Charge-Transfer Spectra of Bis(diamine)copper(II) Complexes and Their Correlation with Other Electronic, Vibrational, and Thermodynamic Properties

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Abstract: The charge-transfer spectra of a series of complexes Cu(diamine)$_2$X$_2$, where diamine is 1,3-propylenediamine, ethylenediamine, *N*-methylethylenediamine, or the symmetric or asymmetric *N,N*-dimethyl- or *N,N*-diethylethylenediamine, and X is H_2O, CH_3OH, a halogen, NO_3^-, BF_4^-, or ClO_4^-, are reported. In most of the complexes there is observed, in the region 30.00–43.00 kK, a single band assigned to the in-plane σ–σ^* transition. In certain of the asymmetric dialkylethylenediamine complexes there are observed two bands which are assigned independently to each of the two types of in-plane σ–σ^* transition. Excellent linear correlations are observed between this ultraviolet charge-transfer transition and the metal–ligand stretching frequencies and crystal field ($x^2 - y^2 \leftarrow xy$) in-plane transition, in the solid state. All the data are discussed in terms of a previously described model of tetragonal distortion. The possibility of obtaining the heats of formation of these complexes from a detailed consideration of their electronic spectra is discussed in depth in the light of a reasonable correlation between such heats of formation and the electronic transition energies of the molecules. Finally the ultraviolet spectra of certain thermochromic derivatives in this series provide evidence of an interaction between the axial group X and the alkyl groups on the tertiary nitrogen atoms.

We have recently published a series of articles[1–5] demonstrating, in the series M(diamine)$_2$X$_2$ (M = Co(II), Ni(II), and Cu(II)), how metal–nitrogen stretching frequencies and electronic d–d transitions are influenced by the extent of tetragonal distortion occurring in these complexes. In the copper complexes a linear relationship[1] was observed between the square of a metal–nitrogen stretching frequency (whose assignment was substantiated by metal isotopic substitution experiments)[3] and the visible band maximum. The data were explained in terms of increasing in-plane bond strength as the axial ligand became a weaker donor or as the in-plane ligand became more bulky. An essentially similar argument was used to explain the variation in metal–nitrogen stretching frequencies in the cobalt(II) and nickel(II) complexes, also substantiated by isotopic experiments,[4] taking into account the differences in structural chemistry between these last two elements and copper(II).

Of particular importance was the observation that with appropriate counterions heavily substituted ethylenediamines provide greater in-plane field strengths than ethylenediamine itself, which is counter to arguments based on thermodynamic experiments in aqueous media (stability constants, free energy, and enthalpy changes, etc.).[6–8] This anomaly was explained in terms of competition between in-plane ligand and axial ligand for the copper electron density; in the case of aqueous media, water can apparently successfully compete in the presence of a heavily substituted ethylenediamine residue. This is not the case for all other anions.

The arguments employed, since they infer steadily increasing in-plane bond strengths in appropriate series of complexes, are subject to test by any alternate means of assessing in-plane bond strengths. Yokoi and Isobe[9] had assigned the ultraviolet absorption observed in aqueous solutions of some of these complexes to a σ–σ^* type charge-transfer transition. If this assignment is substantiated a correlation between these band energies and the data previously obtained should exist; this is so demonstrated here. In support of the basic principles previously discussed,[1–5] Paoletti, *et al.*,[10] have recently reported a direct correlation between the enthalpies of formation of certain diamine copper complexes in aqueous solution and their visible band maxima.

Experimental Section

All the complexes have been previously described in this series.[1,3] Analytical procedures were employed to assure purity before spectroscopic data were obtained. Solid state spectra were recorded *via* transmittance through a sample held between quartz plates in an Applied Physics Cary 14 spectrometer. The sample was finely ground using a "Wig-L-Bug" (Crescent Dental Manufacturing Co., Chicago, Ill.) and mulled with Dow Corning 200 Fluid (Viscosity 2,500,000 centistokes) which is transparent down to at least 44,000 cm^{-1}. The d–d spectra were recorded with the same mull although all such data had been obtained previously[1] using Nujol mulls supported on filter paper. The d–d data used in this paper are those recorded with the Dow Corning mull; they differ slightly in some cases from those previously reported.[1] The differences are believed to be due to the fact that such absorption is fairly broad and often asymmetric, making it difficult to identify band centers accurately. Such band centers may shift slightly as a function of particle size and mulling agent. In order to test the procedure for obtaining ultraviolet spectra, a mull was prepared with naphthalene. The spectrum so obtained, inclusive of vibronic progressions, was identical with that available in the literature.

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

(2) A. B. P. Lever and E. Mantovani, *Inorg. Chim. Acta*, **5**, 429 (1971).

(3) G. W. R. Canham and A. B. P. Lever, *Can. J. Chem.*, **50**, 3866 (1972).

(4) A. B. P. Lever and E. Mantovani, *Can. J. Chem.*, **51**, 1567 (1973).

(5) A. B. P. Lever, E. Mantovani, and J. C. Donini, *Inorg. Chem.*, **10**, 2424 (1971).

(6) *Chem. Soc. Spec. Publ.*, **No. 6** (1957).

(7) R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 740 (1972).

(8) D. L. Leussing, *Inorg. Chem.*, **2**, 77 (1963).

(9) H. Yokoi and T. Isobe, *Bull. Chem. Soc. Jap.*, **42**, 2187 (1969).

