Synthesis and Crystal Structures of Novel One-dimensional Polymers, $[\{M(bpen)X\}_\infty]$ [$M = Cu^I, X = PF_6^-$; $M = Ag^I$, $X = ClO_4^-$; bpen = *trans*-1,2-bis(2-pyridyl)ethylene] and $[\{Cu(bpen)(CO)(CH_3CN)(PF_6)\}_\infty]$†

Susumu Kitagawa,* Shinji Matsuyama, Megumu Munakata* and Tsunehiko Emori
Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka 577, Japan

The new polymeric compounds $[\{M(bpen)X\}_\infty]$ [$M = Cu^I$, $X = PF_6^-$, **1**; $M = Ag^I$, $X = ClO_4^-$, **2**; bpen = *trans*-1,2-bis(2-pyridyl)ethylene] and $[\{Cu(bpen)(CO)(CH_3CN)(PF_6)\}_\infty]$ **3** have been synthesised and their structures determined by X-ray crystallography: **1**, monoclinic, space group $P2_1/n$, $a = 13.653(8)$, $b = 9.288(3)$, $c = 11.232(3)$ Å, $\beta = 96.89(3)°$ and $Z = 4$; **2**, triclinic, space group $P\bar{1}$, $a = 7.569(1)$, $b = 13.253(5)$, $c = 6.757(1)$ Å, $\alpha = 92.24(3)$, $\beta = 104.05(1)$, $\gamma = 78.41(3)°$ and $Z = 2$; **3**, triclinic, space group $P\bar{1}$, $a = 9.882(8)$, $b = 12.126(9)$, $c = 8.173(8)$ Å, $\alpha = 93.33(9)$, $\beta = 102.10(9)$, $\gamma = 106.90(7)°$ and $Z = 2$. The complexes show an infinite-chain structure of macrocations with non-interacting PF_6^- or ClO_4^- anions. Compounds **1** and **2** are unique polymers having a linear co-ordination geometry, characteristic of d^{10} metals. They differ in the mode of polymerization, being of rectangular and triangular wave chain types, respectively. A non-coplanar structure between the pyridyl and olefinic groups of the co-ordinated bpen is recognized, indicative of the importance of intermolecular interaction in crystal packing. Compound **3** has a tetrahedral form of copper(I) as a repeating unit, involving a single CO molecule, which exhibits a short C=O distance [1.104(6) Å] irrespective of the normal ν(CO) value (2088 cm^{-1}). Proton NMR spectra of the copper(I)–bpen systems demonstrate that the solution species has a dimeric structure having two bridging bpen, where the olefinic moiety is co-ordinated to copper(I), dissimilar to the co-ordination mode of **1**. A difference in chemical shifts between the PF_6^- and ClO_4^- salts is observed, indicative of the interaction of ClO_4^- with copper(I). The polymeric complex is predominantly obtained from the PF_6^- salt. The formation and the structure of CO or C_2H_4 adducts in solution have also been examined by ^1H NMR spectroscopy.

Infinite-chain structures are of substantial interest in understanding the solid-state chemistry of metal complexes.[1] The recent advent of polymeric copper complexes,[2] which have very good conductivity, has added an intriguing dimension to Group 11 metal complex chemistry, prompting one to prepare a well ordered assembly of copper and silver complexes.[3] Copper(I) can have a wide variety of geometrical structures,[4] from two- to six-co-ordinate, providing various types of solid structures as relevant building blocks. Reports on infinite-chain complexes of Group 11 metals with organic ligands having π electrons are still sparse although several famous complexes have been known for three decades.[5]

Here we report the synthesis and structural characterization of a new type of chain compound, $[\{M(bpen)X\}_\infty]$ [bpen = bis(2-pyridyl)ethylene; $M = Cu^I$, $X = PF_6^-$, **1**; $M = Ag^I$, $X = ClO_4^-$, **2**] in which the co-ordination geometry of the metal atoms is linear, unique in their metal polymers,[3,4] and where the mode of polymerization is different for the two metals. Moreover, an interesting CO adduct having infinite-chain structure has also been obtained. The solution species and their equilibria have been examined by use of ^1H NMR spectroscopy.

Experimental

All operations were carried out under an atmosphere of purified argon. Solvents were dried by conventional methods and distilled under argon. The salt $[Cu(CH_3CN)_4]PF_6$ was prepared according to the literature,[6] $[Cu(C_2H_4)(ClO_4)]$ was obtained by the reduction of $Cu(ClO_4)_2{\cdot}6H_2O$ by copper wire, whose preparation has been mentioned previously,[7] and $AgClO_4$ was obtained from Wako Chemicals. The compound *trans*-1,2-bis(2-pyridyl)ethylene was purchased from Aldrich Chemicals.

Preparation of Complexes.—$[\{Cu(bpen)(PF_6)\}_\infty]$ **1**. A methanol solution (5 cm^3) of bpen (18.2 mg, 0.1 mmol) was added to $[Cu(CH_3CN)_4]PF_6$ (37.3 mg, 0.1 mmol) and stirred. The solution soon became yellow, and white microcrystals were precipitated. The crystals were filtered off and washed with methanol. Yield 66%.

The yellow filtrate was transferred to a glass tube and kept for 1 d at room temperature. Colourless crystals were obtained, one of which was used for X-ray crystallography. The crystals are insoluble in methanol and acetone. Raman: ν(C=C) 1629 cm^{-1}. ^1H NMR (the filtrate): δ 7.72, 7.89, 7.39, 8.56 and 7.78 for H^2, H^3, H^4, H^5 and H^{11} respectively.

$[\{Ag(bpen)(ClO_4)\}_\infty]$ **2**. A methanol solution (5.0 cm^3) of bpen (18.2 mg, 0.1 mmol) was gently added to a methanol (5 cm^3) solution of $AgClO_4$ (20.3 mg, 0.1 mmol). The mixture obtained was filtered and the colourless filtrate transferred to a glass tube, which was kept at room temperature for 10 d in a dark place. Colourless crystals were obtained, one of which was used for X-ray crystallography. Raman: ν(C=C) 1631 cm^{-1}.

