

The 5145-Å (19,435 cm^{-1}) exciting line, which yielded resonance Raman spectra with the higher concentration sample and the solid,³ falls within the absorption band of Re_3Cl_9 solutions, which exhibit a maximum near 19,400 cm^{-1} .⁴

In agreement with the literature on metal-metal bonding,³ the 256, 505, 755, and 1009 cm^{-1} series is assigned to the fundamental Re-Re totally symmetric cluster breathing mode (A_1' in idealized D_{3h} point group) and its first three overtones. The 216- cm^{-1} band is not appropriate for the E' cluster mode, which is expected at the A_1' wave numbers divided by $(2^{1/2})$.¹⁰ This extra band is characteristic of the spectra of solid¹¹ and aggregated iodine⁸ where a weak (189 \pm 1)- cm^{-1} satellite band was observed beside the 180- cm^{-1} fundamental. This feature is due to out-of-phase stretching of I_2 molecules in the unit cell. Notice that the 216- cm^{-1} band is absent in the isolated spectrum of Figure 1(a). We believe the 216- cm^{-1} band is best explained as out-of-phase Re-Re cluster breathing modes of Re_3Cl_9 units in the aggregate formed in the matrix. This band shows some resonance intensity enhancement but is weaker than the signal from the totally symmetric cluster fundamental.

The intense fundamental at 277 cm^{-1} labeled ν_c in Figure 1(a) and its overtone series are assigned to the symmetric Re-Re cluster breathing mode (A_1') in the isolated Re_3Cl_9 molecular unit. The shift to lower wave number is characteristic of aggregation and intermolecular bonding which gives a 256- cm^{-1} fundamental for the matrix aggregate and a 250- cm^{-1} fundamental in the solid where intermolecular bonding is complete.

The broader subseries of bands which appear 72, 142, and 211 cm^{-1} shifted below the fundamental and first two overtones clearly originate with the resonance-enhanced Re-Re cluster mode. These subbands are attributed to combination bands involving, most probably, some other totally symmetric mode and ν_c . Three other totally symmetric modes that should strongly couple with ν_c are symmetric stretching modes of the out-of-plane chlorines and the bridged chlorines, and a symmetric Cl-Re-Cl valence angle bending mode involving the out-of-plane chlorines on each Re atom. The best present assignment for the 72- cm^{-1} combination band series is to the symmetric valence angle bending mode of the out-of-plane chlorines, ν_b . Thus, the bands in the isolated monomeric Re_3Cl_9 resonance Raman spectrum, reading right to left, are ν_c , $\nu_c + \nu_b$, $\nu_c + 2\nu_b$, $\nu_c + 3\nu_b$, $2\nu_c$, $2\nu_c + \nu_b$, $2\nu_c + 2\nu_b$, $2\nu_c + 3\nu_b$, $3\nu_c$, These assignments are listed in Table I.

It is also interesting to note the much more rapid decrease in overtone intensity for the aggregate, as compared to isolated Re_3Cl_9 , in Figure 1. The same effect was found for matrix-isolated iodine.⁸

Acknowledgment. The authors gratefully acknowledge support for this research by the National Science Foundation under Grant GP-38420X and an Alfred P. Sloan Fellowship for L.A.

Registry No. Re_3Cl_9 , 14973-59-2.

References and Notes

- W. F. Howard, Jr., and L. Andrews, *J. Am. Chem. Soc.*, **95**, 2056 (1973); *Inorg. Chem.*, **14**, 409 (1975).
- L. Andrews and R. C. Spiker, Jr., *J. Chem. Phys.*, **59**, 1863 (1973); L. Andrews, *J. Am. Chem. Soc.*, **95**, 4487 (1973).
- J. San Filippo, Jr., and H. J. Sniadoch, *Inorg. Chem.*, **12**, 2326 (1973).
- F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1402 (1964).
- A. Büchler, P. E. Blackburn, and J. L. Stauffer, *J. Phys. Chem.*, **70**, 685 (1966).
- L. Andrews, *J. Chem. Phys.*, **54**, 4935 (1971).
- D. A. Hatzebuhler and L. Andrews, *J. Chem. Phys.*, **56**, 3398 (1972).
- W. F. Howard, Jr., and L. Andrews, *J. Raman Spectrosc.*, in press.
- W. Kiefer and H. J. Bernstein, *Mol. Phys.*, **23**, 835 (1971).
- C. O. Quicksall and T. G. Spirio, *Inorg. Chem.*, **7**, 2365 (1968).
- A. Anderson and T. S. Sun, *Chem. Phys. Lett.*, **6**, 611 (1970).