(10) R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Inorg. Chem.*, **12**, 1961 (1973); P. Paoletti, private communication, 1972.

Table I. Visible Absorption Data[a] (kK)

Species	X						
	H_2O	MeOH	Cl	Br	BF_4	ClO_4	NO_3
Cu(en)$_2$X$_2$	18.18 (1.78)	17.97 (1.88)[e]	18.69	18.46	19.56	19.25	18.98
Cu(*sym*-Me$_2$en)$_2$X$_2$	17.71 (2.01)	17.84 (2.0)[f]	18.17	18.00	18.78	18.79	18.45
Cu(*asym*-Me$_2$en)$_2$X$_2$	17.78 (2.19)	18.02 (2.15)[f]	17.21	17.40	18.67	18.94	18.90
Cu(*sym*-Et$_2$en)$_2$X$_2$	17.16 (1.99)	16.05 (2.23)[e]	16.05	16.16	18.89	18.73	18.05
Cu(*asym*-Et$_2$en)$_2$X$_2$	16.97 (2.15)	17.02 (2.31)[f]	16.33	15.95	19.64	20.64	21.82[b] 16.81[c]
Cu(1,3-DAP)$_2$X$_2$	17.64 (2.03)	17.70 (2.06)[f]	17.97	17.00	16.08	17.60[d]	18.14

[a] Solution data in water or methanol; log of the extinction coefficient in parentheses. Other data recorded in the solid state. Abbreviations: en = ethylenediamine; *sym*-Me$_2$en = *N,N'*-dimethylethylenediamine; *asym*-Me$_2$en = *N,N*-dimethylethylenediamine; *sym*-Et$_2$en = *N,N'*-diethylethylenediamine; *asym*-Et$_2$en = *N,N*-diethylethylenediamine; Meen = *N*-methylethylenediamine; 1,3-DAP = 1,3-propylenediamine. [b] Red isomer. [c] Blue isomer. [d] Very asymmetric absorption. [e] Bromide complex was dissolved in methanol. [f] Nitrate was dissolved in methanol (see text).

Results and Discussion

Band Assignment. There have been few reports dealing with the charge-transfer, *i.e.*, ultraviolet, spectra of copper complexes of aliphatic amines. An early report[11] indicated the existence of absorption in the 200–250 nm region, and such absorption was subsequently studied by Yokoi and Isobe.[9] These workers studied the aqueous solution spectra of a series of copper bis(diamine) complexes and compared these results against covalency parameters obtained from electron spin resonance experiments and against estimated ionization potentials for the free ligands. In addition to the d–d band near 17,000 cm^{-1} they reported ultraviolet absorption between 35,000 and 43,000 cm^{-1} assigned to a transition from the e_u bonding orbitals to the $d_{x^2-y^2}$ antibonding orbital (see Figure 1). This transition was shown to increase linearly in energy with increasing ionization potential (estimated) of the ligand.

Table I reports visible and Table II ultraviolet spectra of representative complexes of ethylenediamine, *N*-methylethylenediamine, symmetric and asymmetric *N,N*-dimethyl- and -diethylethylenediamines, and 1,3-diaminopropane in the solid state, in aqueous and in methanol solution. Experiments revealed that the aqueous solution spectra were essentially independent of the counterion, suggesting that the dominant species in water is Cu(diamine)$_2$(H$_2$O)$_2^{2+}$. For those complexes in common, our aqueous data agree well with the band positions reported by Yokoi and Isobe for both d–d and ultraviolet bands. However, in the case of the species Cu(*sym*-Me$_2$en)$_2$(H$_2$O)$_2^{2+}$ we obtained a symmetric ultraviolet absorption band in contrast to the asymmetric band reported by the earlier workers.[9] In the methanol solution the dominant species is likely to be Cu(diamine)$_2$(MeOH)$_2^{2+}$, but some contribution from Cu(diamine)$_2$X$^+$ is probable.[12] As would be expected, the solid state spectra are dependent upon the nature of the counterion X, with which they vary quite remarkably. The nature of the visible band, and its dependence upon X, has been previously discussed in detail.[1]

The ligands are transparent in the ultraviolet spectrum, at least to the limits of the experiments carried out here; therefore, the absorption in the ultraviolet region must be d–d, charge transfer, or Rydberg in nature. Since the d–d spectra of copper(II) complexes with these ligands do not occur,[13] above about 25,000 cm^{-1}, such transitions cannot be invoked for the ultraviolet absorption. Moreover Rydberg absorption is also excluded since it would be anticipated at far higher energies.[13,14] A charge-transfer explanation for the ultraviolet absorption seems highly probable. Two types of charge-transfer absorptions may be generally considered, *viz.*, metal to ligand or ligand to metal. The first possibility may be safely excluded in this case on the basis that (a) many of the ligands involved, namely saturated diamine, water, perchlorate, etc., do not possess any accessible acceptor orbitals and (b) a brief study of the ultraviolet spectra[15] of the corresponding diamine complexes of the more readily oxidizable metals Co(II) and Ni(II) showed that their ultraviolet absorption lay at higher energies than in the copper complexes. Such data may be utilized, with care,[16] to infer that the charge transfer is from ligand to metal.[13,14]

