

Metal-Nitrosophenolato Complexes

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Metal-nitrosophenolato complexes consist of a metal ion (most commonly copper(II)) flanked by typically two or more 2-nitrosophenolate ligands. The syntheses of them demonstrate a privileged introduction of a nitroso (and a hydroxyl via the Baudisch reaction) group to an aromatic ring. These complexes first appeared in the literature as early as 1939, and a range of applications has subsequently been published. However, optimisations of the preparative sequences were not considered, and as such, the reactions have seldom been utilised in recent years; indeed, there remains confusion in the literature as to how such complexes form.

Keywords: C-nitrosation ; copper complexes ; Baudisch reaction ; nitrosophenols ; ortho-nitrosophenols ; regioselective aromatic functionalisation

1. Introduction to Metal-Nitrosophenolato Complexes

Metal-nitrosophenolato complexes consist of a metal ion (most commonly copper(II)) flanked by typically two or more 2-nitrosophenolate ligands. The structures of the nitrosophenols (both as ligands and free molecules) are known to resonate between the nitrosophenol and the quinone-monoxime forms ^{[1][2][3]}. Although the monoxime is considered to dominate, most literature representations display the nitrosophenol form, often for clarity and simplicity. Interestingly, the nitrosophenolato complexes are often highly coloured and reported to possess only limited solubility in most common organic solvents and water. Historically, the complexes have featured in a wide range of publications most often-based upon their colourimetric properties, although in recent years, both the metal complexes and their 2-nitrosophenol ligands have received little attention, becoming an almost forgotten class of molecules. However, one compound that has gained current commercial applicability ^[4] is an iron *tris*(1-nitroso-2-naphtholato), a dye known as 'pigment green 8' (**Figure 1**) ^[5] ^{[6][7]}. This vivid green species has found widespread application in concrete, textiles, paint and rubber colouration.

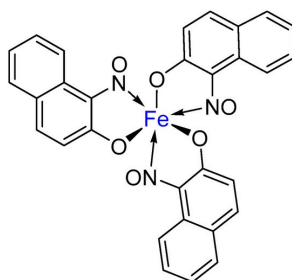


Figure 1. The molecular structure of the commercially available dye, 'Pigment green 8' (aka 'Pigment Green B') ^[6].

2. Metal-Nitrosophenolato Complexes in Nature

Remarkably, substituted iron *tris*(nitrosophenolato) complexes are naturally biosynthesised by particular Streptomyces bacteria as specialised antibiotics ^{[8][9][10][11]}. Ferroverdin (**Figure 2**) was the first confirmed natural product to be isolated ^[8], although this was rapidly followed by the related Viridomycin A, Actinoverdin and Viridomycin E ^[12]. These complexes were found to target certain bacteria by disrupting their cell membranes; however, the free ligands were determined to be more effective than the corresponding iron complexes ^[13]. Interestingly, despite the presence of three negatively charged ligands, the complexes all exist in the Fe(II) oxidation state, with the overall negative charge counterbalanced with a sodium or equivalent cation ^{[9][14]}. It should, however, be acknowledged that this general characterisation is not universally accepted ^[12], and is complicated by the fact that the compounds are redox active and that, although the complexes are largely inert ^[13], ligands can be added/removed under a range of mild conditions ^[14]. Interestingly, these complexes were biosynthesised by the Streptomyces by incubation in a ferrous environment (e.g., with FeSO₄) with carbon sources such as fructose and alanine in an assumingly complex pathway that is not extensively discussed ^[12], phosphate sources were also provided in most cases ^[11]. They were eventually identified as secondary metabolites and did not appear to assist in

the regulatory uptake of iron into the cell [12]. The same iron complexes have now also been synthesised, using Cronheim's copper-mediated nitrosation method (to be discussed in due course), followed by transmetallation to the ferrous complex [12][13][15].

