyl complex is formed which is significantly more stable than all other Cu(I) complexes present in solution, a plot of the cell potential vs. the log of the partial pressure of CO should be linear with a slope of 0.059 for this ratio.[8] As shown in Figure 1 the plot is not even linear.

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Table I. Total Chloride $[\mathrm{Cl}]_t$, Total Copper $[\mathrm{Cu}]_t$, Solution Density ρ, and Cell Potential $E(\mathrm{Cu})$ on Copper Indicator Electrode for Solutions Investigated Potentiometrically

expt	$[\mathrm{Cl}]_t$,[a] M	$[\mathrm{Cu}]_t$,[a] M	ρ, g/mL	$-E(\mathrm{Cu})$, V $P_{\mathrm{CO}} = 0$
1	1.982 ± 0.008	0.175 ± 0.001	1.045	0.1352
2	4.445 ± 0.005	0.320 ± 0.002	1.095	0.2059
3	5.470 ± 0.004	0.345 ± 0.001	1.111	0.2323
4	5.964 ± 0.007	0.340 ± 0.001	1.118	0.2380
5	0.630 ± 0.002	0.00345 ± 0.00003	1.008	0.1649
6[b]	4.553 ± 0.006	0.00293 ± 0.00003	1.185	0.2967
7	5.294 ± 0.004	0.00456 ± 0.00004	1.083	0.3484
8	9.102 ± 0.007	0.00316 ± 0.00003	1.155	0.4366

[a] Errors represent 1 standard deviation. [b] NaCl added rather than HCl to make up total chloride concentration. HCl added to all other solutions.

The Raman spectrum of one of these solutions[13] in the presence of CO shows one symmetric peak in the carbonyl stretching region (ν_{CO} 2100 cm^{-1}). The shift to lower wavenumbers, compared to the free CO molecule,[14] indicates that a carbonyl complex has been formed. The presence of only one carbonyl frequency suggests that there may be only one carbonyl complex formed in major amounts in the solution.

Since changes in the cell potential are strictly reversible with changes in P_{CO}, the equilibrium partial pressure of CO (Figure 1), they cannot be the result of oxidation of Cu(I) by oxygen (an irreversible process) or reduction of Cu(I) by CO (also irreversible). Furthermore, constant potential readings with changes in $\mathrm{CO_2}$ pressure (Figure 1) show that the Pt electrode is actually monitoring the $\mathrm{Cu^{2+},Cu^{+}}$ couple and not the $\mathrm{CO_2,CO}$ couple. Changes in $E(\mathrm{Pt})$ must, therefore, be due only to changes in $\mathrm{Cu^+}$ activity resulting from the formation of the carbonyl complex. Curvature in the plot shown in Figure 1 must mean that the copper carbonyl formed is not substantially more stable than one or more of the Cu(I) chloro complexes which are also present in the solution.

The main conclusion from most previous investigations[15,16] is that $\mathrm{CuCl_2^-}$ and $\mathrm{CuCl_3^{2-}}$ should be the predominant chloro complexes present in most of the solutions examined by this study.[17] Evidence has also been obtained to suggest the existence of one or more polynuclear complexes[18] such as $\mathrm{Cu_2Cl_4^{2-}}$.[15] While the following derivation, which develops the relationship between $E(\mathrm{Pt})$ and the partial pressure of CO, considers only these three chloro complexes, the inclusion of other chloro complexes in this treatment will not alter the final results.

If total copper determined analytically is assumed to be entirely copper(I), then the total molal concentration of copper in solution, m_{Cu}, is equal to the sum of the molalities of the $\mathrm{Cu^+}$ ion, the three chloro complexes, and the Cu(I) carbonyl complex

$$m_{\mathrm{Cu}} = m_{\mathrm{Cu^+}} + m_{\mathrm{CuCl_2^-}} + m_{\mathrm{CuCl_3^{2-}}} + 2m_{\mathrm{Cu_2Cl_4^{2-}}} + rm_{\mathrm{Cu}_r(\mathrm{CO})_x\mathrm{Cl}_y{}^{r-y}} \quad (3)$$

where r, x, and y represent the number of copper atoms, carbonyls, and chlorides, respectively, which are bound together in the carbonyl complex. If molal concentrations are assumed equal to molal activities, $m_{\mathrm{Cu^+}} = a_{\mathrm{Cu^+}}$, $m_{\mathrm{CuCl_2^-}} = a_{\mathrm{CuCl_2^-}}$, etc., then the activities of the complexes can be expressed in terms of the stability constants β_2, β_3, β_{24}, and β_{CO} for the complexes and P_{CO}, $a_{\mathrm{Cu^+}}$, and $a_{\mathrm{Cl^-}}$, the activity of chloride ion in solution, as obtained from eq 4–7. This substitution yields eq 8. The expression for $a_{\mathrm{Cu^+}}$ obtained from

