Table I. Carbon and Oxygen Core Binding Energies for $Fe(CO)_5$

	E_B,[a] eV	FWHM,[a] eV
C 1s		
$Fe(CO)_5$	293.72 (4)	1.17 (4)
CO reference	296.24[b]	1.05 (8)
O 1s		
$Fe(CO)_5$ (treated as 1 peak)	540.02 (5)	1.42 (4)
CO reference	542.57[b]	1.27 (11)
$Fe(CO)_5$ (treated as 2 peaks)[c]	539.71 (4)	1.09 (5)
	540.50 (6)	1.27 (14)
CO reference	542.57[b]	1.10 (7)

[a] The uncertainty in the last digit (estimated as twice the standard deviation determined by the least-squares fit) is indicated parenthetically. [b] For the binding energies of the carbon monoxide reference we use the values of S. R. Smith and T. D. Thomas, *J. Electron Spectrosc. Relat. Phenom.*, 8, 45 (1976). [c] Area ratio constrained to 2:3.

is statistically significant with an acceptable confidence level of >99.999%. The spectral parameters are summarized in Table I.

The conclusion that the C 1s peak cannot be deconvoluted, whereas the O 1s peak can be deconvoluted, is reasonable in view of the simple valence-bond picture of back-bonding, which indicates that back-bonding causes a change in the formal charge of the oxygen atom but no change in the formal charge of the carbon atom. The conclusion is also consistent with the calculations which show essentially identical charges for the equatorial and axial carbon atoms but significantly different charges for the equatorial and axial oxygen atoms.

The fact that the deconvoluted peak of higher intensity in the O 1s $Fe(CO)_5$ spectrum (the peak due to the equatorial CO groups) is of lower binding energy than the deconvoluted peak of lower intensity is in qualitative agreement with the prediction that the equatorial oxygen atoms are more negatively charged than the axial oxygen atoms. The result indicates that the back-bonding to the equatorial CO groups is greater than that to the axial CO groups and is consistent with the well-established rule that, in trigonal-bipyramidal d^8 complexes, strong π-acceptor ligands preferentially coordinate at equatorial positions.[16-18] The magnitude of the binding energy shift between the deconvoluted peaks (0.8 eV) is higher than the predicted values, but the agreement is satisfactory in view of the uncertainties associated with the measured and predicted values.

Experimental Section

The gas phase spectra were obtained using the Uppsala high-resolution spectrometer.[13] Carbon monoxide gas was introduced into the ionization chamber as a reference, and its O 1s and C 1s spectra were recorded simultaneously with those of $Fe(CO)_5$. The raw spectral data were analyzed using the nonlinear least-squares fitting program GAMET.[19] Each data point (counts per channel) was weighted by the reciprocal of its magnitude. A mixed Gaussian–Lorentzian function

$$f(x) = \frac{h}{\alpha\left[1+\left(\frac{x-\mu}{\lambda}\right)^2\right]+(1-\alpha)\left[\exp\left(\frac{x-\mu}{\lambda}\right)^2\right]}$$

was used to represent each core-level line. Combinations of two or three of these lines plus a linear background were used to fit the experimental spectra. The parameters μ, λ, h, and α measure the peak position, line width, peak height, and "mixing ratio", respectively. For the C 1s spectrum the best fit was obtained using $\alpha = 0.97$ (97% Lorentzian character) for all peaks. For the O 1s spectrum the best fit was obtained using $\alpha = 0.60$ for all peaks. We believe that the different mixing ratios required for the oxygen and carbon lines may be attributed to differences in vibrational broadening.[20]

Acknowledgment. This work was supported by the U.S. Energy Research and Development Administration and the National Science Foundation.

Registry No. $Fe(CO)_5$, 13463-40-6.

