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Pyridine-containing nickel(II) bis-formazanates: synthesis, structure, and electrochemical study

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Five diamagnetic nickel(II) complexes with pyridine-containing formazans of composition 2L • M were synthesized by slow diffusion. X-ray diffraction study of three of these complexes demonstrated that the nickel atoms are coordinated by four nitrogen atoms of two ligands and are in a square-planar environment. The nickel atoms lie on inversion centers. The chelate six-membered rings Ni—N—N—C—N—N are nonplanar due to noncovalent repulsions between the closely arranged aryl groups. Data from NMR spectroscopy, electronic absorption spectroscopy, and electrochemistry (cyclic voltammetry and rotating disk electrode) show that all complexes have similar structures in solution.

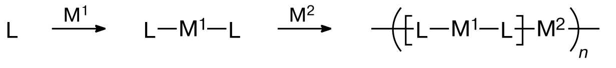
Key words: formazans, formazanates, metalloligands, nickel complexes, cyclic voltammetry, X-ray diffraction study, electronic absorption spectroscopy.

In the last third of the 20th century, supramolecular chemistry, which has been earlier the subject of a few studies on selective complexing agents and molecular recognition, became a rapidly developing field of chemistry.[1] Extensive studies have been carried out on the chemistry of supramolecular polymers, *i.e.*, high-molecular-weight compounds composed of repeated low-molecular-weight fragments linked to each other by noncovalent interactions.[2] Coordination polymers consisting of an organic molecule and a metal atom/ion as two components, which are linked to each other by a coordination bond, are considered by many researchers as promising materials possessing the semiconducting, optical, and magnetic properties.[3,4] These properties are largely determined by a virtually infinite series of combinations of inorganic and organic components of structural polymers. However, an empirical search for such combinations becomes increasingly less advantageous and attractive.

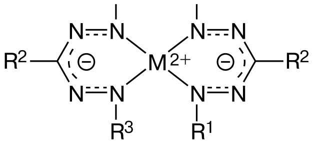
Instead of methods based on the use of simple organic ligands, procedures with the use of "complex" ligands including one or several metal atoms have gained increasing acceptance. Complex ligands provide an approach to numerous structures containing at least two exodentate groups, which can form additional coordination bonds. We will refer to such compounds as metalloligands.

The formation of a coordination polymer with the use of metalloligands as building blocks can be represented by Scheme 1, which involves the synthesis of the metalloligand by the reaction of an organic component L with metal M^1 followed by the reaction of this metalloligand with metal M^2. Compounds, which can form chelates with the central metal ion with retention of the donor centers directed outward, are commonly used as the organic component L.[5—7]

Scheme 1



Formazans and their complexes are convenient substrates for the construction of metalloligands due to the presence of a potentially chelating chromophoric group and the possibility of introducing electron-donating substituents at positions 1, 3, and 5. The deprotonated form of formazan, in which the negative charge is delocalized throughout the conjugated chain, is generally involved in complexation with metal salts to form six-membered metal chelates **A** in which the hydrogen atom is replaced by metal.[8] Complexes with Co^{II}, Ni^{II}, Cu^{II}, Cd^{II}, Pd^{II}, and Zn^{II} containing the MN_4 coordination unit have been synthesized by this method and characterized.[9—18]



A

R^1, R^3 = Ar, Het;
R^2 = Alk, Ar, Het;
M = Co^{2+}, Ni^{2+}, Cu^{2+},
Cd^{2+}, Pd^{2+}, Zn^{2+}

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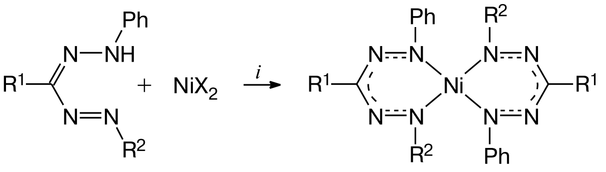
As for the design of metalloligands, it should be noted that formazans containing heterocyclic substituents (Het are benzazoles,[19—24] azoles,[25] pyridines,[26—29] quinolines,[28—35] or pyrimidines[36]) were described in the literature. Nevertheless, in spite of numerous known heteroaryl-substituted formazans, these compounds have not been used for the synthesis of metalloligands.

In the present study, we examined the formation of nickel-containing metalloligands based on formazans bearing the pyridine substituents at position 3 or 5 (Scheme 2). The resulting complexes were characterized by X-ray diffraction, microanalysis, NMR spectroscopy, and electronic absorption spectroscopy. In addition, the electrochemical properties of these compounds were studied.

Scheme 2



1a—d **2a—d**

i. Slow diffusion, CH_2Cl_2 or MeCN, EtOH, 20 °C.

1, 2	R¹	R²	X
a	3-py	Ph	OAc^-, ClO_4^-
b	4-py	Ph	OAc^-
c	Ph	3-py	OAc^-, Cl^-, ClO_4^-, NO_3^-
d	Ph	Ph	OAc^-, Cl^-

Note. The reaction **1a** + $Ni(ClO_4)_2$ produces the bis-pyridinium salt **2a**$H_2^{2+} \cdot 2ClO_4^-$.

