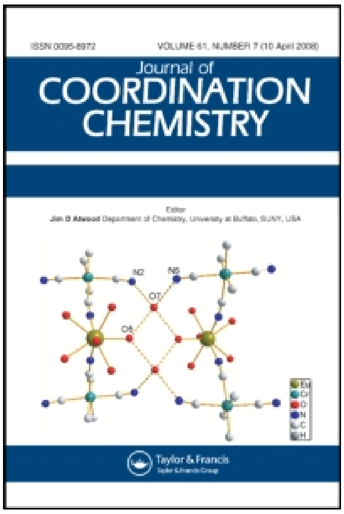

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ESR DETERMINATION OF THE STABILITY CONSTANTS OF COBALOXIME(II)—PYRIDINE MIXED COMPLEXES IN METHANOL

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The stability constants of the 1:1 and 1:2 mixed complexes of bis(dimethylglyoximato)cobalt(II) with pyridine have been determined between 41 and −30°C in methanol, by means of an iteration procedure based on changes in the solution esr spectra. At 24°C, $K_1 = 175$ and $K_2 = 0.83$ M^{-1}. The thermodynamic parameters are $\Delta H_1 = \Delta H_2 = -(3.9 \pm 0.2)$ kcal/mol; $\Delta S_1 = -(2.8 \pm 0.6)$, $\Delta S_2 = -(13.5 \pm 0.8)$ cal/mol.K.

INTRODUCTION

The square planar Co(DH)$_2$ (DH—monoanion of dimethylglyoxime), referred to as cobaloxime(II), forms 1:1 and 1:2 mixed complexes with pyridine,[1] whose stability constants are, however, unknown. In benzene only the 5-coordinate, 1:1 species was found to exist[2] even in the presence of a large excess of pyridine. The existence of the 6-coordinate, 1:2 complex in CH_2Cl_2 and in water has been inferred from the 5-fold shf splitting observed on the esr spectra of *frozen* solutions.[3] In noncoordinating solvents the 1:1 mixed complex was found to dimerize.[3]

In the present paper, we report a study of mixed complex formation between cobaloxime(II), abbreviated Co, and pyridine in methanol. For the determination of the stepwise stability constants, we devised a method based on the changes in the *solution* esr spectra, accompanying mixed complex formation.

EXPERIMENTAL SECTION

The esr spectra were recorded on a JES–ME–3X/Q instrument in the X-band. The sample holders were glass capillaries with identical inner diameters. The esr signal of the glass was separately recorded and taken into correction. All amplitudes were referred to a manganese standard.

Solutions were prepared in an atmosphere of argon by mixing deaerated methanolic solutions of cobalt(II) perchlorate, dimethylglyoxime and pyridine, then transferring the solution in a closed system into the sample holder. 1 mol of sodium hydroxide was added for each mol of dimethylglyoxime. The latter was purified by multiple sublimation. Other chemicals were of analytical grade.

The results were evaluated on a type LGP 21 digital computer.

RESULTS

The esr spectra of methanolic solutions containing a constant concentration of cobaloxime(II) and varying amounts of pyridine are shown in Figure 1. The spectra are superpositions of 3 individual spectra characteristic of the species Co, Copy and Copy$_2$. Provided that these individual spectra are known, the concentrations of all species can be computed from the spectrum of any solution, and thus the stability constants can be calculated.

Since there are two successive equilibria in the system under consideration, viz.

$$\mathrm{Co} + py \overset{K_1}{\rightleftarrows} \mathrm{Copy} \text{ and } \mathrm{Copy} + py \overset{K_2}{\rightleftarrows} \mathrm{Copy_2}$$

it is not generally possible to prepare solutions containing 100% Copy. Also, if K_2 is small, the high pyridine concentration required to effect full formation of Copy$_2$ may cause solubility problems which, in turn, may impose an inconvenient upper limit on the overall Co concentration. High *py* concentrations may also modify the shape of the signal owing to possible changes in the relaxation mechanisms. Consequently, the pure, individual esr spectra of Copy and Copy$_2$ cannot be recorded directly.