$[\{Cu(bpen)(CO)(CH_3CN)(PF_6)\}_\infty]$ **3**. A methanol solution (5 cm^3) of bpen (18.2 mg, 0.1 mmol) was added to $[Cu(CH_3CN)_4]PF_6$ (37.3 mg, 0.1 mmol) and stirred. Then carbon monoxide gas was bubbled into the yellow solution for 20 min, and the colourless solution obtained was transferred to a glass tube under a carbon monoxide atmosphere and kept for a few weeks at 5 °C. Pale yellow crystals were obtained, one of

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

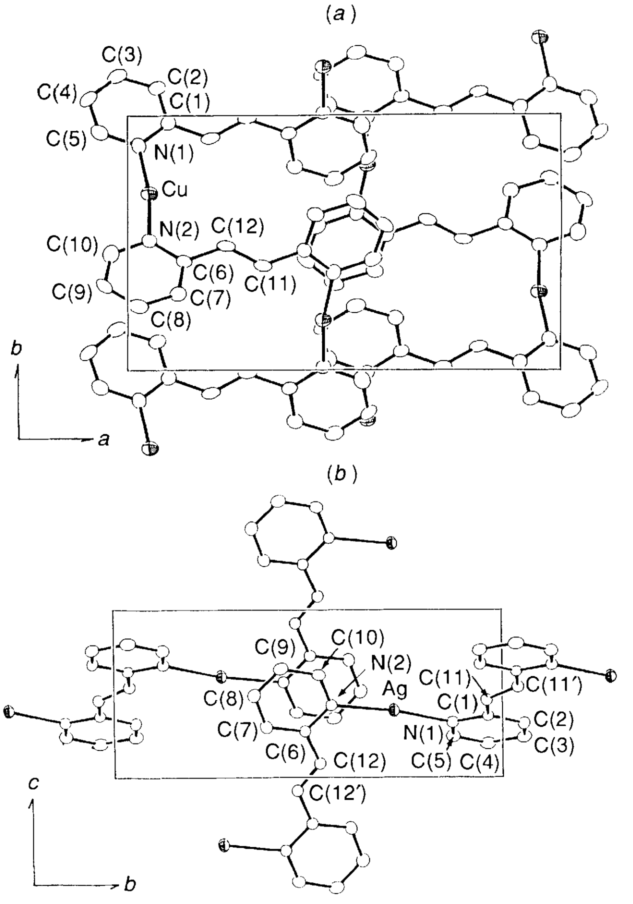


Fig. 1 ORTEP views of portions of macrocations of (*a*) $[\{Cu(bpen)(PF_6)\}_x]$ and (*b*) $[\{Ag(bpen)(ClO_4)\}_x]$. The thermal ellipsoids enclose 30% probability

which was used for X-ray crystallography. IR (KBr disk): ν(CO) 2088, ν(CN) 2120 cm^{-1}. Raman: ν(C=C) 1631 and 1642 cm^{-1}. ^{1}H NMR (−90 °C, [$^2H_4$]methanol, reaction solution atom numbering as in crystal structures. C^{11} denotes both ethylenic protons of bpen): δ 8.17, 8.17, 7.67, 8.74 and 7.94 for H^2, H^3, H^4, H^5 and H^{11} respectively.

bpen. Crystals of bpen were obtained by recrystallization from methanol. ^{1}H NMR ([$^2H_4$]methanol): δ 7.64, 7.83, 7.31, 8.54 and 7.62 for H^2, H^3, H^4, H^5 and H^{11} respectively. Raman: ν(C=C) 1639 cm^{-1}.

$[\{Cu(\mu\text{-}bpen)(ClO_4)\}_2]$ **4**. A methanol solution (1 cm^3) of bpen (2.7 mg, 0.015 mmol) was added to a methanol solution (2.0 cm^3) of $[Cu(C_2H_4)(ClO_4)]$ (0.015 mmol) and stirred under an ethylene atmosphere. After the ethylene was purged with argon, the solution was filtered. The filtrate was sealed in a glass tube and kept at 5 °C for 3 d. Yellow microcrystals were obtained. (Found: C, 41.80; H, 3.00; N, 7.95. Calc. for $C_{12}H_{10}ClCuN_2O_4$: C, 41.75; H, 2.90; N, 8.10%). ^{1}H NMR ([$^2H_4$]methanol, redissolved crystals): δ 7.74, 7.93, 7.43, 8.59 and 7.81 for H^2, H^3, H^4, H^5 and H^{11} respectively.

Physical Measurements.—UV/VIS spectra were recorded with a Hitachi 150-20 spectrophotometer, IR and Raman spectra with JASCO FT/IR-8000 and JEOL JRS-400T laser Raman spectrophotometers, respectively, and ^{1}H NMR spectra with a JEOL GSX-270 spectrometer operating in the Fourier-transform mode (16 K data points, spectral width 3500 Hz after 100–200 pulses) at ambient temperature ($SiMe_4$ as internal reference).

Crystallography.—General crystallographic data and procedures for this paper are as follows. As a rule, crystals were glued on top of a glass fibre. For each compound unit-cell constants were determined from the geometric parameters of 20 well centred reflections with 2θ values in the range 20–32°. Then, a unique data set was measured to a 2θ limit predetermined from the scope of the data, using a Rigaku AFC6B automated diffractometer fitted with a monochromatic Mo-Kα radiation source (λ = 0.710 73 Å) and operating in conventional ω–2θ scan mode at 25 °C. *N* Independent reflections were obtained, N_o with $F_o > 3\sigma(F_o)$ being considered 'observed' and used in the block-diagonal least-squares refinement after analytical absorption corrections. Full-matrix refinement was used for the smaller structures. The structure was solved by direct methods (MULTAN 78).[8] After anisotropic least-squares refinement for non-hydrogen atoms, all hydrogen atoms were located in the Fourier difference map, but their parameters were not refined. Residuals at convergence (*R* and *R'*) are estimated on $|F|$. Atomic scattering factors and anomalous dispersion terms were taken from ref. 9. Computation was carried out on the FACOM 780 computer at the Data Processing Center of Kyoto University by using the program system KPPXRAY. The positional parameters for each compound are listed in Tables 1–4.

Departures from the above occurred for complex **3**. The PF_6^- anion is disordered with the site occupancies of 7:3 for equatorial F(3A), F(4A), F(5A) and F(6A) *vs*. F(3B), F(4B), F(5B) and F(6B), whereas those for the axial F(1) and F(2) are 1:1. The minor model B comprises the anion rotated by *ca*. 45° from the model A around the F(1)–P–F(2) axis. For the final refinement the multiplicities were fixed at those values. The significance of the minor sites was verified by the stable refinement and the fact that the parameters derived for the minor anion are within acceptable ranges.

