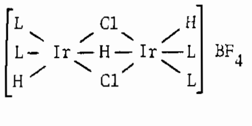
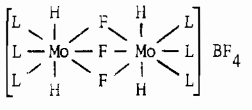


3 (L = PPh$_3$)

hydride protons, like those of **1**, relax relatively rapidly. The data also show there is a difference between the relaxation times of the bridging and terminal hydrides. Possibly the ligand protons make a greater contribution to the relaxation of the latter.[9]

Our final example[2c] is $[(\mathrm{MoH_2(PMePh_2)_3})_2(\mu\text{-F})_3]\mathrm{BF_4}$ (**4**). Here the hydride proton relaxes faster (0.21 s) than any of the hydride protons in **1**–**3**, about 2 times as fast as the PMe protons and about 8 times as fast as the PC$_6$H$_5$ protons in **4**.



4 (L = PMePh$_2$)

We conclude that hydrides can indeed have a relaxation time different, either faster or slower, from those of other protons in a metal complex. This can lead to integration anomalies, but careful control of the experimental conditions (in particular a sufficiently long delay time) can alleviate these problems. Satisfactory integrals for **1**–**4** (theoretical ±1%) can be obtained at 490 MHz with a 5° pulse and 4-s delay time.

Experimental Section

Complexes **1**,[3] **2**,[4] **3**,[8] and **4**[2c] were obtained by literature methods. T_1 measurements were made at 490 MHz as described in Table II. All relaxation times are the result of a computer fitting of ca. 20 observations over the range of $0.1T_1$–$5T_1$ and allowing 30-s recovery time between acquisitions. In all cases strict first-order behavior was observed in the recovery of magnetization. Integration measurements on **1** were made at 90 MHz on an FX-90 Q instrument (see Table I).

Acknowledgment. We thank the Army Research Office for funding, Dr. G. Hlatky for a sample of **4**, A. Habib for a sample of **2**, and Professors K. G. Caulton, J. W. Faller, J. Prestegard, and K. Zilm for helpful comments.

Registry No. **1**, 75494-79-0; **2**, 22276-37-5; **3**, 96149-07-4; **4**, 87656-09-5.

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(9) Chemical shift anisotropy (CSA) does not contribute significantly to relaxation, because we find that T_1 for MH is no slower for **3** at 250 MHz than at 490 MHz; any CSA contribution[7] should vary as H_0^2. Efficient dipolar relaxation is therefore presumably the factor responsible for the rapid relaxation observed.

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Lewis Base Adducts of Group 11 Metal Compounds.† 14. Crystal Structures of the 1:2 Binuclear Adducts of Copper(I) Halides with Some 2(4)-Mono- and Dimethyl-Substituted Pyridine Bases and Quinoline

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Coinage metal halides, MX, may, in many cases, be recrystallized from solution in nitrogen base, L, to yield adducts, MXL$_n$. Where the ligand bulk of the base is small, *n* may be as high as 3, as has been demonstrated structurally for nitrogen rather than phosphine base complexes, by structure determination of the adducts obtained by recrystallizing copper(I) chloride, bromide, and iodide from 3-methylpyridine.[2] With increased steric bulk, as when, e.g., 2- rather than 3-methylpyridine is used, *n* is reduced to 2, leading, in the case of copper(I) iodide with 2-methylpyridine, to the formation of a bis(μ-halo)-bridged dimer[3] in which the coordination number of the metal remains at 4 but now comprises two halogen and two base ligands, rather than yielding a monomeric species with a 1:3 copper halide to ligand base ratio. With a further increase in steric bulk of the base, as e.g., to 2,6-dimethylpyridine, the coordination number attainable by the metal is reduced to 3 as in, e.g., mononuclear iodobis(2,6-dimethylpyridine)copper(I) on the one hand[3] from neat base or binuclear bis(μ-iodo)bis(2,6-dimethylpyridine)dicopper(I) from acetone solution on the other.[4] In the latter sterically uncrowded species, the copper–copper distance is very short (2.586 (5) Å); as steric crowding and coordination number about the copper rise, the copper–copper distance is observed to increase, being 2.866 (3) Å in the binuclear 1:2 adduct of copper(I) iodide with quinoline[3] and 3.083 (3) Å in the adduct with 2-methylpyridine.[3] For the 1:1 adducts of copper(I) chloride, bromide, and iodide with 2,9-dimethyl-1,10-phenanthroline, a hiatus is observed, the chloride being mononuclear with a three-coordinate copper atom and the bromide and iodide binuclear with four-coordinate copper.[5] Elsewhere, we show chloro-, bromo- and iodobis(2,6-dimethylpyridine)copper(I) to be mononuclear;[2] the iodo/2-methylpyridine analogue is binuclear, but with the longest copper–copper distance (3.083 (3) Å) hitherto observed in complexes of that type. Given the nature of the result with the 2,9-dimethyl-1,10-phenanthroline adducts, and the meager structural information on analogous chloride and bromide systems, we considered it not unlikely that a similar discontinuity might be observed throughout the copper(I) chloride, bromide, and iodide series of 1:2 adducts with 2-methylpyridine or a similar base, providing an opportunity to examine more closely the factors leading to dissociation in complexes with monodentate ligands of this type. Accordingly, we report in this paper the synthesis and structure determinations of the 1:2 copper chloride and bromide adducts with 2-methylpyridine (**1** and **2**) (the iodide has been already determined),[3] the chloride, bromide, and iodide series with 2,4-dimethylpyridine (**3**–**5**), and the chloride and bromide adducts with quinoline, (**6** and **7**), the iodide having already been determined[3] to display an intermediate Cu···Cu distance (see above).

Experimental Section

In the work described in this and the following paper, complexes were prepared in all cases by recrystallization under argon of the parent halide from its solution in hot pure base as off-white or fluorescent crystals; because of the air-sensitive nature of the compounds and the readiness with which base is readily lost in compounds such as these with high copper(I) halide:ligand base ratios, their characterization depends primarily on the crystallographic work.

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† In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) (a) Griffith University. (b) University of Western Australia.

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0020-1669/85/1324-1950$01.50/0

