Inorg. Chem. **1980**, *19*, 2414–2416

complex decomposes for either complex (see above and ref 4)] or a mode III heterolytic mechanism in which the emerging carbanion is protonated by solvent. For the latter possibility, two kinetically indistinguishable mechanisms have been discussed:[4] mechanism I in which dissociation of an equatorial methyl proton leads to a dianionic intermediate which decomposes to yield an alkyl ligand carbanion and mechanism II in which hydroxide ion directly attacks the equatorial ligand system leading to concerted expulsion of the organic ligand as a carbanion. Although these two mechanisms could presumably be distinguished by their solvent deuterium isotope effects, the complications arising from secondary isotope effects due to extensive deuteration of the cobaloxime moiety and the very small magnitude of the observed isotope effect ($k_1^{OH^-}/k_1^{OD^-} = 1.03 \pm 0.07$) make such a distinction impossible.

It is surprising to find that $CH_3Co(D_2H_2)OH^-$[4] is 22.5-fold more reactive in the alkane forming reaction than $CH_3CH_2Co(D_2H_2)OH^-$ (Table II), considering the small difference in electron inductive effect for the two organic ligands ($\sigma^* = 0$ for CH_3, $\sigma^* = -0.10$ for CH_3CH_2[22]). This result strongly suggests either that one of the two complexes is anomalously reactive or that the mechanism of alkane formation is not the same for both complexes. The lack of any significant formation of side product in the $CH_3CH_2Co(D_2H_2)OH^-$ case also seems to support the latter conclusion. Further experiments are in progress to attempt to clarify this question.

Acknowledgment. The authors are grateful to Drs. Andrew Armstrong and Richard Dickinson for their able assistance in the operation of the Du Pont Model 321 GC/MS system.

Registry No. $CH_3CH_2Co(D_2H_2)OH_2$, 26025-30-9; $CH_3CH_2Co(D_2H_2)OH^-$, 73926-34-8; CH_3CH_3, 74-84-0; $CH_2{=}CH_2$, 74-85-1; $CH_3CH_2Co(D_2H_2)py$, 25360-57-0.

---

[22] Taft, R. W. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; Chapter 13.

Contribution from the Department of Chemistry,
University of Stirling, Stirling FK9 4LA, Scotland

Enthalpy of Combustion of a Copper Complex. Standard Enthalpy of Formation of Bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II)

R. M. CLAY and W. V. STEELE*

Received October 22, 1979

The standard energy of combustion of bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II) has been determined by oxygen aneroid rotating-bomb calorimetry. Nitric acid was used as solvent for the solid products of combustion in order to produce a well-defined homogeneous final solution of copper(II) nitrate in excess nitric acid. The work reported is the first known application of rotating-bomb calorimetry to an organocopper compound. A standard enthalpy of formation, $\Delta H_f°(C_{10}H_{24}N_6O_6Cu(c)) = -639.4 \pm 4.0$ kJ mol^{-1}, was derived from the experimental data and was used, together with enthalpy of solution data, to derive the enthalpy of formation of the complex ion in aqueous solution. This latter value was in close agreement with a direct calorimetric value.

Introduction

The phenomenon that some macrocyclic ligands in aqueous solution form more stable complexes with metal ions than the analogous open-chain ligands with the same donor groups has been termed the macrocyclic effect.[1] Since the first reported example of this effect, which involved the copper complex of a hexamethyl derivative of a 14-membered tetraaza macrocycle,[1] a great deal of interest has been shown in the thermodynamic origins of this extra stability. Early conflicting studies assigned the extra stability to wholly entropy[2] or wholly enthalpy[3] terms based on enthalpy values obtained from temperature-dependent stability constant studies. More recently[3-7] direct calorimetric determinations of enthalpy values have shown that the entropy term is always favorable and that the enthalpy term is dependent on the matching of the size of the macrocyclic ligand aperture to that of the metal ion. For the octahedral complexes of copper(II) and nickel(II) with 1,4,8,11-tetraazacyclotetradecane (L_1) and 1,4,8,11-tetraazaundecane (L_2), ΔH values for the metathetical reaction

$$ML_2^{2+}(aq) + L_1(aq) = ML_1^{2+}(aq) + L_2(aq) \qquad (1)$$

which represents the macrocyclic effect are −19.7[6] and −20.5 kJ mol^{-1},[7] respectively. These values have been obtained from the calorimetrically determined enthalpy change associated with the formation reactions, namely

$$M^{2+}(aq) + L(aq) = ML^{2+}(aq) \qquad (2)$$

which were measured for both ligands, L_1 and L_2. The experimental conditions used in the determinations were extreme (pH 14), and some collaboration of the results seemed desirable especially since they did not agree with ΔH values obtained indirectly. We decided, therefore, to determine the standard enthalpies of formation of both ligands and their copper complexes, in the form of their nitrate salts, by oxygen aneroid bomb calorimetry and by combining these data with the corresponding enthalpies of solution to obtain an independent value for the macrocyclic enthalpy.

