of the exchange process.[19]   The other possibility, I_d mechanism, requires very strong preferential solvation by DMSO and seems less likely.[20]

Because the solvent mixtures possess lower dielectric

(19) S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, **91**, 2236 (1969).
(20) C. H. Langford and H. G. Tsiang, *Inorg. Chem.*, **9**, 2346 (1970).

constants, there should be an increase in the concentration of second-sphere perchlorate ion pairs relative to pure DMSO.   Apparently this effect does not significantly alter the ligand-exchange parameters.[21]

(21) A referee has suggested that ion association may be sufficiently large in pure DMSO that the addition of nitromethane or methylene chloride cannot significantly increase the amount of ion pairing. This might lead to a Winstein special salt effect.[17]

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The Far-Infrared and Electronic Spectra of Some Bis-Ethylenediamine and Related Complexes of Copper(II) and the Relevance of These Data to Tetragonal Distortion and Bond Strengths

BY A. B. P. LEVER* AND E. MANTOVANI

The far-infrared spectra (500–200 cm^{-1}) of the complexes Cu(N-N)$_2$X$_2$ are assigned [(N-N) = ethylenediamine, 1,3-propylenediamine, and symmetric and asymmetric N,N-dimethyl- and N,N-diethylethylenediamines and X = Cl, Br, I, NCS, ClO$_4$, BF$_4$, and NO$_3$].   A straight-line correlation is observed between the square of the highest metal–nitrogen stretching vibration and the energy of the main electronic d–d band.   The position of a complex on the line is a measure of its tetragonal distortion and of the in-plane bond strength.

While the far-infrared spectra of complexes of the more simple ligands such as the halogens, ammonia, carbon monoxide, nitric oxide, and oxygen have been studied and the metal–ligand vibrational modes have been identified unequivocally,[1] *systematic* studies with more complex ligands are generally unavailable, and the identification of metal–ligand modes is less secure.   The purpose of this work is to identify the metal–nitrogen stretching modes in ethylenediamine complexes of the first-row transition metals and to see whether relationships may be derived between these data and other properties, such as electronic transition energies and thermodynamic parameters.   It is realized that metal–ligand stretching frequencies are rarely "pure," coupling with other normal modes of vibration of the same symmetry, in the molecule, generally being expected. The question of whether such coupling is so important as to invalidate any bonding or structural conclusions is explored.   Certainly if the complex has high symmetry the possibility of other modes of vibration occurring with the same symmetry and with similar energies, such that coupling is important, is minimized.

Copper complexes of the general formula Cu(N-N)$_2$X$_2$ where N-N = ethylenediamine, 1,3-propylenediamine, and the symmetric and asymmetric N-substituted dimethyl- and diethylethylenediamines and X = Cl, Br, I, NCS, BF$_4$, NO$_3$, and ClO$_4$ are discussed.   A number of corresponding cobalt(II) and nickel(II) complexes are included for comparison purposes, but detailed dis-

cussion of these latter derivatives will be presented elsewhere.[2]

Some of the complexes were deuterated, the amine hydrogen atoms being replaced, to facilitate identification of the various normal modes of vibration.

Experimental Section

Preparation of the Complexes.—Most of the complexes have been prepared previously; references thereto are indicated in Table I.

Previously unknown complexes were prepared by the general method of mixing stoichiometric amounts of the copper salt and the appropriate ligand in ethanol followed, where possible, by recrystallization from the same solvent.   A purple isomer of the previously reported Cu($asym$-Et$_2$en)$_2$(NO$_3$)$_2$ complex was obtained by heating this complex to 160°.   It cannot be recrystallized.

Deuteration.—This was achieved by dissolving or wetting the complex with deuterium oxide and pumping to dryness, the procedure being repeated until an infrared spectrum indicated absence of –NH stretching modes near 3200 cm^{-1}.   In some cases a few drops of the free ligand were added to suppress decomposition.   The integrity of the complex was assured by comparison of the electronic spectra thereof with that of the hydrogen analog starting material.   However many of the complexes decomposed when treated in this manner.

Spectroscopic Techniques.—Far-infrared spectra were recorded as Nujol mulls on polythene plates with a Beckman IR-12 spectrophotometer.   Electronic spectra were also recorded *via* transmittance through Nujol mulls using an Applied Physics Cary 14 spectrophotometer.

Results and Discussion

X-Ray structural data are available for many of the

(1) D. M. Adams, "Metal Ligand and Related Vibrations," Edward Arnold, London, 1967.

(2) (a) A. B. P. Lever and E. Mantovani, to be submitted for publication; (b) *Inorg. Chim. Acta*, in press.

TABLE I

ANALYTICAL DATA AND REFERENCES TO X-RAY
DATA AND PREVIOUS LITERATURE

Complex[v]	Analyses, %				Ref	
	Copper		Halogen		Prev lit	X-Ray
	Calcd	Found	Calcd	Found		
Cu(en)₂Cl₂			27.9	28.0	a, b	...
Cu(en)₂Br₂	18.5	18.0	46.6	46.4	a	...
Cu(en)₂I₂	14.5	14.8			a	...
Cu(en)₂(NCS)₂	21.2	20.6	38.8	38.9	a	n
Cu(en)₂(ClO₄)₂	16.6	16.3			a, b	o
Cu(en)₂(BF₄)₂	17.8	17.5			t	t
Cu(en)₂(AgI₃)₂	7.0	6.6	56.0	55.9	c	u
Cu(en)₂(NO₃)₂	20.7	20.7			a	p
Cu(en)₃(BF₄)₂	15.2	15.0			w	...
Cu(1,3-DAP)₂Cl₂			25.1	25.4	d	...
Cu(1,3-DAP)₂Br₂			43.0	43.4	d	...
Cu(1,3-DAP)₂I₂	13.6	13.3			d	...
Cu(1,3-DAP)₂(NO₃)₂	18.9	19.0			e	e
Cu(1,3-DAP)₂(ClO₄)₂	15.5	15.5			s	...
Cu(1,3-DAP)₂(BF₄)₂	16.5	16.3			w	
Cu(1,3-DAP)₃(BF₄)₂	13.8	14.1			w	
Cu(asym-Me₂en)₂Cl₂	20.5	20.3			w	...
Cu(asym-Me₂en)₂Br₂	15.9	15.9	40.0	40.0	w	
Cu(asym-Me₂en)₂(NO₃)₂	17.5	17.3			f	
Cu(asym-Me₂en)₂(ClO₄)₂	14.5	14.9			r	
Cu(asym-Me₂en)₂(BF₄)₂	15.4	15..1			w	
Cu(sym-Me₂en)₂Cl₂			22.8	23.2	w	...
Cu(sym-Me₂en)₂Br₂			40.0	40.3	g, h	h
Cu(sym-Me₂en)₂(NO₃)₂	17.5	17.6			i	i
Cu(sym-Me₂en)₂(ClO₄)₂	14.5	14.9			h, r	h
Cu(sym-Me₂en)₂(BF₄)₂	15.4	15.2			w	
Cu(asym-Et₂en)₂Cl₂			19.3	19.2	j, k	...
Cu(asym-Et₂en)₂Br₂	14.0	13.8			j, k	...
Cu(asym-Et₂en)₂(NO₃)₂	15.1	15.0 (14.8)[x]			j, k	...
Cu(asym-Et₂en)₂(ClO₄)₂	12.8	12.4			j, k, l, r	...
Cu(asym-Et₂en)₂(BF₄)₂	13.5	13.3			j	...
Cu(sym-Et₂en)₂Cl₂			19.3	19.4	w	...
Cu(sym-Et₂en)₂Br₂			35.1	35.3	m	...
Cu(sym-Et₂en)₂(NO₃)₂	15.1	14.9			m	q
Cu(sym-Et₂en)₂(ClO₄)₂	12.9	12.7			l, m, r	...
Cu(sym-Et₂en)₂(BF₄)₂	13.5	13.2			w	

