Aqueous Solution Studies of O-Tolyl Biguanide Complexes of Cobalt(II), Copper(II), and Nickel(II).

JOSEPH R. SIEFKER and LESLIE J. JARDINE, Indiana State University

Abstract

The o-tolyl biguanide complexes of bipositive cobalt, copper, and nickel were found to be only slightly soluble in aqueous solutions. The maximum solubilties at 25 degrees centrigrade appeared to be approximately 0.005 molar. The nickel and copper complexes were quite stable in solution. The cobalt (II) complex decomposed gradually, perhaps by oxidation to a cobalt (III) complex.

The extent of formation of complexes in solution was studied by a spectrophotometric method. A method of successive approximations was applied to the absorption data to calculate the dissociation constant and the molar absorptivity of each complex. The final calculated values for $Cu(C_6H_{14}N_5)_2^{++}$ were $K = 1.12 \times 10^{-7}$ and $\epsilon = 373$ at 350 $m\mu$. Those for $Ni(C_6H_{14}N_5)_2^{++}$ were $K = 2.67 \times 10^{-7}$ and $\epsilon = 77.7$ at 450μ.

In a previous report, certain o-tolyl biguanide complexes were studied in 1-methyl-2-pyrrolidinone as the solvent (6). Metal salts, o-tolyl biguanide, and complexes of the ligand with various cations are quite soluble in this solvent. For this reason, solution studies were first made in 1-methyl-2-pyrrolidinone.

Careful solubility studies showed that o-tolyl biguanide and its complexes have maximum solubilities in water in the range of 0.005 to 0.01 M. Spectrophotometric tests of various solutions indicated that enough absorption of light occured in these relatively dilute aqueous solutions to permit studies of the complexes. The present study was thus made to allow comparison of the parameters of molar absorptivities and dissociation constants, in aqueous and nonaqueous solvents.

Although the biguanides contain five nitrogen atoms, only two of these are involved in chelate formation, as has been shown by various investigators, including Ray and Saha (4). Curd and Rose (1) suggested a slightly different structure for the complex, but again found bidentate ligand behavior. The data presented by Siefker and Wence (6) and the present data further verify that the ligand does coordinate in a bidentate fashion. An excellent review of many references concerned with biguanide coordination chemistry appearing prior to 1961 has been published by Ray (3). Although complexes of biguanides and guanylureas in general have been studied in quite some detail, the complexes of o-tolyl biguanide specifically have received relatively little attention.

Experimental

Solutions were prepared following the method of continuous variations of Job (2). In this method, the total concentration of metal ion plus ligand is kept constant. Several solutions are prepared with the extreme at one end containing only metal ion with no ligand, and that at the other end containing only ligand with no metal ion. For the present studies, nine or ten solutions containing intermediate amounts of metal ion and ligand were prepared.

The o-tolyl biguanide was obtained from Monsanto Chemical Company. All inorganic salts were reagents of the highest analytical grade that could be purchased. The ligand was used in the form, o-tolyl biguanide • ½ H_2O, and was not dried. Because of a possibility of decomposition, the anhydride was not used. Some of the inorganic salts were dried and weighed in the anhydrous form. Others decomposed readily at elevated temperatures and were weighed as hydrated salts to avoid this problem.

A Perkin-Elmer Model 202 recording UV-visible spectrophotometer was used to scan spectra of solutions containing only inorganic salts, solutions containing only o-tolyl biguanide, and solutions containing complexes of metal ions and o-tolyl biguanide. For precise absorbance determinations at selected wavelengths, a Beckman Model DU quartz spectrophotometer equipped with 1-cm. cuvettes was used. All data were collected at approximately 25°C.

Most of the solutions studied were quite stable. Some of the solutions did show a change in absorbance with time. The solutions containing Co(II) and o-tolyl biguanide gave absorbance readings which drifted enough that meaningful results could not be obtained.

Data for the $Cu(NO_3)_2$ and o-tolyl biguanide system are given in Table 1. At 350 mμ the Cu(II) and ligand solutions showed very little absorption while the complex showed high absorption, thus the wavelength of 350 mμ was chosen for the study of this system.

TABLE 1

Conc. Cu(II) ($\times 10^3$ M)	Conc. o-tolyl big. ($\times 10^3$M)	Absorbance at 350 mμ
0.00	5.00	0.037
0.50	4.50	0.172
1.00	4.00	0.367
1.50	3.50	0.490
2.00	3.00	0.565
2.50	2.50	0.500
3.00	2.00	0.361
3.50	1.50	0.244
4.00	1.00	0.168
4.50	0.50	0.0854
5.00	0.00	0.000

For $Ni(NO_3)_2$ and o-tolyl biguanide, the unmixed solutions showed little absorption at 450 mμ while mixed solutions containing the complex showed maxima at this wavelength. The choice of this wavelength for the study of the second system is thus obvious. The data are shown in Table 2.

A wavelength of 390 mμ was used for the third system. $Co(NO_3)_2$ and o-tolyl biguanide absorbed slightly at this wavelength while the

TABLE 2

Conc. Ni(II) (X 10^3 M)	Conc. o-tolyl big. (X 10^3M)	Absorbance at 450 mμ
0.00	5.00	0.0015
0.50	4.50	0.057
1.00	4.00	0.080
1.50	3.50	0.098
1.67	3.33	0.102
2.00	3.00	0.082
2.50	2.50	0.069
3.00	2.00	0.060
3.50	1.50	0.039
4.00	1.00	0.021
4.50	0.50	0.018
5.00	0.00	0.002

complex absorbed light to a considerable extent. Data are shown in Table 3, but these data cannot be considered to be highly accurate values because the solutions were unstable and the readings drifted with time.

