Cationic Copper(I) Isocyanide Complexes, [Cu(CNR)$_4$]$^+$ (R = CH$_3$, C(CH$_3$)$_3$ and 2,6-(CH$_3$)$_2$C$_6$H$_3$): Preparations, Spectroscopic Properties and Reactions with Neutral Ligands. A Comparison of the Vibrational Spectra of [Cu(CNCH$_3$)$_4$]$^+$, [Cu(NCCH$_3$)$_4$]$^+$ and [Cu(NCCD$_3$)$_4$]$^+$

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Abstract

The copper(I) isocyanide complexes [Cu(CNR)$_4$]X (R = Me, CMe$_3$, or xylyl; X = PF$_6^-$ or ClO$_4^-$) have been prepared and characterized using IR, Raman and ^{1}H NMR spectroscopy. Subsequent reactions with neutral chelating ligands have afforded the pseudotetrahedral complexes [Cu(CNMe)$_2$(bipy)]PF$_6$, [Cu(CN-t-Bu)$_2$L$_2$]PF$_6$ (L$_2$ = bipy, phen, DAB, or dppe) and [Cu(CNxylyl)$_2$(2,9-Me$_2$phen)]·PF$_6$, (bipy = 2,2'-bipyridyl, phen = 1,10-phenanthroline, DAB = N,N'-di-tert-butylethylenediimine, and dppe = 1,2-bis(diphenylphosphino)ethane). A detailed study of the vibrational spectra of the related species [Cu(CNMe)$_4$]ClO$_4$, [Cu(NCMe)$_4$]ClO$_4$ and [Cu(NCCD$_3$)$_4$]ClO$_4$ has also been carried out and assignments proposed. The acetonitrile ligands of [Cu(NCMe)$_4$]ClO$_4$ are easily replaced by other Group V donor ligands, the complexes [CuL$_4$]ClO$_4$ (L = PPh$_3$, As Ph$_3$, or SbPh$_3$) having been isolated.

Introduction

The first tetrakis(aryl isocyanide)copper(I) cations, [Cu(CNR)$_4$]$^+$ (R = Ph and *p*-MeC$_6$H$_4$), isolated as their chlorides, were reported in 1952 [1] and since then other alkyl [2] and aryl [2–4] analogues have been described. A few [Cu(CNR)$_4$]$^+$ cations involving unsaturated isocyanides (R = allyl, vinyl, allenyl, or propargyl) are also known [2, 5]. Almost all of these cations have been isolated as their perchlorate or tetrafluoroborate salts. Apart from a detailed study of the ^{13}C NMR spectra of some of the above cations [2, 6], the only other spectroscopic information that is generally available on these compounds is their IR

active ν(C≡N) stretching frequencies. The lone tetrakis(isocyanide)copper(I) complex to have been structurally characterized is [Cu(CNMe)$_4$]BF$_4$ in which tetrahedral coordination around the copper is achieved by four almost linear methyl isocyanide ligands [7].

In contrast to the quite wide range of copper(I) isocyanide complexes of the general type Cu(CNR)$_n$X, where X is a coordinated anion (*e.g.* halide, cyanide, acetylacetonate, phenylacetylide, phenoxide, t-butoxide, carboxylate or η^5-cyclopentadienyl) and n = 1–3 depending on the nature of the anionic ligands and their number, very few copper(I) isocyanide complexes containing other neutral ligands have been reported. Bailey and Mays [4] have isolated the cations [Cu(CNEt)(PPh$_3$)$_3$]$^+$, [Cu(CNC$_6$H$_4$-*p*-OMe)(PPh$_3$)(phen)]$^+$ and [Cu(CNC$_6$H$_4$-*p*-OMe)$_2$L$_2$]$^+$ (L$_2$ = 2PPh$_3$, dppe, or bipy) as their hexafluorophosphate salts and more recently [Cu(CNC$_6$H$_{11}$)$_2$L$_2$]BPh$_4$ (L$_2$ = en or tmen) have been reported [8]. However, none of these complexes have been prepared by direct substitution reactions of [Cu(CNR)$_4$]$^+$ cations, but rather by the reactions of copper(I) halide complexes with isocyanides or the abstraction of halide from CuX(CNR)$_2$ complexes (X = Cl or Br) using AgPF$_6$ in the presence of other neutral ligands.

In view of this rather limited amount of information on these cationic isocyanide species, we have prepared three [Cu(CNR)$_4$]$^+$ salts and studied some representative reactions with a number of bidentate chelating ligands. We have also examined the vibrational spectra of [Cu(CNMe)$_4$]ClO$_4$, [Cu(NCMe)$_4$]ClO$_4$ and [Cu(NCCD$_3$)$_4$]ClO$_4$. Since it is known [7] that the structure of [Cu(CNMe)$_4$]BF$_4$ is very similar to that of [Cu(NCMe)$_4$]ClO$_4$ [9], the bond distances and angles in the two cations showing no significant differences, it was expected that closely related vibrational spectra would be found. In order to aid assign-

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ments, the acetonitrile-d_3 complex was also prepared and its IR and Raman spectra recorded.

Experimental

Starting Materials

Methyl isocyanide [10], tert-butyl isocyanide [11] and N,N'-di-tert-butylethylenediimine [12] were prepared according to standard literature procedures. All other neutral ligands, including 2,6-dimethylphenyl isocyanide, were obtained from commercial sources.

