Inorganica Chimica Acta, 25 (1977) L113–L114

A Soluble, Polymeric 5-Phenyltetrazolate-bridged Ni(II) Complex

L. RICHARDS,* S. N. BOW**

Department of Chemistry, York College of the City University of New York, Jamaica, New York 11451

J. L. RICHARDS,* K. HALTON

Department of Chemistry, Herbert H. Lehman College of the City University of New York, Bronx, New York 10468, USA

Received October 12, 1977

In recent years considerable interest has been expressed in soluble, polynuclear transition metal complexes. A number of soluble complexes containing a few metal centers have been reported [1], but only one high molecular weight complex, an iron/hydroxy/nitrate compound, has been described [2–4]. It was shown to have a spheroidal shape. We wish to report the preparation and characterization of a soluble, high molecular weight polymeric transition metal complex containing Ni^{2+} and 5-phenyltetrazolate which has a rigid, rod-like shape in solution. We believe this to be the first report of a soluble, extended structure polymer containing transition metal ions in its backbone.

When aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and sodium 5-phenyltetrazolate*** (hereinafter NaT) are mixed together so that the final concentration of NaT ranges from near its maximum solubility of 0.6 *M* to less than 10^{-4} *M* and the T^- to Ni^{2+} ratio ranges from 0.1 to 20, a blue precipitate of $NiT_2 \cdot 3H_2O$ forms immediately. *Anal.* Calcd. for $NiT_2 \cdot 3H_2O$: Ni, 14.58; C, 41.71; H, 3.97; N, 27.81. Found: Ni, 13.84; C, 41.56; H, 3.99; N, 27.67. Upon standing some of the blue precipitate dissolves. If the T^- to Ni^{2+} ratio in a solution is at least five, all of the precipitate dissolves after an hour or two to yield a clear, viscous, pink–purple solution. Solutions which are at least 0.25 *M* in T^- cannot be poured at room temperature; those of lower concentration are less viscous and foam readily when agitated. Membrane filtration (membrane pore size 50 Å) of a solution initially 0.02 *M* in Ni^{2+} and 0.2 *M* in T^- yielded a clear material which, when moist, could be stretched in sheet form or pulled out into a long thread. Once formed, all of the solutions are quite stable. They show no signs of decomposition over a period of months at room temperature and they can be heated to 80 °C without visible change. If heated above 80 °C, $NiT_2 \cdot 3H_2O$ begins to precipitate.

A pink–purple precipitate of $NaNiT_3 \cdot 7H_2O$ was isolated from a concentrated pink–purple solution which had been slowly evaporated to dryness by rapidly washing the residue with large amounts of methanol to remove excess NaT. *Anal.* Calcd. for $NaNiT_3 \cdot 7H_2O$: Na, 3.58; Ni, 9.13; C, 39.21; H, 4.51; N, 26.14. Found: Na, 3.34; Ni, 9.12; C, 39.62; H, 4.52; N, 26.48. Solutions with the same final Ni^{2+} and T^- concentrations prepared either by dissolving solid $NaNiT_3 \cdot 7H_2O$ in a NaT solution or by mixing solutions of $Ni(NO_3)_2 \cdot 6H_2O$ and NaT have identical visible absorption spectra. If solid $NaNiT_3$ is allowed to stand in methanol for any length of time, it partially decomposes to the blue NiT_2. Because isolation of pure $NaNiT_3$ is difficult, other studies reported here were conducted on solutions of the compound made by mixing appropriate solutions of Ni^{2+} and T^- without first isolating the solid.

