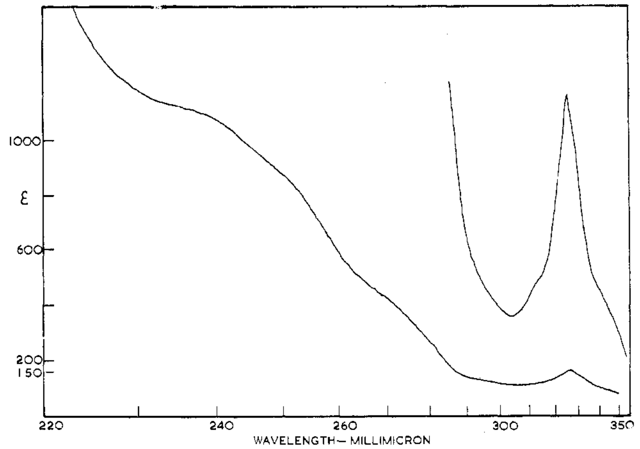

Figure 9.—Ultraviolet spectrum of chromium(II) acetate monohydrate in 95% ethanol. The band system at 326 mμ is also recorded at a higher concentration.

fold to higher energies). The counterpart of band II would certainly be obscured by the more intense $^1A \rightarrow {}^1W$ transitions while the corresponding band III of chromous acetate is believed to be the strong absorption wing which extends through the ultraviolet region. An interesting feature of the chromium(II) acetate spectrum is the presence of a relatively sharp peak at ~30,700 cm^{-1} which appears to sit on a broader band. This may be an n(s,p) excitation to the "nonbonding $d_{xz,yz}$[11] orbitals" or possibly one of the components of $np_\pi \rightarrow (xy)$. Alternatively it may be a d–d type of intraconfigurational transition corresponding to a quintet → singlet excitation in the monomer. Several states arising from the free ion term ^1I have essentially the same configuration as the ground quintet of the monomer. The observed intensity appears to be too large for this assignment.

Experimental Section

Methods of preparing amine- and chloro-substituted derivatives of copper acetate have been described in the literature.[35,36] The electronic spectra were recorded on a Beckman DK-2 diffuse-reflectance and a Shimadzu Seisakusho spectrophotometer. Extinction coefficients were always based on monomeric formula weights. Magnetic measurements on the pyridine derivatives were made by the Gouy-tube method, in the temperature range 90–340°K. The observed $\chi_M(T)$ curves closely resembled those of copper butyrate and copper dicarboxylate pyridine derivatives.[23,25]

Acknowledgments.—L. D. acknowledges the award of a CSIRO senior postgraduate studentship. We thank Dr. R. Robson for drawing our attention to the π-streamer representation shown in Figure 6.

---

(35) R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2960 (1959).

(36) S. Yamada, H. Nishikawa, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 1278 (1960).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CORNELL UNIVERSITY, ITHACA, NEW YORK

Mixed Complexes of Copper(I) Cyanides(1)

BY DEREK COOPER AND ROBERT A. PLANE

Received July 18, 1966

The mixed ligand complexes Cu(phen)CN, Cu(bipy)CN, $Cu(P(C_6H_5)_3)_2CN$, and $Cu(As(C_6H_5)_3)_2CN$ have been prepared. Unlike the compounds $CuCN \cdot NR_1R_2R_3$, these compounds are stable toward oxidation and loss of the other ligands. The compounds appear to have a polymeric structure possibly involving N–Cu bridging of the cyanide ligand and apparently owe their stability to both this structure and some π bonding.

Mixed ligand complexes are currently of interest because of the possibility of observing mutual modifications of the bonding of the individual ligands. Although mixed cyanide–halide complexes of both gold(III)[2] and platinum(II)[3] have been reported, an investigation of complex copper(I) cyanide ions in aqueous solution has shown that mixed ligand complexes are not formed with halide ions as potential ligands.[4] The reaction of solid cuprous cyanide with aqueous halide ions also produced the tricyanocuprate(I) ion, $Cu(CN)_3^{2-}$, and not the mixed ligand complex.[4] The reaction of copper(I) cyanide with amines and with methyl iodide has been reported in the early literature[5,6] to produce addition compounds of the type $CuCN \cdot RNH_2$ or $CuCN \cdot CH_3I$, which readily lose the addend at reduced pressure or on heating and which are readily oxidized in air. Although structures of most of these compounds are not known, the compound $CuCN \cdot NH_3$ has recently been studied by X-ray analysis.[7] This compound was found to consist of layers of bridged copper cyanide molecules with ammonia molecules between the layers; the ammonia was however lost on standing for 3 days.