Contribution from the Department of Chemistry, University of California, Davis, California 95616

Experimental Complications in Studies of the Reaction of Copper(II) with Penicillamine and Related Thiols

W. K. Musker* and C. H. Neagley

Received November 5, 1974

AIC40766M

We have observed unusual experimental complications during our examination of some intensely colored mixed-valence copper complexes¹ formed by partial reduction of copper(II) by certain thiols. Mixed-valence complexes are of interest because they are present in some multi-copper proteins.^{2,3} In the single-copper proteins stellacyanin⁴ and plastocyanin⁵ a copper to sulfur bond has been proposed, yet the redox chemistry associated with the interaction of copper with thiols is unclear. Drugs such as penicillamine which react with copper(II) to cause partial reduction and give intensely colored complexes have been used successfully in the treatment of chronic copper toxicity (Wilson's disease),^{6,7} yet the reaction between penicillamine and copper(II) has not been well characterized. Recently, research has been directed toward an understanding of the reactions between copper(I) and copper(II) and ligands containing the disulfide group.^{8,9}

Our examination of the reaction of copper(II) with penicillamine in aqueous solution reveals that certain important factors which greatly influence the course of the reaction and which relate to the composition of the colored species both in solution and in the solid state have not been reported before.¹⁰⁻¹⁴ These factors must be considered in future discussions of the reactivity of copper in the presence of both thiol and disulfide groups. To circumvent some of the problems encountered with penicillamine, the reaction of a more simple ligand, α -mercaptoisobutyric acid, MIBA, was examined in detail.

Experimental Section

Cupric chloride (Matheson Coleman and Bell) was refluxed with thionyl chloride and dried under vacuum. Cuprous chloride was prepared by reduction of cupric chloride with sodium sulfite. D(-)- and DL-penicillamine and D(-)-penicillamine disulfide (Aldrich) were used without purification. α -Mercaptoisobutyric acid (MIBA) was prepared using the procedure of Biilmann.¹⁵ MIBA disulfide, MIBA(SS), was prepared by oxidizing MIBA with copper chloride, mp 197-200°. Anal. Calcd for $\text{C}_8\text{H}_{14}\text{S}_2\text{O}_4$: C, 40.34; H, 5.88. Found: C, 40.30; H, 6.01.

The electronic absorption spectra were measured with a Cary 14 spectrophotometer. Magnetic susceptibilities were determined by the Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the standard. ESR spectra were obtained using a Varian E-4 spectrometer. Infrared spectra were obtained using a Perkin-Elmer 237B spectrometer. Analytical and molecular weight data were obtained by Galbraith Laboratories Inc., Knoxville, Tenn. Copper analyses were done by electrogravimetry.

Preparation of Complexes. Complexes were prepared by mixing an aqueous CuCl_2 solution ($\sim 10^{-3} M$) with a freshly prepared aqueous thiol solution ($\sim 10^{-3} M$) usually in 0.1 M acetate. Both solutions were purged before mixing with purified nitrogen. The solutions were normally mixed in a flask after introduction via metal-tipped syringes. In some of the penicillamine reactions, however, a syringe pump was used to ensure reproducible mixing. In these reactions the solutions were passed through a small mixing chamber (approximately 0.2 ml in volume) before entering the flask.

The complexes were also prepared in solution by combining solid CuCl with the disulfide in aqueous solution in the presence of 0.1 M acetate. Penicillamine disulfide was quite soluble, whereas MIBA(SS) was initially present as a slightly soluble solid. In these reactions all solutions and flasks were purged with nitrogen. The formation of the products and the dissolution of the insoluble solids occurred over a period of hours.