Crystal data. **1**, $C_{12}H_{10}CuF_6N_2P$, M = 390.73, monoclinic, space group $P2_1/n$, a = 13.653(8), b = 9.288(3), c = 11.232(3) Å, β = 96.89(3)°, U = 1414.0 Å^3, Z = 4, D_c = 1.835 g cm^{-3}, $F(000)$ = 776, μ = 17.21 cm^{-1}. Specimen size: 0.30 × 0.30 × 0.25 mm. $2\theta_{max}$ = 60°; N,N_o = 3750, 1367; R,R' = 0.055, 0.053.

2, $C_{12}H_{10}AgClN_2O_4$, M = 389.57, triclinic, space group $P\bar{1}$, a = 7.569(1), b = 13.253(5), c = 6.757(1) Å, α = 92.24(3), β = 104.05(1)°, γ = 78.41(3)°, U = 644.2 Å^3, Z = 2, D_c = 2.008 g cm^{-3}, $F(000)$ = 384, μ = 17.70 cm^{-1}. Specimen size: 0.30 × 0.30 × 0.30 mm. $2\theta_{max}$ = 60°; N,N_o = 4188, 3550; R,R' = 0.033, 0.043.

3, $C_{15}H_{13}CuF_6N_3OP$, M = 459.80, triclinic, space group $P\bar{1}$, a = 9.882(8), b = 12.126(9), c = 8.173(8) Å, α = 93.33(9), β = 102.10(9), γ = 106.90(7)°, U = 909(1) Å^3, Z = 2, D_c = 1.680 g cm^{-3}, $F(000)$ = 460, μ = 13.13 cm^{-1}. Specimen size: 0.20 × 0.20 × 0.15 mm. $2\theta_{max}$ = 55°; N,N_o = 4765, 3421; R,R' = 0.046, 0.056.

bpen, $C_{12}H_{10}N_2$, M = 182.23, monoclinic, space group $P2_1/n$, a = 7.310(5), b = 12.252(5), c = 5.654(5) Å, β = 107.05(6)°, U = 484.2 Å^3, Z = 2, D_c = 1.250 g cm^{-3}, $F(000)$ = 192, μ = 0.71 cm^{-1}. Specimen size: 0.30 × 0.30 × 0.30 mm. $2\theta_{max}$ = 60°; N,N_o = 1678, 499; R,R' = 0.065, 0.063.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Crystal Structures of Complexes **1** *and* **2**.—Fig. 1 indicates a portion of each polymer. The single-crystal X-ray diffraction analysis reveals that compound **1** (or **2**) is composed of non-interacting PF_6^- (or ClO_4^-) anions and $\{[Cu(bpen)]^+\}_x$ (or $\{[Ag(bpen)]^+\}_x$) macrocations. The cation of **1** is an infinite one-dimensional chain just like a continuous rectangular wave running parallel to the monoclinic *b* axis. The basic repeating unit is two-co-ordinate $Cu(py)_2$ (py = pyridine), whose mode of polymerization is such that a bpen which is co-ordinated to a copper atom also acts as a ligand for a second neighbouring copper. The ethylene group of a bpen is nearly perpendicular to

Table 1 Atomic positional parameters* for $[\{Cu(bpen)(PF_6)\}_\infty]$

Atom	*x*	*y*	*z*
Cu	0.4492(1)	0.1949(1)	0.7424(1)
P	0.7182(2)	0.0477(2)	0.9552(2)
F(1)	0.7392(4)	0.1908(7)	1.0261(7)
F(2)	0.7016(4)	−0.0950(6)	0.8829(6)
F(3)	0.8330(3)	0.0206(5)	0.9679(5)
F(4)	0.6043(3)	0.0763(6)	0.9371(5)
F(5)	0.7264(4)	0.1332(6)	0.8359(5)
F(6)	0.7094(4)	−0.0421(7)	1.0710(5)
C(1)	0.4053(5)	0.4701(8)	0.8404(6)
C(2)	0.4313(5)	0.6106(8)	0.8772(7)
C(3)	0.5247(6)	0.6597(8)	0.8729(7)
C(4)	0.5907(5)	0.5701(9)	0.8322(7)
C(5)	0.5644(5)	0.4358(9)	0.7970(7)
C(6)	0.1298(5)	0.4282(7)	0.8653(6)
C(7)	0.1167(5)	0.2981(9)	0.9203(7)
C(8)	0.0261(6)	0.2508(8)	0.9342(7)
C(9)	−0.0538(5)	0.3309(8)	0.8978(7)
C(10)	−0.0386(5)	0.4587(9)	0.8447(7)
C(11)	0.3087(5)	0.4111(7)	0.8493(7)
C(12)	0.2257(5)	0.4870(7)	0.8512(7)
N(1)	0.4738(4)	0.3824(7)	0.8010(5)
N(2)	0.0508(4)	0.5109(6)	0.8294(5)

* Estimated standard deviations are given in parentheses.

Table 2 Atomic positional parameters* for $[\{Cu(bpen)(CO)(CH_3CN)(PF_6)\}_\infty]$

Atom	*x*	*y*	*z*
Cu	0.6533(0)	0.7866(0)	0.2760(0)
P	0.1995(1)	0.7388(1)	−0.1830(1)
F(1)	0.0541(3)	0.7376(3)	0.1290(4)
F(2)	0.3436(3)	0.7414(3)	−0.2357(4)
F(3A)	0.1034(5)	0.6577(5)	−0.3473(5)
F(3B)	0.155(1)	0.6121(6)	−0.242(1)
F(4A)	0.2914(5)	0.8027(5)	−0.0094(6)
F(4B)	0.2496(9)	0.8745(6)	−0.130(1)
F(5A)	0.1865(7)	0.6217(5)	−0.1002(9)
F(5B)	0.273(1)	0.729(1)	−0.000(1)
F(6A)	0.2047(7)	0.8481(5)	−0.2631(9)
F(6B)	0.130(1)	0.760(1)	−0.370(1)
O(1)	0.6165(5)	0.9055(4)	−0.0255(5)
N(1)	0.4885(2)	0.6444(2)	0.3024(3)
N(2)	0.7410(3)	0.8946(2)	0.5048(3)
N(3)	0.8149(3)	0.7105(2)	0.2669(4)
C(1)	0.4348(3)	0.5465(2)	0.1901(3)
C(2)	0.3282(3)	0.4510(3)	0.2160(4)
C(3)	0.2774(4)	0.4525(3)	0.3599(5)
C(4)	0.333(5)	0.5505(3)	0.4748(4)
C(5)	0.4369(3)	0.6433(3)	0.4413(4)
C(6)	0.6845(3)	0.9727(2)	0.5669(4)
C(7)	0.7601(4)	1.0496(3)	0.7108(4)
C(8)	0.8947(4)	1.0479(3)	0.7944(4)
C(9)	0.9517(4)	0.9680(3)	0.7349(4)
C(10)	0.8728(3)	0.8941(3)	0.5908(4)
C(11)	0.4944(3)	0.5463(2)	0.0398(4)
C(12)	0.5398(4)	0.9717(3)	0.4750(4)
C(13)	0.6272(4)	0.8623(3)	0.0896(5)
C(14)	0.9063(4)	0.6756(3)	0.2581(4)
C(15)	1.0276(5)	0.6324(4)	0.2487(6)

