

SPECIAL ISSUE: ENVIRONMENTAL CHEMISTRY

# Dithiocarbamates as hazardous remediation agent: A critical review on progress in environmental chemistry for inorganic species studies of 20<sup>th</sup> century

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Review

**Abstract** This article provides a critical review and a wide range of applications of dithiocarbamates (DTCs) in environmental samples. The characteristics of DTCs are reviewed with particular emphasis on inorganic speciation studies using state-of-the-art analytical instrumentation coupled with computational methods of analysis.

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## 1. Introduction

Dithiocarbamates (DTCs), a group of small organic molecules with a strong chelating ability toward inorganic species have extensively been used in the agricultural industry for more than 80 years. In recent years their applications have not only become apparent as pesticides and fungicides, but also widely used as vulcanization accelerators in the rubber industry. Moreover, DTCs are also of biological importance due to their antibacterial, antituberculosis and antifungal properties. Their anti-oxidant properties make them even more valuable compounds, among them are disodium ethylenebisdithiocarbamate (commercially known as Nabam), its zinc and manganese complexes

(Zineb and Maneb) and the zinc and iron complexes of dimethyldithiocarbamic acid (Ziram and Ferbam). The insolubility of metal salts (with the exception of sodium and other alkali and alkaline earth metals) and the capacity of the DTCs to form stable metal-complexes are mainly responsible for the extensive use of this class of compounds as superior ligands. Therefore, DTCs exhibit strong binding properties with a number of transition metal ions resulting in stable colored complexes.

Most of these reagents have been employed in the determination of toxic heavy metal ions at trace and ultra-trace levels. The quantitative determination is often carried out by spectroscopy, although other techniques such as gravimetry, fluorimetry, titrimetry, neutron activation analysis (NAA), turbidimetry, voltammetry and chromatography are less widely used.

Today, yearly consumption of DTCs is between 25,000 and 35,000 metric tonnes, and most of the DTCs applied as fungicides are classified by the World Health Organization (WHO) as being hazardous (WHO, 1988 & 2005). Existing reviews merely highlighted an array of analytical methods for the analysis of DTCs and their potential degradation products in

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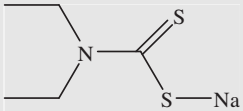
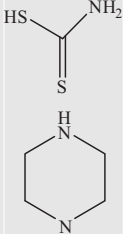
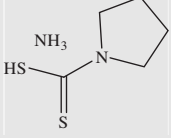
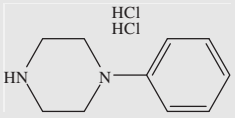
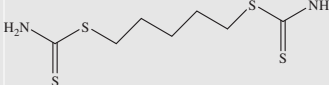
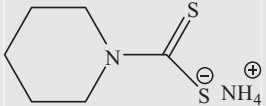
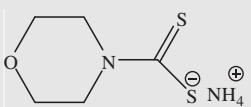
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**Table 1** Structures of DTCs and their physical properties reported in the literature.

DTCs	Structures	Physical properties	Citation
Diethyldithiocarbamate		Molecular weight: 171.26 melting point: 93–95 °C solubility: water	Liu et al. (2000), Cesur (2003), Sarang et al. (2012), Arfana et al. (2012)
Piperazinedithiocarbamate		Molecular weight: 179.05 boiling point: 149.3 °C solubility: water	Cesur et al. (2000)
Ammonium Pyrrolidine dithiocarbamate		Molecular weight: 164.3 melting point: 153–155 °C solubility: water	Gordeeva et al. (2002), Laghari et al. (2010), Ramesh et al. (2002)
Phenylpiperazine dithiocarbamate		Molecular weight: 235.15 melting point: 158–160 °C solubility: water	Cesur et al. (2000)
Pentamethylene dithiocarbamate		Molecular weight: 254.45 melting point: 423.14 solubility: water	Arain et al. (2002)
Ammonium piperidine-1-carbodithioate		Molecular weight: 178.38 melting point: 196–199 °C solubility: water	Venkatasubba Naidu et al. (2011b), Kanchi et al. (2011, 2012, 2013)
Ammonium morpholine dithiocarbamate		Molecular weight: 198.29 melting point: 182–185 °C solubility: water	Venkatasubba Naidu et al. (2011a), Kanchi et al. (2011, 2012, 2013)

environmental samples, pharmaceutical and in foodstuff (Szo-lar, 2007) Accordingly, this review article aims to provide an extensive overview of the inorganic speciation studies of DTCs related to environmental chemistry using a variety of state-of-the-art analytical techniques including the application of computational chemistry to better understand the DTC–metal complexation as a strong remediation agent.

## 2. Chemistry of DTCs

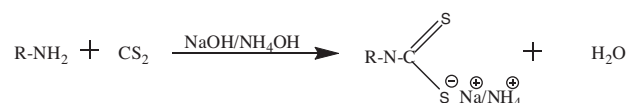
For ease of reference, some of the DTC structures and their physical properties reported in the literature are tabulated in Table 1.

### 2.1. Synthesis of DTCs

DTCs are formed by the exothermic reaction between carbon disulfide and either ammonium or a primary/secondary amine in the presence of sodium hydroxide or excess amine. *N*-substituted dithiocarbamic acids are generally prepared as their

substituted ammonium or sodium salts by the reaction of carbondisulfide (CS<sub>2</sub>) with a primary/secondary amine in alcoholic (Hester and Rohm, 1953) or aqueous solution (Martin, 1959).

In order to conserve the more valuable amine, it is a common practice to use an alkali metal hydroxide to form the salt. Ammonium dithiocarbamate was prepared (Thorn and Ludwig, 1962) by the reaction of ammonia and carbon disulfide as shown in Scheme 1. The free dithiocarbamic acid can be obtained by treatment of ammonium dithiocarbamate with cold acid and decomposes to thiocyanic acid and hydrogen sulfide. Monoalkyldithiocarbamates are formed from the exothermic reaction between carbon disulfide and a monoalkylamine; which after a while decomposes, in alkali solution and more

**Scheme 1** General synthesis reaction of DTCs.

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