Lewis-base Adducts of Group 11 Metal(I) Compounds. Part 58.[1] Syntheses, *X*-Ray Structures, and Far-infrared Spectra of the Novel $[CuX_2(\text{bidentate ligand})]^-$ (X = Cl or Br) Anion Salts of the $[Cu(dpa)_2]^+$ Cation and the Dimeric Iodide $[(dpa)CuI_2Cu(dpa)]$ * [dpa = di(2-pyridyl)amine]

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Reaction of copper(I) halides (CuX, X = Cl, Br, or I) in acetonitrile solution with di(2-pyridyl)amine(dpa) yields 1:1.5 adducts with the chloride and bromide, a 1:1 adduct with the iodide, and a 1:2 adduct with the chloride. The compounds have been characterized by spectroscopic and single-crystal *X*-ray methods. The 1:1 iodide is a dimer, $[(dpa)CuI_2Cu(dpa)]$, of a type familiar with other bidentate nitrogen base ligands, but the 1:1.5 complexes are ionic, formulated as $[Cu(dpa)_2]^+[Cu(dpa)X_2]^-$, containing the first structurally characterized $[Cu(dpa)_2]^+$ cations and $[CuX_2(\text{bidentate ligand})]^-$ anions, while the 1:2 chloride is $[Cu(dpa)_2]^+Cl^-$. In the $[Cu(dpa)_2]^+$ cation mean Cu–N is *ca.* 2.00 Å, while in the $[Cu(dpa)X_2]^-$ anions Cu–N is *ca.* 2.05 Å and Cu–Cl and Cu–Br 2.369(2), 2.302(2) and 2.490(6), 2.439(6) Å respectively. The dpa ligand in all cases is essentially planar. The far i.r. spectra of the anions show bands at 214 cm^{-1} (chloride) and 160 cm^{-1} (bromide) which can be assigned to the asymmetric stretching mode of the CuX_2 unit.

In previous papers in the present series we have recorded studies of the complexes formed with the copper(I) halides, CuX (X = Cl, Br, or I), with bidentate ligands, L. From neat *N,N,N',N'*-tetramethylethylenediamine[2] (tmen), 1:1 complexes have been obtained, the iodide being a dimer, as is the bromide $[(tmen)CuX_2Cu(tmen)]$, while the chloride disproportionates to ionic $[Cu(tmen)_2]^+[CuCl_2]^-$. With 1,10-phenanthroline (phen) (from acetonitrile as solvent), 1:1 iodide[3] and bromide[4] adducts were obtained; the iodide again is a dimer, but the bromide is ionic, $[(phen)CuI_2Cu(phen)]$ and $[Cu(phen)_2]^+[CuBr_2]^-$ respectively. With 2,9-dimethyl-1,10-phenanthroline[3] (dmphen) substituent effects come into play and the bromide and iodide are dimeric $[(dmp)CuX_2Cu(dmp)]$ while the chloride is monomeric, [Cu(dmp)Cl]. The ligand tmen is a ligand of larger bite than phen; in the present paper we examine the nature of complexes obtained by the reaction of an N,N-bidentate of even larger bite, di-(2-pyridyl)amine (dpa), with the copper(I) halides. Structural studies, reported here, show the iodide to be a 1:1 dimer, consistent with all other bidentate nitrogen base–copper(I) iodide complexes studied to date. The chloride and bromide complexes, however, are ionic compounds containing the $[Cu(dpa)_2]^+$ cation and novel $[Cu(\text{N,N-bidentate ligand})X_2]^-$ anions, characterized here by *X*-ray structure determination and far-i.r. spectroscopy. The 'parent' $[Cu(dpa)_2]^+Cl^-$ has also been characterized.

Experimental

Synthesis.—$[Cu(dpa)_2]^+Cl^-$. The ligand dpa (0.5 g) was added to a solution of CuCl (0.2 g) in degassed CH_3CN (10 cm^3) under argon. Orange crystals of the compound precipitated immediately, m.p. (decomp.) > 150 °C (Found: C, 54.1; H, 4.0; N, 19.0. Calc. for $C_{20}H_{18}ClCuN_6$: C, 54.4; H, 4.1; N, 19.0%).

$[Cu(dpa)_2]^+[Cu(dpa)Cl_2]^-$. The ligand dpa (0.35 g) was added to a solution of CuCl (0.5 g) in degassed acetonitrile (40 cm^3) under argon. This resulted in mixed red and yellow precipitates which redissolved on warming in a water-bath to give a clear yellow solution. This was allowed to cool slowly, then stored at −20 °C overnight to give well formed yellow crystals of the complex, m.p. (decomp.) > 150 °C (Found: C, 50.7; H, 3.8; N, 17.9. Calc. for $C_{30}H_{27}Cl_2Cu_2N_9$: C, 50.6; H, 3.8; N, 17.7%).

$[Cu(dpa)_2]^+[Cu(dpa)Br_2]^-$. The ligand dpa (0.24 g) was added to a solution of CuBr (0.2 g) in degassed acetonitrile (20 cm^3) resulting momentarily in a clear orange solution, followed by immediate crystallization of yellow crystals of the complex. Addition of an excess of dpa to the solution did *not* result in crystallization of orange crystals of $[Cu(dpa)_2]^+Br^-$ by analogy with the chloride sample; m.p. (decomp.) > 150 °C (Found: C, 45.2; H, 3.4; N, 15.9. Calc. for $C_{30}H_{27}Br_2Cu_2N_9$: C, 45.0; H, 3.4; N, 15.8%).

