Table II. The Carbonyl Stretching Frequencies of the Iron–Phosphine Complexes

Compd	CO stretch (cm^{-1}) in $CHCl_3$ solvent
$(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2[Fe(CO)_4]_2$ (I)	2057 m, 1977 m, 1938 s, 1933 sh
$(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2[Fe(CO)_4]_2$ (II)	2047 m, 1975 m, 1936 s, 1930 sh
$(C_6H_5)_2P(CH_3)_4P(C_6H_5)_3[Fe(CO)_4]_2$ (III)	2045 m, 1973 m, 1935 s, 1928 sh
$(C_6H_5)_2PCH_2P(C_6H_5)_2[Fe(CO)_4]_2$ (IV)	2053 m, 1980 m, 1946 s, 1938 s
$(C_6H_5)_2PCH_2P(C_6H_5)_2Fe(CO)_4$ (V)	2052 m, 1978 m, 1943 s, 1937 s
$(C_6H_5)_2PCH_2P(C_6H_5)_2Fe(CO)_3$ (VI)	1989 s, 1919 m, 1909 s
$(C_6H_5)_2PCH_2P(C_6H_5)_2Fe_2(CO)_7$ (VII)	2049 s, 1994 s, 1982 m, 1951 sh, 1940 m, 1923 s, 1754 m

VII is unique to the reaction with bis(diphenylphosphino)methane. The elemental analysis and molecular weight data are compatible with a composition of two iron atoms, seven carbonyls, and one phosphine ligand. The infrared spectrum of VII is quite complex and contains seven absorptions, six in the terminal and one on the bridging carbonyl region. The mechanism by which VII is formed in the reaction is not clear; however, separate infrared experiments indicate VII can be formed by two different routes. When $Fe_2(CO)_9$ is photolyzed with benzene solutions of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ for 24 hr, VII is produced. The photolysis of IV in benzene solution for 12 hr also produces VII. Probably both of these routes are operative under the reaction conditions. Thermal reaction[2] of $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ with $Fe_2(CO)_9$ did not produce an analog of VII and photolyses of I in benzene over a 6-day period also does not yield an analog of VII.

The structure of VII is not definitively established by either its infrared or pmr spectrum. These spectra are compatible with a structure in which the phosphine is a chelating ligand replacing two terminal carbonyls on one iron atom of $Fe_2(CO)_9$ or its tautomer $(OC)_4Fe(\mu\text{-}CO)Fe(CO)_4$[6] or with a structure in which the phosphine replaces a terminal carbonyl on each iron atom of the tautomer and serves as a bridging ligand. The apparent inability of a better chelating phosphine $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$ to form an analog of VII favors the latter structure.[3]

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corporation, and the California State University, Fullerton Foundation, for the support of this research.

Registry No. I, 14977-13-0; II, 52843-15-9; III, 52843-16-0; IV, 52843-17-1; V, 52843-12-6; VI, 52843-13-7; VII, 52843-14-8.

References and Notes

(1) J. Lewis, R. S. Nyholm, S. S. Bandhu, and H. H. B. Stiddard, *J. Chem. Soc.*, 2825 (1964).
(2) W. R. Cullen and D. A. Harbourne, *Can. J. Chem.*, **47**, 3371 (1969).
(3) During the editorial processing of this note, F. A. Cotton and J. M. Troup published a paper (*J. Amer. Chem. Soc.*, **96**, 4422 (1974)) in which an alternative preparation and the X-ray structure of $(C_6H_5)_2PCH_2P(C_6H_5)_2Fe_2(CO)_7$ were reported. The structural features suggested here based on chemical and spectral evidence are in agreement with the results of Cotton and Troup.
(4) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **8**, 1464 (1969).
(5) F. A. Cotton, K. I. Hardcastle, and G. A. Rusholme, *J. Coord. Chem.*, **2**, 217 (1973).
(6) F. A. Cotton and J. M. Troup, *J. Amer. Chem. Soc.*, **96**, 1233 (1974).