To synthesize metalloligands, *viz.*, nickel-based bis-formazanates, we used formazans containing the pyridine substituents in different positions of the main chain, such as 3-(3-pyridyl)-1,5-diphenylformazan (**1a**), 3-(4-pyridyl)-1,5-diphenylformazan (**1b**), and 5-(3-pyridyl)-1,3-diphenylformazan (**1c**), as well as 1,3,5-triphenylformazan containing no pyridine substituents (**1d**) as the reference compound. Formazans **1a—d** have been synthesized and characterized earlier.[26,28,29,37]

Known methods for the preparation of bis-formazanates are based on rapid mixing of ethanolic or acetone solutions of the ligand and a nickel salt at room temperature[16,19,25] or on heating.[9,10,14,15,38] Single crystals suitable for X-ray diffraction were grown by recrystallization of the primary reaction products. We synthesized nickel bis-formazanates by slow diffusion of an ethanolic solution of a nickel salt into a solution of the ligand in CH_2Cl_2 or MeCN. This method is commonly used for the synthesis of supramolecular infinite ensembles.[7] For the systems under study, this approach allowed us to prepare complexes as single crystals immediately during the synthesis. In particular, we succeeded for the first time in isolating single crystals of nickel bis-triphenylformazanate **2d**, which has been known for at least 65 years.[9,10]

We chose nickel acetate, chloride, perchlorate, and nitrate as metal-containing components (see Scheme 2). It should be noted that not all reactions of nickel salts with formazans **1a—d** produce bis-formazanates. For ligand **1a**, we succeeded in preparing bis-formazanate **2a** only by the reaction of this ligand with nickel acetate and perchlorate. In the latter case, perchloric acid generated in the exchange reaction interacts with the pyridine substituent to form bis-pyridinium salt **2a**$H_2^{2+} \cdot 2ClO_4$. In turn, ligand **1b** gives bis-formazanate **2b** only with nickel acetate. In other cases, the reactions of ligands **1a,b** afford complexes of unknown composition. The reaction of ligand **1c** with all the nickel salts used produced bis-formazanate **2c**. Bis-formazanate **2d** was prepared by the reaction of ligand **1d** with nickel acetate or chloride. Complex **2d** has been synthesized earlier.[9,10,38]

Nickel(II) bis-formazanates are known[15] to be diamagnetic. Hence, we studied complexes **2** by ^1H NMR spectroscopy. Complexes **2a**$H_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$ and **2c,d** were isolated from the reaction mixtures as single crystals suitable for X-ray diffraction study.

The resulting complexes are insoluble in deuterochloroform. Hence, NMR studies were carried out in DMSO-d_6. The use of DMSO-d_6 instead of deuterochloroform does not lead to substantial changes in the spectra of the ligand, which was exemplified by the spectra of ligand **1c**. Hence, all characteristic spectroscopic features of the complexes can be assigned to their specific structural parameters. In the ^1H NMR spectra of products **2**, signals at δ 14 belonging to the N—H protons of the starting formazans are absent, which is indicative of the presence of the deprotonated form of formazan in the structures of the complexes. Like the spectra of the ligands, the spectra of complexes **2a**, **2a**$H_2^{2+} \cdot 2ClO_4^-$ and **2b,d** are characterized by the equivalence of the signals of the phenyl substituents at the first and fifths atoms of the formazan chain. However, this fact for the ligands is attributed to fast exchange of the acidic hydrogen atom, whereas for the complexes, this is accounted for by the fact that both phenyl groups are in the identical environment, due to which the signals for the protons of the corresponding rings are equivalent.

For all complexes **2**, there are particular changes in the chemical shifts of protons compared to those observed in the spectra of the ligands. The signals for the protons of the aryl substituent at the third carbon atom of the formazan chain remain unchanged (compounds **2a**$H_2^{2+} \cdot 2ClO_4^-$ and **2b**) or are shifted only slightly (the other compounds). The signals for the *ortho* protons of the phenyl rings at the first and fifth nitrogen atoms of the formazan chain are shifted downfield by 0.04 ppm (for

Table 1. Data from electronic absorption spectroscopy for formazans **1** and their complexes **2**

Compound	Solvent	EAS, λ_{max}/nm (logε)
1a	MeOH	309 (4.23), 473 (3.90)
	DMF	309 (4.40), 481 (4.15)
1b	MeOH	319 (4.23), 468 (3.95)
1c	MeOH	291 (4.37), 472 (3.95)
1d	MeOH	298 (4.27), 484 (3.98)
2a	MeOH	309 (4.48), 358 (4.42), 424 sh, 774 (3.17)
2a$H_2^{2+} \cdot 2ClO_4^-$	DMF	303 (4.24), 363 (4.02), 424 (3.79), 560 sh, 684 (3.18)
2b	MeOH	281 (4.57), 335 (4.55), 365 (4.52), 404 (3.49), 749 (3.23), 770 (3.22)
2c	DMF	309 (4.50), 357 sh, 436 (3.92), 658 (3.22)
2d	DMF	305 (4.24), 357 sh, 437 (3.99)

complexes **2a** and **2a**$H_2^{2+} \cdot 2ClO_4^-$, the downfield shift is 0.15 ppm). The signals for the *meta* and *para* protons of these phenyl rings coalesce and are shifted upfield by 0.2—0.4 ppm (these signals are observed at δ 7.12—7.15 for all complexes). Such shifts of the signals for the *meta* and *para* protons can be attributed to the mutual influence of the closely spaced aryl groups (see below).