$[(dpa)CuI_2Cu(dpa)]$. The ligand dpa (0.22 g) was added to a solution of CuI (0.25 g) in degassed acetonitrile (20 cm^3) to give a yellow solution from which yellow crystals of the complex formed as its acetonitrile solvate, m.p. (decomp.) > 150 °C (Found: C, 35.4; H, 2.9; N, 13.8. Calc. for $C_{12}H_{12}CuIN_4$: C, 35.8; H, 3.0; N, 13.9%). Samples were sealed in capillaries for the crystallographic work.

Far-i.r. Spectra.—These were recorded at *ca.* 298 K as petroleum jelly mulls between Polythene plates on a Digilab FTS-60 Fourier-transform Spectrometer employing a FTS-60V vacuum optical bench and a 6.25-μm mylar beam splitter.

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Non-hydrogen atom co-ordinates for $[Cu(dpa)_2]^+Cl^-$

	Ligand A			Ligand B		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Cu	0.506 28(5)	0.898 97(2)	0.247 77(4)			
N(1)	0.470 6(3)	1.000 4(1)	0.162 6(2)	0.532 0(3)	0.788 9(1)	0.198 8(2)
C(12)	0.338 0(3)	1.041 3(2)	0.124 0(2)	0.666 0(3)	0.749 5(2)	0.240 6(2)
C(13)	0.318 5(3)	1.112 7(2)	0.065 9(2)	0.684 6(3)	0.679 2(2)	0.193 9(2)
C(14)	0.439 0(4)	1.141 9(2)	0.051 1(3)	0.558 1(4)	0.646 8(2)	0.107 0(3)
C(15)	0.577 7(4)	1.100 9(2)	0.092 1(3)	0.416 9(4)	0.684 5(2)	0.067 1(3)
C(16)	0.587 0(3)	1.031 5(2)	0.145 4(3)	0.409 6(3)	0.754 7(2)	0.113 2(3)
N(2)	0.292 6(3)	0.896 1(1)	0.239 3(2)	0.713 4(3)	0.896 9(1)	0.383 4(2)
C(22)	0.181 7(3)	0.949 4(2)	0.184 1(2)	0.814 6(3)	0.836 7(2)	0.408 7(2)
C(23)	0.030 0(3)	0.941 6(2)	0.170 1(2)	0.946 7(4)	0.832 4(2)	0.510 3(3)
C(24)	−0.008 0(4)	0.875 7(2)	0.211 3(3)	0.976 9(5)	0.891 7(2)	0.585 0(3)
C(25)	0.103 2(4)	0.818 4(2)	0.265 6(3)	0.877 1(5)	0.955 6(2)	0.558 1(3)
C(26)	0.249 2(4)	0.831 3(2)	0.277 1(2)	0.749 4(4)	0.955 4(2)	0.459 0(3)
N(3)	0.213 0(2)	1.016 2(1)	0.138 3(2)	0.793 7(2)	0.776 4(1)	0.334 3(2)
Cl	0.940 94(7)	0.145 10(4)	0.076 17(6)			

Structure Determinations.—Unique data sets were measured within the specified $2\theta_{max.}$ limits at *ca.* 295 K using Syntex $P2_1$ and Enraf-Nonius CAD-4 four-circle diffractometers, fitted with monochromatic Mo-K_α radiation sources ($\lambda = 0.7106_9$ Å) and operating in conventional 2θ—θ scan mode. N Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the large-block least-squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Residuals at convergence are conventional R,R' on $|F|$, statistical weights derived from $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0005\ \sigma^4(I_{diff})$ being used. Neutral atom complex scattering factors were employed;[5] computation used the XTAL 83 program system[6] implemented by S. R. Hall on a Perkin-Elmer 3240 computer. The structures are illustrated in Figures 1 and 2 (also showing atom labelling); atomic co-ordinates are given in Tables 1—3.

Crystal data. $[Cu(dpa)_2]^+Cl^-$, $C_{20}H_{18}ClCuN_6$, $M = 441.4$, monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), $a = 9.676(2)$, $b = 16.823(6)$, $c = 13.642(6)$ Å, $\beta = 117.15(3)°$, $U = 1\,976$ Å^3. D_c $(Z = 4) = 1.48$ g cm^{-3}, $F(000) = 904$, $\mu_{Mo} = 11.9$ cm^{-1}, specimen $0.13 \times 0.31 \times 0.30$ mm, $A^*_{min.,max.} = 1.16$, 1.26, $2\theta_{max.} = 50°$, $N = 3\,454$, $N_o = 2\,527$, $R = 0.034$, $R' = 0.038$.

$[Cu(dpa)_2]^+[Cu(dpa)Cl_2]^-$, $C_{30}H_{27}Cl_2Cu_2N_9$, $M = 711.6$, monoclinic, space group $P2_1/n$ [C^5_{2h}, no. 14 (variant)], $a = 9.582(4)$, $b = 22.532(8)$, $c = 13.893(5)$ Å, $\beta = 91.58(3)°$, $U = 2\,999$ Å^3, D_c $(Z = 4) = 1.58$ g cm^{-3}, $F(000) = 1\,448$, $\mu_{Mo} = 15.6$ cm^{-1}, specimen cuboid, 0.20 mm, $A^*_{min.,max.} = 1.30$, 1.35, $2\theta_{max.} = 40°$, $N = 3\,005$, $N_0 = 1\,994$, $R = 0.047$, $R' = 0.033$.