$$\beta_2 = a_{\mathrm{CuCl_2^-}}/a_{\mathrm{Cu^+}}a_{\mathrm{Cl^-}}^{2} \qquad \text{for } \mathrm{CuCl_2^-} \quad (4)$$

$$\beta_3 = a_{\mathrm{CuCl_3^{2-}}}/a_{\mathrm{Cu^+}}a_{\mathrm{Cl^-}}^{3} \qquad \text{for } \mathrm{CuCl_3^{2-}} \quad (5)$$

$$\beta_{24} = a_{\mathrm{Cu_2Cl_4^{2-}}}/a_{\mathrm{Cu^+}}^{2}a_{\mathrm{Cl^-}}^{4} \qquad \text{for } \mathrm{Cu_2Cl_4^{2-}} \quad (6)$$

$$\beta_{\mathrm{CO}} = a_{\mathrm{Cu}_r(\mathrm{CO})_x\mathrm{Cl}_y{}^{r-y}}/a_{\mathrm{Cu^+}}^{r}P_{\mathrm{CO}}^{x}a_{\mathrm{Cl^-}}^{y} \qquad \text{for } \mathrm{Cu}_r(\mathrm{CO})_x\mathrm{Cl}_y{}^{r-y} \quad (7)$$

$$m_{\mathrm{Cu}} = a_{\mathrm{Cu^+}}[1 + \beta_2 a_{\mathrm{Cl^-}}^{2} + \beta_3 a_{\mathrm{Cl^-}}^{3} + 2\beta_{24}a_{\mathrm{Cu^+}}a_{\mathrm{Cl^-}}^{4} + r\beta_{\mathrm{CO}}a_{\mathrm{Cu^+}}^{r-1}P_{\mathrm{CO}}^{x}a_{\mathrm{Cl^-}}^{y}] \quad (8)$$

eq 8 is substituted into eq 1 to yield

$$E(\mathrm{Pt}) = X_1 + 0.059 \log [1 + \beta_2 a_{\mathrm{Cl^-}}^{2} + \beta_3 a_{\mathrm{Cl^-}}^{3} + 2\beta_{24}a_{\mathrm{Cu^+}}a_{\mathrm{Cl^-}}^{4} + r\beta_{\mathrm{CO}}a_{\mathrm{Cu^+}}^{r-1}P_{\mathrm{CO}}^{x}a_{\mathrm{Cl^-}}^{y}] \quad (9)$$

where

$$X_{\mathrm{I}} = E^\circ{}_{\mathrm{Cu^{2+},Cu^+}} - E(\mathrm{SCE}) + 0.059 \log (a_{\mathrm{Cu^{2+}}}/m_{\mathrm{Cu}}) \quad (10)$$

Rearrangement of eq 9 yields the final result

$$10^z = I + r\beta_{\mathrm{CO}}a_{\mathrm{Cu^+}}^{r-1}P_{\mathrm{CO}}^{x}a_{\mathrm{Cl^-}}^{y} \quad (11)$$

where

$$z = (E(\mathrm{Pt}) - X_{\mathrm{I}})/0.059 \quad (12)$$

and

$$I = 1 + \beta_2 a_{\mathrm{Cl^-}}^{2} + \beta_3 a_{\mathrm{Cl^-}}^{3} + 2\beta_{24}a_{\mathrm{Cu^+}}a_{\mathrm{Cl^-}}^{4} \quad (13)$$

If all terms are essentially constant except for $E(\mathrm{Pt})$ and the partial pressure of carbon monoxide, P_{CO}, then a plot of 10^z vs. P_{CO}^{x} will be linear for the appropriate value of x.[19] As shown in Figure 1 this plot is nicely linear for $x = 1$. Since all terms pertaining to the chloro complexes appear only in the intercept (eq 13), the value of x obtained from the slope is independent of any assumptions made about the nature of the copper(I) chloro complexes which are also present in the solution.

It remains to determine the number of copper atoms, r, and chlorine atoms, y, which are also present in the carbonyl complex. As discussed previously, the value of r is expected to be 1 if the number of CO molecules in the complex is 1.

