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Prepration of Dimethyldithiocarbamate(DMC) by Reductive Disulfide Bond Breaking of Tetramethylthiuram(TMT) Disulfide in Presence of Mg++

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Abstract

The Mg(II) complex [Mg2(DMC)2((μ-DMC)2] has been synthesized directly from thiram ligand, containing a disulfide bond and characterized by elemental analysis and spectroscopic methods. Surprisingly thiram, undergoes a reductive disulfide bond scission upon reaction with Zn2+ in methanolic media to give the Mg complex. The crystal structure of Mg++ complex has been determined by single crystal X-ray diffraction. Mg is +2 coordinate, with four nearly identical tetrahedral bonds and a longer fifth bond being similar to some reported [Mg(dtc)2(L)] complexes. The crystal structure of this complex is built up of dimeric units, [Mg(dmdtc)(μ-dmdtc)2], so that each unit has two thiocarbamate groups, one wholly bound to a zinc atom as a bidentate ligand and the other in a bridging coordination mode between the two Mg++ atoms. This structure clearly shows scission of the disulfide bond in the thiram ligand to give two dimethyldithiocarbamate ligands coordinated to the Mg(II) ion.

Keywords: DMC, TMC , Ligand etc,

Introduction

Dithiocarbamates are an important class of compounds with a variety of chemical properties and biological effects that are utilized in agriculture as fungicides and pesticides, in rubber chemistry, and in therapeutic applications such as the treatment of alcoholics, acute metal poisoning, and Wilson’s disease . The most prevalent therapeutic application of these compounds is in the treatment of alcoholics with disulfiram (N,N-tetraethylthiuram disulfide).chelation to the copper containing enzyme aldehyde dehydrogenase . Such redistribution of zinc may be explained based on the formation of lipophilic metal chelates In this work, we report the synthesis and characterization of Mg(II) dithiocarbamate complex using an analogue of disulfiram, i.e. thiram as the ligand source which undergoes concomitant S-S bond scission and coordination to Mg(II).

Experimental-

Infrared spectra from KBr pellets were collected on a FT-IR JASCO 680 plus spectrophotometer in the range 4000-400 cm-1. UV-Vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. 1H NMR spectra were obtained on a Bruker AVANCE III 400 spectrometer (400 MHz). Materials and General Methods Synthesis of [Mg++(dmc)2(μ-dmc)2] RESULTS AND DISCUSSION Synthesis and Characterization [Mh2(DMC)2(μ-DMC)2] was directly synthesized by the reaction of tetramethylthiuram disulfide and Mg(OAc)2.2H2O in a 1:1 molar ratio in methanol/CHCl3 solution. Notably, the disulfide bond is reduced to two dimethyldithiocarbamate ligands, by the reductive solvent (methanol) in the presence of . Description of

of the Structure of [Mg2(DMC)2(μ- DMC)2] The crystal structure of [Mg2(DMC)2(μ-DMC)2] with atomic numbering scheme, and the selected bond distances and angles are listed in Table 2. This complex crystallizes in monoclinic space group C2/c. Chemistry of [Mg2(DMC)2(μ-DMC)2] Compound [Mg2(dmdtc)2(μ-dmdtc)2] Empirical formula C6H12N2S4Mg Formula weight 264 Temperature (K) 100 (2) Crystal system Monoclinic Space group C2/c α (°) 90.00 β (°) 102.192(2) γ (°) 90.00 V (Å3) 2295.72(15) mode between the two Mg(II) atoms. This structure clearly shows that the thiram ligand has undergone scission of the disulfide bond to give two dimethyldithiocarbamate ligands coordinated to the Mg(II) ion in two different coordination modes. Mg is 4+1-coordinate, the four tetrahedral bonds are 2.332 to 2.427 Å, and the fifth bond (Mg1…S4) is 3.062 Å. In the reported [Mg2(dtc)2(μ-dtc)2] complexes the four short bonds are between 3.31 and 3.48 Å while the fifth bonds are mostly 3.82-3.95 Å

Conclusion-

Magnesium dimethyldithiocarbamate complex from tetramethyl- thiuram disulfide (thiram) ligand. The reaction of the disulfide ligand (thiram) with Mg(II) in reductive solvents (alcoholic medium) has led to the reductive cleavage of the S-S bond and formation of dimeric Mg complex, $[Mg_2(dmdtc)_2(\mu\text{-}dmdtc)_2]$.

References-

1. Bednar RA. Reactivity and pH-dependence of thiol conjugation to N-ethylmaleimide -Detection of a conformational change in chalcone isomerase. *Biochemistry.* 1990;29:3684–3690. [PubMed] [Google Scholar]

2. Nagy P. Kinetics and mechanisms of thiol-disulfide exchange covering direct substitution and thiol oxidation-mediated pathways. *Antioxid Redox Signal.* 2013 [PMC free article] [PubMed] [Google Scholar]

3. Nelson JW, Creighton TE. Reactivity and ionization of the active site cysteine residues of DsbA, a protein required for disulfide bond formation in vivo. *Biochemistry.* 1994;33:5974–5983. [PubMed] [Google Scholar]

4. Pinitglang S, Watts AB, Patel M, Reid JD, Noble MA, Gul S, Bokth A, Naeem A, Patel H, Thomas EW, Sreedharan SK, Verma C, Brocklehurst K. A classical enzyme active center motif lacks catalytic competence until modulated electrostatically. *Biochemistry.* 1997;36:9968–9982. [PubMed] [Google Scholar]

5. Gilbert HF. Molecular and cellular aspects of thiol-disulfide exchange. *Adv Enzymol Relat Areas Mol Biol.* 1990;63:69–172. [PubMed] [Google Scholar]

6. Hansen RE, Ostergaard H, Winther JR. Increasing the reactivity of an artificial dithiol-disulfide pair through modification of the electrostatic milieu. *Biochemistry.* 2005;44:5899–5906. [PubMed] [Google Scholar]

7. Roos G, Foloppe N, Messens J. Understanding the pK_a of redox cysteines: The key role of hydrogen bonding. *Antioxid Redox Signal.* 2013;18:94–127. [PubMed] [Google Scholar]

8. Bulaj G, Kortemme T, Goldenberg DP. Ionization-reactivity relationships for cysteine thiols in polypeptides. *Biochemistry.* 1998;37:8965–8972. [PubMed] [Google Scholar]

9. March J. *Advanced Organic Chemistry.* John Wiley. New York: 1985. [Google Scholar]

10. Shaked Z, Szajewski RP, Whitesides GM. Rates of thiol-disulfide interchange reactions involving proteins and kinetic measurements of thiol pKa values. *Biochemistry.* 1980;19:4156–4166. [PubMed] [Google Scholar]

11. Iversen R, Andersen PA, Jensen KS, Winther JR, Sigurskjold BW. Thiol-disulfide exchange between glutaredoxin and glutathione. *Biochemistry.* 2010;49:810–820. [PubMed] [Google Scholar]

12. Houk J, Whitesides GM. Structure reactivity relations for thiol disulfide interchange. *J Am Chem Soc.* 1987.109:6825–6836. [Google Scholar]

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