$[Cu(dpa)_2]^+[Cu(dpa)Br_2]^-$, $C_{30}H_{27}Br_2Cu_2N_9$, $M = 800.5$, monoclinic, space group $P2_1/n$, $a = 9.681(2)$, $b = 23.104(8)$, $c = 13.871(4)$ Å, $\beta = 90.37(2)°$, $U = 3\,102$ Å^3. D_c $(Z = 4) = 1.71$ g cm^{-3}, $F(000) = 1\,592$, $\mu_{Mo} = 39$ cm^{-1}, specimen $0.30 \times 0.07 \times 0.07$ mm, $A^*_{min.,max.} = 1.28$, 1.32, $2\theta_{max.} = 40°$, $N = 2\,905$, $N_o = 1\,230$, $R = 0.084$, $R' = 0.067$.

$[(dpa)CuI_2Cu(dpa)]\cdot 2CH_3CN$, $C_{24}H_{24}Cu_2I_2N_8$, $M = 805.4$, orthorhombic, space group $Pcab$ [D^{15}_{2h}, no. 61 (variant)], $a = 17.575(3)$, $b = 12.946(2)$, $c = 12.328(4)$ Å, $U = 2\,805$ Å^3, D_c $(Z = 8) = 1.91$ g cm^{-3}, $F(000) = 1\,552$, $\mu_{Mo} = 39$ cm^{-1}, specimen 0.18 mm polyhedral spheroid, $A^*_{min.,max.} = 1.51$, 1.66, $2\theta_{max.} = 45°$, $N = 2\,202$, $N_o = 1\,596$, $R = 0.043$, $R' = 0.030$.

Abnormal features. Data for the bromide were very weak and limited in scope and would only support meaningful refinement of isotropic thermal parameters for C and N. For the iodide, difference-map artefacts were successfully modelled and refined in terms of a fully occupied acetonitrile solvate molecule; the nitrogen atom was assigned on the basis of thermal parameter behaviour and methyl hydrogen atoms subsequently inferred from difference maps. These results are consistent with the analysis.

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

Discussion

Results of the single-crystal structure determinations of the adducts of copper(I) chloride, bromide, and iodide with dpa are consistent with their formulation as 1:2, 1:1.5, 1:1.5, and 1:1 complexes respectively as above, the iodide being an acetonitrile monosolvate.

In the iodide the complex is found to be of the dimeric $[LCuI_2CuL]$ form, familiar already for the examples L = tmen, phen, or dmphen; in the present case, one half of the dimer (with associated solvent) is the asymmetric unit of the structure, the other half being generated by a crystallographic inversion centre. Molecular $N_2CuI_2CuN_2$ core geometries are given in Table 4, in comparison with those for the above examples, showing a number of features of interest; we exclude from our commentary the dmphen example where substituent effects already discussed in detail elsewhere,[3] cause a gross asymmetry in the structure. First, we note that, despite considerable variation in parameters relating to the nitrogen atoms, the CuI_2Cu core geometry is remarkably insensitive to such changes; further comparison with a summary of $L'_2CuI_2CuL'_2$ core geometries (L′ = monodentate N-base ligand without a 2 substituent, *viz.* pyridine or 3,5-dimethylpyridine) given elsewhere[7] shows a similar insensitivity to whether the ligand L is bidentate or replaced by L'_2 = two monodentate ligands. Perturbation of these geometries, however, is readily achieved in both cases by incorporation of a 2-methyl substituent in the ligands of either type. In the present system, in respect of the nitrogen bases, we observe a considerable change in ligand 'bite,' as measured by the N–Cu–N angle, increasing from phen (*ca.* 80°) to tmen *ca.* 84°) to dpa (*ca.* 95°); this is *not* paralleled by a corresponding monotonic variation in Cu–N distance, that for the present system being by far the shortest (mean 2.04 Å) and that for the aliphatic tmen system the longest (mean 2.17_5 Å). The dpa ligand is substantially planar (not only in the present iodide, but also the chloride and bromide complexes

Table 2. Non-hydrogen atom co-ordinates for $[Cu(dpa)_2]^+[Cu(dpa)X_2]^-$ (X = Cl or Br)