Table I. Crystal Data

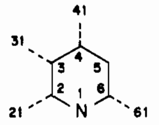
	compd						
	1	2	3	4	5	6	7
formula	CuCl(2-Mepy)$_2$ ($C_{12}H_{14}ClCuN_2$)	CuBr(2-Mepy)$_2$ ($C_{12}H_{14}BrCuN_2$)	CuCl(2,4-Me$_2$py)$_2$ ($C_{14}H_{18}ClCuN_2$)	CuBr(2,4-Me$_2$py)$_2$ ($C_{14}H_{18}BrCuN_2$)	CuI(2,4-Me$_2$py)$_2$ ($C_{14}H_{18}CuIN_2$)	Cu$_2$Cl$_2$(quin)$_4$·quin ($C_{45}H_{35}Cl_2Cu_2N_5$)	Cu$_2$Br$_2$(quin)$_4$·quin ($C_{45}H_{35}Br_2Cu_2N_5$)
M_r	285.3	329.7	313.3	357.8	404.9	843.8	932.8
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic	monoclinic	monoclinic
space gp	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)	$P\bar{1}$ (C_i^1, No. 2)	$P2_1/n$ (C_{2h}^5, No. 14)	$P2_1/n$ (C_{2h}^5, No. 14)
a/Å	9.563 (4)	9.591 (3)	10.229 (8)	10.363 (9)	10.784 (9)	23.96 (3)	24.01 (2)
b/Å	9.090 (4)	9.185 (4)	9.084 (5)	9.149 (7)	9.263 (7)	7.323 (6)	7.431 (6)
c/Å	8.906 (4)	9.041 (5)	8.270 (5)	8.259 (6)	8.259 (5)	23.06 (2)	23.12 (2)
α/deg	108.29 (3)	108.57 (4)	105.45 (4)	104.88 (6)	104.57 (5)		
β/deg	117.26 (3)	117.76 (3)	96.24 (5)	94.75 (6)	93.89 (6)	106.82 (8)	106.97 (6)
γ/deg	95.04 (3)	94.38 (3)	92.36 (5)	94.73 (6)	97.51 (6)		
V/Å^3	628.3 (4)	643.7 (5)	734.3 (8)	750 (1)	787.3 (9)	3873 (6)	3945 (5)
D_{calcd}/g cm^{-3}	1.51	1.70	1.54	1.59	1.83	1.45	1.57
Z	2	2	2	2	2	4	4
F(000)	292	328	324	360	396	1728	1872
μ_{Mo}/cm^{-1}	18.5	46.5	15.8	40.0	33.1	13.2	33.1
specimen mm	0.36 × 0.10 × 0.09	0.30 × 0.10 × 0.06	0.40 × 0.16 × 0.12	0.45 × 0.20 × 0.25	0.40 × 0.18 × 0.12	spheroid, ~0.2	spheroid, ~0.25
range A^a	1.14–1.21	^{b}	1.19–1.31	^{b}	1.44–1.81		
$2\theta_{max}$/deg	50	50	50	60	60	40	40
N	2242	2209	2415	3942	4242	3613	3291
N_o	1442	1596	1808	2522	3217	1885^a	2437^a
R	0.034	0.043	0.041	0.034	0.051	0.078	0.059
R'	0.038	0.050	0.053	0.038	0.107	0.085	0.070

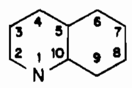
^{a} Including 680 calculated greater than 3σ (510 for bromide); no absorption correction. ^{b} Not recorded.

Crystallography

For the crystallographic work, specimens were routinely transferred wet with mother liquor to capillaries and sealed under an argon atmosphere; melting points and densities were not determined. The general procedure adopted for structure determination in this and the following paper is as follows; in each case, data specific to each compound are summarized in Table I.

General Data. Unique data sets were measured within a present $2\theta_{max}$ limit at 295 K using Syntex $P\bar{1}$ and $P2_1$ four-circle diffractometers fitted with monochromatic Mo Kα radiation sources (λ = 0.71069 Å) and operating in conventional $2\theta/\theta$ scan mode (variable scan speed 2.4° min^{-1} minimum; background time 0.5 times total scan time).[6] N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered observed and used in the full-matrix least-squares refinement (minimizing $\sum(w\|F_o\| - \|F_c\|^2)$ after analytical absorption correction and solution of the structure by vector methods. Anisotropic thermal parameters were refined for the non-hydrogen atoms; except in **1**, where $(x, y, z)_H$ were refined, $(x, y, z, U_{iso})_H$ were constrained at estimated values. Residuals on $|F|$ quoted at convergence are conventional R and R', reflection weights being $(\sigma^2(F_o) + 0.0005(F_o)^2)^{-1}$. No problems with extinction were encountered. Neutral complex scattering factors were used;[7] computation used the X-RAY 76 program system[8] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Non-hydrogen atom labeling in the ligands is as follows:





Refined atom coordinates (normally non-hydrogen atoms) are given in Tables II–IV; standard deviations are given parenthetically throughout.

Abnormal Features. In complex **1**, the precision of the data permitted refinement of all hydrogen atom positional parameters; these are recorded in the main text. Although the data:parameter ratio is not high, the resulting geometries are reasonable and the results credible.

For complexes **6** and **7**, the accessible data were limited, probably, with the benefit of hindsight, as a consequence of the very high thermal motion on the ligands and, in particular, on the molecular of solvent that accompanies each dimer. The solvent is very poorly defined, would not refine satisfactorily (typical $\sigma(x, y, z)_{C,N}$ ($\times 10^3$) being (1, 6, 1)), and was constrained after a couple of initial least-squares cycles to approximately define its position. In order to optimize the information obtained from the marginal quality data, reflections for which $I_{calcd} > 3\sigma(I)$ were included in the refinement. In **6**, anisotropic thermal parameters were refined for Cu, Cl, N; for the other non-hydrogen atoms, the isotropic form was refined. In both **6** and **7** U_{iso} for the solvent non-hydrogen atoms were constrained at idealized estimates.

Discussion

In **1–5**, the structure determination establishes/confirms the stoichiometry of the species in question as that of an adduct with a 1:2 copper(I) halide:base ratio. In all cases, the complexes crystallize in a triclinic cell. Compounds **1** and **2** are isomorphous with each other, but *not* with the previously studied iodide analogue, and have been refined with the same coordinate settings; compounds **3–5** are isomorphous with each other and have similarly been refined with similar settings. In all cases, the asymmetric unit of the structure is one $XCuL_2$ formula unit, but the basic structural unit is a bis(μ-halo)-bridged dimer $[L_2CuX_2CuL_2]$,

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(6) Dampawan, P.; Huntrakul, C.; Raston, C. L.; Reutrakul, V.; White, A. H. *J. Sci. Soc. Thailand* **1977**, *3*, 14.

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Table II. Atom Coordinates for 1 and 2

