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Mixed valent/geometry, linear, tetranuclear nickel complex bearing ONO pincer ligand exhibiting hitherto unknown ligation mode

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Abstract

A hitherto unknown linear, tetranuclear nickel(II/III) complex possessing both square planar and pentagonal bipyramidal geometry around the metal ions was obtained from the reaction of ONO pincer ligand (*E*)-*N*-(2-hydroxybenzylidene)acetohydrazide with [NiCl₂(PPh₃)₂] precursor complex in methanol medium. The novel ONO ligand and its nickel complex were characterized by using elemental analysis, UV-visible, FT-IR, ¹H and ¹³C NMR spectral data. The identity of the tetranuclear complex crystallized in triclinic crystal system with P-1 space group was confirmed by single-crystal XRD study. Density Functional Theory (DFT) calculations performed for the optimization of the titled nickel complex by considering the presence as well as the absence of coordinated solvent molecules in the input coordinates revealed that the optimized structures are energetically somewhat disfavored but its formation in the experiment

could be attributed to the participation of packing forces that stabilizes the molecule it in the solid state.

Keywords: ONO pincer ligand, Tetranuclear, Nickel(II/III) complex, Single-crystal XRD, DFT calculations.

1. Introduction

Nowadays, researchers focus their attention to the rational design and synthesis of coordination complexes with interesting structural properties [1,2]. Particularly, achieving polynuclear transition-metal complexes is a fascinating area of inorganic chemistry research [3,4] mainly due to their applications in various field including, catalysis [5], magnetism [6], luminescence[7], sensors [8] and non-linear optics [9]. The formation of polynuclear complexes mainly depends on the ligand design and their coordination behavior [10,11]. In this regard, numerous reports are available on the synthesis of salen type ligands and their multinuclear complexes as the prototype [12-13].

After the invention of pincer ligands by Moulton and Shaw in 1976 [14], tremendous reports were made on their transition-metal complexes. Owing to their high thermal stability and numerous applications as potential catalysts [15], sensors [16], synthons for metallo-dendrimers [17] and in medicinal chemistry as biomarkers [18], pincer ligands are considered to be a group of privileged molecules to construct transition metal complexes with novel properties. Variety of pincer ligands incorporating NCN, PCN, NNN, PCP, PNP, CNC and CCC donor atoms were developed [19,20]. In spite of, ONO pincer ligands and their metal complexes are handful in the literature. On the other hand, polynuclear complexes incorporating pincer ligand were very rarely reported.

Very recently, Karvembu and co-workers [21] reported the synthesis of a trinuclear nickel(II) complex incorporating pyridine based ONO pincer ligand. To the best of insight, there were no reports available for the mixed geometry nickel complex in the literature and hence we feel that the present work is the first report for the mixed geometry nickel complex. As a part of our ongoing journey towards the synthesis and catalytic applications of novel pincer complexes [22-28], we present in this article, the synthesis and structural features of a tetranuclear nickel complex possessing both bivalent and trivalent ions networked through ONO pincer ligand.

2 Experimental procedures

2.1 Materials

Reagent grade chemicals were utilized without further purification unless otherwise specifically mentioned. The solvents utilized in this study were purified and dried according to standard procedures [29]. Acethydrazide, salicylaldehyde and [NiCl₂(PPh₃)₂] were purchased from Sigma-Aldrich and used as received.

2.2 Physical measurements

Microanalyses (C, H and N) were performed on a Vario EL III Elemental analyzer. A Nicolet Avatar Model FT-IR spectrophotometer was used to record the infrared spectra (4000–400 cm⁻¹). A Jasco V-630 spectrophotometer was used to collect the electronic spectra. Melting points were determined with a Lab India instrument and are uncorrected.¹H and ¹³C NMR spectra were recorded in CDCl₃ as solvent on BRUKER 400 and 100 MHz instruments, respectively.