Contribution No. 2544 from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Triarylstibine Complexes of Rhodium(I). II[1]

Philip E. Garrou and George E. Hartwell*

Received April 19, 1974 AIC40256S

Previous investigations have shown that although Rh(I) phosphine complexes are four coordinate, the analogous stibine complexes prefer to be five coordinate in the solid state.[1] Furthermore the reaction of $Rh_2Cl_2(CO)_4$ with PPh_3 resulted in the isolation of $Rh_2Cl_2(CO)_x(L)_{4-x}$ (x = 1–3) dependent on the P/Rh ratio,[2] but the analogous SbR_3 reactions gave no evidence for the existence of such dimeric complexes.[1] Recently[3] the reactions of $Rh_2Cl_2(CO)_x(C_2H_4)_{4-x}$ (x = 1–3) with PR_3 were reported as more suitable routes to complexes of the type $Rh_2Cl_2(CO)_x(L)_{4-x}$ (x = 1–3). As a continuation of our studies on Rh(I) stibine complexes, the study of $Rh_2Cl_2(CO)_x(C_2H_4)_{4-x}$ (x = 1–3) with SbR_3 was undertaken in an attempt to observe dimeric stibine complexes and further compare Rh(I) stibine and phosphine reactions.

Experimental Section

All reactions were carried out under an atmosphere of argon. Solvents were dried and deaerated prior to use. The ligand $(p\text{-}CH_3C_6H_4)_3Sb$[4] and the complexes $Rh_2Cl_2(CO)_4$,[5] $Rh_2Cl_2(C_2H_4)_4$,[6] and $Rh_2Cl_2(CO)_x(C_2H_4)_{4-x}$[3] ($x$ = 1–3) were prepared by literature methods.

Infrared Solution Studies. The reaction of $Rh_2Cl_2(CO)_x(C_2H_4)_{4-x}$ (x = 1–3) with SbR_3 (R = Ph or $p\text{-}CH_3C_6H_4$) was monitored using a Perkin-Elmer 621 ir spectrometer in the 2100–1900-cm^{-1} region during the addition of aliquots of SbR_3 in $CHCl_3$ to 0.05×10^{-3} *M* solutions of the dimers in $CHCl_3$. A portion of the solution was withdrawn by syringe 1 min after addition of the aliquot and the solution spectrum recorded, the portion was then returned and another aliquot added. Figures 1 and 2 include a grating and scale change at 1980 cm^{-1}.

Results and Discussion

As described previously,[3] reaction of 1 mol of $Rh_2Cl_2(CO)_4$ (Y_0) with $^1/_3$, 1, or 3 mol of $Rh_2Cl_2(C_2H_4)_4$ (Y_4) resulted in high concentrations of $Rh_2Cl_2(CO)_3(C_2H_4)$ (Y_1), $Rh_2Cl_2(CO)_2(C_2H_4)_2$ (Y_2), or $Rh_2Cl_2(CO)(C_2H_4)_3$ (Y_3), respectively.

Ethylene was found to be readily displaced from Y_1, Y_2, or Y_3 by phosphines of various basicities, to give phosphine-substituted complexes.[3] The following ir absorptions were observed when the reaction of Y_1, Y_2, or Y_3 with SbR_3 was monitored in $CHCl_3$ solution.

Reaction of $Rh_2Cl_2(CO)_3(C_2H_4)$ (Y_1) with SbR_3 (Figure 1). At Sb/Rh = 0, absorptions due to Y_1 were observed at 2098 and 2038 cm^{-1}. At Sb/Rh = 0.5, absorptions at 2095, 2060, and 2015 cm^{-1} were observed in addition to the absorptions of Y_1. At Sb/Rh = 1.6, absorptions due to Y_1 were absent and absorptions at 2090, 2060, 2015, and 1966 cm^{-1} were present. At an Sb/Rh = 2.5, only the absorption at 1966 cm^{-1} remained.