The penicillamine and MIBA complexes slowly precipitate from

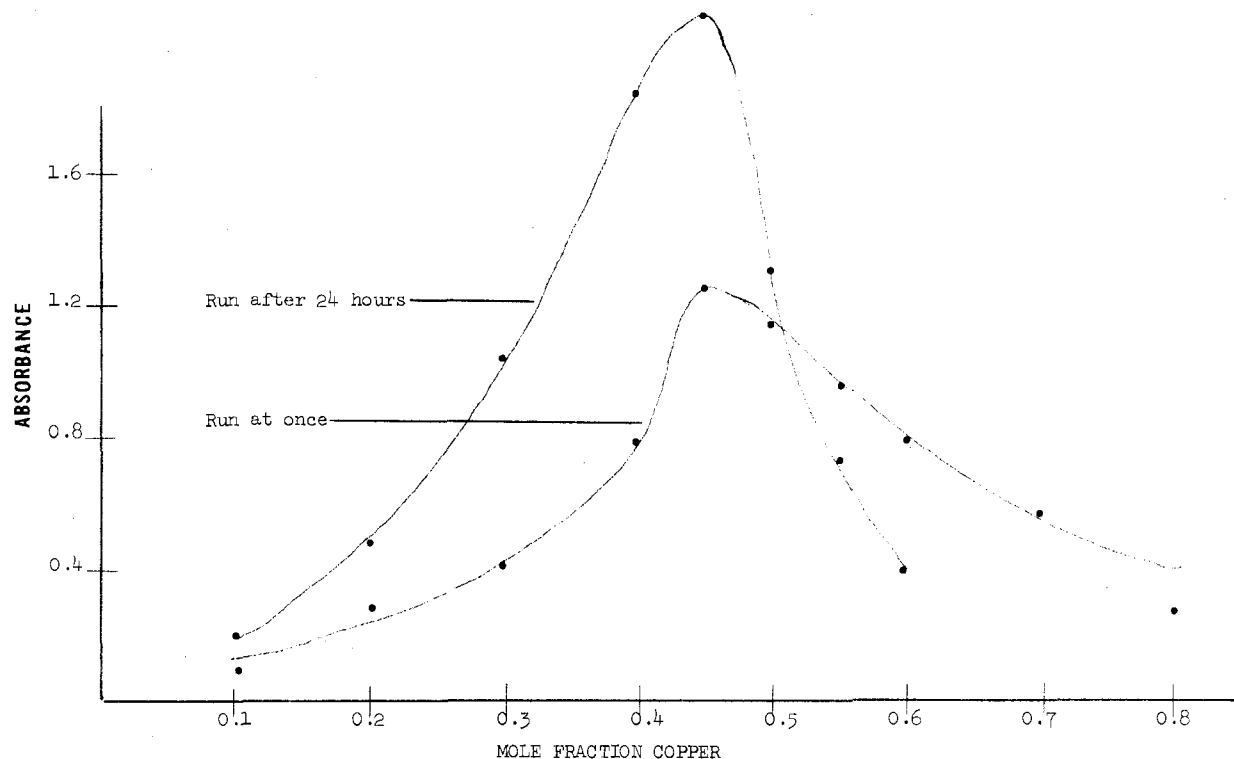


Figure 1. Job's plot for CuCl_2 + penicillamine (λ 520 nm).

solution in the presence of certain organic solvents. With penicillamine the purple product precipitated upon addition of solvents such as ethanol, THF, and acetonitrile. With MIBA the brown product was obtained upon addition of an excess of THF to the unbuffered solution. The products could not be crystallized. Since the purple complexes precipitate as amorphous solids, the elemental analyses varied over narrow ranges for each sample obtained. The results reported are for a representative sample which was successively reprecipitated and dried. Anal. Found for copper-penicillamine complex: C, 23.9; H, 4.5; N, 5.3; S, 12.8; Cu, 32.2; Cl, 1.6. Found for Cu-MIBA complex: C, 22.2; H, 3.9; S, 14.7; Cu, 33.9; Cl, 1.8.

Results and Discussion

Penicillamine. When penicillamine is treated with copper(II) in aqueous solution at concentrations from 10^{-2} to 10^{-3} M in 0.1 M acetate adjusted to pH ~ 6.2 , a purple solution is formed. The complex is most stable in the pH range from 4 to 7. The following experimental problems are encountered.

a. The initial absorbance of solutions made by mixing CuCl_2 and penicillamine under a variety of experimental conditions is not reproducible and varies by as much as 20% under identical conditions. The *rate of mixing* seems to be the major reason for the variation. By the use of a syringe pump with a small mixing chamber, the irreproducibility of the absorbance can be minimized but not eliminated (variation $\sim 3\%$).

b. Using the syringe pump the maximum absorption (520 nm; ϵ 1400) is achieved for a solution having 0.54 mole fraction penicillamine and 0.46 mole fraction CuCl_2 . (Figure 1). The initial absorption of solutions having a mole fraction of penicillamine greater than 0.5 *increases* slowly over a period of 24 hr and then stabilizes. The absorbance remains at this value for several months before decreasing slowly. However, below a mole fraction of 0.5, the initial absorption *decreases* slowly with time, and below a mole fraction of 0.3, the solution *completely decolorizes* in 24 hr.

c. Beer's law is not obeyed when solutions of varying initial concentrations are mixed. However, dilution of colored solutions already formed does follow Beer's law over a concentration range of 10^{-3} – 10^{-5} M. Precipitation occurs at concentrations greater than 10^{-2} M.

d. A purple precipitate can be obtained if THF is added

to aqueous solutions of the complex. The stoichiometry of the precipitated material reveals that the ratio of copper to ligand is not a simple integer. Part of the difficulty arises from the fact that *the precipitate always contains chloride (minimum $\sim 1.5\%$) corresponding to $\text{Cl}^-:\text{Cu}^{2+}$ ratio of 0.1*. The precipitate cannot be recrystallized and repeated dissolution and reprecipitation do not appreciably reduce the quantity of chloride present in the solid. However, the ratio of carbon to sulfur indicates that the ligand has not decomposed and that neither acetate nor THF is incorporated into the solid.

e. Actually Cl^- (or Br^-) is *required* to achieve and maintain the maximum intensity of the solution. Only a fleeting color is observed if $\text{Cu}(\text{ClO}_4)_2$ is used and a white precipitate forms within a few hours if thiocyanate or cyanide ions are present. A continuous variation study of copper and chloride reveals that a $\text{Cl}^-:\text{Cu}^{2+}$ ratio of 1.6 is required at a ratio of penicillamine to copper of 1:1. However, *if a large excess of chloride is present*, the color of the solution is discharged in several hours.