2.3 Synthesis of H₂L

The ligand (*E*)-*N*⁻(2-hydroxybenzylidene)acetohydrazide (H₂L) was synthesized from the condensation of equimolar quantities of salicylaldehyde (0.185 g, 1 mmol) and acethydrazide (0.185 g, 1 mmol) in methanol medium under reflux for 5 h. Yield: 0.098 g, 85%. Melting point: 125 °C. Elemental Analysis calc. for (%) C₉H₁₀N₂O₂: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.45; H, 5.71; N, 15.68. UV-visible (solvent: DMSO, nm): 281, 288, 302, 322, 357. Selected IR bands (KBr, *v* in cm⁻¹): 3051 (N–H), 2977 (O–H), 1682 (C=O), 1605 (C=N). ¹H NMR in CDCl₃: 11.8 (s, 1H), 11.1 (s, 1H), 9.8 (s, 1H), 7.53 (dd *J* = 8.0, 8.0 *Hz*, 1H), 7.39 (t *J* = 4.0 *Hz*, 1H), 7.31 (d *J* = 8.0 *Hz*, 1H), 7.27 – 7.19 (m, 1H). ¹³C NMR in CDCl₃: 162.7, 160.3, 144.1, 129.4, 129.3, 128.7, 128.1, 127.8, 21.5.

2.4 Synthesis of [Ni₄(L)₄(H₂O)₂(OCH₃)₂]

To a methanolic solution (35 mL) of the ligand (H₂L) (1 equiv.) was refluxed with equimolar solution of $[NiCl_2(PPh_3)_2]$ in the same solvent in presence of KOH for 8 h. After 20 days, an orange color needle-like crystal suitable for X-ray analysis was obtained on the slow evaporation of the solvent. Yield: 65%. Elemental Analysis calcd for (%) C₄₃ H₆₀ N₈ Ni₄ O₁₆: C, 43.78; H, 5.13; N, 9.50. Found: C, 43.76; H, 5.20; N, 9.55. UV-visible (solvent: DMSO, nm): 266, 315, 359, 372. Selected IR bands (KBr, v in cm–1): 3062 (H₂O), 2919 (C–O), 1603 (C=N), 1556 (C=N–N=C), 1200 (imidolate –N=C–O).

2.5 X-ray crystallography

X-ray quality single-crystals of complex **1** were grown by slow evaporation of the corresponding methanol-chloroform solutions (1:1). An orange needle-like piece measuring 0.25 x 0.17 x 0.13 mm³ was mounted on a loop with oil. Data was collected at -143°C on a Nonius Kappa CCD FR590 single crystal X-ray diffractometer, Mo-radiation. Crystal-to-detector distance was 30 mm and exposure time was 30 seconds per degree for all sets. The scan width was 2°. Data collection was 99% complete to 25° in ϑ . A total of 10152 merged reflections were collected covering the indices, -14<=h<=14, -13<=k<=14, -17<=l<=19. 6591 reflections were symmetry independent and the R_{int} = 0.0892 indicated that the data was of average quality. Indexing and unit cell refinement indicated a triclinic P lattice. The space group was found to be P $\overline{1}$ (No.2).

The data was integrated and scaled using hkl-SCALEPACK [30]. This program applies a multiplicative correction factor (S) to the observed intensities (I) and has the following form:

$$S = (e^{-2B(\sin^2\theta)/\lambda^2})/\text{scale}$$

S is calculated from the scale and the B factor determined for each frame and is then applied to I to give the corrected intensity (I_{corr}). Solution by direct methods (SHELXS, SIR97 [31]) produced a complete heavy atom phasing model consistent with the proposed structure. The structure was completed by difference Fourier synthesis with SHELXL97 [32,33]. Scattering factors are from Waasmair and Kirfel [34]. Hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C---H distances in the range 0.95-1.00 Angstrom. Isotropic thermal parameters U_{eq} were fixed such that

they were $1.2U_{eq}$ of their parent atom Ueq for CH's and $1.5U_{eq}$ of their parent atom U_{eq} in case of methyl groups. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares.

The structure, in addition to the shown solvent, contains disordered water and methanol. The contribution of the disordered solvent to the diffraction pattern was removed with SQUEEZE [35,36]. The dimeric complex contains a center of inversion.

2.6 DFT calculations

DFT calculations were carried out with the program package Gaussian 09 Revision C.01 [37]. The ground state geometries were optimized without symmetry constraints using the B3LYP [38] functional in combination with 6-31G(d) [39] basis set for non-metals and LANL2DZ [40] basis set with effective core potential for metal ions have been used for all the calculations. The initial geometry coordinates have been extracted from the crystal structure of the molecule.