	Chloride			Bromide		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Anion						
X(1)	0.229 9(2)	0.127 85(8)	0.102 6(1)	0.246 2(4)	0.126 1(2)	0.100 8(3)
X(2)	0.136 9(2)	0.064 09(8)	0.356 8(1)	0.128 4(3)	0.065 2(2)	0.367 3(3)
Cu	0.095 4(1)	0.060 67(4)	0.192 84(8)	0.095 5(4)	0.058 9(2)	0.193 1(3)
N(1)	−0.111 4(6)	0.052 6(3)	0.152 9(4)	−0.115(2)	0.056(1)	0.148(2)
C(12)	−0.164 3(8)	0.004 7(3)	0.107 3(5)	−0.157(3)	0.009(1)	0.111(2)
C(13)	−0.309 2(8)	0.002 0(4)	0.085 3(6)	−0.311(3)	0.005(1)	0.089(2)
C(14)	−0.393 2(8)	0.047 2(4)	0.109 3(6)	−0.392(3)	0.051(1)	0.116(2)
C(15)	−0.340 2(9)	0.096 3(4)	0.155 8(6)	−0.326(3)	0.101(1)	0.163(2)
C(16)	−0.200 0(8)	0.096 5(3)	0.177 4(6)	−0.194(3)	0.102(1)	0.173(2)
N(2)	0.140 0(6)	−0.023 0(2)	0.147 2(4)	0.132(2)	−0.022(1)	0.151(2)
C(22)	0.051 2(8)	−0.059 2(3)	0.098 9(5)	0.048(3)	−0.056(1)	0.105(2)
C(23)	0.093 4(10)	−0.114 3(3)	0.067 4(6)	0.080(3)	−0.113(1)	0.077(2)
C(24)	0.228 1(10)	−0.132 3(3)	0.086 6(6)	0.211(4)	−0.132(1)	0.090(2)
C(25)	0.318 2(9)	−0.095 3(3)	0.135 7(6)	0.299(3)	−0.101(1)	0.144(2)
C(26)	0.271 2(9)	−0.041 8(3)	0.164 6(6)	0.269(3)	−0.045(1)	0.164(2)
N(3)	−0.085 1(6)	−0.042 3(2)	0.080 1(4)	−0.091(2)	−0.040(1)	0.083(2)
Cation						
Cu	0.794 8(1)	0.347 68(4)	0.145 28(8)	0.801 9(5)	0.344 7(2)	0.145 4(3)
Ligand A						
N(1)	0.816 5(6)	0.435 3(2)	0.139 6(4)	0.825(2)	0.429(1)	0.144(2)
C(12)	0.709 1(7)	0.472 4(3)	0.124 0(5)	0.732(3)	0.469(1)	0.131(2)
C(13)	0.728 3(8)	0.532 1(3)	0.103 3(6)	0.745(3)	0.526(1)	0.111(2)
C(14)	0.860 7(8)	0.554 8(3)	0.099 0(6)	0.870(3)	0.549(1)	0.111(2)
C(15)	0.972 3(8)	0.517 8(3)	0.116 1(5)	0.975(3)	0.510(2)	0.123(3)
C(16)	0.946 2(8)	0.459 3(3)	0.134 7(6)	0.956(3)	0.452(1)	0.139(2)
N(2)	0.584 8(6)	0.348 3(2)	0.142 0(4)	0.599(2)	0.348(1)	0.145(2)
C(22)	0.511 5(7)	0.398 7(3)	0.135 4(5)	0.526(3)	0.399(1)	0.140(2)
C(23)	0.364 4(8)	0.397 9(3)	0.133 3(5)	0.376(3)	0.397(1)	0.132(2)
C(24)	0.297 2(8)	0.345 2(3)	0.140 4(6)	0.319(3)	0.344(1)	0.133(2)
C(25)	0.375 1(8)	0.293 2(3)	0.147 8(6)	0.381(3)	0.293(1)	0.143(2)
C(26)	0.515 5(8)	0.296 7(3)	0.147 5(5)	0.522(3)	0.300(1)	0.142(2)
N(3)	0.571 9(6)	0.454 0(2)	0.131 2(4)	0.595(2)	0.450(1)	0.128(2)
Ligand B						
N(1)	0.886 8(6)	0.307 3(2)	0.034 5(4)	0.894(2)	0.306(1)	0.032(2)
C(12)	0.986 4(7)	0.267 3(3)	0.044 1(5)	0.993(3)	0.265(1)	0.042(2)
C(13)	1.070 3(7)	0.250 4(2)	−0.030 8(5)	1.087(2)	0.250(1)	−0.036(2)
C(14)	1.044 9(8)	0.273 5(3)	−0.120 7(5)	1.056(3)	0.274(1)	−0.116(2)
C(15)	0.936 6(8)	0.313 8(3)	−0.134 3(5)	0.944(3)	0.312(1)	−0.143(2)
C(16)	0.862 7(8)	0.328 7(3)	−0.055 5(6)	0.876(3)	0.326(1)	−0.056(2)
N(2)	0.899 1(6)	0.299 3(2)	0.246 0(4)	0.907(2)	0.298(1)	0.242(2)
C(22)	0.982 0(7)	0.253 6(3)	0.225 1(5)	0.990(3)	0.254(1)	0.224(2)
C(23)	1.037 1(8)	0.216 8(3)	0.297 5(5)	1.047(3)	0.221(1)	0.297(2)
C(24)	1.010 2(8)	0.228 7(3)	0.389 9(5)	1.023(2)	0.229(1)	0.390(2)
C(25)	0.928 6(8)	0.277 3(3)	0.413 8(5)	0.941(3)	0.279(1)	0.414(2)
C(26)	0.875 0(8)	0.310 2(3)	0.339 8(5)	0.891(3)	0.308(1)	0.342(2)
N(3)	1.017 6(6)	0.239 4(2)	0.131 8(4)	1.028(3)	0.241(1)	0.129(2)

discussed below), with no pyridine–pyridine interplanar dihedral angle exceeding 18° and mean (central)N–C distances in the more precisely determined examples (chloride, iodide) being $\lesssim 1.40$ Å.

