

The Far Infrared and Electronic Spectra of Mono-
(Ethylenediamine) and Related Complexes of Copper(II).
An Example of the *Trans* Effect, and the Influence
of Axial Interactions Upon the In-Plane Bond Strength

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The vibrational (far infrared) and electronic spectra of the complexes $\text{Cu}(\text{N}-\text{N})\text{X}_2$ (where (N-N) is ethylenediamine, 1,3-propylenediamine, 1,4-butylenediamine, and the symmetric and anti-symmetric N,N-dimethyl and diethylethylenediamines, and $\text{X}=\text{Cl}$, Br, NO_3 , or NCS) are reported.

Correlations are demonstrated between metal nitrogen and metal ligand (X) stretching frequencies which are interpreted with the electronic spectra in terms of increasing tetragonal distortion and increasing in-plane bond strength. The nature of the Cu-X bond influences the frequency of the Cu-N vibration via a *trans* influence. These conclusions are supported by a simple force constant analysis of the problem and are generally interpreted in terms of the effective charge on the copper atom.

Introduction

We recently reported¹ an analysis of the far infrared and electronic spectra of copper complexes containing two diamine ligands (of the general formula $\text{Cu}(\text{N}-\text{N})_2\text{X}_2$) and showed that these data may be related to the extent of tetragonal distortion in these complexes and also to the in-plane bond strength. We now report a detailed analysis of the far infrared spectra of derivatives of the general formula $\text{Cu}(\text{N}-\text{N})\text{X}_2$ where (N-N) is ethylenediamine, 1,3-propylenediamine, 1,4-butylenediamine, or the symmetric or antisymmetric N,N-dimethyl or N,N-diethylethylenediamines, and X is a halogen, pseudohalogen or nitrate group.

Experimental Section

Most of the complexes have been previously reported (see Table I for references) and were prepared by the literature methods. New complexes of 1,3-diaminopropane and 1,4-diaminobutane were prepared by mixing stoichiometric proportions of the amine and metal salt in ethanol, and recrystallising, where possible, from the same solvent. Far infrared spectra were recorded as Nujol mulls with a Beckman IR 12

spectrometer, whilst electronic transmittance spectra were also recorded as Nujol mulls (on filter paper) using a Cary 14 spectrometer. Low temperature electronic spectra were obtained using a Beckman VLT-2 variable temperature cell with quartz windows. Metal and halogen analyses (Table I) were obtained by the Authors using standard gravimetric or potentiometric techniques.

Results and Discussion

In our previous study¹ of the complexes $\text{Cu}(\text{N}-\text{N})_2\text{X}_2$ a novel correlation was observed between the in-plane copper nitrogen stretching vibration and the crystal field splitting energy of this CuN_4 chromophore, as a function of the axial ligand X. It was shown that these spectra reflected changes in tetragonal distortion and that as the distortion towards a square increases,

Table I. Analytical data

Complexes	Metal Analyses		Anion Analyses		Reference
	Req.	Found	Found	Req.	
$\text{Cu}(\text{En})\text{Cl}_2$	32.6	32.9			a,b,c
$\text{Cu}(\text{En})\text{Br}_2$	22.4	22.3			c
$\text{Cu}(\text{En})(\text{NCS})_2$			48.4	48.5	a
$\text{Cu}(\text{Sym-Me}_2\text{en})\text{Cl}_2$			31.9	31.7	a,c
$\text{Cu}(\text{Sym-Me}_2\text{en})\text{Br}_2$			51.3	51.6	a,c,d
$\text{Cu}(\text{Sym-Me}_2\text{en})(\text{NCS})_2$			43.3	43.3	a
$\text{Cu}(\text{Sym-Me}_2\text{en})(\text{NO}_3)_2$	23.0	22.9			c
$\text{Cu}(\text{Asym-Me}_2\text{en})_2\text{Cl}_2$	28.5	28.6			a,c
$\text{Cu}(\text{Asym-Me}_2\text{en})\text{Br}_2$			51.3	51.5	c
$\text{Cu}(\text{Asym-Me}_2\text{en})(\text{NCS})_2$			43.3	43.5	a
$\text{Cu}(\text{Sym-Et}_2\text{en})\text{Cl}_2$			28.3	28.7	c
$\text{Cu}(\text{Sym-Et}_2\text{en})\text{Br}_2$			47.1	47.5	a,c
$\text{Cu}(\text{Sym-Et}_2\text{en})(\text{NO}_3)_2$	20.9	21.1			c
$\text{Cu}(\text{Asym-Et}_2\text{en})\text{Cl}_2$	25.3	25.4			a,c
$\text{Cu}(\text{Asym-Et}_2\text{en})\text{Br}_2$	18.7	19.1			c
$\text{Cu}(\text{Asym-Et}_2\text{en})(\text{NO}_3)_2$	20.9	20.7			c
$\text{Cu}(1,4\text{-DAP})\text{Cl}_2$	30.5	30.6	34.0	34.1	e
$\text{Cu}(1,3\text{-DAP})\text{Br}_2$	21.3	21.1	53.7	53.9	e
$\text{Cu}(1,3\text{-DAP})(\text{NO}_3)_2$	24.3	23.9	47.4	47.6	e
$\text{Cu}(1,4\text{-DAB})\text{Cl}_2$	28.5	28.7	31.9	32.1	e
$\text{Cu}(1,4\text{-DAB})\text{Br}_2$	20.4	20.4	51.3	51.2	e