3 Results and discussion

3.1 Synthesis of H₂L and tetranuclear nickel complex

The ONO pincer lignad (H₂L) was prepared in 85% yield by facile condensation reaction of equimolar quantities of salicylaldehyde and acethydrazide in ethanol medium (Scheme 1). The molecular formula and structure was confirmed through elemental analysis and spectroscopic techniques. Reaction of H₂L in methanol with bis(triphenylphosphine)nickel(II) dichloride, [NiCl₂(PPh₃)₂] in presence of KOH provided complex **1** (Scheme 2). The molecular structure of complex **1** is quite unexpected. Based on the well known coordination modes of the present ligand, the formation of mononuclear nickel(II) complex with tridentate ONO pincer ligand and

triphenylphosphine as ancilary ligand was straightforward. To our surprise, a mixed valent, tetranuclear nickel(II/III) complex was realized. The final proof for the formation of ligand bridged structure of complex **1** was corroborated through single-crystal XRD.



Scheme 2: Synthesis of tetranuclear Ni(II/III) complex 1 containing the bridging ONO

pincer ligand (H₂L).

3.2 Spectroscopic properties

Infrared spectra of the ligand (H₂L) and its nickel complex have been collected using KBr pellets. IR spectra of free ligand (H₂L) showed the N–H and C=O stretches appears at 3051 and 1682 cm⁻¹, respectively [41]. However these absorptions were not observed in the spectrum of complex **1** and thus confirmed the deprotonation of the amide functionality of the tridentate pincer ligand. The C=N stretching of the free ligand (H₂L) observed at 1615 cm⁻¹ was shifted to a lower wave number in the case of complex 1 and appeared at 1603 cm⁻¹. The strong and sharp band appeared at 1556 cm⁻¹ is owing to the presence of conjugated C=N–N=C fragment of complex **1**. The imidolate (–N=C–O) functionality of complex **1** showed its vibration at 1200 cm⁻¹. Another medium intensity band observed at 1089 cm⁻¹ is assigned as due to the phenolate C–O stretching of coordinated ligand in complex **1**. The above IR spectral features indicated that the ONO pincer ligand (H₂L) was coordinated to nickel ion through the phenolate oxygen, azomethine nitrogen and imidolate oxygen in a binegative tridentate fashion [42].

The electronic spectrum of ligand (H₂L) and its nickel complex were recorded in dimethylsulfoxide at room-temperature and it was found that charge-transfer transitions dominate in all the spectra. The spectral profile of free ligand and its complex are very similar. The absorption spectra of ligand show two bands at 281 and 322 nm and three shoulders at 288, 302 and 357 nm. In the same way, spectra of complex **1** display two bands at 266 and 359 nm followed by two shoulders at 315 and 372 nm. Thus, the longer and shorter wavelength absorptions exhibited by complex **1** is due to complex based charge transfer and ligand centered transitions, respectively [43].

The proton NMR spectrum of the pincer ligand recorded in CDCl₃ showed a singlet at 11.8 ppm owing to the presence of highly deshielded OH proton. The downfield resonances observed at 11.1 and 9.82 ppm were attributed to the azomethine and amide protons of the pincer ligand. A sharp singlet appeared at 2.14 ppm is responsible for methyl proton. All the other aromatic protons were observed as multiplet in the region of 7.19 to 7.55 ppm [44]. ¹³C NMR spectra of the ligand showed a sharp signal at 162.7 ppm due to the amide carbon atom. The signal corresponding to azomethine carbon was found at 144.1 ppm. Moreover, methyl carbon atom of the free ligand was observed at 21.5 ppm. The signals observed in the region 127.8-129.4 ppm which were assigned to the aromatic carbon atoms of the free ligand [45]. However, owing to the presence of mixed valent nickel ions in the complex **1**, no meaning full NMR spectrum was obtained.