The overall dimer configuration is of considerable interest. Systems $L'_2CuX_2CuL'_2$ have been synthesized and structurally characterized for all X, but full sequences for specific ligands are only available for the hindered L′ = 2-methyl- and 2,4-dimethylpyridine. For the former, trends in the Cu···Cu distance are erratic; for the latter, the three compounds are isostructural and Cu···Cu increases monotonically from 2.995(3) (Cl), 3.091(3) (Br), to 3.140(3) Å (I), although it is not clear that in the absence of hindrance in the base this is necessarily a trend to be expected. In particular we note that for the bidentate ligand 2,9-dimethyl-1,10-phenanthroline (dmphen) the isostructural pair $[(dmp)CuX_2Cu(dmp)]$, X = Br or I, exhibit a reverse trend with Cu···Cu 3.097(1) and 3.024(2) Å respectively, although ligand strain appears greater in the bromide. For whatever reason, for the sequences of bidentate bases so far studied, dimers are generally established for the iodide, sometimes for the bromide, and never for the chloride, ligand disproportionation or monomer formation occurring and reducing the average co-ordination number of the copper atom. Thus for L = tmen the chloride is $[CuL_2]^+[CuCl_2]^-$, for phen the bromide is $[CuL_2]^+[CuBr_2]^-$, and for dmphen the chloride is [CuLCl]. In examining factors which

Table 3. Non-hydrogen atom co-ordinate for [(dpa)CuI$_2$Cu(dpa)]

Atom	*x*	*y*	*z*
I	0.449 60(3)	0.141 96(4)	0.083 07(5)
Cu	0.564 68(6)	0.019 43(8)	0.047 42(9)
N(1)	0.624 2(4)	−0.030 3(5)	0.178 4(5)
C(12)	0.698 3(5)	−0.008 3(6)	0.196 1(7)
C(13)	0.737 4(5)	−0.047 6(7)	0.285 9(8)
C(14)	0.701 9(6)	−0.109 2(8)	0.357 1(8)
C(15)	0.626 8(6)	−0.136 7(8)	0.338 0(8)
C(16)	0.592 3(5)	−0.096 1(7)	0.250 6(9)
N(2)	0.651 7(4)	0.108 2(5)	−0.012 4(5)
C(22)	0.721 8(5)	0.108 8(6)	0.031 5(7)
C(23)	0.780 4(5)	0.168 8(6)	−0.013 8(8)
C(24)	0.766 1(5)	0.222 8(7)	−0.104 2(9)
C(25)	0.695 6(6)	0.220 5(7)	−0.151 9(8)
C(26)	0.640 5(5)	0.162 1(7)	−0.102 3(7)
N(3)	0.738 9(4)	0.054 0(5)	0.125 6(6)
Acetonitrile solvent			
N(0)	0.908 2(5)	0.008 6(8)	0.127 0(8)
C(0)	0.957 9(7)	−0.050 8(10)	0.123 2(8)
C(01)	1.016 0(6)	−0.122 7(8)	0.119 4(9)

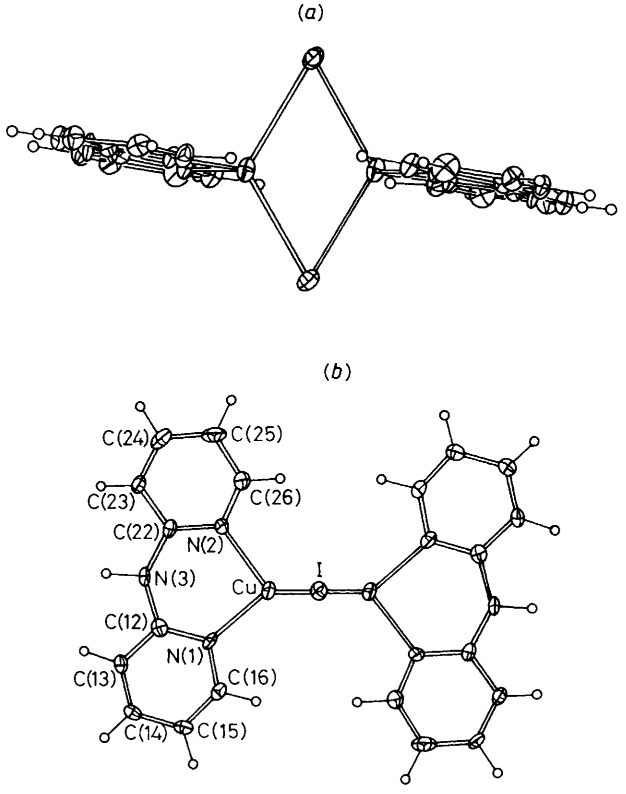

Figure 1. Projections of [(dpa)CuI$_2$Cu(dpa)]: (*a*) perpendicular to the CuI$_2$Cu plane; (*b*) perpendicular to the Cu $\cdots$ Cu line, in the CuI$_2$Cu plane. 20% Thermal ellipsoids are shown for the non-hydrogen atoms, together with atom labelling. Hydrogen atoms have an arbitrary radius of 0.1 Å

