Inorganica Chimica Acta, 28 (1978) 119–122
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Synthesis and Characterization of a Soluble, Polymeric 5-Phenyltetrazolate-Bridged Aquo Cobalt(II) Complex

L. RICHARDS*, M. LaPORTE and R. MAGUIRE[†]

Department of Chemistry, York College of the City University of New York, Jamaica, N.Y. 11451, U.S.A.

J. L. RICHARDS* and L. DIAZ, Jr.

Department of Chemistry, Herbert H. Lehman College of the City University of New York, Bronx, N.Y. 10468, U.S.A.

Received September 16, 1977

A soluble, high molecular weight polymer, [Co($C_6H_5CN_4$)$_2$(H_2O)$_2$]$_n$, has been prepared and characterized. Osmotic pressure measurements indicate the polymer has a molecular weight on the order of 10^4 to 10^5. Viscosity measurements indicate the molecule behaves as a rigid, rod-like particle in solution. The proposed structure for the polymer is one in which each Co^{2+} is connected by two bridging tetrazolates to form a rigid, linear chain. Hydrogen bonds between the two waters on each adjacent Co^{2+} are also postulated. The properties of the cobalt polymer are similar to those of a recently reported nickel polymer, [Ni($C_6H_5CN_4$)$^-$]$_n$, though the structures and net charges of the two compounds are different.

Introduction

We recently reported the first example of a soluble, rod-like polymer containing transition metal ions in its backbone [1]. The polymer, composed of Ni^{2+} and 5-phenyltetrazolate, has a molecular weight on the order of 10^5. Its monomer unit is tris(5-phenyltetrazolato)nickel(II). In the polymer each of the 5-phenyltetrazolates serves as a bridging ligand between two Ni^{2+}'s. The polymer is unusual both because it is soluble and because it has a rigid, linear structure. Only one other soluble, high molecular weight transition metal polymer, an iron-hydroxy-nitrate compound, has been reported and it has a spherical structure [2].

We now wish to report the preparation and characterization of a second rod-like, soluble transition metal polymer. This compound contains Co^{2+}, 5-phenyltetrazolate and water. Data are presented here which permit formulation of the monomer unit and establish the nature of the coordination around the metal ion. Intrinsic viscosities and molecular weight values for the polymer are reported and a structure for the polymer is proposed.

The new compound exhibits the same unusual physical behavior in solution as the earlier reported nickel polymer, but its composition and structure are different.

Experimental

Preparation of Tetrazoles and Tetrazolates

5-Phenyltetrazole and 5-(*p*-nitro-phenyl)tetrazole were synthesized using procedures reported in the literature [3]. The tetrazoles were recrystallized until a constant melting point was achieved. Sodium 5-phenyltetrazolate** (hereinafter NaT) and sodium 5-(*p*-nitro-phenyl)tetrazolate (hereinafter Na *p*-NO_2-T) were prepared by titrating the appropriate tetrazole with NaOH to pH 8.2. Water was removed from the salt by rotary evaporation at reduced pressure. The resulting salt was stored in a vacuum desiccator.

Preparation of Co(II) 5-Phenyltetrazolate Complexes

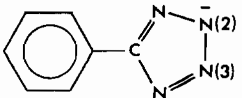
Aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ (ACS reagent grade) and NaT were mixed together to yield solutions whose final Co^{2+} concentrations ranged from 0.06 to 0.001 *M* and whose T^- to Co^{2+} ratios were between twenty and ten. In all solutions pink precipitates formed immediately. In ten to twenty minutes the precipitates dissolved to yield highly viscous, clear yellow solutions. Spectral analysis indicated the formation of a new compound. A yellow solid could not be isolated in pure form from the viscous yellow solution. Yellow solutions with the same spectral properties and viscosities as the above solutions could be prepared using $CoCl_2 \cdot 6H_2O$ (ACS reagent grade) instead of $Co(NO_3)_2 \cdot 6H_2O$.

---

*Authors to whom correspondence should be addressed.

[†] National Science Foundation Undergraduate Research Program Participant.

