

Soluble, Polymeric Fe(II) Tetrazolate Complexes

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Received August 8, 1985

Recent investigations have established that 5-phenyltetrazolate** is capable of bridging Co^{2+} and Ni^{2+} ions to form high molecular weight, rigid rod-like polymers which are soluble and stable in solution [1, 2]. To date, these are the only such species reported in the literature. We now wish to report the synthesis and characterization of two additional members of this family of compounds, those containing Fe^{2+} and either 5-phenyltetrazolate or 5-*p*-methylphenyltetrazolate. We also report the preparation of an insoluble compound containing Fe^{2+} and 5-*p*-nitrophenyltetrazolate. The data presented here suggest that the stability of the soluble long chain compounds is related to π -electron effects and that their solubility depends on charge delocalization in the polymer molecule or its ability to form hydrogen bonds to the solvent.

When oxygen-free aqueous solutions of $\text{Fe}(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and sodium 5-phenyltetrazolate (hereinafter NaT) are mixed to yield solutions in which the T^- to Fe^{2+} ratios are ten or more and final Fe^{2+} concentrations range from 0.025 M to less than 0.0025 M, highly viscous red solutions form within hours. Chromophore formation is virtually complete after one day. In contrast to other metal-tetrazolate preparations, no precipitate is observed when the reagents are mixed.

When oxygen-free aqueous solutions of $\text{Fe}(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and sodium 5-*p*-methylphenyltetrazolate (Na *p*- CH_3T) are mixed to yield solutions in which the T^- to Fe^{2+} ratios are ten or more and final Fe^{2+}

concentrations are between 0.025 and 0.0025 M, a brownish-red precipitate of $\text{Fe}(\text{p-CH}_3\text{T})_2 \cdot 3\text{H}_2\text{O}$ forms. *Anal.* Calcd. for $\text{Fe}(\text{p-CH}_3\text{T})_2 \cdot 3\text{H}_2\text{O}$: Fe, 13.05; C, 44.86; N, 26.16; H, 4.71%. Found: Fe, 13.90; C, 44.77; N, 25.59; H, 4.34%. (All analyses were performed by Galbraith Laboratories Inc., Knoxville, Tenn.). If the mixture is kept under N_2 at 6 °C for one or two days, the precipitate dissolves and highly viscous red solutions result.

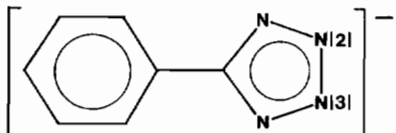
When oxygen-free, aqueous solutions of $\text{Fe}(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and sodium 5-*p*-nitrophenyltetrazolate (Na *p*- NO_2T) are mixed so the *p*- NO_2T^- to Fe^{2+} ratios are ten or more, a bright yellow precipitate of $\text{Fe}(\text{p-NO}_2\text{T})_2 \cdot 9\text{H}_2\text{O}$ forms. *Anal.* Calcd. for $\text{Fe}(\text{p-NO}_2\text{T})_2 \cdot 9\text{H}_2\text{O}$: C, 28.11; H, 4.38; N, 23.41; Fe, 9.34%. Found: C, 28.00; H, 4.38; N, 23.52; Fe, 9.00%. If the mixture is kept under N_2 at room temperature or 6 °C, this precipitate does not dissolve.

The coordination number of the metal and the stoichiometry of the chromophoric unit in the two soluble compounds were determined spectrophotometrically. Visible spectra of solutions in which the ligand to metal ratio was at least ten were recorded. Maximum absorbances were observed at 523 nm ($\epsilon = 180 \text{ M}^{-1} \text{ cm}^{-1}$) and 515 nm ($\epsilon = 220 \text{ M}^{-1} \text{ cm}^{-1}$) for the $\text{Fe}^{2+}/\text{T}^-$ and $\text{Fe}^{2+}/\text{p-CH}_3\text{T}^-$ compounds respectively. These maxima are typical of metal-to-ligand charge transfer bands for low spin, six coordinate Fe(II) compounds in which ligands are bound through a nitrogen [3]. Limiting absorbances were obtained at a ligand to metal ratio of eight for the T^- and ten for the *p*- CH_3T^- compound. Continuous variation studies were conducted in which the mole ratio was varied from zero to one and the total molarity held constant at 0.04 M for the T^- and 0.025 M for the *p*- CH_3T^- compound. In both cases maxima were obtained at mole fraction $\text{Fe} = 0.25$ which corresponds to the monomer formulas FeT_3^- and $\text{Fe}(\text{p-CH}_3\text{T})_3^-$.

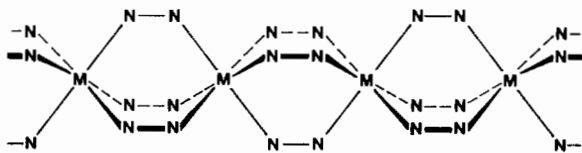
Viscosity measurements were made on both compounds to estimate number average molecular weights using solutions which were 0.004 M in Fe^{2+} and 0.08 M in ligand. At various time intervals after solution preparation, several dilutions were made and their viscosities measured at 20 °C. To determine the intrinsic viscosity, $[\eta]$, for each species, extrapolations to $c = 0$ were made for both $(1/c)(\eta'/\eta - 1)$ and $(1/c) \ln(\eta'/\eta)$ (where c is the concentration of monomer in ml g^{-1} and η' and η are the viscosities of solution and solvent respectively). Values of $[\eta]$ for the T^- compound were 4300 ml g^{-1} after one week and 4900 ml g^{-1} after two weeks. For the *p*- CH_3T^- compound, the values were 1100 ml g^{-1} and 2200 ml g^{-1} , respectively, for the same time intervals.