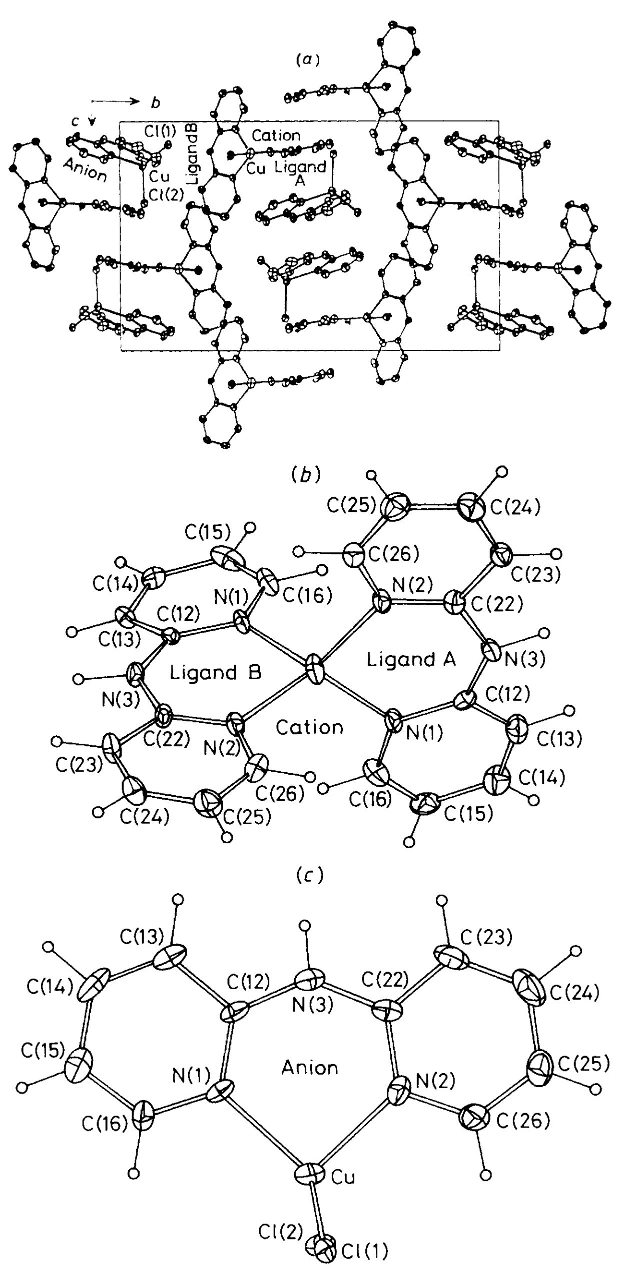

Figure 2. (*a*) Unit-cell contents of [Cu(dpa)$_2$]$^+$[Cu(dpa)Cl$_2$]$^-$ projected down *a*; (*b*) the cation, projected down a pseudo-two-fold axis; (*c*) the anion, projected normal to the ligand plane

may assist in explaining why only the iodide is dimeric for dpa, it is of interest to note [Figure 1(*b*)] the ligand disposition; for L = phen, the dimer [(phen)CuI$_2$Cu(phen)] displayed in Figure 1 of ref. 3 is found to be quite devoid of ligand strain, so much so that the CuI$_2$Cu core is non-planar. The increased bite of the dpa ligand (*vis-à-vis* phen) in the present examples means that this situation no longer obtains, Figure 1(*b*) strongly being suggestive of the evasion of interligand hydrogen interactions across the core, consistent with the H(16) $\cdots$ H(26) estimate of 2.6 Å and correlating with the asymmetry in the Cu–I distances. In this context, our inability to obtain the chloride and bromide as 1:1 dimers is not surprising.

Chloride and bromide structures consistent with an ionic formulation, are, surprisingly, not the 1:1 stoicheiometry of [Cu(dpa)$_2$]$^+$[CuX$_2$]$^-$, which might be expected on the basis of the above precedents and which we have been unable to obtain (at least from acetonitrile solution), but, rather, 1:1.5 stoicheiometry consistent with [Cu(dpa)$_2$]$^+$[Cu(dpa)X$_2$]$^-$, and in the case of the chloride also 1:2, [Cu(dpa)$_2$]$^+$Cl$^-$, in which both copper atoms retain a co-ordination number of four. The cation is the first of this type to be structurally characterized with dpa as a bidentate ligand; we compare it with

Table 4. Molecular $N_2CuI_2CuN_2$ core geometries (iodide) (distances in Å, angles in °). Values pertain to [LCuI$_2$CuL] (L = symmetrical N,N-bidentate ligand) systems

	L = dpa[a]	tmen[b]	phen[c]	dmphen[c]
Cu–I	2.608(1)	2.605(5)	2.589(1)	2.673(1)
Cu–I′	2.649(1)	2.596(5)	−2.632(1)	2.563(1)
Cu–N(1)	2.029(7)	2.13(2)	2.078(6)	2.094(6)
Cu–N(2)	2.051(7)	−2.21(2)	−2.103(6)	2.092(5)
Cu ··· Cu	2.606(1)	2.566(4)	2.609(2)	3.024(2)
I ··· I	4.566(1)	4.491(3)	4.454(2)	4.276(1)
N(1)–Cu–N(2)	94.6(3)	84.4(8), 82.9(11)	80.8(2), 79.7(2)	80.4(2)
I–Cu–I′	120.58(4)	119.3(1), 119.5(1)	118.53(4), 116.85(4)	109.48(4)
Cu–I–Cu′	59.42(3)	59.1(1), 59.1(1)	59.96(4), 60.38(4)	70.52(4)
I–Cu–N(1)	117.3(2)			
I–Cu–N(2)	107.3(2)	111.3(7)	111.7(2)	106.4(2)
I′–Cu–N(1)	106.4(2)	−114.3(8)	118.1(2)	−124.6(1)
I′–Cu–N(2)	107.1(2)			

[a] This work. [b] Ref. 2. [c] Ref. 3.

