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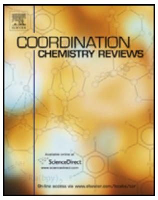

Review

The coordination chemistry of dithiophosphonates: An emerging and versatile ligand class

Werner E. van Zyl[a,*], J. Derek Woollins[b]

[a] School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa
[b] EaStCHEM School of Chemistry, University of St. Andrews, Fife KY16 9ST, United Kingdom

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ABSTRACT

The phosphor-1,1,-dithiolate class of compounds is the heavier and “softer” congener of the more popular phosphonate derivatives. It contains the S_2P functionality as a common feature and several sub-categories are known which include the dithiophosphato $[S_2P(OR')_2]^-$ (R' = typically alkyl), dithiophosphinato $[S_2PR_2]^-$ (R = alkyl or aryl), and dithiophosphonato $[S_2PR(OR')]^-$ (R = typically aryl or ferrocenyl, R' = alkyl) monoanionic ligands. The amidodithiophosphonato derivative of the type $[S_2PR(NR')]^-$, is rare.

Abbreviations: ac-py, acetylpyridine; Ar, 4-anisyl (4-C_6H_4OMe); ^{t}Bu, tertiary butyl; COD, 1,5-cyclooctadiene; Cp, cyclopentadienyl; Cp*, pentamethylcyclopentadienyl; DCM, dichloromethane; DME, dimethylformamide; dppa, bis(diphenylphosphino)amine; dppm, bis(diphenylphosphino)methane; dppe, bis(diphenylphosphino)ethane; dppb, bis(diphenylphosphino)butane; en, ethylenediamine; Et, ethyl; Fc, ferrocenyl; FcLR, ferrocenyl Lawesson's Reagent; LR, Lawesson's Reagent; ^{i}Pr, iso-propyl; Me, methyl; OAc, acetate; Ph, phenyl; py, pyridine; solv, solvent; THF, tetrahydrofuran; tptz, 2,4,6-tris(2-pyridyl)-1,3,5-triazine.

* Corresponding author.
E-mail address: vanzylw@ukzn.ac.za (W.E. van Zyl).

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Potential dianionic monoester variants such as $[H_2S_2P(=Q)(OR)]$ and $[H_2S_2P(=Q)R]$ (Q = O, S) have also been investigated. This review focuses on the dithiophosphonato $[S_2PR(OR')]^-$ ligand derivatives which have emerged as an interesting ligand choice to investigate coordination complexes. This review summarizes all reported coordination compounds utilizing dithiophosphonates with an emphasis on structure and coordination modes. It is apparent that the vast majority of compounds reported to date center around only certain metals and a large section thus remain unexplored, leaving tremendous scope and opportunity for further investigation.

1. Introduction

Dithio-organophosphorus compounds have found widespread use, not only in basic academic research, but also in diverse and important industrial areas. Applications range from anti-oxidant additives in the oil- and petroleum-industry [1] particularly zinc dithiophosphates used as a lubricant additive (anti-oxidant) for the past 60 years [2,3] paving the way for new technology [4]; agricultural pesticide derivatives [5,6]; and metal ore extraction reagents and flotation agents in the mining industry [7]. Within the realm of "green chemistry", Anastas and co-workers recently suggested a structural modification in organophosphorus compounds to reduce toxicity could be achieved by replacing the present oxono analogs as acetylcholinesterase (AChE) inhibitors by the less reactive thiono analogs [8]. Aspects of the related thio- and selenophosphinic acid [9] and xanthate [10] ligands has been reviewed, but the last detailed review that covered the title ligand class as a subset of other compounds occurred in 1995 and included only 5 entries [11]. During the past two decades, however, research endeavors facilitating the formation of monoanionic dithiophosphonato ligands of the type $[S_2PR(OR')]^-$, and their systematic study as useful complexing agents for transition metal centers have grown substantially. An updated review of the topic is thus highly desirable. The present review covers all the reported coordination complexes of dithiophosphonato ligands until mid-2012 and focuses on those compounds that contain reported X-ray crystal structures.