Reaction Procedures

All reactions involving compounds of the type $[Cu(NCMe)_4]X$ ($X = ClO_4^-$ or PF_6^-) or $[Cu(CNR)_4]X$ ($R = Me$, CMe_3, or xylyl) were carried out in an atmosphere of nitrogen and all solvents were dried over molecular sieves and deoxygenated by purging with nitrogen gas prior to use.

In those cases where complexes were prepared by very similar procedures, only details of representative recipes will be given.

A. Preparation of copper(I)–acetonitrile and –isocyanide Complexes

(i) $[Cu(NCMe)_4]X$ ($X = ClO_4^-$ and PF_6^-)

The white crystalline complexes $[Cu(NCMe)_4]X$ were prepared by standard literature procedures [13–15]. The samples were recrystallized from a chloroform–ethanol mixture (1:2), washed with diethyl ether and dried in vacuo before further use. Anal. (for the perchlorate): Calcd. for $C_8H_{12}ClCuN_4O_4$: C, 29.37; H, 3.70; Cu, 19.4. Found: C, 29.49; H, 3.75; Cu, 19.3.

The complex $[Cu(NCCD_3)_4]ClO_4$ was prepared in an identical manner using copper(I) oxide (0.30 g, 0.21 mmol) in 5 ml of acetonitrile-d_3 and 5 ml of 2 M aqueous perchloric acid.

(ii) $[Cu(CNMe)_4]ClO_4$

The reaction between a quantity of $[Cu(NCMe)_4]$-ClO_4 (1.0 g, 3.056 mmol) and methyl isocyanide (1.47 g, 35.8 mmol) in stirred methanol (25 ml) was carried out for 5 h in a stoppered flask at room temperature. The solution was filtered to remove colourless crystals which were washed with diethyl ether and petroleum ether. The product was recrystallized from a dichloromethane–diethyl ether mixture (1:2), and the colourless needles obtained were washed with diethyl ether and dried in vacuo; yield 0.85 g (85%). Anal. Calcd. for $C_8H_{12}ClCuN_4O_4$: C, 29.37; H, 3.70. Found: C, 29.03; H, 4.21.

The product $[Cu(CNMe)_4]ClO_4$ is stable with respect to oxidation and decomposition in light and air at ambient temperature, and is slightly soluble

in polar solvents, such as $CHCl_3$, CH_2Cl_2, MeCN, Me_2CO, MeOH, and EtOH. The spectroscopic properties of this complex are as follows: ^1H NMR (in $CHCl_3$-d_1) δ 3.35 (s, CH_3NC). IR spectrum: Nujol mull $\nu(C\equiv N)$ 2212(s) and 2181(sh) cm^{-1} (2210(s) cm^{-1} in CH_2Cl_2).

(iii) $[Cu(CNR)_4]PF_6$ ($R = Me$, CMe_3, and xylyl)

Typically, a quantitiy of $[Cu(NCMe)_4]PF_6$ (1.0 g, 2.68 mmol) was dissolved in 25 ml of acetone, then a slight excess of the appropriate isocyanide ligand (6 equivalents) was added to the reaction mixture which was then stirred at room temperature for 30 min. The colourless solution was reduced in volume under a stream of nitrogen gas, and the addition of diethyl ether precipitated a white crystalline product that was separated by filtration, washed with diethyl ether, and dried in vacuo; yields were in the range 90–95%. Anal. Calcd. for $C_8H_{12}CuF_6N_4P$: C, 25.78; H, 3.25. Found: C, 25.91; H, 3.43. Calcd. for $C_{20}H_{36}CuF_6N_4P$: C, 44.40; H, 6.71; N, 10.36. Found: C, 44.67; H, 7.04; N, 10.41. Calcd. for $C_{36}H_{36}CuF_6N_4P$: C, 58.98; H, 4.95. Found: C, 59.78; H, 5.44.

The spectroscopic properties of complexes are as follows: (1) $[Cu(CNMe)_4]PF_6$ ^1H NMR (acetone-d_6) δ 3.44(t) $J(^{14}N-^1H) = 2.4$ Hz, CH_3NC. IR spectrum: Nujol mull $\nu(C\equiv N)$ 2213(s) and 2176(w) cm^{-1} (2211(s) and 2176(w) cm^{-1} in CH_2Cl_2). (2) $[Cu(CNCMe_3)_4]PF_6$ ^1H NMR (acetone-d_6) δ 1.51 (s, $CNCMe_3$). IR spectrum: Nujol mull $\nu(C\equiv N)$ 2182(s) and 2147(sh) cm^{-1} (2180(s) and 2144(sh) cm^{-1} in CH_2Cl_2). (3) $[Cu(CNxylyl)_4]PF_6$ ^1H NMR (acetone-d_6) δ 2.56 (s, 24H, CH_3), 7.40 (s, 12H, aryl). IR spectrum: Nujol mull $\nu(C\equiv N)$ 2157(s) cm^{-1} (2163(s) cm^{-1} in CH_2Cl_2).

