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Synthesis and crystal structure of a zwitterionic nickel(II) complex

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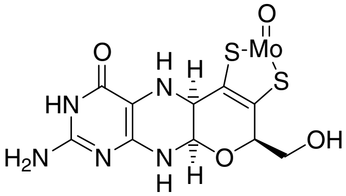
Abstract

The crystal structure of complex **3**, a Ni(II)(dppe) ligated in a square planar arrangement by a novel S, N-ligand, has been determined at 123 K. The neutral and air stable complex is of interest as it shows an apparently zwitterionic structure, one counter-anion to the Ni(II) being delocalised into the backbone of the ligand. Support for this conclusion comes from an analysis of bond lengths in the complex **3**, the crystal structure of which is presented and the result of a density functional calculation performed on the complex. A discussion of the mechanism leading to the observed product is presented.

Keywords: Nickel; dppe; Aza-thiol ligand; Zwitterion; Density functional calculation

The molybdenum dependent oxygen-transfer enzymes are essential to all life [1]. Enzymes isolated and characterised from this diverse family to date share a structurally conserved cofactor. This cofactor has been called the molybdenum cofactor and the general structure, as determined by protein crystallography, is shown. Additional ligation on the metal is not shown, but may be provided by a second pterin–dithiolene or serine, cysteine or selenocysteine, while the free hydroxyl group may be replaced by a phosphate–dinucleotide, in the case of bacterial sources of the co-factor.



Molybdenum cofactor

We are engaged in research directed at elucidation of the mechanism by which the molybdenum cofactor allows electron transfer between the active site (molybdenum) via the reduced tricyclic pterin to one of a number of different biological redox centres, this being dependant on the class of oxygen-transfer enzyme. An interest in modelling essential features of this process led us to attempt to prepare the nickel dithiolene complex **1** (Scheme 1).

We had expected dithiolene complex **1** to be readily formed by hydrolysis of the precursor ligand **2c**, followed by transmetallation to Ni(II)dppe ($Ph_2PCH_2CH_2PPh_2$). Though none of the dithiolene **1** was identified, a novel nickel complex **3** was isolated. This had apparently resulted from incomplete hydrolysis of the ligand **2c** under the conditions employed, prior to the complexation with $NiCl_2 \cdot$ dppe. The structure of this product **3** was elucidated by X-ray crystallographic analysis and is presented here. A comparison of the structure with that of the parent ligand **2c** is made together with a consideration of the novel zwitterionic structure and a discussion of the likely mechanism leading to the formation of complex **3**.

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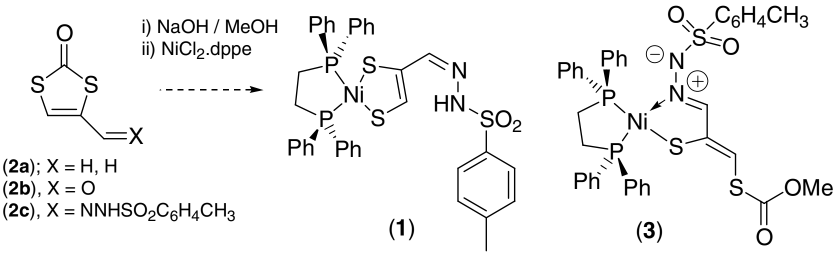


Scheme 1.

The aldehyde **2b** was prepared in 70% yield from the dithiolene **2a** by oxidation employing selenium dioxide in refluxing dioxane. Aldehyde **2b** has previously been made, in a 45% yield, by a di-*iso*-butylaluminium hydride (DiBAl) mediated reduction of the corresponding methylcarboxylate substituted dithiolene [2]. This route is, however, accompanied by over-reduction, which gives the corresponding alcohol. Thus, the route reported here, in one step from the readily available methyldithiolene **2a**, represents an improved synthesis of the aldehyde **2b**. Reaction of the aldehyde **2b** with toluenesulfonylhydrazide in ethanol gave the sulfonylhydrazone **2c** in 93% yield. ^{1}H, ^{13}C NMR and mass spectral data were consistent with the proposed structure and for the purposes of comparison with the complex **3** an X-ray crystallographic analysis was performed, the result of which is shown in Fig. 1.