f. After the purple solid is precipitated from solution by adding THF, the remaining solution exhibits a pale blue color which can be attributed to the copper(II) complex of penicillamine disulfide $(\text{CuRSSR})_2$.⁹ The presence of the disulfide complex was suggested by a comparison of its electronic absorption spectrum and ESR spectrum with those of an authentic sample. By a series of experiments, we have found that penicillamine disulfide when added to the original solution competes significantly with penicillamine for available copper(II). If a mixture of penicillamine and penicillamine disulfide is added to a solution containing copper(II) chloride, only a faint purple color forms immediately, but the color grows in intensity slowly over a period of hours. However, the intensity of the color never reaches the level exhibited by the solution in the absence of penicillamine disulfide. Similarly, if penicillamine disulfide is added to the purple solution shortly after mixing, the maximum absorbance is not obtained, but, if penicillamine disulfide is added several days after mixing, the maximum absorbance is maintained. The result cannot be attributed solely to a reoxidation of copper(I) by disulfide before the mixed-valence complex can be formed, since the

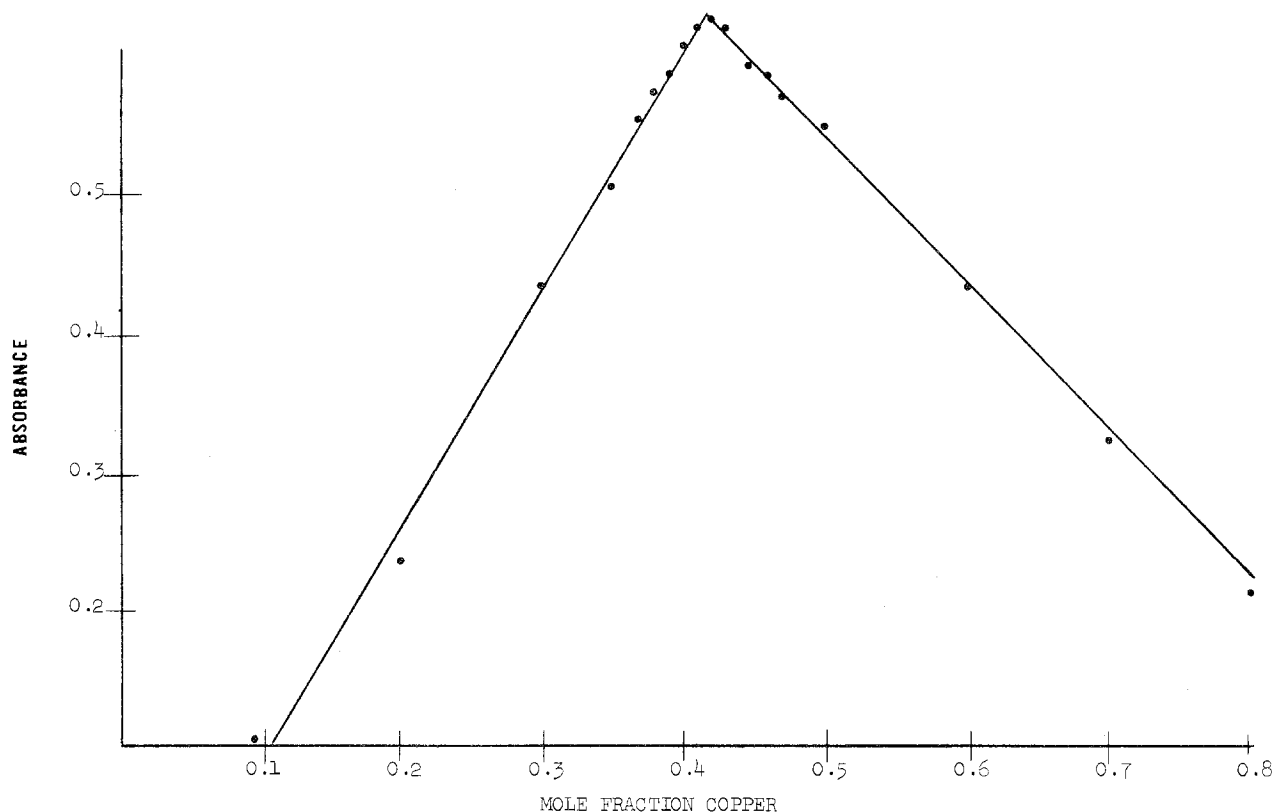


Figure 2. Job's plot for $\text{CuCl}_2 + \text{MIBA}$ (λ 485 nm).

reaction of MIBA with copper(II) is not inhibited by MIBA(SS). Likewise, the presence of amino acids, such as glycine, does not inhibit the formation of the purple complex.

g. The magnetic moment of the purple precipitate has a μ_{eff} of 1.22 BM, at 25° , but it does not display an ESR spectrum either in the solid state or in aqueous solution when the reprecipitated solid is redissolved. Apparently the signal is so broad that it cannot be resolved. However, the initial solution gives an ESR signal which can be attributed to the copper disulfide complex.

h. Other observations of the reaction of penicillamine with copper(II) include the fact that precipitation occurs both in phosphate buffer at pH 6.2 or in a solution which is neutralized by concurrent addition of sodium hydroxide. Oxygen has no effect on the reaction except that it causes the decomposition of penicillamine. The purple complex, once formed, is stable to oxygen. The purple complex can also be obtained by treatment of CuCl with penicillamine disulfide.¹⁶ Water appears to be required for the reaction—no purple color is observed in methanol, ethanol, or DMSO.

