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Formation of a Cobalt(II) Complex with the Ligand 2,4,6-Tripyridyl-s-Triazine. Reduction in Solution to the Univalent State

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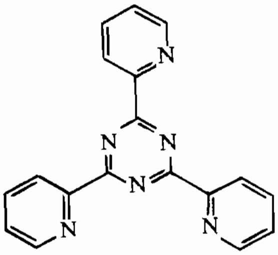
The formation of a cobalt complex involving the ligand 2,4,6-tripyridyl-s-triazine (TPTZ) is reported. Spectral data, magnetic susceptibility measurements, and conductance values are compatible with a six coordinate, high spin cobalt(II) complex, which in solution is found to be polarographically reducible to a formally univalent state. The reduction potentials of $Co(TPTZ)_2^{2+}$ *and* $Co(terpy)_2^{2+}$ *are compared and discussed (terpy = 2,2′,2″–terpyridine).*

Introduction

The synthesis of the terpyridine-like tridentate ligand, 2,4,6-tripyridyl-s-triazine (TPTZ) was first accomplished by Case and Koft,[1] and the compound is now commercially available. It has been extensively used in analytical procedures[2,3] involving divalent iron. However, the solution chemistry of this interesting ligand with other transition metals has not been extensively reported. We would like now to report on the polarographic behavior of the bis(2,4,6-tripyridyl-s-triazine) cobalt(II) cation.



TPTZ

Experimental Section

Materials. All chemicals used were of reagent grade. The 2,4,6-tripyridyl-s-triazine was used as received from the G. Frederick Smith Company.

Preparation of the bis(2,4,6-tripyridyl-s-triazine) cobalt(II) nitrate monohydrate. Two ml of a 0.2 *M* stock solution of cobalt(II) nitrate hexahydrate in ethanol was added to 25 ml of an ethanolic solution of excess TPTZ. A reddish brown precipitate formed, which was collected, filtered, washed with ethanol, air dried, and dried *in vacuo* for 12 hr. The analysis was consistent with the composition $Co(TPTZ)_2(NO_3)_2 \cdot H_2O$. *Anal.* Calcd. for $C_{36}H_{24}N_{14}H_2O$: C, 52.33; H, 3.15; N, 23.74. Found: C, 52.30; H, 3.16; N, 23.50.

Solutions. For the conductance measurements, the solid complex was dissolved (0.001 *M*) in methanol. For all other experimental measurements, an aqueous solution of cobaltous nitrate was added to an appropriate amount of TPTZ in ethanol. Final solutions were made to contain 50% ethanol by volume. With the exception of the continuous variations method, measurements were made with a molar ratio of TPTZ to cobalt of at least 4 to 1, in order to insure formation of the bis complex in solution.

Physical Measurements. Electronic absorption spectra were taken with a Cary Model 14 recording spectrophotometer.

Polarograms were obtained with an Indiana Instrument and Chemical Corp. Controlled Potential and Derivative Voltammeter, Model ORNL-1988A, in conjunction with a Moseley Model 7001 X-Y recorder. An aqueous silver-silver chloride electrode (saturated NaCl) was used as the reference electrode.

The circuit for the controlled potential electrolysis was fabricated from Philbrick type P25A operational amplifiers and type P66A booster amplifiers.

Conductance values were measured using an Industrial Instruments Inc., Model RC–16B conductivity bridge and a dip type cell with a cell constant of 0.1 cm^{-1}.

The determination of magnetic susceptibility was made at room temperature by the Faraday method. Standard $Hg[Co(NCS)_4]$ was used as a calibrant. Diamagnetic corrections were made using Pascal's constants.

Elemental analyses were performed by Gailbraith Microanalytical Laboratories, Knoxville, Tenn.

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[1] F. H. Case and E. Koft, *J. Am. Chem. Soc., 81,* 905 (1959).

[2] P. Collins, H. Diehl and G. F. Smith, *Anal. Chem., 31,* 1862 (1959).

[3] H. Diehl and G. F. Smith, « The Iron Reagents: Bathophenanthroline, Bathophenanthroline-disulfonic Acid, 2,4,6-Tripyridyl-s-triazine, Phenyl-2-pyridyl Ketoxime », 2nd ed, G. Frederick Smith Chemical Co., Columbus, Ohio, 1965.

Results and Discussion

The solution spectrum of the triazine complex shows two bands in the visible region centered at 19,00 cm^{-1} (525 nm) and 20,800 cm^{-1} (480 nm) with molar extinction coefficients of approximately 550 and 670, respectively.