a) M.E. Farago and J.M. James, *Inorg. Chem.*, **4**, 1706 (1965); b) G. Giusepette and F. Mazzi, *Rend. Soc. mineral Ital.*, **11**, 202 (1955); c) P. Pfeiffer and H.J. Glaser, *J. prakt. Chem.*, **151**, 134 (1938); d) D.W. Meek and S.A. Ehrhardt, *Inorg. Chem.*, **4**, 584 (1965); e) This work.

(1) A. B. P. Lever and E. Mantovani, *Inorg. Chem.*, **10**, 817 (1971).

Table II. Electronic Spectroscopic Data (cm⁻¹) (Mull Transmittance)

Complexes		Internal <i>d-d</i> transitions		Charge Transfer
CuenCl ₂	rt.	14,160	(15,750)	
	lt.	13,970	(16,340)	
CuenBr ₂	rt.	(13,440)	15,080	
	lt.	13,930	15,850	(24,810)
Cuen(SCN) ₂	rt.	15,270	(17,390)	(24,270)
	lt.	(13,000)	15,080	(16,000) (18,080) (25,970)
Cu(Asym-Me ₂ en)Cl ₂	rt.		15,240	
	lt.		15,820	
Cu(Asym-Me ₂ en)Br ₂	rt.	(13,790)	15,240	(23,250)
	lt.	(13,570)	15,650	23,750
Cu(Asym-Me ₂ en)(NCS) ₂	rt.	(14,810)	17,540	
	lt.	(15,240)	17,950	
Cu(Sym-Me ₂ en)Cl ₂	rt.	14,000	(15,480)	
	lt.	13,850	15,800	
Cu(Sym-Me ₂ en)Br ₂	rt.	(12,900)	15,385	(22,830)
	lt.	(13,260)	15,360	(24,000)
Cu(Sym-Me ₂ en)(NCS) ₂	rt.	(14,290)	17,040	
	lt.	(14,820)	17,360	(22,220)
Cu(Sym-Me ₂ en)(NO ₃) ₂	rt.	(14,290)	16,310	
	lt.	14,660	17,180	
Cu(Asym-Et ₂ en)Cl ₂	rt.	(12,990)	14,600	
	lt.	(13,120)	14,080	15,850
Cu(Asym-Et ₂ en)Br ₂	rt.	(13,120)	14,860	(22,730)
	lt.	(13,120)	15,670	(23,150)
Cu(Asym-Et ₂ en)(NO ₃) ₂	rt.		16,670	
	lt.	(13,910)	17,985	
Cu(Sym-Et ₂ en)Cl ₂	rt.	(14,815)	(16,130)	
	lt.	(12,380)	15,150	
Cu(Sym-Et ₂ en)Br ₂	rt.	(12,500)	14,160	16,180
	lt.	(12,900)		
Cu(Sym-Et ₂ en)(NO ₃) ₂	rt.	(11,630)	(13,330)	16,930 (22,530)
	lt.	(11,820)	13,440	15,500 (24,100)
Cu(Sym-Et ₂ en)(NO ₃) ₂	rt.	(12,160)	(15,290)	16,890
	lt.	(14,285)		
Cu(1,3-DAP)Cl ₂	rt.	(12,840)	15,270	17,950 (25,840)
	lt.	(14,035)		
Cu(1,3-DAP)Br ₂	rt.	(12,900)	15,600	
	lt.	(12,410)	(13,790)	15,900
Cu(1,3-DAP)(NO ₃) ₂	rt.	(12,900)		
	lt.	(12,900)	(13,790)	15,670
Cu(1,4-DAB)Cl ₂	rt.	(14,810)	15,970	
	lt.	(14,200)	16,340	
Cu(1,4-DAB)Br ₂	rt.	(14,285)	16,920	
	lt.		15,150	
Cu(1,4-DAB)(NO ₃) ₂	rt.	(13,560)	15,820	
	lt.		15,110	
Cu(1,4-DAB)Br ₂	rt.	(13,160)	15,900	(25,000)
	lt.			