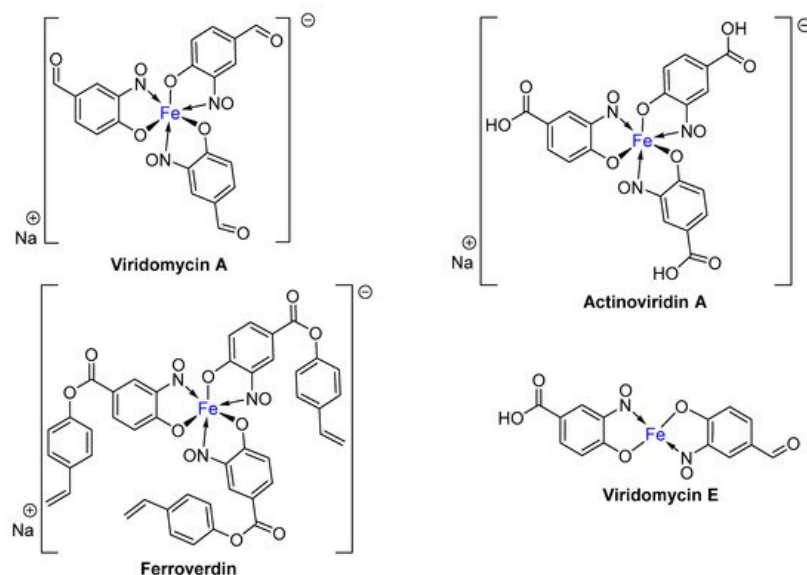


Figure 2. The structures of four antibiotics isolated from *Streptomyces* bacteria, Viridomycin A [13], Actinoverdin A, Ferroverdin [9] and Viridomycin E. Viridomycin E has been described in only a single publication [12] and could well exist preferentially as the hexadentate sodium salt, equivalent to the other 3 examples.

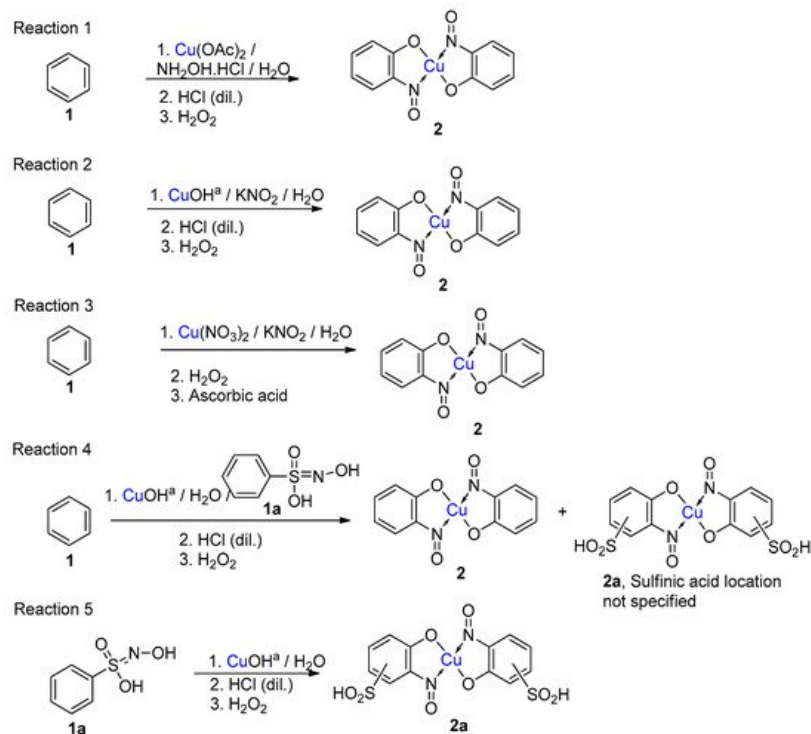
3. A Brief History of Metal-Nitrosophenolato Synthesis

The very first appearance of metal-nitrosophenolato complexes was reported by Eugène Millon [16] in 1849, involving the formation of a mercury(II) complex. As indicated, such complexes are usually highly coloured, which inspired their continued preparation and isolation; indeed, the first fully isolated example appeared as early as 1900, but was originally misidentified as an *ortho*-nitrophenol complex of mercury with four pendant ligands [17]. It has now been comprehensively shown that this isolated compound was actually the corresponding mercuric-nitrosophenolato complex [18][19]. The analytical value of these intensely coloured complexes has over the years been widely exploited via the 'Millon reagent' or 'Millon test'. This test has been used as a qualitative detection method for tyrosine, as well as other phenol functional molecules present in solution [14][17].