B. Mixed Donor Complexes of Copper(I) Containing Both Isocyanide and Nitrogen or Phosphorus Donating Ligands

(i) $[Cu(CNMe)_2(bipy)]PF_6$

A mixture of $[Cu(CNMe)_4]PF_6$ (0.5 g, 1.34 mmol) and bipy (0.5 g, 3.20 mmol) in 30 ml of 1-propanol was refluxed for 48 h. The solution was cooled to 0 °C and the pale yellow needles which precipitated were separated by filtration, washed with diethyl ether, and dried in vacuo; yield 0.51 g (86%). Anal. Calcd. for $C_{14}H_{14}CuF_6N_4P$: C, 37.62; H, 3.14. Found: C, 38.06; H, 3.06. The spectroscopic properties of this complex are as follows: ^1H NMR (acetone-d_6) δ 3.40 (s, 6H, CH_3NC), 7.80 (td, 2H, bipy), 8.21 (td, 2H, bipy), 8.54 (d, 2H, bipy), 8.96 (d, 2H, bipy). IR spectrum: Nujol mull $\nu(C\equiv N)$ 2213(s), 2193(s), 2164(sh) cm^{-1}.

Alternatively, the above compound can be prepared from $[Cu(NCMe)_4]PF_6$. The complex $[Cu(NCMe)_4]PF_6$ (0.5 g, 1.34 mmol) was dissolved in 15 ml of ethanol and to the stirred solution was

added an ethanol solution (30 ml) of 2,2'-bipyridyl (0.21 g, 1.35 mmol) and methyl isocyanide (0.15 ml, 2.70 mmol). This mixture was stirred at room temperature for 30 min and then the solution evaporated to dryness under a stream of nitrogen to yield the pale yellow complex [Cu(CNMe)$_2$(bipy)]-PF$_6$. Recrystallization of the complex was achieved using an acetone–diethyl ether mixture (1:2); yield 0.54 g, (91%).

(ii) [Cu(CNCMe$_3$)$_2$(bipy)]PF$_6$

This primrose yellow complex was obtained by procedures analogous to those described in section B(i); yield 82%. *Anal.* Calcd. for C$_{20}$H$_{26}$CuF$_6$N$_4$P: C, 45.24; H, 4.90. Found: C, 45.29; H, 4.97. The spectroscopic properties of this complex are as follows: electronic absorption spectrum (CH$_2$Cl$_2$): 383(sh) nm. ^{1}H NMR (acetone-d_6) δ 1.40 (s, 18H, CNCMe$_3$), 7.70 (td, 2H, bipy), 8.15 (td, 2H, bipy), 8.50 (d, 2H, bipy), 8.88 (d, 2H, bipy). IR spectrum: Nujol mull ν(C≡N) 2188(s), 2168(s), 2138(w) cm^{-1}.

(iii) [Cu(CNCMe$_3$)$_2$(DAB)]PF$_6$

This orange-yellow compound was obtained by procedures analogous to those in section B(i); yield 80%. *Anal.* Calcd. for C$_{20}$H$_{38}$CuF$_6$N$_4$P: C, 44.24; H, 7.05. Found: C, 44.38; H, 7.19. The spectroscopic properties of this complex are as follows: ^{1}H NMR (acetone-d_6) δ 1.42 (s, 18H, CNCMe$_3$), 1.49 (s, 18H, t-Bu of DAB), 8.30 (s, 2H, N–H of DAB). IR spectrum: Nujol mull ν(C≡N) 2197(s) and 2176(s) cm^{-1} (2190(s) and 2168(s) cm^{-1} in CH$_2$Cl$_2$).

(iv) [Cu(CNCMe$_3$)$_2$(phen)]PF$_6$

This pale yellow compound was obtained by procedures analogous to those outlined in section B(i), yield 85%. *Anal.* Calcd. for C$_{22}$H$_{26}$CuF$_6$N$_4$P: C, 46.71; H, 4.72. Found: C, 46.38; H, 5.27. The spectroscopic properties of this complex are as follows: ^{1}H NMR (acetone-d_6): δ 1.48(s, 18H, CNCMe$_3$), 8.12 (multiplet, 2H, phen), 8.17 (s, 2H, phen), 8.78 (dd, 2H, phen), 9.32 (dd, 2H, phen). IR spectrum: Nujol mull ν(C≡N) 2189(s) and 2170(s) cm^{-1}.

(v) [Cu(CNCMe$_3$)$_2$(dppe)]PF$_6$

This colourless compound was obtained upon refluxing a mixture of [Cu(CNCMe$_3$)$_4$]PF$_6$ (0.5 g, 0.92 mmol), dppe (0.55 g, 1.38 mmol), and KPF$_6$ (0.2 g, 1.16 mmol) in 40 ml of ethanol for 48 h. Recrystallization of the compound could be achieved using an acetone–toluene solvent mixture (1:2); yield 75%. IR spectrum: Nujol mull ν(C≡N) 2188(s) cm^{-1}.

(vi) [Cu(CNxylyl)$_2$(Me$_2$phen)]PF$_6$

This off-white complex was obtained by refluxing a mixture of [Cu(CNxylyl)$_4$]PF$_6$ (0.235 g, 0.32 mmol) and 2,9-dimethyl-1,10-phenanthroline (0.20

g, 0.96 mmol) in 1-propanol for 5 days. Cooling the resulting dark orange-red solution to 0 °C yielded the complex which was collected by filtration, washed with diethyl ether, and dried *in vacuo*. The compound was recrystallized from a dichloromethane-diethyl ether mixture (1:2); yield 0.17 g (78%). *Anal.* Calcd. for C$_{32}$H$_{30}$CuF$_6$N$_4$P: C, 56.57; H, 4.42. Found: C, 55.54; H, 4.73. The spectroscopic properties of this complex are as follows: ^{1}H NMR (acetone-d_6): δ 2.39 (s, 12H, CH$_3$ of xylyl), 3.32 (s, 6H, CH$_3$ of 2,9-Me$_2$phen). IR spectrum: Nujol mull ν(C≡N) 2147(s) and 2125(s) cm^{-1} (2143(s) cm^{-1} in CH$_2$-Cl$_2$).