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(6) We used literature values of the C–O stretching force constants for ten of the compounds for which we have O 1s binding energies. We calculated the following force constants (in mdyn/Å) from literature values of the vibrational frequencies: $C_6H_6Cr(CO)_3$, 15.17; $C_7H_7V(CO)_3$, 15.13; $C_7H_8Fe(CO)_3$, 16.23; $C_4H_6Fe(CO)_3$, 16.25; $C_5H_5V(CO)_4$, 15.56; $Cl_3SiMn(CO)_5$, 16.75 (ax), 17.07 (eq). Literature values were taken from the references given in ref 5. The multiplicity-weighted average C–O stretching frequencies and weighted average stretching force constants are very closely proportional, with a correlation coefficient of 0.998; $\langle \nu_{CO} \rangle = 62.8\langle k_{CO} \rangle + 986$, where ν_{CO} is given in cm^{-1} and k_{CO} is given in mdyn/Å.
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(19) The computer program GAMET was written by C. E. R. Lederer at the Lawrence Berkeley Laboratory, Berkeley, Calif.
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Solubility of the Dithionates of Binuclear Ions

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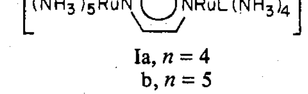
The binuclear ions Ia–c were first described by Creutz and



Ia, $n = 4$
b, $n = 5$
c, $n = 6$

Taube.[2] These workers prepared the ions Ia–c, where ammonia L was one of several ligands, e.g., water, chloride, pyrazine, etc. Only the symmetric ions, where L was ammonia, have been isolated as solid salts. Those compounds were isolated as tosylates or perchlorates from quite concentrated mother liquors. The general method of synthesis for ions of the kind Ia is the reaction between the pyrazinepentaammineruthenium(II) ion and an appropriately substituted aquatetraammineruthenium(II) ion. This latter ion is generated by reduction of the corresponding ruthenium(III) species by zinc amalgam or solutions of vanadium(II) salts. Thus the crude reaction mixtures contain not only the desired binuclear ion but also unreacted mononuclear species Zn^{2+} or V^{3+} and buffering ions for control of acidity.

Due to an interest in obtaining pure salts of ions Ia–c where L = water or chloride (for ESCA studies), a search for a reasonably convenient method to isolate those ions from a solution was undertaken. It was desired to avoid having to use column chromatography for several reasons: (a) the products and reagents are sensitive to oxygen and nitrogen, (b) large amounts of eluate must be evaporated during the isolation, and (c) ligand exchange and hydrolysis can occur by long exposure to aqueous solution.

Experimental Section

In a preliminary test, a nearly saturated solution of the tosylate Ia (L = NH_3) was added to test tubes containing saturated solutions of sodium fluoborate, perchlorate, iodide, chloride, sulfate, and dithionate. The test tubes were sealed, scratched, and examined for precipitate. Only sodium dithionate produced a precipitate. This was a dark red amorphous solid which, when separated by centrifugation, left the solution essentially colorless. It was also noted that this precipitate did not form upon addition of sodium dithionate if the solution already had a high concentration of other salts. The red precipitate was insoluble in pure water, but quite soluble in strong solutions of noncomplexing salts. The electronic spectrum of the resulting solution was identical with that of Ia (L = ammonia), thus disproving the initial suspicion that the dithionate had somehow caused decomposition of the binuclear ion.

This property not only was viewed as a potential tool for the isolation of the desired compounds but also was interesting in its own right. It was therefore decided to investigate the phenomenon further.

Many of the complexes described in the text were synthesized from published literature.[3-12] Others were synthesized by chemical and electrochemical methods and these will be published later. All starting chemicals were of reagent quality. The purity of the synthesized complexes was checked with spectral measurements and routine chemical analysis.

The spectra were run on a Beckman Acta IV spectrophotometer which covers, near-infrared, visible, and ultraviolet regions. The infrared spectra were recorded on a Perkin-Elmer 337 spectrometer, using pressed KBr pellets. For temperature control, a Lauda K-2R thermostat was used.

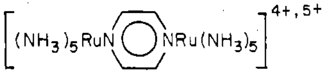
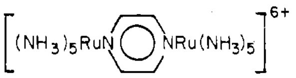
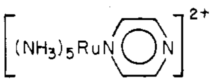
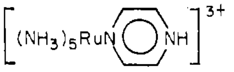
Results and Discussion

The solubilities of the dithionates were conducted by dissolving approximately 10 mg of the compound in question in a minimum amount of water and adding 1 mL of a saturated solution of sodium dithionate to the test tube. The test tubes were cooled for a few hours and checked for precipitate. We obtained the electronic spectra of supernatants of solutions which produced precipitates. In all cases but one, $RuPzH^{3+}$, the precipitation was found to be essentially quantitative. All the precipitates formed were found to be readily soluble in solutions of high ionic strength. The results are summarized in Table I along with the abbreviations used in the text. The ions which form insoluble dithionates have two things in common: (a) all are binuclear, (b) all have a charge of at least 4+.