The next big development in the preparation of metal-nitrosophenolato compounds was realized by the Austrian chemist, Oskar Baudisch, during the early part of last century [20][21]. The developed synthesis represents a very interesting and novel functionalisation of an aromatic ring (such as benzene), where a hydroxy and nitroso moiety are added with defined *ortho*-regioselectivity. The functional aromatics are formed in the presence of a metal ion, typically copper(I) or (II) and hence post reaction, the compounds remain co-ordinated to the metal, forming a stable dimeric complex (in the case of copper). Advances in the fundamental understanding of this sequence, which has become known as the 'Baudisch reaction', including its underlying mechanism, have been explored in several publications, but the experimental results and conclusions have never been reviewed in a comprehensive fashion, and despite multiple recent advances in copper-mediated nitrosation procedures [22][23], the related Baudisch scheme has been neglected.

4. Introduction to the Baudisch Reaction

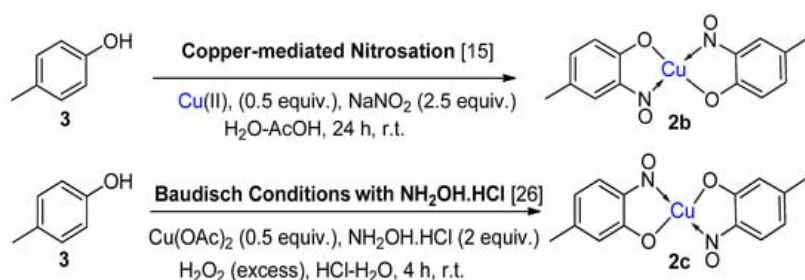
While not being a commonly encountered or formally recognised named reaction, the term 'Baudisch reaction' has become synonymous with specific processes that synthesise metal-nitrosophenolato compounds. In the original reported work, Baudisch employed a range of copper(I) and (II) sources and 'Merck's Superoxol' (historic, commercial name for aqueous hydrogen peroxide) with benzene [20][21]. In addition, either hydroxylamine or a nitrous acid source was further supplied to introduce the corresponding nitroso moiety, hence forming complexes as the end product (Scheme 1 and Scheme 2). Baudisch in his reports proposed that the mechanism was much the same whether hydroxylamine or a nitrite source was used, although findings from later publications to be discussed cast significant doubts over this conclusion.



Scheme 1. Five different reactions (1–5) that Baudisch chose to publish, across two publications, which have subsequently become known as the Baudisch reaction [20][21]. ^aBaudisch states in the literature that ‘freshly prepared yellow cuprous hydroxide’ was used; it is known that this is not a stable entity, so the actual active substance could well be an alternative such as cuprous oxide, Cu_2O .

5. Copper-Mediated Aromatic Nitrosation

An alternative, but related scheme that produces metal-nitrosophenolato complexes converging from phenolic starting materials was reported by Cronheim, several years after Baudisch’s original discoveries [15]. In this reaction aqueous nitrosation conditions (nitrite salt with acid) were used, and hence the process most likely occurs via an aromatic C-nitrosation, where the copper plays a crucial, yet undisclosed, role. This approach has been used to synthesise several derivatives disclosed in other publications and is also therein loosely referred to as the Baudisch reaction [18][24][25]. It should be noted that Cronheim and others’ opinion was that this route was distinct from the Baudisch conditions, as often a different major product is generated under the Baudisch conditions. A representative example which clearly distinguishes between these processes is transposed regioselectivity, as seen in the below transformations (Scheme 2).



Scheme 2. A clear distinction between copper-mediated aromatic nitrosation of phenols and the Baudisch conditions is demonstrated by the reporting of a different major product from the same starting material (3) [15][26].

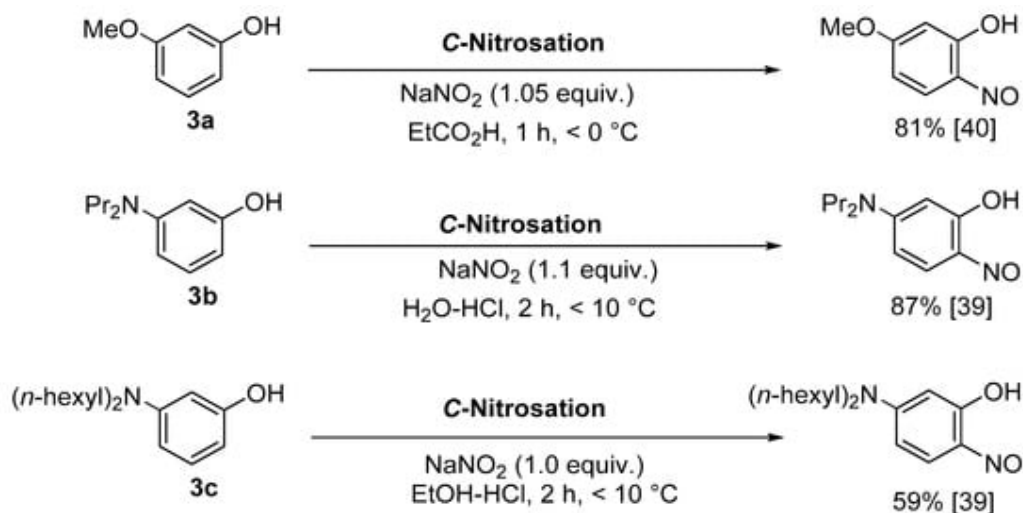
6. Additional Syntheses of Metal-Nitrosophenolato Complexes