**The structure and numbering convention for phenyltetrazolates is as follows:



A pink precipitate of $CoT_2 \cdot 2H_2O$ formed when the viscous, yellow solution was heated. The precipitate was filtered, rapidly washed with methanol, air dried and analyzed. *Anal.* Calcd for $CoT_2 \cdot 2H_2O$: Co, 15.28; C, 43.61; H, 3.67; N, 29.07. Found: Co, 15.02; C, 42.91; H, 3.63; N, 28.48%. (This and all other analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.) A similar pink compound, $CoT_2 \cdot 3H_2O$, was made by adding methanol to the viscous yellow solution. The resulting precipitate was filtered, washed with methanol and air dried. *Anal.* Calcd for $CoT_2 \cdot 3H_2O$: C, 41.68; H, 3.97; N, 27.79. Found: C, 40.82; H, 3.82; N, 27.10%. The two pink compounds had identical IR spectra.

Preparation of Co(II) 5-(p-Nitro-phenyl)tetrazolate Complexes

Aqueous solutions of $Co(NO_3)_2 \cdot 6H_2O$ and Na p-NO_2-T were mixed together to yield solutions with final Co^{2+} concentrations of 0.01 to 0.02 M and p-NO_2-T^- to Co^{2+} ratios of ten. A yellow precipitate, $Co(p\text{-}NO_2\text{-}T)_2 \cdot 9H_2O$, formed immediately. The precipitate was filtered, washed with water and air dried. *Anal.* Calcd for $Co(p\text{-}NO_2\text{-}T)_2 \cdot 9H_2O$: Co, 9.82; C, 27.95; H, 4.33; N, 23.29. Found: Co, 9.69; C, 27.85; H, 4.04; N, 23.01%. A pink precipitate, $Co(p\text{-}NO_2T)_2 \cdot 4H_2O$, formed when methanol was added to the yellow precipitate. The compound was filtered and air dried [4]. *Anal.* Calcd for $Co(p\text{-}NO_2\text{-}T)_2 \cdot 4H_2O$: Co, 11.55; C, 32.88; H, 3.13. Found: Co, 11.72; C, 33.42; H, 3.00%.

Physical Methods

UV–VIS spectra were recorded on Beckman Model M-VI and GCA/McPherson Model 707K spectrophotometers. When recording an absorption spectrum, the appropriate tetrazolate solution was used as a reference. When recording absorbance for the continuous variation study, the appropriate Co^{2+} solutions were used as references and corrections were made for small amounts of scattering.

IR spectra were recorded on a Beckman Model 4240 spectrophotometer.

Potentiometric measurements were made using a Leeds and Northrup Model 7407 pH meter for the titrations and a Princeton Applied Research Model 170 Electrochemistry System for half-wave potentials.

Viscosities were measured at 10.0 °C in modified Ostwald–Fenske viscometers with flow times for water of 369.4 sec and 34.7 sec. Flow times for all solutions were long enough so that kinetic corrections could be ignored.

Molecular weights were determined using a modified Wagner–Schulz osmometer with Type RC-51 Schleicher and Schuell membranes (50 Å pore size). Initial liquid levels were set both above and below the expected final level. Readings were taken for five to eight days. The capillary rise contribution to the height was determined separately by permitting the polymer solution to rise freely in the same piece of capillary tubing.

Membrane filtration was achieved by applying up to twelve atm pressure of N_2 gas to a solution contained in the osmotic pressure apparatus.

Densities were measured at 10.0 °C using a 25 ml pycnometer calibrated with water.

Results and Discussion

The transition metal compound we are reporting here has extraordinary physical properties. Solutions which are 0.06 M in Co^{2+} and 0.48 M in T^- are so viscous at room temperature they cannot be poured. More dilute solutions are also very viscous and foam when agitated. Concentrated solutions made by membrane filtration can be stretched into thread or sheet form. Such behavior suggests the species in solution is a polymer.

The yellow solutions that form when solutions of T^- and Co^{2+} are mixed at T^- to Co^{2+} ratios greater than seven are fairly stable at room temperature. However, if heated gently or treated with methanol or ethanol, the solutions immediately yield a pink precipitate, $CoT_2 \cdot 3H_2O$. If these solutions are cooled again, the yellow viscous solutions re-form. Solutions in which the T^- to Co^{2+} ratio is higher than seven are more resistant to formation of pink precipitate.