The electronic absorption spectra of arylformazans **1** show[21—24,34,36,39—44] characteristic bands in the visible and near-UV regions at 300 and 480 nm (Table 1). The spectra of complexes **2** have additional bands at 360 and 660—760 nm compared to the absorption spectra of the ligands. These bands are assigned to charge transfer from the nickel ion to the ligand,[16,17,20,21,45] which is responsible for the black color of the complexes.

The crystallographic data and other parameters for complexes **2a**$H_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$ and **2c,d** are given in Table 2. The molecular structures of these complexes and selected geometric parameters are presented in Figs 1—3, respectively.

According to the X-ray diffraction data, compounds **2a**$H_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$ and **2c,d** are complexes of composition 2L•M. In all these structures, the nickel atoms lie on inversion centers and are surrounded by four nitrogen atoms. The coordination environment of the metal atom is a planar square. Known monoligand nickel complexes with acyclic 1,5-diarylformazans are characterized

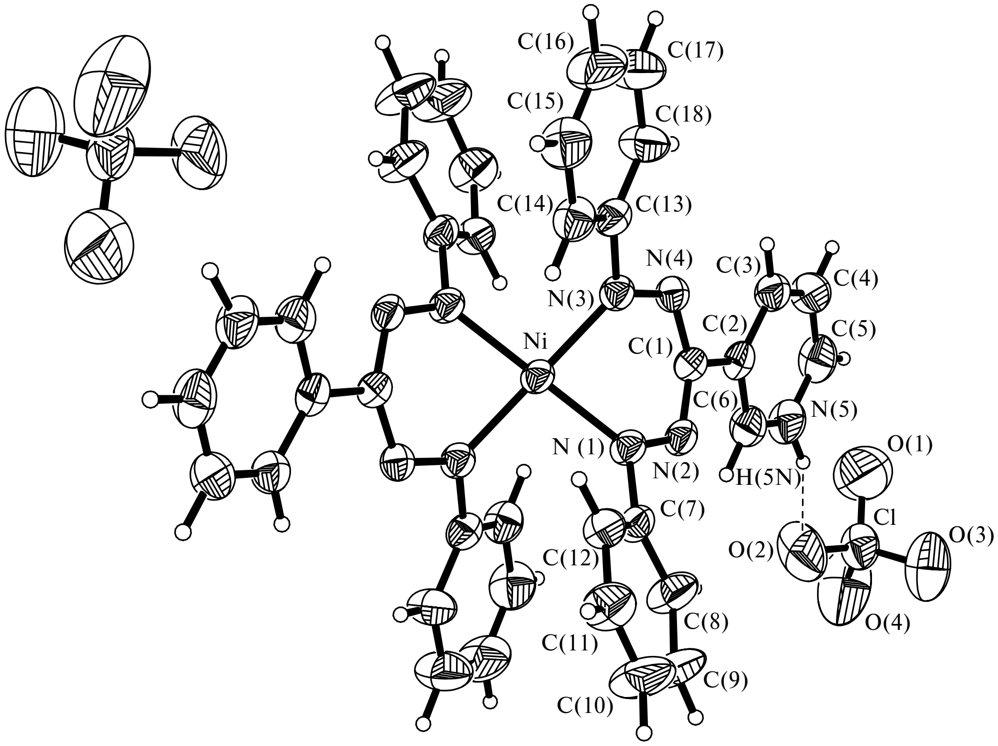


Fig. 1. Molecular structure of the complex **2a**$H_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$ projected onto the NiN_4 plane. The solvate water molecules are omitted. The intramolecular O(2)...H(5N) hydrogen bond is indicated by a dashed line. Selected bond lengths/Å: Ni—N(1), 1.874(4); Ni—N(3), 1.879(4); N(1)—N(2), 1.299(5); N(1)—C(7), 1.424(6); N(2)—C(1), 1.335(6); N(3)—N(4), 1.302(5); N(3)—C(13), 1.424(6); N(4)—C(1), 1.336(6); C(1)—C(2), 1.467(6). Selected bond angles/deg: N(1a)—Ni—N(3), 95.63(16); N(1)—Ni—N(3), 84.37(16); N(2)—N(1)—C(7), 114.6(4); N(2)—N(1)—Ni, 121.4(3); C(7)—N(1)—Ni, 123.3(3); N(1)—N(2)—C(1), 118.7(4); N(4)—N(3)—C(13), 115.0(4); N(4)—N(3)—Ni, 122.0(3); C(13)—N(3)—Ni, 122.4(3); N(3)—N(4)—C(1), 118.3(4); N(2)—C(1)—N(4), 125.7(4); N(2)—C(1)—C(2), 116.3(4); N(4)—C(1)—C(2), 116.7(4).