A linear plot of 10^z vs. P_{CO} will have a slope S which is related to the chloride activity. If the complex is polynuclear and r is greater than 1, then S will also depend on the $\mathrm{Cu^+}$ activity.

$$S = r\beta_{\mathrm{CO}}a_{\mathrm{Cu^+}}^{r-1}a_{\mathrm{Cl^-}}^{y} \quad (14)$$

Although $a_{\mathrm{Cu^+}}$ and $a_{\mathrm{Cl^-}}$ appear to change little as CO pressure is increased over any particular solution, they will differ significantly from solution to solution because of the large variation in total copper and total chloride present (Table I). If $r = 1$ as we expect, then the complex is a monomer and a plot of the log of the slopes S from all solutions studied vs. the log of the chloride activity for each solution will be linear with a slope equal to y, the number of chlorides present in the carbonyl complex (eq 15).

$$\log S = \log \beta_{\mathrm{CO}} + y \log a_{\mathrm{Cl^-}} \quad (15)$$

The slope S can be readily determined for each solution (Table II). Rather than attempting to determine one value for $a_{\mathrm{Cl^-}}$ which requires an exact knowledge of the populations of all complexes present, a range of reasonable values for $a_{\mathrm{Cl^-}}$ was determined for each solution.[20] Each of the predominant chloro complexes, $\mathrm{CuCl_2^-}$, $\mathrm{CuCl_3^{2-}}$, and $\mathrm{Cu_2Cl_4^{2-}}$, removes two or three chlorides per copper atom from the total chloride concentration measured analytically. Thus, a maximum value for the free or uncomplexed chloride present in solution can be determined by assuming that each copper atom removes two chloride ions. A minimum value for free chloride can be determined by assuming that each copper atom removes three chloride ions from solution. Molar chloride concentration was converted to molal chloride using the solution density (Table I) and this was then converted to chloride activity using the

Table II. Cell Potential E(Pt) on a Platinum Electrode with the Corresponding Partial Pressure of Carbon Monoxide P_{CO} for Solutions Studied Potentiometrically at 23 (±1) °C

expt	E(Pt), V	P_{CO}, Torr	expt	E(Pt), V	P_{CO}, Torr	expt	E(Pt), V	P_{CO}, Torr
1	0.0898	0	3	0.1657	0	6	0.2083	0
	0.0964	117		0.1685	91		0.2116	137
	0.1044	296		0.1741	258		0.2153	297
	0.1099	448		0.1796	455		0.2195	491
	0.1185	756		0.1834	645		0.2244	764
2	0.1733	0	4	0.1741	0	7	0.1887	0
	0.1754	75		0.1785	108		0.2037	135
	0.1805	226		0.1816	213		0.2106	293
	0.1861	413.5		0.1877	431		0.2157	491
	0.1913	638		0.1922	632		0.2222	745
			5	0.0748	0	8	0.2317	0
				0.0887	127		0.2429	130
				0.0995	296		0.2470	286
				0.1095	483		0.2523	514
				0.1184	751		0.2578	722

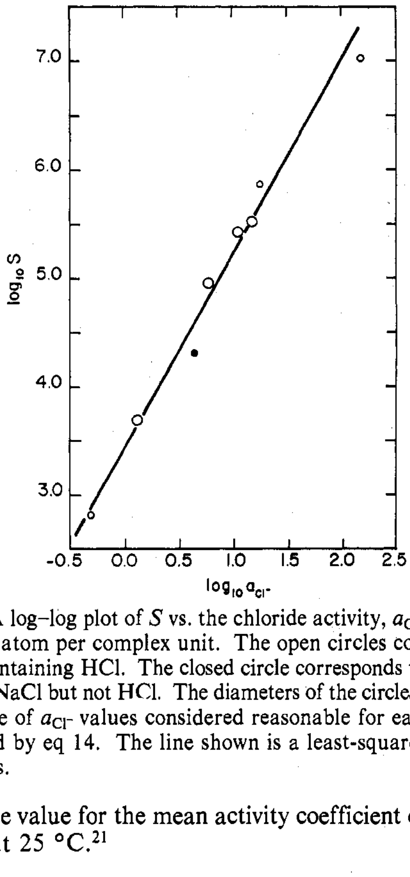

Figure 2. A log–log plot of S vs. the chloride activity, a_{Cl^-}, assuming one copper atom per complex unit. The open circles correspond to solutions containing HCl. The closed circle corresponds to a solution containing NaCl but not HCl. The diameters of the circles correspond to the range of a_{Cl^-} values considered reasonable for each solution. S is defined by eq 14. The line shown is a least-squares fit for all eight points.

appropriate value for the mean activity coefficient of HCl, $\gamma_\pm$, in water at 25 °C.[21]

$$a_{Cl^-} = \gamma_\pm m_{Cl^-} \qquad (16)$$

Figure 2 shows the plot of log S vs. log a_{Cl^-} where a_{Cl^-} represents the range of chloride activities considered reasonable for each solution. The plot is reasonably linear over a wide range of Cu^+ activities (7.9×10^{-13}–1.0×10^{-7} m) and Cl^- activities (0.48–150 m). The slope of the line using all eight points is 1.7. By exclusion of the point at highest chloride concentration the slope becomes 1.9. Since small changes in m_{Cl^-} result in large variations in a_{Cl^-} at very high chloride ion concentration, it is not possible to say whether this is really a small deviation from linearity or is simply the result of an error in the m_{Cl^-} estimate for this one point.