Though we could not isolate a pure form of the yellow compound from the solution, we were able to characterize it by determining the oxidation state of cobalt and the geometry and stoichiometry of the yellow compound in solution from electrochemical, spectrophotometric and titration studies.

To determine if the Co^{2+} was being oxidized as the yellow solution formed, the cobalt present in the compound was electrochemically reduced. The measured half-wave potential for a solution 0.001 M in Co^{2+} and 0.01 M in T^- in 0.1 M KCl was -1.13 V; that for a solution 0.001 M in $CoCl_2$ in 0.1 M KCl was -1.22 V. The fact that the potentials are within 0.1 V of each other strongly indicates that the cobalt in the polymer remains Co^{2+}.

UV–VIS spectral studies of the yellow viscous solution show absorption maxima at 290 nm ($\epsilon = 365\ M^{-1}\ cm^{-1}$), 458 nm ($\epsilon = 18\ M^{-1}\ cm^{-1}$) and a band which has a maximum at $\lambda > 800$ nm ($\epsilon_{800} = 3.5\ M^{-1}\ cm^{-1}$). These absorption maxima are different from those exhibited by aqueous solutions of either $CoCl_2$ or NaT and they are typical of six coordinate Co(II) compounds containing ligands which are bound to the cobalt through a nitrogen atom [5]. Limiting absorbances were found at T^- to Co^{2+} ratios of seven.

Continuous variation studies were performed, in which the sum of the number of mol of Co^{2+} and T^-

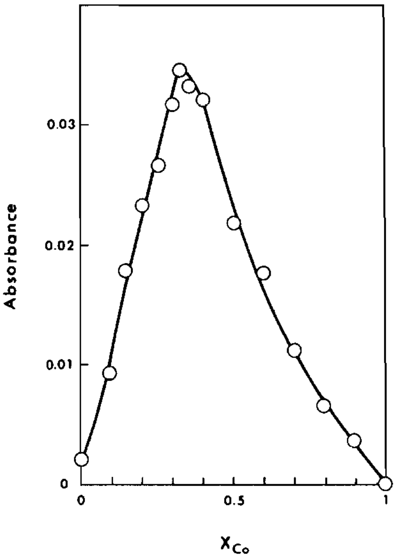


Fig. 1. Continuous variation study of $CoCl_2 \cdot 6H_2O$ and NaT.

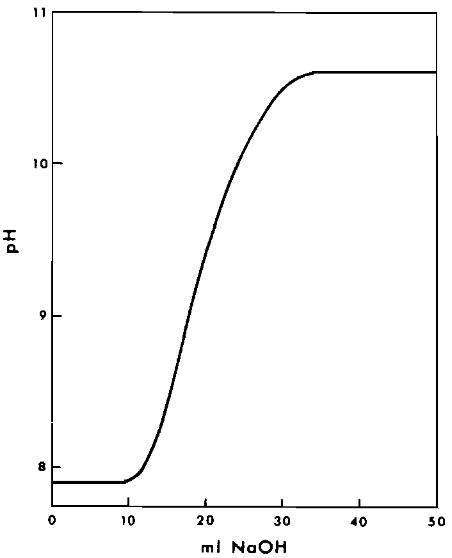


Fig. 2. pH titration curve for the addition of 0.010 *M* NaOH to a solution of cobalt polymer containing 0.20 mmol Co^{2+}.

was kept constant at 0.3 mmol and the mol fraction of Co^{2+}, X_{Co}, was varied from 0 to 1. Maximum absorbance at 458 nm, indicating maximum chromophore formation, was found to be at $X_{Co} = 0.33$ (Figure 1) which corresponds to a T^- to Co^{2+} ratio of two.