C. Substitution Reactions of [Cu(NCMe)$_4$]ClO$_4$ using Group V Donor Ligands

(i) [Cu(PPh$_3$)$_4$]ClO$_4$

Triphenylphosphine (3.5 g, 13.3 mmol) and [Cu(NCMe)$_4$]ClO$_4$ (1.0 g, 3.06 mmol) were reacted in refluxing chloroform (20 ml) for 2 h. Addition of ethanol (10 ml) and cooling to 0 °C afforded colourless crystals of the product which were recrystallized from a chloroform–ethanol mixture (1:2), washed with diethyl ether and dried *in vacuo*; yield 3.20 g (86%). *Anal.* Calcd. for C$_{72}$H$_{60}$ClCuO$_4$P$_4$: C, 71.34; H, 5.00. Found: C, 70.80; H, 4.98.

Attempts to prepare partially substituted products of the type [Cu(NCMe)$_{4-x}$(PPh$_3$)$_x$]ClO$_4$ (x = 1–3) by using reduced molar proportions of the phosphine were unsuccessful. Such reactions merely led to reduced yields of [Cu(PPh$_3$)$_4$]ClO$_4$.

(ii) [Cu(EPh$_3$)$_4$]ClO$_4$ (E = As and Sb)

These complexes were prepared in an identical manner to the tetrakis(triphenylphosphine) complex; yields *ca.* 70%. *Anal.* Calcd. for C$_{72}$H$_{60}$As$_4$-ClCuO$_4$: C, 61.42; H, 4.30. Found: C, 61.50; H, 4.10. Calcd. for C$_{72}$H$_{60}$ClCuO$_4$Sb$_4$: C, 54.90; H, 3.84. Found: C, 54.60; H, 3.60. Attempts to prepare complexes of the type [Cu(NCMe)$_{4-x}$(EPh$_3$)$_x$]ClO$_4$ (x = 1–3) were unsuccessful. Reduced yields of [Cu(EPh$_3$)$_4$]ClO$_4$ complexes were the only products.

Physical Measurements

Infrared (IR) spectra of Nujol and hexachlorobutadiene mulls were recorded on an IBM Instruments IR 32 Fourier transform spectrometer (4000–400 cm^{-1}), a Perkin-Elmer 599B spectrophotometer (4000–200 cm^{-1}) and a Digilab FTS-20B spectrometer (500–50 cm^{-1}). Raman spectra were obtained from samples held in capillary tubes using a Spex 1401 double monochromator in conjunction with a Lexel 81 Ar$^+$ laser (514.5 nm line). A photomultiplier cooled to −15 °C and photon-counting detection were employed. Calibration was achieved using indene or by argon lines present when the interference filter was removed. Routine ^{1}H NMR spectra

were recorded using a Perkin-Elmer R32 90 MHz spectrometer. Resonances were referenced internally usually to the residual protons in the incompletely deuterated solvents. Electronic absorption spectra were recorded on dichloromethane solutions using an IBM instruments 9420 UV-visible spectrophotometer.

Elemental microanalyses were performed by Dr. H. D. Lee of Purdue University microanalytical laboratory or by Butterworths Laboratories. Copper was determined by EDTA titration using PAN indicator.

Results and Discussion

Four tetrakis(isocyanide) cationic complexes of copper(I) $[Cu(CNR)_4]X$ (R = Me, X = ClO_4 and PF_6; R = CMe_3 and xylyl, X = PF_6) have been prepared by displacement of acetonitrile ligands from the analogous $[Cu(NCMe)_4]X$ complexes by use of excess isocyanide. The reactions were carried out in either methanol or acetone at room temperature and excellent yields of ca. 90% were easily achieved. The products are stable with respect to oxidation and decomposition in air and light at room temperature. The complexes with R = Me and CMe_3 have previously been isolated as their tetrafluoroborate salts [2], but no xylyl isocyanide complexes of copper(I) appear to have been reported prior to this work.

Displacement of acetonitrile ligands from $[Cu(NCMe)_4]^+$ has been used on a number of occasions to prepare other copper(I) complexes, such as $[CuL_4]^+$ (L = various amines) [16] and two-coordinate $[CuL_2]^+$ (L = imidazoles, pyrazoles and hindered pyridines) [17]. Indeed, we have further shown in the present work that the Group V ligands EPh_3 (E = P, As, or Sb) will replace all four acetonitrile ligands of $[Cu(NCMe)_4]ClO_4$ to give high yields of the tetrahedral complexes $[Cu(EPh_3)_4]ClO_4$. Although the complexes with E = P [18] and E = As [19] have been prepared previously by reduction of hydrated copper(II) perchlorate using an excess of the appropriate Group V donor in ethanol as both reductant and ligand, they have not been prepared by direct replacement of the ligands of a copper(I) complex cation. To our knowledge $[Cu(SbPh_3)_4]\cdot ClO_4$ has not been isolated previously. These syntheses, therefore, further illustrate the value of $[Cu(NCMe)_4]^+$ as starting material for the preparation of a variety of other copper(I) complexes.

