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СИНТЕЗ И СТРОЕНИЕ МАКРОЦИКЛИЧЕСКОГО БИЯДЕРНОГО КОМПЛЕКСА НИКЕЛЯ(II) С 5-(4-ПИРИДИЛ)ТЕТРАЗОЛАТОМ В КАЧЕСТВЕ СОЛИГАНДА

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Биядерный комплекс никеля(II) $[Ni_2L^mClO_4]^+$, где L^m представляет собой 24-членный макроциклический гексааза-дитиофенолятный лиганд, при реакции с 5-(4-пиридил)тетразолом ($PyrCN_4H$) образует биядерный комплекс $[Ni_2L^m(PyrCN_4)]^+$. Новый комплекс был выделен в виде солей перхлората или тетрафенилбората и охарактеризован на основании данных элементного анализа и ИК-спектроскопии. Структура $[Ni_2L^m(PyrCN_4)]BPh_4 \cdot MeCN$ определялась с помощью рентгеноструктурного анализа на монокристалле, который показал, что тетразолат проявляет N2,N3-мостиковую координацию, генерируя диоктаэдрическое ядро $N_3Ni(\mu\text{-}S)_2(\mu\text{-}N_4CPyr)NiN_3$.

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Ключевые слова: макроциклические лиганды; никелевые комплексы; тетразолаты; рентгеноструктурный анализ.

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SYNTHESIS AND STRUCTURE OF MACROCYCLIC DINICKEL(II) COMPLEX WITH 5-(4-PYRIDYL)TETRAZOLATE AS COLIGAND

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The dinuclear nickel(II) complex $[Ni_2L^mClO_4]^+$, where L^m represents a 24-membered macrocyclic hexaaza-dithiophenolate ligand, reacts with 5-(4-pyridyl)tetrazole ($PyrCN_4H$) to give the dinuclear complex $[Ni_2L^m(PyrCN_4)]^+$. The new complex was both isolated as perchlorate or tetraphenylborate salts and characterised by elemental analysis and IR spectroscopy. The structure of $[Ni_2L^m(PyrCN_4)]BPh_4 \cdot MeCN$ was determined by single crystal X-ray diffraction, showing that tetrazolate units are in a N2,N3-bridging mode to generate dioctahedral $N_3Ni(\mu\text{-}S)_2(\mu\text{-}N_4CPyr)NiN_3$ core.

Keywords: macrocyclic ligands; nickel complexes; tetrazolates; X-ray diffraction analysis.

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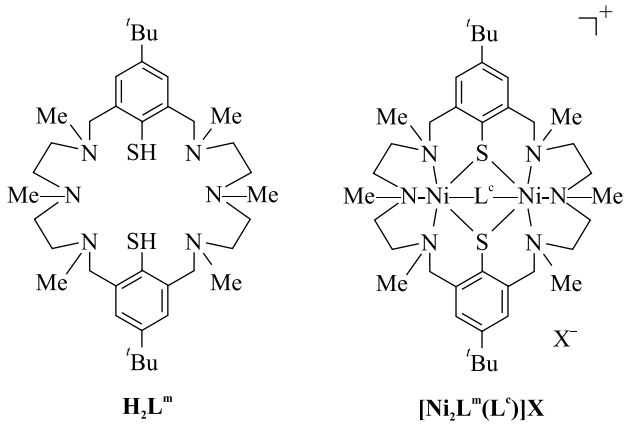
Introduction

Binuclear complexes with Robson-type ligands [1; 2] have diverse coordination chemistry, since their metal centers, rigidly bound in the cavity of the chelating macrocycle, are available for coordination with a wide range of coligands. Due to the close proximity of metal cations, they represent a good model for testing the possibility of bridging coordination of ambident ligands. Moreover, such complexes are useful objects for studies of the mechanism of magnetic exchange interactions in binuclear systems and predicting molecular magnetism caused by the interaction of magnetic centers through bridging ligands.

24-Membered hexaaza-dithiophenolate macrocycle H_2L^m is one of representative Robson-type ligands (fig. 1). Till now range of its binuclear complexes $[Ni_2L^m(L^c)]X$ were synthesised and characterised. These include complexes with simple inorganic anions, various carboxylates and thiolates as coligands L^c [2].



