Cr^{2+} added. We are presently in the process of investigating a wider range of metal nitrosyls with the intention of pursuing the last possibility offered above.

Experimental Section

$[Ru(NH_3)_5NO]Cl_3$ was prepared by saturating a concentrated solution of $Ru(NH_3)_6^{3+}$ (pH <2 with HCl) with NO(g) for 1-2 hr.[13] Addition of NaCl precipitated the nitrosyl complex as the chloride salt. The solid was then washed with acetone and anhydrous ether. $[Co(NH_3)_5NO]Cl_2$ was prepared[24] by the addition of a degassed solution of $CoCl_2$ to a cold, degassed solution of aqueous ammonia (12%). The solution was saturated with NO for 3 hr resulting in the formation of a black precipitate. The crystalline, black solid was washed with absolute alcohol and anhydrous ether and stored in a vacuum desiccator. $CrNO^{2+}$ was prepared by two different methods. (1) Stock solutions of $CrNO^{2+}$ were prepared by the dropwise[21] addition of 0.5 *M* Cr^{2+} (10 ml/20 min) to a stirred solution of 200 ml of 0.1 *M* $HClO_4$. The latter solution was saturated with NO by means of a gas dispersion tube. After removing the NO from solution, the red solution was stored at 5°. Aliquots of the stock solution were purified by adsorption of the complex onto Dowex 50W-X8, 200-400 mesh (in the H^+ form). The red band was eluted with 0.5 *M* $HClO_4$. (2) The black $[Co(NH_3)_5NO]Cl_2$ was ground into a fine powder and placed inside a vial. The vial was stoppered with a rubber septum cap and purged with dry argon. A solution containing an equal number of moles of Cr^{2+} was injected directly into the vial.

Nitric oxide (chemically pure, Matheson Gas Products) was purified by vigorous scrubbing through towers of molecular sieve (−78°), solid KOH, and 5 *M* NaOH, respectively. All gases were passed through a final, common scrubbing tower of 0.1 *M* NaCl. Before and after the NO gas flow, argon was admitted to our all-glass system by rotation of a three-way stopcock (placed between the 5 *M* NaOH and 0.1 *M* NaCl towers). Chromium(II) perchlorate solutions were prepared (under argon) by the reduction of $Cr(H_2O)_6^{3+}$ with amalgamated zinc. Stock solutions of Cr(III) perchlorate were prepared by reduction of primary standard $K_2Cr_2O_7$ with acidic H_2O_2 and boiling the solution for several hours.[21] The solution was cooled overnight, and the $KClO_4$ was removed by filtration. Stock solutions of Fe^{2+} were prepared by treatment of iron wire (Baker and Adamson, reagent grade) with $HClO_4$.[25]

The solubility of NO was determined by injecting an aliquot of an NO-saturated solution (at 25.0° and 1 atm) into an excess of O_2-saturated water. The resulting NO_2^- was determined quantitatively.[26,27]

All reactants and products were characterized by their uv-vis spectra, their behavior on a cation-exchange column, and their ir spectra (KBr disks).

Registry No. $Ru(NH_3)_5NO^{3+}$, 37874-79-6; $Co(NH_3)_5NO^{2+}$, 38402-80-1; $CrNO^{2+}$, 40187-02-8; chromium, 7440-47-3.

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Correspondence

A Linear Relationship between the Enthalpy of Formation and the Frequency of the Maximum in the Electronic Absorption Spectra of the Copper(II)-Tetramine Complexes

Sir:

Recently a considerable amount of experimental material relating to the reactions between 3d metal ions and linear aliphatic tetramines has been reported.[1] In particular for copper(II) it has been found that complexes containing a system of three fused chelate rings in which five- and six-membered rings alternate, *e.g.*, $[Cu(2,3,2\text{-tet})]^{2+}$ [2] and $[Cu(3,2,3\text{-tet})]^{2+}$,[3] are more stable than complexes in which the chelate rings are either all five-membered (2,2,2-tet[4a]) or six-membered (3,3,3-tet[4b]).[5] Furthermore calorimetric titrations have shown that the greater stability is due to a more favorable enthalpic contribution.[1] The more negative $\Delta H°$ reflects the capacity of the ligand to place the donor atoms in positions better suited to the steric requirements of the copper(II) ion (probably at the corners of a square plane) thus giving a configuration with less strain as is also shown by the construction of molecular models. The formation of both $[Cu(2,3,2\text{-tet})]^{2+}$ [6] and $[Cu(3,2,3\text{-tet})]^{2+}$ [7] is more exothermic even than that of $[Cu(en)_2]^{2+}$ [8] with two separated five-membered rings, so that any cumulative steric strain must be considered absent in these compounds.

In the solid state, salts of $[Cu(2,3,2\text{-tet})]^{2+}$, which has the highest heat of formation in the series under consideration, are bright red, while complexes of the other ligands have the usual blue-purple color. In other words both in the solid state and in solution the frequency of the electronic absorption maximum of the complex $[Cu(2,3,2\text{-tet})]^{2+}$ is higher than those of the corresponding complexes of homologous ligands.

This led us to think that there must be a relation between the thermodynamic and the spectral properties of these complexes.

Figure 1 shows the ΔH of formation of these complexes plotted against the frequency of the maximum in their electronic absorption spectra in aqueous solution. The least-squares equation describing the relation is $-\Delta H° = 3.75\bar{\nu}_{max} - 43.36$ ($\Delta H°$ being expressed in kcal mol^{-1} and $\bar{\nu}_{max}$ in kK). The linear relationship between these two quantities is not a completely unexpected result. In fact it has been found that the values of $\Delta H°$ become more negative as the coordinate bonds formed by the equatorially coordinated ligand become stronger.[6]

On the other hand, it was shown that the frequency of the maximum of the d-d band could be considered as an approximate measure of the in-plane bond strength (*i.e.*, the

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[5] Linear aliphatic tetramines of the type $H_2N(CH_2)_lNH(CH_2)_mNH(CH_2)_nNH_2$ are denoted by the symbol *l,m,n*-tet. Furthermore en is for ethylenediamine and tn is for 1,3-propanediamine.

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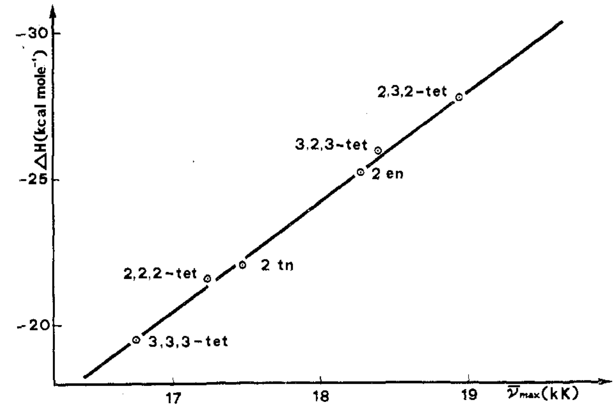

Figure 1. Enthalpies of formation *vs.* the frequencies of the maximum of the electronic spectra of copper(II)–tetramine complexes in aqueous solution at 25°.

transition $x^2 - y^2 \leftarrow xy$).[9] More recent work shows that this approximation does not hold in some cases.[10]

However, a large number of experimental data[9,10] suggest that for complexes of the general type CuL_2X_2 (where L is an aliphatic diamine and X is an inorganic mononegative anion) the maximum of the d–d band is linearly correlated to the square of the metal–nitrogen stretching vibration, which undoubtedly furnishes a measure of the strength of the copper–nitrogen coordinative bond.