A further alternative synthetic approach would be to generate the free 2-nitrosophenol compounds first and then react them in a secondary process with a metal salt (e.g., copper(II) chloride). A copper ion, for example, will readily combine with 2-nitrosophenol under a range of monophasic or biphasic solvent systems, due to the substantial binding affinity [1][15][27]. Indeed, the thermodynamic stability of the copper-nitrosophenolato complexes is such that the biphasic reaction of a ligand in an organic solvent with a copper(II) salt in water is often completed quantitatively in only a few minutes [15]. Free 2-nitrosophenols can be made by partial oxidation of 2-aminophenols, in some cases [28], as well as a simple C-nitrosation of a phenol [27][29][30][31]. The scope of this particular approach however appears limited to certain 5-substituted-2-nitrosophenols and *ortho* nitrosoanaphthols [1][31][32].

In contrast, the ligands can be freed from the complexes through the action of a strong acid. These reactions were demonstrated by Cronheim to show the formation and decomplexation of these complexes, as visualised by substantial colourimetric differences. The recovered yields for the free ligands were not reported; but Cronheim described 'relatively low yields', which is expected due to the nitrosophenol compounds' strong ligand binding affinity and the temperamental acid-stability of the free ligands. A much improved technique allowing simple isolation of the 2-nitrosophenol involves the use of a copper-scavenger, which coordinates with a higher binding affinity and thus selectively displaces the chelating nitrosophenol ligands [24].

The ligand-metal association method is not as applicable as might first be expected due to problems with isolating the free 2-nitrosophenol compounds. Indeed, there are only very limited experimental procedures documenting the preparation and isolation of 2-nitrosophenols. It is a common misconception that C-nitrosation of phenols predominantly produce the corresponding 2-nitrosophenol regioisomer, as per the general expectation for an S_EAr process [29][33][34]. Conversely, unless there is a blocking group at the 4-position or a very strongly directing or bulky group at the 3-position, nitrosation of phenols occurs almost exclusively *para* to the hydroxyl group [35]. This occurs because even though the 2-nitrosophenol is the kinetic product, owing to the ability of the nitroso group to undergo migration to a more favourable position of the Wheland intermediate, the thermodynamic 4-substituted product is almost the sole isolated adduct [21][36]. It should also be noted that examples of 4-substituted-2-nitrosophenols are still relatively rare and mainly historical, the one recent publication [37] describing the preparation, isolation and characterisation of four such compounds has since been retracted, hence the existence of these compounds remains unconfirmed. Electronics also play an important role as aromatics with electron-withdrawing substituents are generally inert to nitrosation (hence why poly nitrosation is rarely observed), to a greater extent even than nitration [38], with toluene being about the least electron-rich aromatic known to undergo C-nitrosation [28][32][34].

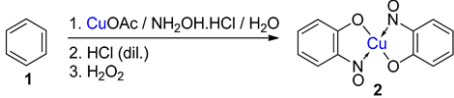
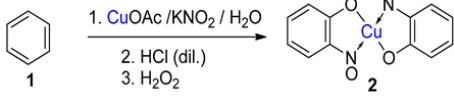
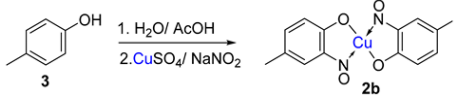
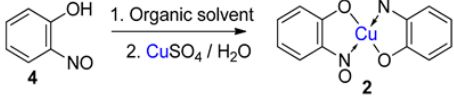
This preference for *para*-nitrosation is seemingly altered in the Baudisch conditions where the formation of a complex stabilises the 2-nitrosophenol ligand against rearrangement. Complexation also helps prevent condensation/decomposition or oxidation to the nitro derivative [18][36], factors which likely explain why free 2-nitrosophenol compounds are so rarely reported and characterised in the literature. Despite their highly reactive nature, a small collection of publications describe the synthesis and isolation of 2-nitrosophenols possessing a meta substituent, rather than a *para* 'blocking' group (Scheme 3) [31][39][40]. In each case, the metal substituent was a π -donor comparable in strength to or exceeding the phenol directing group, hence attenuating the natural preference for *para*-nitrosation relative to the phenol.