Figure 1 represents a simplified molecular orbital scheme relevant to the complexes under discussion. For reasons which will become clear later in the discussion, it is convenient to assume, initially, that the complexes have D_{4h} symmetry, *i.e.*, the molecular orbital diagram is representative of a *t*-CuN$_4$X$_2$ complex. The π bonding levels of the X group have been omitted for clarity; there is no evidence that they are involved in any of the observable absorption. The ultraviolet absorption does not vary in the same manner as the energy of the π levels of X. In particular the transition energies in the chlorides and bromides are very similar and alternate in relative energy according to the nature of the in-plane amine. On the basis of the previous discussion there are two possible parity allowed transitions, namely

$$2b_{1g} \longleftarrow a_{2u}\ (^2A_{2u} \longleftarrow {}^2B_{1g}) \qquad \text{(i)}$$

and

$$2b_{1g} \longleftarrow e_u\ (^2E_u \longleftarrow {}^2B_{1g}) \qquad \text{(ii)}$$

We note that complexes of the symmetrically substituted amines are formally of D_{2h} symmetry, while those of the asymmetrically substituted amines will have C_{2h} symmetry, assuming that the ring methylene groups adopt the appropriate symmetric conformation.

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(11) G. Basu and S. Basu, *Anal. Chim. Acta*, **21**, 187 (1959).

(12) R. Barbucci, P. Paoletti, and L. Fabbrizzi, *J. Chem. Soc., Dalton Trans.*, 2593 (1972).

(13) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968.

(14) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962.

(15) B. P. Kennedy and A. B. P. Lever, unpublished observations.

(16) W. Byers, B. F.-C. Chou, A. B. P. Lever, and R. V. Parish, *J. Amer. Chem. Soc.*, **91**, 1329 (1969).

Table II. Ultraviolet Spectra[a] (kK)

	X						
Species	H_2O	MeOH	Cl	Br	BF_4	ClO_4	NO_3
$Cu(en)_2X_2$	43.86 (3.78)	40.05 (3.81)[f]	36.77	36.06	43.27	39.67	38.73 41.37[b]
Cu(*sym*-$Me_2en)_2X_2$	38.28 (3.89)	37.84 (3.85)[g]	35.17	34.65	38.21	38.78	35.45
Cu(*asym*-$Me_2en)_2X_2$	35.55 (3.67) 40.82 sh	35.30 (3.71)[g] 38.80 sh	33.97	32.56	39.39	33.91	37.11
Cu(*sym*-$Et_2en)_2X_2$	39.26 (3.70)	36.71 (3.67)[f]	33.48	33.58	36.36	36.10	35.34
Cu(*asym*-$Et_2en)_2X_2$	38.71 (3.56)	33.33 (3.52)[g]	33.57	*e*	31.10	31.27	29.63[c]
		39.67 (3.55)	42.11		40.42	41.31	33.96[d]
Cu(1,3-DAP)$_2X_2$	40.47 (3.81)	43.22 (3.73)[g]	34.60	37.23 35.45 sh	37.36	36.23	37.94

[a] Log of the extinction coefficient in parentheses after solution data in water and in methanol; other data were recorded in the solid state. [b] Nitrate absorption. [c] Red isomer. [d] Blue isomer (see ref 1). [e] Compound did not mull well and failed to yield reproducible spectra. [f] Bromide complex dissolved in methanol. [g] Nitrate complex dissolved in methanol (see text). The species $Cu(Meen)_2(H_2O)_2^{2+}$ absorbs at 18.1 (0.92) and 40.44 (3.37) kK in aqueous solution. The solid state spectrum of Cu(*sym*-$Et_2en)_2(NO_3)_2 \cdot 2H_2O$ absorbs at 17.54 and 35.65 kK. The quadridentate amines plotted in Figure 5 absorb at: (2-2-2) 39.08 (3.72); (2-3-2) 41.22 (3.78) 40.44 sh (mean position used in graph); (3-2-3) 39.26 (3.83); (3-3-3) 37.55 (3.84) kK (log ε), in aqueous solution.

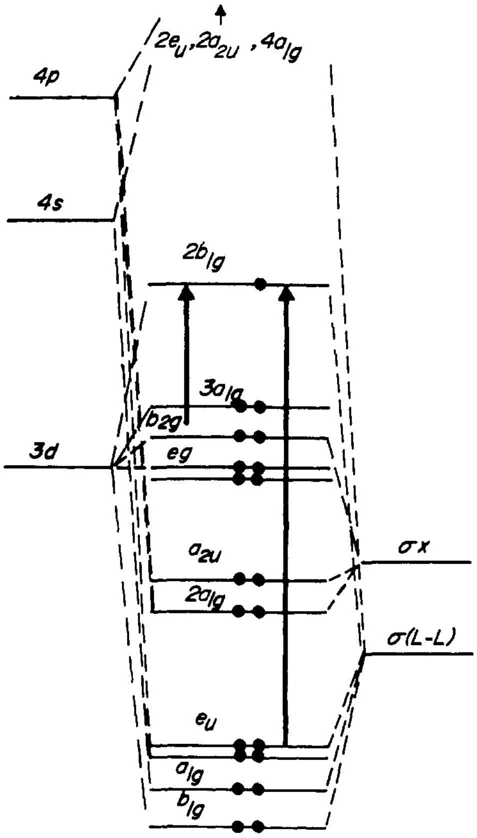

Figure 1. A molecular orbital diagram for $Cu(L\text{-}L)_2X_2$ complexes assuming D_{4h} symmetry. (The π orbitals of X are omitted for clarity.)

