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.

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

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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

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

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.*

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

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

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

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 $\Delta H(CuL)_{aq} - \Delta H(L)_{aq}$ 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

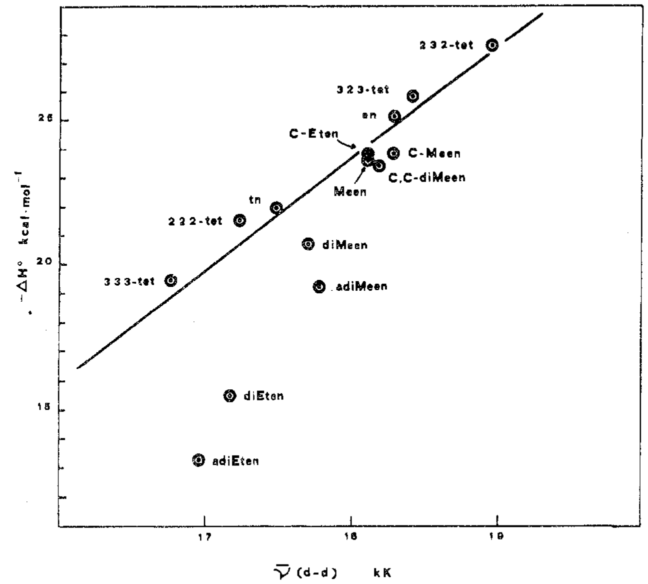

Figure 1. Relationship between ΔH_{aq} and ν(d–d) for a series of bidentate and tetradentate ligand complexes. 222-tet etc. refer to the various chain length linear tetradentate *mnp*-tet ligands referred to in the text. The equation of the line is $\Delta H = 46.4 - 3.896\nu$(d–d), and the coefficient of variation is 0.92%.

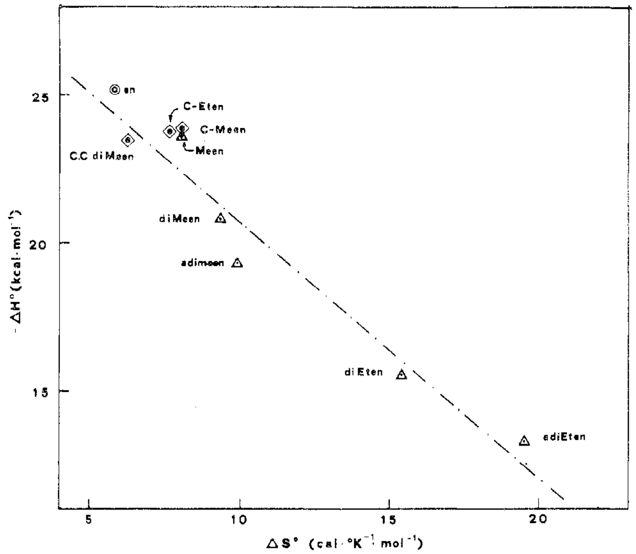

Figure 2. Relationship between ΔH_{aq} and ΔS for the series of bidentate and tetradentate ligand complexes.

the line the process of desolvation of the ligand and of the metal ion and solvation of the complex releases a greater number of water molecules for these complexes than for those which are well behaved.

Such a conclusion may be supported by more detailed consideration of the entropy changes. Thus in Figure 2 values of ΔH_{aq} for reaction 1 are plotted against ΔS; as the heat of reaction decreases, ΔS becomes more positive.

Assuming that the entropy changes associated with the loss of freedom of the individual ligands are small and/or similar, the variation in ΔS should parallel the number of water molecules released. Thus these data confirm that the process of desolvation is more extensive in the *N*-alkyl-substituted derivatives than in the other complexes.

Alkyl groups on the nitrogen atoms impede the formation of hydrogen bonds between the complex and solvent water. Such a desolvation effect will increase as the size of the hydrophobic alkyl group increases. As predicted, the diethyl complexes do show a more pronounced deviation than the dimethyl derivatives, and further the asymmetric compounds deviate more than the symmetric. Alkyl groups substituted on the aliphatic carbon chain are less likely to impede hydrogen-bond formation and they are indeed well behaved, within the limits of the experiment.