Scheme 3. Three literature procedures for the successful synthesis, isolation and characterisation of 3-substituted-2-nitrosophenols [39][40]. Yields refer to pure, isolated compounds.

Consequently, not all metal-nitrosophenolato complexes can be formed when metal salts are combined with free 2-nitrosophenols [41]. Several failed attempts to synthesise complexes have been reported [1]; however, investigating the experimental approach it is not clear if this was as a result of complex instability or actually unsuccessful synthesis of the ligand in the first place. In general, there are four principal synthesis routes to the discussed complexes, and although their preparations can be problematic, the corresponding complexes can often be readily obtained by simple precipitation. Some representative reaction conditions are summarised in **Table 1** and will be discussed further in more detail subsequently.

Table 1. General conditions reported to produce metal-nitrosophenolato complexes, highlighting a representative copper example for each case.

Description	Accepted Starting Materials
<p>Baudisch conditions with hydroxylamine</p> 	<p>A range of aromatics including benzene, phenols, catechols, naphthalenes and phenylsulfonic acids [20][42][43].</p>
<p>Baudisch conditions with nitrous acid</p> 	<p>Shown to accept benzene. Similar aromatics expected to work, though scope not investigated [20].</p>
<p>Copper-mediated aromatic nitrosation</p> 	<p>Phenols with sufficiently electron-rich aromatic ring and at least one non-functionalised carbon atom <i>ortho</i> to the phenol [15][41].</p>
<p>Association of free 2-nitrosophenols with copper</p> 	<p>Stable 2-nitrosophenol compounds [1][15][41].</p>

All experiments can be conducted at room temperature.

7. Scope of Metal-Nitrosophenolato Synthesis

While the mechanism of the Baudisch reaction implies that almost any aromatic should be able to form a copper-nitrosophenolato complex, in practice, the Baudisch conditions have not been extensively investigated for their scope. More commonly, this approach has been relegated in favour of either the copper (or other metal)-mediated phenol nitrosation procedure or the direct complexation of the free-ligand with a metal salt (it is worth noting that these latter schemes are still often unhelpfully referred to as the 'Baudisch reaction'). For this reason, there is often a strong correlation between the number of available literature references for a given nitrosophenol ligand and that of the related metal complex. The exception is for 4-substituted-2-nitrosophenols, such as 4-chloro-2-nitrosophenol, where there has been no reliable confirmation of existence for the free ligand, whereas the corresponding metal complex has been repeatedly reported. The sub-class of *o*-nitrosonaphthols appears to form the most popular complexes, probably because several *o*-nitrosonaphthols are more stable and are also commercially available [44]. A range of metals have thus been utilised in their complexation. Historically, these were initially smaller, first-row transition metals, though larger metals have subsequently been found to form complexes too, including (but not limited to) gold [15], palladium [45], ruthenium [46] and more recently even samarium [47].

8. Properties of Metal-2-Nitrosophenolato Complexes

One of the first publications highlighting the properties of a vast assortment of metal-nitrosophenolato complexes came from German chemist, Georg Cronheim [15], whose team prepared and analysed over 50 different complexes. It was also suggested in this seminal publication that the free 2-nitrosophenol ligands were isolated from these complexes; however,

yields, purities, stabilities or structural data were not provided to support this statement. It was found that stable complexes formed with a variety of metal +2 centres, especially mercury(II), nickel(II), iron(II), cobalt(II) and palladium(II). Other metals in different oxidation states, including silver(I) and gold(III) were also found to have affinity for the free 2-nitrosophenols. Interestingly, if insufficient free nitrosophenol was present for complete conversion to the *bis*-ligated complexes, mono-ligated complexes were selectively formed. These could be easily distinguished by their different solubilities, because the bi-ligated complexes were organic soluble but not aqueous, and the reverse was true for the mono-ligated. The majority of the complexes reported were prepared using Baudisch conditions; however, as 4-substitued-2-nitrosophenolato complexes cannot be made in this way, they were instead generated using what appears to be the first record of a copper-mediated nitrosation of phenols procedure (excluding examples of the Millon test [16]).