As the ions $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ are known to

---

(1) This work was supported by Grant GP2643 from the National Science Foundation.

(2) L. H. Jones, *Inorg. Chem.*, **3**, 1581 (1964).

(3) L. H. Jones and J. M. Smith, *ibid.*, **4**, 1677 (1965).

(4) D. Cooper and R. A. Plane, *ibid.*, **5**, 16 (1966).

(5) E. G. J. Hartley, *J. Chem. Soc.*, 780 (1928).

(6) W. Peters, *Z. Anorg. Allgem. Chem.*, **89**, 191 (1914).

(7) D. T. Cromer, A. C. Larson, and R. B. Roof, Jr., *Acta Cryst.*, **19**, 192 (1965).

stabilize copper(I) with respect to oxidation[8] and as the cyanide ion is generally recognized as being capable of π-bond formation, it seemed reasonable to attempt to prepare mixed cyano complexes using other potential ligands which were capable of π bonding. We report here an investigation using triphenylphosphine, triphenylarsine, 1,10-phenanthroline, and α,α'-bipyridine as the potential ligands for mixed complex formation with copper(I) cyanide.

Experimental Section

Copper(I) cyanide was prepared by the method of Barber[9] and dried under vacuum over anhydrous magnesium sulfate. α,α'-Bipyridine, 1,10-phenanthroline, triphenylphosphine, and triphenylarsine were used as supplied by the Eastman Kodak Co. Bis(1,10-phenanthroline)copper(I) perchlorate and bis(α,α'-bipyridine)copper(I) perchlorate were prepared according to the method described by Schilt and Taylor.[10]

Preparation of 1,10-Phenanthrolinecopper(I) Cyanide.—Finely ground, freshly prepared copper(I) cyanide (0.5 mmole) was added to a solution of 1,10-phenanthroline (3.0 mmoles) in dry methanol (200 ml) under nitrogen and stirred vigorously for 3 days. The volume was reduced by approximately half under vacuum and the product, 1,10-phenanthrolinecopper(I) cyanide, was filtered off, washed copiously with methanol, and dried in a vacuum desiccator (0.03 mmole, 60%). Uncomplexed copper(I) cyanide which is occasionally present can be detected by the C–N vibrational frequency at 2060 cm^{-1} in the infrared and can be removed by grinding the product to a fine powder and further stirring in a solution of 1,10-phenanthroline in methanol. *Anal.* Calcd for $C_{12}H_8N_2CuCN$: C, 57.89; H, 2.99; N, 15.57. Found: C, 57.73; H, 2.92; N, 15.46.

Preparation of α,α'-Bipyridinecopper(I) Cyanide.—α,α'-Bipyridinecopper(I) cyanide was prepared in a manner analogous to that of 1,10-phenanthrolinecopper(I) cyanide. *Anal.* Calcd for $C_{10}H_8N_2CuCN$: C, 53.76; H, 3.28; N, 17.10. Found: C, 52.84; H, 3.26; N, 17.05.

Preparation of Bis(triphenylphosphine)copper(I) Cyanide.—Freshly prepared copper(I) cyanide (0.2 mmole) and triphenylphosphine (10.0 mmoles) were heated in a sealed tube *in vacuo* to 150° for 8 hr. The tube was opened on cooling and the remaining glassy compound was vigorously stirred with acetone (in the tube) until the glassy compound had disappeared. The mixture was filtered and the fine white precipitate of bis(triphenylphosphine)copper(I) cyanide was copiously washed with acetone and dried in a vacuum desiccator (0.14 mmole, 70%), mp 182.5–183.5°. *Anal.* Calcd for $(C_{18}H_{15}P)_2CuCN$: C, 72.36; H, 4.92; N, 2.28. Found: C, 72.43; H, 4.91; N, 2.24.