3.3 Crystal structure

Single-crystal X-ray structure of complex **1** was determined in order to identify the coordination mode of the pincer ligand with nickel. The crystallographic data and structure refinement of the nickel complex **1** and the selected bond angle (°) and lengths (Å) are summarized in Table 1 and 2 respectively and are within the reported range [46,47]. Complex **1** crystallizes in triclinic crystal system with P-1 space group. The crystal unit consists of a tetranuclear molecule through the combination of asymmetric unit and its symmetry inversion containing four nickel ions (Figure 1). An oxidation states of nickel centre are Ni(II) and Ni(III). The pincer ligand coordinate to the Ni1 *via* the phenolate oxygen, azomethine nitrogen, deprotanated imidol oxygen and the fourth site was occupied by the sharing of the azomethine

nitrogen of the next unit of the same pincer ligand as dianionic tridentate manner to form the five and six membered chelate rings around nickel 1 center.

However, the Ni2 centre is quite different from Ni1 in a way that it was ligated by two deprotanated oxygen atoms, azomethine nitrogen and a methoxide ion formed from the solvent molecule methanol and a molecule of water. The coordinated solvent molecules are trans to the pincer ligand. In addition, these asymmetric unit and its symmetry inverted moiety was connected through the phenolate oxygen and a direct metal-metal bond between Ni2–Ni2# to form pentagonal bipyramidal geometry. The bond distance between the Ni2–Ni2 is 3.084(1). In addition, two non-coordinated methanol molecules are also present in the crystal lattice of the complex **1**. Interestingly, the solvent molecules those were coordinated to the inner nickel(III) ions were accounted for the stabilization of the regular rhombus like structure existing between the said metal centers.[48]

Hydrogen bonding appears to be very important for the stabilization of the crystal structure. The present tetranuclear complex **1** also shows the occurrence of intramolecular hydrogen bondings. A hydrogen bond between phenoxide oxygen atom of coordinated pincer ligand and hydrogen atoms of non coordinated methanol moleculewas observed. Then, another hydrogen bond between the oxygen atom of the coordinated water molecule and the methanol hydrogens those were clearly displayed in the packing diagram of the complex **1** shown in Figure 2. The intramolecular hydrogen bonding parameters are given in Table 3.

The bond angle of O2–Ni1–O1 and N1–Ni1–N4 are 179.44 (13) and 170.88(17) respectively. This suggests that the geometry around Ni 1 was slightly deviated from those of a regular square planar. The bond length of N2–Ni1 is 1.829 Å and it is shorter than N3–Ni1

(1.915 Å). The axial Ni2–O6 bond distance is 2.126 Å and it is longer than Ni2–O5 (2.098 Å). The five interior angles in the pentagon determined from the XRD data are 72.01° which is very close to the expected value for an idealized pentagon (72.0°).

Our sincere effort on the literature survey of nickel complexes possessing mixed geometry around the metal ions of the same molecule confirmed that there is no such example was reported. However, voluminous literature is available on the chemistry and structure of square-plannar nickel systems. In spite of, only few reports are available for the pentagonalbipyramidal geometry of seven coordinated nickel complexes. G. J. Palenik was the first to report seven coordinated pentagonal-bipyramidal complexes of Ni(I1) and Cu(11) prepared from the reaction of 2,6-diacetylpyridinebissemicarbazone with either Ni(NO₃)₂.6H₂O or Cu(NO₃)₂.3H₂O [49]. Consequently, the same research group documented the reaction of 2,6diacetylpyridinebis(benzoic acid hydrazone) with Ni(NO₃)₂.6H₂O and Co(NO₃)₂.3H₂O those yielded the pentagonal-bipyramidal complexes of the composition [Co(DAPBH)(H₂O)(NO₃)]⁺ NO₃⁻ and [Ni(DAPBH)(H₂O),]²⁺(NO₃⁻)₂.2H₂O, respectively [50]. Later, C. Pelizi and co-workers reported the structure of a seven coordinated Ni(II) complex containing 2,6-diaeetylpyridine bis(2-hydroxybenzoylhydrazone) ligand [51]. But, a nickel complex made up of both mixed valence/geometry remains unpublished so far. Hence, the complex 1 obtained in our present study is a class of very rare example to show the presence of mixed valence/geometry around the metal ions of nickel complex. Also, among the known coordination modes of pincer ligands towards several metal ions, this is yet another addition exhibited by the said ligand system towards nickel ions.