rt. = room temp. lt. = liq. N₂ temp. Shoulders in parentheses.

so does the in-plane stretching frequency and bond strength.

In these mono-ligand complexes the in-plane chromophore is now *cis* CuN₂X₂ so that as X changes the in-plane chromophore also changes, thus making the problem rather more difficult. Moreover whilst many X-ray structural studies have been completed with the 1:2 (metal to diamine) complexes, few such studies have been reported for the 1:1 (metal to diamine) derivatives. Nevertheless it is evident that there will be two limiting structures for these complexes, namely a square planar complex, with no axial perturbation, and a six coordinate complex in which a number of Cu(N-N)X₂ units are stacked together such that the X groups of one molecule axially interact with an adjacent copper atom in a tetragonally distorted octahedral array.² The possibility of a five

coordinate or distorted tetrahedral environment about the copper ions must however also be considered.

It will be demonstrated that consideration of both the far infrared and electronic spectra does allow statements to be made about the nature of the environment around the metal ion in these complexes, and notwithstanding that the 1:1 complexes present a less favourable case for study than the 1:2 compounds, some chemically useful conclusions can be drawn.

Electronic Spectra. All the complexes exhibit a broad band in the visible region which is generally resolvable at liquid nitrogen temperature into two main peaks often with one or more shoulders to lower energy (Table II).

For a given ligand X, the band positions show, with few exceptions, very little dependence upon the amine. In the chloride series, for example, the two main bands lie in the regions 13,560 to 14,160, and 15,335 to 16,340 cm⁻¹ which seems to imply that all the chlo-

(2) G. Giuseppetti and F. Mazzi, *Rend. Soc. mineral Ital.*, 11, 202 (1955).

Table III. Far Infrared (500 cm^{-1} - 190 cm^{-1}) Spectra and Force Constant Data.