The coordination sphere of the metal centers in the monomers and dimers contains essentially identical ligands, and, therefore, there is no a priori reason to expect great differences in their polarizabilities, "hard–soft" properties, or effective dimensions. The forces between adjacent dithionate ions and metal centers should, therefore, be similar for the monomeric and the dimeric species.

Each binuclear ion interacts with eight dithionate ions, which in turn interact with eight different binuclear ions. The relative insolubility of these compounds seems to be due to the fact that they are composed of linear cations with multiple charges on each end, cross-linked by doubly charged linear anions.

Table I. Results of the Mixing of Sodium Dithonate Solution with Strong Solutions of Several Compounds

Compd	Abbreviation	Results
	$diRuPz^{4+,5+}$	Red ppt, formed instantly, quant
		Light orange ppt, formed instantly, quant
		No ppt
	$RuPzH^{3+}$	Red-brown ppt, moderately soluble
$[(NH_3)_5Ru(H_2O)]^{2+,3+}$		No ppt
$[(NH_3)_5RuN_2]^{2+}$		No ppt
$[(NH_3)_5RuN_2Ru(NH_3)_5]^{4+}$		Light yellow needles, quant
$[(NH_3)_5RuN_2Ru(NH_3)_5]^{5+}$		Light green ppt, quant
$[(NH_3)_5RuN_2Os(NH_3)_5]^{4+}$		Yellow needles, quant
$[(NH_3)_5RuN_2Os(NH_3)_5]^{5+}$		Light blue ppt, quant
$[(NH_3)_4(H_2O)RuN_2Os(NH_3)_5]^{5+}$		Light blue ppt, quant
$[(NH_3)_5OsN_2]^{2+}$		No ppt
$[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$	Ru-red	No ppt
$[(NH_3)_3RuCl_3Ru(NH_3)_3]^{2+}$	Ru-blue (?)	No ppt
$[(NH_3)_5RuOV(H_2O)_4SO_4]^{2+}$	$RuOV^{2+}$	No ppt

This tentative hypothesis is supported by the fact that the two binuclear compounds in Table I which do not form precipitates have only two positive charges, i.e., Ru-blue and $RuOV^{2+}$. Furthermore, the pentaamminepyrazineruthenium ion forms a moderately insoluble dithionate only when it is in the protonated form, with a total of three positive charges. In the unprotonated form, no precipiate was observed.

To obtain a more quantitative idea of the behavior of binuclear dithionates, the solubility of the dithionate salt of $diRuPz^{5+}$ was determined as a function of the concentration of several noncomplexing salts. The choice of the mixed valence ion $diRuPz^{5+}$ was due to the air sensitivity of the $diRuPz^{4+}$ ion, which would otherwise have been used.

Composition of $diRuPz^{5+}$ Dithionate. A 15-mg sample of $diRuPz^{5+}$ tosylate was dissolved in 15 mL of water. Aliquots of a 0.030 M solution of sodium dithionate were added. After each addition the solution was agitated for 3 min and centrifuged, and the amount of binuclear ion remaining in the supernatant was determined spectrophotometrically. The results are shown in Figure 1. Point A represents the saturation point, at which the solid starts forming. At point B, the concentration of the binuclear ion becomes quite low, and the precipitation is no longer stoichiometric. The slope of the line between points C and D should reflect the stoichiometry of the precipitate. A linear regression of those points was formed, yielding a slope of 0.401 and a correlation coefficient of 0.993. The ratio of $diRuPz^{5+}$ to dithionate is therefore 1:2.49 or 2:4.98.

The precipitate obtained in this experiment was washed with water and alcohol and dried. A weighed sample was dissolved in a few milliliters of concentrated solution of magnesium chloride, then diluted in a volumetric flask. The absorptivity

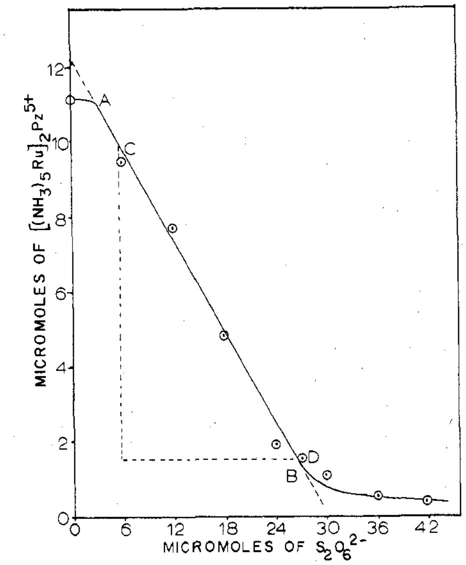


Figure 1. Precipitation of μ-pyrazine-decaamminediruthenium(5+) with sodium dithionate. The ratio of the complexion to dithionate is found to be 2:5.

of the solution was consistent with the $diRuPz^{5+}$ to dithionate ratio of 2:5.