[a] J. M. Proctor, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968). [b] W. R. McWhinnie, *J. Inorg. Nucl. Chem.*, **26**, 21 (1964). [c] A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2552 (1963). [d] P. Neogi and K. L. Mandal, *J. Indian Chem. Soc.*, **16**, 433 (1939). [e] A. Pajunen, *Suom. Kemistilehti B*, **42**, 15 (1969). [f] M. Griffil, *J. Phys. Chem.*, **71**, 3284 (1967). [o] D. W. Meek and S. A. Ehrhardt, *Inorg. Chem.*, **4**, 584 (1965). [h] R. Näsänen, I. Virtano, and H. Myllymäki, *Suom. Kemistilehti B*, **39**, 200 (1966). [i] A. Pajunen, *ibid.*, B, **42**, 261 (1969). [j] W. E. Hatfield, T. S. Piper, and U. Klabunde, *Inorg. Chem.*, **2**, 629 (1963). [k] H. Ojima and K. Sone, *Naturwissenschaften*, **51**, 105 (1964). [l] P. Pfeiffer and H. Glase, *J. Prakt. Chem.*, [2] **151**, 134 (1938). [m] F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.*, **76**, 211 (1954). [n] B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 254 (1964). [o] A. Pajunen, *Ann. Acad. Sci. Fenn.*, *Ser. A2*, 138 (1967). [p] Y. Komiyama and E. C. Lingafelter, *Acta Crystallogr.*, **17**, 1145 (1964). [q] R. Näsänen and E. Lukkonen, *Suom. Kemistilehti B*, **41**, 27 (1968). [r] H. Yokoi and T. Isobe, *Bull. Chem. Soc. Jap.*, **42**, 2187 (1969). [s] P. Pfeiffer, E. Schmitz, and A. Böhm, *Z. Anorg. Allg. Chem.*, **270**, 287, 291 (1952). [t] D. S. Brown, J. D. Lee, B. G. A. Nelson, B. J. Hathaway, I. M. Proctor, and A. A. G. Tomlinson, *Chem. Commun.*, 369 (1967). [u] R. Stomberg, *Acta Chem. Scand.*, **23**, 3498 (1969). [v] Abbreviations: en, ethylenediamine; 1,3-DAP, 1,3-propylenediamine; *sym-* and *asym-*Me₂en, symmetric and asymmetric *N,N*-dimethylethylenediamine; *sym-* and *asym-*Et₂en, symmetric and asymmetric *N,N*-diethylethylenediamine. [w] Previously unreported. [x] Previously unreported purple isomer.

ing distance, and a tetragonally distorted octahedral complex also with an in-plane CuN_4 stoichiometry but with axially coordinating X groups. The complexes discussed here will fall at or between these extremes depending upon the relative effective crystal field strengths of the in-plane amine and the axial ligand X. The most strongly coordinating axial ligands (such as the halogens and pseudohalogens) will tend to coordinate to the copper atom and form tetragonally distorted octahedra, in which ΔDq (the difference in in-plane and out-of-plane field strengths)[3] will be small. The smallest value of ΔDq will be observed in complexes of the $Cu(en)_3{}^{2+}$ ion, which may be assumed to contain the least tetragonally distorted copper ion. When X is perchlorate, nitrate, or tetrafluoroborate, ions which are generally regarded as being only weakly coordinating, coordination may occur to yield strongly tetragonally distorted octahedra in which ΔDq is large. In the limit the X groups are uncoordinated and $\Delta Dq = Dq$ (in-plane). Clearly the value of ΔDq which will reflect the degree of distortion may vary considerably and will depend not only on the electronic characteristics of the ligands but also, and very importantly, upon the steric interactions between the in-plane and axial ligands.

The electronic spectra of these complexes generally exhibit[4,5] a broad structureless band in the visible region, whose maximum ranges from 14,000 to about 22,000 cm⁻¹ depending upon the in-plane amine and the axial ligand. The highest energies are observed with the weakly coordinating axial ligands and it is clear that the position of this band is a useful indication of the degree of tetragonal distortion. As the axial field strength weakens, be it for electronic or steric reasons, the in-plane strength increases due to increasing involvement of the copper orbitals with the in-plane ligands. Similar effects have been observed with tetragonal nickel complexes[3,6] but to a lesser degree. As ΔDq in the nickel series increases, a small increase in the in-plane field strength may be observed[6] until ΔDq reaches a value at which there is an abrupt discontinuous change to a diamagnetic square-planar complex in which the nickel in-plane bond length has been markedly decreased and the in-plane field strength markedly increased.[3,4]

The existence of continuous series of copper complexes in which the tetragonal distortion varies widely permits a penetrating study of this distortion by various physical means. In the nickel series ΔDq may be evaluated from the electronic spectra of the complexes in terms of the radial integral Dt.[3] In the copper complexes the poor resolution of the electronic transition energies generally precludes this calculation. The low-temperature electronic spectra of these complexes[5] are somewhat better resolved and a shoulder near 14,000 cm⁻¹ may frequently be observed. This shoulder is

complexes under discussion (see footnotes to Table I for references). Two extreme structures may be recognized: a square-planar complex with an in-plane CuN_4 stoichiometry, the anionic X groups being beyond bond-

(3) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).

(4) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968, Chapter 9.

(5) I. M. Proctor, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc. A*, 1678 (1968).

(6) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **7**, 795 (1968).

assigned[5] to the $x^2 - y^2 \leftarrow z^2$ transition, while the main band envelope contains both the $x^2 - y^2 \leftarrow xy$ (whose energy equals the in-plane $10Dq$)[4] and the $x^2 - y^2 \leftarrow xz, yz$ transitions. The difference in energy between the main band envelope and the shoulder is not simply a function of Dt (it can be shown to be $10Dq_{xy} - 5Dt - 4Ds \simeq 7Dq_{xy} + 3Dq_z - 4Ds$) and so is not a direct measure of the tetragonal distortion. However it can certainly be expected that the separation will *decrease* with *increasing* tetragonal distortion (provided Ds is positive) and this is observed; in the halo complexes $Cu(en)_2X_2$ the separation is of the order of 4 kK, while when X is perchlorate or tetrafluoroborate, it is of the order of 2 kK.[5]