Table 2. X-ray data collection and refinement statistics for complexes **2a**$H_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$ and **2c,d**

Compound	**2a**$H_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$	**2c**	**2d**
Molecular formula	$C_{36}H_{34}Cl_2N_{10}NiO_{10}$	$C_{36}H_{28}N_{10}Ni$	$C_{38}H_{30}N_8Ni$
Molecular weight	896.34	659.39	657.42
Crystal dimensions/mm	0.44×0.10×0.08	0.34×0.22×0.06	0.29×0.26×0.19
Crystal system		Triclinic	
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	7.748(2)	7.993(2)	8.022(2)
b/Å	10.934(2)	10.619(2)	10.820(2)
c/Å	12.674(3)	10.996(2)	11.077(2)
α/deg	101.53(3)	114.03(3)	113.45(3)
β/deg	95.01(3)	94.91(3)	95.35(3)
γ/deg	104.83(3)	110.74(3)	111.63(3)
V/Å^3	1006.1(4)	767.8(3)	786.8(3)
Z	2	1	2
d_{calc}/g cm^{-3}	1.479	1.426	1.387
μ/mm^{-1}	0.684	0.677	0.659
F(000)	462	342	342
T/K	293(2)	293(2)	293(2)
θ Scan range/deg	1.66—25.17	2.11—25.47	2.09—25.97
Ranges of indices of reflections	$-9 \le h \le 0$, $-12 \le k \le 13$, $-15 \le l \le 15$	$0 \le h \le 9$, $-12 \le k \le 12$, $-13 \le l \le 13$	$-9 \le h \le 0$, $-12 \le k \le 13$, $-13 \le l \le 13$
Number of measured reflections	3898	3200	3312
Number of independent reflections (R_{int})	3606 (0.0284)	2848 (0.0157)	3077 (0.0245)
Number of parameters in refinement	271	266	250
R_1 ($I \ge 2\sigma(I)$)	0.0554	0.0302	0.0250
wR_2 (based on all reflections)	0.1101	0.0731	0.0626
Goodness-of-fit on F^2	0.985	0.922	0.887
Residual electron density (max/min)/e Å^{-3}	1.128/−0.332	0.371/−0.305	0.263/−0.253
CCDC refcode	610465	610466	611500

by the planar chelate Ni—N(Ar)—N—C(Ar)—N—N(Ar) ring.[46,47] Bis-ligand complexes of 1,5-diarylformazans can have two different types of structures due to repulsions between the aryl substituents. In one case, the metal chelate rings are twisted about the C(3)—Ni—C(3) axis, the chelate rings remaining planar, whereas the coordination environment of the metal atom being tetrahedrally distorted. This type was found in the structure of copper(II) bis-formazanate.[13] In another case, the square-planar environment of the metal atom is retained, but the metal chelate rings are distorted due to deviation of the metal atom from the plane through four nitrogen atoms of the chelate ring. Such structures are typical of divalent nickel[15,16] and palladium.[11]

Like the nickel complexes of 1,5-diarylformazans described in the literature,[15,16] complexes **2a**$H_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$ and **2c,d** belong to the second structural type with nonplanar metal chelate rings (Fig. 4). The deviations of the nickel atoms from the mean N_4 planes in the compounds under study are given in Table 3. This table also lists the dihedral angles between these planes and the planes of the NiN_4 rings.

As can be seen from Fig. 4, the aryl substituents at the first and fifths nitrogen atoms of the formazan chain are located at certain distances from each other. Analysis of these distances (see Table 3) shows that the aryl groups of the adjacent ligand molecules are linked to each other by π—π interactions, which is also manifested in the ^{1}H NMR spectra.

In the molecular structure of complex **2c**, the phenyl rings at position 3 of the ligands are disordered due to a twist about the C(1)—C(7) bond by an equal angle. The position of the nitrogen atom in the pyridine ring is statistical, and this atom is disordered over two positions. One of several possible orientations is shown in Fig. 2. The phenyl rings at position 3 of the ligands in the molecular