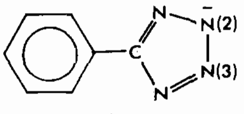
Viscosity measurements were made on 2.00×10^{-3} *M* and 4.00×10^{-3} *M* Ni^{2+} solutions in which the T^- to Ni^{2+} ratio was 20. Measurements were made at 18.0 °C using Cannon–Fenske type viscometers having flow times of 275.4 and 336.9 seconds for water. Reference solutions contained T^- at the same concentration as the corresponding polymer solutions. Densities were measured at 18.0 °C using a 25 ml pycnometer. At various time intervals several dilutions of each parent solution were made and the intrinsic viscosity for the solute, $[\eta]$, was determined by extrapolating the quantities $(1/c)[(\eta'/\eta) - 1]$ and $(1/c)\ln(\eta'/\eta)$ to infinite dilution (η' and η are the viscosities of the solution and solvent respectively and c is the concentration of Ni^{2+} in units of g NiT_3^-/ml). Values of $[\eta]$ for the 2.00×10^{-3} *M* Ni^{2+} solutions at 0.3, 8 and 14 days were 270, 700 and 1400 ml/g respectively. The corresponding values of $[\eta]$ for the 4.00×10^{-3} *M* Ni^{2+} solutions were 1200, 2700 and 3000 ml/g. At longer times viscosities are even greater. Such high intrinsic viscosities suggest that the solute has a high molecular weight and that it may have an extended, rigid structure.* The steady increase in

---

*Authors to whom correspondence should be addressed.

**National Science Foundation Undergraduate Research Program Participant.

***The structure and numbering convention for 5-phenyltetrazolate is as follows:



The sodium salt was made by titrating pure tetrazole [5] to pH 8.2 and flash evaporating to dryness.

*Two notable examples of substances for which $[\eta] > 1000$ ml/g are native collagen (M.Wt. = 3.45×10^5, $[\eta] = 1150$ ml/g) and DNA (M.Wt. = 6×10^6, $[\eta] = 5000$ ml/g). These molecules have relatively rigid triple and double helical structures respectively. Random coil polymers seldom have $[\eta] > 1000$ and when they do their molecular weights are on the order of 10^7 or greater [6].

[η] indicates that molecules are joining to form longer polymeric molecules.

Osmotic pressure measurements were made using a modified Wagner–Schulz osmometer [7]. Readings made after eight days on 2.00×10^{-3} M Ni^{2+} solutions with Ni^{2+} to T^- ratios of 20 indicated there were 150 to 300 Ni^{2+}'s per polymer molecule which corresponds to a number average molecular weight of 0.75 to 1.5×10^5.

The geometry and stoichiometry of the chromophoric species in solution was determined by spectrophotometric studies on solutions of the polymer. The UV–VIS spectrum of the pink–purple viscous solutions shows absorption maxima at 334 nm ($\epsilon = 11.1$ M^{-1} cm^{-1}), 520 nm ($\epsilon = 6.1$ M^{-1} cm^{-1}) and a band which has a maximum at $\lambda > 800$ nm ($\epsilon_{750} = 4.5$ M^{-1} cm^{-1}). This spectrum is consistent with octahedral coordination around Ni^{2+} and is in good agreement with reported spectra for other octahedral Ni^{2+} tetrazolate complexes [8]. Limiting absorbances for the compound were reached when the T^- to Ni^{2+} ratio was seven.

A continuous variation study was conducted in which 5.00×10^{-3} M aqueous solutions of Ni^{2+} and T^- were mixed in various mol ratios and allowed to react overnight. Using Ni^{2+} solutions at the same concentration as references, Job's plot showed a maximum in absorbance at mol fraction $Ni^{2+} = 0.25$ when absorbance was measured at 520 nm and corrected for a small amount of scattering. This maximum corresponds to a T^- to Ni^{2+} ratio of three, which is in agreement with the analysis of solid $NaNiT_3 \cdot 7H_2O$.