Reaction of $Rh_2Cl_2(CO)_2(C_2H_4)_2$ (Y_2) with SbR_3 (Figure 2). At Sb/Rh = 0, absorptions due to Y_2 were observed at 2028 and 2031 cm^{-1}. At Sb/Rh = 0.8, absorptions at 2060, 1975, and 1966 cm^{-1} were observed in addition to the absorptions due to Y_2. At Sb/Rh = 1.65, absorptions due to Y_2 were absent while absorptions were present at 2060 and 1966 cm^{-1}. Additional SbR_3 caused the 2060-cm^{-1} absorption to diminish until at Sb/Rh = 2.5 only the absorption at 1966 cm^{-1} remained.

---

* To whom correspondence should be addressed at Dow Chemical U.S.A., Eastern Research Laboratory, Wayland, Mass. 01778.

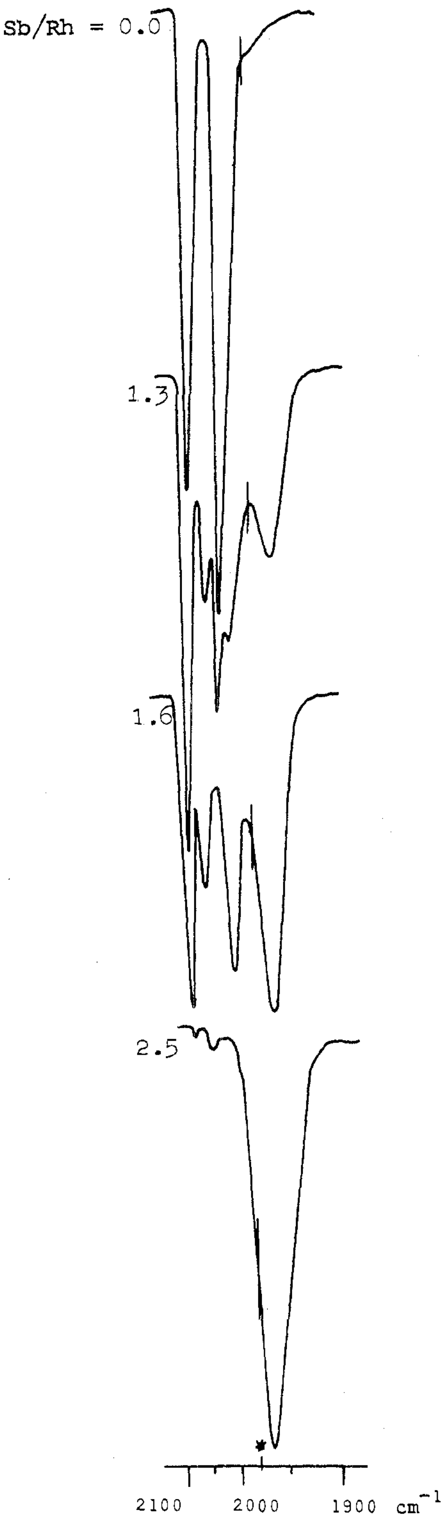


Figure 1. Infrared spectra in $CHCl_3$ of $Rh_2Cl_2(CO)_3(C_2H_4)$; Y_1 with $SbPh_3$.