Plots derived from eq 14 for other integer values of r are not linear. This establishes one copper atom per complex. Since one solution contained chloride only in the form of NaCl rather than HCl and the slope S still falls on the line in Figure 2, the complex does not appear to contain H^+.[22]

If only one carbonyl complex is formed to an appreciable extent in the solution, the most reasonable formula of this species would appear to be $Cu(CO)Cl_2^-$. These results cannot exclude the existence of other carbonyl complexes in minor amounts nor the possibility that a mixture of monomers with identical carbonyl stretching frequencies and an average of about two chlorides per copper atom exists instead. Since y exceeds 1, one or more of the complexes must be anionic. This is in agreement with an earlier electrolysis study[3b] which showed that the carbonyl is attracted to the positive anode where CO is evolved.

On the basis of *only* the dichloro formulation, the stability constant β_{CO} can be estimated from the intercept of the plot in Figure 2. The value appears to be about 2×10^6 m^{-2} atm^{-1} which is the same order of magnitude as the stability constants for the $CuCl_2^-$ and $CuCl_3^{2-}$ complexes.[23]

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Registry No. $Cu(CO)Cl_2^-$, 68629-61-8; CuCl, 7758-89-6; CO, 630-08-0.

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Simple Alkyne Adducts of $MoO(S_2CNR_2)_2$

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It has recently been shown that $MoO(S_2CNEt_2)_2$ can reversibly bind acetylene in solution whereas no binding between the complex and ethylene was observed.[1] Spectroscopic evidence demonstrated that the alkyne is bound cis to the oxo group and is in the plane which is perpendicular to the MoO bond vector. This geometry, which is readily predicted using simple bonding arguments, is identical with those found with the structurally characterized adducts of the activated alkene tetracyanoethylene[2] and the activated alkyne ditoluoylacetylene.[3] The actual isolation of acetylenic adducts has been accomplished up to this time in only those cases where the alkyne bears strongly activating substituents as in $RC{\equiv}CR'$ ($R = R' = CH_3C_6H_4CO$[3] or CH_3CO_2[4] and $R = CH_3CO_2$, $R' = H$[5]). We now wish to report the isolation and characterization of several adducts of $MoO(S_2CNMe_2)_2$ and $MoO(S_2CNEt_2)_2$ with the simpler alkynes acetylene, phenylacetylene, and diphenylacetylene.

Experimental Section

All manipulations were performed either under vacuum or in an argon atmosphere. Anhydrous, air-free CH_2Cl_2 was obtained by equilibration over P_2O_5 followed by distillation under vacuum. The oxomolybdenum(IV) complexes were prepared by a published procedure.[6] All other materials were reagent grade. Elemental analyses were obtained from Galbraith Laboratories. Infrared spectra were obtained using a Perkin-Elmer Model 283 spectrophotometer while ^1H NMR spectra were determined at 220, 100, and 60 MHz using Varian HR-220, XL-100, and T-60 spectrometers, respectively.

The alkyne complexes were prepared according to the following general procedure. The addition of 5 mmol of the alkyne to 25 mL of CH_2Cl_2 containing 0.6 mmol of either $MoO(S_2CNEt_2)_2$ or $MoO(S_2CNMe_2)_2$ rapidly discharged the initial rose color and caused the appearance of a bright orange-yellow color. The reaction is virtually heterogeneous when $MoO(S_2CNMe_2)_2$ is used but it is homogeneous when $MoO(S_2CNEt_2)$ is employed. For the latter, concentration followed by slow introduction of hexane by distillation causes the deposition of bright yellow crystals which can be removed by filtration. With the exception of the compound formed with diphenylacetylene, the analytical results shown in Table I are in accord with the formulation $MoO(alkyne)(S_2CNR_2)_2$. With diphenylacetylene, however, the product is $MoO(PhC_2Ph)(S_2CNEt_2)_2\cdot{}^1/_2PhC{\equiv}CPh$. The additional alkyne in this compound is undoubtedly a guest in the lattice since it was easily removed by either washing with hexane or extensive exposure to a dynamic vacuum.