H_2L^m **$[Ni_2L^m(L^c)]X$**

Fig. 1. Structure of Robson-type ligand H_2L^m and its complexes $[Ni_2L^m(L^c)]X$: X – anion, L^c – coligands

Among azoles, attractive as N,N′-bridging coligands, only pyrazole derivatives were explored before our joint research [3; 4]. Previously, we found that tetrazole and its 5-R-substituted derivatives RCN_4H, where R = H, Me, Ph, react readily with complex $[Ni_2L^mCl]^+$ or $[Ni_2L^mClO_4]^+$ to give $[Ni_2L^m(RCN_4)]^+$ ones [5] (fig. 2). Under same conditions bistetrazoles $HN_4C—X—CN_4H$, where X = 1,3-C_6H_4, 1,4-C_6H_4, NH, give the tetranuclear complexes $[(Ni_2L^m)_2(N_4C—X—CN_4)]^{2+}$ [6; 7]. X-ray crystallography of these complexes isolated as BPh_4 salts, showed that tetrazolates ligands bind to the $[Ni_2L^m]^{2+}$ fragment as bidendate bridges through their two endocyclic nitrogen atoms N2 and N3. Bistetrazolates join two dinuclear $[Ni_2L^m]^{2+}$ fragments through the same nitrogen atoms.

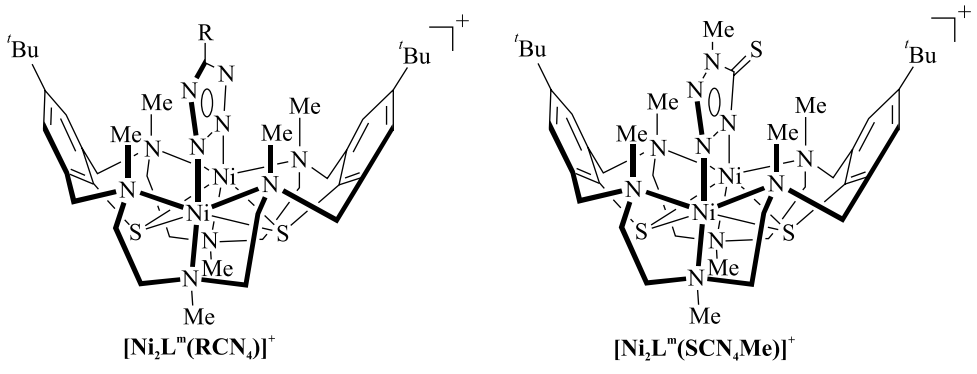


Fig. 2. Complexes of $[Ni_2L^m]^{2+}$ with tetrazole derivatives

1-Methyltetrazole-5-thiole ($HSCN_4Me$) reacts with $[Ni_2L^mClO_4]^+$ to give complex $[Ni_2L^m(SCN_4Me)]BPh_4$ with N3,N4-bridging mode of tetrazole-5-thiolate coligand [8] (see fig. 2). Here we describe the synthesis and characterisation of novel dinickel macrocyclic hexaaza-dithiophenolate complex bearing another functionally substituted tetrazolate coligand, 5-(4-pyridyl)tetrazolate. It should be noted that coordination chemistry of this ligand is poorly explored. Only several Cu(I) [9], Cu(II) [10–14], Cd(II) [15–18], Mn(II) [17], Ni(II) [19], Zn(II) [9; 20–23], Pb(II) [24], Co(II) [25] complexes with coordinated 5-(4-pyridyl)tetrazolate were structurally characterised till now.

Materials and methods

All reactions were carried out under inert atmosphere. The complex $[Ni_2L^m(ClO_4)]ClO_4$ was prepared according to the literature procedure [26; 27]. 5-(4-Pyridyl)tetrazole have been prepared by the cycloaddition of sodium azide to 4-cyanopyridine [28]. All other starting materials were commercially obtained and used without further purification. IR spectra were recorded on a Bruker Vector 27 FT-IR spectrometer (USA) using KBr pellets. Elemental analyses were performed with a Vario EL elemental analyser (*Elementar*, USA). ESI mass spectra were recorded with a 7 Tesla Apex II instrument (*Bruker Daltonics*, USA).