If the preparation is carried out in air, heating for an extended period leads to the formation of impurities of a cyanato complex (identified as such by infrared spectroscopy).

Preparation of Bis(triphenylarsine)copper(I) Cyanide.—This compound was prepared in a manner analogous to that of bis(triphenylphosphine)copper(I) cyanide, mp 179–181°. Infrared spectra of the original preparation showed the presence of unreacted CuCN. The product was subsequently recombined with excess triphenylarsine twice, after which the spectrum showed no uncombined CuCN. However, the final analysis indicates some 2 mole % CuCN. *Anal.* Calcd for $(C_{18}H_{15}As)_2CuCN$: C, 63.30; H, 4.30; N, 2.00. Found: C, 62.01; H, 4.19; N, 2.33.

Attempts were made to prepare the triphenylstibine analog of these compounds using the same technique. Although the copper(I) cyanide did dissolve in a gross excess of triphenylstibine, uncomplexed copper(I) cyanide was always detected in the product.

Visible and ultraviolet spectra were recorded on a Bausch and Lomb 505 recording spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 521 grating spectrometer using pressed potassium iodide pellets and solutions in 2-aminoethanol. For solution spectra, only the frequencies in the C–N region (2000–2200 cm^{-1}) were recorded. Molecular weights were determined cryoscopically in 2-aminoethanol.

Results

The reaction of finely divided, freshly precipitated copper(I) cyanide with methanolic solutions of 1,10-phenanthroline or α,α'-bipyridine (written as L-L when the two bidentate ligands are not distinguished) under nitrogen resulted in the formation of a brown compound of empirical formula Cu(L-L)CN. The reaction of solid copper(I) cyanide with a gross excess (100-fold) of either triphenylphosphine or triphenylarsine in a sealed tube *in vacuo* at *ca.* 120° led to the formation of the white compounds CuL_2CN (L is triphenylphosphine or triphenylarsine where the two are not distinguished). When the preparation was attempted using triphenylstibine, copper(I) cyanide was found to dissolve in a sufficient excess of the molten ligand, but on precipitation the product was found to be at least half uncomplexed copper(I) cyanide. This reaction was not further investigated. Preparations initially carried out open to the air led to the formation of cyanato compounds as impurities; these were not further investigated.

Possible structures for these compounds consistent with the analyses are the simple monomeric form Cu(L-L)CN, an ionic form $Cu(L\text{-}L)_2^+Cu(CN)_2^-$, structures involving cyanide bridging, and, for the heterocyclic ligands, structures involving bridging of the bidentate ligands. The latter case seems unlikely for steric reasons and this structure is not further considered.

Of the remaining structures, the ionic form can be discounted in the case of the heterocyclic ligands by comparison with the analogous perchlorates $Cu(L\text{-}L)_2ClO_4$. The perchlorate complexes exhibit absorption bands at 242, 261, 293, and 435 mμ for $Cu(bipy)_2^+$ and 223, 241 (sh), 267, 285 (sh) and 435 mμ for $Cu(phen)_2^+$ (sh = shoulder), whereas the cyanide complexes have bands at 234, 241 (sh), 254 (sh), 261 (sh), 291, and 303 (sh) mμ, for Cu(bipy)CN, and at 231, 241 (sh), 254 (sh), 261 (sh), 284, and 303 (sh) mμ for Cu(phen)CN.

This spectral difference is taken to indicate the absence of the ion $Cu(L\text{-}L)_2^+$ from solutions of the cyano complexes. Unfortunately the same approach could not be used for the phosphine and arsine complexes but consideration of the infrared spectra suggests that the ionic form, $CuL_4^+Cu(CN)_2^-$, is unlikely. The compound $KCu(CN)_2$ has been prepared and exhibits two well-distinguished infrared cyanide stretching frequencies at 2085 and 2105 cm^{-1}. Both frequencies are infrared active because the ion $Cu(CN)_2^-$ is nonlinear, as shown by X-ray analysis.[11] It is reasonable therefore to expect two infrared-active C–N frequencies for the ionic form under discussion (unless, in this case, the ion should become linear). In fact,

---

[8] D. Cooper and R. A. Plane, *Inorg. Chem.*, **5**, 1677 (1966).