An increase in the in-plane field strength arising from a tightening up of the in-plane bonds when the axial interaction is weakened should be reflected in the vibrational properties of the system, in particular the in-plane copper–nitrogen stretching frequency (or, better, force constant), and also in the bond strengths of the complexes produced. Thus the energy of the visible band maximum, reflecting as it does the in-plane field strength, should be related to the vibrational properties of the in-plane interaction and perhaps to the stability constants. The stability constants in aqueous solution decrease in the sequence[7,8]

en > *sym*- and *asym*-Me$_2$en > *sym*- and *asym*-Et$_2$en   (1)
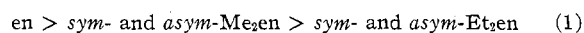
In these studies, water undoubtedly occupies the axial sites. Comparison of the *aqueous* solution electronic spectra of the nitrate complexes shows that these absorption maxima do indeed fall into the above sequence (1); *viz.*, for $Cu(N-N)_2(NO_3)_2$ (visible maximum, cm^{-1}; stability constant log β_2):[7] N–N = en (18,315; 20.0) > *asym*-Me$_2$en (17,760; 16.0) > *sym*-Me$_2$en (17,670; 16.3) > 1,3-DAP (17,575; 16.6) > *sym*-Et$_2$en (17,120; 15.6) > *asym*-Et$_2$en (17,035; 13.7). The ligands are ordered according to the visible absorption maximum and follow the general sequence (1). Although for a given alkyl group a strict parallelism between log β_2 and the absorption maximum does not hold, the discrepancies are probably within the experimental error. In the solid state the sequence of absorption maxima is essentially the same except for the position of the *asym*-Et$_2$en complex which has an exceptionally high energy, placing it above ethylenediamine itself. X-Ray structural data are available (see Table I) for the complexes of *sym*-Et$_2$en, *sym*-Me$_2$en, and 1,3-DAP and reveal that the NO$_3$ groups occupy coordinating sites along the z axis of the molecule (in-plane xy). These three complexes show doubling of the medium-intensity nitrate combination band near 1750 cm^{-1}, a fact which is indicative[9] of nitrate coordination, while the *asym*-Et$_2$en complex only shows one strong band indicative of ionic uncoordinated nitrate.[9] In the chloro and bromo complexes the absorption spectra follow the same general sequence (1) but the position of 1,3-diaminopropane varies. It seems credible therefore that the electronic

spectra may be reliably used as a criterion for the field strengths of the in-plane ligands, for the in-plane bond energies, and even for the stability constants in solution if a homologous series of complexes is chosen so that changes in entropy from one complex to another can be minimized. There is evidence of a decrease in bond enthalpy in the alkyl-substituted ethylenediamines[8] so that the lower values for the stability constants for these species do not arise solely from unfavorable entropy changes (see below).

This argument becomes particularly convincing if, as will be demonstrated below, the electronic spectra are also related to the in-plane vibrational properties of the complexes.

Far-Infrared Spectra.—Metal–nitrogen vibrational frequencies have been reviewed by Durig and Wertz,[10] and it is evident that there is still considerable confusion in the literature as to the position of the metal–nitrogen stretching modes in ethylenediamine complexes.

The number of bands to be expected is uncertain. The actual symmetry of the molecules will be very low and all four possible metal–nitrogen stretching modes should theoretically be observable. However the effective symmetry may be at least as high as D_{2h} if the metal is unaffected by the carbon atoms of the ligands and in this case two metal–nitrogen stretching modes should be active in the infrared spectrum. In the extreme situation when only the in-plane CuN$_4$ microsymmetry is considered, the group is D_{4h} and only one metal–nitrogen stretching mode is expected.

In general asymmetrically substituted ligands give rise to a more complex spectrum than symmetric ligands, as would be anticipated. Thus more skeletal vibrations (see below) are frequently observed in the former complexes. Depending upon the metal–ligand interaction, this lower symmetry may, or may not, affect the metal–nitrogen modes. The data (500–200 cm^{-1}) and assignments are presented in Table II and Figure 1. It should be emphasized that the identification of skeletal and metal–nitrogen modes listed in the appropriate columns of this table does not necessarily imply that all such modes have been identified. The column "other bands" infers unidentified absorptions which may therefore contain unidentified metal–nitrogen or skeletal vibrations.

In the earlier literature[11] bands above 500 cm^{-1} were assigned to metal–nitrogen stretching vibrations in first-row transition metal–ethylenediamine complexes. Durig[12] suggested that the Pd–N modes in palladium-(II)–ethylenediamine complexes are found between 430 and 520 cm^{-1}; if correct, this infers that first-row divalent metal–nitrogen modes would be expected below 500 cm^{-1}. Krishnan and Plane[13] using Raman spectroscopy assigned bands near 400 cm^{-1} to metal–nitrogen

(7) K. W. Sykes, Ed., *Chem. Soc., Spec. Publ.*, **No. 6** (1956).
(8) F. Basolo and R. K. Murmann, *J. Amer. Chem. Soc.*, **76**, 211 (1954).
(9) N. F. Curtis and Y. M. Curtis, *Inorg. Chem.*, **4**, 804 (1965).

(10) J. R. Durig and D. W. Wertz, *Appl. Spectrosc.*, **22**, 627 (1968).
(11) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 1112 (1961); *Spectrochim. Acta*, **17**, 68 (1961).
(12) J. R. Durig, R. Layton, D. Sink, and B. Mitchell, *ibid.*, **21**, 1367 (1965).
(13) K. Krishnan and R. A. Plane, *Inorg. Chem.*, **5**, 852 (1966).