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**The structure and numbering convention for 5-phenyltetrazolate is



The values for $[\eta]$, coupled with the information on stoichiometry in solution, make it clear that both the T^- and $p\text{-CH}_3T^-$ compounds are soluble polymers of the same type as $(\text{NiT}_3^-)_n$ and have the formulas $(\text{FeT}_3^-)_n$ and $[\text{Fe}(p\text{-CH}_3\text{T})_3^-]_n$, respectively. The backbone structure of all three compounds can be illustrated schematically as follows (where M = metal and only N(2) and N(3) of each ligand is shown):



Values of the number average molecular weight, M_n , were estimated for the soluble Fe^{2+} polymers using the empirical equation $[\eta] = KM^\alpha$ [4] in conjunction with data on the Ni^{2+} and Co^{2+} polymers. For the Ni^{2+} and Fe^{2+} compounds, α is assumed to have the maximum theoretical value for rigid rods of 1.8 because the three covalently bonded bridges per monomer unit are expected to make these polymers extremely rigid. (α for the Co^{2+} polymer, in which one third of the bridges are based on hydrogen bonding, has a value of 1.7 [5].) K was determined to be 5.79×10^7 for $(\text{MT}_3^-)_n$ type polymers from osmotic pressure and viscosity measurements on the Ni^{2+} polymer. An error limit of about $\pm 30\%$ is associated with K because of uncertainty in the osmotic pressure measurements. Average molecular weights for $(\text{FeT}_3^-)_n$ in solutions which were 0.004 M in Fe^{2+} and 0.08 M in T^- are 3.0×10^5 after one week and 3.3×10^5 after two weeks, corresponding to 620 and 670 monomer units respectively. For the $[\text{Fe}(p\text{-CH}_3\text{T})_3^-]_n$ polymer the corresponding values for the same solution concentrations and time intervals are 0.9×10^5 (190 monomers) and 1.1×10^5 (220 monomers).

When the data on the iron compounds are combined with those available for other metal tetrazolate compounds, three general observations about these species may be made. First, reactions of metal ions with tetrazolates in solution usually result in the formation of insoluble compounds which analyze as ML_2 (L = ligand). This phenomenon is observed for compounds containing both unsubstituted [6] and substituted tetrazolates such as 5-trifluoromethyl [7], 5-nitro and 5-chloro [8], and 5-amino [9] as well as the 5-phenyl and substituted 5-phenyltetrazolates [1, 2, 10]. Little is known about the structures of the ML_2 solids except that the tetrazolates appear σ -bonded to the metal [11]. Second, soluble metal-tetrazolates appear to form only when the tetrazolate has a phenyl group substituted in the five position and the solvent is water. However, the presence of the phenyl group does not invariably result in a soluble polymer. Third, of the first series transition metals, only 2+

ions with d^6 , d^7 , d^8 and d^9 electron configurations (*i.e.* Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+}) are known to produce the highly viscous solutions which indicate the presence of rod-like polymers.

Since soluble polymers appear to form only when the ligand has a large delocalized π system and the metal has a minimum of six d electrons which, in low spin octahedral complexes completely occupy the t_{2g} orbitals (which are also of π symmetry), it is likely that π effects play an important role in determining the stability of these systems. Given the structures of the soluble polymers, overlap of the ligand π^* and metal t_{2g} orbitals could create a single delocalized π system extending over the whole molecule. Such a system would serve to stabilize the polymer if the overlap is large enough and a favorable amount of electron density is present.

The phenyl group on the tetrazolate ring may serve to increase the π^*-t_{2g} overlap by changing the energies of the ligand π^* orbitals. Since it is generally considered an electron donor, it may also provide more electron density to the extended π system. The fact that Fe^{2+} does not form a soluble polymer when the phenyl group is substituted with the electron-withdrawing nitro group may indicate that the minimum electron density needed for compound formation is provided by a d^6 ion and the 5-phenyltetrazolate ligand.

The solubility of the $(\text{ML}_3^-)_n$ polymers is probably a result of the charge on the polymer and the ability of the aromatic π system of the ligand to delocalize that charge. Presumably the interaction between water and the partial charge on the phenyl group is sufficient to stabilize the polymer in solution. The solubility of the neutral cobalt polymer, $(\text{CoT}_2(\text{H}_2\text{O})_2)_n$, may derive from the ability of the two waters per monomer unit to form hydrogen bonds to the solvent.

Acknowledgements

We wish to acknowledge support from the donors of the Petroleum Research Fund administered by the American Chemical Society and grants from the City University of New York, PSC-CUNY Research Award Program, the George N. Shuster Foundation, and the President's Research Award Program of York College.

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