[9] H. J. Barber, *J. Chem. Soc.*, 125 (1924).

[10] A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

[11] D. T. Cromer, *J. Phys. Chem.*, **61**, 1388 (1959).

only one CN stretching frequency was observed for each complex at 2105 and at 2125 cm^{-1} for $Cu(P(C_6H_5)_3)_2CN$ and $Cu(As(C_6H_5)_3)_2CN$, respectively. Although the presence of the ion $Cu(CN)_2^-$ cannot be rigorously excluded, this observation, along with comparison with the heterocyclic compounds, suggests that this ion is not present.

Consideration of the infrared spectra of the solid state and of solutions of these complexes is helpful in discussing the monomeric and polymeric structures which are possible for these compounds. The complexes all showed a lowering of the C–N stretching frequency on going from the solid to solution. Data are given in Table I. Bridging of a $C\equiv N$ group *via* the nitrogen is expected to lead to an increase in the $C\equiv N$ frequency.[12] Although this is not always the case (as for example in $KCu(CN)_2$[13]), the converse is that an increased $C\equiv N$ frequency almost certainly indicates bridging of the CN. It is therefore suggested that there is some degree of bridging in the solid state, presumably by interaction of the nitrogen with an adjacent copper atom. Molecular weight determinations for the complexes Cu(L-L)CN in 2-aminoethanol indicate a monomeric structure in solution, but values for the complexes CuL_2CN could not be obtained because of the lower solubilities of these compounds.

TABLE I

INFRARED $C\equiv N$ FREQUENCIES, CM^{-1}

Compound	Solid	Soln[a]
Cu(bipy)CN	2100	2090
Cu(phen)CN	2105	2085
$Cu(As(C_6H_5)_3)_2CN$	2125	2095
$Cu(P(C_6H_5)_3)_2CN$	2105	2080

[a] Solutions in 2-aminoethanol.

In order to investigate the relative stability of the mixed complexes toward air oxidation in solution, the following experiments were done. Copper(I) cyanide was treated with methanolic solutions of 2-aminoethanol or α,α'-bipyridineamine, and oxidation of the copper(I) was seen to occur within a few seconds and deep blue solutions were obtained. When, however, copper(I) cyanide was treated with methanolic solutions of α,α'-bipyridine–2-aminoethanol or α,α'-bipyridine–2-aminoethanol–α,α'-bipyridineamine, a yellow-brown solution of the copper(I) complex was obtained which was stable toward oxidation. The same results were obtained when *o*-phenanthroline was substituted for α,α'-bipyridine. This evidence was taken to indicate that α,α'-bipyridine and *o*-phenanthroline stabilize the copper(I) cyanide more than the copper(II) state in solution, whereas α,α'-bipyridineamine and 2-aminoethanol stabilize the Cu(II) more than the Cu(I) in solution.

Discussion

The structures suggested for the complexes described in this work differ from those reported for similar compounds of copper(I) which do not contain the cyanide ligand. For example, compounds of empirical formulas CuSCN·phen and CuSCN·bipy have been shown by spectrophotometric measurements in nitrobenzene to contain the ion $Cu(L\text{-}L)_2^+$ by comparison with $Cu(phen)_2ClO_4$ and $Cu(bipy)_2ClO_4$.[14] In the thiocyanato complexes the nitrogen atoms are expected to be bound to the copper atom[15] and only the more weakly binding sulfur atoms are available for contributing to a polymeric structure. In the cyanide complexes the nitrogen atoms are by comparison eminently situated for this form of intermolecular bridging. Compounds prepared from copper(I) halides and tertiary phosphine[16–18] or arsine[16,19] ligands (L) are of the type $(CuLX)_4$, $(CuL_4)(CuX_2)$, CuL_3X, and CuL_2NO_3. In all but the last case, CuL_2NO_3, the copper atom is four-coordinated. For CuL_2NO_3 it was not possible to distinguish bidentate and monodentate nitrate coordination.[19] The results presented here suggest that for the compounds CuL_2CN and Cu(L-L)CN, four-coordination is maintained by the bridging of the nitrogen atom with an adjacent copper atom. It appears therefore that N–Cu bonding may be important in determining the structures of these compounds. The compounds were prepared in an attempt to stabilize a copper(I) cyanide mixed complex by means of other π-acceptor ligands. It is pertinent to inquire if there is any positive indication of π bonding.