The standard enthalpies of formation and solution of both ligands, L_1 and L_2, have been reported in ref 8. Here we report the determination of the standard enthalpy of formation of bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II) ($CuL_1(NO_3)_2$). The authors believe that this is the first re-

---

[1] S. K. Cabbiness and D. W. Margerum, *J. Am. Chem. Soc.*, **91**, 6540 (1969).

[2] M. Kodma and E. Kimura, *J. Chem. Soc., Dalton Trans.*, **116**, 2341 (1976).

[3] F. P. Hinz and D. W. Margerum, *Inorg. Chem.*, **13**, 2941 (1974).

[4] A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *J. Chem. Soc., Chem. Commun.*, 244 (1977).

[5] A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chim. Acta*, **22**, L25 (1977).

[6] A. Anichini, L. Fabbrizzi, P. Paoletti, and R. M. Clay, *J. Chem. Soc., Dalton Trans.*, 577 (1978).

[7] L. Fabbrizzi, P. Paoletti, and R. M. Clay, *Inorg. Chem.*, **17**, 1042, (1978).

[8] R. M. Clay, M. Micheloni, P. Paoletti, and W. V. Steele, *J. Am. Chem. Soc.*, **101**, 4119 (1979).

0020-1669/80/1319-2414$01.00/0

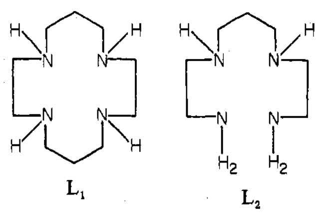


Figure 1.

ported rotating-bomb combustion calorimetric determination of the standard enthalpy of formation of an organocopper compound. The methodology developed here should open the way to measurements of the standard enthalpies of formation of other copper(II)–organo compounds and should be applicable, in particular, to copper complexes containing amino acids.

Experimental Section

Materials. The sample of 1,4,8,11-tetraazacyclotetradecane (L_1) used in this work was a portion of that purified earlier for the determination of its enthalpy of formation.[8]

Bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II) was prepared by adding equimolar quantities of a solution of AnalaR copper nitrate trihydrate in ethanol to a solution of L_1 in ethanol. The purple product, which separated, was twice recrystallized from water and dried at 353 K in vacuo. The calorimetric sample was stored in a desiccator over P_2O_5 until use since it was found to be slightly hygroscopic. Elemental analysis (C, H, and N) for the sample corresponded, within acceptable limits, to that required by the molecular formula. In the absence of any other method of determination, gravimetric analysis for copper[9] was used to give a quantitative estimate of purity. A solution of 0.15 g of the complex in 0.050 dm^3 of water was warmed, and 1.5 g of $K_2S_2O_8$ was added in small portions to oxidize the organic part of the complex. The copper in the resulting solution was determined gravimetrically as the salicylaldoximate:[9] calcd, 16.38%; found, 16.37 ± 0.06% (mean of duplicate analyses).

$Cu(NO_3)_2 \cdot 3H_2O$ was taken from a freshly opened sample of BDH AnalaR grade, stored in a tightly sealed bottle under dry nitrogen, and was used without further purification. The benzoic acid used was BDH thermochemical standard, and the 2.00 mol dm^{-3} HNO_3 was prepared by accurate dilution of BDH "Aristar" concentrated reagent using deionized water.

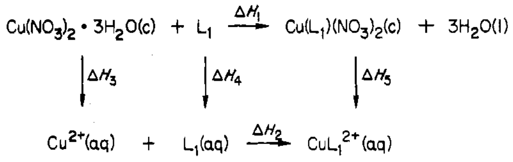
Calorimetric Method. The aneroid rotating-bomb calorimeter and the auxiliary equipment have been described previously.[10] In a series of trial experiments on the combustion of $CuL_1(NO_3)_2$ varying conditions of oxygen pressure, auxiliary combustion aids, and various concentrations of nitric acid were used in an attempt to obtain complete combustion and homogeneous solution. Reproducible results of complete combustion and dissolution of all solid products were obtained by using lightly pressed pellets of $CuL_1(NO_3)_2$ burned with pellets of thermochemical benzoic acid under an initial oxygen pressure of 3.2 MPa at 298.15 K in the presence of 0.0250 dm^3 of 2.000 mol dm^{-3} HNO_3. The thermochemical benzoic acid accounted for two-thirds of the heat output of the combustion reaction. Attempts to lessen this resulted in the formation of a solid black mass in the crucible, insoluble in the bomb solution but partially soluble in aqua regia. The oxygen used was purified by passage over heated cupric oxide to remove any combustible material.

