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.

References and Notes

(1) Author to whom correspondence should be addressed.

(2) C. Creutz and H. Taube, *J. Am. Chem. Soc.*, **95**, 1086 (1973).
(3) C. Creutz, Ph.D., Dissertation, Stanford University, 1970.
(4) B. Folkesson, *Acta Chem. Scand.*, **26**, 4008 (1972).
(5) E. E. Mercer and L. W. Grey, *J. Am. Chem. Soc.*, **94**, 6426 (1972).
(6) F. Bottomley and S. B. Tong, *Can. J. Chem.*, **49**, 3739 (1971).
(7) H. de Smedt, A. Parsoons, and L. deMaeyer, *Inorg. Chem.*, **13**, 90 (1974).
(8) A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967).
(9) C. M. Elson, J. Gulens, and J. A. Page, *Can. J. Chem.*, **49**, 207 (1971).
(10) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965).
(11) D. F. Harrison and H. Taube, *J. Am. Chem. Soc.*, **89**, 5706 (1967).
(12) R. H. Magnuson, Ph.D., Dissertation, Stanford University, 1974.

(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.

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Thermochemical Consequences of π Delocalization in Metal–Biguanide Complexes

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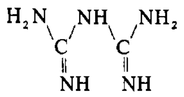
Biguanide, I (abbreviated bgu), is a compound which exhibits some peculiar properties: (1) it has a large proton affinity in aqueous solution, its basic strength[1] being only slightly lower than the hydroxyl ion (pK = 13.25); (2) it forms stable metal complexes acting as a bidentate ligand, and it has 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).



I

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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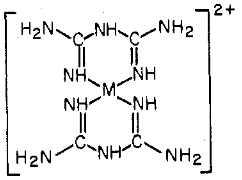
strongly exothermic, and the largely negative enthalpy change more than compensates for the remarkably unfavorable entropy contribution.

If one considers aqueous interactions of nitrogen ligands with copper(II) ions, reactions of bgu in both the first and second step are the most exothermic we have encountered (heat evolved per nitrogen atom coordinated).[7] Corresponding ΔH° values for the analogous ethylenediamine complexes are remarkably lower: $Cu(en)^{2+}$, 12.6 kcal mol^{-1}; $Cu(en) + en \rightarrow Cu(en)_2^{2+}$, 12.6 kcal mol^{-1}.[8] The formation of $Cu(bgu)_2^{2+}$ is also more exothermic than the reaction of copper(II) with the strongly coordinated macrocyclic ligand cyclam.[9] Analogously, formation of $Ni(bgu)_2^{2+}$ involves a remarkably more negative enthalpy change than the reference amine complex $Ni(en)_2^{2+}$.[10]

The aqueous complexes presumably have a tetragonal or square geometry, as suggested by x-ray studies of $Ni(bgu)_2Cl_2$[11] and of the copper complexes with the related molecule ethylenebis(biguanide).[12]

It is remarkable that the energy of the σ in-plane interaction for copper(II) bgu complexes is comparable with that for analogous ethylenediamine complexes. The energy of the d–d absorption band for $Cu(bgu)_2^{2+}$ and $Cu(en)_2^{2+}$, which furnishes a measure of the copper–nitrogen in-plane interaction,[13] is nearly the same (1.87 and 1.83 μm^{-1}, respectively). Therefore, other effects than simple metal–donor σ bonding must contribute to the large exothermicity. On the basis of x-ray analysis,[11] structure II has been presumed for the 1:2 complexes. Furthermore, all the C–N distances in the coordinated biguanide molecule are intermediate between those expected for a single and a double bond, showing that coordination involves some delocalization of π electrons over the entire molecular framework. The existence of a pπ (ligand)–dπ (metal) bond has been demonstrated by ^{1}H NMR data.[11] Therefore, the ligand stabilization, due to the π delocalization, and formation of metal–nitrogen π bonds are both responsible for the high exothermicity of the complex formation. The larger heat effect of $Cu(bgu)_2^{2+}$ in comparison with Ni(II) reflects a quite general behavior: the $\Delta H^\circ (CuL_2)/\Delta H^\circ (NiL_2)$ ratio for bgu (1.53) is in agreement with those found for corresponding polyamines (en, 1.40;[8,10] triethylenetetramine, 1.54;[14] and trimethylenediamine, 1.50[15]). A further interesting point is that the second step of chelation of bgu to the copper(II) ion is more exothermic than the first one. This behavior in not unusual in coordination of bidentate ligands to aqueous 3d metals; e.g., in the case of the Ni–ethylenediamine system, $\Delta H_2^\circ = -9.4$ and $\Delta H_1^\circ = -8.9$. This has been ascribed[16] to the fact that coordination of the first ligand molecule causes a large dehydration of the metal ion, which is an endothermic process, while the addition of the second ligand liberates less water molecules, and the overall exothermicity is reduced. Undoubtedly, this "solvation effect" can operate in the Cu–bgu system. Furthermore, addition of a second bgu molecule makes the π-resonating system more extended, causing a larger π delocalization over the molecular framework, and this would favor the second step from the point of view of the enthalpy.