The infrared spectra of complexes of transition metal ions with both 1,10-phenanthroline and α,α'-bipyridine have been the subject of previous examinations.[10,20] Whereas characteristic changes occur in the spectrum of the organic molecule on complex formation, the shifts offer no correlation with the properties of the metal atom. Even the region of the spectrum below 500 cm^{-1} which is associated with skeletal bending modes and metal–nitrogen vibrations and which would be expected to show the greatest variation with the metal ion does not show any ordered change from metal to metal. The spectra of the mixed cyano complexes, Cu(L-L)CN, are similar to those of the nonmixed compounds $Cu(L\text{-}L)_2ClO_4$. Where differences occur, the lines in the cyano complexes are generally closer to those of the uncomplexed ligand than are those of the nonmixed complexes. For example, the strong line at 1580 cm^{-1} (skeletal stretch) of bipyridyl is at 1588 cm^{-1} in CuCN(bipy) and 1598 cm^{-1} in $Cu(bipy)_2ClO_4$; the 1268-cm^{-1} line (C–H in-plane bend) of bipyridyl is at 1274 cm^{-1} in CuCN(bipy) and 1280 cm^{-1} in $Cu(bipy)_2ClO_4$. Similarly the skeletal stretching vibration of phenanthroline at 1560 cm^{-1} is at 1564 cm^{-1} in CuCN(phen) and 1576

---

(12) R. D. Gillard, *J. Inorg. Nucl. Chem.*, **21**, 1321 (1965).

(13) V. Lorenzelli and F. Gasmunco, *Atti. Accad. Nazl. Lincei, Rend., Classe. Sci. Fis., Mat. Nat.*, **35**, 524 (1963).

(14) C. M. Harris, private communication, quoted by W. W. Brandt, F. P. Dwyer, and E. C. Gyarfar, *Chem. Rev.*, **54**, 959 (1954).

(15) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 173.

(16) F. G. Mann, D. Purdie, and A. F. Wells, *J. Chem. Soc.*, 1505 (1936).

(17) G. Costa, G. Pellizer, and F. Rubessa, *J. Inorg. Nucl. Chem.*, **26**, 961 (1964).

(18) F. A. Cotton and D. M. L. Goodgame, *J. Chem. Soc.*, 5267 (1960).

(19) R. S. Nyholm, *ibid.*, 1257 (1952).

(20) R. G. Inskeep, *J. Inorg. Nucl. Chem.*, **24**, 763 (1962).

cm^{-1} in $Cu(phen)_2ClO_4$. Our assignments follow those made previously for zinc(II) and mercury(II) complexes.[21] Changes in the infrared absorption spectra of iron complexes of phenanthroline and bipyridine have been cited as evidence in support of the postulation of enhanced π-bond formation,[20] but changes of similar magnitude are not observed for similar complexes with other metals. The changes in the infrared spectra are evidently not sufficient for the discussion of structures involving π bonding.