Attempts to prepare mixed ligand pseudo-tetrahedral complexes of the general type $[Cu(NCMe)_{4-x}(EPh_3)_x]ClO_4$ (x = 1–3) by use of a deficiency of EPh_3 substituent were unsuccessful, the only products isolated were the fully substituted derivatives $[Cu(EPh_3)_4]ClO_4$.

The tetrakis(isocyanide) products have been characterized by microanalysis, IR $\nu(C\equiv N)$ band positions and ^1H NMR spectroscopy. Details are given in the Experimental Section. The $\nu(C\equiv N)$ frequencies lie in the range 2220–2140 cm^{-1} as expected [20] for terminal isocyanide ligands. Although free alkyl isocyanides display long-range $^{14}N-^1H$ coupling, metal isocyanide complexes do not usually show this feature. However, we have previously [21] found that the silver(I) analogue $[Ag(CNMe)_4]ClO_4$ shows $^{14}N-^1H$ coupling of ca. 2.5 Hz, and in the case of $[Cu(CNMe)_4]PF_6$ we find that $J(^{14}N-^1H) = 2.4$ Hz.

The tetrakis(isocyanide)copper(I) complexes have been reacted with the bidentate chelate ligands 2,2'-bipyridyl, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, N,N'-di-tert-butylethylenediimine and 1,2-bis(diphenylphosphino)ethane. The method usually employed was to react the $[Cu(CNR)_4]PF_6$ species with an excess of the chelate ligand in refluxing 1-propanol or ethanol. Although more than sufficient chelating ligand was present to achieve complete substitution of the four isocyanide ligands, it was found that only two isocyanide ligands were replaced. The products were, therefore, invariably of the type $[Cu(CNR)_2(chelate)]PF_6$ and in all reactions that were attempted, excellent yields (75% or better) were obtained after recrystallization. Analytical results and IR $\nu(C\equiv N)$ band positions are given in the Experimental. These complexes are air-, moisture- and light-stable.

It is also apparent that complexes of the above type can be prepared in a single step by displacement of all four acetonitrile ligands from $[Cu(NC-Me)_4]PF_6$ employing an ethanolic mixture of a chelate ligand and isocyanide in a 1:2 molar ratio. For example, the complex $[Cu(CNMe)_2(bipy)]PF_6$ has been prepared in 91% yield by this route. The advantage of this approach is that the intermediate tetrakis(isocyanide)copper(I) cations do not need to be prepared and also that the substitution reactions proceed rapidly in ethanol at room temperature. In contrast to this, the substitution reactions employing $[Cu(CNR)_4]PF_6$ need to be carried out in refluxing solvents in order to achieve a reasonable reaction rate. The $[Cu(CNR)_2(chelate)]PF_6$ complexes are likely to be pseudotetrahedral as has been shown by a single-crystal X-ray diffraction study of $[Cu(CNCy)_2(tmen)]BPh_4$ [8], (tmen = $Me_2NCH_2CH_2NMe_2$), one of only four previously isolated complexes of this type [4, 8].

The Vibrational Spectra of $[CuL_4]ClO_4$, (L = MeNC, MeCN or CD_3CN)

In view of current interest in the vibrational spectra of transition metal isocyanide [21, 22] and nitrile [23, 24] complexes and their importance as starting materials for a wide range of syntheses, the IR and Raman spectra of the above copper(I)

complexes have been examined. The perdeuterated complex was employed to support assignments for the acetonitrile complex. The assumption has been made that, to a first approximation, the spectra can be regarded as arising from a combination of the vibrations of isolated T_d ClO_4^- anions, CH_3 or CD_3 groups with local C_{3v} symmetry, together with $[Cu(C{\equiv}N{-}C)_4]^+$ or $[Cu(N{\equiv}C{-}C)_4]^+$ moieties. It was further assumed that the individual $Cu{-}C{\equiv}N{-}C$ or $Cu{-}N{\equiv}C{-}C$ groups are linear producing $[Cu(CNC)_4]^+$ or $[Cu(NCC)_4]^+$ ions of T_d symmetry. The number of normal modes of each symmetry species for these groupings will therefore be $3A_1 + 3E + 6T_2 + 2T_1$, the A_1 and E modes being Raman-active, the T_2 modes IR and Raman-active and the T_1 modes inactive. Justification for this approach

comes from the solid state structures of $[Cu(CNMe)_4]BF_4$ [7] and $[Cu(NCMe)_4]ClO_4$ [9]. In the former complex [7] the six C–Cu–C angles of each of the three cations in the asymmetric unit do not deviate more than $\pm4°$ from the ideal tetrahedral angle and the $Cu{-}C{\equiv}N{-}$ and $-C{\equiv}N{-}C{-}$ angles are within 5° of being linear. In $[Cu(NCMe)_4]ClO_4$ [9] there are also three cations in the asymmetric unit, the N–Cu–N angles fall within the range 106–113° and the $Cu{-}N{\equiv}C{-}$ and $-N{\equiv}C{-}C{-}$ angles range from 169–179° and 176–180°, respectively.

The approximate descriptions of the normal modes and proposed assignments are listed in Table I. The perchlorate anion fundamentals require little comment, the frequencies being close to those of the free ion. All four fundamentals are Raman-active and,

TABLE I. Vibrational Spectra (cm^{-1}) of Solid $[CuL_4]ClO_4$, L = CH_3NC, CH_3CN and CD_3CN.