Note that the ΔH_{aq} *vs.* ν(d–d) correlation implies that as the metal–ligand interaction decreases, both ΔH_g and ν(d–d) should approach zero;[6,7] in other words a plot of ΔH_g *vs.* ν(d–d) should pass through the origin. Extrapolation of the ΔH_{aq} *vs.* ν(d–d) plot to zero electronic energy does not pass through the origin but intercepts the ΔH_{aq} axis at +46.4 kcal/mol. If it may be assumed that the relationship between ΔH_g and ν(d–d) is indeed of the form $\Delta H_g = f\nu$(d–d) (where f is a constant), then the bracketed terms in eq 3 sum to −46.4 kcal/mol. This procedure provides an attractive approach toward the evaluation of outer-sphere solvation energies which are very difficult to obtain by other routes. If this value is accepted for the solvation energy terms we may evaluate ΔH_g for each of the complexes. Use of eq 3 then leads to values in the range −65 to −73 kcal/mol for the *gas-phase enthalpy*; such numbers are considerably lower than might be anticipated for the enthalpy of four Cu–N bonds. This anomaly may arise because the premise that $\Delta H_g = f\nu$(d–d) is incorrect or because there is inaccurate extrapolation of the ν(d–d) *vs.* ΔH_{aq} line as a consequence of insufficient experimental data. Clearly further work is necessary to answer these questions. Equally clearly this procedure does show exceptional promise as a means of obtaining highly desirable thermodynamic quantities which can only very rarely be directly measured.

Finally, we have previously demonstrated[7] a similar relationship between thermodynamic parameters and σ–σ^* transition energies in these complexes. It was pointed out that such a correlation should be meaningful in the solid state but that in solution "solvent effects" might render an apparent correlation fortuitous and that further solution data should be sought. Indeed a plot of ΔH_{aq} *vs.* $E(\sigma$–$\sigma^*)$ for the ten well-behaved complexes in Figure 1 is badly scattered. This arises not because there is a breakdown in the model itself but presumably because small changes in solvation energy from one complex to another have a marked effect upon the relative stabilization of the ground and excited electronic states of the molecule.[7]

Experimental Section

All the complexes have been previously described. They were prepared (as perchlorates) by the literature methods and analyzed satisfactorily. Thermodynamic data $\Delta H°$ and $\Delta S°$ have been published for all but two complexes.[6,10-13] Data for diEten and adiEten for reaction 1 (0.5 *M* NaClO$_4$, T = 25°) were obtained by direct calorimetric titration using published procedures.[11,12] Appropriate combination of ΔH values with the reported ΔG data[14,15] gives ΔS. (See below.)

	$-\Delta H$, kcal/mol	ΔS, eu
Cu(diEten)$_2^{2+}$	15.5 ± 0.4	19.5 ± 1.4
Cu(adiEten)$_2^{2+}$	13.2 ± 0.4	15.4 ± 1.2

Most of the spectroscopic data have been previously reported.[2,6,7,13] Additional data obtained with a Beckman DK 2A instrument, are given below (aqueous solution, molar extinction coefficients in parentheses).

	ν(d–d), kK	$\nu(\sigma$–$\sigma^*)$, kK
Cu(Meen)$_2^{2+}$	18.11 (89)	40.32 (6240)
Cu(*C*-Meen)$_2^{2+}$	18.28 (70)	43.29 (4830)
Cu(*C,C*-diMeen)$_2^{2+}$	18.18 (84)	42.92 (4210)

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Registry No. Cu(diEten)$_2$$^{2+}$, 52918-69-1; Cu(adiEten)$_2$$^{2+}$, 46754-10-3; Cu(Meen)$_2$$^{2+}$, 36421-64-4; Cu(C-Meen)$_2$$^{2+}$, 17992-12-0; Cu(C,C-diMeen)$_2$$^{2+}$, 52918-70-4.

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A Case for Covalent Bonding in Lanthanide Trihalides

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Many of the properties of lanthanide compounds, particularly complexes, have been interpreted as supporting the argument that bonding to the lanthanide atom is substantially electrostatic.[1] However, there have been suggestions that covalent bonding may be important in chelates,[2] and a pyramidal structure has been suggested for PrF$_3$,[3] which would not be expected if bonding were purely ionic. In addition, it has been shown that covalent bonding must be invoked to account for the observed dissociation energies of LnX (X = O, S, Se, Te) molecules,[4] and a σ-bonded lutetium alkyl has recently been prepared and its structure established by X-ray diffraction.[5]

An appropriate model for bonding in the lanthanide trihalide molecules should account for the bond strength of these molecules. Thermodynamic and spectral data in the literature provide a basis for calculations testing the ionic model and assessing whether a covalent model may be appropriate. The approach used here is to calculate atomization energies of the molecules and to apply first an ionic model and then a covalent model in an attempt to account for observed trends, these models being considered the only reasonable ones for these molecules.