Table 5. Cation core geometries (distances in Å, angles in °); values pertain to [CuL$_2$]$^+$ (L = symmetrical N,N-bidentate ligand) systems

	[Cu(dpa)$_2$]$^+$[a]			[Cu(tmen)$_2$]$^+$[b]	[Cu(phen)$_2$]$^+$[c]	
Cu–N(A1)	2.003(2)	1.988(5)	1.97(2)	2.15(1)	2.045(8)	2.006(8)
Cu–N(A2)	2.018(3)	2.011(6)	1.96(2)	2.15(1)		2.071(5)
Cu–N(B1)	2.022(3)	2.013(6)	2.01(2)	2.16(1)	2.053(9)	
Cu–N(B2)	2.014(2)	2.018(5)	2.00(2)	2.13(1)		
N(A1)–Cu–N(A2)	95.0(1)	95.6(2)	94.1(9)	86.0(4)	81.4(3)	82.2(3)
N(B1)–Cu–N(B2)	93.8(1)	93.8(2)	93.5(9)	85.3(4)	80.9(3)	
N(A1)–Cu–N(B1)	127.1(1)	111.8(2)	112.1(9)	122.9(4)		
N(A1)–Cu–N(B2)	112.5(1)	121.0(2)	118.9(9)	121.6(4)	109.7(3)	115.8(3)
N(A2)–Cu–N(B1)	103.7(1)	116.4(2)	117.6(9)	123.1(4)	−144.7(2)	−146.0(3)
N(A2)–Cu–N(B2)	128.1(1)	119.7(2)	122.3(9)	122.5(5)		

[a] Values are for [Cu(dpa)$_2$]$^+$Cl$^-$ and [Cu(dpa)$_2$]$^+$[Cu(dpa)X$_2$]$^-$ (X = Cl or Br) respectively. [b] Ref. 2. [c] Ref. 4; the two values are for the perchlorate and dibromocuprate respectively. For data from ref. 4, the atom designation has been set in conformity with the present system.

Table 6. Anion core geometries (distances in Å, angles in °)

	Chloride	Bromide
Cu–X(1)	2.369(2)	2.490(6)
Cu–X(2)	2.302(2)	2.439(6)
Cu–N(11)	2.051(6)	2.13(2)
Cu–N(12)	2.039(6)	1.99(2)
X(1)–Cu–X(2)	114.86(8)	113.5(2)
N(11)–Cu–N(12)	92.5(2)	93.5(9)
X(1)–Cu–N(11)	116.7(2)	115.6(6)
X(1)–Cu–N(12)	107.7(2)	109.2(6)
X(2)–Cu–N(11)	114.2(2)	114.2(6)
X(2)–Cu–N(12)	107.9(2)	108.7(7)

[Cu(tmen)$_2$]$^+$ and [Cu(phen)$_2$]$^+$ in Table 5. As might be expected, the hierarchy of 'bite' angles found for the ligands in this sequence remains as established above for their iodide complexes; a similar hierarchy of Cu–N distances is also found, shorter overall in the dpa adducts by perhaps 0.02 Å.

The anions (Table 6) are novel; we are aware of no other examples for monodentate N-base [CuL′$_2$X$_2$]$^-$ or bidentate [CuLX$_2$]$^-$ stoicheiometry. The Cu-X distances in [CuCl$_2$]$^-$ and [CuBr$_2$]$^-$ are typically 2.08_6[3] and 2.21_6 Å[4] respectively, by comparison with the present (mean) values of 2.33 and 2.46_5 Å. The angle X–Cu–X in the present species is somewhat above the tetrahedral value, as might be expected in consequence of being opposed to a ligand bite angle well below it, and comparable, as is the Cu–N distance, to the value of the iodide dimer. The N–Cu–N angles correspond to a normalized bite of 1.45, and the X–Cu–X angles of 114.9 (Cl) and 113.5° (Br) correspond to effective bond-length ratios R(X/N) of 0.89(Cl) and 0.91(Br) in agreement with expected values for a halide ligand compared with an unchanged bidentate ligand.[8]

One final feature worthy of note is the presence of strong hydrogen-bonding interactions involving the amine hydrogen. In [Cu(dpa)$_2$]$^+$Cl$^-$, Cl ··· H(3A)($1 + x, y - 1, z$) is 2.2_7 Å and Cl ··· H(3B)($2 - x, \frac{1}{2} + y, \frac{1}{2} - z$) 2.1_8 Å is very short; comparable effects are seen in [Cu(dpa)$_2$]$^+$[Cu(dpa)Cl$_2$]$^-$: H(3B) ··· Cl(1)($1 + x, y, \bar{z}$), H(3A) ··· Cl(2)($\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$), and H(3)(anion) ··· Cl(1)($\bar{x}, \bar{y}, \bar{z}$) are 2.1_1, 2.3_0, and 2.3_7 Å, with counterparts in the bromide of 2.4_1, 2.4_4, and 2.4_3 Å. The iodide appears devoid of close contacts.