Class	Description	Activity	L = CH_3NC		L = CH_3CN		L = CD_3CN	
			IR	R	IR	R	IR	R
ClO_4^- Fundamentals (T_d)								
A_1	ClO sym. str.	R		928(38)		926(47)		926(39)
E	OClO deg. def.	R		452(7)		450(8)		449(7)
T_2	ClO deg. str.	IR/R	1089vs,br	1091(3)	1080vs,br	1077(2)	1078vs,br	1075sh
T_2	OClO deg. def.	IR/R	622vs	619(9)	620vs	617(5)	620vs	615(7)
CH_3 or CD_3 Fundamentals (C_{3v})								
A_1	$CH_3(CD_3)$ sym. str.	IR/R	2950s	2948(52)	2930s	2931(60)	2105s	2106(43)
A_1	$CH_3(CD_3)$ sym. bend	IR/R	1402m	1398(19)	1360m	1360(31)	1093m	1090(2)
E	$CH_3(CD_3)$ asym. str.	IR/R	3010s	3014(5)	2998s	2996(7)	2252vs	2245(4)
E	$CH_3(CD_3)$ asym. bend	IR/R	1430m ⎫ 1415m ⎭	1431(3) 1408(20)	1417m	1420(3)	a	1017(1)
E	$CH_3(CD_3)$ rock	IR/R	a		1020s	1020(3)	842s^c	844(40)^c
$Cu(C{\equiv}N{-}C)_4$ or $Cu(N{\equiv}C{-}C)_4$ Fundamentals (T_d)								
A_1	$C{\equiv}N/N{\equiv}C$ str.	R		2205(100)		2265(100)^c		2278(100)^c
A_1	CuC/CuN str.	R		236(2)		215(19)		219(4)
A_1	N–C/C–C str.	R		906(5)		930sh		837(40)
E	CuCN/CuNC def.	R		377(2)				
E	CCuC/NCuN def.	R						
E	$C{\equiv}N{-}C/N{\equiv}C{-}C$ bend	R				369sh		350sh
T_2	$C{\equiv}N/N{\equiv}C$ str.	IR/R	2213vs ⎫ 2182sh ⎭	2224(6)	2265s	2265(100)^c	2275s	2278(100)^c
T_2	CuC/CuN str.	IR/R	258m	257(12)	268m	268(11)		230(2)
T_2	CuCN/CuNC def.	IR/R	367w ⎫ 325w ⎭		150s,br			
T_2	CCuC/NCuN def.	IR/R						
T_2	$C{\equiv}N{-}C/N{\equiv}C{-}C$ bend	IR/R	200s		390ms	385(24)	359s	355(29)
T_2	N–C/C–C str.	IR/R	948sh ⎫ 934m ⎭	b	925m	b	842s^c	844(40)^c
T_1	CuCN/CuNC def.	inactive						
T_1	$C{\equiv}N{-}C/N{\equiv}C{-}C$ bend	inactive						
A_1	CH_3 sym. bend + C–C sym. str.	IR/R			2290s	2294(27)		

^{a}Hidden by broad T_2 ClO stretch.　^{b}Hidden by intense A_1 ClO stretch.　^{c}Coincident bands.

as expected, the symmetric stretch is the most intense of the four bands. The appearance of this band at 926 cm^{-1} for [Cu(NCMe)$_4$]ClO$_4$ prevents direct observation of the T$_2$ C–C stretching mode but fortunately this band is clearly evident at 925 cm^{-1} in the IR spectrum. The two IR-active perchlorate modes are present as very strong bands in the IR spectra of all three complexes at ca. 1080 and ca. 620 cm^{-1}. The broadness and intensity of the T$_2$ Cl–O stretching mode prevents detection of both the CH$_3$ rocking mode of [Cu(CNMe)$_4$]ClO$_4$ and the CD$_3$ asymmetric bending mode of [Cu(NCCD$_3$)$_4$]ClO$_4$ in the IR spectra of these complexes. The latter band can be observed as a very weak feature in the Raman spectrum of the perdeuterated complex but the CH$_3$ rocking mode of the isocyanide complex has not been detected. This band is not observed in the Raman spectra of free methyl isocyanide [25] and [Re(CNMe)$_6$]PF$_6$ [22].

A nitromethane solution Raman spectrum of [Cu(NCMe)$_4$]ClO$_4$ confirms the perchlorate assignments, the band at 928 cm^{-1} being polarized (ρ ~0.15) and the bands at 620 cm^{-1} and 470 cm^{-1} being depolarized.

Bands associated with the methyl stretching, bending and rocking modes of [Cu(CNMe)$_4$]ClO$_4$ and [Cu(NCMe)$_4$]ClO$_4$ have been assigned by consideration of their frequencies in the vibrational spectra of methyl isocyanide [25] and acetonitrile [26, 27] respectively. Should C_{3v} symmetry be appropriate, all such bands will be both IR- and Raman-active. This situation is indeed found and, as expected, the A$_1$ modes are particularly prominent in the Raman spectra. On coordination to copper(I) the two CH$_3$ stretching modes (A$_1$ + E) for both MeNC and MeCN show little shift, whereas the two methyl bending modes (A$_1$ + E) of these ligands show shifts of between 15 and 30 cm^{-1} to lower frequencies. As expected, the methyl fundamentals are considerably affected by deuteration. The A$_1$ symmetric stretch which is observed at 2930 cm^{-1} for the H isotopic species [Cu(NCMe)$_4$]$^+$ is found as a strong band in both the IR and Raman spectra of [Cu(NCCD$_3$)$_4$]$^+$ at 2105 cm^{-1}. The E asymmetric stretch of the latter cation appears as a weak band in the Raman and as a strong band in the IR at ca. 2250 cm^{-1} compared with 2998 cm^{-1} for the H isotopic species. These bands are therefore found near ν(N≡C) in the spectra, but comparison with free CD$_3$CN [28] removes any confusion over the assignments.