* Estimated standard deviations are given in parentheses.

the *b* axis. In linear-chain copper(I) compounds[4,5] this two-co-ordination of the copper(I) monomer unit is quite rare, while three- and four-co-ordinate copper(I) monomer units are common.

The cation of **2** also shows infinite one-dimensional chains just like a continuous triangular wave (zigzag mode) running parallel to a diagonal axis of the triclinic cell. The basic repeating unit is similar to that of **1**, indicative of an uncommon structure in polymeric silver compounds.

Table 3 Atomic positional parameters* for $[\{Ag(bpen)(ClO_4)\}_\infty]$

Atom	*x*	*y*	*z*
Ag	0.6853(0)	0.2780(0)	0.3975(0)
Cl	0.9092(1)	0.2221(0)	0.9497(1)
C(1)	0.7410(3)	0.0365(2)	0.3660(4)
C(2)	0.6794(3)	−0.0552(2)	0.3193(4)
C(3)	0.4950(4)	−0.0560(2)	0.2388(4)
C(4)	0.3720(3)	0.0373(2)	0.2002(4)
C(5)	0.4396(3)	0.1260(2)	0.2428(4)
C(6)	0.6468(3)	0.5072(2)	0.2728(4)
C(7)	0.6840(4)	0.6067(2)	0.2987(5)
C(8)	0.7737(4)	0.6368(2)	0.4874(5)
C(9)	0.8249(4)	0.5676(2)	0.6491(5)
C(10)	0.7892(4)	0.4711(2)	0.6138(4)
C(11)	0.9349(3)	0.0401(2)	0.4604(4)
C(12)	0.5476(4)	0.4708(2)	0.0795(4)
N(1)	0.6198(3)	0.1276(2)	0.3264(3)
N(2)	0.7034(3)	0.4391(2)	0.4305(3)
O(1)	0.9289(4)	0.1136(2)	0.9542(5)
O(2)	0.7232(3)	0.2668(2)	0.8436(5)
O(3)	1.0379(4)	0.2511(3)	0.8525(6)
O(4)	0.9449(5)	0.2594(3)	1.1518(5)

* Estimated standard deviations are given in parentheses.

Table 4 Atomic positional parameters* for *trans*-1,2-bis(2-pyridyl)ethylene

Atom	*x*	*y*	*z*
C(1)	0.7902(4)	0.0659(2)	0.0836(6)
C(2)	0.6959(5)	0.0520(3)	0.2591(7)
C(3)	0.5508(6)	0.1202(3)	0.2656(7)
C(4)	0.5008(5)	0.2017(3)	0.0938(7)
C(5)	0.5982(5)	0.2107(3)	−0.0741(7)
C(11)	0.9467(4)	−0.0053(3)	0.0738(6)
N(1)	0.7407(4)	0.1459(2)	−0.0854(5)

* Estimated standard deviations are given in parentheses.

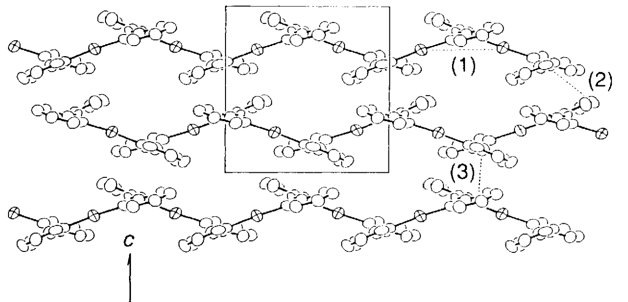


Fig. 2 Projection of the chain structure of $[\{Cu(bpen)\}_n]^{n+}$ along the *a* axis, showing the framework of the non-planar polymeric chain. Dashed lines show the nearest-neighbour atom contacts: (1) Cu ··· Cu 7.17; (2) C(1) ··· C(3′) 3.46; (3) C(1) ··· C(4′) 3.69 Å. Primes denote atoms in the neighbouring chain

Table 5 provides a list of important bond distances and angles. The co-ordination geometry of the metal in both compounds **1** and **2** indicates a deviation from linearity. The N–Cu–N angle of 168.2(2)° for **1** is close to that of pyridine derivatives, $[Cu(dmpy)_2]ClO_4$ (170°) (dmpy = 2,4-dimethylpyridine),[10] but smaller than that of other two-co-ordinate copper(I) complexes, (170–180°).[10] On the other hand, the Cu–N_{av} distance of 1.884(6) Å falls within the range 1.86–1.94 Å.[11] In the case of **2** the bond distance Ag–N_{av} of 2.162(3) Å falls within the common values, and the angle N–Ag–N 169.6(1)° is at the lower end (172–180°) for two co-ordinate silver complexes having N-donors.[12] Because **1** and **2** reveal a similar co-ordination geometry, the difference in the polymerization mode is attributable to the counter anion.