	1 (X = Cl)			2 (X = Br)		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.35807 (7)	0.36301 (7)	0.31516 (7)	0.3489 (1)	0.3577 (1)	0.3028 (1)
X	0.6209 (1)	0.3488 (1)	0.5381 (1)	0.62615 (8)	0.34120 (7)	0.54080 (9)
			Ligand A			
N(1)	0.3733 (4)	0.3141 (4)	0.0858 (4)	0.3680 (6)	0.3118 (6)	0.0793 (7)
C(2)	0.2873 (5)	0.3609 (5)	−0.0504 (5)	0.2827 (8)	0.3598 (8)	−0.0546 (9)
C(21)	0.1593 (7)	0.4395 (8)	−0.0403 (8)	0.1541 (10)	0.4381 (10)	−0.0465 (10)
H(21a)	0.198 (7)	0.535 (7)	0.062 (8)	0.205	0.532	0.069
H(21b)	0.104 (7)	0.386 (7)	−0.002 (8)	0.076	0.368	−0.045
H(21c)	0.088 (7)	0.446 (7)	−0.146 (8)	0.091	0.477	−0.137
C(3)	0.3167 (6)	0.3369 (6)	−0.1938 (6)	0.3142 (10)	0.3359 (10)	−0.1954 (10)
H(3)	0.255 (5)	0.381 (5)	−0.274 (6)	0.256	0.373	−0.290
C(4)	0.4323 (6)	0.2625 (7)	−0.2006 (7)	0.4288 (10)	0.2617 (11)	−0.2007 (10)
H(4)	0.457 (6)	0.249 (6)	−0.282 (7)	0.454	0.241	−0.297
C(5)	0.5168 (6)	0.2105 (7)	−0.0647 (7)	0.5132 (9)	0.2082 (11)	−0.0666 (11)
H(5)	0.591 (6)	0.159 (6)	−0.063 (7)	0.595	0.149	−0.072
C(6)	0.4852 (5)	0.2382 (5)	0.0751 (6)	0.4800 (8)	0.2369 (9)	0.0712 (9)
H(6)	0.546 (5)	0.210 (5)	0.180 (6)	0.541	0.201	0.168
			Ligand B			
N(1)	0.1634 (4)	0.2469 (4)	0.3097 (4)	0.1579 (6)	0.2436 (6)	0.3010 (7)
C(2)	0.1322 (5)	0.0938 (5)	0.2895 (6)	0.1291 (8)	0.0905 (8)	0.2804 (9)
C(21)	0.2407 (8)	−0.0024 (7)	0.2548 (10)	0.2354 (10)	−0.0046 (9)	0.2398 (13)
H(21a)	0.361 (7)	0.048 (7)	0.336 (8)	0.350	0.047	0.338
H(21b)	0.219 (8)	−0.041 (8)	0.148 (8)	0.229	−0.007	0.131
H(21c)	0.241 (7)	−0.099 (8)	0.272 (9)	0.222	−0.115	0.227
C(3)	−0.0001 (6)	0.0279 (6)	0.2991 (7)	0.0018 (9)	0.0235 (9)	0.2944 (11)
H(3)	−0.008 (6)	−0.076 (6)	0.288 (7)	−0.018	−0.084	0.286
C(4)	−0.1001 (6)	0.1169 (7)	0.3253 (8)	−0.0967 (9)	0.1128 (10)	0.3278 (11)
H(4)	−0.183 (6)	0.071 (6)	0.332 (7)	−0.183	0.070	0.342
C(5)	−0.0693 (6)	0.2710 (6)	0.3434 (7)	−0.0698 (8)	0.2683 (9)	0.3453 (9)
H(5)	−0.138 (5)	0.341 (5)	0.364 (6)	−0.141	0.334	0.364
C(6)	0.0634 (5)	0.3327 (6)	0.3362 (6)	0.0585 (7)	0.3279 (8)	0.3323 (9)
H(6)	0.090 (5)	0.438 (5)	0.352 (6)	0.079	0.439	0.346

Table III. Non-Hydrogen Atom Coordinates for 3–5

	3 (X = Cl)			4 (X = Br)			5 (X = I)		
atom	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
Cu	−0.13718 (6)	0.05081 (6)	0.00717 (6)	−0.13845 (5)	0.05116 (5)	0.00337 (5)	−0.1350 (2)	0.0462 (1)	0.0009 (2)
X	0.0454 (1)	0.1577 (1)	−0.1111 (1)	0.05741 (4)	0.16675 (4)	−0.11713 (4)	0.06573 (7)	0.17858 (7)	−0.12274 (8)
					Ligand A				
N(1)	−0.1604 (3)	0.2153 (4)	0.2192 (4)	−0.1627 (3)	0.2180 (3)	0.2111 (3)	−0.1654 (8)	0.2149 (8)	0.2026 (10)
C(2)	−0.1937 (4)	0.3581 (5)	0.2222 (5)	−0.1951 (3)	0.3574 (4)	0.2075 (4)	−0.2006 (9)	0.3490 (11)	0.1929 (12)
C(21)	−0.2298 (6)	0.3920 (6)	0.0552 (6)	−0.2280 (5)	0.3845 (6)	0.0391 (6)	−0.2328 (13)	0.3746 (14)	0.0263 (16)
C(3)	−0.1948 (4)	0.4704 (4)	0.3736 (4)	−0.1959 (3)	0.4717 (4)	0.3557 (4)	−0.2008 (11)	0.4659 (11)	0.3334 (13)
C(4)	−0.1576 (4)	0.4405 (4)	0.5276 (5)	−0.1634 (3)	0.4478 (4)	0.5109 (4)	−0.1684 (10)	0.4509 (10)	0.4947 (13)
C(41)	−0.1556 (4)	0.5609 (5)	0.6924 (5)	−0.1636 (5)	0.5701 (5)	0.6716 (5)	−0.1699 (14)	0.5746 (15)	0.6495 (16)
C(5)	−0.1214 (4)	0.2955 (5)	0.5216 (5)	−0.1295 (4)	0.3042 (4)	0.5125 (4)	−0.1332 (11)	0.3089 (13)	0.5047 (12)
C(6)	−0.1247 (4)	0.1876 (4)	0.3695 (5)	−0.1310 (4)	0.1956 (4)	0.3630 (4)	−0.1338 (11)	0.2015 (10)	0.3595 (13)
					Ligand B				
N(1)	−0.2679 (3)	−0.0538 (4)	−0.1975 (4)	−0.2682 (3)	−0.0520 (3)	−0.2000 (3)	−0.2685 (8)	−0.0500 (9)	−0.1963 (10)
C(2)	−0.3763 (4)	−0.1390 (5)	−0.1918 (5)	−0.3790 (4)	−0.1371 (4)	−0.1929 (4)	−0.3787 (11)	−0.1268 (15)	−0.1858 (14)
C(21)	−0.4001 (5)	−0.1593 (7)	−0.0228 (6)	−0.4058 (5)	−0.1561 (8)	−0.0243 (6)	−0.4060 (15)	−0.1323 (18)	−0.0096 (16)
C(3)	−0.4615 (4)	−0.2134 (6)	−0.3365 (6)	−0.4620 (4)	−0.2077 (5)	−0.3364 (5)	−0.4659 (11)	−0.1999 (19)	−0.3296 (16)
C(4)	−0.4341 (4)	−0.2012 (5)	−0.4930 (5)	−0.4335 (4)	−0.1986 (4)	−0.4933 (5)	−0.4365 (12)	−0.1894 (16)	−0.4884 (15)
C(41)	−0.5205 (6)	−0.2836 (8)	−0.6519 (7)	−0.5209 (5)	−0.2766 (9)	−0.6517 (7)	−0.5281 (15)	−0.2640 (27)	−0.6424 (19)
C(5)	−0.3210 (5)	−0.1149 (5)	−0.4980 (5)	−0.3182 (4)	−0.1142 (5)	−0.5001 (5)	−0.3238 (12)	−0.1082 (14)	−0.4984 (14)
C(6)	−0.2434 (4)	−0.0436 (5)	−0.3499 (5)	−0.2404 (4)	−0.0433 (4)	−0.3542 (4)	−0.2414 (11)	−0.0433 (12)	−0.3557 (13)

centrosymmetric about a crystallographic inversion center. In spite of the rather similar cell dimensions throughout and the centrosymmetric disposition of the dimer, the sets [**1**, **2**, $(ICuL_2)_2$] and [**3**, **4**, **5**] are not isomorphous. **1** and **2**, however, *are* isomorphous with the previously described 1:2 adduct of silver(I) bromide with 2-methylpyridine[9] and are presented in a compatible setting; a cell contents figure is given in the earlier publication, together with a molecular projection normal to the Ag_2Br_2 plane. In the present report, we, therefore, present only a cell contents figure and molecular projection for **4** (Figure 1) as representative of the series **3**–**5**. For **6** and **7** the structure determination establishes the stoichiometry of the complex to be the 1:2 adduct, again as a dimer, together with a molecule of solvent present with each dimer. It is of interest to note that a rather similar packing disposition occurs in the iodide, already studied elsewhere, so that it also occurs as a solvate, but with *two* solvent molecules per dimer. We also note the postulation elsewhere[10] of adducts of the stoichiometry of **3** and **4** as monomers.

