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Review

Molecular and supramolecular chemistry of mono- and di-selenium analogues of metal dithiocarbamates

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ABSTRACT

This bibliographic review summarises the coordination chemistry of mono- and di-selenium analogues of metal dithiocarbamate ligands, $[RR'NCS_2]^-$, as revealed by X-ray crystallography and spectroscopy (⁷⁷Se NMR and infrared). The Se-ligands are usually chelating but, bridging modes, up to μ_4 , are known. Reflecting the larger size, greater polarisability and presence of a polar-cap (σ -hole), selenium atoms are more likely to be involved in secondary-bonding (chalcogen-bonding) than sulphur when a competition exists. Isostructural relationships are established across the series in about one-third of the structures.

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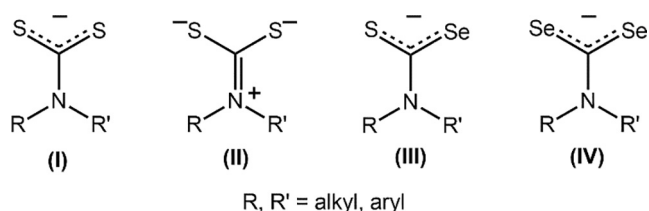
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1. Introduction

Dithiocarbamate ligands, (I), comprise the most important member of the 1,1-dithiolate class of ligands and their metal complexes are ubiquitous in coordination chemistry. The significant contribution of up to 40% of canonical form (II) to its electronic structure make dithiocarbamate ligands very effective chelators for metal centres and thus, practically all accessible elements of the Periodic Table form compounds with the dithiocarbamate ligand. Besides fundamental chemistry, e.g., the ability of dithiocarbamate ligands to stabilise higher than usual oxidation states, traditionally metal dithiocarbamates were of interest for applications such as in the vulcanisation of rubber, in agriculture and as flotation agents in the mining industry. More current applications relate to the exploration of their roles in biology, such as pharmaceutical potential [1,2], e.g., as anti-cancer and anti-microbial agents, radiopharmaceuticals [3] and in chelation therapy [4], as single-source precursors for the production of nanomaterials [5,6] and even for the generation of coordination polymers [7]. Reflecting the above, the structural chemistry of dithiocarbamates has attracted considerable attention for a long time and has been reviewed periodically [8–11].



In comparison to the very widely studied dithiocarbamates, the chemistry of selenium analogues, selenothiocarbamates (III) and diselenocarbamates (IV), is, relatively speaking, in its infancy. While dithiocarbamates are typically and readily prepared by reacting a secondary (sometimes primary) amine with CS₂ in the presence of base (usually alkali metal or ammonia), there are challenges associated with synthesising selenium analogues owing to the need to access C(S)Se and CSe₂, if an analogous procedure is to be followed to those employed for dithiocarbamates. When C(S)Se is available, the reaction to form selenothiocarbamates, with additional precaution, can be carried out as for the preparation of dithiocarbamates [12]. A second procedure, which may be more convenient, has been described very recently [13]. Here, in appropriate stoichiometric quantities, elemental sodium is reacted with selenium powder to generate Na₂Se, followed by reaction with Me₂NC(=S)Cl to form Na[Se(=S)CNMe₂]. The diselenocarbamates are prepared in a similar fashion to that described for dithiocarbamates but, freshly prepared CSe₂ is recommended as are low temperatures and vigorous stirring [14]. The main motivation for synthesising selenium analogues of dithiocarbamates is to generate effective single-molecule precursors for potential semiconductor compounds as detailed below.

Over and above the consideration of molecular structures, secondary-bonding interactions important for supramolecular association have also been identified in the crystal structures described herein. Secondary-bonding interactions are well known and have been periodically reviewed [15–17], including in the context of metal dithiocarbamate chemistry for which it has been shown that steric effects can moderate supramolecular association mediated by M···S interactions leading to distinctive aggregation patterns [18–20]. Beyond structural chemistry, secondary-bonding involving chalcogens, while generally weak, are proven

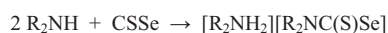
to be of importance in the design of materials and in catalysis [21]. Indeed, there has been renewed interest in recent years in secondary-bonding, mirroring the increasing interest in supramolecular chemistry in general, in fact so much so, that new terms have emerged for secondary-bonding depending on the Group the electrophilic atom belongs to, i.e., tetrel-, pnictogen- and chalcogen-bonding for elements of Groups 14, 15 and 16, respectively [22]. These efforts have led to an explanation of the seemingly curious observation often noted with secondary-bonding in that two ostensibly electron-rich species are engaged in an attractive interaction. This phenomenon can be explained in terms of an anisotropic distribution of electron density leading to a so-called polar-cap or σ-hole concept [23–26]. In the context of the present discussion, for a covalent bond involving a chalcogen (Ch) atom, i.e., R–Ch, the outer lobe of the p-orbital forming this bond has an uneven distribution of electron-density with the region at the tip of the bonding vector being electron-deficient. This effect increases with increasing size of the element and so where competition between sulphur and selenium is possible, selenium would normally participate preferentially in secondary-bonding interactions.

This bibliographic review is arranged in the following manner: the significantly less numerous selenothiocarbamate structures are discussed before the diselenocarbamates. As a general principle, the structures of the oxidation products are described before salts, transition metal complexes and main group element compounds of the respective ligands. Within each category, the complexes/compounds are covered in order of groups of the Periodic Table. Within each group, the structures of lighter elements are described before heavier congeners, binary compounds before mixed ligand species, and neutral molecules before charged species. Data employed in this review were extracted in the form of Crystallographic Information Files (CIF's) with three-dimensional atomic coordinates archived from the Cambridge Structural Database [27] with structural interrogation largely dependent on PLATON [28]. All crystallographic diagrams are original, being drawn with DIAMOND [29]. Structures with disorder were omitted only in cases where the disorder led to ambiguous chemistry. In addition to structures determined by X-ray crystallography, information about structures revealed by ⁷⁷Se NMR spectroscopy and infrared spectroscopy are also included. The use of ⁷⁷Se NMR in research, a tool not usually available in the study of dithiocarbamates, was first reported in 1973 [30] and has enabled the determination of useful structural information in solution of organoselenium compounds in general, and selenothiocarbamates and diselenocarbamates in particular [31,32].

2. Selenothiocarbamate structures

Two general approaches have been established for the synthesis of dialkylselenothiocarbamates. The first of these approaches is directly analogous to the common method used for the synthesis of the corresponding dithiocarbamates, namely the reaction of CSSe with the appropriate dialkylamine, yielding the dialkylammonium salt (Scheme 1).

More recently, owing to the difficulty of obtaining CSSe, dialkylselenothiocarbamates have been prepared from Na₂Se, generated in situ by reaction of sodium and selenium powder, and the corresponding dialkylthiocarbamyl chloride (Scheme 2); see for example [13].



Scheme 1.

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