O-Tolyl Biguanide Complexes of Some Transition Metal Ions in 1-Methyl-2-Pyrrolidinone

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The biguanides contain five nitrogen atoms and are remarkable coordinating agents. The general formula of a biguanide is $R_2NC(:NH)NHC(:NH)NR_2$, where R represents an alkyl, aryl, or hydrogen group. Only two of the five nitrogen atoms are involved when biguanides coordinate with metal ions to form complex ions. The complexes which form are chelates containing six-membered rings. Usually two or three biguanide molecules coordinate with each metal ion.

The ligand used in this study, o-tolyl biguanide, has the formula, $o\text{-}CH_3C_6H_4NHC(:NH)NHC(:NH)NH_2$. The compound is a bidentate ligand. The coordination chemistry of this ligand has not been extensively investigated, although the literature contains several references to certain other biguanides. Ray has prepared a comprehensive review listing most of the important papers concerning biguanide coordination chemistry published prior to 1961 (3). Some of the first biguanide complexes of cobalt and copper were prepared by Rathke in 1879 (2). However, the Co (II) compound was first isolated in the pure state by Ray and Ghosh in 1943 (4). In general, most of the quantitative studies of relatively pure biguanide complexes have been done since 1935. The present study was undertaken to find the dissociation constants and the molar absorptivities of four o-tolyl biguanide chelates.

Experimental

The solvent used in these studies was 1-methyl-2-pyrrolidinone purchased from Matheson, Coleman and Bell. O-tolyl biguanide is quite soluble in this solvent as are many inorganic salts. Further, the various complexes formed in this study were soluble in the solvent. Thus all the species used were soluble, and all the data reported below were obtained with solutions.

Most of the inorganic salts were used as the nitrates. Because of decomposition, these cannot be dried in ovens in the usual fashion. Instead, the hydrated salts were weighed and placed in 1-methyl-2-pyrrolidinone solutions and then dried with 2,2-dimethoxypropane. A ten percent excess of drying agent was added. The reaction is quantitative and proceeds as follows:

$$(CH_3)_2C(OCH_3)_2 + H_2O = CH_3C(:O)CH_3 + 2CH_3OH.$$
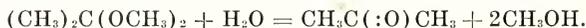
A Perkin-Elmer Model 202 recording UV-visible spectrophotometer was used to scan spectra of solutions containing only inorganic salts, solutions containing only o-tolyl biguanide, and solutions containing complexes of metal ions and o-tolyl biguanide. For precise absorbance determinations at selected 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. When drifting was noticed, the absorbance data were taken with freshly prepared solutions.

The first system studied contained various amounts of $Co(NO_3)_2$ and o-tolyl biguanide. The data are listed in Table 1. The solution containing only $Co(NO_3)_2$ had a spectrum showing an absorbance peak at 525 mμ. This solution absorbed very little light at 400 mμ. The solution containing the complex showed characteristic absorption at 380 mμ. Therefore the latter wavelength was used to study the complex.

The second system involved complexes of $Cu(NO_3)_2$ and o-tolyl biguanide. The data are given in Table 2. The spectrum of a solution containing only $Cu(NO_3)_2$ showed a peak at 800 mμ and practically no absorbance at 500 mμ. The complex had a peak at 610 mμ. The optimum wavelength for the study was 540 mμ.

The third system was composed of $Ni(NO_3)_2$ and o-tolyl biguanide (see Table 3). The spectrum of a solution containing $Ni(NO_3)_2$ had one absorbance peak at 750 mμ and a second at 400 mμ. The spectrum of a solution of the complex had a maximum at 410 mμ. At wavelengths slightly greater than 400 mμ the absorbance of the Ni(II) fell much more rapidly than that of the complex solution. Therefore, 460 mμ was the wavelength which permitted the study of this system.

The fourth system contained $CrCl_3$ and o-tolyl biguanide. Solutions of $CrCl_3$ showed maxima at 500 mμ while solutions of complex showed maxima at 470 mμ. Below 450 mμ the absorbance of the Cr(III) dropped off rapidly. Thus, 390 mμ was deemed the best wavelength for the study of the complex.

Calculations and Results

Job's method of continuous variations was applied to the spectrophotometric data to determine the most stable complex in each case (1, 6). The absorbance data in Tables 1, 2, and 3 show that maxima occur at a ratio of one part metal ion to two parts ligand; therefore, the most stable complexes are of the form $M(\text{o-tolyl biguanide})_2^{++}$, where M represents Co(II), Cu(II), and Ni(II), respectively. The absorbance data in Table 4 indicate a maximum in the formation of a complex at a ratio of one part metal ion to 3 parts ligand; therefore, the most stable complex is $Cr(\text{o-tolyl biguanide})_3^{+++}$.

The data were analyzed to permit the calculation of the dissociation constant and the molar absorptivity of the most stable complex of each metal ion. A method of successive approximations as given in a previous paper was used in a modified form (5). The dissociation of a complex ion may be written as

$$MX_n = M + nX$$
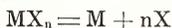
and the dissociation constant as

$$K = \frac{[M][X]^n}{[MX_n]} \tag{1}$$

Let ϵ_M = molar absorptivity of the metal ion, ϵ_X = molar absorptivity of the ligand, and ϵ_C = molar absorptivity of the most stable complex ion.

Then the total absorbance, A, for any solution containing metal ion and ligand is given by

$$A = \epsilon_M[M] + \epsilon_X[X] + \epsilon_C[MX_n] \tag{2}$$

assuming that the concentrations of intermediate complex ions are insignificant. In all the cases studied, solutions of the pure ligand absorbed light to no appreciable extent, thus ϵ_X was essentially zero and the second term was omitted from equation (2).