α -Mercaptoisobutyric Acid (MIBA). An intensely colored brown complex (λ_{max} 485 nm; ϵ 1500) which is formed when CuCl_2 is treated with α -mercaptoisobutyric acid, MIBA, exhibits more ideal solution behavior and consequently is more amenable to study. No mixing problem is encountered; the intensity of initial absorption does not vary with time and appears to persist indefinitely up to 50° ; Beer's law holds over a concentration range from 10^{-2} to 10^{-5} M; Job's plots can be created from absorbance values obtained at all mole fractions of CuCl_2 and MIBA (Figure 2) or of CuCl and MIBA(SS) (Figure 3). MIBA(SS) is formed in the reaction of CuCl_2 and MIBA and is isolated in 35% yield. In contrast to the penicillamine system, MIBA(SS) does not form a complex with copper(II) and therefore does not inhibit the reaction.

Although some color appears in the absence of chloride, chloride is also required to achieve maximum conversion to the colored Cu -MIBA complex. However, the quantity re-

quired is much less with MIBA than with penicillamine—a $\text{Cl}^-:\text{Cu}^{2+}$ ratio of 0.1 is sufficient. Even though the quantity of chloride required is low, small amounts ($\sim 2\%$) of chloride are still present in the solid material precipitated with THF and purified by successive dissolution and reprecipitation. Here again, the solid cannot be crystallized and elemental analysis does not correspond to a simple stoichiometry between copper and ligand. That extensive decomposition of the complex does not occur in the process of precipitation and solution is evident from the fact that the redissolved material has an absorbance $>96\%$ of that of the original solution. With perchlorate, tetrafluoroborate, nitrate, or fluoride ions present the maximum wavelength of the colored complex was shifted to 505 nm and the color was much less intense (ϵ_{max} 800). The absorbance values were not reproducible and the complex was not stable on dilution. However, by adding chloride to solutions containing $\text{Cu}(\text{ClO}_4)_2$ the color was intensified to its maximum absorbance value. The reaction of CuBr_2 with MIBA gives a purple complex (λ_{max} 485 nm; ϵ_{max} 1300) which is similar to that obtained with CuCl_2 . In the presence of iodide, cyanide, and thiocyanate, the solution decolorizes and a white precipitate is formed.

Based on the ideal solution behavior of CuCl_2 with MIBA and of CuCl with MIBA(SS), Job's method of continuous variations was applied to both systems and the maxima were related to the stoichiometry. The extent of oxidation and reduction was determined in the following way. By subsequently adding CuCl to the reaction mixture prepared by mixing CuCl_2 and MIBA at the optimum absorbance of the colored species, an intensification of absorbance (Table I) was observed which could be quantitatively related to the amount of MIBA(SS) formed in the reaction. Similarly, by subsequently adding MIBA to the reaction mixture prepared by mixing CuCl and MIBA(SS), an intensification of absorbance was also observed (Table II) which could be related to the amount of copper(II) formed in this reaction. Note that the addition of other reagents did not cause an appreciable change in the absorbance.