This experiment disproved the suspicion that the precipitate might contain other anions or cations in its lattice.

Solubility of $diRuPz^{5+}$ Dithionate as Function of Ionic Strength. The solubility of sparingly soluble salts as a function of ionic strength is described by the Debye–Hückel limiting law

$$\log \gamma_{\pm} = -0.5091|Z_+Z_-|I^{1/2}$$

where $\gamma_{\pm}$ is the mean activity coefficient, Z_+ and Z_- are the charges of the cations and anions, respectively, and I is the ionic strength.

The mean activity coefficient is defined as $\gamma_{\pm} = (\gamma_+^{\nu_+}\gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)}$ where γ_+ and γ_- are the individual activity coefficients for the cations and anions, respectively, and ν_+ and ν_- are their respective numbers.

The concentration of $diRuPz^{5+}$ in the solution was determined spectrophotometrically, and the mean activity coefficient was easily determined.

First, the solubility of the material was measured in distilled water and found to be $<10^{-6}$ M. At this concentration, it is reasonable to assume that the mean activity coefficient equals 1.[13] The solubility was then measured in solutions of increasing ionic strength, and the activity coefficient was derived.

The salt dissolves as follows:

$$(diRuPz^{5+})_2(dith^{2-})_5 \rightleftharpoons 2(diRuPz^{5+}) + 5(dith^{2-}) \quad (1)$$

and

$$[dith^{2-}] = {}^5/_2[diRuPz^{5+}] \quad (2)$$

The solubility constant is defined as

$$\bar{K}_{sp} = \gamma_+^2[diRuPz^{5+}]^2\gamma_-^5[dith^{2-}]^5 \quad (3)$$

When the ionic strength is around 10^{-5} the solubility constant can be represented as

$$K_{sp} = [diRuPz^{5+}]_0^2[dith^{2-}]_0^5 \quad (4)$$

since the activity coefficients approach 1.

Substituting eq 2 into eq 3 and 4, one obtains

$$K_{sp} = \gamma_+^2\gamma_-^5[diRuPz^{5+}]^7(5/2)^5 = [diRuPz^{5+}]^7(5/2)^5$$

Hence

$$\gamma_{\pm}^7 = \gamma_+^2\gamma_-^5 = [diRuPz^{5+}]^7/[diRuPz^{5+}]_0^7$$

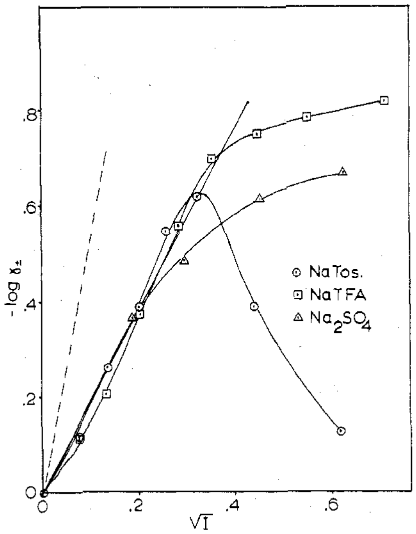


Figure 2. Activity of the μ-pyrazine-decaamminediruthenium(5+) dithionate as a function of the ionic strength. The dashed line is predicted by the Debye–Hückel limiting law. The complex probably forms ion pairs.

Thus the measurement of the mean activity coefficient as a function of the ionic strength amounted to nothing more than measuring the absorbance of solutions with increasing ionic strengths saturated with the binuclear dithionate.