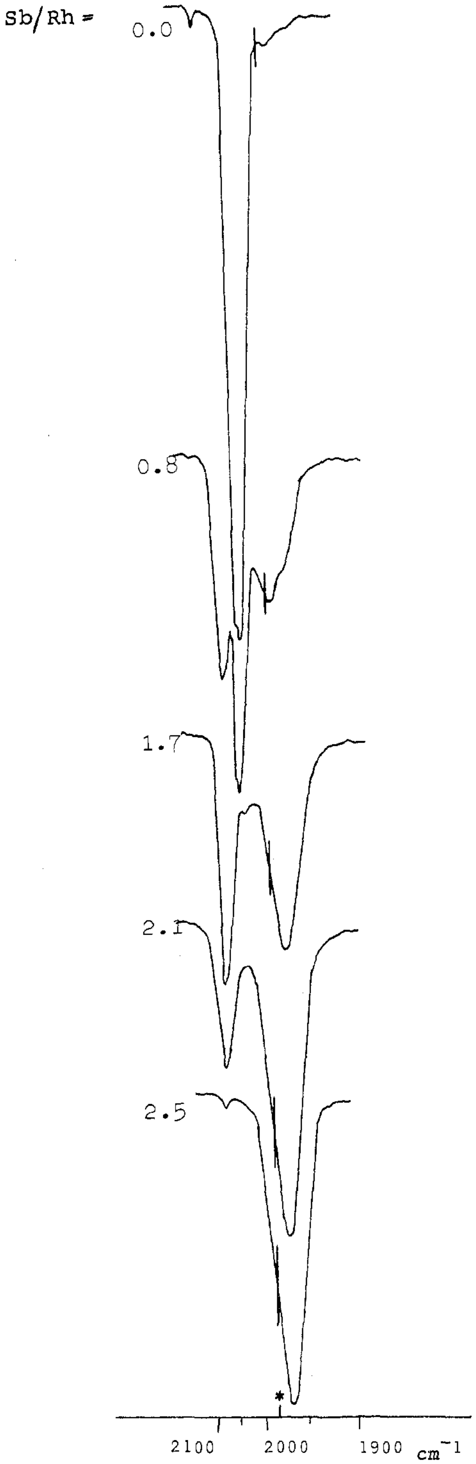


Figure 2. Infrared spectra in $CHCl_3$ of $Rh_2Cl_2(CO)_2(C_2H_4)_2$; Y_2 with $SbPh_3$.

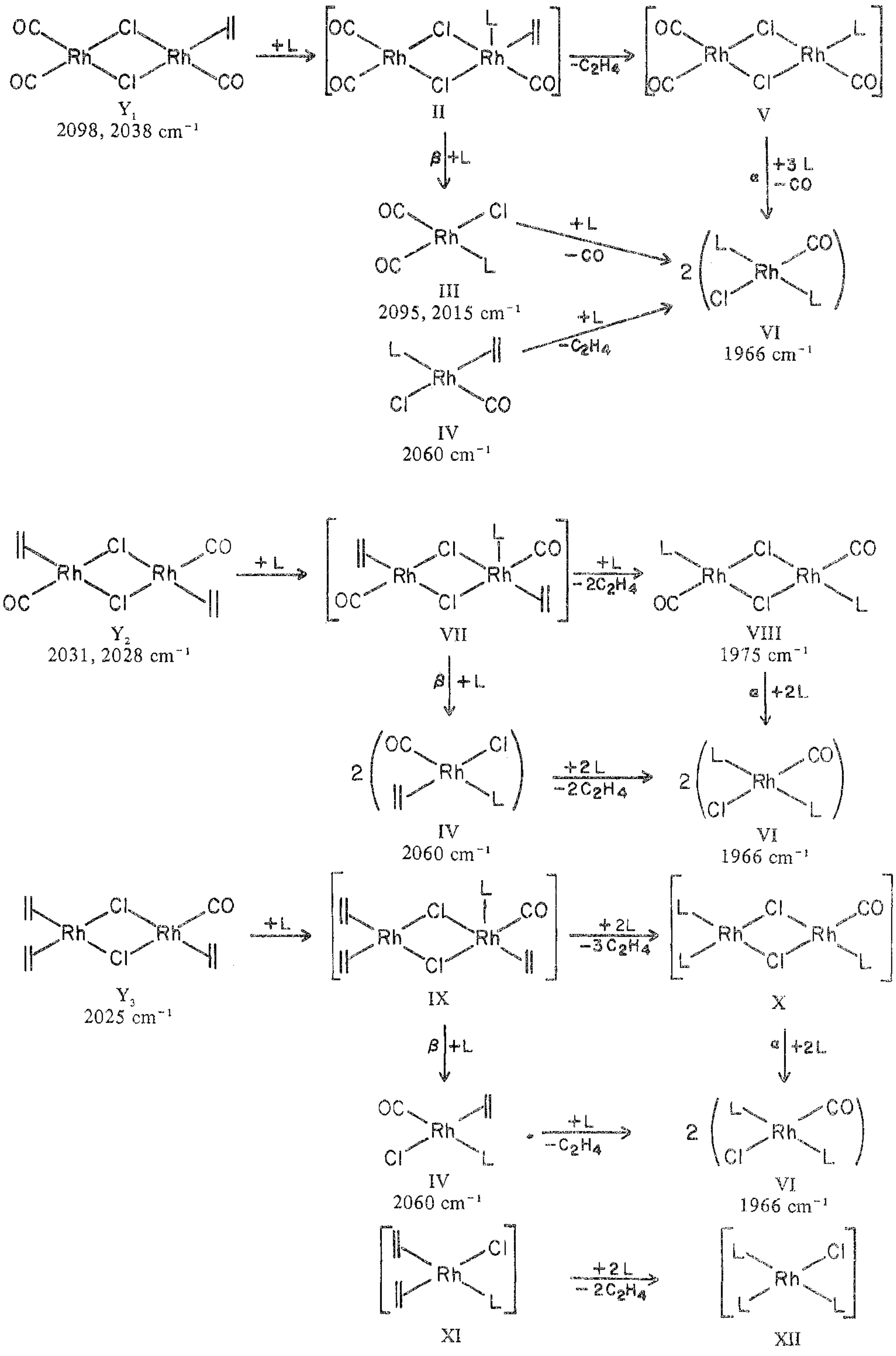
Reaction of $Rh_2Cl_2(CO)(C_2H_4)_3$ (Y_3) with SbR_3. At Sb/Rh = 0, an absorption due to Y_3 was observed at 2025 cm^{-1}. At Sb/Rh = 0.5, an absorption at 2060 cm^{-1} was observed in addition to the absorption due to Y_3. Further addition of SbR_3 caused a decrease in the bands at 2025 and 2060 cm^{-1}, as an absorption at 1966 cm^{-1} grew. At Sb/Rh = 2.60, only the 1966-cm^{-1} band remained.