It is relevant that in most cases the intensities of absorption of the asymmetric ligands are greater than those of the symmetric ligands, reflecting the lower symmetry of the former. Transition i, while parity allowed, is orbitally forbidden in both D_{4h} and D_{2h}. It should therefore not be observed in complexes of the symmetric amines. While this transition is allowed in C_{2h}, we invoke the concept of the "symmetry ascent selection rule"[17] to argue that its intensity is likely to be very small in the asymmetric complexes. Transition ii, on the other hand, is orbitally allowed in all

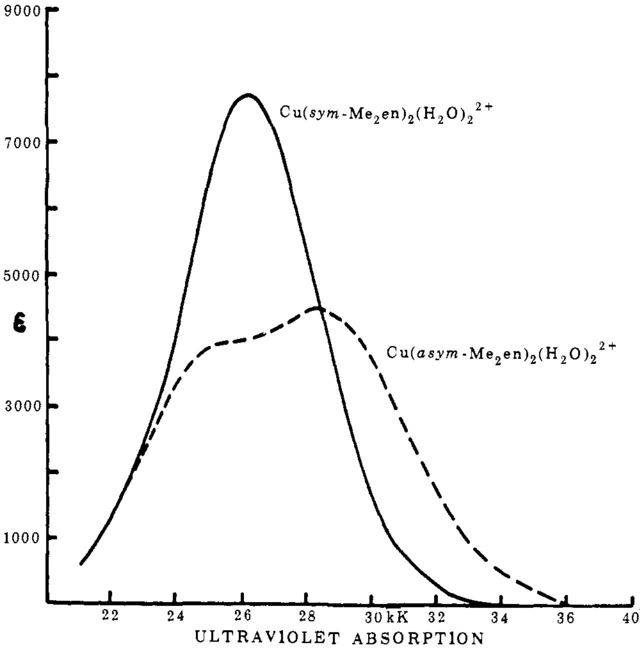

Figure 2. The ultraviolet spectra of Cu(*sym*-$Me_2en)_2(H_2O)_2^{2+}$ and Cu(*asym*-$Me_2en)_2(H_2O)_2^{2+}$ in aqueous solution.

these groups. We conclude, in agreement with Yokoi and Isobe,[9] that the ultraviolet absorption in these complexes does indeed arise from the $^2E_u \leftarrow {}^2B_{1g}$ transition (in D_{4h}). The e_u orbital primarily involves the σ bonding orbitals of the in-plane amine ligands, in combination with the metal p_x and p_y orbitals. It is relevant that Yokoi and Isobe demonstrated a fairly good linear relationship between the ultraviolet band maximum and the (estimated) ionization potential of the amine ligand. They showed that the smaller the ionization potential, and the stronger the basic character of the ligand, the lower was the ultraviolet band energy.

In D_{2h} symmetry this transition should split into two allowed transitions. The spectra of the symmetric amine complexes exhibit a single broad band (Table II, Figure 2), whose bandwidth at half-height is of the order of 8000 cm^{-1}. While this breadth may in part arise through some splitting of the ^2E_u state, it should be recognized that even in the absence

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(17) B. R. Hollebone, A. B. P. Lever, and J. C. Donini, *Mol. Phys.*, 22, 155 (1971).

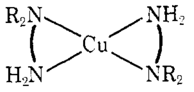
of any splitting a very broad band would be expected. This transition may be classified as a σ–σ^* transition and the equilibrium metal–ligand distance in the ^2E_u state is going to be markedly longer than in the $^2B_{1g}$ ground state. Such conditions lead to broad bands.[13,14] Similarly in C_{2h} symmetry two transitions may be anticipated, and in the case of the asymmetric amine complexes, two bands are indeed frequently observed (Tables II and III, Figure 2). The possibility that one of these two bands is in fact transition i (above) seems excluded both on the argument previously cited and because the intensities of the two bands observed in the asymmetric amine complexes are roughly one-half of the intensities observed in the spectra of the symmetric amine complexes. In assigning a C_{2h} point group symmetry to the asymmetric amine complexes we assume a trans configuration (I); molecular models suggest the cis configuration would be crowded. Moreover an X-ray structural determination[18] of Ni(*asym*-$Et_2en)_2(NO_2)_2$ reveals a trans configuration.

Table III. Thermochromic Complexes of *asym*-Diethylethylenediamine (Effect of Temperature upon the Electronic Transitions (kK))

Complex	Temp, °C	d–d transition	σ–σ^{*a} I	II
Cu(*asym*-$Et_2en)_2(ClO_4)_2$	−190	21.86	32.58	41.43
	0	21.13	31.26	41.34
	25	20.64	31.27	41.31
	78	19.74	30.65	41.37
Cu(*asym*-$Et_2en)_2(BF_4)_2$	−190	21.95	32.38	41.53
	0	21.29	32.20	41.67
	78	19.02	30.4 sh	41.46
Cu(*asym*-$Et_2en)_2Cl_2{}^b$	−190	16.96	33.59	42.10
	25	16.33	32.69	42.10

[a] I refers to the Et_2N–Cu–NEt_2 bond; II refers to the H_2N–Cu–NH_2 bond (see structure I in text). [b] This complex is not obviously thermochromic and is included for comparison purposes. The data were all obtained from Dow Corning grease mulls. The room temperature data vary slightly from those previously published.[5] See the Experimental Section.

