Inorganica Chimica Acta, 26 (1978) L10

Simple Method for the Separation of Meso and Racemic 2,3-Butanediamines

E. J. BILLO and J. R. VITIELLO

Department of Chemistry, Boston College, Chestnut Hill, Ma. 02167, U.S.A.

Received November 12, 1977

The ethylenediamine analog, 2,3-butanediamine (bn), has been the subject of many studies of the effect of steric crowding on complexation equilibria or kinetics [1]. *Meso* and *d,l* isomers of this ligand are possible; reduction of dimethylglyoxime with Raney nickel yields the *m*-bn and *dl*-bn in about 3:1 ratio. The isomers have been separated by fractional crystallization of the dihydrochlorides from anhydrous methanol [2], the solubility of *m*-bn being 0.7 g/100 cm^3 while that of *dl*-bn is 7 g/100 cm^3. Separation by fractional crystallization is time-consuming, and although the *meso* isomer could be obtained quite pure, we found that the *d,l* isomer was difficult to free from the less soluble *meso*.

We report a simple procedure for purification of *dl*-bn, based on the difference in formation constants of the nickel(II) tris chelates of the isomeric diamines.

When *dl*-bn forms a five-membered chelate ring with a metal ion, both methyl substituents can occupy equatorial positions, minimizing steric repulsions. The *meso* isomer, however, is unable to adopt such a favorable conformation. As a result, the formation constants of the *m*-bn chelates are significantly smaller than those of *dl*-bn. The formation constant difference is particularly great for formation of the tris complexes: $\log K_3$ (*dl*-bn) = 4.31, $\log K_3$ (*m*-bn) = 2.89 for Ni(II) [3]. Hence, when Ni^{2+} reacts with a mixture of the isomeric diamines, the tris chelate which is isolated is the more stable *dl*-bn complex.

Procedure

The diamine mixture was obtained from the Wyandotte Chemicals Corporation or was synthesized [2]. The dihydrochloride salt of the isomer mixture was prepared by addition of concentrated HCl to an aqueous solution of the diamine, followed by evaporation. The solid was extracted twice with boiling absolute methanol and the residue (*m*-bn) recrystallized from methanol. The combined extracts were concentrated and impure *dl*-bn, containing a significant amount of the *meso* isomer, was recovered. The purity of the isomers was established by NMR (D_2O solvent): *m*-bn showed a sharp doublet at 1.64 and 1.53 ppm, while the impure *dl*-bn, even after several recrystallizations, exhibited a doublet at 1.58 and 1.48 ppm, with a weak pair of lines at the *m*-bn positions.

To 12.5 g of the impure *dl*-bn dihydrochloride (0.078 mol) in 40 ml of water was added 7.6 g of $Ni(NO_3)_2\cdot 6H_2O$ (0.026 mol) and 8.5 ml of saturated NaOH solution. The violet tris complex which crystallized was filtered and while still moist* was placed in a flask, excess saturated NaOH added, and the released diamine steam-distilled. The dihydrochloride may be isolated from the concentrated aqueous distillate. NMR of the dihydrochloride in D_2O showed a single sharp doublet at 1.58 and 1.48 ppm, with no detectable *meso* isomer.

Acknowledgment

We thank Dr. W. K. Langdon of Wyandotte Chemicals Corporation for a gift of 2,3-diaminobutane.

References

1 See for example L. D. Pettit and J. L. M. Swash, *J. Chem. Soc. Dalton Trans.*, 697 (1977); F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York (1967) p. 162.

2 F. H. Dickey, W. Ficket and H. J. Lucas, *J. Am. Chem. Soc.*, *74*, 944 (1952).

3 L. G. Sillen and A. E. Martell (eds.), "Stability Constants", The Chemical Society, London (1964).

---

*Organic nitrate salts are potentially explosive. It is not recommended that the complex be dried.