Using the symbol C_M to represent the total analytical concentration of metal ion added to the solution, and C_X to represent the total concentration of ligand, equation (2) can be written as

$$A = \epsilon_M (C_M - [MX_n]) + \epsilon_C[MX_n] \tag{3}$$

and equation (1) can be written as

$$K = \frac{(C_M - [MX_n]) \, (C_X - n[MX_n])^n}{[MX_n]} \tag{4}$$

For solutions containing only metal salt, equation (2) becomes

$$A = \epsilon_M[M] \tag{5}$$

Thus the measurement of the absorbances of a series of solutions containing only metal ion permitted the calculation of ϵ_M.

The calculations were done by two methods. First, data were substituted directly into equation (5) and ϵ_M calculated. Secondly, graphs of [M] versus A were made and ϵ_M was determined from the slope of the line in each plot. This gave a check concerning the agreement of the absorbance data to Beer's law and gave statistical value to the determined ϵ_M. The values found were: $\epsilon_{Co} = 19.75$ at 380 mμ, $\epsilon_{Cu} = 1.30$ at 540 mμ, $\epsilon_{N1} = 8.90$ at 460 mμ, and $\epsilon_{Cr} = 10.2$ at 390 mμ.

The data given in Tables 1-4 were used to calculate approximate values for ϵ_C. The data were plotted and an approximate ϵ_C was calculated for each of the systems by choosing a point where the metal ion concentration was very low and the ligand concentration was relatively high. Under such conditions, the concentration of the metal ion in solution is practically zero and the concentration of the complex ion, MX_n, is nearly equal to the analytical concentration of the metal ion; that is, nearly all the solvated metal ion is converted to complex ion. Thus, as an approximation, equation (3) becomes $A = \epsilon_C[MX_n]$ or $A = \epsilon_C C_M$ and an approximate ϵ_C could be calculated.

The calculation was continued by using the absorbance data at the maximum of each curve, that is, at the point where the complex was formed most strongly in each case. The known values for A, ϵ_M, C_M, and the approximate value for ϵ_C were substituted into equation (3), permitting calculations of the approximate concentrations of the complex ions. The data were then substituted into equation (4) to allow the calculation of an approximate dissociation constant.

The data at the first point, that is, at low C_M and high C_X, were substituted into equation (4) and by using the approximate K previously determined at the maximum point, the concentration of the complex ion could be determined. In all cases, this was lower than the value used in the first approximation since a small portion of the solvated metal ion was not converted to the complex ion. Thus a better approximation for the concentration of the complex ion was now available, and this value was substituted into equation (3) to permit the calculation of a better value for ϵ_C. This value for ϵ_C was used again at the second point, the maximum on the curve, to obtain a better value for the concentration of the complex using equation (3). Then a better value for K was calculated at point 2 and this value used again at point 1 in the same fashion as discussed above. These calculations were repeated for each system until no change was noted in ϵ_C or K, indicating that the approximate values had converged to the actual values. Usually three or four cycles of calculations were required.

The final calculated values for $Co(C_6H_{14}N_5)_2^{++}$ were $K = 1.14 \times 10^{-11}$ and $\epsilon_C = 642$ at 380 mμ. Those for $Cu(C_6H_{14}N_5)_2^{++}$ were $K = 1.98 \times 10^{-7}$ and $\epsilon_C = 72.6$ at 540 mμ. The results for $Ni(C_6H_{14}N_5)_2^{++}$ were $K = 1.60 \times 10^{-7}$ and $\epsilon_C = 88.1$ at 460 mμ. For $Cr(C_6H_{14}N_5)_2^{+++}$ the corresponding values were $K = 4.21 \times 10^{-11}$ and $\epsilon_C = 708$ at 390 mμ.

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TABLE 1

Conc. Co(II) (X 10³ M)	Conc. o-tolyl big. (X 10³ M)	Absorbance at 380 mμ
4.00	0.00	0.079
2.80	1.20	0.178
2.40	1.60	0.343
2.00	2.00	0.514
1.80	2.20	0.645
1.60	2.40	0.672
1.40	2.60	0.833
1.20	2.80	0.768
0.80	3.20	0.368
0.00	4.00	0.000

TABLE 2

Conc. Cu(II) (X 10^2 M)	Conc. o-tolyl big. (X 10^2 M)	Absorbance at 540 mμ
2.00	0.00	0.026
1.40	0.60	0.143
1.20	0.80	0.200
1.00	1.00	0.264
0.90	1.10	0.303
0.80	1.20	0.369
0.70	1.30	0.428
0.60	1.40	0.424
0.50	1.50	0.355
0.40	1.60	0.260
0.00	2.00	0.003

TABLE 3

Conc. Ni(II) (X 10^2 M)	Conc. o-tolyl big. (X 10^2 M)	Absorbance at 460 mμ
2.00	0.00	0.178
1.40	0.60	0.319
1.20	0.80	0.374
1.00	1.00	0.428
0.80	1.20	0.489
0.70	1.30	0.538
0.60	1.40	0.492
0.50	1.50	0.438
0.40	1.60	0.343
0.30	1.70	0.254
0.00	2.00	0.002

TABLE 4

Conc. Cr(III) (X 10^2 M)	Conc. o-tolyl big. (X 10^2 M)	Absorbance at 390 mμ
1.00	0.00	0.102
0.70	0.30	0.115
0.60	0.40	0.123
0.50	0.50	0.128
0.45	0.55	0.140
0.40	0.60	0.200
0.35	0.65	0.481
0.30	0.70	0.908
0.25	0.75	1.600
0.20	0.80	1.610
0.10	0.90	0.925
0.05	0.95	0.354
0.00	1.00	0.001