Table 5 Selected bond distances (Å) and angles (°)

(*a*) $[\{Cu(bpen)\}_n]^{n+}$			
Cu–N(1)	1.878(6)	Cu–N(2)	1.890(6)
N(1)–C(5)	1.338(9)	N(2)–C(6)	1.346(8)
N(1)–C(1)	1.354(9)	N(2)–C(10)	1.343(9)
C(1)–C(11)	1.44(1)	C(6)–C(12)	1.44(1)
C(11)–C(12)	1.33(1)		
N(1)–Cu–N(2)	168.2(2)	Cu–N(1)–C(1)	124.8(5)
Cu–N(1)–C(5)	117.3(5)	Cu–N(2)–C(6)	127.0(4)
Cu–N(2)–C(10)	115.3(4)	C(1)–C(11)–C(12)	125.8(6)
C(6)–C(12)–C(11)	125.7(6)		
(*b*) $[\{Cu(bpen)(CO)(CH_3CN)\}_n]^{n+}$			
Cu–N(1)	2.057(3)	Cu–N(2)	2.083(4)
Cu–N(3)	2.075(4)	Cu–C(13)	1.835(4)
N(1)–C(5)	1.338(4)	N(2)–C(6)	1.355(4)
N(1)–C(1)	1.355(4)	N(2)–C(10)	1.346(4)
C(1)–C(11)	1.470(5)	C(6)–C(12)	1.465(5)
C(12)–C(12′)	1.293(9)	N(3)–C(14)	1.116(5)
C(11)–C(11′)	1.309(6)	C(14)–C(15)	1.455(7)
C(13)–O(1)	1.104(6)		
N(1)–Cu–N(2)	109.7(1)	N(1)–Cu–N(3)	100.2(1)
N(1)–Cu–C(13)	119.5(1)	N(2)–Cu–N(3)	101.3(1)
N(2)–Cu–C(13)	114.9(1)	N(3)–Cu–C(13)	108.6(2)
Cu–N(1)–C(1)	123.0(2)	Cu–N(1)–C(5)	119.6(2)
Cu–N(2)–C(6)	126.1(2)	Cu–N(2)–C(10)	116.5(2)
Cu–C(13)–O(1)	176.3(5)	N(3)–C(14)–C(15)	178.8(3)
C(1)–C(11)–C(11′)	124.4(3)	C(6)–C(12)–C(12′)	126.3(4)
(*c*) $[\{Ag(bpen)\}_n]^{n+}$			
Ag–N(1)	2.158(3)	Ag–N(2)	2.166(3)
N(1)–C(5)	1.348(3)	N(2)–C(6)	1.353(3)
N(1)–C(1)	1.353(3)	N(2)–C(10)	1.347(3)
C(1)–C(11)	1.461(3)	C(6)–C(12)	1.457(4)
C(12)–C(12′)	1.318(3)	C(11)–C(11′)	1.325(3)
N(1)–Ag–N(2)	169.6(1)	Ag–N(1)–C(1)	125.9(2)
Ag–N(1)–C(5)	115.8(2)	Ag–N(2)–C(6)	123.3(2)
Ag–N(2)–C(10)	118.2(2)	C(1)–C(11)–C(11′)	125.2(3)
C(6)–C(12)–C(12′)	125.6(3)		
(*d*) bpen			
N(1)–C(1)	1.342(4)	N(1)–C(5)	1.326(5)
C(11)–C(11′)	1.305(5)	C(1)–C(11)	1.453(6)
C(1)–N(1)–C(5)	117.0(3)	N(1)–C(1)–C(2)	121.1(3)
N(1)–C(1)–C(11)	117.5(3)	C(2)–C(1)–C(11)	121.4(3)

The pyridine ring contact between the nearest-neighbour chain in compound **1** is 3.46 Å (Fig. 2), indicative of π–π stacking interactions.[13] Evidently, no metal–metal interaction occurs because of the long distance (7.1 Å) of the nearest-neighbour copper atoms.

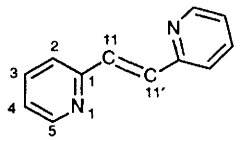
Crystal Structure of Complex **3**.—The carbonyl complex **3** also gives an infinite one-dimensional chain (Fig. 3), which is composed of non-interacting PF_6^- anions and $\{[Cu(bpen)(CO)(CH_3CN)]^+\}_\infty$ macrocations. The macrocations run parallel to a diagonal axis of the triclinic cell. The basic repeating unit is four-co-ordinate $[Cu(py)_2(CO)(CH_3CN)]$, whose mode of polymerization is such that a bridging bpen is co-ordinated to two copper atoms in a similar manner as in **1** and **2**. The midpoint of the ethylene group sits on the crystallographic inversion centre.

The two Cu–N(py) distances, 2.057(3) and 2.083(4) Å, are close to that of $[Cu(py)_4]ClO_4$,[14] while Cu–N(nitrile) 2.075(4) Å is longer than that of $[Cu(CH_3CN)_4]ClO_4$ [average 1.98(2)].[15] In the case of the bond angles around the copper atom, the average deviation from a tetrahedron (109.5°) is only +0.2 and −0.9° for N(py)–Cu–N(py) and C(13)–Cu–N(nitrile), respectively, while larger deviations are found for N(py)–Cu–$C(13)_{av}$ (+7.7) and N(py)–Cu–$N(nitrile)_{av}$ (−8.7°), indicating that both CO and CH_3CN incline at *ca.* 8° from a tetrahedral bond direction.

It is worth noting that the Cu–C(13) distance, 1.835(4) Å, is the longest in four-co-ordinate copper(I) complexes (1.73–1.82 Å) so far synthesised.[16–22] The C–O distance is at the shortest end (1.10–1.148 Å) and shorter than the value (1.128 Å) of metal-free CO.[23] To the best of our knowledge only one carbonyl copper polymer, $[\{Cu(CO)(C_2H_5SO_3)\}_\infty]$,[24] has been crystallographically characterized. The Cu–C and C–O bond distances of the tetrahedral copper moiety fall within the range mentioned above, but quite a high ν(CO) (2128 cm^{-1}) is observed, indicative of a high positive charge or low electron density on the copper which is attributed to a weak copper–sulphonate interaction.[24] This ν(CO) is in contrast to that (2088 cm^{-1}) of **3** which falls within the normal range (2060–2090 cm^{-1}).[16–22] This is because **3** contains N-donor ligands, where the electron density on the copper atom increases and π back-bonding interaction is involved in the Cu–CO bond more than in the case of the sulphonate group. Although the π back bonding contributes to the Cu–CO bond, its structural parameters reveal the predominance of σ bonding. At present there are no positive data to show that the Cu–CO bonding in the carbonylated polymer complex **3** is weak. In practice, the crystals did not lose CO when exposed to air. Thus the collection of the X-ray diffraction data was successful.

Olefinic C=C *Bond Distances*, r.—The crystals of complexes **2** and **3** contain structurally different types of bpen. The two C=C distances, r_a and r_b, are listed in Table 5. Inspection of *r* and ν(C=C) reveals that the decreasing order in *r* corresponds well with that of increasing ν(C=C); 1629 [**1**, 1.33(1)] < 1631 [**2a**, 1.325(4); **b**, 1.318(5); **3b**, 1.309(1)] < 1639 [bpen, 1.305(5) Å] < 1642 cm^{-1} [**3a**, 1.293(1) Å]. A relation $r \propto \nu(C{=}C)^{-1}$ holds for these polymers in the solid state.