A later study, by Charalambous et al. [41], investigated the properties of additional metal-2-nitrosophenolato complexes and addressed some of the common misconceptions made in the earlier literature. Using infrared spectroscopy, it was discovered that the nitrosophenol ligands readily tautomerise to the more favoured *o*-benzoquinone monoxime structure (Figure 3), and the same is true for the free nitrosophenols [29].

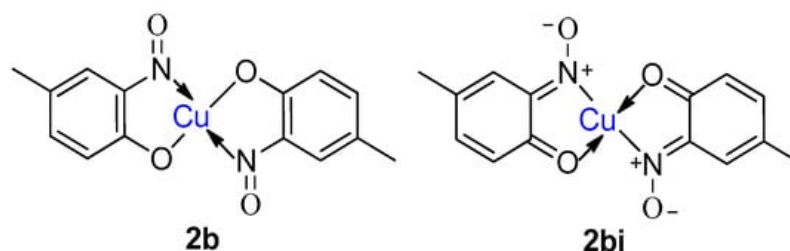


Figure 3. The possible tautomers of copper(II) *bis*(4-methyl-2-nitrosophenol), (2b, 2bi).

It was not possible at the time to determine whether the metal atom coordinated to the nitrogen or the oxygen atom of the nitroso group. It has now been confirmed using single crystal X-ray diffraction (XRD) analysis that coordination is through the nitrogen (Figure 4) [29][48]. A Jahn-Teller distorted octahedral geometry is adopted, with the two aromatic ligands forming an equatorial plane and the axial positions occupied due to oligomerisation, with the phenolic oxygen typically as the donor, although its distance is a little outside the primary coordination sphere of the copper and instead within the Van der Waal's radii [49]. This structure occurs for only completely dried, anhydrous compounds, otherwise a water (or another solvate, e.g., ethanol) is found sitting at the apex of the structure in the place of a neighbouring phenol oxygen. Almost all other published structures (where two nitrosophenolato ligands are present, with a single additional small donor) share the back-to-back square-based pyramid geometry, apart from one example, which reports a distorted trigonal bipyramid [50].

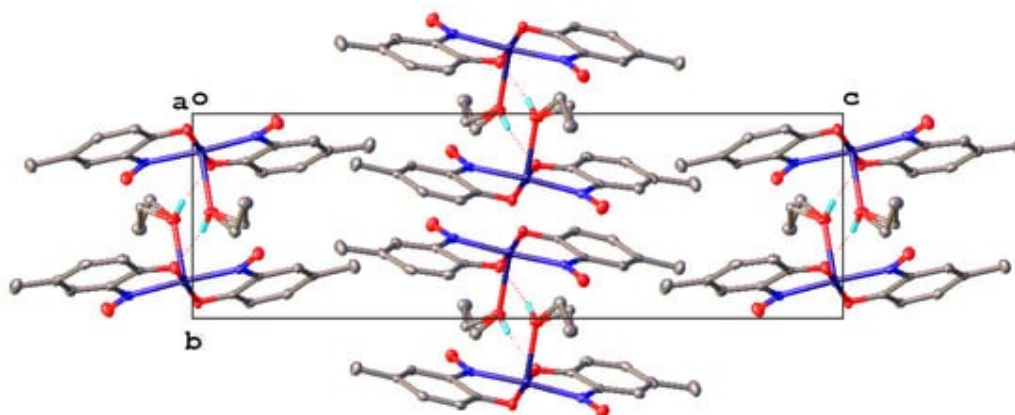


Figure 4. The unit cell of the obtained crystal structure of copper(II) *bis*(4-methyl-2-nitrosophenol) with ethanol as a solvate [41][51].

In all cases studied, when the copper complex is prepared the system tends to adopt a *bi*-ligated dimer unit as a maximum whereas other metals, such as the higher oxidation states of cobalt(III) or the larger iron (II or III) ions have been known to accommodate an additional nitrosophenol ligand, i.e., retaining an octahedral hexacoordinate structure bearing 3 ligands (Figure 5) [52] (although with nitrosophenols bearing larger substituents, e.g., 4-bromo-2-nitrosophenol, complexes remain *bis*-ligated, at least with Co(III)) [53]. These findings were fully supported by elemental analysis and UV-VIS absorbance data and proved at the time most revealing as up to this stage all complexes were assumed to be limited to just one or two nitrosophenol ligands [3][43].