<div align="center">

Table II

Electronic and Far-Infrared Spectra

</div>

	Visible	Ring	ν(M–N)	CH₃ twist	Other bands[a]
enH₂²⁺(Cl⁻)₂		476 s			250 vs, 238 vs
Cu(en)₂Cl₂	18,520	460 s	406 s, 326 s		237 s, 218 m
Deuterio isomer		460 s	393 s, 312 m		(230), 218 m
Cu(en)₂Br₂	18,420	460 s	403 s, 324 s		(245), 225 s
Cu(en)₂I₂	18,080	460 m	400 s, 318 m		258 m, 233 s
Cu(en)₂(NCS)₂	19,050	482 s[b]	412 s, 309 w		472 s,[b] 263 m, 237 s, 225 m
Cu(en)₂(NO₃)₂	18,940	485 s	421 vs, 331 s		318 w, (275), 232 s, 224 s
Cu(en)₂(ClO₄)₂	19,000	474 m	412 s, 312 m		272 w, 210 s
Cu(en)₂(BF₄)₂	19,510	474 m	414 s, 330 m		357 s,[c] 300 w, 205 s
Cu(en)₂(AgI₂)₂	19,300	474 m	412 m		198 m
Cu(en)₃(BF₄)₂	17,100	462 m	392 m, 317 m		356 m,[c] 279 w, 215 s
Ni(en)₂(AgI₂)₂	Square	500 s	395 m		232 vs
Ni(en)₂(NO₃)₂	Trans O_h	449 s	381 vs, 294 m		320 s, 232 s, 220 s
Ni(en)₂Br₂	Cis O_h	432 m	357 s, 310 m, 275 s		232 s, 224 m, 208 m
sym-Me₂enH₂²⁺(Cl⁻)₂		480 w, 471 w		298 vs	(221), 215 s
Cu(sym-Me₂en)₂Cl₂	17,390	450 vs, 400 s	374 vs	299 vs	277 w, 260 m, 254 w, 230 m
Cu(sym-Me₂en)₂Br₂	17,600	454 vs, 402 s	375 vs	300 vs	(275), 262 m, (254), 231 m
Cu(sym-Me₂en)₂(NO₃)₂	18,180	459 s, 408 s	377 m	302 vs	275 m, 232 s
Deuterio isomer		447 s, 393 s	372 m	302 vs	275 m, 232 s
Cu(sym-Me₂en)₂(ClO₄)₂	18,870	465 m, 413 m	378 s	303 s	236 m
Cu(sym-Me₂en)₂(BF₄)₂	18,790	464 s, 410 m	378 s	303 m	(357),[c] 355 m,[c] 280 m, 233 m
Ni(sym-Me₂en)₂(NCS)₂	O_h	454 m, 420 s	393 s, 350 s	284 s?	473 s,[d] 241 s, 226 w
Co(sym-Me₂en)₂Cl₂	O_h	452 m, 417 m	374 s, 339 s	(300 vw)	269 s, br, 237 m, 214 m, br
sym-Et₂enH₂²⁺(Cl⁻)₂		481 w, 415 w		297 vs	(277), (245), (216)
Cu(sym-Et₂en)₂Cl₂	15,770	497 m, (435)	388 w	295 vs	(277), (218), 207 s
Cu(sym-Et₂en)₂Br₂	15,920	497 vs, 444 w	390 m	295 vs	(275), 240 w, 223 m
Cu(sym-Et₂en)₂(NO₃)₂	18,020	458 m, 431 m	409 w, 348 m	348 m	292 m, 275 w, 240 m, 221 w
Deuterio isomer		450 m, 425 m	386 w, 340 w	308 s	290 w, 275 w, 240 m, 221 w
Cu(sym-Et₂en)₂(ClO₄)₂	18,940	460 w, 431 s	385 s, 319 m	306 s	276 m, 237 m, 219 w
Cu(sym-Et₂en)₂(BF₄)₂	18,650	457 m, 428 m	390 s, (345)	307 s	359 w[c] (289)
Ni(sym-Et₂en)₂Cl₂	Trans O_h	433 s	377 s	290 s	494 s, (277), 213 s, br
Co(sym-Et₂en)₂Cl₂	Trans O_h	425 s	365 s, 349 w	279 s	487 s, (270), 215 vs
Cu(asym-Me₂en)₂Cl₂	16,920	455 m, 430 m, 415 w	375 m	298 vs	267 s, 232 s, 215 m
Cu(asym-Me₂en)₂Br₂	17,210	460 m, 430 m, 420 w	380 s	295 vs	255 s, ~200 s
Cu(asym-Me₂en)₂(NO₃)₂	18,480	465 m, 440 m	394 s	300 s	274 m, (238), 221 s
Deuterio isomer		454 m, 438 m	390 s	298 s	274 m, (238), 221 s
Cu(asym-Me₂en)₂(ClO₄)₂	18,830	463 m, 441 s	398 s	299 m	276 m, 236 w, 221 s
Cu(asym-Me₂en)₂(BF₄)₂	18,790	467 m, 439 s	394 s	304 s	358 s,[c] 267 w, 228 m
Ni(asym-Me₂en)₂Cl₂	Trans O_h	450 m, 430, 412 w	380 s, (360)	292 s	480 vs, 260 vs, 238 s, (217)
Ni(asym-Me₂en)₂I₂	Square	453 m	396 m	305 m	480 m, 275 w, 240 s
Co(asym-Me₂en)₂Cl₂	Trans O_h	469 s, 440 m, 403 s		(295)	497 s, 260 s, 244 s, 233 w, 221 m
Co(asym-Me₂en)₂I₂	Trans O_h	475 vs, 445 m	356 s	289 vs	(275), 246 w
Ni(asym-Me₂en)₂(NCS)₂	Trans O_h	437 s, 412 m	355 s, 332 m	(280)?	470 vs, 260 s, 218 s
Cu(asym-Et₂en)₂Cl₂	16,370	478 s, 414 s	388 w, 360 w	304 s	268 w, 228 s
Cu(asym-Et₂en)₂Br₂	15,950	485 w, 470 w, 420 m	385 m, 348 m	290 vs	323 m, 257 s
Cu(asym-Et₂en)₂(NO₃)₂	21,460	478 s	414 vs, 368 s	298 s	318 m, 277 w, 240 w, 220 w
Cu(asym-Et₂en)₂(NO₃)₂[e]	17,600	485 vs	395 w, (328)	311 s	(282), 260 m, 254 m, 205 s
Cu(asym-Et₂en)₂(ClO₄)₂	20,700	480 m, 462 s, (420)	405 vs, 345 s	283 s	
Cu(asym-Et₂en)₂(BF₄)₂	19,450	491 m, (483), (420)	406 m, (350)	281 s	357 s,[c] 274 s
Ni(asym-Et₂en)₂Br₂	Square	445 m, 435 w	380 s, 340 m	318 s?	(262), 240 s, br
Ni(asym-Et₂en)₂Cl₂	Trans O_h	430 m, 400 m	350 s, 335 s	287 s	262 s, 220 m
Co(asym-Et₂en)₂Cl₂	Trans O_h	419 m, 390 m	348 w, 332 m	285 m	499 vs, 254 m, 215 s, br
1,3-DAPH₂²⁺(Cl⁻)₂		450 w, 428 s, 409 w			(292), 238 w, 220 w, 210 w
Cu(1,3-DAP)₂Cl₂	18,180	410 s	368 vs		295 w, (250), 231 w, 211 s
Cu(1,3-DAP)₂Br₂	17,000	410 s	364 s		298 w, 275 w, 253 m, 220 w
Cu(1,3-DAP)₂I₂	18,210	410 s	365 s, 356 w		304 w, 256 m
Cu(1,3-DAP)₂(NO₃)₂	18,050	458 w, 408 s	365 s, 337 m		500 s, 295 w, 257 m, 207 s
Deuterio isomer		412 w, 386 s	343 s, 320 m		462 s, 252 s, 207 s
Cu(1,3-DAP)₂(ClO₄)₂	17,700	459 m, 414 s	365 s		300 w, 275 w, 242 w, 220 w
Cu(1,3-DAP)₂(BF₄)₂	17,600	417 m	368 s		(360),[c] 303 w, 287 w, 256 w, 249 w, 226 w
Cu(1,3-DAP)₃(BF₄)₂	15,950	497 s, 392 m	344 m		354 m,[c] 250 m
Ni(1,3-DAP)₂(NO₃)₂	Trans O_h	435 w, 381 m	353 s, (332)		324 m, 253 s, 215 s, br
Ni(1,3-DAP)₂Cl₂	Cis O_h	370 s	332 vs, (325), (275)		487 vs, 244 m, 220 s, br

[a] May include unidentified ring or metal–nitrogen vibrations. [b] One of these bands is the ring vibration and one is a bending mode of the NCS group.   An arbitrary choice has been made in this table. [c] BF₄ vibrations. [d] NCS bending mode. [e] Purple isomer.
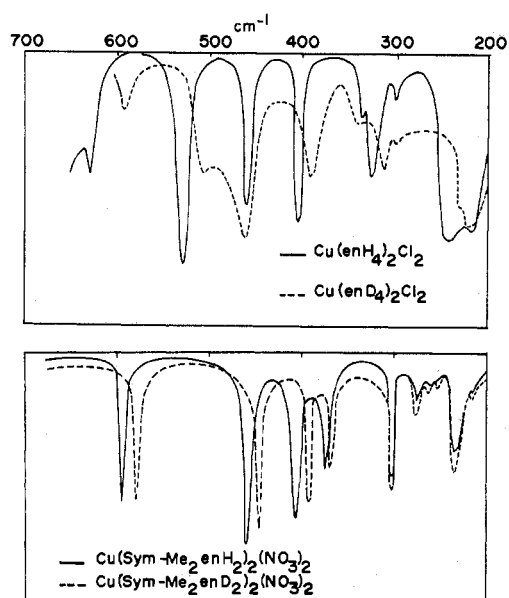
Figure 1.—The far-infrared spectra of $Cu(en)_2Cl_2$ and $Cu(sym-Me_2en)_2(NO_3)_2$ and their N-deuterated analogs.

stretching modes in zinc–, cadmium–, and mercury–ethylenediamine derivatives. In a recent study of chromium(II)–ethylenediamine derivatives[14] in which spectra were recorded from about 450 cm^{-1} no bands were assigned to metal–nitrogen vibrations implying that these lie below 450 cm^{-1}. It is anticipated that the metal–nitrogen stretching modes in ethylenediamine complexes would lie at similar or perhaps lower energies than the corresponding modes in metal–ammonia complexes since the effective mass of the nitrogen atom has been increased and the force constant, though it might increase slightly through chelation,[13] will not change very much. In the first-row transition metal hexaammines these frequencies lie[1] near 300–350 cm^{-1} and in the tetraammines [of Cu(II), Zn(II), and Hg(II)] near 400 cm^{-1}; *e.g.*, ν(Cu–N) of $Cu(NH_3)_4Cl_2$ lies at 420 cm^{-1}. Thus copper–nitrogen stretching modes in ethylenediamine complexes are expected near 400 cm^{-1} and certainly not above 500 cm^{-1}. The earlier assignment[11] of ν(Cu–N) at 538 cm^{-1} (in $Cu(en)_2PtCl_4$) must be considered in error.