In Table I the ν(C–C) stretches of the acetonitrile complex are suggested to be virtually coincident with the A$_1$ ν(ClO) of the ClO$_4^-$ ion at 926 cm^{-1} and the corresponding ν(C–C) stretch of the perdeuterated complex is assigned to a band at 837 cm^{-1}. This implies coupling between ν(C–C) and other modes,

and since the isotope shift for the CH$_3$ and CD$_3$ symmetric bending modes is not as expected for isolated modes, it is reasonable to suggest coupling between ν(C–C) and these symmetric bends. The CD$_3$ rocking mode is also found in this part of the spectrum of the D isotopic species.

Figure 1 shows the ν(N≡C) (for [Cu(NCMe)$_4$]$^+$ and [Cu(NCCD$_3$)$_4$]$^+$) or ν(C≡N) (for [Cu(CNMe)$_4$]$^+$)
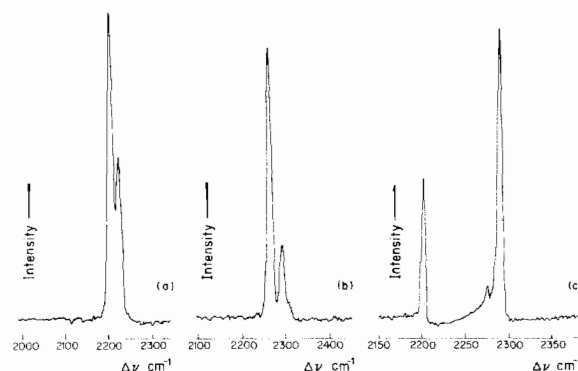
Fig. 1. Solid state Raman spectra of: (a) [Cu(CNMe)$_4$]ClO$_4$, (b) [Cu(NCMe)$_4$]ClO$_4$, and (c) [Cu(NCCD$_3$)$_4$]ClO$_4$.

stretching region of the Raman spectra of the three complexes*. For [Cu(CNMe)$_4$]ClO$_4$, two intense bands (A$_1$ + T$_2$) are found in the Raman spectrum at 2224 and 2205 cm^{-1} in agreement with a T_d approximation. In further agreement with this approach just one very strong IR active ν(C≡N) band (T$_2$) is found in CH$_2$Cl$_2$ solution at 2210 cm^{-1}. In the solid state IR spectrum the main band at 2213 cm^{-1} has a shoulder at 2182 cm^{-1}. The assignments for ν(C≡N) in the Raman spectrum are based on the assumption that the A$_1$ mode will give rise to the more intense band. These ν(C≡N) bands are found some 40 and 60 cm^{-1} higher, respectively, than that for free MeNC, (2165 cm^{-1}) [25]. For H$_3$B·CNMe an increase in ν(C≡N) on coordination of ca. 150 cm^{-1} was related [29] to an increase in C≡N force constant rather than to significant coupling with other modes. For the copper(I) complex a force constant increase would be consistent with a strengthening of the C≡N bonds as indicated by structural data on [Cu(CNMe)$_4$]BF$_4$ [7]. The average C≡N bond length of 1.114 Å for the four copper(I) cations in the asymmetric unit compares with 1.156 Å for methyl isocyanide itself [30].

Unlike [Cu(CNMe)$_4$]ClO$_4$, only one strong band assignable to ν(N≡C) has been detected in the IR and Raman spectra of both [Cu(NCMe)$_4$]ClO$_4$ and

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*For convenience we write these modes as ν(N≡C) and ν(C≡N) to accord with the Cu–ligand bonds being represented as Cu–N≡C–R and Cu–C≡N–R, respectively.

$[Cu(NCCD_3)_4]ClO_4$, (Fig. 1). The additional bands in both the IR and Raman spectra of the per-deuterated complex are assigned to the CD_3 stretches. For the H isotopic species the additional band at *ca.* 2290 cm^{-1} in both the IR and Raman spectra is attributed to a combination band arising from the A_1 CH_3 symmetric bend and the A_1 C–C stretch. Many studies on acetonitrile complexes [23] have shown that this combination band gains intensity by Fermi resonance with $\nu(N≡C)$. Such Fermi resonance is, or course, essentially absent in the perdeuterated complex. The assignment of these two bands for the H isotopic species as $\nu(N≡C)$ and an A_1 combination is supported by nitromethane solution Raman data. Bands found at 2298 and 2270 cm^{-1} are both polarized. The increase in $\nu(N≡C)$ (upon coordination) for the H and D isotopic species of *ca.* 15 cm^{-1} is much smaller than that usually, but not invariably, observed for σ-bonded nitrogen donor acetonitrile complexes but is indicative of increased CN stretching force constants on coordination as a result of increasing CN σ-bond strengths. This is in agreement with a decrease in the C≡N bond length from 1.157 Å for CH_3CN to an average of 1.13 Å for the $3[Cu(NCMe)_4]^+$ cations in the asymmetric unit [9]. The increase in $\nu(N≡C)$ on coordination of CH_3-CN to either copper(I) chloride or bromide is similarly small (*ca.* 20 cm^{-1}) [27]. The D isotopic species has $\nu(N≡C)$ some 13 cm^{-1} higher than that of the H isotopic species, (2278 and 2265 cm^{-1} respectively), because of the absence of a Fermi resonance shift in the former.