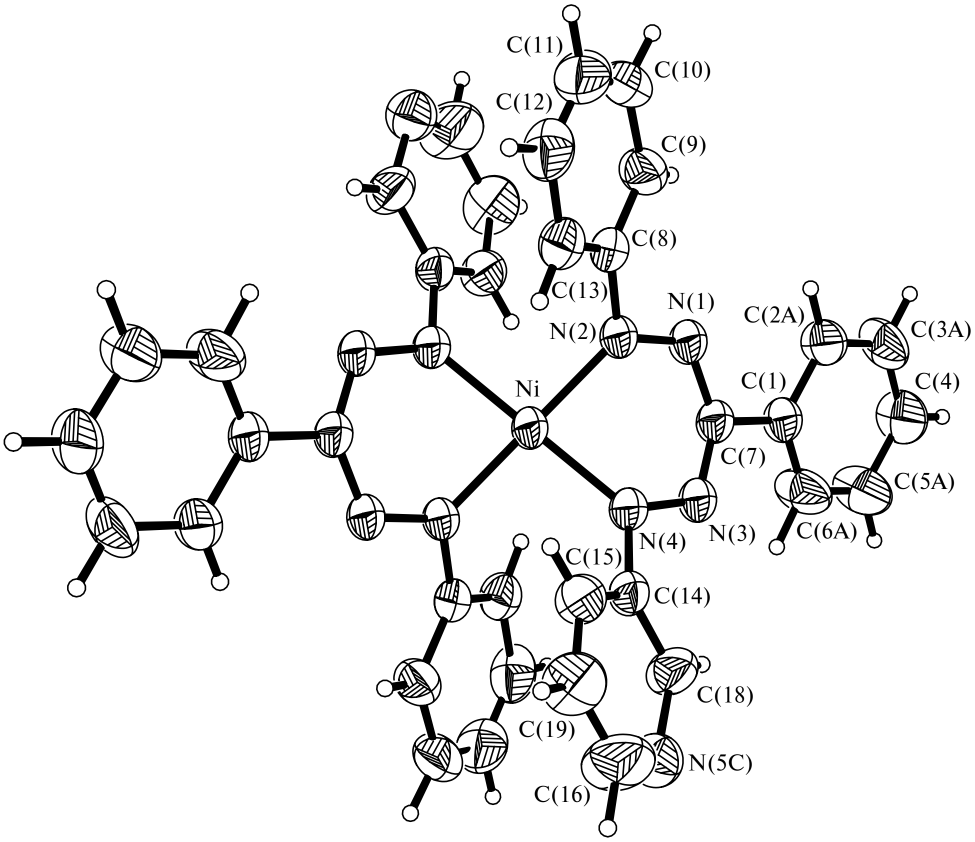


Fig. 2. Molecular structure of complex **2c** for one orientation of the phenyl and pyridine rings projected onto NiN_4 the plane. Selected bond lengths/Å: Ni—N(2), 1.8723(17); Ni—N(4), 1.8778(16); N(1)—N(2), 1.299(2); N(1)—C(7), 1.347(3); N(2)—C(8), 1.422(3); N(3)—N(4), 1.296(2); N(3)—C(7), 1.331(3); N(4)—C(14), 1.421(3); C(1)—C(7), 1.483(3). Selected bond angles/deg: N(2a)—Ni—N(4), 94.93(8); N(2)—Ni—N(4), 85.07(8); N(2)—N(1)—C(7), 119.37(16); N(1)—N(2)—C(8), 113.65(15); N(1)—N(2)—Ni, 122.98(13); C(8)—N(2)—Ni, 122.93(12); N(4)—N(3)—C(7), 119.89(16); N(3)—N(4)—C(14), 113.47(15); N(3)—N(4)—Ni, 123.02(13); C(14)—N(4)—Ni, 123.13(12); N(3)—C(7)—N(1), 124.71(17); N(3)—C(7)—C(1), 117.48(17); N(1)—C(7)—C(1), 116.40(17).

Table 3. Distances and angles between selected fragments in the molecules of complexes $\mathbf{2a}H_2^{2+}\cdot 2ClO_4^{-}\cdot 2H_2O$ and **2c,d**

Parameter	$\mathbf{2a}H_2^{2+}\cdot 2ClO_4^{-}\cdot 2H_2O$	**2c**	**2d**
Dihedral angle between the N_4 and NiN_4 planes/deg	40.5	37.0	37.2
Deviation of the Ni atom from the mean N_4 planes/Å	0.904	0.832	0.831
Deviation of the C atom of the formazan chain from the mean N_4 planes/Å	0.208	0.198	0.198
Distance between the N_4 planes/Å	1.808	1.664	1.662
Distance between the centroids of the nearest Ph rings/Å	3.934(1)	3.774(1)	3.829(1)
Distance between the closest C atoms of the nearest Ph rings/Å	3.101(1)	3.018(1)	3.034(1)

structure of complex **2d**, like those in the structure of complex **2c**, are disordered over two positions. One of several possible orientations is shown in Fig. 3.