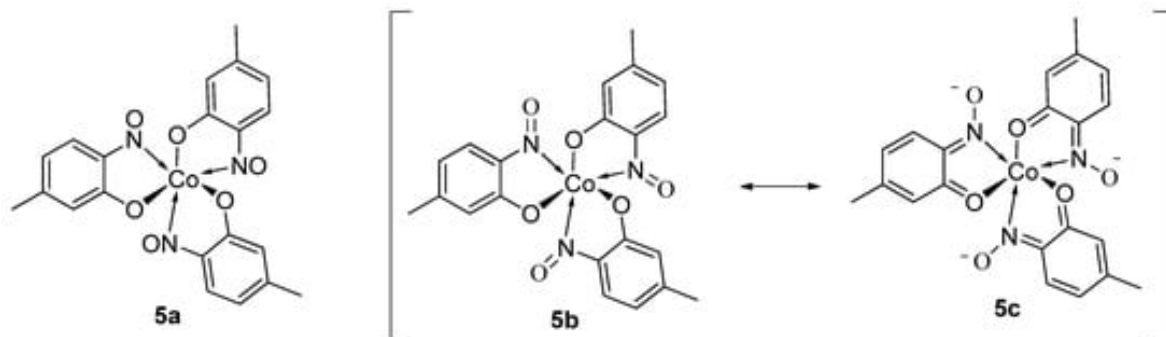
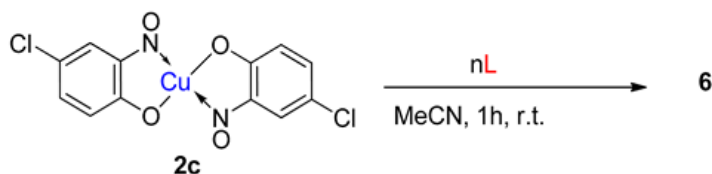


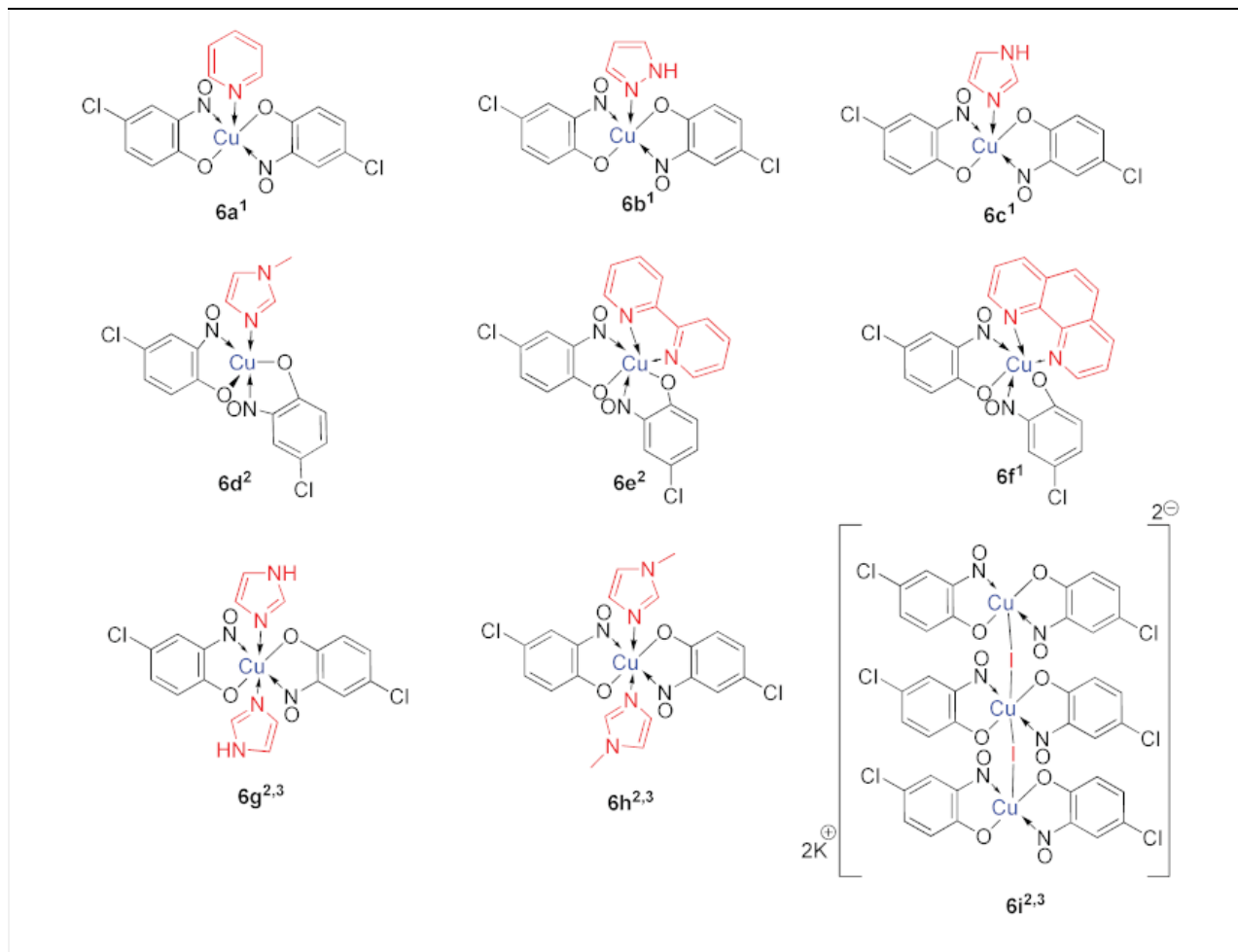
Figure 5. The suggested structure of Cobalt(III) *tris*(4-methyl-2-nitrosophenolato) (**5a**) as specified in the publication by Mahmoud et al. and tautomeric forms (**5b,c**) indicating potential hydrogen bond donor sites ^[54].