The free ligands generally absorb in the region[14,15] 500–300 cm^{-1}, the vibrations concerned involving in-plane skeletal vibrations of the framework. Rocking modes of the NH_2 groups may also occur near or above 500 cm^{-1}. Upon bidentate coordination of the ligand to a metal ion, the skeletal modes involve in-plane vibration of the five or six membered ring so formed and will therefore be alluded to here as "ring" vibrations. Such "ring" vibrations may be expected to be coupled mechanically to some extent with the metal–nitrogen vibrational modes. Ligands with a CH_3 group exhibit a twisting vibration of this group near 300 cm^{-1}. The spectra of the complexes will, in addition, include metal–nitrogen stretching and bending vibrations.

(14) A. Earnshaw, L. F. Larkworthy, and K. C. Patel, *J. Chem. Soc. A,* 1339 (1969).

(15) A. Sabatini and S. Califano, *Spectrochim. Acta,* **16**, 677 (1960).

In order to rationalize the data the following working criteria were adopted.

(1) Bands occurring in the spectra of the complexes in the region 500–200 cm^{-1} which do not appear in the free ligand or its hydrochloride were assumed to involve vibration of the metal. While site symmetry effects may give rise to ligand bands in the complexes which are absent from the free ligand, such effects are expected to be random. Thus, if consistency is sought *via* study of a large number of complexes, such random effects should factor out.

In assigning a band to a metal–nitrogen mode we infer that this band is predominantly metal–nitrogen in origin but understand that other vibrations will contribute to the potential energy.

(2) The ν(Cu–X) modes in these complexes, because of the long axial Cu–X bond (or absence of such a bond), are expected at very low frequencies and, with the possible exception of X = Cl, will not arise above 200 cm^{-1}. They will therefore not be considered in this study.

(3) In the ammino derivatives NCuN bending modes occur[1] near 250 cm^{-1} and are therefore expected to lie at or below 250 cm^{-1} in the complexes under discussion. Such bending modes are generally intense, while the stretching modes are of variable intensity and can be very weak.[1] The free ligands also absorb in this region as a consequence of out-of-plane skeletal vibrations.

(4) "Ring" vibrations should have frequencies with comparatively little dependence on the nature of the metal ion. Metal–nitrogen stretching frequencies, on the other hand, should have frequencies sensitive to the nature of the metal ion. However if coupling between these modes is severe, both will be affected by change of metal.

Changes in the conformation of the ligand are also likely to invalidate this criterion. Indeed ring mode frequencies may prove useful in identifying conformational isomerism.

(5) Comparison of the spectrum of a complex with the spectrum of the corresponding complex where the N–H protons have been replaced by deuterium may be useful. "Ring" vibrations have energies which may or may not be sensitive to deuteration depending upon the degree of mixing of this mode with NH modes of vibration. Both situations are observed. The CH_3 twisting mode and metal–halogen stretching modes are generally insensitive to deuteration in practice, although coupling could in principle negate this. A metal–nitrogen ($-NH_2$–M or $-NHR$–M) mode is expected to decrease in energy upon substitution of H for D by some 5–25 cm^{-1}. The only absolute criterion which may be employed is that bands which do not shift upon deuteration do not involve $-NH_2$–M or $-NHR$–M modes and will generally be ligand vibrations (save for M–Hal). It would be dangerous however to apply this criterion to the asymmetric disubstituted ethylenediamine complexes.

Powell and Sheppard[11] also studied the spectra of some deuterio derivatives. The bands they assigned to metal–nitrogen modes, above 500 cm^{-1}, decreased in

energy by a considerable amount on deuteration. In the case of the complex $Cu(en)_2PtCl_4$ the band at 538 cm^{-1} assigned to $\nu(Cu-N)$ decreased by 70 cm^{-1}. This is far greater than could be justified on the basis of such a small change in mass and provides further evidence of the error in these assignments.

It is convenient to discuss the data for each of the ligands in turn.

Ethylenediamine Complexes.—Ethylenediamine itself absorbs at 468 and 327 cm^{-1} as a consequence of a skeletal in-plane vibration (ν_9) and an NH_2 torsional vibration (ν_{22}), respectively.[14] The hydrochloride complex also exhibits a skeletal vibration at 476 cm^{-1}, but there is no torsional band near 327 cm^{-1}. In this last study[16] strong out-of-plane skeletal vibrations were observed at 250 and 238 cm^{-1}. All the bis(ethylenediamine)copper complexes presented here (Table II) exhibit a band between 460 and 485 cm^{-1} which can be attributed to the skeletal or "ring" vibration. Two additional bands are noted above 300 cm^{-1} near 320 and 400 cm^{-1}. In the spectrum of the deuterated complex $Cu(enD_4)_2Cl_2$ the band at 460 cm^{-1} is retained, confirming that it is not a metal–nitrogen mode, while the additional bands cited above decrease in energy by some 15 cm^{-1}. The Raman study of zinc–, cadmium–, and mercury–ethylenediamine derivatives[13] also assigns a band near 480 cm^{-1} to a skeletal bending vibration. These observations provide evidence for the assignments of the bands near 400 and 320 cm^{-1} as metal–nitrogen stretching modes. The complexes exhibit strong multiple absorption between 200 and 275 cm^{-1} attributable to out-of-plane ring vibrations and metal–nitrogen bending vibrations. The strong band at 237 cm^{-1} in $Cu(en)_2Cl_2$ decreases to 230 cm^{-1} upon deuteration while the band at 218 cm^{-1} is unshifted. It is probable therefore that the former is the bending vibration while the latter is the skeletal vibration.

In the square nickel complex $Ni(en)_2^{2+} \cdot 2AgI_2^-$[17] two bands are observed between 300 and 500 cm^{-1}, namely, at 395 and 500 cm^{-1}. These are assigned to the metal–nitrogen and ring modes, respectively. The nickel–nitrogen stretching frequency in diamagnetic square-planar nickel–amine complexes is expected to lie near 400 cm^{-1},[18] and it is not unreasonable that the ring frequency will increase because of the tightness of the nickel–nitrogen bond, the latter being expected to be some 0.2 Å shorter than a copper(II)–nitrogen bond[19] (see also below).

In paramagnetic octahedral nickel complexes on the other hand, a "ring" band appears somewhat below 460 cm^{-1} (Table II), again consistent with the somewhat weaker metal–nitrogen bond relative to the square complexes and the copper complexes, and the band near 400 cm^{-1} in the copper complexes is replaced by a band at considerable lower energy assigned to the nickel–ni-

trogen stretching frequency. These nickel complexes, which will be discussed in detail elsewhere,[2] provide further evidence for the correctness of the assignments for the copper complexes.

sym-N,N'-Dimethylethylenediamine Complexes.—The ligand hydrochloride exhibits[16] two bands at 471 and 480 cm^{-1} ascribable to skeletal vibrations and a band at 298 cm^{-1} due to a CH_3 twisting vibration. The copper complexes also exhibit two bands between 400 and 500 cm^{-1} which may readily be ascribed to ring vibrations, although, through coupling, they do shift on deuteration in this case. The complexes also show a strong band near 300 cm^{-1} ascribable to the CH_3 twisting mode. In addition, all of the complexes have a band near 375 cm^{-1} which is assigned to a metal–nitrogen mode. This mode is expected to lie at a somewhat lower energy than in the ethylenediamine complexes because the effective mass of the nitrogen atom has increased through methylation.