Complex	Ring	$\nu(\text{M-N})$	$\nu(\text{M-N})$	$\tau(\text{CH}_3)$	$\nu(\text{M-X})$	Other bands ^a
Cu(en)Cl ₂	475s	375s [0.944]	317s	—	267s [1.04]	285m 218s
—D		362s	312s	—	267s	— 220s
Cu(en)Br ₂	470s	370s [0.933]	302s	—	187s [0.813]	278m, 228m
—D		360s	290m	—	187s	— 228m
Cu(en)(NCS) ₂	473s	374s [0.965] ^b	323m, 318m	—	259m 249m [1.41] ^b	282m [NCS 2137s, 2110s, 794m, 457m]
Cu(Sym-Me ₂ en)Cl ₂	481w 427w 449s	395m [1.02]	352s	282s	307s 208s [1.41]	262s
Cu(Sym-Me ₂ en)Br ₂	454s	388m [1.01]	353m	288s	227m [1.22]	370m, 263s
Cu(Sym-Me ₂ en)(NO ₃) ₂	457s 427s	391w [1.03]	386w	298s	326s [0.839]	(234) 221s, 212w
Cu(Sym-Me ₂ en)(NCS) ₂	464m 431s	399s [1.09]	384m	290s	309vs [0.668]	256w, 231m, 229m, 204s NCS, 2121s, 2075s, 800m, 487s
Cu(Asym-Me ₂ en)Cl ₂	447m 425s	380s [0.935]	—	283m	302s [1.37]	(392) 248m, 207w
—D	445m 425s	373s	—	283m	302s	(392) 248m, 207w
Cu(Asym-Me ₂ en)Br ₂	450m 428s	376s [0.940]	—	286m	233m [1.29]	264s
Cu(Asym-Me ₂ en)(NCS) ₂	460m 425s	380s [0.989]	—	286s	307vs [0.659]	499s, 260w, 231m, 225m, 204w [NCS 2141s, 2075s, 784m, 483m]
Cu(Sym-Et ₂ en)Cl ₂	492s	397s [1.02]	—	298s	312s [1.47]	272m, 252m
Cu(Sym-Et ₂ en)Br ₂	464m	387s [1.00]	—	285s	229m [1.24]	279s, 229m
Cu(Sym-Et ₂ en)(NO ₃) ₂	447m 413s	402m [1.09]	366m	296s	332s [0.870]	496m, 260m, 227m
Cu(Asym-Et ₂ en)Cl ₂	468m 427m	398s [1.06]	350m	305m	280s [1.14]	332w, 242m, 225m
Cu(Asym-Et ₂ en)Br ₂	470m 422m	395s [1.06]	350m	298s	198s [0.914]	330w, 245s
Cu(Asym-Et ₂ en)(NO ₃) ₂	480s 427s	401s [1.09]	343s	290s	321s [0.810]	261m, 225vs
Cu(1,3-DAP)Cl ₂	416s	341s [0.742]	—	—	286s, 208s [1.25]	237m
—D	457s 403m	327m	—	—	286m, 208s	232m
Cu(1,3-DAP)Br ₂	498s 411s	333s [0.752]	—	—	199s [0.927]	245s
Cu(1,3-DAB)(NO ₃) ₂	450m 418w	365s (347) [0.904]	—	—	314m [0.777]	300w, 232m, 220m
Cu(1,4-DAB)Cl ₂	383s	335w [0.739]	—	—	272s, 253s [1.10]	260s
Cu(1,4-DAB)Br ₂	381s	338w [0.768]	—	—	212s [1.06]	263s

[] = Calculated force constants in $\text{md}/\text{\AA}$, with $f_{\text{NX}} = .1 \text{ md}/\text{\AA}$. ^b $f_{\text{NX}} = 0.2 \text{ md}/\text{\AA}$ — with $f_{\text{NX}} = 0.1$, equations fail to solve D = N-deuterated amine complex () = shoulders. a) 'Other bands' includes bands due to the thiocyanate group, as indicated, and may include unidentified metal ligand vibrations.

ride complexes have similar structures. In the bromide series the higher energy band lies within the narrow range 15,310 to 15,970 cm^{-1} but there is a somewhat larger variation (about 1700 cm^{-1}) in the energies of the lower band. In the nitrate complexes the lower energy band varies by about 1300 cm^{-1} and the higher by about 1000 cm^{-1} .

It is concluded that all the complexes may be regarded to have a CuN_2X_2 in-plane microsymmetry with a varying interaction from adjacent molecules along the z axis. This interaction is undoubtedly present in all the complexes since an isolated four-coordinate CuN_2X_2 chromophore would absorb at higher energies than observed here.³ In the case of the nitrate complexes, the axial interaction probably arises through interaction with a second oxygen atom of the nitrate group (*i.e.* the nitrate group bonds in an asymmetric bidentate mode) as recently observed⁴ in the complex $\text{Cu}(2\text{-Picoline})_2(\text{NO}_3)_2$.

For a given ligand, the electronic energies shift, as a function of X in the spectrochemical series:



implying an increase in the d orbital splitting in that order. A detailed interpretation of the electronic spectra of both the $\text{Cu}(\text{diamine})\text{X}_2$ and $\text{Cu}(\text{diamine})_2\text{-X}_2$ series of complexes will be presented elsewhere.