These observations are consistent with the reaction pathways in Scheme I. The observed carbonyl stretching frequencies are indicated beneath each species. The brackets indicate species not detected by solution ir in the ν_{CO} region.

An intermediate (IV) with ν_{CO} at 2060 cm^{-1} can be observed in each reaction. In the reaction with Y_1, the appearance of III, which was previously identified in the reaction of $Rh_2Cl_2(CO)_4$ with SbR_3,[1] suggests formation by the cleavage of II by L and thus IV should also be formed.

An isomer of IV with the CO trans to Cl was rationalized as a possible intermediate in an analogous phosphine study but was neither isolated nor observed.[3] An increase in the stability of metal–olefin complexes containing SbR_3 rather than PPh_3 has previously been observed for *trans*-$RhClL_2(C_2H_4)$.[7,8] Since the isomer of IV with the CO trans to the Cl would be

Scheme I



expected to have a ν_{CO} similar to that of VI, and not as high as the observed value of 2060 cm^{-1}, the structure we propose for IV has the ethylene trans to chlorine as in *trans*-RhClL$_2$(C$_2$H$_4$).

The presence of IV as an intermediate in the reaction of Y$_2$ is consistent with the cleavage of VII by L. The absorption at 1975 cm^{-1} observed at Sb/Rh < 1 is reasonable for the dimeric species, VIII, since ν_{CO} (CHCl$_3$) for Rh$_2$Cl$_2$(CO)$_2$(PPh$_3$)$_2$ is at 1979 cm^{-1}.

The presence of IV in the reaction of Y$_3$ is consistent with the cleavage of IX by L. The final product observed in solution for the reactions of Y$_1$, Y$_2$, and Y$_3$ was VI, identified by ν_{CO} (CHCl$_3$) 1966 cm^{-1}.

It thus appears that the proposed dimeric intermediates (II, VII, and IX) may give dimeric complexes (V, VIII, and X respectively) by displacement of C$_2$H$_4$ or they may be cleaved, before C$_2$H$_4$ displacement, by the attack of a second L (pathway β).