Figure 1: ORTEP diagram of the tetranuclear Ni complex 1 with thermal ellipsoids at the 50% probability level. Disorder omitted for clarity.



Figure 2: Unit cell packing diagram of complex 1 showing intramolecular hydrogen bonding.

Table 1: Crystal data and structure refinement for complex 1.

Description			
CCDC Number	1564190		
Empirical formula	C ₄₃ H ₆₀ N ₈ Ni ₄ O ₁₆		
Formula weight	1179.83		
Temperature	130(2) K		
Wavelength	0.71073 Å		
Crystal system	Triclinic		
Space group	P -1		
Unit cell dimensions	$a = 10.6361(18) \text{ Å}$ $\alpha = 72.679(10)^{\circ}$		
	b = 11.173(2) Å β = 66.527(9)°.		
	$c = 14.522(2) \text{ Å}$ $\gamma = 60.449(10)^{\circ}.$		
Volume	1365.9(4) Å ³		
Z	1		
Density (calculated)	1.434 Mg/m^3		
Absorption coefficient	1.427 mm^{-1}		
F(000)	614		
Crystal size	$0.25 \text{ x} 0.17 \text{ x} 0.13 \text{ mm}^3$		
Theta range for data collection	2.11 to 28.36°.		
Index ranges	-14<=h<=14, -13<=k<=14, -17<=l<=19		
Reflections collected	10152		
Independent reflections	6591 [R(int) = 0.0892]		
Completeness to theta=25.00°	99.0 %		
Max. and min. transmission	0.8362 and 0.7168		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	6591 / 8 / 337		
Goodness-of-fit on F ²	0.880		
Final R indices [I>2sigma(I)]	R1 = 0.0641, wR2 = 0.1411		
R indices (all data)	R1 = 0.1363, wR2 = 0.1617		
Largest diff. peak and hole	1.003 and -0.778 $e.\text{\AA}^{-3}$		

N(2)-Ni(1)	1.829(4)
N(3)-Ni(1)	1.915(3)
O(1)-Ni(1)	1.799(3)
O(2)-Ni(1)	1.837(3)
N(4)-Ni(2)	1.990(3)
O(3)-Ni(2)	2.043(3)
O(4)-Ni(2)	2.009(3)
O(4)-Ni(2)#1	2.034(3)
O(5)-Ni(2)	2.098(4)
O(6)-Ni(2)	2.127(4)
O(4)-Ni(2) #2	2.034(3)
Ni(2)-Ni(2)#1	3.084(1)
N(1)-N(2)-Ni(1)	115.4(3)
N(2)-Ni(1)-N(3)	173.88(17)
O(1)-Ni(1)-O(2)	179.44(13)
N(3)-N(4)-Ni(2)	113.9(3)
O(4)-Ni(2)-O(3)	169.78(11)
N(4)-Ni(2)-O(3)	79.23(13)
N(4)-Ni(2)-O(4)	90.56(14)
N(4)-Ni(2)-O(4)#1	171.11(14)
O(4)-Ni(2)-O(4)#1	80.58(13)
O(4)#1-Ni(2)-O(3)	109.64(12)
Ni(2)-O(3)-Ni(2)#1	99.42(13)
O(5)-Ni(2)-O(6)	172.5(8)
O(3)-Ni(2)-O(5)	87.1(10)
N(4)-Ni(2)-O(6)	89.83(14)
O(4)#1-Ni(2)-O(6)	89.62(13)
O(3)-Ni(2)-O(6)	90.12(14)
Ni(2)-O(4)-Ni(2)#1	99.42(13)

Table 2: Selected bond lengths (Å) and angles (°) for the complex 1.

D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)	
O(5)-H(5O)O(6)#1	0.80	2.37	3.06(4)	144.1	0
O(5)-H(5O)O(4)	0.80	2.47	2.99(3)	123.9	
O(5)-H(5P)O(8)	0.81	1.99	2.78(3)	166.6	
O(7)-H(7O)O(8)	0.84	1.71	2.53(4)	168.8	
O(8)-H(8O)O(2)	0.84	1.92	2.751(5)	173.2	
O(9)-H(9O)O(6)	1.00	2.56	3.510(8)	158.6	

Table 3. Hydrogen bond parameters for complex **1** [Å and °].