Molecular $N_2CuX_2CuN_2$ core parameters are given in Table

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[9] Healy, P. C.; Mills, N. K.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1985**, 111.

[10] Goher, M. A. S. *Acta Chim. Acad. Sci. Hung.* **1979**, *99*, 307.

Table IV. Non-Hydrogen Atom Coordinates for 6 and 7

	6 (X = Cl)			7 (X = Br)		
atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu(1)	0.4396 (1)	0.1358 (5)	0.3031 (1)	0.44064 (8)	0.1374 (3)	0.30216 (8)
Cu(2)	0.5589 (1)	0.1567 (4)	0.2742 (1)	0.55895 (8)	0.1478 (3)	0.27003 (8)
X	0.5347 (2)	0.3417 (8)	0.3470 (2)	0.53497 (6)	0.3436 (2)	0.34702 (6)
X′	0.4776 (2)	−0.0570 (8)	0.2405 (2)	0.47494 (7)	−0.0711 (2)	0.23340 (7)
Ligand 1A						
N(1A1)	0.3810 (7)	0.308 (2)	0.2518 (7)	0.3796 (6)	0.301 (2)	0.2488 (5)
C(1A2)	0.398 (1)	0.475 (4)	0.243 (1)	0.3927 (6)	0.465 (3)	0.2398 (7)
C(1A3)	0.364 (1)	0.602 (3)	0.205 (1)	0.3559 (9)	0.589 (2)	0.2007 (8)
C(1A4)	0.309 (1)	0.558 (3)	0.171 (1)	0.3024 (10)	0.529 (3)	0.1696 (8)
C(1A5)	0.232 (1)	0.315 (4)	0.144 (1)	0.2289 (10)	0.289 (3)	0.1466 (8)
C(1A6)	0.214 (1)	0.141 (4)	0.155 (1)	0.2141 (9)	0.120 (4)	0.1575 (11)
C(1A7)	0.252 (1)	0.024 (4)	0.194 (1)	0.2539 (11)	0.008 (3)	0.1972 (10)
C(1A8)	0.305 (1)	0.074 (4)	0.226 (1)	0.3080 (8)	0.066 (3)	0.2265 (7)
C(1A9)	0.326 (1)	0.252 (3)	0.219 (1)	0.3253 (9)	0.241 (2)	0.2175 (7)
C(1A10)	0.289 (1)	0.377 (3)	0.178 (1)	0.2859 (8)	0.352 (3)	0.1765 (7)
Ligand 1B						
N(1B1)	0.4372 (7)	−0.021 (3)	0.3746 (7)	0.4371 (5)	−0.016 (2)	0.3729 (6)
C(1B2)	0.458 (1)	−0.187 (4)	0.378 (1)	0.4561 (8)	−0.183 (3)	0.3775 (7)
C(1B3)	0.465 (1)	−0.298 (4)	0.430 (1)	0.4615 (8)	−0.296 (3)	0.4273 (10)
C(1B4)	0.447 (1)	−0.242 (3)	0.476 (1)	0.4456 (8)	−0.230 (3)	0.4757 (8)
C(1B5)	0.409 (1)	0.017 (4)	0.523 (1)	0.4096 (8)	0.024 (3)	0.5218 (8)
C(1B6)	0.387 (1)	0.196 (5)	0.520 (1)	0.3889 (11)	0.192 (3)	0.5158 (10)
C(1B7)	0.382 (1)	0.295 (5)	0.463 (2)	0.3851 (12)	0.298 (3)	0.4640 (11)
C(1B8)	0.399 (1)	0.214 (4)	0.416 (1)	0.3989 (8)	0.224 (3)	0.4172 (8)
C(1B9)	0.422 (1)	0.039 (3)	0.423 (1)	0.4200 (7)	0.049 (2)	0.4208 (7)
C(1B10)	0.426 (1)	−0.060 (3)	0.475 (1)	0.4247 (7)	−0.055 (3)	0.4741 (7)
Ligand 2A						
N(2A1)	0.5536 (6)	0.322 (2)	0.1996 (7)	0.5547 (5)	0.306 (2)	0.1955 (5)
C(2A2)	0.535 (1)	0.487 (4)	0.201 (1)	0.5369 (6)	0.476 (3)	0.1937 (7)
C(2A3)	0.526 (1)	0.613 (3)	0.152 (1)	0.5290 (7)	0.590 (2)	0.1429 (9)
C(2A4)	0.537 (1)	0.559 (3)	0.101 (1)	0.5405 (8)	0.528 (3)	0.0945 (8)
C(2A5)	0.573 (1)	0.309 (4)	0.046 (1)	0.5751 (8)	0.279 (3)	0.0420 (8)
C(2A6)	0.593 (1)	0.133 (4)	0.045 (1)	0.5952 (10)	0.110 (3)	0.0439 (9)
C(2A7)	0.601 (1)	0.025 (4)	0.095 (1)	0.6018 (8)	0.007 (3)	0.0941 (11)
C(2A8)	0.588 (1)	0.082 (4)	0.148 (1)	0.5875 (8)	0.069 (3)	0.1449 (8)
C(2A9)	0.566 (1)	0.261 (3)	0.148 (1)	0.5665 (7)	0.244 (3)	0.1439 (8)
C(2A10)	0.557 (10)	0.379 (3)	0.097 (1)	0.5600 (7)	0.351 (3)	0.0926 (8)
Ligand 2B						
N(2B1)	0.6258 (6)	−0.024 (2)	0.3066 (6)	0.6277 (7)	−0.026 (2)	0.3057 (5)
C(2B2)	0.615 (1)	−0.196 (3)	0.324 (1)	0.6179 (8)	−0.195 (3)	0.3204 (8)
C(2B3)	0.657 (1)	−0.329 (3)	0.344 (1)	0.6590 (10)	−0.323 (3)	0.3439 (8)
C(2B4)	0.712 (1)	−0.282 (4)	0.351 (1)	0.7148 (11)	−0.284 (3)	0.3509 (9)
C(2B5)	0.787 (1)	−0.055 (4)	0.341 (1)	0.7871 (10)	−0.053 (4)	0.3397 (11)
C(2B6)	0.798 (1)	0.106 (4)	0.323 (1)	0.7983 (10)	0.117 (4)	0.3233 (11)
C(2B7)	0.756 (1)	0.247 (4)	0.302 (1)	0.7543 (11)	0.239 (3)	0.3031 (9)
C(2B8)	0.698 (1)	0.198 (3)	0.298 (1)	0.6971 (9)	0.199 (3)	0.2965 (8)
C(2B9)	0.684 (1)	0.024 (3)	0.314 (1)	0.6843 (10)	0.017 (3)	0.3131 (6)
C(2B10)	0.729 (1)	−0.108 (3)	0.336 (1)	0.7299 (10)	−0.108 (3)	0.3367 (8)
Solvent (See Text)						
C,N(1)	0.248	0.911	0.524	0.248	0.892	0.521
C(2)	0.292	0.751	0.542	0.291	0.741	0.542
C(3)	0.278	0.592	0.519	0.281	0.575	0.521
C(4)	0.241	0.485	0.482	0.236	0.482	0.481
C(5)	0.152	0.463	0.414	0.151	0.508	0.417
C(6)	0.108	0.622	0.396	0.117	0.825	0.420
C(7)	0.113	0.804	0.415	0.112	0.659	0.403
C(8)	0.166	0.894	0.458	0.164	0.922	0.463
C(9)	0.197	0.775	0.479	0.200	0.781	0.480
C(10)	0.196	0.603	0.459	0.198	0.616	0.461