Synthesis of $[Ni_2L^m(PyrCN_4)]ClO_4$. Triethylamine (22 mg, 0.22 mmol) was added to a solution of 5-(4-pyridyl)tetrazole (18.4 mg, 0.125 mmol) in methanol (20 mL). Complex $[Ni_2L^m(ClO_4)]ClO_4$ (110 mg, 0.113 mmol) was added and the resulting green solution stirred for 20 h. A solution of $LiClO_4 \cdot 3H_2O$ (321 mg, 2.00 mmol) in methanol (5 mL) was then added to the green solution. After further stirring for 1 h, the green precipitate was filtered off, washed with cold ethanol, and dried in air. The yield of complex was 90 mg (77 %). Complex was characterised by elemental analyses and IR spectroscopy.

Elemental analysis for $C_{44}H_{68}ClN_{11}Ni_2O_4S_2$ (1029.33): C 51.21, H 6.64, N 14.93 %; found C 51.39, H 6.74, N 15.10 %;

IR (KBr), cm^{-1}: 3431 (strong (s)), 2961 (s), 2866 (s), 2029 (weak (w)), 1639 (medium (m)), 1610 (m), 1559 (w), 1490 (m), 1461 (s), 1426 (m), 1397 (w), 1364 (m), 1310 (w), 1265 (w), 1238 (w), 1204 (m), 1149 (m), 1090 (s, $\nu_3(ClO_4^-)$), 1058 (s), 1040 (s), 1021 (w), 998 (w), 930 (w), 916 (m), 881 (w), 829 (m), 809 (w), 754 (w), 701 (w), 626 (m, $\nu_4(ClO_4^-)$), 566 (w), 536 (w), 489 (w), 418 (w).

Synthesis of $[Ni_2L^m(PyrCN_4)]BPh_4$. A solution of $NaBPh_4$ (171 mg, 0.5 mmol) in methanol (5 mL) was added to a solution of $[Ni_2L^m(PyrCN_4)]ClO_4$ (52 mg, 0.05 mmol) in methanol (25 mL) and stirred for 1 h at ambient temperature. The green solid was filtered, washed with ethanol and dried in air. The yield of complex was 55 mg (88 %). Complex was characterised by elemental analyses and IR spectroscopy.

Elemental analysis for $C_{68}H_{88}BN_{11}Ni_2S_2$ (1251.85): C 65.24, H 7.09, N 12.31 %; found C 65.89, H 7.46, N 12.10 %;

IR (KBr), cm^{-1}: 3434 (s), 3056 (m), 3034 (m), 2999 (m), 2965 (s), 2863 (s), 1938 (w), 1611 (m), 1580 (m), 1560 (w), 1480 (s), 1464 (s), 1423 (m), 1394 (w), 1362 (m), 1311 (w), 1290 (w), 1264 (m), 1235 (m), 1201 (w),

1153 (w), 1132 (w), 1124 (w), 1108 (w), 1074 (s), 1056 (s), 1040 (s), 991 (w), 981 (w), 931 (m), 913 (w), 881 (m), 836 (w), 825 (m), 817 (m), 807 (w), 751 (m), 733 (s, ν(BPh_4^-)), 703 (s, ν(BPh_4^-)), 667 (w), 632 (m), 611 (m), 565 (w), 537 (w), 471 (w), 418 (w).

Crystal structure determination. Data collection was performed at 180(2) K on a STOE IPDS-2T image plate diffractometer (Germany) equipped with a sealed Mo X-ray tube and a graphite monochromator crystal (λ(MoK_α) = 0.710 73 Å). Data reduction and numerical absorption correction were done with *STOE X-Area* software (X-Area version 1.70). The structure was solved by direct methods using *SHELXS-2104* [29] and refined with *SHELXL-2018* [30] and *OLEX2* [31]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included on idealised positions applying the riding model. One *tert*-butyl group was found to be disordered over two sites. A split atom model was applied to account for this disorder to give site occupancy factors of 0.75/0.25. Selected crystallographic data are summarised in table 1.