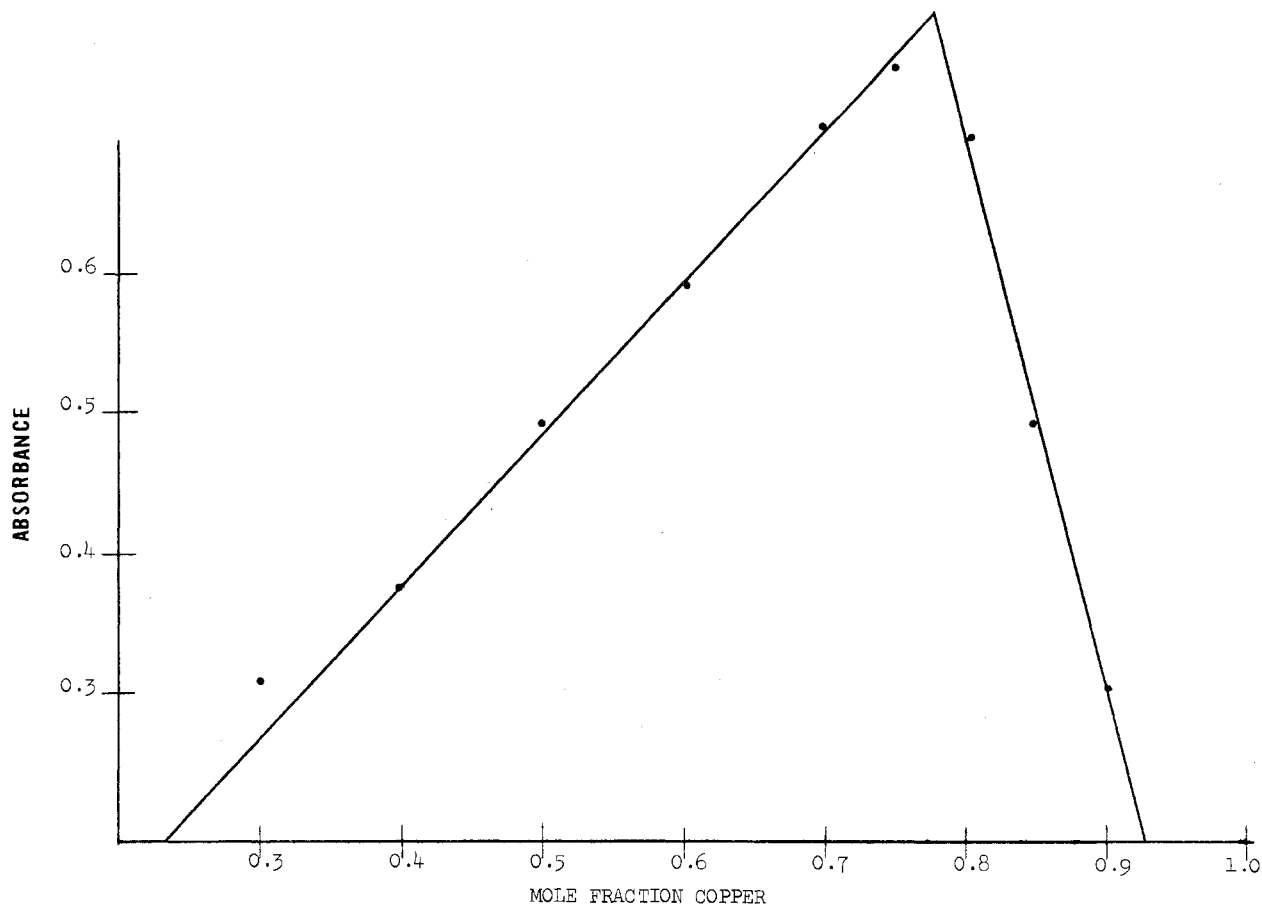


Figure 3. Job's plot for $\text{CuCl} + \text{MIBA}(\text{SS})$ (λ 485 nm).

Table I. Specific Additions to CuCl_2 Plus MIBA Solution (0.44 Mole Fraction Copper) (λ 485 nm)

Added reagent	Absorbance	Added reagent	Absorbance
None	0.68	MIBA	0.70
CuCl_2	0.67	MIBA(RSSR)	0.66
CuCl	1.10		

Table II. Specific Additions to CuCl Plus MIBA(SS) Solution (0.75 Mole Fraction Copper) (λ 485 nm)

Added reagent	Absorbance	Added reagent	Absorbance
None	0.76	MIBA	1.12
CuCl_2	0.76	MIBA(RSSR)	0.81
CuCl	0.82		

Before the stoichiometry of the Cu -MIBA complex is discussed, several additional experiments will be described. The conductivity of the redissolved solid was observed to be very low suggesting that the complex essentially behaves as a nonelectrolyte. However, to ensure that the trace of chloride was not serving simply as the counterion of a complex of high molecular weight, an attempt was made to exchange the chloride for tetrafluoroborate. However, no exchange was observed. The pH of the redissolved solid is 6.9 indicating that the complexed MIBA has no ionizable protons and must be doubly deprotonated in the complex. The infrared spectrum of the sample confirmed the absence of $-\text{SH}$ and $-\text{COOH}$ absorptions. The magnetic susceptibility of the precipitated solid ($\mu_{\text{eff}} = 1.27 \text{ BM}$) shows the copper is probably present in a mixed-valence state.

Therefore, if the trace of chloride is ignored, the assumption can be made that each molecule of the purple complex contains an even number of copper(I) atoms. This is required to balance the doubly deprotonated MIBA and ensure nonelectrolyte

Table III. Predicted Spectral Parameters ($L = \text{MIBA}$)

	$\text{CuCl}_2 + \text{MIBA}$		$\text{CuCl} + \text{MIBA}(\text{SS})$	
	A^a	B^b	C^c	D^d
Obsd	0.40-0.44	56-68	0.75-0.79	39-47
$\text{Cu}_2^{\text{I}}\text{Cu}^{\text{II}}\text{L}_2$	0.43	100	0.80	33
$\text{Cu}_2^{\text{I}}\text{Cu}^{\text{II}}\text{L}_3$	0.44	67	0.77	25
$\text{Cu}_2^{\text{I}}\text{Cu}^{\text{II}}\text{L}_4$	0.45	50	0.75	20
$\text{Cu}_2^{\text{I}}\text{Cu}^{\text{II}}\text{L}_6$	0.47	33	0.73	14
$\text{Cu}_4^{\text{I}}\text{Cu}^{\text{II}}\text{L}_3$	0.42	133	0.82	40
$\text{Cu}_4^{\text{I}}\text{Cu}^{\text{II}}\text{L}_4$	0.43	100	0.80	33
$\text{Cu}_4^{\text{I}}\text{Cu}^{\text{II}}\text{L}_5$	0.44	80	0.78	29
$\text{Cu}_5^{\text{I}}\text{Cu}^{\text{II}}\text{L}_4$	0.41	150	0.83	43
$\text{Cu}_6^{\text{I}}\text{Cu}^{\text{II}}\text{L}_5$	0.42	120	0.81	38
$\text{Cu}_6^{\text{I}}\text{Cu}^{\text{II}}\text{L}_6$	0.43	100	0.80	33
$\text{Cu}_6^{\text{I}}\text{Cu}^{\text{II}}\text{L}_7$	0.43	86	0.79	30