Far-i.r. Spectra.—The far-i.r. spectra of the 1:1.5 chloro- and bromo-complexes are shown in Figure 3. Halogen-sensitive bands occur in the region below 200 cm^{-1}. Two ν(Cu–X) bands are expected in the far-i.r. region. Assuming an idealized C_{2v} structure for the non-linear CuX$_2$ unit, these arise from the symmetric (A_1) and asymmetric (B_1) stretching modes. In the closely related anionic complex [Cu(PPh$_3$)Br$_2$]$^-$ these bands have been assigned at 195 (B_1) and 150 cm^{-1} (A_1).[9] We have recently shown that ν(Cu–X) can be empirically correlated with the Cu–X bond length r in a range of CuX complexes which contain a single terminal Cu–X bond.[10] For CuCl and CuBr complexes this relationship may be represented by equation (1)

$$\nu/\text{cm}^{-1} = b(r/\text{Å})^{-m} \qquad (1)$$

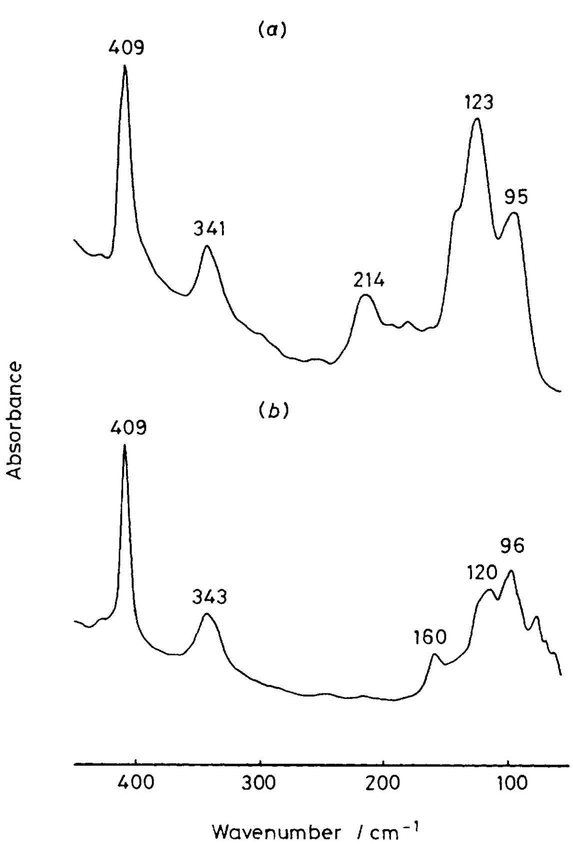

Figure 3. Far-i.r. spectra (50—450 cm^{-1}) of the $[Cu(dpa)X_2]^-$ (X = Cl or Br) complexes

Table 7. Observed and calculated metal–halogen stretching frequencies

Complex	ν(Cu–X)/cm^{-1} Obs.	ν(Cu–X)/cm^{-1} Calc.	f_r/N m^{-1}
$[Cu(PPh_3)Br_2]^{-}$ [a]	195	189 (B_1)	60
$[Cu(dpa)Br_2]^{-}$ [b]	160	165 (B_1)	44
	—	133 (A_1)	
$[Cu(dpa)Cl_2]^{-}$ [b]	214	216 (B_1)	54
	—	188 (A_1)	

[a] Ref. 9. [b] This work.

where b = 13 800 and 18 000 and m = 4.9 and 5.2 for X = Cl and Br respectively. The present complexes contain two halogen atoms terminally bound to the same copper atom, and so are significantly different in structure to those for which equation (1) was obtained. However, we have noted that the wavenumber of the more intense, higher-frequency (B_1) ν(Cu–Br) mode of the complex $[Cu(PPh_3)Br_2]^-$ is predicted very well by this equation [mean Cu–Br bond length r = 2.377 Å; calculated ν(Cu–Br) 189 cm^{-1}, observed value 195 cm^{-1}]. Applying the same calculation to the $[Cu(dpa)X_2]^-$ species, we obtain ν(Cu–X) 216 and 165 cm^{-1} for X = Cl and Br respectively. On this basis the observed bands at 214 and 160 cm^{-1} can be assigned to the B_1 ν(Cu–X) modes for the X = Cl and Br respectively. The A_1 modes should occur at lower frequency, but this region of the spectrum is partly obscured by strong ligand bands which occur in the region 90—120 cm^{-1}. In order to estimate the frequencies of the A_1 modes the metal–halogen stretching frequencies were calculated by carrying out a normal-co-ordinate analysis on an isolated C_{2v} CuX_2 unit with an X–Cu–X bond angle of 115°. A simple diagonal force field was used. This involves a Cu–X bond stretching force constant f_r and an X–Cu–X angle bending force constant f_α. With f_α set equal to 0.1 f_r, f_r was varied and the vibrational frequencies calculated to give the best fit of the calculated to the observed frequencies. The results are given in Table 7, together with those obtained previously in a similar calculation on the $CuBr_2$ unit in $[Cu(PPh_3)Br_2]^-$.[9] For both $[Cu(dpa)X_2]^-$ species, weak bands or shoulders occur at the wavenumbers predicted for the A_1 modes. However, these are not well enough resolved to allow definite assignments for these modes. The force constants f_r in Table 6 show reasonable relationships to one another, and this provides further support for the assignments on which they are based. Thus, the value for the four-co-ordinate $[Cu(dpa)Br_2]^-$ is smaller than that for the three-co-ordinate $[Cu(PPh_3)Br_2]^-$, and the value for $[Cu(dpa)Cl_2]^-$ is greater than that for $[Cu(dpa)Br_2]^-$. Both of these trends are in line with those observed previously for species with one terminal Cu–X bond.[10]

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