A 10-mg sample of $diRuPz^{5+}$ tosylate was dissolved in 10 mL of water. A 2-mg portion of silver trifluoroacetate was added to oxidize all traces of the $diRuPz^{4+}$ present. A saturated solution of sodium dithionate was added slowly, dropwise. The solution was stirred for 1 min between each addition to promote crystal growth. When no more precipitate formed, the suspension was centrifuged and the supernatant discarded. The solid was washed with water at least five times. The solid was again suspended in 10 mL of water, agitated for 15 min, and centrifuged. The absorbance of the supernatant was measured and used to calculate $[diRuPz^{5+}]$.

The ionic strength of the supernatant was increased by adding a weighed amount of sodium trifluoroacetate. The mixture was again agitated for 15 min at 24 °C and centrifuged and the absorbance of the supernatant measured. This operation was repeated until the desired range of ionic strengths had been covered.

This experiment was repeated using sodium tosylate and sodium sulfate. The results are shown in Figure 2.

The reason for the decreasing portion in curve (1) is that when the concentration of sodium tosylate reaches 0.1 M, the binuclear ion starts precipitating as a tosylate salt.

It is evident that at ionic strengths below 0.15, the relation between $-\log \gamma_{\pm}$ and the square root of I is fairly linear. The solid line is the least-squares fit to those points for which $I \leq 0.15$. The slope of this line is 1.94. The valence factor $|Z_+Z_-|$ for $diRuPz^{5+}$ dithionate is 10, so the slope predicted by the Debye–Hückel limiting law is 5.09, as shown by the dotted line in Figure 2. The relative consistency of the slope for the three different electrolytes suggests that the compound does not dissolve as eq 1 indicates. Rather, the compound probably dissociates into ion pairs or clusters which have a valence factor of approximately 4 (i.e., 1.94:0.509). These hypothetical ions could be of the kind $(2diRuPz^{5+}\cdot 4dith^{2-})^{2+}\cdot dith^{2-}$ (i.e., $Z_+Z_- = 4$) or there could be ion pairs and clusters with an average valence factor of 4.

The Debye–Hückel limiting law has been found to be fairly accurate for spherical ions of low charge (±1 or ±2) and dilute solutions. Extrapolations to highly charged linear ions must therefore be considered rather speculative. However, the slope of 1.94 is interesting.

Before a more general conclusion about the solubility of binuclear dithionates can be formulated, a series of compounds would have to be studied in the same ways as was done here. Additional evidence for the degree of ion pairing in solution could be obtained by conductance studies.

Irrespective of the theoretical implications of the solubility behavior of binuclear dithionates, this behavior has been found most useful for the isolation and purification of several binuclear ions. This is exemplified in our isolation of the novel compound μ-dinitrogen-decaamminediruthenium(II,III) dithionate.

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Registry No. $(diRuPz^{4+})(dith^{2-})_2$, 64814-01-3; $(diRuPz^{5+})_2(dith^{2-})_5$, 64825-51-0; $(diRuPz^{6+})(dith^{2-})_3$, 64814-02-4; $(RuPzH^{3+})_2(dith^{2-})_3$, 64814-04-6; $([(NH_3)_5RuN_2Ru(NH_3)_5]^{4+})(dith^{2-})_2$, 64814-06-8; $([(NH_3)_5RuN_2Ru(NH_3)_5]^{5+})_2(dith^{2-})_5$, 64871-83-6; $([(NH_3)_5RuN_2Os(NH_3)_5]^{4+})(dith^{2-})_2$, 64814-09-1; $([(NH_3)_5RuN_2Os(NH_3)_5]^{5+})_2(dith^{2-})_5$, 64871-84-7; $([(NH_3)_4(H_2O)RuN_2Os(NH_3)_5]^{5+})_2(dith^{2-})_5$, 64871-85-8.

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(13) If one assumes complete dissociation for the 5:2 electrolyte the $\gamma_{\pm}$ will be 0.95, at 10^{-6} M in distilled water. This will introduce a correction factor of 0.71 for the K_{sp} in eq 4.

Contribution from the Istituto Chimica Generale ed Inorganica,
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Thermochemical Consequences of π Delocalization in Metal-Biguanide Complexes

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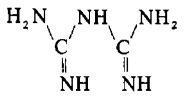

I

Biguanide, I (abbreviated bgu), is a compound which exhibits some peculiar properties: (1) it has a large proton affinity in aqueous solution, its basic strength[1] being only slightly lower than the hydroxyl ion (pK = 13.25); (2) it forms stable metal complexes ~~acting~~ as a bidentate ligand, and it has a strong preference toward square coordination (e.g., $Ni(bgu)_2^{2+}$ and $Cu(bgu)_2^{2+}$ have a square geometry and are more stable by about two orders of magnitude than the corresponding complexes with the reference ligand ethylenediamine);[2] and (3) it stabilizes unusually high oxidation states of metals (e.g., Ag(III)[3] and Ni(III)[4]). Thermodynamic aspects of the interaction of biguanide with aqueous protons have been recently investigated,[5] and it has been shown that the extreme basicity is a result of an exceptional enthalpy of protonation (the most exothermic protonation reaction reported to date).