Hydrolysis of the sulfonylhydrazone **2c** employing two equivalents of sodium methoxide in methanol was followed to completion (disappearance of starting material, as judged by TLC analysis of the reaction mixture). Upon addition of the $NiCl_2 \cdot$ dppe, a red colour formed immediately. Chromatographic purification of the crude product, on silica gel, yielded one principal product. This air stable red crystalline solid was found to be soluble in organic solvents. X-ray crystallographic analysis at 123 K showed the compound to have the structure **3** shown in Fig. 2 and both ^{1}H NMR and mass spectral data were consistent with this analysis. Interesting features of the structure shown in Fig. 2 are the planarity of the ligand arranged around the square planar Ni(II) and the absence of both a counter-ion in the lattice and a proton at the N-2 position of the structure. Thus, the ligand is a dianion, balancing the charge on the nickel and resulting in a neutral complex.

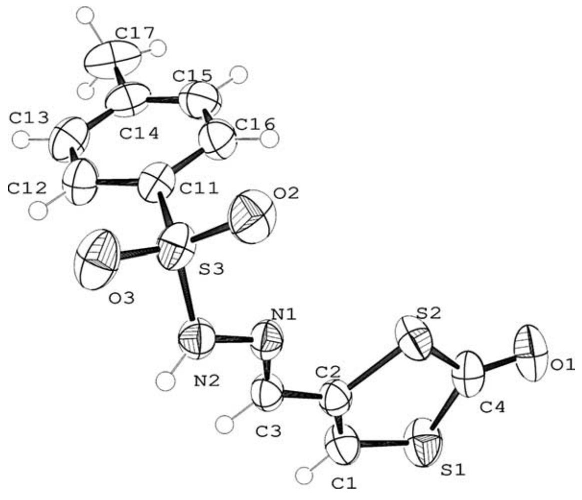


Fig. 1. ORTEP diagram for pro-ligand **2c** showing the atom-labelling scheme and 50% probability ellipsoids. Selected bond lengths (Å): C1–C2 1.332(4), C2–C3 1.450(3), C3–N1 1.274(3), N1–N2 1.391(3), N2–S3 1.650(2), S3–O2 1.430(2), S3–O3 1.426(2).

Various canonical forms can be drawn to account for the distribution of charge in this structure (Scheme 2).

Significantly, no canonical form allows the de-localised charge in the ligand backbone to cancel the development of positive charge at N1. Support for the likely contribution of each of the canonical forms shown comes from an examination of the bond lengths.

The bond lengths in the complex **3** are consistent with contributions from each of the canonical forms (I)–(III) shown (Fig. 2). Thus, the bonds C1–C2, C3–N1 and the two S3–O bonds are longer, while the bonds C2–C3,

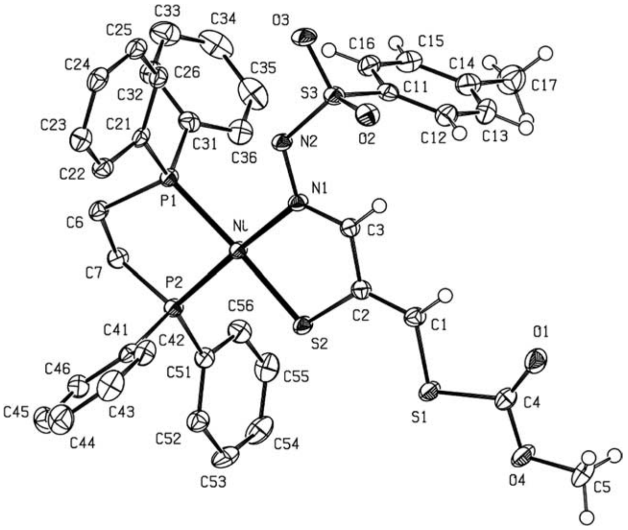
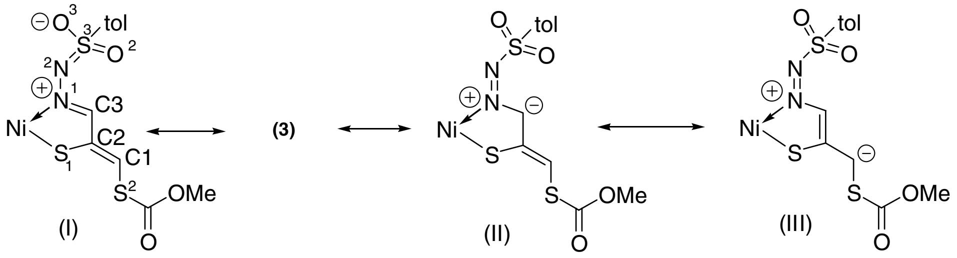