Observation of IV indicates that a significant portion of the reactions proceed *via* pathway β in contrast to the reported phosphine reactions[3] which, except for P(C$_6$H$_{11}$)$_3$, proceed to yield dimers analogous to VIII before undergoing cleavage *via* pathway α. Observation of VIII indicates that dimeric complexes containing R$_3$Sb may be present at *low* Sb/Rh ratios but these species are either quick to react with additional R_3Sb to produce VI (pathway α) or simply are not favored because of cleavage of the original dimeric intermediates (pathway β). Whatever the reason, their concentration is to low to be observed at Sb/Rh > 1.

Attempted isolation of the products of the reactions of Y_1, Y_2, or Y_3 at various Sb/Rh ratios gave only $RhCOCl(R_3Sb)_2$ and $RhCOCl(R_3Sb)_3$.

The reaction of $P(C_6H_{11})_3$ by a pathway similar to β was rationalized as due to the steric bulk of the ligand.[3] Steric size can be determined by methods previously outlined.[9,10] Our calculations of the cone angles show $SbPh_3$ to be less bulky (*ca.* 13° smaller cone angle) than PPh_3 whose reaction with Y_2 proceeds *via* the dimer $Rh_2Cl_2(CO)_2(PPh_3)_2$. Since the SbR_3 reactions follow pathway β, steric considerations do not appear to be the controlling factor. The smaller steric interaction of SbR_3 is, however, probably responsible for the observed preference for five coordinate Rh(I) complexes[1] and the nondissociative nature of four coordinate Ni(0) and Pd(0) complexes.[11,12]

Registry No. Y_1, 49694-03-3; Y_2, 12306-60-4; Y_3, 49634-54-0; $SbPh_3$, 603-36-1.

References and Notes

(1) P. E. Garrou and G. E. Hartwell, *J. Organometal. Chem.*, **69**, 445 (1974).
(2) J. Gallay, D. de Montauzon, and R. Poilblanc, *J. Organometal. Chem.*, **38**, 179 (1972).
(3) A. Maisonnat, P. Kalck, and R. Poilblanc, *Inorg. Chem.*, **13**, 661 (1974).
(4) T. B. Brill and G. G. Long, *Inorg. Chem.*, **11**, 225 (1972).
(5) J. A. McCleverty and G. Wilkinson, *Inorg. Syn.*, **8**, 211 (1966).
(6) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).
(7) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A.*, 1711 (1966).
(8) J. T. Mague and G. Wilkinson, *J. Chem. Soc. A.*, 1736 (1966).
(9) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).
(10) C. A. Tolman, W. C. Seidel, and L. W. Gosser, *J. Amer. Chem. Soc.*, **96**, 53 (1974).
(11) P. E. Garrou and G. E. Hartwell, submitted for publication.
(12) The complexes $M(PPh_3)_4$ have been shown to be substantially dissociated according to the equilibria $M(PPh_3)_4 \rightleftarrows M(PPh_3)_3 + PPh_3$ (M = Ni, Pd). C. A. Tolman, W. C. Seidel, and D. H. Gerlach, *J. Amer. Chem. Soc.*, **94**, 2669 (1972).

Contribution from the Istituto di Chimica Generale ed
Inorganica, dell'Universita di Firenze, Florence, Italy 50132,
and from the Chemistry Department, York University,
Downsview, Ontario M3J 1P3, Canada

Enthalpy and Entropy Studies with Copper(II)-Bis(diamine) Complexes and Some Comments on Solvation Energy and Gas-Phase Enthalpies

C. Bianchini,[1a] L. Fabbrizzi,[1a] P. Paoletti,*[1a] and
A. B. P. Lever*[1b]

Received May 29, 1974 AIC40346X

Measurements of the enthalpy of formation of a metal complex in aqueous media provide a facile means quantitatively to evaluate and compare metal–ligand interactions. One must nevertheless bear in mind that the measured energy, generally of the order of tens of kilocalories per mole, is a balance of several terms of differeing sign. Thus the formation of the complex and its solvation are exothermic, while the desolvation of the ligand and of the metal ion are endothermic. These individual terms may be of the order of hundreds of kilocalories per mole.