The possibility that the lower of the two ring modes is really the metal–nitrogen mode is eliminated by consideration of the octahedral cobalt and nickel complexes which also show two ring bands, the lower of which are higher in energy than those exhibited by the copper complexes. It is not considered likely that the $\nu(Co-N)$ and $\nu(Ni-N)$ vibrations would be higher in energy than $\nu(Cu-N)$ for corresponding complexes.

sym-N,N'-Diethylethylenediamine Complexes.—The ligand exhibits[16] two skeletal bands at 415 and 481 cm^{-1}, while the metal complexes show one or two bands in this region. The chloro- and bromocopper derivatives differ markedly from the other complexes in this respect, a difference which is also reflected in their electronic spectra.

Additional bands falling in the region 300–440 cm^{-1} are assigned to metal–nitrogen stretching modes as indicated in Table II. In the chloro- and bromocopper complexes the observation of a band near 390 cm^{-1} assigned to $\nu(Cu-N)$ is consistent with the data presented in the section above.

asym-N,N-Dimethylethylenediamine Complexes.—Most of the complexes exhibit two bands between 400 and 500 cm^{-1} assignable as ring vibrations, while a few have a third weak low-energy band. One or sometimes two additional bands are observed between 320 and 400 cm^{-1} which are assigned to metal–nitrogen vibrations. The CH_3 twisting vibration is near 300 cm^{-1} in the copper complexes but is less obvious in some of the cobalt and nickel complexes. Deuteration affects both the ring vibrations and the metal–nitrogen modes. The position of the copper–nitrogen stretching frequency is quite compatible with the data presented above, while, as expected, the cobalt– and nickel–nitrogen modes in the octahedral complexes lie at somewhat lower energies. In the square nickel derivative the nickel–nitrogen mode is increased to 390 cm^{-1} also in agreement with previous observations.

asym-N,N-Diethylethylenediamine Complexes.—The halocopper complexes exhibit two bands between 400 and 500 cm^{-1} and two bands between 350 and

(16) R. J. Mureinik and W. Robb, *Spectrochim. Acta, Part A*, **24**, 377 (1968).

(17) A. B. P. Lever, J. Lewis, and R. S. Nyholm, *J. Chem. Soc.*, 2552 (1963).

(18) A. B. P. Lever, B. S. Ramaswamy, S. H. Simonsen, and L. K. Thompson, *Can. J. Chem.*, **48**, 3076 (1970), and references therein.

(19) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958).

400 cm^{-1} which can be reasonably assigned to ring and metal–nitrogen vibrations, respectively. The perchlorate and tetrafluoroborate complexes show only one band in the 350–400-cm^{-1} region but have a band just above 400 cm^{-1} which is probably a metal–nitrogen mode. Additional bands between 420 and 500 cm^{-1} can then be assigned to ring modes. The nitrate complex has a spectrum similar to that of the halides except that the relative intensities of the bands are very different. The strong band at 414 cm^{-1} is assigned to the metal–nitrogen mode, rather than a ring mode as might at first be anticipated because (i) the perchlorate, nitrate, and tetrafluoroborate probably have similar structures and the first strong ring band in the perchlorate and tetrafluoroborate complexes is observed above 450 cm^{-1} and (ii) heating the nitrate complex to 160° converts it to a purple isomeric form[2a] in which the 414-cm^{-1} band is missing and is replaced by a weak band at 395 cm^{-1} while other band energies are essentially unchanged. The electronic energy of the purple isomer is also reduced relative to the red complex (see vibrational–electronic correlation below). The perchlorate complexes exhibit thermochromism (see Table I, ref *j*) as does the tetrafluoroborate in our hands.[2a] In the case of this compound, mulling the sample causes discoloration so that data taken at room temperature may not be reliable; thus the data in Table II were recorded at 78° when a homogeneously colored mull was obtained.

1,3-Diaminopropane Complexes.—The free ligand hydrochloride absorbs strongly at 428 cm^{-1} and weakly at 450 and 209 cm^{-1} as a consequence of in-plane skeletal vibrations. The complexes have very simple spectra in the region 300–500 cm^{-1} with two bands near 370 and 410 cm^{-1}. The assignment in Table II is made by comparing these data with the data for the 1:1 complexes[2b] Cu(1,3-DAP)X$_2$, which exhibit a band near 415 cm^{-1} and a second band which varies in energy from 333 to 365 cm^{-1} according to the nature of X. The two bands are assigned to the ring vibration and copper–nitrogen vibration, respectively, because (i) the metal–nitrogen mode is expected to be sensitive to the nature of X and (ii) the ring mode frequencies do not change markedly[2b] in going from the 1:1 complexes Cu(amine)X$_2$ to the 1:2 complexes Cu(amine)$_2$X$_2$.

This assignment rests on less secure grounds than those made previously; it is rather unsatisfactory in that changing from ethylenediamine to propylenediamine should not unduly alter the effective weight of the coordinating nitrogen atom and the metal–nitrogen stretching frequencies in the two series of complexes should be similar. We return to this point later.

The assignment for the nickel complexes follows because the reverse assignment would lead to the observation of an exceptionally low ring frequency and to nickel–nitrogen stretching frequencies comparable to those of the copper complexes, which is not anticipated.

Correlation between Electronic and Vibrational Data.—There is a correlation between the electronic and vibrational data, such that as the in-plane bond

strength increases, *i.e.*, as the structure approaches a square, both the metal–ligand stretching frequency and the electronic transition frequency generally increase. For a given in-plane ligand the effective reduced mass of the Cu–N bond should remain constant, so that, neglecting coupling for the moment, the square of the metal–ligand stretching frequency should be proportional to the force constant for the bond.

A plot of the square of the metal–ligand stretching frequency against the electronic transition energy maximum reveals a remarkable correlation between these two quantities for most of the complexes (Figure 2). With few exceptions an essentially straight-line plot is obtained. It is evident that the complexes with the greater tetragonal distortion, the most square complexes, lie near the top of each line, while the least distorted complexes lie near the bottom; it is particularly gratifying that the almost octahedral Cu(en)$_3$$^{2+}$ ion also lies on the line, at the bottom of the ethylenediamine series, and that the two isomeric Cu(*asym*-Et$_2$en)$_2$(NO$_3$)$_2$ complexes also fit.

The existence of this correlation is itself an indication of the reliability of the assignments which have been made and infers that the problem of coupling is not a serious factor. The correlation also confirms that the electronic transition energies do indeed reflect the in-plane bond energies as had been postulated. With the exception of the complexes of *sym*-Me$_2$en, there is no obvious correlation between the ring frequencies and the electronic maxima. In these latter complexes the ring frequencies do increase with increasing tetragonality and increasing electronic transition energy; a straight-line plot can be obtained, and it is evident that coupling between the metal–ligand and ring modes must be significant.