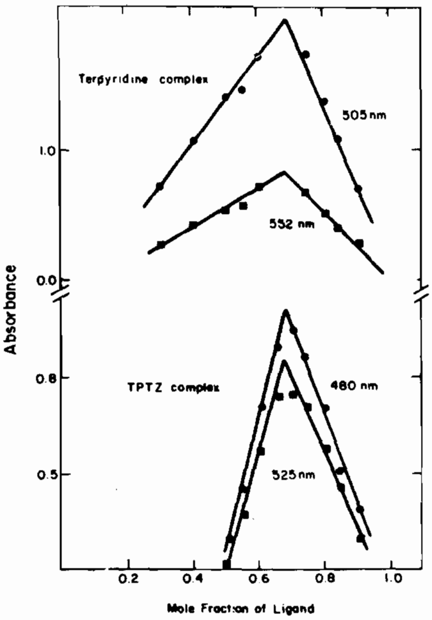

Figure 1. Plot of absorbance versus mole fraction of ligand for complexes of cobalt with TPTZ and terpyridine. For individual runs, the sum of the cobalt plus ligand concentrations was equal to 5.0 *mM*.

At each of these wavelengths a continuous variations plot was made to establish the stoichiometry of the complex in solution. These plots are shown in Figure 1. The maximum absorbance occurs at a ligand mole fraction of 0.68, indicating a combining ratio of TPTZ to cobalt of two to one. Also shown for comparison are curves of $Co(terpy)_2^{2+}$ under identical solution conditions. In addition, a value of 152 ohm^{-1} cm^{-2} mol^{-1} was found for the molar conductance of $Co(TPTZ)_2(NO_3)_2 \cdot H_2O$, in good argreement with the value of 157 ohm^{-1} cm^{-2} mol^{-1} reported by Taylor and Busch[4] for the similar nickel(II) complex, $Ni(TRI)_2(NO_3)_2 \cdot H_2O$, a 2:1 electrolyte in solution (TRI = tribenzo [b, f, j][1,5,9] triazacycloduodecine). These results show the complex cobalt cation to be $Co(TPTZ)_2^{2+}$. Also, the solid state cobalt complex possesses a room temperature magnetic moment of 4.78 B.M., which is in the expected range for high spin cobalt(II).

Polarograms of millimolar concentrations of $Co(TPTZ)_2^{2+}$ were taken using 0.3 *M* ammonium chloride as background electrolyte (Figure 2, curve A). A well developed reduction wave occurs at –0.359 volt *vs.* Ag/AgCl electrode. Solutions containing ligand alone in 0.3 *M* NH_4Cl did not show any reduction until a voltage of –0.6 v *vs.* Ag/AgCl electrode was reached. It was concluded that the reduction wave of the complex was diffusion controlled, since the variation of the limiting current with the square root of mercury column height was linear. The height of the diffusion current was comparable to that obtained for the one electron reduction of $Co(terpy)_2^{2+}$ previously reported.[5]

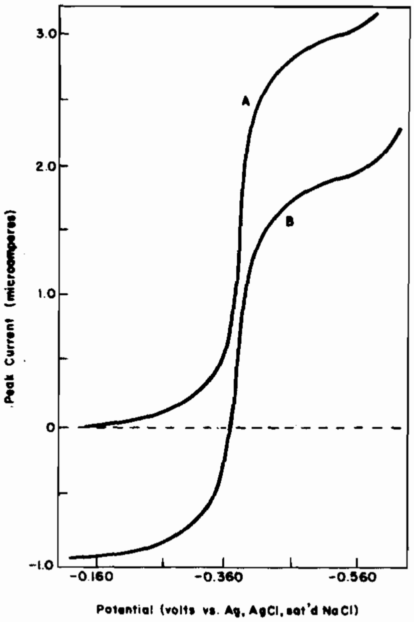

Figure 2. Curve A: Polarogram of 1.0 *mM* $Co(TPTZ)_2^{2+}$ with excess TPTZ in 50% ethanol-water, using 0.3 *M* ammonium chloride as background electrolyte. Curve B: Polarogram of the same solution after electrolysis at –0.525 v *vs.* Ag/AgCl reference electrode.