In the crystal structure of $\mathbf{2a}H_2^{2+}\cdot 2ClO_4^{-}\cdot 2H_2O$, one of the oxygen atoms of the perchlorate anion (O(2)) is linked to the H(5N) atom by a strong hydrogen

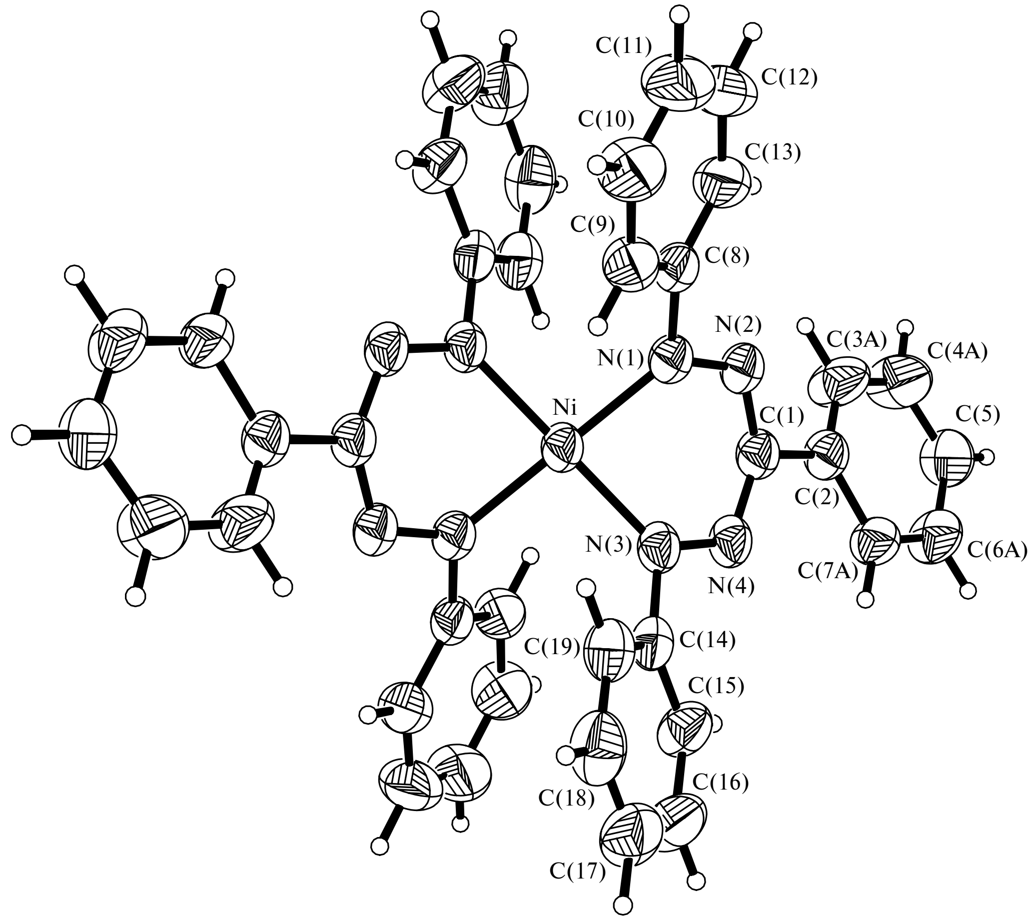


Fig. 3. Molecular structure of complex **2d** for one orientation of the phenyl rings projected onto the NiN_4 plane. Selected bond lengths/Å: Ni(1)—N(3), 1.8754(15); Ni(1)—N(1), 1.8776(14); N(1)—N(2), 1.3011(17); N(1)—C(8), 1.429(2); N(2)—C(1), 1.337(2); N(3)—N(4), 1.2991(17); N(3)—C(14), 1.426(2); N(4)—C(1), 1.342(2); C(1)—C(2), 1.481(2). Selected bond angles/deg: N(3)—Ni(1)—N(1a), 94.83(7); N(3)—Ni(1)—N(1), 85.17(7); N(2)—N(1)—C(8), 113.40(13); N(2)—N(1)—Ni(1), 122.91(11); C(8)—N(1)—Ni(1), 123.36(10); N(1)—N(2)—C(1), 119.64(14); N(4)—N(3)—C(14), 113.61(13); N(4)—N(3)—Ni(1), 123.06(12); C(14)—N(3)—Ni(1), 122.95(10); N(3)—N(4)—C(1), 119.30(14); N(2)—C(1)—N(4), 125.02(15); N(2)—C(1)—C(2), 117.05(15); N(4)—C(1)—C(2), 116.56(15).

bond (O(2)...H(5N), 1.884 Å; O(2)...N(5), 2.844(7) Å; O(2)...H(5N)—N(5), 159.5°).

The electrochemical properties of complexes **2** were studied by cyclic voltammetry (CV) and at a rotating disk electrode (RDE) (Fig. 5, Table 4).

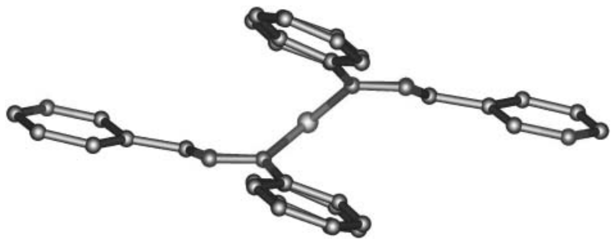
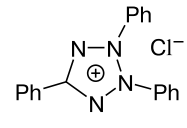


Fig. 4. Molecular view of **2a** in the structure of $\mathbf{2a}H_2^{2+} \cdot 2ClO_4^- \cdot$ $\cdot 2H_2O$ along the line between the N(1) and N(3) atoms. The H atoms, perchlorate anions, and water molecules are omitted.