It may be worthwhile to speculate briefly about the nature of such a correlation since additional chemical information may be extracted from consideration of the slopes and intercepts of the lines obtained. A good correlation may also be achieved between the electronic transition energy maximum and the stretching frequency itself, rather than its square. Thus the data while demonstrating that a correlation exists do not provide convincing information about the order of the relationship. The insensitivity of the correlation toward the power of the metal–ligand stretching frequency probably arises because of the comparatively narrow range of vibrational frequencies which may be correlated. Further data are being sought to clarify this problem.

If the bonding is discussed within the ionic model, then $Dq = 5\mu\overline{r^4}/6a^6$ where μ is the dipole induced at the ligand by the metal ion, $\overline{r^4}$ is the mean fourth-power radius of the d electrons on the copper ion, and a is the metal–ligand distance. In that the force constant is also inversely proportional to the sixth power of the metal–ligand distance,[20] the two quantities may readily be related, and the slope of the resulting plot will in-

(20) J. A. Ladd, W. J. Orville-Thomas, and B. C. Cox, *Spectrochim. Acta*, **20**, 1771 (1964).

Figure 2.—The electronic transition maximum *vs.* the square of the frequency of the highest energy metal–nitrogen stretching mode. A particularly poor correlation is observed with the perchlorate and tetrafluoroborate complexes of *sym*-Et₂en. The metal–nitrogen modes may be misassigned in this case; a better, though not perfect, correlation is obtained by assigning the lower energy ring modes in these compounds to metal–nitrogen modes. However there is no supporting evidence for this alternate assignment. In the *asym*-Et₂en plot, the lower of the two perchlorate points refers to a 78° measurement, the tetrafluoroborate point was recorded at 78°, and the lower of the two nitrate points is the purple isomer (see Experimental Section). Note that the scales of the various diagrams differ and that the slopes of the various lines do differ. The equations of the lines are as follows (percentage standard deviations in parentheses): en, $(\nu(M-N))^2 = 7.817\nu_{elec} + 19,600$ (~0.2%); *asym*-Me₂en, $(\nu(M-N))^2 = 8.418\nu_{elec} - 1159$ (~0.3%); *asym*-Et₂en, $(\nu(M-N))^2 = 4.256\nu_{elec} + 80,864$ (<0.2%) (excludes ClO₄⁻); *sym*-Me₂en, $(\nu(M-N))^2 = 2.000\nu_{elec} + 105,316$ (<0.1%); *sym*-Et₂en, $(\nu(M-N))^2 = 7.369\nu_{elec} + 34,544$ (<0.1%) (excludes BF₄⁻ and ClO₄⁻); 1,3-DAP, $(\nu(M-N))^2 = 6.420\nu_{elec} + 19,071$ (~0.8%).

volve μ, the induced dipole. Thus the slope may provide information about the degree of ionicity and covalency in the metal–ligand bond. It is interesting to observe how the slope does vary from one complex to another (see Figure 2 legend).

An alternative approach to a correlation between the electronic and vibrational data can be phrased in molecular orbital language. The highest energy orbital in the d orbital manifold is the $x^2 - y^2$ orbital which is strongly σ antibonding with respect to the molecular plane. Its energy will increase (and the transition energy will increase) as the in-plane bond strength increases. Qualitative relationships may be derived[21] between the heat of dissociation of a bond and its stretching frequency or force constant (regarding the bond as a diatomic oscillator) and it is generally regarded that the force constant of a bond will increase with the bond strength. Thus the slope of the relationship may again yield information about the covalency of the bond. Further studies are in progress with other series of complexes in order to see how general this relationship is and to provide further information of the nature of the correlation; at present, additional speculation would not be fruitful.

A number of general observations may be made from the data presented here.

(i) As expected, complexes with nitrate, perchlorate, or tetrafluoroborate generally have higher electronic

transition energies and higher metal–nitrogen stretching frequencies and therefore will have higher copper–nitrogen bond energies than the corresponding halogen complexes.

(ii) As the nucleophilicity of the counterion decreases, the antisymmetric disubstituted ligands form complexes with a stronger copper–nitrogen bond than the symmetrically disubstituted complexes. Thus for ClO₄⁻, NO₃⁻, BF₄⁻, and Cl⁻, the *asym*-Et₂en complexes have higher electronic and vibrational energies than the corresponding complexes of *sym*-Et₂en; with Br⁻, the reverse is true. With the dimethyl ligands, the changeover comes above Cl⁻, the symmetric Me₂en ligand forming stronger complexes with NO₃⁻, BF₄⁻, and ClO₄⁻, while with Br⁻ and Cl⁻ the stabilities are evidently very similar.

(iii) The very high electronic transition energies of the *asym*-Et₂en complexes with copper nitrate, perchlorate, and, to a lesser extent tetrafluoroborate, imply very high copper–nitrogen bond energies in these instances.

(iv) The halide complexes, though evidently only weakly tetragonally distorted, do not lie in the same sequence for all the complexes. It is particularly surprising that the iodide complex is the least distorted in the ethylenediamine series but the most distorted in the 1,3-diaminopropane series. It seems possible that the extra carbon atoms in the propanediamine ligand do interact sterically with the large iodide ion and thereby increase the distortion in the complex.

(21) S. Glasstone, "Textbook of Physical Chemistry," Macmillan, London, 1953.

(v) 1,3-diaminopropane appears to form weaker complexes than ethylenediamine as indicated by both lower metal–nitrogen stretching frequencies and electronic transition frequencies for most anions.

In order to explain the above observations, a number of different and often opposing factors must be considered. The stabilities of aminemetal complexes generally fall with increasing alkyl substitution,[7] a fact which is in part attributable to unfavorable entropy changes as the number of atoms in the ligand increases but is also due to a steric interaction between the in-plane and axial ligands such that the overall bond enthalpies in the octahedral complex decrease.[8] However in the absence of steric effects the in-plane bond enthalpies should increase with increasing alkyl substitution since the inductive effect of these substituents will decrease the ionization potential of the ligand and increase its polarizability. Hence in square or very strongly tetragonally distorted octahedral complexes, the bond enthalpies in the substituted amines might exceed those in ethylenediamine itself.

Equating the lower metal–nitrogen stretching frequencies and lower electronic transition energies with essentially six-coordinate complexes and the converse with essentially four-coordinate complexes, it is evident that the copper–nitrogen bond strengths in the six-coordinate ethylenediamine complexes greatly exceed those in any of the other complexes (neglecting for the moment the complexes of 1,3-diaminopropane). Clearly in six-coordinate complexes of the substituted amines, interligand repulsion plays a dominant role and weakens the in-plane interaction.

In the four-coordinate complexes, however, the differences between ethylenediamine and the substituted ligands is diminished, and the asymmetric diethylethylenediamine complexes are especially strong. Here the interligand repulsion does not apparently weaken the in-plane interaction. The greater strength of the copper–nitrogen bonds in the ethyl- rather than the methyl-substituted derivatives can then be ascribed to the increase in polarizability of the ligand. Those steric interactions which are present are apparently minimized by placing both alkyl groups on the same nitrogen atom, since it is evident that the antisymmetric ligands form stronger bonds in these square complexes than the symmetric ligands.

A recent esr study[22] of alkyl-substituted ethylenediaminecopper complexes has revealed that the covalency of the copper–nitrogen bond, as indicated by the coefficient of the $d_{x^2-y^2}$ orbital in the in-plane bonding molecular orbital, does indeed increase with increasing alkyl substitution, the asymmetric diethylethylenediamine derivative showing the most marked effect.

The propylenediamine complexes are apparently anomalous in having much lower metal–nitrogen stretching frequencies than those of ethylenediamine. The electronic transition energies of the 1,3-DAP derivatives, although slightly less than those of en, are not concomitant with the metal–nitrogen stretching fre-

quencies; moreover it is known[7] that the stability constants for the formation of copper complexes with these two ligands are very similar.