Two Raman active $\nu(N–C)$ stretches are predicted $(A_1 + T_2)$ for a T_d $[Cu(CNC)_4]^+$ unit, the T_2 mode also being IR active. However, only one such band (906 cm^{-1}) can be assigned in the Raman spectrum. The other is found in the IR spectrum at 934 cm^{-1} and will therefore be hidden in the Raman spectrum by the strong $\nu(ClO)$ at 928 cm^{-1}. The $\nu(N–C)$ stretch of free MeNC is found at 928 cm^{-1} [25]. There are also problems over the assignments of $\nu(CC)$ for $[Cu(NCMe)_4]ClO_4$, again as a result of near-coincidence with $\nu(ClO)$ in the Raman spectrum. However, an IR band at 925 cm^{-1} can be assigned to the T_2 $\nu(CC)$ mode. Assignment of $\nu(CC)$ for $[Cu(NCCD_3)_4]ClO_4$ is also not firmly based because of the presence of the CD_3 rocking mode in the same region.

The remaining bands in the vibrational spectra of these complexes all appear below 400 cm^{-1}. The bands observed for $[Cu(CNMe)_4]ClO_4$ in both the Raman and IR spectra are, at best, of moderate intensity and in view of the few assured assignments of $\nu(MC)$ and $\delta(M–C≡N)$, any proposals must be regarded as tentative. By analogy with other metal isocyanide [22] and metal carbonyl complexes, bands of higher frequency are assigned (Table I) to $\delta(CuCN)$ and those of lower frequency to $\nu(CuC)$

vibrations. Thus, Raman bands at 257 and 236 cm^{-1} are assigned to the T_2 and A_1 $\nu(CuC)$ vibrations, the former also being found as a medium intensity band in the IR spectrum. The remaining band in the IR spectrum at 200 cm^{-1} is tentatively assigned to a $\delta(Me–NC)$ vibration. This is in accord with similar assignments of strong or medium intensity bands at *ca.* 184 cm^{-1} in the IR spectra of $[M(CNMe)_6]^+$ (M = Mn and Re) [22] and at 202 cm^{-1} in the IR spectrum of $[Ag(CNMe)_4]ClO_4$ [21], much shifted from $\delta(Me–NC)$ of free MeNC at 288 cm^{-1} [25]. Bands assignable to $\delta(CCuC)$ deformations have not been observed but are likely to be of very low frequency.

Two bands in the Raman spectra of both $[Cu(NCMe)_4]ClO_4$ and its perdeuterated analogue can be assigned to $\delta(C–C≡N)$ modes, one of the bands also appearing in the IR spectra. Shifts to lower frequencies for the D isotopic species may result from coupling with the CD_3 rocking mode. A nitromethane solution of the H isotopic complex shows a depolarized Raman band at 385 cm^{-1} ascribed to a $\delta(C–C≡N)$ vibration. The two weak Raman bands at 268 and 215 cm^{-1} for $[Cu(NCMe)_4]ClO_4$ and at 230 and 219 cm^{-1} for $[Cu(NCCD_3)_4]ClO_4$ are assigned to $\nu(Cu–N)$ stretching modes. A band at 268 cm^{-1} is also observed in the IR spectrum of the H isotopic species but no analogous band is evident in the IR spectrum of the perdeuterated complex. Reports of metal–nitrogen stretching frequencies for acetonitrile complexes are relatively few [23], most of the assignments being, at best, tentative because of difficulties in detecting the weak $\nu(MN)$ bands in both the IR and Raman spectra. Bands assigned to $\nu(MN)$ vibrations are likely to be coupled with $\delta(MNC)$, $\delta(NMN)$ and $\delta(CCN)$ deformations, as recently discussed [24] for *cis*-$[PtCl_2(NCMe)_2]$ We believe our assignments to be reasonable since the Raman spectra of $[CuX(NCMe)]_n$ contain medium–intensity bands at 266 cm^{-1} (X = Cl) and 253 cm^{-1} (X = Br) assigned to $\nu(CuN)$ stretching modes [27]. Furthermore, the IR spectrum of $[Cu(NCMe)_4]$-SO_3F [31] contains a weak band at 260 cm^{-1}. Other workers [32] have suggested that strong IR bands at 163 cm^{-1} for $[Cu(NCMe)_4]X$ (X = ClO_4^-, $GaCl_4^-$, $InCl_4^-$ and BF_4^-) should be assigned as $\nu(CuN)$. This, however, leaves unassigned weak bands at 220–240 cm^{-1} for these complexes. A strong, broad band at *ca.* 150 cm^{-1} in our IR spectrum of $[Cu(NCMe)_4]ClO_4$ may be associated with either a $\delta(CuNC)$ or a $\delta(NCuN)$ deformation.

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