As can be seen from these data, oxidation of the complexes occurs in one quasireversible step, except for irreversible oxidation of compound **2b** (the number of electrons transferred in each electrochemical step, which was experimentally determined by comparing with the ferrocene current, is in a range of 0.2—0.4 due, apparently, to electrode passivation during electrochemical measurements). The resulting radical cations are unstable on the time scale used (the lifetime <5 s), because we observed a pair of related peaks in the reverse cathodic sweep of the CV curve (see Fig. 5, the reduction peak *A* and the oxidation peak *B*). The potentials of these peaks are exactly equal to the reduction potential of 2,3,5-triphenyltetrazolium chloride (**3**), which we have synthesized and studied by electrochemical methods earlier,[37] and the oxida-



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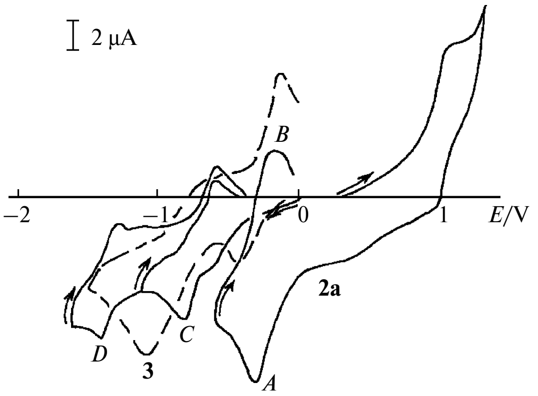

Fig. 5. Cyclic voltammograms of complex **2a** (solid line) and compound **3** (dashed line) (DMF, Bu_4NBF_4, Ag/AgCl/KCl(sat.), 20 °C, Pt electrode).

Table 4. Electrochemical oxidation (E^{Ox}) and reduction (E^{Red}) potentials of compounds **2a—d** measured by the CV method (E_p is the peak potential) and at an RDE ($E_{1/2}$ is the half-wave potential)[a]

Compound	$E_{1/2}^{Ox}$	E_p^{Ox} [b]	$-E_{1/2}^{Red}$	$-E_p^{Red}$ [c]
	V			
2a	1.04	1.01 (−0.34, 0.89)	0.64	0.74 (0.63), 1.31 (1.23)
2a$H_2^{2+}\cdot 2ClO_4^-$	0.98	1.05 (−0.30, 0.96)	0.24, 0.70	0.58, 0.76 (0.56), 1.36 (1.24)
2b	1.02	1.04 (−0.32)	0.65	0.74 (0.65)
2c	0.96	1.00 (−0.28, 0.94)	0.68	0.73 (0.68), 1.13 (1.03)
2d	0.90, 1.40	0.92 (−0.40, 0.87), 1.41	0.77	0.79 (0.72), 1.23 (1.04)

[a] DMF, Bu_4NBF_4, Ag/AgCl/KCl(sat.), 20 °C, a Pt electrode.

[b] The potentials of the reverse cathodic peaks are given in parentheses.

[c] The potentials of the reverse anodic peaks are given in parentheses.

tion potential of reduction product **3** (−0.49 and −0.28 V, respectively).

Hence, oxidation of the compounds under study affords radical cations, which rather rapidly decompose to give the tetrazolium cation and, apparently, a dimeric product with the nickel—nickel bond (LNi—NiL). The formation of dimeric (polymeric) products leads to Pt-electrode passivation, which apparently decreases the observed anodic current.

The CV curves have two quasireversible reduction peaks (see Fig. 5, the peaks *C* and *D*), whose potentials are virtually equal to the reduction potentials of substituted formazans **1**. We have studied the electrochemical properties of the latter compounds earlier.[37] Therefore, the initial electronic changes upon both oxidation and reduction are concentrated at the conjugated system of four nitrogen atoms of the formazan chain.

To reveal the influence of protonation of the pyridine nitrogen atoms on the electrochemical characteristics of the complexes, we also studied the redox properties of the complex **2a**$H_2^{2+}\cdot 2ClO_4^-$. As can be seen from Table 4, protonation of the pyridine nitrogen atoms does not lead to changes in the electrochemical potentials. This is evidence that the nature of the aryl substituents is of little importance. The early reduction peak (−0.58 V, see Table 4) is in the reduction region of the protons of $HClO_4$.[48]

To summarize, we synthesized and structurally characterized previously unknown nickel(II) complexes with formazans containing the pyridine fragments at positions 1 or 3. Such compounds are promising building blocks for the construction of complex infinite polyheterometallic ensembles. Preliminary ^1H NMR monitoring experiments demonstrated that the reaction of metalloligand **2c** with silver(I) nitrate in DMSO-d_6 produced new complexes. The structures and properties of these complexes are the subject of further investigations.