Far Infrared Data. The methods utilised in assigning the far infrared spectra of the 1:1 derivatives ($\text{Cu}(\text{N-N})\text{X}_2$) are identical to those discussed in detail for the 1:2 derivatives¹ ($\text{Cu}(\text{N-N})_2\text{X}_2$) and therefore will not be repeated here. Suffice to say that the spectrum for a given pair of ligands in the 1:1 series is very similar to that of the corresponding 1:2 complex. The principle difference is the presence of the $\nu(\text{Cu-X})$ modes in the 1:1 spectrum these generally being absent from the 1:2 spectra because the Cu-X bond is a long axial bond giving rise to a low energy vibrational usually outside the range of the spectrometer.

The assignments are presented in Table III. The inplane skeletal (ring vibrations) are found, as previously noted,¹ between 400 and 500 cm^{-1} , whilst the $\nu(\text{Cu-N})$ vibrations, which decrease slightly upon N-deuteration of the amine appear in the region 330-400 cm^{-1} . The $\nu(\text{Cu-X})$ modes are strongly X sensitive and are unaffected by N-deuteration. They fall in ranges consistent with the presence of tetragonally distorted octahedral copper complexes.^{3,5}

It is recognised, of course, that a vibration identified as a metal ligand in origin will undoubtedly be coupled to other vibrations in the molecule. The label «metal nitrogen» or «metal halogen» implies that this vibration makes a predominant contribution to the potential distribution.

The data in Table III immediately reveal that these

(3) M. Keeton, A. B. P. Lever, and B. S. Ramaswamy, *Can. J. Chem.*, **48**, 3185 (1970).

(4) A. F. Cameron, R. H. Nuttall, and D. W. Taylor, *J. Chem. Soc.*, **D** 865 (1970).

(5) M. Keeton and A. B. P. Lever, *Spectrochim. Acta*, **26A**, 2173 (1970).

metal ligand vibrations are quite sensitive to small structural changes arising from changing the amine.

Consideration of the data leads to the following statements:

1) the copper nitrogen frequency (higher when there are two) is dependent upon the group X and shifts to higher energy (with one exception) in the same sequence (1) as the electronic bands.

2) If the data are plotted as a function of amine (Figure 1) then some interesting regularities are observed. An approximately straight line relationship is observed between the $\nu(\text{Cu-X})$ and $\nu(\text{Cu-N})$ vibrations for all the amine ligands except ethylene-diamine and N,N-diethylethylenediamine. Moreover slopes of all the lines so obtained are 2 as determined from a least squares analysis of the data. The fact that the slopes are the same, and that the same ligands are always exceptions would seem to indicate that this relationship is genuine and not spurious.

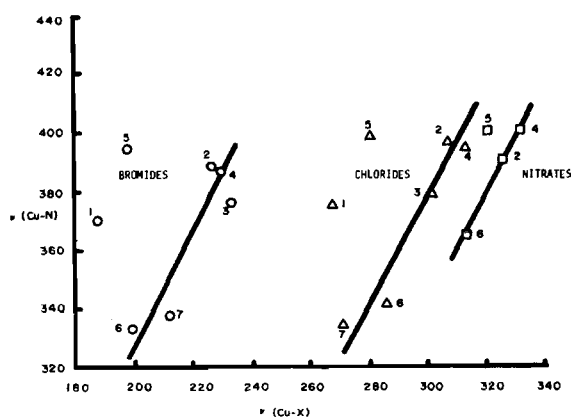


Figure 1. A plot of the highest metal nitrogen frequency versus the highest metal halogen (or nitrate) frequency, in the series $\text{Cu}(\text{N-N})\text{X}_2$. All lines have a slope of 2 [Derived by least squares analysis]. Ligands: 1, En; 2, Sym-Me₂en; 3, Asym-Me₂en; 4, Sym-Et₂en; 5, Asym-Et₂en; 6, 1,3-DAP; 7, 1,4-DAB.

In considering relationships of this sort, one should seek a correlation between the fundamental properties concerned, namely the force constants. Only in the absence of severe coupling and of changes in the reduced mass, will it be reasonable to assume that relationships between sets of frequencies also infer similar relationships between the corresponding force constants. In the relationship (2), since all the derivatives on a given line have the same in-plane CuN_2X_2 microsymmetry and differ only in the substitution upon the nitrogen atoms, the reduced masses will be effectively unaltered. If coupling to other internal modes of the molecule (within the amine) or to the lattice is important then it is extremely unlikely that such a good correlation would have been observed. We conclude that, as was the situation in the 1:2 complexes¹ coupling is either small, or makes an approximately constant contribution throughout the series. In the 1:2 series the unimportance of coupling could be rationalised in terms of the fairly high symmetry of the complexes making it less likely that vibrations of the same symmetry description would occur close in energy.