For the mixed complexes with triphenylphosphine and triphenylarsine, CuL_2CN, comparison of the infrared spectra of the complexes with those of the uncomplexed ligand clearly indicate coordination. Most of the vibrations associated with the aromatic rings are expected to occur in the same region irrespective of the substituent, but new lines occur at 1710 and 1715 cm^{-1} for $Cu(P(C_6H_5)_3)_2CN$ and $Cu(As(C_6H_5)_3)_2CN$, respectively. The prominent lines at 1090 and 1075 cm^{-1} in $P(C_6H_5)_3$ and $As(C_6H_5)_3$ also show a marked increase in intensity relative to the neighboring lines for the complexes $Cu(P(C_6H_5)_3)_2CN$ and $Cu(As(C_6H_5)_3)_2CN$. The lines which show the most prominent shifts on coordination are those associated with carbon–phosphorus and carbon–arsenic vibrations. In both cases the 690-cm^{-1} peak is shifted to 700 cm^{-1}, and the lines at 425 cm^{-1} ($P(C_6H_5)_3$) and 475 cm^{-1} ($As(C_6H_5)_3$) show an increase of 5–7 cm^{-1} on complex formation. The lines at 415 and 370 cm^{-1} ($P(C_6H_5)_3$) and 465 and 308 cm^{-1} ($As(C_6H_5)_3$) also show shifts of the same order. In view of the similarity of the spectra of triphenylphosphine and triphenylarsine, it is not surprising that the mixed complexes show only small changes.

Thus, the spectral evidence does not give direct evidence for either the presence or absence of significant metal–ligand bonding. Furthermore, the observation that the solid structures formed involve CN bridging of Cu atoms could indicate that the stability of these complexes is due solely to this stabilization and not to π bonding. However, the solution experiments must not be overlooked. It was shown that in methanol the ligands α,α'-bipyridine and *o*-phenanthroline stabilize Cu(I) more than Cu(II) while N-donor ligands having less π-bonding capability (α,α'-bipyridineamine, 2-aminoethanol, ethylenediamine,[8] and ammonia[8]) stabilize Cu(II) more than Cu(I). Apparently, π bonding does indeed play a role in stabilizing the mixed complexes of Cu(I). That this should be the case is consistent with the discussion of Kida concerning the importance of π bonding on mixed complex formation.[22] He notes, for example, that $Co(CN)_4(bipy)^-$ exists while $Co(CN)_4(en)^-$ is not known.

---

[21] K. Krishnan and R. A. Plane, unpublished work.

[22] S. Kida, *Bull. Chem. Soc. Japan*, **34**, 962 (1961).

Contribution from the Department of Chemistry, University of California,
Berkeley, California 94720, and William Ramsay and Ralph Forster
Laboratories, University College, London, W.C.1, England

Metal Complexes of Unsaturated Tertiary Phosphines and Arsines. III. Group VI Metal–Olefin Complexes. An Unusual Metal-Catalyzed Olefin Isomerization[1,2]

By L. V. Interrante, M. A. Bennett, and R. S. Nyholm

Received July 2, 1966

The preparation of a new chelating ligand, 2-allylphenyldiphenylphosphine (AP), and its application to the synthesis of the first monoolefin complexes of all three zerovalent group VI metals are described. The molecular formula of these complexes [$C_{21}H_{19}PM(CO)_4$; M = Cr, Mo, W] and their infrared spectra are consistent with coordination of both the phosphorus atom and a C=C bond to the group VI metal. However, nmr results show that the position of the C=C bond has been shifted upon coordination of the olefin to the metal and that the ligand in these complexes is the isomeric compound, 2-propenylphenyldiphenylphosphine. Moreover, by independent synthesis of both the *cis* and *trans* forms of this propenyl ligand and their corresponding group VI metal complexes it has been possible to show further that the coordinated olefin has the *cis* configuration. This isomerization of AP to the higher energy isomer of 2-propenylphenyldiphenylphosphine is discussed in light of previous transition metal catalyzed olefin isomerizations. The lowering in the C=C stretching frequency upon coordination of 2-*cis*-propenylphenyldiphenylphosphine to the zerovalent group VI metals is determined from infrared spectral measurements and is used to assess the degree of interaction between olefin and metal in these complexes.

Introduction

Recently, we reported the preparation of monoolefin complexes of all three zerovalent group VI metals.[3] The olefinic ligand used in this preparation was the new compound 2-allylphenyldiphenylphosphine (AP). At that time preliminary nmr results in-

---

[1] Presented in part at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[2] Part II: M. A. Bennett, G. J. Erskine, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, in press.

[3] M. A. Bennett, L. V. Interrante, and R. S. Nyholm, *Z. Naturforsch.*, **20b**, 633 (1965).