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1.

3.4 DFT studies of the complex 1

To understand the formation of complex **1**, we applied the DFT calculations to evaluate thermodynamic feasibility of it. The geometry optimization for nickel complexes with and without solvent molecules was carried out by DFT calculations. Initial geometry for nickel complex was obtained from crystallographic information file. Optimized structures shown in Figure 3 and 4 with relative energies suggested that the structure of complex **1** is destabilized compared with the experimentally observed linear tetranuclear nickel complex. Though the isolation of complex **1** is unlikely on the basis of molecular stability obtained from DFT studies, it was realized experimentally. Hence, we assumed that the role played by the coordinated solvent molecules and the packing forces existed in the solid state could have been the driving force for the formation of a stable complex **1** from the reaction that was described in this study. [52]. The energy parameters calculated from DFT studies corresponding to the optimized geometries of the complex **1** shown below did tell us that the possibility of formation of

complex **1** in the selected reaction is supported only in the presence of coordinated solvent molecules around the inner nickel(III) ions. The other optimized structure with Total Energy E (SCF) of -1950383.08 kcal/mol obtained by omitting the coordinated solvent molecules around the metal ions was not a favorable one. Hence, it is clear that the DFT studies also supported the formation of a linear, tetranuclear nickel complex **1** comprising a set of bivalent nickel ions at the periphery and an equal number of trivalent ions in the inner part of the molecule possessing a stable four coordinated square planar geometry around the ions in the former positions while a seven coordinated pentagonal bipyramidal geometry including a Ni–Ni bond between them in the later positions. This study extended a new dimension to the well known chelation behavior of pincer ligands towards nickel ions.



Figure 3: Direct (a) and side (b) views of optimized geometries for complex **1** with coordinated solvent molecules; Total Energy E (SCF) = -2190716.66 kcal/mol.



Figure 4: Direct (a) and side (b) views of optimized geometries for complex 1 without solvent molecules; Total Energy E (SCF) = -1950383.08 kcal/mol.

4. Conclusion

In this paper, we report the synthesis of a new ONO pincer ligand and its nickel complex. The structure of the novel complex reported herein was confirmed by using various analytical techniques such as elemental analysis, UV-visible, FT-IR, ¹H and ¹³C NMR. The single-crystal XRD data of the synthesized nickel complex revealed an interesting tetranuclear composition of the complex made up of two different nickel environments in terms of coordination type and number. Specifically, the peripheral nickel ions are bivalent and square planar whereas the set of inner ions are trivalent nickel with seven coordination around them. Interestingly, the pincer ligand exhibited a diverse ligation in this tetranuclear nickel complex such as (i) a dianionic tridentate behavior towards the peripheral nickel ions as well as (ii) a trianionic pentadentate bridging behavior through the phenolate oxygen atoms those bridging the inner set of nickel ions and one of the nitrogens of the same pincer bound to the peripheral nickel ions in addition to the normally expected tridentate dianionic mode of the pincer observed towards the peripheral bivalent nickel ions of the complex 1. Apart from the oxygen bridges observed, a Ni-Ni direct metal-metal bond was also present to make the coordination around the inner nickel ions as seven. This kind of versatile coordination behavior exhibited by the selected ONO pincer ligand would certainly create a current of interest among coordination/material chemists with particular interest on the synthesis and magnetic properties of multinuclear mixed valent complexes. The present research work not only represents a successful structural study of a linear teranuclear nickel pincer complex but will also trigger some interest for the development of new coordination complexes of variable oxidation states and geometry facilitated by pincer ligands.

Appendix A.

CCDC 1564190 contains the supplementary crystallographic data for crystal structure reported in this paper and these data can be obtained free of charge via <u>http://www.ccdc.cam.ac.uk/conts/retrieving.html</u>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: <u>deposit@ccdc.cam.ac.uk</u>.