At first sight such a statement cannot be made about these derivatives since their microsymmetry is C_{2v} whilst their site symmetry (at least for the crystallographically determined $\text{Cu}(\text{enCl}_2)$) is at least as low as C_2 . However recent e.s.r. and magnetic anisotropy experiments⁶ with the complex $\text{Cu}(\text{enCl}_2)$ suggest that the effective symmetry is actually as high as D_2 , thus coupling may in fact be minimised for symmetry reasons.

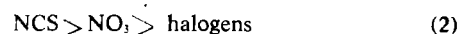
It is conceivable that the trends observed in the copper nitrogen vibrations as a function of X (for a given amine) and which parallel the electronic spectra may be spurious. Whilst the arguments presented above suggest that coupling of the copper nitrogen modes to the lattice and to internal modes of the ligand is not a serious problem, coupling to the copper halogen modes may be severe.

Since we see only one copper nitrogen stretching vibration and only one copper halogen stretching vibration it may be reasonable to discuss these data in terms of a linear triatomic model, viz: N-Cu-X . If coupling across the two N-Cu-X units in the CuN_2X_2 chromophore is important we would expect to see two infrared active Cu-N and Cu-X stretching modes, which is not generally the case. Although additional bands are observed in a few complexes, which could be metal-ligand in origin, in the majority of cases, no more than one of each of the copper ligand stretching modes could be identified.

We have therefore treated the data in terms of a linear triatomic oscillator⁷ in order to solve for the copper nitrogen and copper X force constants (f_N and f_X) respectively. The interaction (coupling) between the stretching modes is accounted for by the interaction force constant f_{NX} .

There being only two observables, f_{NX} is assumed to be 0.1 md/A. The primary force constants are expected near 1.00 md/A (cf. $f(\text{Cu-NH}_3) = 0.84$ md/A)⁸ and interaction constants in triatomic molecules rarely exceed 10% of the primary force constants concerned.⁹ It transpires (see below) that the precise value assumed for f_{NX} does not influence the conclusions which will be reached.

The force constants so derived are given in square brackets in Table III where it is seen that the sequence of Cu-N force constants, as a function of the trans group X, may be written:



Note also that the Cu-X force constants increase in the same sequence. Thus a trans effect is confirmed in these complexes, whereby the nature of the Cu-X bond controls the Cu-N force constant and hence bond strength. The proposed mechanism parallels that of the 1:2 derivatives.¹ As the electronegativity of X decreases (X becomes more polarisable) more charge is transferred to the copper atom, whose effective charge is thereby reduced, and the copper nitrogen interaction is weakened. The thiocyanate

(6) D. E. Billing, R. Dudley, B. J. Hathaway, P. Nichols, and I. M. Proctor, *J. Chem. Soc., A* 316 (1969).

(7) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, « *Molecular Vibrations* », McGraw Hill, Toronto, 1955.

(8) T. Shimanouchi and I. Nakagawa, *Inorg. Chem.*, 3, 1805 (1964).

(9) K. Ramaswamy and V. Ranganathan, *Z. Naturforsch.*, 25b, 675 (1970).

ion gives rise to the strongest *trans effect* since the Cu–NCS bond is the weakest in the series and presumably fairly ionic; thus the copper ion retains a high effective charge.

Whilst the Cu–N frequency in the chloro complexes is almost always higher than in the bromo series, as would be anticipated, there is in fact very little difference between the Cu–N force constants as a function of halogen. If the interaction constant is varied from 0 to 0.3 md/A (*i.e.* from 0–30% of the values of the primary force constants) this has no effect upon sequence (2) although in some cases it does alter the relative order of the halogens. Such a range of f_{NX} undoubtedly contains the correct values.