Atomization energies of LnX$_3$ molecules may be calculated from the thermochemical cycle

$\mathrm{LnX_3(s) = Ln(s) + {}^3/_2X_2}$(std state)	$-\Delta H_f(\mathrm{LnX_3})$
$\mathrm{LnX_3(g) = LnX_3(s)}$	$-\Delta H_s(\mathrm{LnX_3})$
$\mathrm{Ln(s) = Ln(g)}$	$\Delta H_s(\mathrm{Ln})$
${}^3/_2\mathrm{X_2}$(std state) $= \mathrm{3X(g)}$	$\Delta H_f(\mathrm{X})$
$\mathrm{LnX_3(g) = Ln(g) + 3X(g)}$	ΔH_{at}

The data and results of such calculations are given in Table I,[6–19] the values for all entries being at 298.15°K. All entries are rounded to the nearest kilocalorie, and estimated quantities are in parentheses. The assumed uncertainty is ±5 kcal if all quantities are measured and ±10 kcal if one or more estimated values are used. The double periodicity in atomization energy as a function of atomic number has also been noted for the enthalpies of sublimation of the metals[7] (see Table I) and for the dissociation energies of monochalconide molecules.[4,20,21]

The ionic model was assessed in terms of the processes

$\mathrm{Ln^{3+}(X^-)_3(g) = Ln^{3+}(g) + 3X^-(g)}$	$-\Delta H_{ia}$
$\mathrm{Ln^{3+}(g) + 3e^- = Ln(g)}$	$-\Sigma\mathrm{IP}$
$\mathrm{3X^-(g) = 3X(g) + 3e^-}$	3EA
$\mathrm{Ln^{3+}(X^-)_3(g) = Ln(g) + 3X(g)}$	$\Delta H_{at}'$

The ion association energies were calculated assuming trigonal-planar geometry (even though PrF$_3$ is probably not planar). Interionic distances were estimated using the measured value[22] for LaF$_3$ and Pauling's crystal radii,[23] assuming a constant ratio between the sum of the crystal ionic radii and the interionic distance in the gaseous molecule.[14] The relationship used for the calculation was

$$\Delta H_{ia} = \left\{\left[-3\left(\frac{3e^2}{r}\right) + \frac{3e^2}{r\sqrt{3}}\right]\left(1 - \frac{1}{n}\right)\right\}N_0$$
$$= \frac{1}{r\,(\text{Å})}\left(1 - \frac{1}{n}\right)(2.413 \times 10^3 \text{ kcal Å/mol})$$

where r is the interionic distance, e is the electronic charge, n is the Born exponent (9.5 for LnF$_3$, 10.5 for LnCl$_3$, 11.0 for LnBr$_3$, and 12.0 for LnI$_3$), and N_0 is the Avogadro number. Ionization potentials are from the compilation of Martin and coworkers,[24] and electron affinities are values cited by Huheey.[25]

The results of the calculations using the ionic model are given in Table II. Differences between ΔH_{298} (thermochemical values) and ΔH_0 (ionic model) have been neglected. Comparison of values of $\Delta H_{at}'$, calculated from the ionic model, with values of ΔH_{at} based on thermochemical data shows that the ionic model does not account for the observed atomization energies. Furthermore, the discrepancies increase from LnF$_3$ to LnI$_3$. This is most clearly seen in the ratio $\Delta H_{at}'/\Delta H_{at}$. For the LnF$_3$ molecules the ionic model accounts for 80–90% of the observed atomization energy, but for the LnI$_3$ molecules this drops to as low as 27%. Not surprisingly, the ionic model works best for LnF$_3$ molecules, but in addition to increasing departure from ionic behavior with LnCl$_3$, LnBr$_3$, and LnI$_3$ molecules, the extent to which the ionic model accounts for the observed atomization energies itself shows a double periodicity with minima at EuX$_3$ and YbX$_3$. While choosing shorter interionic distances could increase the magnitude of ΔH_{ia} and hence increase $\Delta H_{at}'$, the trend of increasing departure from the ionic model and the double periodicity would remain.

Since the ionic model is seen to have serious deficiencies, the question arises as to whether a covalent model would be any better. This question cannot be answered in full at present because of the complexities of theoretical calculations. However, an assessment can be made as to whether a covalent perspective will account for the observed trends in atomization energies, in particular the double periodicity noted above. The approach used is to calculate atomization energies, not to the