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

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References

- K. T. Mahmudov, M. N. Kopylovich, M. F. C. Guedes da Silva, A. J. L. Pombeiro, Coord. Chem. Rev. 345 (2017) 54.
- 2. C. Fliedel, A. Ghisolfi, P. Braunstein, Chem. Rev. 116 (2016) 9237.
- 3. Y. Li, X. Zhou, Z. L. Chen, H. H. Zou, F. P. Liang, Polyhedron. 119 (2016) 505.
- A. N. Bilyachenko, A. I. Yalymov, A. A. Korlyukov, J. Long, J. Larionova, Y. Guari, A. V. Vologzhanina, M. A. Es'kova, E. S. Shubina, M. M. Levitsky, Dalton Trans. 45 (2016) 7320.
- 5. A. Bhattacharjee, S. Halder, K. Ghosh, C. Rizzoli, P. Roy, New J. Chem. 41 (2017) 5696.
- R. Puentes, J. Torres, C. Kremer, J. Cano, F. Lloret, D. Capucci, A. Bacchi, Dalton Trans. 45 (2016) 5356.
- F. Bai, Y. Ni, Y. Jiang, X. Feng, T. Wuren, L. Zhang, H. Su, J. Mol. Struct. 1131 (2017) 190.
- L. P. Ravaro, T. R. Almeida, R. Q. Albuquerque, A. S. S. de Camargo, Dalton Trans. 45 (2016) 17652.

- V. N. Serezhkin, M. S. Grigoriev, A. R. Abdulmyanov, A. M. Fedoseev, A. V. Savchenkov, S. Y. Stefanovich, L. B. Serezhkina, Inorg. Chem. 56 (2017) 7151.
- 10. H. Han, S. A. Johnson, Organometallics, 25 (2006) 5594.
- 11. P. J. STEEL, Acc. Chem. Res. 38 (2005) 243.
- 12. X. Yang, R. A. Jones, S. Huang, J. Coord. Chem. 273 (2014) 63.
- 13. X. Q. Song, P. P. Liu, Z. R. Xiao, X. Li, Y. A. Liu, Inorg. Chim. Acta. 438 (2015) 232.
- 14. C. J. Moulton, B. L. Shaw, J. Chem. Soc., Dalton Trans. (1976) 1020.
- 15. S. Chakraborty, P. Bhattacharya, H. Dai, H. Guan, Acc. Chem. Res. 48 (2015) 1995.
- 16. L. Tabrizia, H. Chiniforoshan, Sens. Actuators, B. 245 (2017) 815.
- 17. M. Albrecht, R. A. Gossage, M. Lutz, A. L. Spek, G. van Koten, Chem. Eur. J. 8 (2000)6.
- 18. M. Albrecht, G. Rodri'guez, J. Schoenmaker, G. van Koten, Org. Lett. 2 (2000) 3461.
- 19. G. van Koten, Organomet Chem. 40 (2013) 1.
- 20. M. Asay, D. M. Morales, Dalton Trans. 44 (2015) 17432.
- 21. P. Jerome, N. S. P. Bhuvanesh, R. Karvembu, J. Struct. Chem. 57 (2016) 528.
- 22. A. Vignesh, W. Kaminsky, N. S. P. Bhuvanesh, N. Dharmaraj, RSC Adv. 5 (2015) 59428.
- 23. A. Vignesh, W. Kaminsky, N. Dharmaraj, RSC Adv. 5 (2015) 77948.
- 24. A. Vignesh, W. Kaminsky, N. Dharmaraj, Green Chem. 18 (2016) 3295.
- 25. A. Vignesh, W. Kaminsky, N. Dharmaraj, ChemCatChem. 8 (2016) 1.
- 26. A. Vignesh, W. Kaminsky, N. Dharmaraj, J. Organomet. Chem. 824 (2016) 7.
- 27. A. Vignesh, N. S. P. Bhuvanesh, N. Dharmaraj, J. Org. Chem. 82 (2017) 887.
- 28. A. Vignesh, W. Kaminsky, N. Dharmaraj, ChemCatChem. 9 (2017) 1.
- 29. D. D. Perrin, W.L.F. Armarego, D.P. Perrin, Purification of Laboratory Chemicals, second ed., Pergamon, Oxford, 1983.
- Z. Otwinowsky, W. Minor, Methods in Enzymology, in: C.W. Carter, R.M. Sweet (Eds.), Academic Press, New York, 276 (1997) 307.
- 31. a) A. Altomare, C. Burla, M. Camalli, L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G, Moliterni, G. Polidori, R. J. Spagna, Appl. Cryst. 32 (1999) 115;

(b) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Cryst. 26 (1993) 343.

 a) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Gottingen, Germany, 1997.