When 50 ml aliquots of solutions 2.00×10^{-3} M in Ni^{2+} and 4.00×10^{-2} M in T^- were titrated with 5.00×10^{-3} M NaOH, only one equivalence point appeared between pH 7 and 10. The equivalence point was sharp and corresponded to a Ni^{2+} to OH^- ratio of about 85. Since the solutions being titrated contained only Na^+, T^-, Ni^{2+}, NO_3^- and H_2O, the presence of an equivalence point suggests that water is coordinated to Ni^{2+} in the polymer. If one water is coordinated at each end of the polymer, the titration data indicate the polymer contains 170 Ni^{2+}'s per polymer molecule. Two waters coordinated at each end of the molecule corresponds to 340 Ni^{2+}'s per polymer molecule. These results are in reasonable agreement with number of Ni^{2+}'s per polymer molecule obtained from osmotic pressure measurements.

The above solution data indicate the formula for the polymer is $(NiT_3^-)_n$. The only structure consistent with the data is one in which each Ni^{2+} is bound to another Ni^{2+} by three T^-'s, each acting as a bidentate, σ-bonded bridging ligand. Molecular models indicate that coordination through N(2) and N(3) of the tetrazole ring [9] minimizes steric interaction between phenyl groups. This mode of coordination creates three nearly strain-free, six-membered Ni–N rings per Ni^{2+} which should result in a rigid structure for the polymer. The presence of one or two water molecules at each end of the polymer suggested by titrations and osmotic pressure measurements is consistent with the proposed structure since each end of the polymer has three coordination sites which are not occupied by bridging T^-'s and may be filled with water or monodentate T^-.

The partial specific volume of the polymer was found from density measurements at several concentrations to be 0.73 ml/g NiT_3^-. If the polymer molecule is assumed to behave as a rigid, rod-like hydrodynamic particle, this value may be used in conjunction with intrinsic viscosity data and bond lengths to deduce an average molecular weight for the polymer in solution [6]. If it is assumed that no hydration of the polymer occurs in solution, an average length molecule in an eight day old 2.00×10^{-3} M Ni^{2+} solution is calculated to contain 330 monomer units. However, some hydration of the particle is expected. If ten to twenty percent hydration by weight is assumed, the mean number of monomers is found to range from 310 to 290. All of these values are compatible with those obtained directly from experiment.

In addition to the Ni^{2+} 5-phenyltetrazolate polymer, we have also been able to prepare soluble polymers from Fe^{2+}, Co^{2+}, Co^{3+}, Cu^{2+}, Rh^{3+} and Pt^{2+} and 5-phenyl-, 5-(*p*-nitrophenyl)-, and 5-(*p*-methylphenyl)-tetrazolate. We are now in the process of characterizing these species, several of which appear to have interesting magnetic and redox properties.

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. Shuster Foundation.

1 See, for example, C. Creutz and H. Taube, *J. Am. Chem. Soc.*, *95*, 1086 (1973); H. Fisher, G. M. Toma and H. Taube, *ibid.*, *98*, 5512 (1976); G. Kolko, C. R. Frihart, H. N. Rabinowitz and S. J. Lippard, *ibid.*, *98*, 5720 (1976); N. S. Lewis, K. R. Mann, J. G. Gordon II and H. B. Gray, *ibid.*, *98*, 7461 (1976).

2 T. G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils and P. Saltman, *ibid.*, *88*, 2721 (1966).

3 S. E. Allerton, J. Renner, S. Colt and P. Saltman, *ibid.*, *88*, 3148 (1966).

4 T. G. Spiro, G. Bates and P. Saltman, *ibid.*, *89*, 5559 (1967).

5 R. A. Henry and R. Lofquist, *ibid.*, *80*, 3908 (1958).

6 Charles Tanford, "Physical Chemistry of Macromolecules", Wiley, New York, N.Y. (1961) Ch. 6.

7 A. Weissberger and B. W. Rossiter, eds., "Physical Methods of Chemistry", Vol. I, Part V, Wiley–Interscience, New York (1971) p. 333.

8 N. A. Dougherty and C. H. Brubaker, Jr., *J. Inorg. Nucl. Chem.*, *22*, 193 (1961).

9 Other workers have observed this mode of bonding: A. Gaughan, K. S. Bowman and Z. Dori, *Inorg. Chem.*, *11*, 601 (1972).