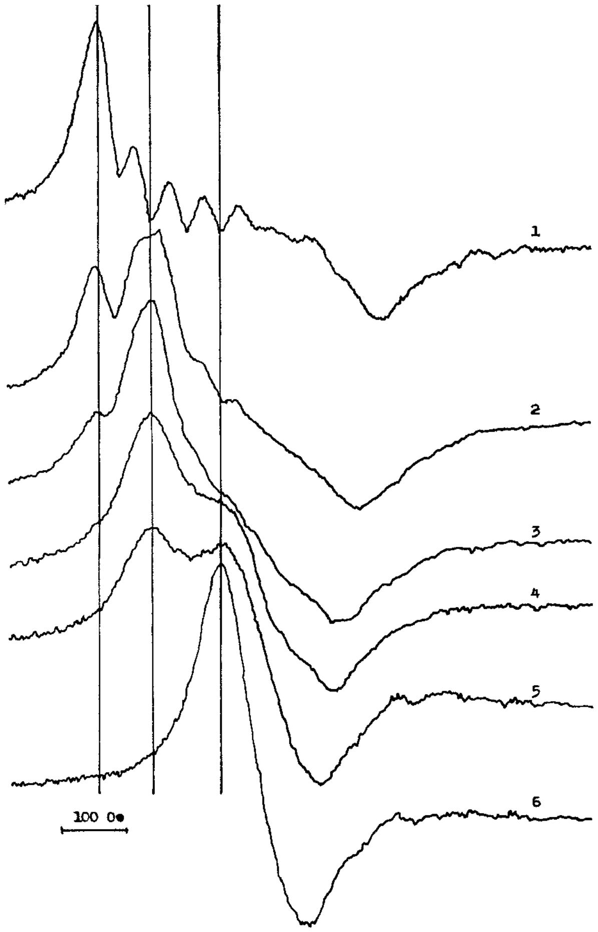

FIGURE 1 Esr spectra of methanolic solutions of CO(DH)$_2$, containing various amounts of pyridine (24°C). $[\mathrm{Co}]_\mathrm{T} = 10^{-2}$ M; Overall pyridine concentration: 1 = zero; 2 = $1.4 \times 10_{-2}$; 3 = 4×10^{-2}; 4 = 0.2; 5 = 0.29; 6 = 2.32 M.

The stability constants were, therefore, determined by means of an iteration procedure performed on a digital computer, involving the following two principal steps:

(1) Determination of the individual esr amplitudes for Copy and Copy$_2$ from K_1 and K_2, which are assumed to be known (the initial estimates of K_1 and K_2 are obtained from preliminary experiments);

(2) Recalculation of K_1 and K_2 from the individual spectral parameters.

The procedure requires a minimum of 5 samples at a given temperature. To ensure rapid convergence, the sample compositions should fulfill the following requirements:

Sample *a*: pure Co,
bx: predominantly Copy, i.e. [Copy]$\gg$[Co], [Copy$_2$],
cx: predominantly Copy$_2$, i.e. [Copy$_2$]$\gg$ [Co], [Copy],
ab: $p \equiv [\mathrm{Copy}]/[\mathrm{Co}] \approx 1$,
bc: $q \equiv [\mathrm{Copy}_2]/[\mathrm{Copy}] \approx 1$.

The first 3 samples approximate the individual esr spectra of the corresponding species, whereas the composition of samples *ab* and *bc* is such as to permit the possible most accurate calculation of K_1 and K_2, respectively. As illustrated by Figure 1, the individual solution spectra of the 3 cobaloxime(II) species are significantly different, revealing 3 distinct maxima marked by vertical lines. The fields corresponding to these maxima will be denoted by indices *1*, *2* and *3*. So far as the solutions are dilute, the individual signal shapes will be independent of the concentration, and the experimental amplitude (A) at a given field can be written as

$$A = a\,[\mathrm{Co}] + b\,[\mathrm{Copy}] + c\,[\mathrm{Copy}_2] \qquad (1)$$

where a, b and c are constants characteristic of the field and the conditions of the measurement. Applying this relationship to the amplitude at field 1 for samples *bx* and *cx*, one obtains

$$A_{1,bx} = a_1[\mathrm{Co}]_{bx} + b_1[\mathrm{Copy}]_{bx} + c_1[\mathrm{Copy}_2]_{bx} \quad (2)$$

$$A_{1,cx} = a_1[\mathrm{Co}]_{cx} + b_1[\mathrm{Copy}]_{cx} + c_1[\mathrm{Copy}_2]_{cx} \quad (3)$$

Similar equations are valid for amplitudes A_2 and A_3, resulting in 3×2 equations, which can be solved pairwise for b_1, c_1, b_2, c_2, and b_3, c_3, provided that the concentrations of the species are known in samples *bx* and *cx*. Signal components a_1, a_2 and a_3 are obtained from the spectrum of sample *a*, containing pure Co.