Potentiometric titrations of solutions containing 1.4 mmol T^- and 0.2 mmol Co^{2+} in 20 to 30 ml of water showed one sharp equivalence point at pH 9.48 when 0.010 *M* NaOH was used as titrant (Figure 2). The equivalence point occurred when 0.2 mmol of OH^- had been added to the solution, which corresponds to one mol of base added per mol of Co^{2+}. Since the solutions being titrated contained only Co^{2+}, Cl^- or NO_3^-, Na^+, T^- and H_2O, the source of the proton must be coordinated water. Unfortunately, a precipitate formed as the pH neared the equivalence point, which limited the information which could be obtained from the titration data. However, the data indicate that at least one water is present in the first coordination shell of Co^{2+}. Since the properties of polymer solutions made with either the chloride or the nitrate salt are the same, it is unlikely that either of these ions is bound directly to Co^{2+}. Therefore, the most probable monomer unit for the polymer is $CoT_2(H_2O)_x$ where x is between two and four depending on whether tetrazolate is mono- or bidentate.

In an attempt to confirm this monomer unit, the analogous p-NO_2-T^- compound was prepared and isolated. It analyzed as $Co(p\text{-}NO_2\text{-}T)_2 \cdot 9H_2O$. Since the behavior of the two yellow compounds is similar (both form pink compounds when heated or treated with methanol, both pink compounds re-form their respective yellow compounds on the addition of water and both contain two tetrazolates per Co^{2+}), the fact that there is no Cl^- or NO_3^- in the isolated compound provides additional support for the proposed composition of the monomer unit for the cobalt-tetrazolate polymer.

In order to determine a molecular weight range for the polymer, osmotic pressure measurements were made on solutions which were 0.002 *M* in Co^{2+} and 0.02 *M* in T^-. Measurements were made in two different osmometers using 0.02 *M* NaT as the solvent. The net heights ranged from 0.8 to 0.3 cm which corresponds to between 60 and 160 Co^{2+}'s per polymer molecule or to molecular weights from 2 to 6×10^4.

Quantitative viscoscity measurements were made to determine the intrinsic viscosity of the polymer. Viscosity measurements were made on solutions with Co^{2+} concentrations between 4.0×10^{-3} and 1.2×10^{-4} *M* and T^- to Co^{2+} ratios between 10 and 100. The measurements were made at 10.0 °C to ensure that precipitates would not form in any of the more dilute solutions. Solutions of NaT of the same concentration present in the polymer solution were used as the reference solvents.

The intrinsic viscosity, $[\eta]$, was determined from the defining equation $[\eta] = \lim[(1/c)(\eta' - \eta)/\eta]$ as c approaches zero, where η' and η are the viscosities of the solution and solvent respectively, and from the quantity $(1/c)\ln(\eta'/\eta)$ [6]. The latter quantity approaches the value of $[\eta]$ more quickly and it was found that, for the concentration range studied, it was usually possible simply to calculate $(1/c)\ln(\eta'/\eta)$ for a given solution without making a series of dilutions for that solution.

Solutions with a T^- to Co^{2+} ratio of ten which were 0.004, 0.003, 0.002 and 0.0015 *M* in Co^{2+} had $[\eta]$'s of 1600, 430, 180 and 110 ml/g after one week and [η]'s of 2200, 760, 230 and 140 ml/g after two weeks respectively. Solutions with a T^- to Co^{2+} ratio of twenty which were 0.004 and 0.002 *M* in Co^{2+} had [η]'s of 5000 and 1300 ml/g after one week and 5700 and 2300 ml/g after two weeks respectively. Solutions with a T^- to Co^{2+} ratio of 100 which were 0.004 *M* in Co^{2+} were too viscous to pour after only a few hours and the [η] for a 0.002 *M* Co^{2+} with a T^- to Co^{2+} ratio of 100 was greater than 3000 ml/g after three days.

Such high intrinsic viscosities are exhibited only by random coil molecules of very high molecular weight ($\sim 10^7$ or greater) and a few rigid, helical molecules of lower molecular weight [7, 8]. Even if allowance is made for the greater molecular weights expected in more concentrated solutions of cobalt polymer, the molecular weight of the polymer alone cannot account for the extremely high [η] values that are observed. It must also be presumed that the molecule has a highly asymmetric shape. Evidence that this assumption is justified comes from the fact that the viscosity values for the cobalt polymer are similar to those found for the nickel compound, which was shown to behave as a rigid, rod-like molecule [1].