In order to determine the reversibility of the reduction process, a polarogram was taken on a solution of $Co(TPTZ)_2^{2+}$ which had been electrolyzed for a suitable length of time at –0.525 volt *vs.* Ag/AgCl electrode. This polarogram (Figure 2, curve B) showed a composite oxidation-reduction wave with equal half-wave potentials for the anodic and cathodic branches. The electrolyzed solution had a deep purple color. Quantitative transfer from the electrolysis cell to the polarographic vessel was carried out under an atmosphere of nitrogen. When the reduced solution of the complex was exposed to air, the reddish brown color of $Co(TPTZ)_2^{2+}$ reappeared and the resulting visible spectrum and polarogram were identical to those obtained for the divalent complex. On all of the recorded polarograms, the sum of the anodic and cathodic currents was constant. When a plot of $\log[i/(i_d-i)]$ *vs.* E was made for the polarogram of Figure 2, a straight line was obtained (Figure 3) with a slope of 57.4 millivolts, indicating that the electrode reduction of the complex involves the transfer of one electron. In addition, the half-wave potential was found to be independent of excess ligand concentration, implying that the coordination number is the same for both the oxidized and reduced forms

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(4) L. T. Taylor and D. H. Busch, *Inorg. Chem.*, *8*, 1366 (1969).

(5) D. J. Macero, r. V. Lovecchio and S. J. Pace, *Inorg. Chim. Acta*, 3, 65 (1969).

of the complex.[6] For these measurements, the molar ratio of TPTZ to cobaltous ion was varied from 2 to 10.

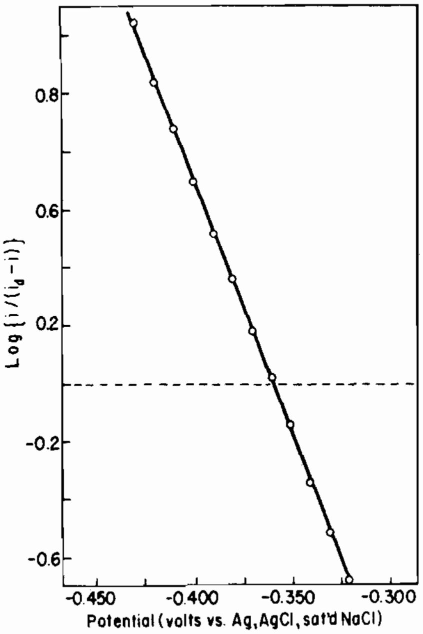

Figure 3. Plot of log[i/(i_d–i)] versus potential for the polarographic reduction of $Co(TPTZ)_2^{2+}$.

It is instructive to consider how the reduction potential of a reversible metal complex is affected when a substitution is made on the ligand. If this substitution does not substantially alter the immediate bonding environment of the central metal ion, then the observed changes in the reduction potentials of the complex can furnish information about the relative energies of metal and ligand orbitals. Studies of this type have been carried out largely by Vlček and co-workers.[6]

One can consider TPTZ as essentially a substituted terpyridine ligand, where substitution occurs at a distance which is sufficiently removed from the field of the metal ion. The measured half-wave potential of $Co(TPTZ)_2^{2+}$ in 50% ethanol-water is –0.36 v which is more positive than that of $Co(terpy)_2^{2+}$ (–0.85 v) under identical conditions. Similarly, the reducion of free TPTZ occurs at a more positive voltage than that observed for free terpyridine, *i.e.* –0.58 v *vs.* –0.94 v, respectively.* Clearly, the change in half-wave potentials for the $Co(TPTZ)_2^{2+}$–$Co(terpy)_2^{2+}$ pair is in the same direction and of the same order of magnitude as the change of reduction potentials for the free ligands. This suggests that in the reduction process, the electron affinity of the complex is highly influenced by the ligand differences. As is implied by the substitution restrictions above, a correlation of this type is strictly valid only if the entropy factors, which are primarily a function of nuclear charge, metal-ligand equilibrium distance, and stereochemical orientation are constant for the different complexes. In this way, the E° values for the electrode reduction of the complexes can be directly related to their electron affinities.[6] In view of the similarity of TPTZ to terpyridine, it is not unreasonable to expect that the ΔS° values for the $Co(TPTZ)_2^{2+}$–$Co(TPTZ)_2^{+}$ redox couple are similar to those of the $Co(terpy)_2^{2+}$–$Co(terpy)_2^{+}$ couple. It should be pointed out however that this is speculative, and more experimental data is needed to substantiate this reasoning.

Acknowledgment. We wish to thank W. A. Baker, Jr. for very helpful discussions, and also P. B. Lutz for measurements of magnetic susceptibility.

[6] A. A. Vlcek, « Progress in Inorganic Chemistry », Vol. 5, F. Albert Cotton, Ed., John Wiley and Sons, Inc., New York, N. Y. (1963).

(*) The potential values chosen for the free ligands were those at which the measured current was equal to 0.15 microamperes. A concentration of 4.0 *mM* ligand was used in each case.