In all iteration steps, the concentrations in samples *bx* and *cx* are calculated by means of K_1 and K_2 obtained in the previous estimate, using the equations:

$$[\mathrm{Co}] = \frac{[\mathrm{Co}]_\mathrm{T}}{1 + p + pq} \qquad (4)$$

$$[\mathrm{Copy}] = [\mathrm{Co}]\,p \qquad (5)$$

$$[\mathrm{Copy}_2] = [\mathrm{Copy}]\,q \qquad (6)$$

where $[\mathrm{Co}]_\mathrm{T}$ is the overall cobaloxime(II) concentration and

$$p \equiv [\mathrm{Copy}]/[\mathrm{Co}] = K_1\,[py] \qquad (7)$$

$$q \equiv [\mathrm{Copy}_2]/[\mathrm{Copy}] = K_2[\mathrm{py}] \qquad (8)$$

The concentration of free pyridine is

$$[py] = [py]_\mathrm{T} - [\mathrm{Co}]_\mathrm{T} + [\mathrm{Co}] - [\mathrm{Copy}_2] \qquad (9)$$

Since $[py]_\mathrm{T}$ in samples *bx* and *cx* is sufficiently high, equation 9 can be simplified to

$$[py] = [py]_\mathrm{T} - [\mathrm{Co}]_\mathrm{T} \qquad (10)$$

with a very good approximation.

Equations 4–10 thus give the concentrations of all species in samples *bx* and *cx* on the basis of an initial estimate for K_1 and K_2. The signal components are subsequently obtained from equations of the form of equation 1.

Samples *ab* and *bc* are now used to calculate a better approximation for the stability constants. K_1 is obtained from the spectrum of sample *ab* on the basis of the following system of equations:

$$\begin{pmatrix} A_{1,ab} \\ A_{2,ab} \\ A_{3,ab} \end{pmatrix} = \begin{pmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{pmatrix} \begin{pmatrix} [\mathrm{Co}]_{ab} \\ [\mathrm{Copy}]_{ab} \\ [\mathrm{Copy}_2]_{ab} \end{pmatrix} \qquad (11)$$

whence

$$p_{ab} = \frac{\begin{vmatrix} a_1 & A_{1,ab} & c_1 \\ a_2 & A_{2,ab} & c_2 \\ a_3 & A_{3,ab} & c_3 \end{vmatrix}}{\begin{vmatrix} A_{1,ab} & b_1 & c_1 \\ A_{2,ab} & b_2 & c_2 \\ A_{3,ab} & b_3 & c_3 \end{vmatrix}} \qquad (12)$$

The new K_1 is calculated from equation 7, which, however, requires the knowledge of the free pyridine concentration ($[py]_{ab}$) in sample *ab*. For this, the following expression can be derived:

$$[py]_{ab} = [py]_{\mathrm{T},ab} - [\mathrm{Co}]_{\mathrm{T},ab}\,\frac{p_{ab} + 2p_{ab}q_{ab}}{1 + p_{ab} + p_{ab}q_{ab}} \qquad (13)$$

The value of q_{ab} is estimated by means of the relationship

$$q_{ab} = p_{ab}K_2/K_1 \qquad (14)$$

using the stability constants from the previous iteration cycle.

K_2 is calculated in an analogous manner, applying equation 8 to sample *bc*. Since in this sample $p_{bc} \approx 100$ and $q_{bc} \approx 1$, the free pyridine concentration is obtained from the following simplified form of equation 13

$$[py]_{bc} = [py]_{\mathrm{T},bc} - [\mathrm{Co}]_{\mathrm{T},bc}\,\frac{1 + 2q_{bc}}{1 + q_{bc}} \qquad (15)$$

Thus the signal components provide us with refined values for K_1 and K_2 on the basis of samples *ab* and *bc*. These stability constants are now used to determine the refined values of the signal components from samples *bx* and *cx*. The cycle is repeated until the difference between the constants from 2 successive iteration steps becomes smaller than a pre-set limit.

The compositions of the solutions used in the experiments and the stability constants obtained at 4 temperatures are listed in Table I. We have used 2 different *ab* samples with an identical set of the remaining samples. The iteration program provided for corrections in the methanol concentration in the case of higher pyridine concentrations.