Table 1

Crystallographic data for $[Ni_2L^m(PyrCN_4)]BPh_4 \cdot MeCN$

Formula	$C_{70}H_{89}BN_{12}Ni_2S_2$
M_r	1290.88
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	20.643(6)
b, Å	14.920(3)
c, Å	22.098(7)
α, deg	90
β, deg	96.97(2)
γ, deg	90
V, Å^3	6756(3)
Z	4
d_{calcd}, g/cm^3	1.269
Crystal size, mm	0.10 × 0.10 × 0.10
μ(MoK_α), mm^{-1}	0.710 73
θ limits, deg	4.54–27.40
Measured reflections	34 776
Independent reflections	14 866
Observed reflections	10 605
No. parameters	811
$R1$ ($R1$ all data)	0.043 5 (0.060 8)
$wR2$ ($wR2$ all data)	0.118 9 (0.113 1)
Max (min) peaks, e/Å^3	0.691 (–0.701)

CCDC-2089298 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via www.ccdc.cam.ac.uk/data_request/cif*.

Results and discussion

Triethylammonium 5-(4-pyridyl)tetrazolate (prepared *in situ* from 5-(4-pyridyl)tetrazole and triethylamine) was found to react easily with the complex $[Ni_2L^m(ClO_4)]ClO_4$ in methanol over 1 h. Complex $[Ni_2L^m(PyrCN_4)]ClO_4$ was obtained in 77 % yield. Further salt metathesis provided $[Ni_2L^m(PyrCN_4)]BPh_4$ in 88 % yield (fig. 3). The synthesised complexes gave satisfactory elemental analyses and were characterised by IR spectroscopy.

The structure of $[Ni_2L^m(PyrCN_4)]BPh_4 \cdot MeCN$ was determined by single crystal X-ray diffraction. Suitable single crystals were obtained by slow evaporation of $[Ni_2L^m(PyrCN_4)]BPh_4$ solution (mixture of acetonitrile and ethanol in the ratio of 1 : 1) at ambient temperature. The ORTEP view of the molecular structure of the

complex cation is presented in fig. 4. Selected bond lengths and angles are summarised in table 2. The metrical data for the other 5-R-tetrazolato complexes $[Ni_2L^m(RCN_4)]BPh_4$ [5] are included for comparison.

The nickel atoms in studied complex show distorted octahedral coordination geometries. Each metal atom is surrounded by two bridging sulfur atoms and three nitrogen atoms of the macrocycle and one nitrogen atom of the tetrazolate group, typical for complexes of the type $[Ni_2L^m(L^c)]^+$. The macrocycle forms a typical bowl-shaped conformation featuring multiatom bridging coligand L^c [2]. The 5-(4-pyridyl)tetrazolate anion binds to the $[Ni_2L^m]^{2+}$ fragment as bidentate bridge *via* the N2 and N3 ring atoms. In $[Ni_2L^m(PyrCN_4)]^+$ the average $Ni—N_{macrocyclic}$ and $Ni—N_{tetrazole}$ bond lengths are very close to those observed for $[Ni_2L^m(RCN_4)]^+$. The Ni···Ni distance of 3.446 Å is also close to one for similar tetrazolate complexes. Thus, the nature of the substituent R at C5 atom of 5-R-tetrazole ring has no significant influence on geometry of coordination polyhedron.

The N—N and N—C distances of the tetrazole ring differ slightly from the corresponding distances of the free 5-(4-pyridyl)tetrazole which exists in two distinct crystalline forms [32]. In both polymorphs pyridine nitrogen atom is protonated giving zwitterionic molecule with negatively charged tetrazole ring. Thus, observed complexation has little effect on the geometry of the negatively charged tetrazole ring. In 5-(4-pyridyl)tetrazole polymorphs the tetrazole and pyridine rings are nearly coplanar, making a dihedral angle of 2.5° and 4.7°. In $[Ni_2L^m(PyrCN_4)]^+$ this angle is somewhat larger having value of 17°.

