



Research paper

Effect of crystal packing and coordinated solvent molecules on metal–ligand bond distances in linear trinuclear nickel compounds with bridging acetato and Schiff base ligands

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ABSTRACT

A combined experimental and theoretical study on the molecular structure of linear trinuclear nickel compounds of general formula $[\text{Ni}_3(\mu\text{-}^Z\text{saltn})_2(\mu\text{-AcO})_2(\text{S})_2]$ ($Z = \text{H}$, **1S**, and Br , **2S**, where S identifies coordinated solvent molecules) is here presented. In these complexes the three metal ions are linked together by bridging acetato ions and tetradentate Schiff base ligands, these last derived from the condensation of 1,3-diaminopropane with two equivalents of 5-Z-salicylaldehyde. Two solvent molecules S can also interact with the terminal nickel ions to complete an octahedral coordination environment. We report the synthesis of $[\text{Ni}_3(\mu\text{-}^{\text{Br}}\text{saltn})_2(\mu\text{-AcO})_2]$ (**2**), and its crystal structure with two coordinated dimethylformamide molecules, $[\text{Ni}_3(\mu\text{-}^{\text{Br}}\text{saltn})_2(\mu\text{-AcO})_2(\text{DMF})_2]$ (**2DMF**). Its comparison with the crystal structure of **2** without solvent, together with the series of compounds **1**, **1DMF**, **1MeOH**, **1DMSO**, **1Py** and **1H₂O** (MeOH = methanol, DMSO = dimethylsulfoxide, Py = pyridine) available in the literature, allows recognising modification in Ni–O and Ni–N coordination bond lengths and peculiar intermolecular contacts between neighbour molecules. In order to discern among the contribution of solvent molecules, crystal packing and substituent Z (H or Br) on bond distances (and angles), we performed a systematic theoretical study on four representative derivatives, namely **1**, **1DFM**, **2** and **2DMF**, with the M06 functional and a careful choice of the best basis set. The results indicate that, while the major modulating factor is the presence or absence of the sixth solvent molecule to the peripheral nickel(II) ion, even if less strongly coordinated with Ni–O/N bond distances > 2.15 Å, $\pi\text{-}\pi$ stacking interactions and C–H $\cdots\pi$ and/or C–Br $\cdots\pi$ non-bonded interactions affect the coordination geometry in a significant way.

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1. Introduction

Metal–ligand (M–L) bond distances in complexes, as derived from X-ray structure determinations, are considered mostly affected by the composition of the coordination sphere around the metal ion and, only to a lesser extent, by crystal packing effects. The presence of short intermolecular contacts involving either the metal centre or, in most cases, the surrounding ligands can actually strongly influence the overall coordination environment around M [1,2]. For example, in our previous systematic investigation on

square planar $[\text{Pt}^{\text{II}}(\text{PPh}_3)_2\text{XY}]^{\text{n}+}$ derivatives, where X and Y can be either anionic (Cl^- , Br^- , I^- , AcO^- , NO_3^- , etc. [3,4]) or neutral (thiourea [5], substituted pyridines, amines [6], PPh_3 [7], etc.), we have demonstrated how the nature and reciprocal position of the different ligands have a direct effect on the $^1J_{\text{Pt-P}}$ coupling constants, giving rise to the so-called *cis* and *trans* influences. The associated X-ray derived M–L bond lengths, however, are modulated in a less clear extent since they also reflect factors as various as ionic or covalent radii, steric hindrance and the crystal packing [3,4,6]. Furthermore, peripheral substituents on ligands can induce higher or lower electron density along the organic skeleton toward the metal, with a consequent tuning effect on the coordination distances, as highlighted in unsymmetrically-substituted salen-type tetradentate Schiff base copper(II) compounds [8]. The modulation given by substituents can be even more subtle, since their involvement in intermolecular contacts can, for example, lead to the stabilization of high or low spin state in iron(II) complexes with

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bis-pyrazolopyridine ligands, with a remarkable change in Fe–N bond lengths [9]; certainly, in this case the different spin state is the driving force for bond modification.

What appears clear in these studies is the difficulty to single out, in the solid state, the effect of each possible modulating factor on M–L distances relying only on X-ray data, since in the crystal structure electronic, steric and crystal packing influences act all together in a cooperative way [1,2,10]. The study of homologous series of compounds where one factor is changed at a time could surely help rationalize trends in geometrical properties [11], though not always feasible. Moreover, crystal packing effects are often overwhelming with respect to subtle electronic effects due to the ligands, so that accurate theoretical calculations on isolated molecules revealed nowadays to be fundamental [12], in addition to experimental data, for the study of the structural properties of metal complexes [4,6,8,9,11], besides providing a reliable prediction of chemical and physical properties [8,13].

In our ongoing research on Schiff base ligands and their copper (II) complexes [8,11,14,15], our interest has been also attracted by nickel(II) derivatives, well-studied for their nonlinear optics (NLO) [16] and catalytic properties [17,18]. An interesting family, also for their magnetic properties, is given by linear trinuclear complexes in which a central nickel(II) ion is connected to two peripheral ones by carboxylato ions (formato [19], acetato [17,19–26], benzoato [17,19], etc.), as well as by bridging phenoxido oxygen atoms of the tetradentate Schiff base ligands that coordinate the two terminal metal ions [17,19–26]. Also similar mixed-metal linear systems are reported [27].