The thermodynamic parameters were determined by plotting the logarithm of K_1 and K_2 against 1/T:

$\Delta H_1 = -(3.9 \pm 0.2)$ kcal/mol;

$\Delta S_1 = -(2.8 \pm 0.6)$ cal/mol.K

$\Delta H_2 = -(3.9 \pm 0.2)$ kcal/mol;

$\Delta S_2 = -(13.5 \pm 0.8)$ cal/mol.K

TABLE I

Sample compositions and the values of the stepwise stability constants K_1 and K_2

Temperature (°C)	K_1 (M_{-1})	K_2 (M_{-1})
	147	0.64
41	115	0.53
average	(131)	(0.58)
	189	0.82
24	161	0.84
average	(175)	(0.83)
	292	1.52
0	309	1.52
average	(300)	(1.52)
	926	3.00
−30	780	3.01
average	(853)	(3.00)

Composition of the samples:

a: $[\mathrm{Co}]_\mathrm{T} = 5 \times 10^{-3}$ M;

bx: $[\mathrm{Co}]_\mathrm{T} = 2 \times 10^{-3}$ M; $[py]_\mathrm{T} = 5 \times 10^{-2}$ M;

cx: $[\mathrm{Co}]_T = 1 \times 10^{-3}$ M; $[py]_T = 2$ M;
ab: $[\mathrm{Co}]_T = 3 \times 10^{-3}$ M; $[py]_T = 3 \times 10^{-3}$ and 9×10^{-3} M;
bc: $[\mathrm{Co}]_T = 2 \times 10^{-3}$ M; $[py]_T = 0.3$ M

DISCUSSION

According to the results presented, the 1:1 and 1:2 mixed complexes of bis(dimethylglyoximato)-cobalt(II) with pyridine are paramagnetic in methanol and there is no evidence for dimerization. The solution esr spectra are consistent with the stepwise coordination of 2 pyridines in the axial positions of the square planar cobaloxime(II) parent species. Although no attempts were made at working under anhydrous conditions, evidence is available that in the absence of pyridine, the axial positions are occupied by methanol molecules. We repeated the determination of K_1 and K_2 under conditions when the water concentration in the system was increased 2-fold. Since the stability constants remained unchanged within experimental error, the composition of the parent cobaloxime(II) must be $Co(DH)_2(CH_3OH)_2$.

It is noteworthy that in the present case the coordination number of the mixed pyridine species predominating at room temperature at a given composition cannot be correctly deduced from the esr spectrum of the frozen solution, regardless of how rapidly the freezing is carried out. This is illustrated by the following results. A methanolic solution with $[\mathrm{Co}]_T = 10^{-2}$M and $[py]_T = 0.1$ M contains about 90% of Copy at 25°C. Upon rapid freezing and cooling to liquid N_2 temperature, a 5-fold shf splitting is observed, which, however, indicates predominance of Copy_2 (at least 90%). The explanation lies in the lability of the cobalt(II) complexes: $K_1K_2 = \beta_2$ becomes so large in the vicinity of the freezing point of methanol that the 90% formation of Copy_2 is thermodynamically possible and the rapidity of the replacement of coordinated methanol permits fast re-establishment of the equilibrium. The important consequence of this is that the presence of 6-coordinate bis(pyridine)cobaloxime(II) at 70 K does not necessarily mean that the same species predominates in the solution at room temperature. The mixed complex Copy_2, although existent at room temperature, is rather unstable and its formation requires high pyridine concentrations.

The method of determination of stepwise stability constants described here can be applied to other low-spin d^7 systems if the solution esr spectrum is sufficiently sensitive to changes in the coordination sphere. In the present case, it seems to be superior to the spectrophotometric technique in both accuracy and sensitivity. The iteration procedure used requires very little computer time. An important condition of applicability is that the life-time of the individual species should be high enough to permit separate observation of the esr signals of the components. The rate constant of methanol exchange[4] in cobalt(II)–methanol complexes is of the order of 10^5–10^6 sec^{-1}. The corresponding life-time is by 2–3 orders of magnitude higher than the 10^{-8} sec equivalent to a line separation of about 30 0e, therefore, the observation of the individual signals is ensured and the spectra of Figure 1 are actually superpositions of the esr spectra of Co, Copy and Copy_2.

Work is in progress on the application of the method to other systems of mixed complexes.

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