Fig. 2. ORTEP diagram for complex **3** showing the atom-labelling scheme and 50% probability ellipsoids. H atoms have been omitted from the dppe ligand for clarity. Selected bond lengths (Å): C1–C2 1.352(3), C2–C3 1.434(3), C3–N1 1.310(3), N1–N2 1.386(2), N2–S3 1.614(18), S3–O2 1.448(16), S3–O3 1.455(17).



Scheme 2. Canonical forms accounting for electron distribution in complex **3**.

N1–N2 and N2–S3 are shorter than the corresponding bonds in the ligand precursor **2c**, though these differences are small and it is evident that both structures **3** and **2c** show bond lengths intermediate between single and double bonds. The canonical form (I) presumably benefits in stability from charge localisation onto the more electronegative oxygen, while forms (II) and (III) from the known ability of sulphur to stabilise adjacent carbanions [3].

This charge distribution is supported by a density functional calculation of the atomic charges, selected values from which are shown in Table 1 [4].

An interesting question concerning the course of the reaction during the hydrolysis and subsequent transmetallation is why the sole product identified is the five membered chelate ring **3**. None of the isomeric six membered chelate ring **4** (Scheme 3) was detected. We suggest two possible explanations. The six membered chelate **4** is thermodynamically less stable and, if formed, spontaneously rearranges, with acyl transfer to the observed product **3**. Another explanation is that the side chain on the protected ligand directs the hydrolysis to give the one regioisomer. Nucleophilic attack of methoxide on the deprotonated ligand presumably results in a tetrahedral intermediate **5**, the collapse of which to yield the observed regioisomer is directed by the Lewis acidity of the sodium cation, itself coordinated to the hydrazide (Scheme 3). It is conceivable that the dianionic nature of the hydrolysis product **6** then slows attack of the second methoxide at the terminal thiocarbonate, the product from which would have been the initially desired dithiolate **1**. We have previously observed the hydrolysis of similar protected dithiolenes lacking potentially acidic side chains to be a facile [5].

Table 1
Selected partial atomic charges calculated for complex **3**

C1	−0.141	N2	−0.542	P1	0.146
C2	0.173	O2	−0.563	S3	1.162
C3	−0.37	O3	−0.567	S2	−0.183
N1	0.308	Ni	−0.234	S1	−0.122

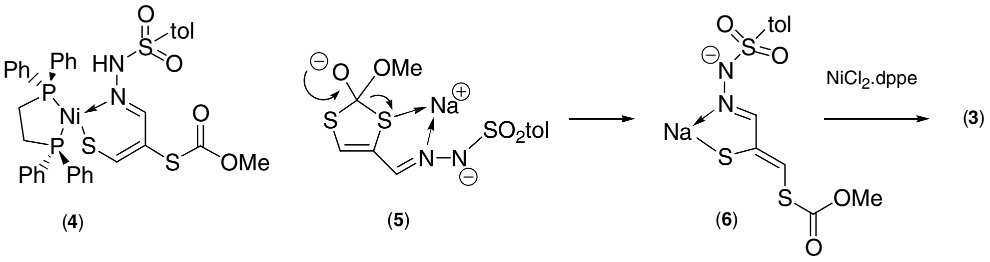
In conclusion, a neutral nickel(II) complex has been isolated, wherein one counterion is delocalised in the ligand backbone and not on a ligating atom.

Acknowledgement

This material is based on work supported by the National Research Foundation under Grant No. 2053652. Financial support from the University of the Witwatersrand is also gratefully acknowledged.

Appendix A. Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic data centre, CCDC No. 221256 for pro-ligand **2c** and CCDC No. 221257 for nickel complex **3**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK or http://www.ccdc.cam.ac.uk. Full experimental details, characterisation for all compounds described in this paper, and crystallographic tables are contained in the



Scheme 3.

supplementary data file. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2004.12.027.

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