In consequence of this, a straight-line correlation between the $\Delta H°$ of formation and the energy of the $x^2 - y^2 \leftarrow xy$ transition in the considered complexes is quite reasonable, even if this electronic transition is not always easily identified.[10]

This empirical relationship allows an estimate of the $\Delta H°$ of formation of tetracoordinated copper(II) complexes to be made using spectrophotometric measurements alone. The application of this method could be very useful for the study of systems for which a traditional thermodynamic determination of $\Delta H°$ by calorimetric titration was difficult. As an example let us take the case of complexes with macrocyclic ligands. The formation constant for the copper(II) complex with tet *a* (tet *a*: 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, meso isomer) has been estimated by a spectrophotometric method; it is by far the highest for any polyamine complex of copper(II) yet investigated.[11]

To emphasize this exceptional stability the term *macrocyclic effect* was introduced. However the reaction between copper(II) and tet *a* is very slow and thus a calorimetric determination of ΔH and a rationalization of the macrocyclic effect in terms of the contributions due to enthalpy and entropy are not possible. On the other hand, an approximate value of $\Delta H°$ can be calculated from our empirical relationship, given the value of $\bar{\nu}_{max}$ (19.6 kK)[12] for the complex. This gives a value for ΔH of −30 kcal mol^{-1}, *i.e.*, a higher value for the heat of formation than those found experimentally for analogous open-chain tetramine complexes. The tet *a* complex contains four successive rings, two five-membered and two six-membered, arranged alternately. The structure of the ligand is such that the donor atoms are in the most favorable positions for the formation of strong coordinate bonds.

From the $\Delta H°$ value calculated in this way and the reported value of $\Delta G°$ it is immediately possible to calculate the $\Delta S°$ of formation for the complex [Cu(tet *a*)]. The value obtained (27 cal deg^{-1} mol^{-1}) is exceptionally high, appreciably higher than the values found for the open-chain tetramines (13–19 cal deg^{-1} mol^{-1}). On coordination the nitrogen atoms of an open-chain tetramine become fixed in a single rigid configuration. Going from a situation in which various configurations are possible (the uncoordinated tetramine) to one with a single fixed configuration (the coordinated tetramine) must cause an appreciable loss of entropy. On the other hand one does not expect a loss of entropy when complexes are formed by a macrocyclic ligand which already has its donor atoms in a rigid configuration suitable for coordination.

On the basis of these results we are able to propose that the *macrocyclic effect* is not simply an enhanced *chelate effect*. The *chelate effect* is essentially an entropy effect while both entropy and enthalpy terms contribute to the *macrocyclic effect*.

Experimental Section. All the complexes were obtained as perchlorates by adding equimolar amounts of $Cu(ClO_4)_2 \cdot 6H_2O$ and of the amine in methanolic solution. Electronic spectra of the aqueous solutions thermostated at 25° were performed with a Beckman DK-2A spectrophotometer.

Spectrophotometric data are as follows [frequency of the maximum, kK (molar absorbance)]: $[Cu(2,2,2\text{-tet})]^{2+}$, 17.24 (150); $[Cu(2,3,2\text{-tet})]^{2+}$, 18.94 (70); [Cu(3,2,3-tet)], 18.40 (92); $[Cu(3,3,3\text{-tet})]^{2+}$, 16.75 (173); $[Cu(en)_2]^{2+}$, 18.28 (61); $[Cu(tn)_2]^{2+}$, 17.48 (69).

Thermochemical data are taken from the appropriate references as reported in the text: $\Delta H°$ of $[Cu(2,2,2\text{-tet})]^{2+}$ and $[Cu(tn)_2]^{2+}$ are taken from ref 13 and 14, respectively.

Registry No. $[Cu(2,2,2\text{-tet})]^{2+}(ClO_4^-)_2$, 40192-39-0; $[Cu(2,3,2\text{-tet})]^{2+}(ClO_4^-)_2$, 40192-40-3; $[Cu(3,2,3\text{-tet})]^{2+}(ClO_4^-)_2$, 40192-41-4; $[Cu(3,3,3\text{-tet})]^{2+}(ClO_4^-)_2$, 40192-42-5; $[Cu(en)_2]^{2+}(ClO_4^-)_2$, 36407-48-4; $[Cu(tn)_2]^{2+}(ClO_4^-)_2$, 40192-44-7.

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