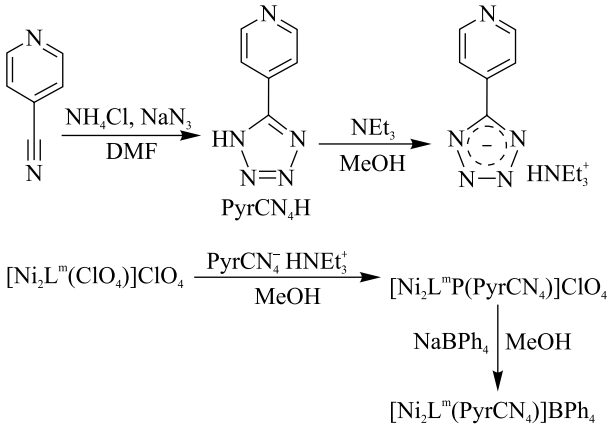


Fig. 3. Preparation of 5-(4-pyridyl)tetrazole and its complexes

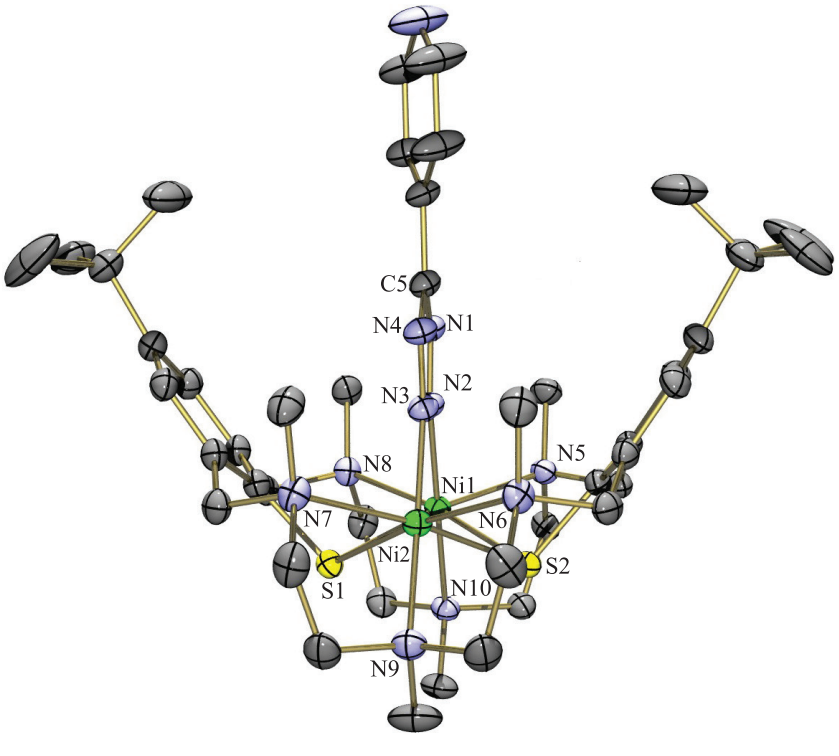


Fig. 4. ORTEP representation of the structure of $[Ni_2L^m(PyrCN_4)]^+$.
Ellipsoids are represented at 50 % probability. H atoms were omitted for clarity

Table 2

Selected interatomic distances (Å) and angles (in degrees) for complexes $[Ni_2L^m(RCN_4)]BPh_4$

Parameters	$[Ni_2L^m(RCN_4)]BPh_4$			
	R = H	R = Me	R = Ph*****	R = 4-Pyr
Ni—$N_{macrocycle}$*	2.239(2)	2.233(2)	2.235(3) [2.233(3)]	2.230(2)
Ni—$N_{tetrazole}$**	2.079(2)	2.067(2)	2.061(3) [2.060(3)]	2.061(3)
Ni—S***	2.4870(8)	2.4855(8)	2.484(1) [2.483(1)]	2.492(1)
Ni1···Ni2	3.455(1)	3.425(1)	3.443(1) [3.450(1)]	3.446(1)
N2—N3	1.367(2)	1.331(3)	1.346(4) [1.360(4)]	1.343(2)
N2—N1	1.325(2)	1.330(3)	1.333(4) [1.320(4)]	1.326(3)
N3—N4	1.317(2)	1.335(3)	1.328(4) [1.317(4)]	1.329(2)
C5—N1	1.331(3)	1.333(4)	1.341(5) [1.347(5)]	1.345(3)
C5—N4	1.341(3)	1.333(4)	1.347(5) [1.354(5)]	1.341(3)
Ni—S—Ni****	88.03(2)	87.12(3)	87.92(4)	87.46(3)