II

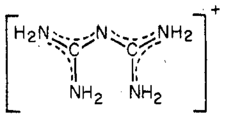
Table II. Thermodynamic Quantities for the Reaction between Biguanide and Copper(II) and Nickel(II) Ions in 0.1 M KCl at 25 °C

Reaction	$-\Delta G^\circ$,[a] kcal mol^{-1}	$-\Delta H^\circ$,[b] kcal mol^{-1}	$-\Delta S^\circ$,[b] cal deg^{-1} mol^{-1}
$Cu^{2+} + bgu \rightleftarrows Cu(bgu)^{2+}$	15.94	17.0 (2)	3.5 (8)
$Cu(bgu)^{2+} + bgu \rightleftarrows Cu(bgu)_2^{2+}$	12.31	20.0 (3)	26 (1)
$Cu^{2+} + 2bgu \rightleftarrows Cu(bgu)_2^{2+}$	28.25	37.0 (2)	29.3 (6)
$Ni^{2+} + 2bgu \rightleftarrows Ni(bgu)_2^{2+}$	18.08	24.2 (4)	20 (1)

[a] Log K values taken from literature at 20 °C were corrected at 25 °C using the ΔH° values with an iterative procedure. [b] The values in parentheses are the standard deviations on the last digit.

It must be emphasized that the strong enthalpy contribution to the solution stability of metal bgu complexes is counteracted by the very unfavorable entropy contribution. The free ligand (I), containing sp^3 nitrogen atoms, is puckered and is thus able to arrange itself in several configurations, rotating around its σ C–N bonds. On the other hand, coordination to a metal ion and consequent π delocalization involve planarization and a complete stiffening of the molecule. It is probably the consequent loss of configurational entropy, which is not compensated by the increase in translational entropy associated with the release of solvational water molecules, that causes an unfavorable entropy contribution. The reaction of nickel(II) is characterized by a less negative ΔS° than the corresponding copper(II) reaction. Aqueous $Cu(bgu)_2^{2+}$ is expected to have a distorted octahedral stereochemistry with two water molecules in the apical position, whereas these water molecules will not be present in the yellow diamagnetic $Ni(bgu)_2^{2+}$ complex, causing an additional favorable contribution to the translational entropy and making the overall ΔS° change less negative.

Coordination of bgu to metal ions involves thermochemical consequences analogous to those observed for protonation.[5] These reactions are both exceptionally exothermic, the most exothermic in their own class, and characterized by negative entropy changes. This substantially reflects that π stabilization of the bgu molecule is induced by binding to the ion. This is particularly evident in protonation of bgu, where the highly symmetric monoprotonated $(bgu)H^+$ ion allows a total delocalization of π electrons (see III).



III

In complex formation, additional contributions due to metal–nitrogen π interaction are also present.

Registry No. $Cu(bgu)_2^{2+}$, 60475-78-7; $Ni(bgu)_2^{2+}$, 64714-54-1.

References and Notes

(1) G. Schwarzenbach and G. Anderegg, *Pharm. Acta Helv.*, **38**, 547 (1963).
(2) *Chem.. Soc., Spec. Publ.*, **No. 25** (1971).
(3) D. Sen, *J. Chem. Soc. A*, 1034 (1969).
(4) D. Sen and C. Saha, *J. Chem. Soc., Dalton Trans.*, 776 (1976).
(5) L. Fabbrizzi, M. Micheloni, P. Paoletti, and G. Schwarzenbach, *J. Am. Chem. Soc.*, **99**, 5574 (1977).
(6) C. Bianchini, L. Fabbrizzi, and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, 1036 (1975).
(7) J. J. Christensen and R. M. Izatt, "Handbook of Metal Ligand Heats", Marcel Dekker, New York N.Y., 1970.
(8) R. Barbucci, L. Fabbrizzi, P. Paoletti, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, 740 (1972).
(9) A. Anichini, L. Fabbrizzi, P. Paoletti, and R.M. Clay, *J. Chem. Soc., Chem. Commun.*, 244 (1977).
(10) M. Ciampolini, P. Paoletti, and L. Sacconi, *J. Chem. Soc.*, 4553 (1960).
(11) T.C. Creitz, R. G. Sell, and D.L. Wampler, *Chem. Comm.*, 1371 (1969).
(12) M. Matthew and N.R. Kunchur, *Acta Crystallogr., Sect. B*, **26**, 2054 (1970).
(13) A. B. P. Lever and E. Mantovani, *Inorg. Chem.*, **10**, 817 (1971).
(14) L. Sacconi, P. Paoletti, and M. Ciampolini, *J.. Chem. Soc.*, 5115 (1961).