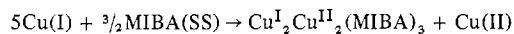
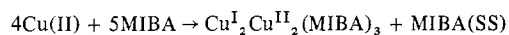
^a Job's plot maximum (mole fraction copper). ^b Percent intensification by CuCl at the maximum. ^c Job's plot maximum (mole fraction copper). ^d Percent intensification by MIBA at the maximum.

behavior. In addition, the magnetic susceptibility data suggest that at least half of the copper in the complex is paramagnetic. Thus, formulations can be ruled out in which copper(I) atoms outnumber copper(II) atoms.

A representative series of hypothetical formulations fulfilling the above requirements is evaluated in Table III in terms of the predicted spectral parameters for Job's plot maximum values (A and C) and intensification values (B and D).

The table shows that of the various formulations $\text{Cu}_2^{\text{I}}\text{Cu}^{\text{II}}(\text{MIBA})_3$ (and its multiples) predicts spectral values in columns A , B , and C closely in agreement with those observed. It is also seen that as the size of the hypothetical unit increases there is no apparent convergence toward any formulation providing a better spectral fit than $\text{Cu}_2^{\text{I}}\text{Cu}^{\text{II}}(\text{MIBA})_3$. Such a product would be formed from copper(II) and MIBA and from copper(I) and MIBA(SS), respectively,

according to



The copper(II):MIBA ratio of 4:5 corresponds to a 0.44 predicted optimum ratio on the copper(II) plus MIBA Job's plot (A), and the copper(I):MIBA(SS) ratio of 10:3 corresponds to a 0.77 predicted optimum ratio on the copper(I) plus MIBA(SS) Job's plot (C). If the 1 mol of MIBA(SS) liberated as the oxidation product in the first reaction is fully converted to colored complex by the addition of excess copper(I), the color intensity should increase 67% corresponding to the formation of an additional 0.67 mol of colored product (B). If the 1 mol of copper(II) formed as oxidation product in the second reaction is converted to colored complex by the addition of excess MIBA, the color intensity should increase 25% in accordance with the formation of 0.25 mol of colored product (D). $\text{Cu}_2\text{Cu}^{\text{II}}_2(\text{MIBA})_3$ thus represents the best fit of the spectral parameters by predicting values which fall within the experimentally observed range in three of the four categories. The one category (D) out of four which does not show agreement between theory and observation involves absorbance intensification of the copper(I) plus MIBA(SS) product. This discrepancy may be resolved if some of the CuCl reactant has been oxidized prior to the formation of the purple complex. The reaction between CuCl and MIBA(SS) was slow because of the limited solubility of both MIBA(SS) and CuCl in aqueous solution. Therefore, a small amount of atmospheric oxidation could have taken place under the conditions of the reaction. Additionally, there was a trace of a copper(II) impurity in the CuCl. The preceding assumption is consistent with the observed extinction coefficient of the solution corresponding to the optimum point on the copper(I) plus MIBA(SS) Job's plot. The extinction coefficient of this solution was predicted to be 1200 and was expected to increase to the full 1500 value upon addition of excess MIBA. In actuality, the optimum solution only had an ϵ_{max} of 1000 but it increased to the expected value of 1500 in the presence of excess MIBA. This suggests that there was sufficient copper present to lead ultimately to full color development, but there was insufficient copper(I) to yield the predicted absorbance with MIBA(SS). The predicted Job's plot optimum value (C) is still within the experimentally observed range if calculated on the basis of the proposed prior oxidation of less than 10% of the CuCl. The precipitated complex contains water and the stoichiometry $\text{Cu}_2\text{Cu}^{\text{II}}_2(\text{MIBA})_3 \cdot 4\text{H}_2\text{O}$ approximates the analytical data obtained for the solid species except that it does not account for the presence of small quantities of chloride. An experimental molecular weight of 790 in H_2O is rather close to the predicted value of 680.

Returning to the penicillamine system, we suggest that the observed complications are primarily due to polymerization, to the inhibition of the reaction by penicillamine disulfide, and to the unusual role of chloride (and bromide) which is still unexplained.

Acknowledgment. We wish to thank the NSF for support of this research.

Registry No. Penicillamine, 52-67-5; MIBA, 4695-31-2; MIBA(SS), 4695-30-1; Cu, 7440-50-8.