The crystallographic structure of metal-free bpen was also determined as the *trans* form shown. It is worth noting that the pyridine and ethylene groups of metal-free bpen are nearly coplanar [dihedral angles (φ)* of 2.8°] while all the co-ordinated bpen ligands studied here show large deviations from planarity. The φ values in co-ordinated bpen in **1**, **3a**, **3b**, **2a** and **2b** are 23.0, 13.2, 31.5, 11.4 and 13.7°, respectively. In the case of **3a** and **3b** the difference in φ is anomalously large. For two-co-ordinate systems the increasing order in the *r* appears to be in good agreement with that in φ: 1.305(5) (2.8, **4**) < average 1.322 (average 12.5, **2**) < 1.33(1) Å (23.0°, **1**). The apparent trend is opposite to that expected from usual considerations concerning conjugated systems, where large φ is accompanied by a shortening of *r* because the bond order is increased by twisting of the $C{=}C(C_5H_4N)$ bond. However, the *r vs.* φ relationship does not apply in the case of **4**. The observed trend is not associated with a pure intramolecular electronic interaction such as π–π interaction with C=C and py moieties, which are perturbed by the metal atom. It is also not simply accounted for by the problem of the X-ray data analysis † because of the good



---

* Defined as the angle between the ethylenic and pyridine ring planes, constituted by C(1)–H(11)–C(11)–C(12)–H(12) and N(1)–C(1)–C(2)–C(3)–C(4)–C(5), respectively.

† A similar phenomenon has been found in the temperature-dependent ethylenic bond distance of (*E*)-2,2′-dimethylstilbene,[25] which is related to the treatment of the anharmonic oscillation of the ethylenic atoms in the data analysis.

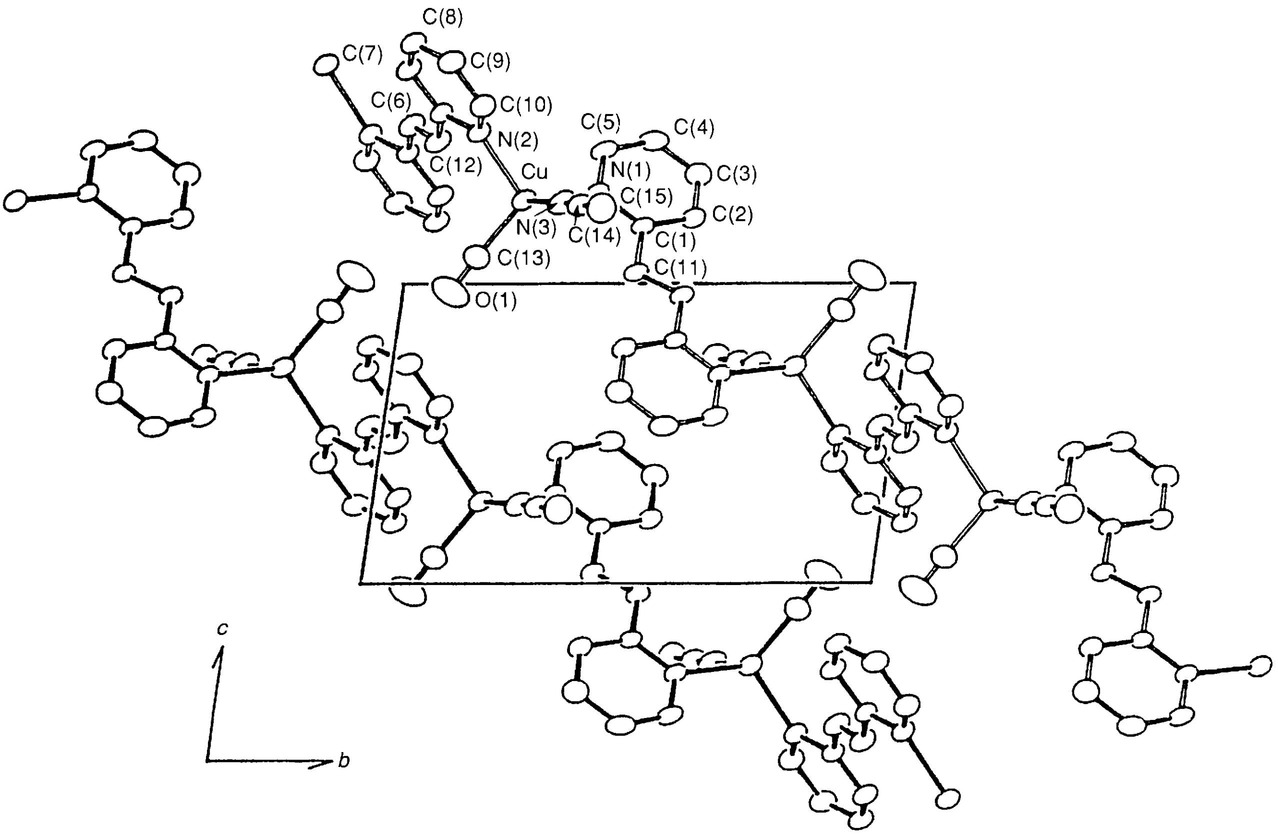


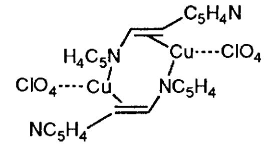
Fig. 3 An ORTEP view of portions of the macrocations of $[\{Cu(bpen)(CO)(CH_3CN)(PF_6)\}_\infty]$. The thermal ellipsoids enclose 30% probability

relationship between *r* and v mentioned above. Most probably, the intermolecular interactions involved in the crystal packing are important in governing the local molecular structure such as dihedral angles and torsion angles. In this context bpen is an ideal ligand for studying such phenomena owing to its high degree of flexibility.