More specifically, our attention was attracted to derivatives whose general formula can be expressed as $[\text{Ni}_3(\mu\text{-}^Z\text{salt})_2(\mu\text{-AcO})_2(\text{S})_2]$ with Z = H (**1S**) and Br (**2S**), where S identifies coordinated solvent molecules. In these compounds, the three nickel ions are linked together by bridging oxygen atoms of tetradentate Schiff base ligands derived from the condensation of 1,3-diaminopropane (tn) with two equivalents of 5-Z-salicylaldehyde (5-Z-salH), and by bridging *syn,syn*- η^1, η^1 - μ -acetato ions. The external nickel ions can be either *penta*-coordinated without solvent molecules S, or *hexa*-coordinated when S is present (Scheme 1). Crystal structures of compounds with Z = H and different solvent molecules (**1** with no solvent [20], **1DMF** with S = dimethylformamide [21,22], **1MeOH** with S = methanol [22], **1DMSO** with S = dimethylsulfoxide [23], **1Py** with S = pyridine [24] and **1H₂O** with S = H₂O, even if with an ethyl substituent on the tn bridge [26]) are available in the literature, providing a chance to explore the effect of different coordinated solvent molecules on the coordination geometry around the nickel(II) ions. Moreover, the crystal structure of **2** with Z = Br and no solvent was also reported, [25] allowing to investigate the effect of peripheral substitutions on the Ni₃ cores. In

addition, the homologous of **1** with 2-hydroxy-1,3-diaminopropane instead of tn, **3** [17], is reported in the literature (Scheme 1).

We were then interested in investigating the effect of adding the sixth coordinated S molecule to the peripheral nickel(II) ions in **2** on Ni–O and Ni–N bond distances, in the same way as reported for **1S** series. Unfortunately, **2** revealed very low solubility and we could obtain crystals suitable for X-ray diffraction of this complex only with coordinated DMF (**2DMF**). We will report therein the structural results on this compound, which will be compared with the ones of **2** [25] so as to highlight the influence of coordinated solvent, and with those of **1** and **1DMF**, to reveal possible substituent effects. The results of a theoretical study on the *gas-phase* molecular structure of **1**, **1DMF**, **2** and **2DMF** will be also presented and compared with the experimental findings in order to finally disclose the effect of intermolecular contacts (crystal packing) on the coordination bond lengths. Structure of **3** will also help with this purpose, due to additional possible intermolecular contacts caused by site-specific structural modification with respect to **1**. All data collections have been performed at room temperature, with only two exceptions (**1Py**, T = 123 K [24], and **1H₂O**, T = 150 K [26]), allowing to exclude in most cases thermal effects on the observed differences.

2. Experimental

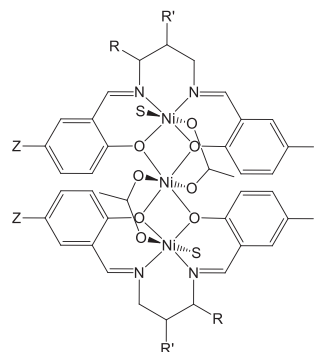
2.1. Materials

All used chemicals were reagent grade, and solvents were used as received. Elemental analyses were performed at the Microanalytical Laboratory at the Università degli Studi di Milano. Infrared spectra were recorded as KBr disks using a JASCO FTIR-4700LE spectrophotometer with a 2 cm⁻¹ resolution, and main bands are given in inverse centimetres.

2.2. Synthesis of $[\text{Ni}_3(\mu\text{-}^{\text{Br}}\text{salt})_2(\mu\text{-AcO})_2]$ (**2**) and $[\text{Ni}_3(\mu\text{-}^{\text{Br}}\text{salt})_2(\mu\text{-AcO})_2(\text{DMF})_2]$ (**2DMF**)

Br-salH (0.201 g, 1.00 mmol) and tn (42.0 μL, 0.499 mmol) were mixed in EtOH (15 mL) and the resulting yellow solution was refluxed for 30 min. Ni(AcO)₂·4H₂O (0.125 g, 0.502 mmol) was added and the green mixture was refluxed for other 30 min and then cooled to room temperature. **2** could be recovered by filtration as light green solid, washed with EtOH, diisopropyl ether (*iPr*2O) and dried in vacuum. Yield in **2**: 0.181 g (92.8%). *Anal. Calc.* for C₃₈H₃₄Br₄N₄Ni₃O₈ (1170.39): C, 39.00; H, 2.93; N, 4.79. Found: C, 39.40; H, 2.74; N, 4.34. IR (KBr pellet; cm⁻¹): ν(C=N) 1633, ν

compound	Z	S	R	R'	ref
1	H	–	H	H	[20]
1DMF	H	DMF	H	H	[21]
1DMF·1MeOH	H	DMF	H	H	[22]
1DMSO	H	DMSO	H	H	[23]
1Py	H	Py	H	H	[24]
1H₂O	H	H ₂ O	Et	H	[26]
2	Br	–	H	H	[25]
2DMF	Br	DMF	H	H	this work
3	H	–	H	OH	[17]



Scheme 1. Representation and codes of the linear trinuclear compounds $[\text{Ni}_3(\mu\text{-}^Z\text{salt})_2(\mu\text{-AcO})_2(\text{S})_2]$.

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