On the other hand some spectroscopic parameters (crystal field and charge-transfer transition energies, metal–ligand stretching frequencies, and force constants, etc.) can qualitatively provide a measure of the metal–ligand interaction in a manner less dependent upon solute–solvent interactions. Recent publications from our laboratories[2-7] have sought to establish a more quantitative relationship between spectroscopic and thermodynamic parameters, which is further extended in this note.

Paoletti and coworkers[6] have recently reported a relationship between the energy of the principal d–d transition in aqueous solution (ν(d–d)) and the enthalpy of reaction 1 in aqueous

$$\mathrm{Cu(H_2O)_6}^{2+} + \mathrm{L(aq)} \rightarrow \mathrm{CuL(H_2O)_2}^{2+} \quad \Delta H_{\mathrm{aq}} \tag{1}$$

solution, where L is a linear aliphatic tetramine of general formula $NH_2(CH_2)_mNH(CH_2)_nNH(CH_2)_pNH_2$, referred to as *mnp* in Figure 1, or represents two diamine species. These complexes possess a tetragonally distorted octahedral structure in aqueous solution with the amines occupying the in-plane sites and water occupying the axial sites.[6,7] One may assume, with some confidence,[2] that the energy of the principal d–d band coincides approximately with the energy of the in-plane transition $xy \rightarrow x^2 - y^2$ and thereby furnishes a measure of the in-plane field strength, Dq_{xy}. The magnitude of Dq_{xy} should be directly proportional to the enthalpy of formation of the complex in the gas phase,[8] *i.e.*

$$\mathrm{Cu^{2+}(g)} + \mathrm{L(g)} \rightarrow \mathrm{CuL^{2+}(g)} \quad \Delta H_{\mathrm{g}} \tag{2}$$

ΔH_g is related to the experimentally measured value, ΔH_{aq}, through the relationship

$$\Delta H_{\mathrm{aq}} = \Delta H_{\mathrm{g}} - [\Delta H(\mathrm{Cu^{2+}})_{\mathrm{aq}} + \Delta H(\mathrm{L})_{\mathrm{aq}} - \Delta H(\mathrm{CuL^{2+}})_{\mathrm{aq}}] \tag{3}$$

where the last three terms are the hydration energies of the species indicated. Since there is a linear relationship[6] between the enthalpy of formation in aqueous media and ν(d–d), the overall magnitude of the three solvation energy terms (in brackets in (3)) must remain essentially constant for the six ligands previously chosen.[9]

We now extend this correlation to include a series of both *N*-alkyl- and *C*-alkyl-substituted ethylenediamines. The ΔH_{aq} *vs.* ν(d–d) correlation for ten complexes is reported in Figure 1; the good linear relationship (coefficient of variation 0.92%) is upheld. These complexes possess a molecular plane containing at least six hydrogen atoms bound to the four coplanar nitrogen atoms. It seems probable that hydrogen bonding to the water outer sphere provides the bulk of the solvation energy of these species. *C*-Alkyl substitution of the ethylenediamine ligand does not seem to interfere with the correlation since complexes of *C*-Meen, *C*-Eten, and *C,C*-Eten lie close to the line. However complexes of the *N*-alkyl-substituted ethylenediamines (diMeen, adiMeen, diEten, and adiEten) lie off the line as a consequence both of the steric effect of the N substituents and of the decrease to four N hydrogen atoms in the molecular plane. For such complexes the measured heat is lower than would be expected on the basis of the visible electronic transition. Referring to eq 3 one may conclude that for the complexes which fall off the line, the term $\Delta H(\mathrm{CuL})_{aq} - \Delta H(\mathrm{L})_{aq}$ is more *endothermic* than for those complexes which lie on the line. Indeed, one may estimate the magnitude of the solvaltion energy difference for complexes lying off the line, relative to those which lie on the line, to be as follows (kcal/mol): diMeen, 1.8; adiMeen, 3.6; diEten, 5.4; adiEten, 6.5. Reaction 1 takes place with a net liberation of a certain number of water molecules as is demonstrated by the positive value of ΔS observed. The solvation energy data given above imply that in the formation of those complexes which lie off