After combustion, the solution from the bomb calorimeter and several washings were combined and diluted to 0.250 dm^3. The solution was then analyzed gravimetrically for copper,[9] by UV spectroscopy for nitrate ion[10,11] and by potentiometric titration with standard sodium hydroxide for total acid. The analytical results showed complete solution of the solid copper products of combustion and stoichiometric quantities of acid and nitrate ion within the sensitivity of the analytical techniques (±0.05%). Mass spectroscopy of a sample of the nitric acid free gas from a combustion run failed to show the presence of any gaseous combustion products other than CO_2.

Table I. Physical Properties at 298.15 K[a]

compd	M_r	ρ/g cm^{-3}	$(\partial e/\partial p)_T$/ J MPa^{-1} g^{-1}	C_p/J K^{-1} g^{-1}
benzoic acid	122.123	1.32	−0.0117	1.21
cyclam[b]	200.326	0.73	(−0.0209)	1.87
$Cu(NO_3)_2 \cdot 3H_2O$	241.601	2.34	(−0.0209)	
filter paper	27.198	1.50	negligible	1.68
$Cu(cyclam)(NO_3)_2$	387.882	1.87	(−0.0209)	2.36

[a] Values in parentheses are estimates. [b] Cyclam = 1,4,8,11-tetraazacyclotetradecane.



L_1 = 1,4,8,11-tetraazacyclotetradecane

Figure 2.

Comparison experiments were used to minimize errors from inexact reduction to standard states caused by the lack of relevant data.[12] The samples in the comparison experiments were pellets of 1,4,8,11-tetraazacyclotetradecane and benzoic acid and 0.0250 dm^3 of 2.000 mol dm^{-3} nitric acid containing copper(II) nitrate. The amounts of these materials were selected so that the energy evolved and the CO_2 produced in the comparison experiment were nearly the same as in the corresponding combustion experiment. The amount of copper(II) nitrate was such that, following dilution with the water produced during the combustion of the samples, a solution was formed of nearly the same amount and concentration as in the combustion experiment.

The standard energy of combustion of 1,4,8,11-tetraazacyclotetradecane has been determined previously[8] as −36.1360 ± 0.0059 kJ g^{-1}. The standard energies of combustion of the filter paper used as a fuse and the benzoic acid were −17.223 kJ g^{-1} and −26.435 kJ mol^{-1}, respectively.

The experimental results are based on 1976 atomic weights.[13] The values in Table I of the density ρ, the specific heat capacity C_p*, and $(\partial e/\partial p)_T$ respectively were used for reducing weighings in air to masses, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states.[14] All values of density were measured in this laboratory. Values for the specific heat capacities were determined on the DSC using sapphire as a standard.[15] The standard state for aqueous nitric acid was $HNO_3 \cdot 100H_2O$. The enthalpy of solution of $Cu(NO_3)_2 \cdot 3H_2O$ in the nitric acid solution was redetermined and found to agree exactly with the value calculated from data in ref 16.

Results and Discussion

The results of a typical combustion and the corresponding comparison experiment for bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)copper(II) are given in Table II. It is impractical to list summaries for all experiments, but values of $\Delta e_c°/M$, the specific energy for the idealized combustion reaction, for all experiments are given in Table III. The idealized combustion reaction is represented by eq 3. The results in

$$C_{10}H_{24}N_6O_6Cu(c) + 16O_2(g) = 10CO_2(g) + 9H_2O(l) + Cu(NO_3)_2 \cdot 3H_2O(c) + 2N_2(g) \quad (3)$$

Table III correspond to a standard molar energy of combustion

---

(9) A. I. Vogel "A Textbook of Quantitative Inorganic Analysis", 3rd ed., Longmans, Green and Co., New York, 1961.

(10) G. A. Heath, G. T. Hefter, and W. V. Steele, *J. Chem. Thermodyn.*, **10**, 395 (1978).

(11) R. P. Buck, S. Singadega, and L. B. Rodgers, *Anal. Chem.*, **26**, 1240 (1954).