A structure for the cobalt polymer consistent with all of the data is one which both T^-'s of the monomer unit serve as bridging ligands, using the N(2) and N(3) atoms to bond to adjacent Co^{2+}'s. This mode of bonding would fill four coordination sites on each Co^{2+} and would result in a rod-like molecule. The remaining two coordination positions would then be filled by H_2O. Models show that hydrogen bonding is possible between adjacent waters. If it occurs, it would provide additional structural rigidity. Models also show that steric interactions are minimized if the T^-'s are either all *cis* or all *trans* to each other. If the T^-'s are *cis* to each other, the result is a helical structure in which the repeat distance corresponds to eight monomer units. The same amount of hydrogen bonding is possible in both configurations.

If the molecule behaves as a rigid, rod-like hydrodynamic particle, one may make use of a theoretical relationship between the viscosity increment, ν, and the intrinsic viscosity to deduce the axial ratio for such a molecule [9, 10]. If no hydration is assumed, $[\eta] = \nu\bar{v}$ where $\bar{v}$ is the partial specific volume of the polymer in solution. Measurements of the densities of several polymer solutions yield a value for $\bar{v}$ of 0.94 ml/g. ν for the polymer solution 0.002 *M* in Co^{2+} and 0.02 *M* in T^- after two weeks was 240 ml/g which corresponds to an axial ratio of 72 [7]. Using molecular dimensions calculated from the two proposed structures for the compound, the polymer length is found to be between 570 and 640 Å which corresponds to between 140 and 160 cobalt ions per polymer chain. Even if hydration to the extent of ten to thirty percent by weight of water is assumed, the number of monomers per polymer is found to range from 150 to 120. The fact that all of these estimates are in good agreement with the values for the polymer length obtained from osmotic pressure measurements provides additional evidence that the polymer has a rigid, rod-like structure.

A comparison of the Co^{2+} and Ni^{2+} polymers shows that they have remarkably similar structures and physical properties. However, there are some differences between them. The principal ones are the number of T^-'s per metal ion and their net charges. They also differ in their rates of formation and decomposition in solution. The cobalt compound appears to polymerize more rapidly – as evidenced by the larger values of [η] for solutions with the same metal and ligand concentrations after the same time intervals – and decompose more rapidly when heated. These facts can be explained by considering the structural differences between the two polymers. Instead of a third bridging tetrazolate ligand, the cobalt compound has two waters which can form hydrogen bonds. The waters are presumably coordinated before polymer formation and hydrogen bonds are more easily made or broken than typical metal–nitrogen bonds.

Acknowledgments

We wish to acknowledge support from the donors of the Petroleum Research Fund administered by the American Chemical Society and grants from the National Science Foundation Undergraduate Research Participation Program and the George N. Schuster Foundation.

References

1 L. Richards, S. N. Bow, J. L. Richards and K. Halton, *Inorg. Chim. Acta, 25,* L113 (1970).
2 T. G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils and P. Saltman, *J. Am. Chem. Soc., 88,* 2721 (1966).
3 W. G. Finnegan, R. A. Henry and R. Lofquist, *J. Am. Chem. Soc., 80,* 3908 (1958).
4 Similar pink and yellow forms of complexes formed from substituted tetrazoles and cobalt(II) have been observed before. See for example, H. B. Jonassen, J. O. Terry and A. D. Harris, *J. Inorg. Nucl. Chem., 25,* 2239 (1963).
5 A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam (1968) p. 320.
6 F. Daniels, R. A. Alberty, J. W. Williams, C. D. Cornwell, P. Bender and J. E. Harriman, "Experimental Physical Chemistry", 7th ed., McGraw-Hill, New York (1970) p. 331.
7 C. Tanford, "Physical Chemistry of Macromolecules", Wiley, New York (1961) Chap. 6.
8 J. Brandrup and E. H. Immergut (eds.), "Polymer Handbook", 2nd ed., Wiley–Interscience, New York (1975) Chap. IV-1.
9 R. Simha, *J. Phys. Chem., 44,* 25 (1940).
10 J. W. Mehl, J. L. Oncley and R. Simha, *Science, 92,* 132 (1940).