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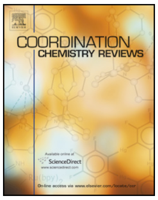

Review

Recent advances in multinuclear metal nitrosyl complexes

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Contents

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This manuscript is dedicated to Prof. Peter C. Ford for his wisdom and friendship.

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ABSTRACT

The coordination chemistry of metal nitrosyls has expanded rapidly in the past decades due to major advances of nitric oxide and its metal compounds in biology. This review article highlights advances made in the area of multinuclear metal nitrosyl complexes, including Roussin's salts and their ester derivatives from 2003 to present. The review article focuses on isolated multinuclear metal nitrosyl complexes and is organized into different sections by the number of metal centers and bridging ligands.

1. Introduction

Nitric oxide (NO) is a gaseous lipophilic radical molecule that plays important roles in several physiological and pathophysiological processes in mammals, including activating the immune response, serving as a neurotransmitter, regulating the cardiovascular system, and acting as an endothelium-derived relaxing factor [1–3]. NO functions in eukaryotes both as a signal molecule at nanomolar concentrations and as a cytotoxic agent at micromolar concentrations [4]. The latter arises from the ability of NO to react readily with a variety of cellular targets leading to thiol S-nitrosation [5], amino acid N-nitrosation [6], and nitrosative DNA damage [7,8].

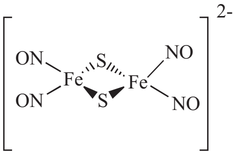
Nitric oxide can readily bind to metals to give metal-nitrosyl (M-NO) complexes [9]. Some of these species are known to play roles in biological NO storage and transport [10–28]. The coordination chemistry of metal nitrosyls has expanded rapidly in the past decades. These complexes have different biological, photochemical, or spectroscopic properties due to distinctive structural features, and are often studied by using electron paramagnetic resonance (EPR), infrared (IR) vibrational frequencies (ν_{NO}), X-ray crystallography, Mössbauer, theoretical calculations, etc. [29–34].

The aim of this review is to highlight advances made in the area of multinuclear metal nitrosyl complexes, including Roussin's salts and their ester derivatives. It summarizes the literature from 2003 to present. There have been several excellent reviews covering different aspects of metal nitrosyl chemistry in recent years [35–42], and we have tried to avoid direct overlap with the subject matter of those articles. This review is focused on recent advances on the synthesis and characterizations of isolated multinuclear metal nitrosyl complexes with structural certainty rather than in situ identifications. It is organized by the number of metal centers and further arranged into different sections based on the type of bridging ligands.

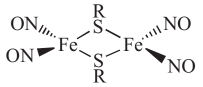
2. Dinuclear metal nitrosyl complexes

2.1. Homodinuclear cluster linked by sulfur – RRS and RRE types

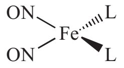
Roussin's Red Salt $[Fe_2(\mu\text{-}S)_2(NO)_4]^{2-}$, (RRS), and Roussin's Red Salt Ester, $[Fe_2(\mu\text{-}SR)_2(NO)_4]$, (RRE), have been known since the mid-nineteenth century [43,44]. They can be considered as the dinuclear form of a dinitrosyl iron complex, (DNIC) [35–46]. The structures of RRS, RRE and DNIC are shown below. RRS and RRE can be generated in situ by directly reacting nitric oxide with proteins containing [Fe–S] clusters, such as rubredoxin and ferredoxin [47]. They were discovered as being bound to the cysteine residues of proteins within body tissues [48]. In addition, the reactions of NO with [4Fe–4S] clusters of Wbl proteins and a Rieske-type protein form RRE [49]. Using synthetic model compounds of [2Fe–2S] and [4Fe–4S], the RRE species were also identified from these reactions [50,51].



RRS



RRE



DNIC

RRE and RRS molecules have been tested for their effects on tumor cell growth and are efficient NO donors that lead to eventual cell death [52,53]. The bactericidal effect on the food-spoilage bacterium *Clostridium sporogenes* is effective in the millimolar range [54]. Some water-soluble RREs act as much slower yet higher stoichiometric NO-release agents with low cytotoxicity toward immortalized vascular endothelial cells [55,56]. Because of many recent discoveries of the biological activities of RRS and RRE, there is a renewed interest in preparing new types of RRS and RRE and investigating their properties.

2.1.1. Preparation and spectroscopic properties of RRS and RRE

RREs may be synthesized through the alkylation of Roussin's Red Salt (RRS) with an alkyl halide or treatment of $Fe_2(\mu\text{-}I)_2(NO)_4$ with an organic thiol compound in the presence of a proton acceptor as shown in Scheme 1 [57].

Lippard et al. reported another way to synthesize RRE. An RRE with *t*-Bu, $[Fe(S\textit{t}Bu)(NO)_2]_2$, **1**, was obtained from the reaction of excess NO with $(Et_4N)[Fe(S\textit{t}Bu)_3(NO)]$. The latter was generated in situ by treating $(Et_4N)_2[Fe(S\textit{t}Bu)_4]$ with 1 mol-equiv. of NO (g) at low temperature (Scheme 2) [58].

Recently we reported two different ways of preparing a series of Roussin's Red Salt Esters $[Fe_2(\mu\text{-}SR)_2(NO)_4]$, **2**, (R = *n*-Pr, **2a**, t-Bu, **2b** or **1**, 6-methyl-2-pyridyl, **2c**, and 4,6-dimethyl-2-pyrimidyl, **2d**). One method is to mix freshly prepared $Fe(NO)_2(CO)_2$ with equal