9. Derivatisation of Complexes

While the organic nitrosophenolato ligands have enormous affinity for small metallic ions, like Cu(II), researchers have been able to derivatise the complexes with additional, neutral ligands. Cronheim first used pyridine as an auxiliary ligand to alter complex solubility ^[15], noting that the new compounds could be formed by simply mixing the copper (or other metal) nitrosophenolato complex with pyridine. Castellani et al. also synthesised several new complexes with additional neutral amine bases, again by simply stirring the parent complex at room temperature in acetonitrile, with a slight excess of the Lewis base (**L**, **6a–f**, **Table 2**) ^[55]. Later, it was discovered that 6-coordinate complexes could be generated by additionally heating the complex with three equivalents of imidazole or *N*-methylimidazole in refluxing acetonitrile (**6g,h**, **Table 2**) ^[50] in order to overcome the interaction of the copper centre with a neighbouring phenolic oxygen atom. Other notable derivatisations recorded include the synthesis of a potassium (μ -iodo) copper nitrosophenolato complex, which comprises copper in both its octahedral and square-based pyramid geometries, bound by two bridging iodides (**6i**, **Table 2**) ^[56].

Table 2. A range of derivatised complexes generated by Castellani and co-workers, starting from copper *bis*(4-chloro-2-nitrosophenolato) with amine Lewis bases ^{[55][56]}.





¹ supported by elemental analysis data. ² supported by a solved crystal structure from XRD analysis [55][56] as well as elemental analysis data. ³ synthesised by refluxing starting complex with 3 equiv. of ligand in MeCN rather than by stated scheme.

The complexes have also been shown to undergo transmetalations. Tamura et al. [18] report the conversion of mercury *bis*(4-methyl-2-nitrosophenolato) to the corresponding copper *bis*(4-methyl-2-nitrosophenolato) in the presence of a simple copper salt (CuSO₄). Remarkably, Charalambous, Castellani and co-workers have been able to synthesise and characterise crystalline nitrosophenolato complexes prepared from alkaline metals, i.e., sodium and lithium, by reacting with sodium and lithium hydroxide respectively [57]. Due to the redox characteristics of the ligands, these may have interesting properties for areas such as energy storage and battery materials [58].

10. Conclusion

The challenges in synthesis, lack of profusion in literature and unique properties of 2-nitrosophenols and their metal salts make them a stimulating target for further study. Across several publications, greater understanding has developed about their properties and the mechanisms to their formation. Applications are demonstrated, but not yet developed—the speciality of the process may afford application in the future. Doubts over specific aspects of the mechanisms proposed remain, and further study and characterisation of the structures proposed would aid in the understanding of the field. A publication [41], completed by our group, represents the initial stages of such as study.

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