(12) W. D. Good and D. W. Scott, *Exp. Thermochem. 1956–1962*, **2**, Chapter 4 (1962).

(13) IUPAC Commission on Atomic Weights 1975, *Pure Appl. Chem.*, **47**, 45 (1976).

(14) W. N. Hubbard, D. W. Scott, and G. Waddington, *Exp. Thermochem. 1956–1962*, **1**, Chapter 5 (1956).

(15) E. M. Barrall and J. F. Johnson, *Tech. Methods Polym. Eval.*, **1**, 2 (1970).

(16) *NBS Tech. Note (U.S.)*, No. **270-4** (1969).

Table II. Bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)-copper(II) (M_r = 387.882): Summary of Typical Combustion and Comparison Experiments[a]

	combustn expt	comparison expt
$m(\text{complex})^b$/g	0.293990	
$m(\text{cyclam})^c$/g		0.151833
$m(\text{Cu(NO}_3)_2\cdot 3\text{H}_2\text{O})$/g		0.1868
m(benzoic acid)/g	0.383733	0.381280
m(filter paper)/g	0.007629	0.007651
$\Delta R_{\text{cor}}/\Omega$	1.1370	1.1404
$n^i(\text{H}_2\text{O})$/mol	1.3060	1.3060
$n^i(\text{HNO}_3)$/mol	0.0500	0.0500
$-\Delta R\epsilon$(calor)/kJ	−15.3800	−15.4257[e]
$-\Delta R\epsilon$(cont)/kJ	−0.3165	−0.3206
ΔE(ign)/kJ	0.0015	0.0016
$\Delta E_W{}^d$/kJ	0.0559	0.0555
$-m\Delta e_c{}^\circ$(benzoic acid)/kJ	10.1441	10.0792
$-m\Delta e_c{}^\circ(\text{cyclam})^c$/kJ		5.4857
$-m\Delta e_c{}^\circ$(filter paper)/kJ	0.1314	0.1318
$-m\Delta e_{\text{soln}}{}^\circ(\text{Cu(NO}_3)_2\cdot 3\text{H}_2\text{O})$/kJ		−0.0075
$m\Delta e_e{}^\circ(\text{complex})^b$/kJ	−5.3636	
$\Delta e_c{}^\circ(\text{complex})^b$/kJ	−18.2442	

[a] The symbols and abbreviations are those of ref 10. [b] Complex = bis(nitrato)(1,4,8,11-tetraazacyclotetradecane)-copper(II). [c] Cyclam = 1,4,8,11-tetraazacyclotetradecane. [d] Items 81-85, 87-91, 93, and 94 of the computation form of ref 14; correction to standard states. [e] Value used to determine ϵ(calor) for the corresponding combustion experiment.

Table III. Summary of Experimental Results: Values of of $\Delta e_c{}^\circ$ at 298.15 K

$-\Delta e_c{}^\circ$/kJ g^{-1}	$-\Delta e_c{}^\circ$/kJ g^{-1}	$-\Delta e_c{}^\circ$/kJ g^{-1}
18.2473	18.2346	mean: 18.2412
18.2442	18.2408	std dev: 0.0018
18.2388	18.2416	

of $\Delta e_c{}^\circ = -7075.4 \pm 4.0$ kJ mol^{-1} and a corresponding standard molar enthalpy of combustion $\Delta H_c{}^\circ = -7085.3 \pm 4.0$ kJ mol^{-1}. The uncertainties are twice the standard deviation of the mean and include the uncertainties in the determined energies of all the materials used. The values $\Delta H_f{}^\circ(\text{CO}_2(\text{g})) = -393.51$ kJ mol^{-1},[17] $\Delta H_f{}^\circ(\text{H}_2\text{O(l)}) = -285.830$ kJ mol^{-1},[17] and $\Delta H_f{}^\circ(\text{Cu(NO}_3)_2\cdot 3\text{H}_2\text{O(c)}) = -1217.1$ kJ mol^{-1} [16] were used to derive a standard enthalpy of formation $\Delta H_f{}^\circ(\text{C}_{10}\text{H}_{24}\text{N}_6\text{O}_6\text{Cu(c)}) = -639.4 \pm 4.0$ kJ mol^{-1}.