Returning to the correlation in Figure 1, it is seen to be excellent for the nitrate complexes, good for the chloride complexes, but rather poor for the bromide derivatives. In this last case coupling contributions may be important, or more likely, there is some distortion towards a tetrahedron in these more covalent derivatives. If the force constants from the earlier calculation are plotted in a similar fashion, approximately straight line correlations are again achieved, with the exception of the same two ligands; the bromide correlation is, however, poor. The slopes of these force constant lines are dependent upon the choice of f_{NX} . It is evident from these remarks that the correlations in Figure 1 are real, and may be interpreted in a manner exactly similar to that employed for the 1:2 complexes.¹

The bulkier amines occur at the top of the lines; they inhibit the approach of adjacent molecules, decrease the axial interaction and therefore the molecules are more strongly tetragonally distorted. Thus proceeding along a line, increasing tetragonal distortion results in stronger in-plane bonding which is reflected in these 1:1 complexes by an increase in both the copper amine and copper X stretching frequencies (and force constants). It is by no means clear why the ligands En and Asym–Et₂en consistently fall off these lines. The answer probably lies in the detailed structures of these derivatives (perhaps the compounds on the line are five coordinate, and those off, six coordinate) and further discussion must await additional X-ray information.

Considering those amines which do fall on the line in Figure 1, this vibrational correlation is paralleled in the chloro and nitrate series by the electronic spectra both d–d bands moving to higher energy as the complex becomes more tetragonal. This is consistent with expectation.¹ In the bromide series there are some discrepancies once again, and distortion of the molecule towards a tetrahedron may account for these.

Comparison of these Results with the Cu(N–N)₂X₂ (1:2) Derivatives. As we have observed the two series of complexes exactly parallel one another, with increasing in-plane force constants (bond energies) and an increasing splitting of the *d* orbital manifold, as the degree of tetragonal distortion increases, (axial interaction decreases).

It is a curious observation however that the $\nu(\text{Cu–N})$ frequencies of the alkyl N–substituted amine derivatives in the 1:1 series are similar to, or slightly higher, than those observed in the 1:2 series, whilst

in the unsubstituted amine series, the frequencies observed in the 1:1 complexes are appreciably lower than those observed in the 1:2 complexes: If the complexes of the 1:2 series are thought of as special examples of the 1:1 complexes with X₂=amine, then the substituted amines are placed at the right hand of sequence (2) and the unsubstituted ligands on the left-hand. Hence the N–alkyl substituted derivatives behave as though they were much more polarisable and transmit much more electron density to the copper atoms, than do the unsubstituted amines. This is exactly to be expected in view of the inductive effect of the alkyl substituents. It may be relevant that the substituted ligands tend to form the most square complexes where the copper atom is sufficiently polarising to make good use of this available electron density.

The correlation between structure, bond strength, vibrational and electronic spectra may ultimately prove useful, as discussed earlier,¹ as a means of obtaining useful thermodynamic information from solid state studies. Of course such studies are not limited to copper complexes, although these have been found to be the most promising. Correlations of the types shown here, and previously,¹ have been noted before, but have generally only been isolated observations and therefore subject to criticism. For example the copper nitrogen band (highest energy) in the series Cu(NH₃)₂X₂ is also very sensitive to the nature of X.¹⁰ In general the frequency of absorption does in fact increase with increasing electronegativity of X, but the correlation is less meaningful, because the structures within this series are more variable.¹⁰ Studies of the copper nitrogen frequencies in the series Cu(NH₃)₄X₂, as a function of X have also been made¹¹ but have not yet been published in detail.

In the series Co(NH₃)₅X²⁺ X=Cl, Br, and I, the highest energy Co–N stretching vibration shifts to lower energy in the sequence of increasing polarisability of the halide.¹² Similar but less marked effects are seen in the series M(NH₃)₆X₂ with various metals as a function of X.¹² In the latter case electron density is perhaps being transferred to the metal atom in some kind of hydrogen bonding process. Of course such small changes in frequency in these last isolated examples may arise from effects quite unrelated to changes in electron density at the metal atom. Coupling to the lattice and changing degrees of hydrogen bonding through the lattice with varying halogen, may be responsible. However having demonstrated that the metal nitrogen frequency is indeed sensitive to the effective charge of the metal atom, we should seriously consider the proposition that the position of the metal nitrogen stretching frequency in a series of closely related complexes may carry considerable information about the nature of the metal ligand bonds.

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