The explanation may lie in the ring size of 1,3-DAP relative to en. In the 1,3-DAP complexes the six-membered ring will be more flexible than the five-membered ring present in the ethylenediamine derivatives. As a consequence the ring frequencies will appear at lower energies, much closer in fact to the metal–nitrogen frequencies. Coupling between these vibrations will be severe and the metal–nitrogen stretching vibrations will be depressed in energy while the ring frequencies will increase.

Evidence for the greater degree of coupling in the 1,3-diaminopropane complexes is inferred from the deuteration studies, since the spectra of the deuteriopropane complex shows much larger shifts from the hydrogen spectrum than observed with the other ligands.

It is evident that the position of an anion on a given line in the absence of a steric interaction provides a measure of its crystal field strength relative to the in-plane ligand. Since steric effects can be excluded in the ethylenediamine series, a spectrochemical series can be drawn from these en data, *viz.*, AgI_2, $< BF_4 <$ $SCN < ClO_4 < Cl < Br < I < en$. The sequence of the halide ions is remarkable and atypical and probably reflects the relatively strong class b behavior of the copper(II) ion.

There appears to be no systematic trend in the copper–nitrogen bond lengths discernible from the comparatively small amount of X-ray data available (with a given ligand).[5] If anything, the admittedly rather poor-quality data seem to suggest that the more octahedral complexes have the shorter copper–nitrogen bond length rather than the longer as would be expected. The expected correlation has been shown to exist however in the $Cu(NH_3)_4X_2$ series[23] where increasing Cu–X bond length parallels decreasing in-plane Cu–NH_3 bond length. Electronic and vibrational correlations would be expected for this series but such a study has not yet been made.

Attempts have been made to obtain Raman spectra of these diaminecopper complexes but so far without success.

These data represent the most extensive correlations of electronic and vibrational data made to date, and their relationship to bond strengths suggests that such studies may provide an alternate means to the evaluation of such quantities. At present there are no alternative methods for the evaluation of the bond strengths of compounds of this kind as a function of the axial ligand.

It has previously been shown[24] that there is a good quantitative relationship between the metal–oxygen stretching force constants in metal acetylacetonates and their stability constants, and this correlation probably extends to their electronic spectra *via* the Irving–

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

(23) B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).

(24) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963, p 220.

Williams relationship. Very recently a straight-line correlation has also been observed[25] between the square of the metal–oxygen stretching frequencies and the first d–d band in the electronic and vibrational spectra of a series of oxymolybdenum(IV) complexes. Thus such

(25) R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc. A*, 1702 (1970).

correlations may be fairly general and undoubtedly merit further investigation.

Symmetrically Disubstituted Ferrocenes. II. Complexes of Ferrocene-1,1'-bis(dimethylarsine) and Ferrocene-1,1'-bis(diphenylarsine) with Group VI Carbonyls[1]

BY J. J. BISHOP[2a] AND A. DAVISON[*2b]

The reaction of the group VI carbonyls with stoichiometric amounts of the arsines ferrocene-1,1'-bis(dimethylarsine) (fdma) and ferrocene-1,1'-bis(diphenylarsine) (fdpa) gave the complexes (fdma)M(CO)$_4$ and (fdpa)M(CO)$_4$, M = Cr, Mo, and W. Prolonged reaction of excess fdma with Mo(CO)$_6$ led to the isolation of μ-fdma-[fdmaMo(CO)$_3$]$_2$ and (fdma)$_2$Mo(CO)$_3$. It is proposed that the former complex has a bridging diarsine and a facial arrangement of donor arsenic atoms in the molybdenum coordination sphere, while the latter complex has one unidentate and one bidentate diarsine with a meridional arrangement of the donor arsenic atoms about the molybdenum atom.

Introduction

We have undertaken a study of the chemistry of symmetrically 1,1'-disubstituted ferrocenes (C$_5$H$_4$L)$_2$Fe, where the substituents are potential donor groups. In the previous communication[1] we have described convenient syntheses of the potential ligands where L = PR$_2$, AsR$_2$, and S$^-$ or SH. This work describes some complexes of the group VI metal carbonyls[3–7] with ferrocene-1,1'-bis(dimethylarsine) (fdma) and ferrocene-1,1'-bis(diphenylarsine) (fdpa).

Experimental Section

General Data.—Microanalyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim (Ruhr), West Germany; Galbraith Laboratories, Inc., Knoxville, Tenn.; Midwest Microlab, Inc., Indianapolis, Ind.; Spang Microanalytical Laboratory, Ann Arbor, Mich.; and at MIT by Dr. Stephen S. Nagy and Mrs. Nancy F. Alvord. Molecular weight determinations were carried out by Midwest Microlab, Inc.

All melting points are corrected and were determined using a Thomas-Hoover "Unimelt" melting point apparatus on samples sealed in evacuated capillaries.

Where sensitive materials were involved, manipulations were carried out in an atmosphere of prepurified nitrogen.

Infrared spectra were recorded on Perkin-Elmer 337 and 521 spectrophotometers. Nuclear magnetic resonance spectra were recorded on Varian Associates T-60, A-60, and HA-100 spectrometers with tetramethylsilane as an internal reference.

Materials.—Reagent grade solvents were used and, when required, were degassed *in vacuo*. Hydrocarbons were dried by refluxing over and distilling from calcium hydride under nitrogen. Diglyme was dried, as above, over lithium aluminum hydride. The arsines ferrocene-1,1'-bis(dimethylarsine) (fdma) and ferrocene-1,1'-bis(diphenylarsine) (fdpa) were prepared as described previously.[1] The technique of Werner and Coffield[8] was used to prepare molybdenum diglyme tricarbonyl. All other chemicals used were of commercial reagent grade and, unless stated below, were used without purification.

Preparations. Tetracarbonylferrocene-1,1'-bis(dimethylarsine)chromium(0).—A mixture of sublimed Cr(CO)$_6$ (2.21 g, 10.0 mmol) and fdmp (3.99 g, 10.1 mmol) in dry diglyme (40 ml) was stirred and brought slowly to reflux (*ca.* 2 hr). The Cr(CO)$_6$ which sublimed from the reaction mixture was returned to the flask periodically by swirling and by scraping the condenser with a nichrome wire spiral which passed through a serum cap such that the system remained closed at all times. The reaction mixture was kept at reflux for 5.0 hr and then evaporated to dryness (65° (0.1 mm)) and maintained under these conditions for 13 hr to remove the unreacted Cr(CO)$_6$. The dark orange residue was extracted, in one portion, with boiling heptane (270 ml). The extract was filtered hot through a bed of Celite. Cooling the filtrate gave fragile yellow needles which were collected, washed with heptane (two 10-ml portions), and dried *in vacuo*; yield 4.21 g (75%), mp 178–179°. *Anal.* Calcd for C$_{18}$H$_{20}$As$_2$CrFeO$_4$: C, 38.74; H, 3.61. Found: C, 38.94; H, 3.78.

The solid is stable to air but its solutions are rapidly decomposed by air. The complex dissolves readily in benzene, chloroform, and acetone.

(1) Part I: J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, submitted for publication.

(2) (a) Petroleum Research Fund Graduate Fellow, 1968–1969. (b) Fellow of the Alfred P. Sloan Foundation, 1967–1969. To whom correspondence should be addressed.

(3) Although no systematic studies have been described, brief reports of symmetrically disubstituted ferrocenes functioning as ligands have appeared.[4–7]

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