The preparation of $MoO(HC_2H)(S_2CNMe_2)_2$ followed the same general procedure and again the reaction was virtually heterogeneous. However, the isolated product had sufficient solubility in CD_2Cl_2 to observe the major features of the ^1H NMR spectrum including the signal due to the bound acetylene. Furthermore, the infrared spectrum of the compound, when taken immediately after its isolation, only contained bands which could be ascribed to the adduct. However, the intensities of these bands slowly diminished while new bands due to $Mo_2O_4(S_2CNMe_2)_2$ appeared. The appearance of the dinuclear complex is due to a reaction with O_2 since the adduct is completely converted to $Mo_2O_4(S_2CNMe_2)_2$ on exposure to air. We assume that the other product is $H_2C{=}CH(S_2CNMe_2)$ since others[5] have observed that the reaction of $MoO(RC_2R')(S_2CNMe_2)_2$ ($R = R' = CF_3$; $R = H$, $R' = CH_3CO_2$) with O_2 from moist air results in the near-quantitative formation of the dinuclear compound and the corresponding alkene addition product. Although we took extreme precautions in preparing a sample of the alkyne adduct for commercial analyses, the analytical results which were returned to us point to decomposition of the adduct and virtually complete formation of the dinucear compound and the alkene in a mole ratio of 1:2. Anal. Calcd: C, 24.3; H, 3.83; N, 7.09; S, 32.5. Found: C, 23.9; H, 3.52; N, 7.18; S, 32.5.

Results and Discussion

Pertinent infrared and ^1H NMR data are included in Table II. Coordination of the alkyne results in a decrease in the MoO stretching frequencies by about 30 cm^{-1} from the values observed with the parent oxomolybdenum(IV) complexes. Similarly, coordination of the alkyne causes a decrease in the carbon–carbon stretching frequency of about 300 cm^{-1}. The NMR spectra of those complexes in which the bound alkyne possesses acetylenic hydrogen atoms revealed considerable deshielding of these atoms as evidenced by their downfield shifts of about 6 ppm relative to the values observed with free alkyne. These observations lend further credence to the suggestion that the formation of these complexes[3] as well as those of the azodicarboxylates[4] involves a formal two-electron oxidative addition of the alkyne to the oxomolybdenum(IV) species. Simple bonding arguments suggest that the bond order of the MoO bond in the latter should be three since the empty d_{xz} and d_{yz} orbitals of the metal can overlap with the filled $p\pi$ orbitals of the oxo ligand. Housing two electrons in the d_{xy} orbital then accounts for the diamagnetism. The bond order of the MoO fragment is then maintained if the alkyne occupies the *xy* plane. The filled d_{xy} orbital can overlap effectively with an empty π^* orbital of the alkyne resulting in a transfer of electron density from the metal to the alkyne. The resulting complex can be described as a pentagonal bipyramid in which the equatorial sites are occupied by the carbon atoms of the alkyne and three sulfur atoms from two bidentate ligands.

Spectroscopic techniques have allowed us to demonstrate that the dynamic equilibrium shown in eq 1 exists when those

$$\mathrm{MoOL_2 + alkyne = MoO(alkyne)L_2} \qquad (1)$$
$$\mathrm{L = S_2CNEt_2}$$

complexes having appreciable solubility are dissolved in CH_2Cl_2. Both bound and dissociated species are observed using NMR spectroscopy as well as infrared spectroscopy[1] even at ambient temperature. The addition of excess alkyne or a decrease in the temperature will cause the equilibrium to shift in favor of the adduct. The spectrum of $MoO(HC_2H)(S_2CNEt_2)_2$ at −55 °C, 100 MHz, and a 25-fold excess of acetylene is shown in Figure 1. Two signals due to the methyl hydrogen atoms of the ligands appear in a 3:1 distribution. A similar distribution can also be observed for the two signals caused by the methylene hydrogen atoms. We have observed a similar pattern in the spectrum of $MoO(PhC_2Ph)(S_2CNEt_2)_2$. This region of the spectrum of $MoO(PhC_2H)(S_2CNEt_2)_2$, however, is complicated somewhat by overlapping resonances due to two possible orientations of the alkyne. Additional comments about the consequences of these orientations appear later in this paragraph. The spectrum of $MoO(RC_2R)(S_2CNEt_2)_2$ ($R = CH_3CO_2$), a compound which does not dissociate appreciably according to eq 1, shows only the simple 3:1 patterns at ambient temperature. The stronger binding of this alkyne is caused by more extensive electron withdrawal ($d_{xy} \rightarrow \pi^*$) demanded by the carboxylate groups. The qualitative similarity of these features in the NMR spectra

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