In the point group C_{2h}, the wave functions for the H_2N–Cu–NH_2 σ bond and the R_2N–Cu–NR_2 σ bond transform according to different representations of the group. Therefore to a first approximation the two observed ultraviolet transitions may be separately identified as σ–σ^* transitions from each of these two types of σ bond. It is clear from the previous discussion and from Yokoi and Isobe's correlation that the lower energy absorption band can be associated with σ–σ^* (R_2N–Cu–NR_2) and the higher with σ–σ^* (H_2N–Cu–NH_2). It is relevant that X-ray structural investigations of[18] Ni(*asym*-$Et_2en)_2(NO_2)_2$ and of[19] bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)bis(*N*,*N*-dimethylethylenediamine)copper(II) show that the M–NR_2 bond is significantly longer than the M–NH_2 bond.



I

Temperature Dependence of the Ultraviolet Transitions in the Thermochromic Complexes of *asym*-Diethylenediamine. The complexes Cu(*asym*-$Et_2en)_2X_2$, where X = ClO_4 and BF_4, have previously[5] been shown to be thermochromic with a color transition from orange–red to purple near room temperature. At low temperatures the strongly tetragonally distorted orange–red form is stable, while at about 78° the more closely octahedral purple form is stable. This change was interpreted in terms of a temperature-dependent variation in the axial copper to X bond length, which increased with decreasing temperature. Barbucci, Fabbrizzi, and Paoletti[20] report ΔH values of about 3000 cal/mol associated with this thermochromic behavior and suggest that the Cu–X bond length is influenced by interaction of the axial group with the alkyl groups on the tertiary nitrogen atoms. Data in Table III reveal that one of the two σ–σ^* transitions, namely that arising from the Et_2N–Cu–NEt_2 bond, is quite temperature dependent, while the other is essentially temperature independent. These data provide convincing evidence of the interaction of the axial group with the tertiary nitrogen atom alkyl groups.

Correlation of Ultraviolet Transition Energy with Visible Band Energy, Metal–Ligand Stretching Frequencies, Enthalpies of Formation, and Tetragonal Distortion. The connection between the metal–nitrogen stretching frequencies in these complexes and their visible band energy, in terms of the degree of tetragonal distortion and the in-plane bond strength, has been established previously.[1–5] It is reasonable to expect that a similar correlation will be found with the ultraviolet absorption. Very recently Paoletti, *et al.*, have reported[10] a direct linear correlation between the enthalpy of formation of several diamine copper complexes in aqueous solution and their visible band energies. A similar correlation between the σ–σ^* transition energy and the enthalpy of formation of the in-plane metal ligand bonds might well be anticipated. Figures 3–5 illustrate the relationships between the ultraviolet band energy and metal–nitrogen stretching frequencies, visible band energies, and enthalpies of formation, respectively. Since the two bands in the asymmetric complex ultraviolet spectra cannot always be resolved, such complexes are excluded from most of the correlations.

Correlation of Ultraviolet Transition Energy with ν(Cu–N) Stretching Frequencies. These data are displayed in Figure 3 for the ethylenediamine and *sym*-dimethylethylenediamine complexes. Two ν(Cu–N) vibrations have been identified.[1,3] There is a good correlation between the electronic transition energy and the vibrational frequencies for both vibrations.

Correlation of Ultraviolet Transition Energy with Visible (d–d) Band Energy. Given a correlation between the d–d band and the metal nitrogen vibrational frequencies, then, accordingly there must be a correlation between the visible and ultraviolet band energies; this exceptionally good correlation is shown in Figure 4. Ideally the ultraviolet transition energy should be plotted against the $x^2 - y^2 \leftarrow xy$ d–d transition;[1,3] in practice the visible band maximum is used.

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[18] M. B. G. Drew, D. M. L. Goodgame, M. A. Hitchman, and D. Rogers, *Proc. Chem. Soc., London*, 363 (1964).

[19] M. A. Bush and D. E. Fenton, *J. Chem. Soc. A*, 2446 (1971).

[20] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Proc. Int. Conf. Coord. Chem., 15th, 1973*, 503, and private communication.

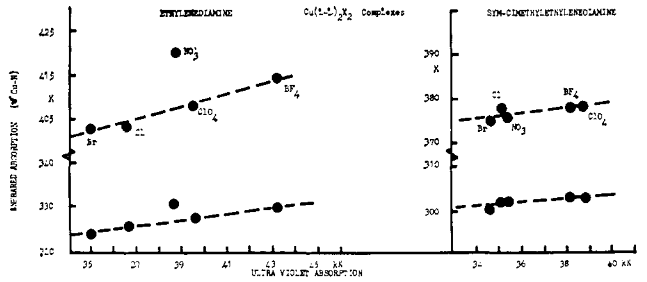

Figure 3. Metal–nitrogen stretching frequencies *vs.* ultraviolet absorption maxima in some $Cu(L-L)_2X_2$ complexes of ethylenediamine and *sym*-dimethylethylenediamine.

This band maximum corresponds directly with the $x^2 - y^2 \leftarrow xz, yz$ transition which obscures the former transition. For most complexes the approximation that both transitions have the same energy is valid.[3] It should be noted that this correlation is not a trivial exercise. In the case of *sym*-diethylethylenediamine a good correlation between the visible band energy and the ν(Cu–N) stretching frequencies[1] was not obtained. Similarly the correlation between these *sym*-Et_2en vibrational energies and the ultraviolet bands is poor. However, the correlation presented for this ligand in Figure 4 is excellent. Vibrational coupling may vitiate the vibrational correlation.