Considering the thermochemical cycle (Figure 2) ΔH_2 represents the enthalpy of formation of the (1,4,8,11-tetraazacyclotetradecane)copper(II) ion in solution. This value can be calculated by combining ΔH_1 with the standard enthalpies of solution ΔH_3, ΔH_4, and ΔH_5, i.e., $\Delta H_2 = \Delta H_1 + \Delta H_5 - \Delta H_3 - \Delta H_4$. We have previously reported[8] $\Delta H_4 = -10.5 \pm 0.7$ kJ mol^{-1} and $\Delta H_f{}^\circ(\text{L}_1) = -115.9 \pm 2.1$ kJ mol^{-1}. Using a TRONAC calorimeter (Model 450), we have determined $\Delta H_3 = +9.6 \pm 0.8$ kJ mol^{-1} and $\Delta H_5 = +22.0 \pm 0.8$ kJ mol^{-1}. Hence $\Delta H_2 = -141.0 \pm 5.0$ kJ mol^{-1}. This value is in excellent agreement with that obtained by direct calorimetry,[6] $\Delta H_2 = -135.6 \pm 2.5$ kJ mol^{-1}. This study therefore strongly indicates the absence of any serious systematic errors in either the rotating-bomb combustion calorimetric method or the earlier reaction calorimetry. However, the presence of possible systematic errors within the assigned uncertainties cannot be excluded and could arise, for example, in the value used for the enthalpy of solution of CO_2 in the bomb liquid which has been taken as equal to that in pure water.

With reference to the macrocyclic effect, it can now be confirmed, at least for the copper complexes with L_1 and L_2 in aqueous solution, that both entropy and enthalpy terms contribute, almost equally, to the increased stability of the macrocyclic complex. This work has confirmed the value of the macrocyclic enthalpy term[4,6] by using an alternative calorimetric method. This in turn vindicates the earlier direct calorimetric method which was performed in strongly alkaline solutions and does not change our contention that the difference in hydration energies of the two ligands has a major influence on the magnitude of the macrocyclic enthalpy.

Wherever possible, we feel that enthalpy values should be determined calorimetrically, rather than indirectly, by the temperature dependence of stability constants. While the direct calorimetric method[4,6] is much simpler to perform, combustion calorimetry could be used with profit if the ligand proved to be essentially insoluble in water or on those occasions when complicated protonation equilibria in aqueous solution prevent the accurate description of the calorimetric reaction.

Registry No. $\text{CuL}_1(\text{NO}_3)_2$, 73746-94-8.

---

(17) CODATA (key values for thermodynamics): *J. Chem. Thermodyn.*, **3**, 1 (1971); *CODTA Bull.*, **5** (1971).

Contribution from the Department of Chemistry,
Stanford University, Stanford, California 94305

Characterization and Reactions of Osmium(IV) Ammines

JOHN D. BUHR, JAY R. WINKLER, and HENRY TAUBE*

Received May 29, 1979

Cis and trans forms of $\text{Os(NH}_3)_4\text{X}_2{}^{2+}$ and of *mer*-$\text{Os(NH}_3)_3\text{X}_3$ (where X is Cl, Br, or I) were prepared by oxidizing the corresponding Os(III) complexes with Fe^{3+}(aq). Acidic solution aquation and disproportionation are sufficiently slow so that ion-exchange methods are applicable to separations and characterization. The osmium(IV) ammines in comparison to the corresponding Os(III) species show LMCT at lower energies and metal to halide stretching frequencies ca. 40 cm^{-1} higher. At high enough acidity the Os(IV)/Os(III) couples are reversible in cyclic voltammetry. Application of this method yielded E_f values for *trans*-$[\text{Os(NH}_3)_4\text{Cl}_2]$, *cis*-$[\text{Os(NH}_3)_4\text{Cl}_2]$, *mer*-$[\text{Os(NH}_3)_3\text{Cl}_3]$, and OsNH_3Cl_5 of 0.73, 0.83, 0.61, and 0.37 V, respectively. As the pH is raised, the values of E_f become acid dependent. A combination of electrochemical and spectrophotometric measurements yielded pK_a values for the four chloro complexes of 4.0, ~1, 4.9, and 6.5, respectively. The relatively higher acidity of the osmium(IV) ammines compared to that of Pt(IV) analogues is attributed to charge transfer from ligands to the unfilled π orbitals of Os(IV).

Introduction

Ammine complexes of metals in the oxidation state 4+ have received little attention, and of this class only those of Pt(IV) have thus far been described. A property of these species which alone makes them worthy of further attention is the high acidity of the coordinated ammonia. For ammonia complexes of metals in the oxidation state 3+, values of pK_a have been estimated for Ru,[1] Co,[2] Rh,[3] and Os[4] of which only that for

---

(1) D. Waysbort and G. Navon, *Inorg. Chem.*, **18**, 9 (1979).