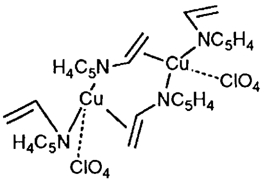
Solution Species.—The ligand bpen reacts with $[Cu(CH_3CN)_4]X$ ($X = PF_6$ or ClO_4) or $[Cu(C_2H_4)(ClO_4)]$ in acetone or methanol to give a yellow solution, which exhibits a shoulder (λ = 350 nm, ε = 1400 dm^3 mol^{-1} cm^{-1}) on the ligand band. This band is assigned metal-to-ligand charge transfer (m.l.c.t.) (Cu→py) because analogous pyridine complexes of copper(I) give a band in the same region, *e.g.* $[Cu(py)_4]^+$ (330 nm).[26] When such complexes are two-co-ordinate, this band tends to be blue shifted, giving pale yellow or colourless crystals.[7,27] The fact that complex **1** is colourless is not an exception because each copper(I) is two-co-ordinate.

When copper(I) perchlorate systems such as $[Cu(CH_3CN)_4]ClO_4$ or $[Cu(C_2H_4)(ClO_4)]$ were used as starting materials the resulting yellow solutions gave only *yellow* crystals of **4**. The elemental analysis reveals $[\{Cu(bpen)(ClO_4)\}_n]$. When the PF_6^- salt was used as a starting material the yellow solution gave *colourless* crystals, which are undoubtedly assigned to **1** as mentioned above.

In order to clarify the structure of the yellow species in solution the yellow crystals of **4** were redissolved and the ^1H NMR spectrum recorded. The protons of bpen were shifted downfield, indicative of co-ordination of the pyridyl N and olefin group: co-ordination shifts ($\delta_C = \delta_{obs} - \delta_{free}$) 0.08, 0.06, 0.08, 0.02 and 0.16 for pyridyl H^2, H^3, H^4, H^5 and olefinic H^{11}, respectively. A downfield shift of the olefinic protons has also been observed for an olefinic α-proton of 2-vinylpyridine(vpy) in dimeric $[Cu_2(\mu\text{-vpy})_2(vpy)_2][ClO_4]_2$ **5**,[28] where the olefin group is co-ordinated to copper(I) is the side-on mode as shown. On this basis the yellow species **4** is also a binuclear copper(I) complex, $[\{Cu(\mu\text{-bpe})(ClO_4)\}_2]$. The ^1H NMR spectrum also demonstrates that this is the only species in solution because there are no other signals. The fact that metal-free pyridyl signals are not observed for **4** is accounted for by a chemical exchange process: $-Cu(^*NC_5H_4)C{=}C(C_5H_4N) \leftrightarrow -Cu(NC_5H_4)C{=}C(C_5H_4N^*)$.



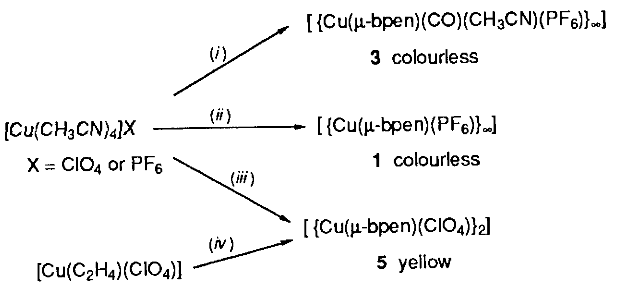
4



5

In the crystal structure of compound **5**,[28] a ClO_4^- anion is placed in the vicinity of copper(I) with a distance ($Cu-O_{av}$) of 2.80(1) Å, implying a weak interaction of ClO_4^- with copper in the solid state. It has also been found that a ClO_4^- anion interacts with copper(I) in $[Cu(bipy)(CH_2{=}CHPh)(ClO_4)]$ (bipy = 2,2′-bipyridine) [Cu–O 2.591(4) Å].[29] In the case of the copper(I)–bpen system in solution a close contact $Cu \cdots ClO_4^-$ is also suspected because there is a clear anion dependence of the species obtained as mentioned above. However, no vibrational confirmation of perchlorate co-ordination to copper in solution was observed. A PF_6^- anion has no co-ordination ability[30] and hence exerts no influence on the environment of the copper(I). The role of ClO_4^- is associated with the solubility of complex **4**, which is the kinetically preferred species; its insolubility results in precipitation, interfering with the progress of the reaction.

In the case of the PF_6^- salt, complex **1** precipitates as soon as the copper(I) salt and bpen are mixed. Complex **1** is insoluble in methanol. Thus, the ^1H NMR spectrum of the yellow filtrate was directly measured. It is similar to that of **4**, but δ_C is slightly different. Because there are no ClO_4^- anions, the solution



Scheme 1 (*i*) bpen, PF_6^-, CO; (*ii*) bpen, PF_6^-; (*iii*) bpen, ClO_4^-; (*iv*) bpen

species is considered to be $[\{Cu(\mu\text{-bpen})L_n\}_2][PF_6]_2$, where L denotes CH_3CN or solvent molecule or no co-ordination.* As a result, the participation of the counter anion is related to the formation of polymeric structures and polymeric **1** can be predominantly prepared by the appropriate selection of starting materials having non-interacting anions such as PF_6^-.

In conclusion, the formation of the polymeric complexes depends on the stability and the solubility of the low-molecular-weight precursor in addition to the requirements of their crystal packing. This is associated with the presence of co-ordinatively unsaturated copper(I) species, which can bind another co-ordinated bpen to give a linking system. In the copper(I)–bpen system, the use of an anion having no co-ordination ability results in polymeric complexes. Thus, the selection of the counter ion is also important in the synthesis of bpen–copper(I) complexes in the solid state.

All the yellow species in solution can readily react with CO, reversibly, to give a quite soluble species. When CO gas is bubbled into the solution the yellow colour disappears, indicative of the formation of an adduct because it has been demonstrated that on the addition of CO the m.l.c.t. band even for four- or five-co-ordinate species undergoes a blue shift to the UV region.[32] Proton NMR shifts reveal the co-ordination of pyridyl and olefin groups; δ_C = 0.40, 0.24, 0.26, 0.16 and 0.29 for H^2, H^3, H^4, H^5 and H^{11}, respectively. On this basis the species in solution is considered to be $[\{Cu(\mu\text{-bpen})(CO)L\}_2]^{2+}$ (L = CH_3CN or solvent). The carbonylated species is equilibrated with uncarbonylated species due to the lability of CO as regards copper(I). This is illustrated by the change in ^1H NMR signals on decarbonylation by purging CO with argon: the signals move continuously upfield and the signals for the two species are not separated. This means that the signals are averaged by a chemical exchange process. In the case of ethylene which is also a good π acid to copper,[29] δ_C = 0.17, 0.01, 0.07, 0.09 and 0.10 for H^2, H^3, H^4, H^5 and H^{11}, respectively. These smaller shifts than those for CO indicate that the affinity of ethylene for the copper(I) species is weaker than that of CO.