V, together with those of related compounds; further comparisons of the CuX_2Cu geometries with those of compounds of different stoichiometry are available in Table VI. For consideration of the molecular geometries, the isomorphous **3**–**5** series represents the most useful starting point. Consideration of Table V shows that, without exception, the core parameters vary monotonically throughout the series. Moreover, there is no series disagreement between those principal stereochemical parameters that might be equivalent on symmetry considerations, e.g., the four N–Cu–X angles γ, γ', δ, δ'. One notes, however, the discrepancy, consistent across the series, between the deviations of the copper atom from the two ligand planes and also between the dihedral angles of the latter to the Cu_2X_2 plane. The copper–nitrogen distance increase is only slight and is at a low level of significance from **3** to **5**; this variation, however, is consistently reproduced in the 2-methylpyridine series. The angle between these two bonds decreases, rather markedly and suddenly, on passing from bromide to iodide **4** to **5**, while the X–Cu–X angle increases in parallel fashion. Changes in both of these angles are the converse of expectations founded on electron pair repulsion theory, whereby the bonding

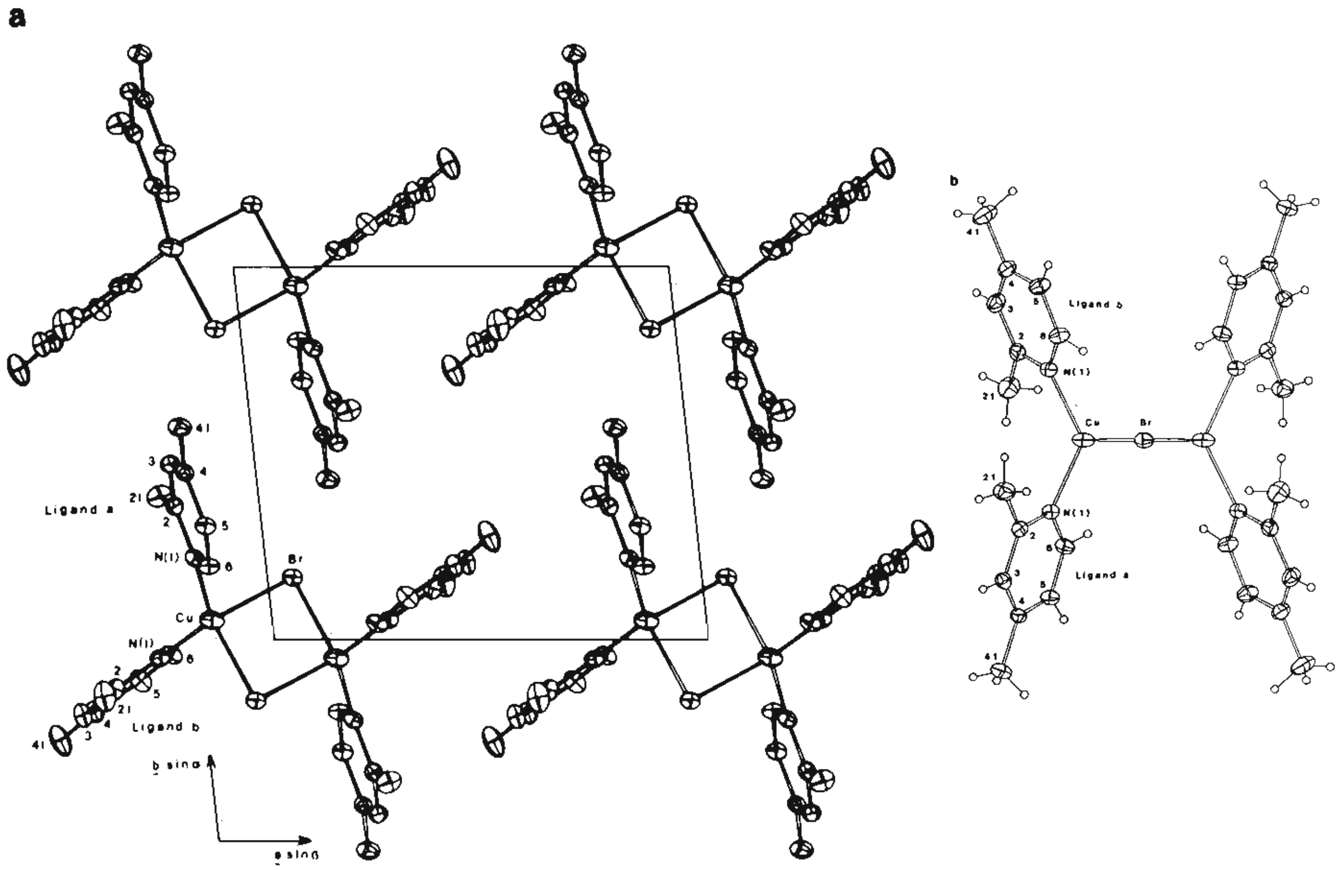


Figure 1. (a) Unit-cell contents of **4** projected down *c*. 20% thermal ellipsoids are shown for the non-hydrogen atoms. (b) Single dimer of **4** projected through the bisector of the copper–copper line in the Cu_2Br_2 plane. The rear bromine atom is masked.

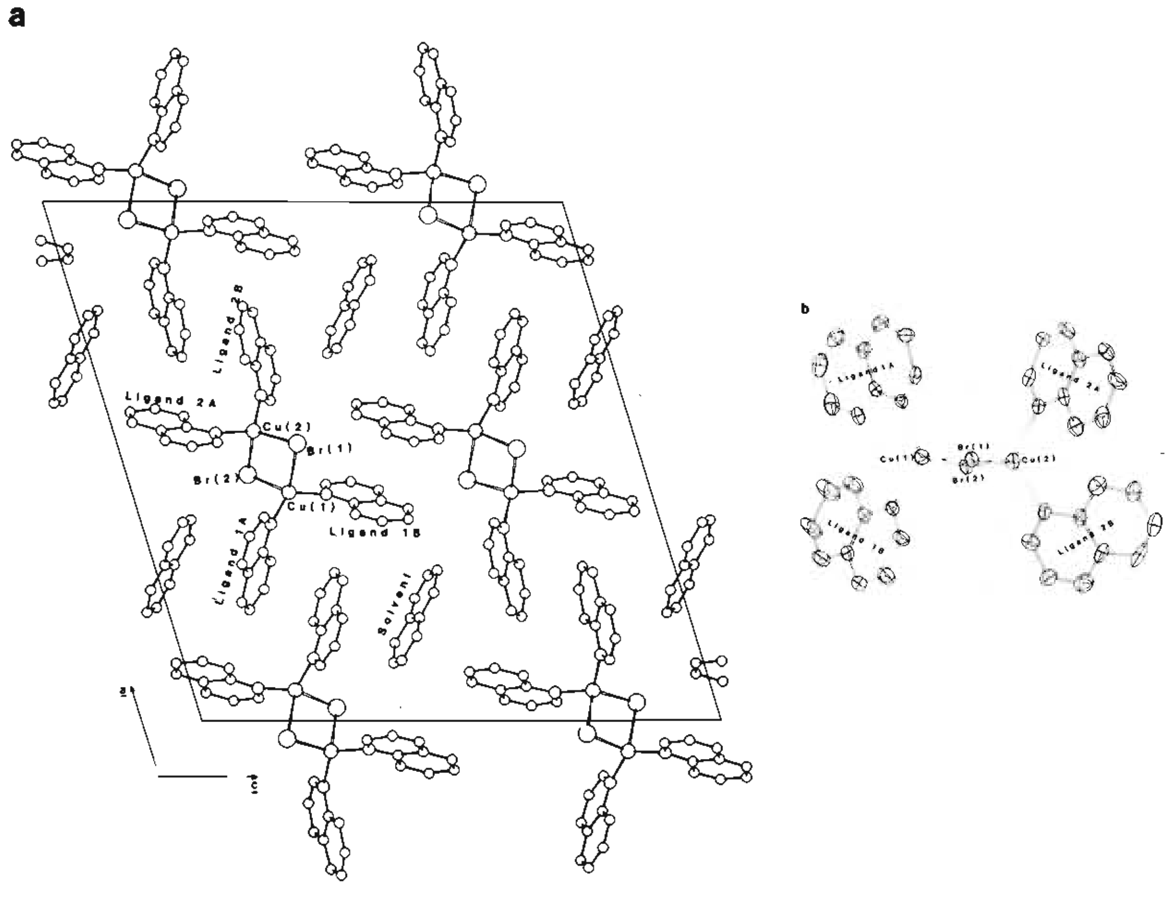
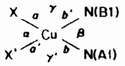