References and Notes

- I. M. Klotz, G. H. Czerlinski, and H. A. Fiess, *J. Am. Chem. Soc.*, **80**, 2920 (1958).
- B. G. Malmstrom in "Oxidases and Related Redox Systems", Vol. 1, T. E. King, Ed., Wiley, New York, N.Y., 1965, p 207.
- G. Morpurgo and R. J. P. Williams in "Physiology and Biochemistry of Hemocyanins", F. Ghirelli, Ed., Academic Press, New York, N.Y., 1968, p 113.

- L. Morpurgo, G. Rotilio, A. Finazzi-Agro, and B. Mondavi, *Arch. Biochem. Biophys.*, **161**, 291 (1974).
- M. T. Graziani, A. Finazzi-Agro, G. Rotilio, D. Barra, and B. Mondavi, *Biochemistry*, **13**, 804 (1974).
- J. M. Walshe, *Q. J. Med.*, **22**, 483 (1953).
- J. M. Walshe in "Biochemistry of Copper", J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N.Y., 1966, p 475.
- T. Otterson, L. G. Warner, and K. Seff, *Inorg. Chem.*, **13**, 1904 (1974).
- J. A. Thich, F. Mastropaolo, J. Potenza, and H. J. Schugar, *J. Am. Chem. Soc.*, **96**, 726 (1974).
- E. J. Kuchinkas and Y. Rosen, *Arch. Biochem. Biophys.*, **97**, 370 (1962).
- W. E. Blumberg and J. Peisach, *J. Chem. Phys.*, **49**, 1793 (1968).
- J. Peisach and W. E. Blumberg, *Mol. Pharmacol.*, **5**, 200 (1969).
- Y. Sugiura and H. Tanaka, *Chem. Pharm. Bull.*, **18**, 368 (1970).
- E. W. Wilson and R. B. Martin, *Arch. Biochem. Biophys.*, **142**, 445 (1971).
- E. Billmann, *Justus Liebigs Ann. Chem.*, **348**, 120 (1906).
- P. Hemmerich in "The Biochemistry of Copper", J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N.Y., 1966, p 15.

Contribution from the Department of Chemistry,
Washington State University, Pullman, Washington 99163

Interconversion Reactions between Substituted Phosphinous Acid-Phosphinito Complexes of Platinum(II) and Their Capping Reactions with Boron Trifluoride-Diethyl Etherate

William B. Beaulieu, Thomas B. Rauchfuss,
and D. Max Roundhill*

Received January 2, 1975

AIC50008B

Recently a number of workers have prepared transition metal complexes of substituted phosphinites and secondary phosphites. The ligands, however, tend to be hydrolytically unstable and the complex obtained contains the coordinated resulting acid and its conjugate base. In earlier work we had found that alkyl diphenylphosphinite complexes of platinum would undergo hydrolysis to give complexes containing co-ordinated diphenylphosphinous acid and diphenylphosphinite¹ groups.^{2,3} From the hydrolysis of $\text{Pt}(\text{ROPPH}_2)_4$ [$\text{R} = \text{Me}$, $n\text{-Bu}$] the three complexes $\text{PtH}(\text{OPPh}_2)(\text{HOPPh}_2)(n\text{-BuOPPh}_2)$, $\text{PtH}(\text{OPPh}_2)(\text{HOPPh}_2)_2$, and $\text{Pt}(\text{OPPh}_2)_2(\text{HOPPh}_2)_2$ were obtained. In a separate study Dixon et al. prepared $\text{Pt}(\text{OPPh}_2)_2(\text{HOPPh}_2)_2$ by treating $\text{PtCl}(\text{OPPh}_2)(\text{HOPPh}_2)_2$ with AgOPPh_2 .⁴ Dixon postulated that the hydrogen atoms on the diphenylphosphinous acid groups were symmetrically H bonded between the diphenylphosphinito and diphenylphosphinous acid moieties. This idea was implicitly understood in our second publication,² and more recently a communication on the single-crystal X-ray structure determination of the compound $\text{Pd}_2(\text{SCN})_2[(\text{OPPh}_2)_2\text{H}]_2$ ⁵ has given further credence to this claim. This bifunctional hydrogen-bonded ligand structurally resembles the anion in $[\text{PtH}(\text{PPH}_3)_3](\text{CF}_3\text{CO}_2)_2\text{H}$.⁶

The hydrolysis of chlorodiphenylphosphine,⁷ trialkyl phosphite,^{8,9} or alkyl diphenylphosphinite^{1,2} complexes of platinum leads to phosphorus-bonded complexes of this hydrogen-bonded six-membered ring system. Since these phosphorus compounds undergo more facile hydrolysis when they are not coordinated to a transition metal,¹⁰ it appears likely that these synthetic routes involve the acid as the reactive species.⁹ A recent communication has indicated that the salts of these acids are not widely recognized as ligands,¹¹ but in this note we will present compelling evidence that the formation of diphenylphosphinous acid-diphenylphosphinito complexes of Pt^{II} by the hydrolysis route involves the intermediacy of diphenylphosphinous acid as the reactant.