While the correlation between the visible and ultraviolet energies measured with solid samples is exceptionally good, data obtained in aqueous, methanolic, or ethanolic solution, also shown in Figure 4, do not fall on the correlation lines. The possibility that the stereochemistry in solution differs from that in the solid state, say *c*-$Cu(diamine)_2(solvent)_2$ rather than trans, seems unlikely in view of the close similarity in the visible absorption spectra of the solids and solutions. A more creditable explanation is a "solvent effect;" charge-transfer transitions are well known to be sensitive to changes in the dielectric nature of the media. It is probable that the $^2B_{1g}$ ground term is more stabilized by the polar solvent than the ^2E_u excited state because of the former's greater charge separation. In support of this we note that as the dielectric constant of the solvent decreases, the species lie closer to the correlation line (*e.g.*, see the data for the *sym*-Et_2en complexes). We return to a discussion of this phenomenon below.

Correlation of Ultraviolet Transition Energy with Enthalpy of Formation. Figure 5 contains a plot of the ultraviolet transition energy *vs.* the available enthalpy data for the formation of $Cu(LL)_2^{2+}$ from Cu^{2+} and the bidentate LL in aqueous solution. The figure also includes data[10,21] for the ligands $H_2N\cdot(CH_2)_n\cdot NH\cdot(CH_2)_m\cdot NH\cdot(CH_2)_n\cdot NH_2$ labeled therein by their *n-m-n* values. In this case the enthalpy data refer to the reaction of 1 mol of the tetradentate ligand with the aquo copper(II) species in water. Of the eight compounds, five lie well on the line while three deviate markedly. In the corresponding relationship between the visible band maximum and enthalpy, discussed by Paoletti, *et al.*,[10] six compounds lie on the line and two deviate slightly; the overall correlation is much better.

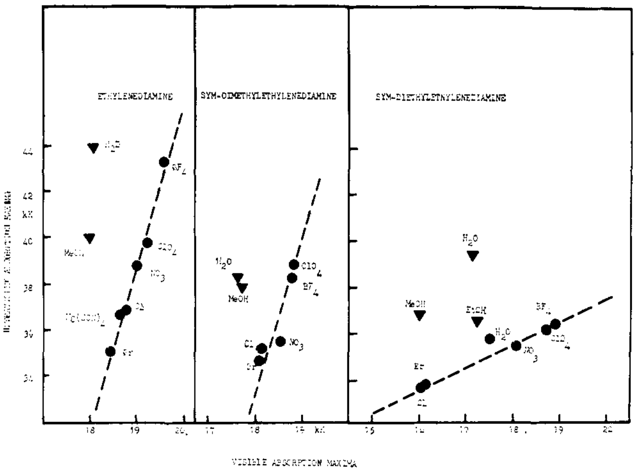

Figure 4. Correlation between ultraviolet and visible absorption maxima in $Cu(L-L)_2X_2$ complexes of ethylenediamine, *sym*-dimethylethylenediamine, and *sym*-diethylethylenediamine. The circles refer to solid state data and the triangles to solution data.

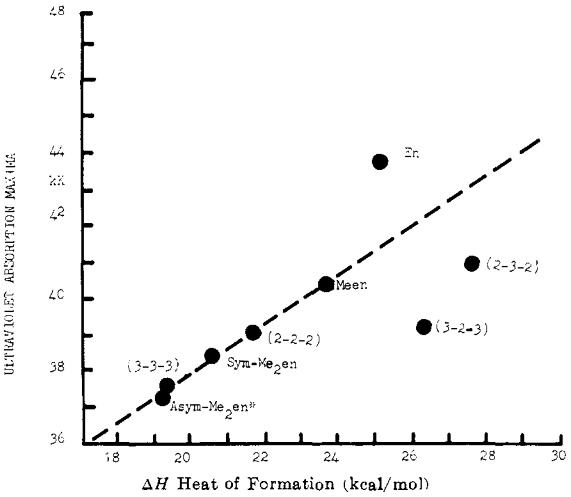

Figure 5. Correlation between the heat of formation in aqueous solution and ultraviolet absorption maxima for some copper amine complexes in aqueous solution. The numerals in parentheses (*n-m-n*) refer to complexes of the quadridentate ligands $H_2N(CH_2)_nNH(CH_2)_mNH(CH_2)_nNH_2$.

Summary

The accumulated vibrational, and electronic (d–d and charge transfer), data provide convincing support for a model of tetragonal distortion in which the in-plane bond strength increases as the axial ligation decreases. The decreasing axial ligation may be facilitated either by using bulky in-plane ligands or weakly coordinating axial ligands.

This work was initiated[1-3] with a view to utilizing solid state vibrational and electronic spectroscopic data to determine the bond strengths in coordination complexes. Most of the work has been carried out with copper(II) because of its comparative spectroscopic simplicity; however, preliminary studies[4] with nickel(II) and cobalt(II) reveal that the concepts have general validity.

Thermodynamic studies with a limited number of amines have enabled Paoletti and his coworkers[10] to correlate visible energies of some diaminecopper complexes with their heats of formation in water solu-

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[21] R. Barbucci, L. Fabbrizzi, and P. Paoletti, *Coord. Chem. Rev.*, 8, 31 (1972).

tion. The correlation of visible energies with charge-transfer data and vibrational frequencies provides, in principle, the link necessary to determine heats of formation from solid-state vibrational and electronic data. While the heat of formation is not directly equal to the in-plane (Cu–L) bond enthalpy, since the former will have solvation energy contributions, it is reasonable to assume that the bond enthalpy (relative to the Cu–H_2O bond) will be the dominant contributor to the magnitude of this heat.