Figure 2. (a) Unit-cell contents of **7** projected down *b*. (b) Single dimer of **7** projected in the Cu_2Br_2 plane.

Table V. $Cu_2X_2N_4$ Core Geometries[a]

	L = 2-Mepy			L = 2,4-Me_2py			L = quin					L = 2-Etpy	L = 3,5-Me_2py
	Cl (1)	Br (2)	*I*	Cl (3)	Br (4)	I (5)	Cl (6)		Br (7)		*I*	*I*	*I*
a	2.433 (2)	2.581 (2)	2.714 (3)	2.478 (2)	2.598 (2)	2.732 (3)	2.675 (6)	2.357 (7)	2.680 (3)	2.493 (3)	2.668 (2)	2.720 (1)	2.6588 (8)
a'	2.476 (2)	2.607 (2)	2.663 (3)	2.459 (2)	2.583 (3)	2.696 (2)	2.381 (7)	2.443 (6)	2.524 (3)	2.537 (3)	2.657 (3)		
b	2.026 (4)	2.027 (7)	2.05 (1)	2.021 (3)	2.031 (3)	2.054 (8)	2.00 (2)	2.08 (2)	2.02 (1)	2.06 (1)	2.104 (5)	2.050 (5)	2.049 (7)
b'	2.031 (4)	2.030 (6)	2.06 (1)	2.025 (3)	2.030 (3)	2.034 (8)	2.02 (2)	2.05 (2)	2.01 (1)	2.07 (2)	2.076 (5)		2.067 (7)
c	3.769 (2)	3.962 (2)	4.407 (3)	3.925 (3)	4.157 (3)	4.428 (3)	3.806 (8)		4.033 (3)		4.487 (4)	4.492 (1)	4.591 (2)
d	3.145 (3)	3.351 (3)	3.083 (3)	2.995 (2)	3.091 (3)	3.140 (3)	3.121 (5)		3.140 (4)		2.866 (3)	3.067 (1)	2.683 (1)
e	3.661 (6) 3.779 (6)	3.732 (8) 3.836 (8)	4.191 (15) 4.015 (12)	3.676 (7) 3.757 (6)	3.718 (6) 3.830 (6)	3.867 (16) 4.015 (14)	3.591 (2) 3.46 (3)	3.54 (3) 3.45 (2)	3.70 (1) 3.59 (2)	3.69 (2) 3.55 (2)	3.825 (7) 3.851 (7)		
α	100.32 (5)	99.56 (5)	110.05 (6)	105.31 (6)	106.73 (5)	109.32 (7)	97.5 (2)	104.9 (2)	101.6 (1)	106.6 (1)	114.87 (5)	111.35 (3)	119.38 (5)
β	122.1 (1)	124.0 (2)	117.9 (2)	130.7 (1)	129.2 (1)	122.4 (4)	131.2 (7)	122.3 (7)	129.8 (6)	121.8 (6)	114.8 (2)	126.4 (2)	110.3 (2)
γ	114.2 (1)	112.2 (2)	106.5 (3)	104.4 (1)	105.3 (1)	107.3 (3)	103.5 (5)	116.0 (4)	103.9 (3)	113.8 (4)	108.1 (1)	108.9 (1)	106.87 (7)
γ'	111.9 (1)	111.5 (2)	104.6 (3)	104.4 (1)	105.2 (1)	107.3 (3)	110.0 (5)	105.0 (4)	107.2 (4)	104.3 (3)	104.1 (1)		
δ	103.1 (1)	103.2 (1)	107.9 (3)	104.5 (1)	103.4 (1)	103.0 (2)	104.2 (5)	106.6 (5)	105.8 (4)	107.3 (4)	107.1 (1)	100.7 (1)	106.67 (7)
δ'	103.4 (1)	103.8 (2)	109.7 (4)	105.3 (1)	105.4 (1)	107.1 (3)	105.3 (6)	99.8 (5)	105.3 (4)	101.4 (5)	108.1 (1)		
ϵ	79.68 (6)	80.45 (6)	69.95 (6)	74.69 (6)	73.27 (5)	70.69 (7)	76.4 (2)	80.6 (2)	74.65 (9)	76.71 (9)	65.14 (2)	68.65 (2)	60.62 (5)
θ_1	66.9	66.8	73.5	75.3	76.1	77.1	77.2	77.2	76.2	76.8	76.7	80.3	
θ_2	62.4	65.4	68.7	70.2	68.9	67.1	76.9	62.4	76.0	62.9	68.9		
χ_1	0.210	0.188	0.065	0.206	0.207	0.267	0.220	0.130	0.154	0.125	0.274	0.230	0.012
χ_2	0.120	0.157	0.123	0.067	0.040	0.100	0.236	0.045	0.254	0.085	0.135		0.091

[a] Atoms generated by the intradimer inversion center are primed. *I* values are drawn from ref 3. Distances are given in Å, and angles, in deg.



N(A1)–Cu–X = δ; X···X' = *c*; N(B1)–Cu–X' = δ'; Cu···Cu' = *d*; Cu–X–Cu' = ϵ; $C(H_3)$···X = *e*. θ_1 and θ_2 are the dihedral angles of ligand 1, 2 planes to the Cu_2X_2 plane. χ_1 and χ_2 are the deviations of the copper atom from ligand 1, 2 planes.