TABLE 3

Conc. Co(II) (X 10^3 M)	Conc. o-tolyl big. (X 10^3M)	Absorbance at 390 mμ
0.00	5.00	0.005
0.50	4.50	0.640
1.00	4.00	0.719
1.50	3.50	0.753
1.67	3.33	0.765
2.00	3.00	0.490
2.50	2.50	0.385
3.00	2.00	0.307
3.50	1.50	0.155
4.00	1.00	0.104
4.50	0.50	0.029
5.00	0.00	0.001

A possible explanation for the instability of the Co(II) complexes might be described in terms of the crystal field theory. The Co might favor a more stable d^6 (Co^{+3}) low spin state to a less stable d^7 (Co^{+2}) high spin state due to the larger crystal field produced by the ligand than by the water itself. The excess electrons of the ligand which contains five nitrogens as compared to the water which contains one oxygen would cause this greater splitting, and a larger crystal field splitting due to the o-tolyl biguanide would be expected.

Calculations and Results

All solutions of the complexes were colored. This can be attributed to the ligand field splitting of the d orbitals of the transition metal ions involved in the complexes, and the following absorption of light energy of a certain wavelength which was used to temporarily excite these electrons to a higher split energy level. Thus, the color observed was due to the absorbance of the energy of the wavelength or wavelengths of light characteristic of the complex and the transmission of other wavelengths.

As was shown by Job (2) and Vosburgh and Cooper (7), the absorption of light is at a maximum when the metal ion and the ligand concentrations are at the ratio of the formula of the most stable complex. As can be seen in Tables 1, 2, and 3, the ratio of metal ion to ligand was 1 to 2 at the maximum absorbance in the present studies, indicating a formula of M(o-tolyl biguanide)$_2^{++}$, where M represents Cu(II), Ni(II), and Co(II), respectively.

Calculations were made to find the molar absorptivities of the hydrated metal ion, the o-tolyl biguanide, and the most stable complex ion, as well as the dissociation constant of the latter.

Let ϵ_M equal molar absorptivity of the metal ion, ϵ_X equal molar absorptivity of the o-tolyl biguanide, and ϵ_C equal molar absorptivity of the most stable complex ion. Then the total absorbance, A, for any solution containing metal ion and ligand is given by

$$A = \epsilon_M [M] + \epsilon_X [X] + \epsilon_C [MX_n] \tag{1}$$

assuming that the concentrations of intermediate complexes are negligible. In the present cases, solutions containing the metal ions absorbed light to the least extent and ϵ_M was taken as zero so that only two terms of equation (*1*) were considered. Using the symbol C_X to represent the total analytical concentration of ligand, equation (*1*) can then be written as

$$A = \epsilon_X (C_X - n [MX_n]) + \epsilon_C [MX_n] \tag{2}$$

With C_n defined as the total analytical concentration of metal ion in the solution, the overall dissociation constant expression can be written as

$$K = \frac{(C_M - [MX_n])\,(C_X - n [MX_n])^n}{[MX_n]} \tag{3}$$

With the molar absorptivity of the ligand being obtained by studies of solutions containing only o-tolyl biguanide, equations (*2*) and (*3*) contain only two unknowns, ϵ_C and K. Because the equations are somewhat complicated, the solution by a direct simultaneous calculation is not readily accomplished, and the equations can more easily be solved by a method of successive approximations, as discussed in previous papers (5, 6).

Data of solutions containing only o-tolyl biguanide were analyzed statistically to obtain the best values for the molar absorptivities at the various wavelengths used in these studies. The values found were: $\epsilon_X = 1.65$ at 350mμ, $\epsilon_X = 3.17$ at 450 mμ and $\epsilon_X = 1.10$ at390 mμ,

Approximate values were obtained for ϵ_C by making calculations with solutions which contained high concentrations of ligand and correspondingly low concentrations of metal ion. In such solutions, the equilibrium is driven strongly in the direction of nearly complete conversion of hydrated metal ions into complex ions. A first approximation for ϵ_C in each case was obtained by assuming that under such conditions the concentration of the complex could be estimated to be equal to the total analytical concentration of metal ion in the solution.

The method of successive approximations was applied in the following fashion. All known and measured values plus the approximate value for ϵ_C were substituted into equation (*2*). This was done using data of solutions having concentrations in the ratio of about 1:2 for metal ion to ligand. Solution of the equation then gave an approximate value for $[MX_n]$ at the specified concentrations. Equation (*3*) was then solved to give an approximate value for K.

Data at a high ligand and low metal ion concentration were then substituted into equation (*3*). The approximate K obtained by the method stipulated above was used and an aproximate $[MX_n]$ was found. This value for $[MX_n]$ was substituted into equation (*2*), and a second value was found for ϵ_C. This value differed slightly from the first approximation, and was a better value, because an approximate equilibrium constant was used the second time.

The new value of ϵ_C was used with the data of the solutions containing the metal ion and ligand in the ratio of approximately 1:2 in the same fashion as stated two paragraphs above. The resulting calculations gave a better value of $[MX_n]$ and subsequently of K.

This better value of K was used as before to find a new value for $[MX_n]$ at a high ligand and low metal ion concentration. The better value for $[MX_n]$ permitted the calculation of a better value for K.

These calculations were repeated back and forth until no changes were noted in ϵ_C or K. Usually four or five cycles of calculations were required to obtain the convergence to the actual experimental values.

The final calculated values for $Cu(C_6H_{14}N_5)_2^{++}$ were $K = 1.12 \times 10^{-7}$ and $\epsilon_C = 373$ at 350 mμ. Those for $Ni\,(C_6H_{14}N_5)_2^{++}$ were $K = 2.67 \times 10^{-7}$ and $\epsilon_C = 77.7$ at 450 mμ.

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