(b) G. M. Sheldrick, Crystal structure refinement with SHELXL. Acta Cryst. 71 (2015) 3.

- 33. S. Mackay, C. Edwards, A. Henderson, C. Gilmore, N. Stewart, K. Shankland, A. Donald, MaXus: a computer program for the solution and refinement of crystal structures from diffraction data. University of Glasgow, Scotland, 1997.
- 34. D. Waasmaier, A. Kirfel, Acta Crystallogr. A. 51 (1995) 416.
- 35. A. Spek, J. Appl. Cryst. 36 (2003) 7; P. van der Sluis, A. L. Spek, Acta Cryst. A46 (1990) 194.
- 36. L. Farrugia, J. Appl. Cryst. 30 (1997) 565.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc. Wallingford CT, (2010).
- 38. (a) A. D. Becke, J. Chem. Phys. 98 (1993) 5648;

(b) C. Lee, W. Yang, R. G. Parr, Phys. Rev. B: Condens. Matter Mater. Phys. 37 (1988)785; (c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, J. Phys. Chem. 98 (1994) 11623.

- 39. (a) G. A. Petersson, M. A. Al-Laham, J. Chem. Phys. 94 (1991) 6081; (b) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, J. Mantzaris, J. Chem. Phys. 98 (1988) 2193.
- 40. W. R. Wadt, P. J. Hay, J. Chem. Phys. 82 (1985) 284.
- 41. P. Krishnamoorthy, P. Sathyadevi, K. Senthilkumar, P. T. Muthiah, R. Ramesh, N. Dharmaraj, Inorg. Chem. Commun. 14 (2011) 1318.
- 42. M. Bagherzadeh, N.A. Mousavi, M. Zare, S. Amali, A. Ellern, L. Keith Woo, Inorg. Chim. Acta 451 (2016) 227.
- 43. S. Saha, S. Pal, C. J. Gomez-Garcia, J. M. Clemente-Juan, K. Harms, H. P. Nayek, Polyhedron, 74 (2014) 1.
- 44. J. Dutta, M. G. Richmond, S. Bhattacharya, Dalton Trans, 44 (2015) 13615.
- 45. S. K. Gupta, P. B. Hitchcock, Y. S. Kushwah, G. S. Argal, Inorg. Chim. Acta. 360 (2007) 2145.
- 46. M. Yoshitake, M. Nishihashi, Y. Ogata, K. Yoneda, Y. Yamada, H. Sakiyama, A. Mishima, M. Ohba, M. Koikawa, Polyhedron, (2017) http://dx.doi.org/10.1016/j.poly.2017.03.043
- B. Terfassa, C. Holzer, J. A. Schachner, P. Cias, H. Krenn, F. Belaj, N. C. Mosch-Zanetti, J. Coord. Chem. 69 (2016) 433.
- 48. R. Herchel, I. Nemec, M. Machata, Z. Trávníček, Dalton Trans. 45 (2016) 18622.
- 49. D. Wester, G. J. Palenik, J. Am. Chem. Soc. 96 (1974) 7565.
- 50. T. J. Giordano, G. J. Palenik, R. C. Palenik, D. A. Sullivan, Inorg. Chem. 18 (1979) 9.
- 51. C. Pelizzi, G. Pelizzi, S. Porretta, F. Vitali, Acta Cryst. C42 (1986) 1131.
- 52. A. Hazari, S. Giri, C. Diaz, A. Ghosh, Polyhedron. 118 (2016) 70.

Graphical abstract



Highlights

- A hitherto unknown coordination behavior of ONO pincer ligand such as dianionic tridentate and trianionic pentadentate towards Ni(II/III) ions in the same complex is explored.
- First report on the square-planar as well as pentagonal bipyramidal geometries around the nickel ions in the same molecule is identified.
- ▶ A tetranuclear nickel complex was stabilized by ONO pincer ligand.