Table VI. M_2X_2 Geometries (Geometrical Parameters Given for the MX_2M Core for Those Adducts of the Copper(I) Halides with Monodentate Nitrogen and Phosphorus Bases for Which Structures Have Been Determined)

stoichiometry of M:X:L	M; X; L	M···M, Å	X···X, Å	X–M–X, deg	M–X–M, deg
1:1:1	Cu; Cl; $P(c\text{-}Hx)_3$ [a]	3.066 (1)	3.439 (3)	96.56 (7)	83.44 (7)
	Cu; I; 2,6-Me_2py [b]	2.586 (5)	4.414 (4)	118.9 (2), 119.3 (2)	60.1 (1), 61.2 (1)
	Cu; I; Me_4pip [c]	2.535 (9)	4.493 (7)	121.2 (3)	58.8 (2)
1:1:2	Cu; I; $P[(Ph)_3SO_2]$ [d]	3.576 (2)	4.109 (1)	98.16 (3), 96.95 (3)	83.40 (5), 79.99 (5)
	Cu; Cl; 2-Mepy	3.145 (3)	3.769 (2)	100.32 (5)	79.68 (6)
	Cu; Cl; 2,4-Me_2py	2.995 (3)	3.925 (3)	105.3 (1)	74.69 (6)
	Cu; Cl; quin	3.121 (5)	3.806 (8)	97.5 (2), 104.9 (2)	76.4 (2), 80.6 (2)
	Cu; Br; 2-Mepy	3.351 (3)	3.962 (3)	99.56 (5)	80.45 (6)
	Cu; Br; 2,4-Me_2py	3.091 (3)	4.157 (3)	106.73 (5)	73.27 (5)
	Cu; Br; quin	3.140 (4)	4.033 (3)	101.6 (1), 106.6 (1)	74.65 (9), 76.71 (9)
	Cu; Br; 2,9-Me_2phen [e]	3.097 (1)	3.876 (1)	102.77 (3)	77.23 (4)
	Cu; I; py [f]	2.699 (5)	4.536 (3)	117.8 (1)	61.6 (1), 61.4 (1)
	Cu; I; 3,5-Me_2py [c]	2.683 (1)	4.591 (2)	119.38 (5)	60.62 (5)
	Cu; I; 2-Mepy [c]	3.083 (3)	4.407 (3)	110.05 (6)	69.95 (6)
	Cu; I; 2,4-Me_2py	3.140 (3)	4.428 (3)	109.32 (7)	70.69 (7)
	Cu; I; quin (quin) [c]	2.866 (3)	4.487 (4)	114.87 (5)	65.14 (2)
	Cu; I; 2,9-Me_2phen [g]	3.024 (2)	4.276 (1)	109.48 (4)	70.52 (4)
	Ag; Br; 2-Mepy [h]	3.080 (5)	4.527 (5)	111.55 (8)	68.45 (8)
	Cu; Cl; 2-Mepy [i]	3.149 (2)	3.759 (2)	100.08 (5)	79.92 (5)
	Cu; Br; 2-Mepy [j]	3.349 (1)	3.962 (1)	99.6 (1)	80.4 (1)
	Cu; I; quin (CH_3CN) [k]	3.137 (2)	4.319 (2)	108.01 (4)	71.99 (6)

[a] Reference 14. [b] Reference 4. [c] Reference 3. [d] Reference 15. [e] Reference 5. [f] Reference 16. [g] Reference 5. [h] Reference 9. [i] Reference 17. [j] Reference 18. [k] Reference 19.

electrons in the metal–halogen bond would be expected to be located further from the metal as the halide size increases. One possible explanation is that electronegativity effects may be overriding expectations based on size, but an alternative explanation is that the geometry of the CuX_2Cu metal core comes to be dominated more extensively by halogen–halogen interactions as the halogen size increases. In none of the present examples (**3**–**5**) is the copper–copper distance so short as to suggest a van der Waals contact; a lower bound for the latter may perhaps be taken as 2.412 (1) Å from the structure of $[[2\text{-}(Me_3Si)_2C(Cu)C_5H_4N]_2]$.[11] By contrast, the iodine–iodine distance (4.4 Å) is close to the Pauling estimate of 4.3 Å[12] and is in keeping with numerous other such distances in such polynuclear systems; the relative discrepancy between the observed halogen...halogen contact distance and van der Waals estimate increases on passing from **5** to **4** to **3** (the Pauling bromine–bromine and chlorine–chlorine estimates are 3.9 and 3.6 Å, respectively)[12] with the angular geometry of the CuX_2Cu system becoming more nearly rectangular. Contacts between the ligand methyl substituents and the halogen atoms are summarized in Table V as *e*; it is seen that constraints of this type increase as the halogen size increases.

For the 2-methylpyridine adducts **1** and **2**, with the iodide a different triclinic phase,[3] trends are less clear-cut, with a more abrupt transition, sometimes not monotonic, occurring in parameter trends between bromide and iodide. In particular, the behavior of the CuX_2Cu core parameters is notably erratic, suggesting that the core is flexible in its response to the development of lattice forces, which may here be greater than usual as changing anion size results in an approach to a different phase. In the chloride and bromide, the halogen...halogen distances (*c* in Table V) are shorter than in their 2,4-dimethylpyridine counterparts by nearly 0.2 Å, a discrepancy that disappears on passing to the iodide; similar discrepancies, but of opposite sign, are found in the copper–copper distances. These differences are, of course, reflected substantially in the associated angular geometry, and particularly so in the ∠N–Cu–X angles, which are observed to divide into two pairs in the chloride and bromide (ca. 103 and 112°), a disparity that is lost in the iodide. As a further test of internal consistency (or lack of it), the iodide geometry may be compared with that of its 2-ethylpyridine counterpart.[3] Variations in distances between the two species are minor; greater disparities are observed in the angular geometry for which the 2-ethylpyridine derivative has a much closer counterpart in the chloride and bromide adducts of 2-methylpyridine. Copper atom deviations from the ligand planes (χ_n in Table V), which are nontrivial (>0.1 Å) generally, are relaxed to <0.13 Å for the 2-methylpyridine/iodide complex. The likely role of interactions between the 2-substituent on the pyridine ring and the halide in influencing the copper–copper distance is emphasized by reference to two other compounds. The high symmetry of the 3,5-dimethylpyridine/iodide adduct[3] may be ascribed to the lack of such contacts; moreover, in this compound, the Cu...Cu distance (*d* in Table V) has now collapsed to 2.683 (1) Å; although I...I has increased to 4.591 (2) Å, this increase is less dramatic, this distance generally lying at or just above 4.4 Å in all compounds regardless of substituent. Other parameters in the 3,5-dimethylpyridine compound change concomitantly with the copper–copper distance reduction, and copper atom deviations from the ligand planes are <0.1 Å. The I–Cu–I angle (α in Table V) is the largest observed, while N–Cu–N (β in Table V) is the smallest. The other relevant compound in this context is the silver(I) bromide/2-methylpyridine complex,[9] *isomorphous* with its copper(I) counterpart. In this complex, the silver(I)–silver(I) distance is 3.080 (5) Å, some 0.27 Å *less* than its anomalous copper(I) analogue. Ag–N = 2.32 (2) and 2.35 (2) Å, suggesting that in this complex the increased Ag–N distance has resulted in diminished substituent/halide interaction, in turn resulting in and permitting a *shortening* of the metal–metal distance in spite of an *increase* in metal radius in that complex. In parallel, in the silver(I) derivative, one notes an extension of the tendency for diminution in domination of the MX_2M geometry by the halide as the relative metal to halide size increases. In the silver complex, the Br...Br distance is 4.527 (5) Å, some 0.56 Å *longer* than in its copper counterpart. In regard to the relatively limited data available for phosphine base analogues (Table VI), we find considerable differences relative to the present system; these will be examined in more detail in a later paper.