2. Dithiophosphonates as a class of phosphor-1,1-dithiolates

The chemistry of the symmetrical dithiophosphato, $[S_2P(OR)_2]^-$ and dithiophosphinato, $[S_2PR_2]^-$ ligands has been well developed [12–19], with reviews specifically aimed at antimony, arsenic and bismuth as well [20–22]. The dithiophosphonato ligand, $[S_2PR(OR')]^-$, however, is far less developed but of interest mainly for the following reasons: (i) it can still be considered comparatively rare in the chemical literature and indeed for the majority of main- and transition-metals scarce to non-existent; (ii) from the reaction between common dimeric precursors (usually Lawesson's Reagent), and any compound that contains a primary or secondary alcohol functionality, a tremendous number of new and varied derivatives can be obtained in a facile manner; (iii) the synthetic methodology allows for control in the design of the ligand (with respect to solubility and materials properties, and steric effects) to perform reactions and yield new products in both organic and also aqueous phases; (iv) the asymmetric nature of the ligand allows for complex *isomers* to be formed which often impose a unique challenge, a feature not possible for the aforementioned symmetrical ligands; and (v) solution and solid state ^{31}P NMR spectroscopy is a valuable tool to obtain mechanistic and structural information.

2.1. Nomenclature

The phosphor-1,1 dithiolate class of compounds is varied and include, among others, the dithiophos*phat*es **A**, dithiophos*phin*ates **B**, dithiophos*pho*nates **C**, and related amidodithiophos*pho*nates **D**, shown with delocalization of electron density across the S—P—S bonds in Chart 1. The dithiophosphonato ligand, **C**, may be described as a *hybrid* of **A** and **B** and represents the major ligand type that is the subject of this review.

For several decades the nomenclature for metal dithiophosphonates has been inconsistently applied. In this regard phosphonic acid, $HPO(OH)_2$, is the parent acid of the phosphon*ate* anion, $[HPO_3]^{2-}$ from which all title ligands in this review are derived. The IUPAC systematic name for $HPO(OH)_2$ is hydridodihydroxydooxidophosphorus while its common name is phosphonic acid. Systematic names are thus seldom used, instead so-called "preferred IUPAC names" (PIN) are used. A PIN is a name that is preferred among two or more IUPAC names, but "the existence of preferred IUPAC names does not prevent the use of other names..." [23]. This implies that as long as there is no ambiguity, the reader being addressed must be considered in the type of nomenclature that is used since no single correct form currently exists. Furthermore, the 1990, 2001, and most recent 2005 IUPAC recommendations of *Nomenclature of Inorganic Chemistry* (Red Book) gives no guidance as to the naming of a phosphonate derivative containing a P—C bond and thio infix [24]. More useful information is found in *Nomenclature of Organic Chemistry* (Blue Book), published in 1979, with a 1993 update and the recent 2004 draft Recommendations [25]. According to these recommendations, the acid R(OR′)P(S)(SH) is named a phosphonodithoic acid, and anions are named by changing the 'ic acid' ending to 'ate', i.e. phosphonodithioate, and neutral salts and esters are both named using the name of the anion derived from the name of the acid. This review will use dithiophosphon*ato* when describing a ligand as a formal coordination entity, and dithiophosphon*ate* when referring to an anion, usually in the context of the deprotonated acid.

2.2. Resonance

The dithiophosphonato ligand can be described by the contributing resonance structures shown in Chart 2.

Depending on the metal type, oxidation state and coordination geometry, resonance structures **E**, **F** or **G** typically predominates. Resonance structures **E** and **F** have been observed for complexes where the ligand binds in a μ_1-fashion (anisobidentate) with a dangling sulfur atom, for example, in many Pb(II), Hg(II), and Zn(II) complexes. Resonance structure **G** predominates in many dinuclear Au(I) complexes, as well as in the common Ni(II) isobidentate chelating mononuclear complexes. Evidence of **G** is usually shown by the two equal P—S bond lengths in the solid state. Structure **H** is unknown for metal dithiophosphonates but included here for completeness as the result of a study by Drew et al. where a comparison in donor strength between dithiophosphates and dithiocarbamates were made [26]. A difference between these two dithio-species was rationalized [27] by proposing the dithiocarbamates, $[S_2C{-}NR_2]^-$, have two negative charges on the sulfur atoms, and a positive charge on the nitrogen (related to **G**), giving enhanced electron density on the sulfur atoms while in resonance **H** "the electron density is diminished by back-donation from the sulfur to the 3d orbitals