Table I.[a] Experimental Details of Microcalorimetric Measurements at 25 °C in 0.1 M KCl

	V_H, μmol s^{-1}	V_M, μmol s^{-1}	V_L, μmol s^{-1}	R, μL s^{-1}	Φ, μcal s^{-1}
			bgu + Cu^{II}		
i	0.02502	0.	0.05086	10.512	
ii	0.02523	0.02154	0.05086	10.512	214.7
i	0.01667	0.	0.03388	8.780	
ii	0.01687	0.02154	0.03388	8.780	143.1
i	0.08004	0.	0.16266	21.870	
ii	0.08024	0.02154	0.16266	21.870	423.7
i	0.02907	0.	0.08892	12.131	
ii	0.02927	0.02154	0.08892	12.131	429.4
i	0.02206	0.	0.06748	10.502	
ii	0.02226	0.02154	0.06748	10.502	408.7
i	0.01472	0.	0.04504	8.790	
ii	0.01492	0.02154	0.04504	8.790	267.6
i	0.01299	0.	0.05975	8.390	
ii	0.01319	0.02154	0.05975	8.390	237.1
i	0.07070	0.	0.21625	21.805	
ii	0.07090	0.02154	0.21625	21.805	444.3
			bgu + Ni^{II}		
i	0.02180	0.	0.66680	11.370	
ii	0.02183	0.00307	0.66680	11.370	44.6
i	0.02180	0.	0.66680	11.840	
ii	0.02183	0.00330	0.66680	11.840	48.3
i	0.02180	0.	0.66680	21.460	
ii	0.02187	0.00798	0.66680	21.460	82.6
i	0.02180	0.	0.66680	23.740	
ii	0.02188	0.00909	0.66680	23.740	90.7

[a] i, Before the reaction; ii, after the reaction. V_H, V_M, and V_L are the flow rates of acid, metal, and ligand. R = total flow rate. Φ = heat flow corrected for dilution. In order to interpret the data in the table see ref 6.

We report the thermodynamic functions $\Delta H°$ and $\Delta S°$ for the reactions of biguanide with nickel(II) and copper(II) ions in 0.1 M KCl at 25 °C.

Experimental Section

Commercial biguanide (Aldrich Europe) was recrystallised from hot DMF, and C, H, and N analyses were satisfactory. Copper(II) and nickel(II) chloride (Erba RP Milano) solutions were analyzed by standard gravimetric techniques.

Enthalpy changes have been determined by a flow-microcalorimetric technique using the flow apparatus LKB-10700-1 and following a described procedure;[6] in this case, peristaltic pumps were replaced by Mettler DV-10 high-precision burets, and the flow rate of each buret was predetermined by means of a resistance box. Complex formation occurred in the microcalorimetric cell by mixing a solution of MCl_2 (M = Cu^{II} or Ni^{II}), slightly acidified in order to prevent hydrolysis, and a solution of biguanide buffered at ca.. 50% with HCl. The effective concentrations of reactant species have been calculated from the reported equilibrium constants by a described procedure.[6] Measured heats were corrected for the enthalpy of deprotonation of $(bgu)H^+$.[5] The design of the experiments and the computer programs have been reported.[6] Experimental details are presented in Table I.

Results and Discussion

The experimental enthalpy changes, $\Delta H°$, and entropy changes, $\Delta S°$, calculated from the appropiate combination of $\Delta H°$ and published $\Delta G°$ values,[1] are reported in Table II. For copper(II), data for the stepwise addition of bgu are presented, but in the case of nickel(II), because the addition of the second molecule of bgu is so favored with respect to the addition of the first one (also in the 1:1 metal to ligand ratio, the formation of $Ni(bgu)_2^{2+}$ strongly predominates with respect to $Ni(bgu)^{2+}$), only the overall reaction of formation of the 1:2 complex has been reported. The considered reactions are

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