The flexibility of the CuX_2Cu core in the presence of constraints resulting in long Cu...Cu distances is further emphasized by consideration of the quinoline derivatives, the chloride and bromide being isomorphous. In the latter derivatives, one independent molecule devoid of crystallographically imposed symmetry comprises the asymmetric unit. One copper–halogen distance only is consistently and abnormally long in both complexes; the degree of abnormality diminishes on passing from chloride to bromide, and in the iodide the molecular core has a crystallographically imposed inversion center with effectively equal Cu–I distances.

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(11) Papasergio, R. I.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1419.

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Cu...Cu in the latter complex is shorter than in the chloride or bromide and shorter than in the remainder of the other iodide complexes with 2-substituted ligands, presumably a consequence of a steric interaction varied by diminished carbon–carbon distance and constrained hydrogen position in the quinoline ligand. In chloride and bromide ∠N–Cu–N angles are particularly large. The precision of determination of ligand geometries is better in the iodide, and it is noted that Cu–N (2.104 (5), 2.076 (5) Å; mean 2.090 Å) distances are above the corresponding distances in those other structures where precision permits a confident estimate (CuCl, Br/2-methylpyridine, mean 2.029 Å; CuCl, -Br, -I/2,4-dimethylpyridine, mean 2.023, 2.031, 2.044 Å, respectively; CuI/3,5-dimethylpyridine, mean 2.058 Å), a result perhaps unexpected in view of the relatively minor differences in base strengths (pK_a for 2-methyl- and 2,4-dimethylpyridine and quinoline are 5.9, 6.8, and 4.9 respectively). It would, however, be expected that increased Cu–X bond order might be reflected in increased X–Cu–X angles, while Cu–N bond order and ∠N–Cu–N should diminish in parallel. While this is true of the quinoline/iodide complex, it does not appear to be the case for the 3,5-dimethylpyridine/iodide adduct.

The theme of the above discussion is that, in the present array of complexes of type $L_2CuX_2CuL_2$, the presence of a 2-substituent on the pyridine base L leads to steric interactions between the base substituent and the halide that have the effect of distorting the CuX_2Cu core so that the Cu...Cu distance is enlarged relative to its value in the complex unconstrained in this manner, i.e. by the presence of substituents of this type. For the iodide, the "unstrained" distance can be less than 2.7 Å (e.g., CuI/3,5-dimethylpyridine, 2.683 (1) Å), while in the "strained" state the maximum Cu...Cu observed is 3.140 (3) Å (CuI/2,4-dimethylpyridine (**5**)). Comparable unstrained values for chloride and bromide complexes are not, so far, available; evidence from the polymeric ···CuX_2CuX_2Cu··· anions suggests Cu...Cu estimates of ~2.7 and 2.85 Å, respectively.[13] The maximum strained values observed for the chloride are remarkably similar to the value observed in the iodide, being 3.145 (3) Å; for the bromide, as discussed already, the maximum observed in the copper(I) bromide/2-methylpyridine adduct (3.351 (3) Å) is extraordinarily long. Values obtained for the 2,4-dimethylpyridine and quinoline analogues of the latter (3.091 (3), 3.140 (3) Å) conform well to the chloride and iodide maxima. The odd bromide value, nevertheless, taken in conjunction with the considerable variability generally observed, e.g., 3.145 (3) and 2.995 (3) Å for the 2-methyl and 2,4-dimethylpyridine/chloride derivatives, suggests that in the "stretched" state steric control of the CuX_2Cu dimensions by the halide...halide van der Waals contact is lost, particularly as halide size decreases, and the core geometry becomes unstable. For three-coordinated copper in $NCuX_2CuX$ systems, minimum Cu...Cu is less, being 2.535 (9) Å (Table VI).

It remains to be finally demonstrated that 2-substituent–halide contacts are the effective cause of the CuX_2Cu core stretch. In the 3,5-dimethylpyridine/iodide adduct where there is no such substituent, it has already been noted that the complex is of high symmetry. In this complex contacts between the 2-carbons of the ligand rings with the iodine are snuggly disposed at 3.881 (5) and 3.877 (5) Å, close to the Pauling aromatic molecule/iodide van der Waals sum of 3.85 Å.[12] In the presence of 2-methyl substituents, rotation of the ligand about the Cu–N bond occurs; consideration of the 2-methyl/iodide contact distances of Table V suggests that this is done in such a manner as to maintain these distances at or near to the van der Waals halide...methyl sum (estimates: 3.8, 3.95, and 4.15 Å for chloride, bromide, and iodide, respectively).[12] Significantly, in a considerable number of cases, the value is *less* (by ~0.15 Å) rather than greater than the estimate. Interligand methyl–methyl contacts in all cases are considerably greater than their van der Waals sum. In the case of **1**, the observed hydrogen atom dispositions are such that within each methyl group H(21c) lies 0.2 Å out of the ligand plane and directed toward H(3), while H(21a,b) lie 0.6–0.7 Å to either side of the plane and H(3). The complexes of quinoline differ from the main pattern; consideration of the molecular projections shows a considerably different ligand disposition in which the substituent ring is oriented so that the 2-carbon of the pyridine ring, rather than the C_6 ring, contacts the halide at distances at or near the aromatic ring/halide contact estimate (3.5, 3.65, and 3.95 Å for chloride, bromide, and iodide, respectively).[12] The increased ∠N–Cu–N angles in the chloride and bromide complexes may be a consequence of the relatively awkward ligand disposition in these complexes, in which the ligand twist about the Cu–N bond is at its greatest; the more "normal" value of ∠N–Cu–N in the iodide together with the decrease in Cu...Cu in that complex presumably indicates some relaxation of strain.

Conclusion

The results of the present study show clearly the steric role of the halide and 2-methyl substituents in pyridine base complexes of copper(I) halides of stoichiometry $XCuL_2$; however, in spite of considerable variation in base profile, dissociation of the binuclear species into a monomer by this means has not yet been achieved.

Note Added in Proof. Recent work,[17-19] which has become available to us since the acceptance of this paper, describes the structure determinations of **1**,[17] **2**,[18] and $[CuI(quin)_2]_2CH_3CN$.[19] Bond length and angle data for the CuX_2Cu cores of these compounds have been included in Table VI for comparison. Data for **1** and **2** are in substantial agreement with the present work. There is a noticeable variation in the core *angular* geometry of quinoline and acetonitrile solvates of the $[CuI(quin)_2]_2$ dimer, emphasizing the ease with which parameters such as Cu···Cu distances can respond to minor changes in chemical environment.

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Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen positional parameters, distances and angles, least-squares planes, and observed and calculated structure factors (82 pages). Ordering information is given on any current masthead page.

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Lewis Base Adducts of Group 11 Metal Compounds.† 15. Structural Studies of Mononuclear Adducts of Copper(I) Halides with Pyridine Bases of Stoichiometry $XCuL_{2,3}$

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In the preceding paper[2] we reported single-crystal structural studies on various pyridine base adducts of the copper(I) halides. $[XCuL_2]_2$, which are binuclear with a four-coordinate metal atom. Elsewhere,[3] we have noted that in the context of the sterically hindered base 2,6-dimethylpyridine (2,6-Me_2py) 1:2 CuI:base adducts may be isolated as mononuclear species, rather than the

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