Concerning the vibrational correlation, the ν(Cu–L) frequency, or preferably force constant, is a measure of the width of the potential well, while the bond enthalpy is a measure of the height of the potential well. Since, for a harmonic oscillator at least, these two quantities are related, force constants, and therefore M–L stretching frequencies, reflect bond strengths, but not necessarily in a simple straightforward fashion.

Our studies have revealed important correlations between the vibrational and electronic data and between the visible and ultraviolet transition energies for series of complexes $Cu(LL)_2X_2$ *for a given LL and changing X*. No such correlations were observed for series in which X is maintained and LL is varied. Thus, in the case of the vibrational correlation changing LL will change the reduced mass of the Cu–L vibration rendering a comparison of the M–L frequencies valueless. Considering the data in Tables I and II, for a given X, there is a trend that as the visible energy increases so does the ultraviolet transition but the correlation is not linear and there are exceptions. A good correlation is only achieved when we are comparing the $xy \rightarrow \sigma^* (x^2 - y^2)$ visible transition against the σ–σ^* ultraviolet transition for a series in which LL is maintained constant. The two transitions concerned lie in the molecular plane and to first approximation changing X may be considered primarily to change the charge on the copper atom. However, it is clear that by maintaining X and changing LL more fundamental changes are being wrought and the relationship between the visible and ultraviolet transition energies cannot be expected to be maintained.

In this context Paoletti's correlation between the visible energies and the heats of formation of a series of different ligands (LL) in water is surprising. Clearly it must be extended to a larger number of amines to establish its validity. Similar comments apply to the correlation in Figure 5. The deviations observed here may reflect varying stabilization of the ground state by the solvent, from one complex to another. However, if one is sure that a particular compound lies on the correlation line, then these data may be used as described by Paoletti, *et al.*,[10] to determine heats of formation without recourse to thermochemical or stability constant measurements, an invaluable procedure. The correlation of the solid state data in Figure 4 provides the most definitive and unequivocal information, there being no solvent effects to interfere. If these lines could be correlated with heats of formation, they should provide reliable numbers free from the uncertainties alluded to above. In the Paoletti procedure one implicitly assumes that a compound adheres to the visible band ΔH correlation in order to calculate a value for ΔH, but this adherence cannot be independently checked. However, using Figure 4, the observation that a compound fits the visible–uv correlation line indicates that the compound is well behaved; thereby the reliability of any ΔH number determined is greatly enhanced.

In order to link the data in Figure 4 to heats of formation, such data for at least two of the compounds on each line are required. One compound may be fitted onto the line, namely $Cu(LL)_2(H_2O)_2{}^{2+}$, by using *solid state* data for these species and assuming that the ΔH values obtained in aqueous solution also apply to the species in the solid state. Although lattice packing effects may alter bond angles or bond lengths to some slight degree, compared with the solution species, such an assumption seems valid. Unfortunately, the preparation of such dihydrated species to check this postulate is not so straightforward. While compounds containing water (usually more than two molecules per copper atom) can, in some cases, be isolated, the water is readily lost on drying generally to yield the anhydrous material or complexes containing species of the type[22] $Cu(LL)_2X(H_2O)^+X^-$ rather than the desired dihydrate. Many of the complexes will crystallize anhydrous from aqueous solution. However, some supporting data do exist. Näsänen, *et al.*,[23] report that the solid state spectrum of $Cu(Meen)_2SO_4 \cdot 4H_2O$, which they believe to contain coordinated water, absorbs at essentially the same frequency as the aqueous solution spectrum. When Cu(*sym*-Et_2en)$_2$(NO_3)$_2$ is recrystallized from water, a dihydrate is obtained which contains coordinated water.[24] The presence of ionic nitrate is indicated by a sharp single peak at 1757 cm^{-1} due to a combination band.[25] The solid state absorption spectrum of this species exhibits a visible band close to that observed in the aqueous spectrum. The ultraviolet band, lies at much lower energies in the solid than in aqueous solution, providing convincing evidence of the "solvent effect" discussed above. The compound does not quite fall onto the correlation line, however (Figure 4).

It therefore seems reasonable that as a first approximation, *one can map onto the correlation lines in Figure 4 a number for the enthalpy of formation of the aquo species at the visible energy corresponding to the aquo species.* Unfortunately similar thermochemical data for a different axial group needed to map a second point are unavailable. Moreover the problems involved in obtaining such data are by no means trivial. Once such information is available then it will be possible to obtain enthalpy data from solid-state electronic spectroscopic data in this series of complexes. This analysis opens the door to the generation of bond enthalpy data from the electronic spectra of complexes not only of copper but of other metals although such systems are likely to be more difficult to work with. One might also note that the observation of independent charge-transfer transitions originating from the σ bonds of each type of copper–nitrogen bond in complexes of the asymmetric ligands leads to the possibility of obtaining enthalpy data for each type of bond.

[22] F. Mazzi, *Rend. Soc. Mineral. Ital.*, **9**, 148 (1953).

[23] R. Näsänen, L. Lemmetti, and M. Tarkkonen, *Suom. Kemistilehti B*, **42**, 169 (1969).

[24] A. Pajunen and E. Luukonen, *Suom. Kemistilehti B*, **42**, 348 (1969).