Acknowledgements

We thank Dr. H. Masuda for measurements of Raman spectra. This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

---

* The ^1H NMR signal of CH_3CN shows a slight co-ordination shift (<0.1 ppm).[31] At present it is difficult to determine whether CH_3CN is co-ordinated or not.

References

1 *Crystal Chemistry and Properties of Materials with Quasi-One-Dimensional Structures*, ed. J. Rouxel, D. Reidel, Dordrecht, 1986.
2 A. Amüller, P. Erk, G. Klebe, S. Hünig, J. U. V. Schutz and H.-P. Werner, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 740.
3 R. D. Willett, *Inorg. Chem.*, 1987, **26**, 3423; M. G. Kanatzidis and S. Huang, *J. Am. Chem. Soc.*, 1989, **111**, 760; G. Mercouri, M. G. Kanatzidis and P. Younbong, *J. Am. Chem. Soc.*, 1989, **111**, 3767.
4 *Advanced Inorganic Chemistry*, eds. F. A. Cotton and G. Wilkinson, Wiley-Interscience, New York, 1988, p. 755; B. J. Hathaway, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, Pergamon, London, 1988, vol. 15, p. 533.
5 M. G. B. Drew, D. A. Edwards and R. Richards, *J. Chem. Soc., Chem. Commun.*, 1973, 124; R. D. Mounts, T. Ogura, and Q. Fernando, *Inorg. Chem.*, 1974, **13**, 802; D. T. Cramer, *J. Phys. Chem.*, 1957, **61**, 1388; P. J. Fisher, N. E. Taylor and M. M. Harding, *J. Chem. Soc.*, 1960, 2303; C. K. Prout and P. M. Rust, *J. Chem. Soc. A*, 1969, 1520; C. Branden, *Acta Chem. Scand.*, 1967, **21**, 1000.
6 D. F. Shriver, *Inorg. Synth.*, 1979, **19**, 90.
7 M. Munakata, M. Maekawa, S. Kitagawa, M. Adachi and H. Masuda, *Inorg. Chim. Acta*, 1990, **167**, 181.
8 MULTAN 78, A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data, Universities of York and Louvain, 1978.
9 International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, vol. 4.
10 L. M. Engelhardt, C. Pakawatchai and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1985, 117; M. Munakata, S. Kitagawa, H. Shimono and H. Masuda, *Inorg. Chim. Acta*, 1989, **158**, 217.
11 T. N. Sorrell and D. L. Jameson, *J. Am. Chem. Soc.*, 1983, **105**, 6013; H. M. J. Hendriks, P. J. M. W. L. Birker, J. V. Rijin, G. C. Verschoor and J. Reedijk, *J. Am. Chem. Soc.*, 1982, **104**, 3607; M. J. Schilstra, P. J. M. W. L. Birker, G. C. Verschoor and J. Reedijk, *Inorg. Chem.*, 1982, **21**, 2637; J. E. O'Conner, G. A. Janusonis and E. R. Corey, *Chem. Commun.*, 1968, 445; I. D. Brown and J. D. Dunitz, *Acta Crystallogr.*, 1961, **14**, 480.
12 T. Yamaguchi and O. Lindqvist, *Acta Chem. Scand., Ser. A*, 1983, **37**, 685 and refs. therein.
13 A. V. Mühldorf, D. V. Engen, J. C. Warner and A. D. Hamilton, *J. Am. Chem. Soc.*, 1988, **110**, 6561.
14 A. H. Lewin, R. J. Michl, P. Ganis, U. Lepore and G. Avitabile, *J. Chem. Soc. Chem. Commun.*, 1971, 1400.
15 I. Csöregh, P. Kierkegaard and R. Norrestam, *Acta Crystallogr., Sect. B*, 1975, **31**, 314.
16 M. I. Bruce and A. P. P. Ostazewski, *J. Chem. Soc., Chem. Commun.*, 1972, 1124; M. R. Churchill, B. D. DeBoer, F. J. Rotella, O. M. Abu Salah and M. I. Bruce, *Inorg. Chem.*, 1975, **14**, 2051.
17 M. Pasquali, F. Marchetti and C. Floriani, *Inorg. Chem.*, 1978, **17**, 1684.
18 M. Pasquali, C. Floriani and A. G. Manfredotti, *J. Chem. Soc., Chem. Commun.*, 1978, 921; *Inorg. Chem.*, 1980, **19**, 1191.
19 R. R. Gagne, R. P. Kreh, J. A. Dodge, R. E. Marsh and M. McCool, *Inorg. Chem.*, 1982, **21**, 254.
20 M. Pasquali, C. Floriani, A. G. Manfredotti and C. Guastini, *J. Chem. Soc., Chem. Commun.*, 1979, 197; *Inorg. Chem.*, 1980, **19**, 2525.
21 M. Pasquali, C. Floriani and A. G. Manfredotti, *Inorg. Chem.*, 1981, **20**, 3382.
22 M. Pasquali, P. Fiaschi, C. Floriani and P. F. Zanazzi, *J. Chem. Soc., Chem. Commun.*, 1983, 613.
23 *Chemisty of the Elements*, eds. N. N. Greenwood and A. Earnshaw, Pergamon, Oxford, 1984, p. 325.
24 G. Doyle, K. A. Eriksen and D. V. Engen, *Inorg. Chem.*, 1983, **22**, 2892.
25 K. Ogawa, H. Suzuki, T. Sakurai, K. Kobayashi, A. Kira and K. Toriumi, *Acta Crystallogr., Sect. C*, 1988, **44**, 505.
26 *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*, eds. K. D. Karlin and J. Zubieta, Adenine, New York, 1983, p. 473.
27 M. Munakata, S. Kitagawa, H. Shimono and H. Masuda, *Inorg. Chim. Acta*, 1989, **158**, 217.
28 M. Munakata, S. Kitagawa, H. Shimono, T. Emori and H. Masuda, *J. Chem. Soc., Chem. Commun.*, 1987, 1798.
29 H. Masuda, K. Machida, M. Munakata, S. Kitagawa and H. Shimono, *J. Chem. Soc., Dalton Trans.*, 1988, 1907.
30 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
31 S. Kitagawa and M. Munakata, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 2743.
32 S. Kitagawa and M. Munakata, *Inorg. Chem.*, 1981, **20**, 2261.

Received 1st March 1991; Paper 1/00970B