Note. * – average values for Ni1—N5, Ni1—N8, Ni2—N6, Ni2—N7 bonds; ** – average values for Ni1—N2, Ni2—N3 bonds; *** – average values for Ni1—S1, Ni1—S2, Ni2—S1, Ni2—S2 bonds; **** – average values for Ni1—S1—Ni2, Ni1—S2—Ni2 angles; ***** – there are two crystallographically independent molecules A and B in the asymmetric unit. Values in square-brackets refer to molecule B.

In previously reported complexes 5-(4-pyridyl)tetrazolate was found to show two coordination modes presented in fig. 5, monodentate mode **I** [11; 15; 17; 22; 24], bidentate of types **II** [16] and **III** [9; 12; 13; 20; 23], tridentate of types **IV** [21], **V** [10; 11; 13; 14; 16; 19] and **VI** [25], tetradentate mode **VII** [9; 10; 13] and pentadentate mode **VIII** [18; 25]. In all cases pyridine nitrogen atom is involved into coordination with metal ions. In $[Ni_2L^m(PyrCN_4)]^+$ we observed novel coordination mode of 5-(4-pyridyl)tetrazolate, namely N2, N3-bridging mode **IX**.

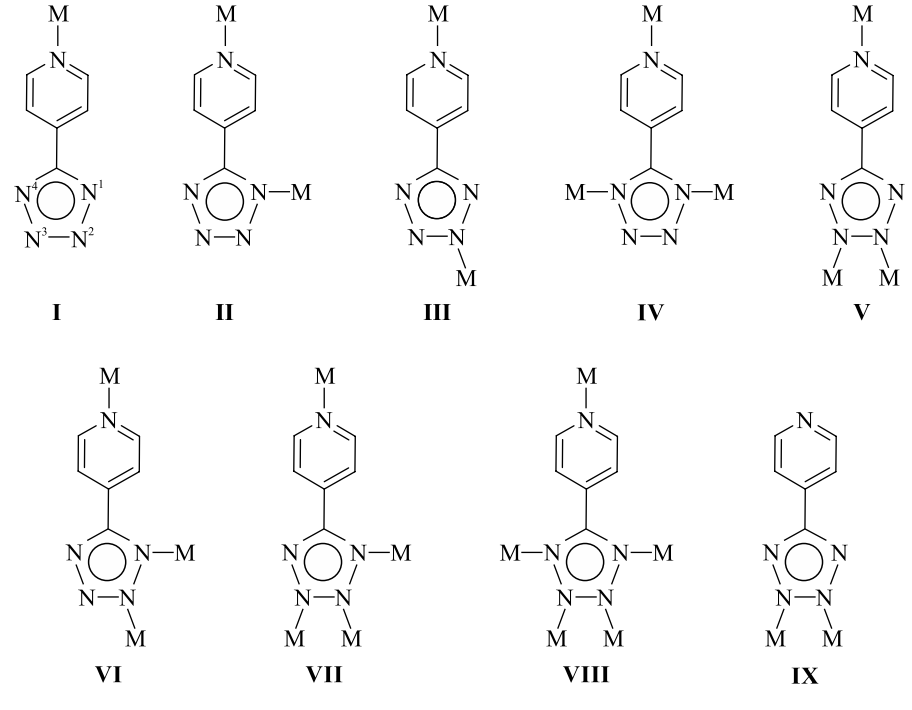


Fig. 5. Coordination modes of 5-(4-pyridyl)tetrazolate with the atom labeling scheme

Conclusion

A novel dinuclear nickel(II) 5-(4-pyridyl)tetrazolate complex supported by macrocyclic hexaaza-dithiophenolate ligand have been synthesised and characterised. X-ray diffraction showed that 5-(4-pyridyl)tetrazolate is coordinated by N2 and N3 atoms of tetrazole ring, whereas pyridine nitrogen atom is not involved into coordination. Presence of this free donor centre causes interest to reported complex as starting material for preparation of oligonuclear complexes by means of targeted assembly.

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