[25] A. B. P. Lever, E. Mantovani, and B. S. Ramaswamy, *Can. J. Chem.*, **49**, 1957 (1971).

Clearly there are still problems in this area despite the "simplicity" of the electronic spectra of copper(II). Some 10% of the 40 or more complexes which have been investigated in these studies are badly behaved and are therefore signalling structural or electronic abnormalities which are at present unclear. Complexes of 1,3-diaminopropane are all badly behaved; compare, for example, Tables I and II. Possibly this reflects the greater conformational freedom of the six-membered rings in these complexes. Once these abnormalities have been explained and understood, and some enthalpy data become available for compounds with a substituent other than water, then the correlations discussed here lay a secure foundation for the evaluation of bond strengths from solid state electronic data.

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The Kinetics of the Positional Isomerization of 2,3-Dimethyl-2-butene. The Heat of Formation of the 2,3-Dimethylbutenyl Radical and the Effect of Methyl Substituents on the Allyl Radical Stabilization Energy[1a]

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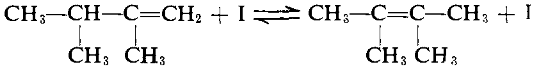
Abstract: The iodine atom catalyzed isomerization, I + 2,3-dimethyl-1-butene $\rightleftharpoons$ 2,3-dimethyl-2-butene + I (k_1, k_2), has been studied from 410 to 530°K. The reaction was found to be surface catalyzed in glass reaction vessels but homogeneous from 477 to 530°K in Teflon coated glass reaction vessels. The rate constant k_1 in this range was given by: $\log (k_1/\text{l. mol}^{-1}\ \text{sec}^{-1}) = (7.36 \pm 0.12) - (6.28 \pm 0.28)/\theta$. From these data the enthalpy of formation of the 2,3-dimethylbutenyl radical (DM-BR) was calculated as: $\Delta H_f°(\text{DM-BR, g, 298}) = 9.6 \pm 1$ kcal mol^{-1}. The bond dissociation energies of the primary C–H bond in 2,3-dimethyl-2-butene is $DH°(\text{C}_\text{p}\text{–H}) = 78.0 \pm 1$, and the tertiary C–H bond in 2,3-dimethyl-1-butene is $DH°(\text{C}_\text{t}\text{–H}) = 76.3 \pm 1$ kcal mol^{-1}. Consequently, the stabilization energy of the dimethylbutenyl radical is 16.7 to 18.5 kcal mol^{-1} depending on the localized model used. When this is compared with the stabilization energies of the allyl and butenyl radicals one is led to the conclusion that the methyl group increases the stabilization energy of the allyl radical by approximately 3 kcal mol^{-1} per group.

Approximately 10 yr ago Benson and Bose[2] proposed a free radical mechanism for the iodine catalyzed positional isomerization of olefins. This was closely followed by a study of the positional isomerization of 2-butene by Egger, Golden, and Benson[3] from which the stabilization energy[4] of the butenyl radical (methallyl) was determined as 12.4 ± 1.4 kcal mol^{-1}. Subsequently, Golden, Rodgers, and Benson[5,6] showed that the stabilization energy of the allyl radical was 9.5 ± 1.4 kcal mol^{-1}, a value recently confirmed by equilibrium studies.[7] In addition to establishing the low value for the allyl radical stabilization energy (*i.e.*, 10–12 rather than 16 to 25 kcal mol^{-1}),[7] these data also indicated that methyl substituents on the allyl radical may increase the stabilization energy. To further pursue this point we have undertaken this study of the kinetics of the iodine atom catalyzed positional isomerization of 2,3-dimethyl-1-butene (eq 1) from which the



$$\underset{\text{(DM-1B)}}{\text{CH}_3\text{—}\underset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{—}\underset{\text{CH}_3}{\underset{|}{\text{C}}}\text{=CH}_2} + \text{I} \rightleftharpoons \underset{\text{(DM-2B)}}{\text{CH}_3\text{—}\underset{\text{CH}_3}{\underset{|}{\text{C}}}\text{=}\underset{\text{CH}_3}{\underset{|}{\text{C}}}\text{—CH}_3} + \text{I} \qquad (1)$$

stabilization energy of the 2,3-dimethylbutenyl radical may be deduced. As this is an allyl radical with three methyl substituents, any such effect should become obvious. The equilibrium constant for reaction 1, needed for the kinetic analysis, has been reported earlier.[8]

Experimental Section

The apparatus has been described in detail previously.[8] Briefly, it consists of a reaction vessel connected to a "hot" box. The temperature of the hot box is maintained at 80–100° so that iodine may be handled and measured up to 40 Torr. The pressure measurements are made in the hot box with a Pace-Wiancko pres-

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[2] S. W. Benson, A. N. Bose, and P. Nangia, *J. Amer. Chem. Soc.*, **85**, 1388 (1963).

[3] K. W. Egger, D. M. Golden, and S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 5420 (1964).

[4] For a discussion of the relative merits of stabilization as opposed to resonance energy see: A. S. Rodgers, M. C. R. Wu, and L. Kuitu, *J. Phys. Chem.*, **76**, 918 (1972).

[5] D. M. Golden, A. S. Rodgers, and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3196 (1966).

[6] D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).

[7] D. M. Golden, N. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969).

[8] A. S. Rodgers and M. C. R. Wu, *J. Chem. Thermodyn.*, **3**, 591 (1971).