Experimental

The course of the reactions and the purity of the resulting compounds were controlled by TLC on a layer of silica gel (Silufol) as the stationary phase. The ^1H NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 on a Bruker-Avance instrument (400 MHz) with the use of signals of the residual protons of the solvents as the internal standard. The electrochemical oxidation and reduction potentials were measured on a PI-50-1.1 potentiostat equipped with a PR-8 programmer. The CV curves and waves at an RDE were recorded on an XY recorder. Tetrabutylammonium tetrafluoroborate of high purity grade (99.8%, Fluka) was used as the supporting electrolyte. The concentration of the electrolytes was 0.05 mol L^{-1}. The electronic absorption spectra in the visible and near-UV regions were measured on a Shimadzu UV-2100 spectrophotometer.

X-ray diffraction study was carried out on an Enraf-Nonius CAD-4 diffractometers at 293 K (β filter, λ(Mo-Kα) = 0.71073 Å, θ/2θ scanning technique). The absorption correction was applied based on the crystal shape. The structure was solved by direct methods (SHELX-97)[49] and refined by the full-matrix least-squares method against F^2 with anisotropic displacement parameters for all nonhydrogen atoms (SHELXL-97).[50] All H atoms were located in difference electron density maps and were not refined. The crystallographic data and X-ray data collection and refinement statistics for compounds **2a**$H_2^{2+}\cdot 2ClO_4^-\cdot 2H_2O$, **2c**, and **2d** are given in Table 2.

5-(3-Pyridyl)-1,3-diphenylformazan (1c) was synthesized according to a known procedure[29] as a dark-claret-colored powder with a green tint, the yield was 65%, m.p. 175 °C (from diethyl ether) (*cf.* lit. data[29]: m.p. 169 °C). Found (%): C, 71.46; H, 4.86;

N, 23.41. $C_{18}H_{15}N_5$. Calculated (%): C, 71.74; H, 5.02; N, 23.24. ^{1}H NMR ($CDCl_3$), δ: 15.35 (s, 1 H, NH); 8.82 (s, 1 H, α'-H$_{Py}$); 8.62 (d, 1 H, α-H$_{Py}$, J = 3.9 Hz); 8.12 (d, 2 H, o-H$_{Ph(2)}$, J = 7.1 Hz); 8.06 (d, 1 H, γ-H$_{Py}$, J = 8.0 Hz); 7.78 (d, 2 H, o-H$_{Ph(1)}$, J = 7.6 Hz); 7.51 (t, 2 H, m-H$_{Ph(2)}$, J = 7.7 Hz); 7.46 (t, 2 H, m-H$_{Ph(1)}$, J = 7.4 Hz); 7.34—7.43 (m, 3 H, p-H$_{Ph(2)}$, p-H$_{Ph(1)}$, β-H$_{Py}$). ^{1}H NMR (DMSO-d$_6$), δ: 13.59 (s, 1 H, NH); 8.99 (d, 1 H, α'-H$_{Py}$, J = 2.4 Hz); 8.41 (dd, 1 H, α-H$_{Py}$, J_1 = 4.8 Hz, J_2 = 1.5 Hz); 8.12 (ddd, 1 H, γ-H$_{Py}$, J_1 = 8.1 Hz, J_2 = 3.6 Hz, J_3 = 1.2 Hz); 7.95 (d, 2 H, o-H$_{Ph(2)}$, J = 6.6 Hz); 7.93 (d, 2 H, o-H$_{Ph(1)}$, J = 6.9 Hz); 7.55 (t, 2 H, m-H$_{Ph(2)}$, J = 7.5 Hz); 7.38—7.51 (m, 5 H, m-H$_{Ph(1)}$, p-H$_{Ph(2)}$, p-H$_{Ph(1)}$, β-H$_{Py}$).

Synthesis of complexes 2 (slow diffusion). Ethanol (3 mL) was very slowly added to a solution of formazan **1** (0.166 mmol) in MeCN or CH_2Cl_2 (4 mL) until stratification was achieved. A solution of a nickel salt (0.083 mmol) in EtOH (5 mL) was slowly added to the ethanolic layer. The reaction solution was kept for 25 days. The resulting crystals or powder were separated from the mother liquor, washed with diethyl ether, and dried in air.

Nickel(II) bis[3-(3-pyridyl)-1,5-diphenylformazanate] (2a) was synthesized from a solution of formazan **1a** in MeCN and nickel acetate tetrahydrate; the yield was 86%, a black crystalline powder, m.p. >320 °C. Found (%): C, 65.15; H, 4.46; N, 21.00. $C_{36}H_{28}N_{10}Ni$. Calculated (%): C, 65.37; H, 4.57; N, 21.18. ^{1}H NMR (DMSO-d$_6$, 20 °C), δ: 9.24 (br.s, 1 H, α'-H$_{Py}$); 8.66 (br.s, 1 H, α-H$_{Py}$); 8.38 (br.s, 1 H, γ-H$_{Py}$); 7.82 (br.s, 4 H, o-H$_{Ph}$); 7.61 (br.s, 1 H, β-H$_{Py}$); 7.12 (br.s, 6 H, m-H$_{Ph}$, p-H$_{Ph}$).

Nickel(II) bis[3-(3-pyridyl)-1,5-diphenylformazanate] dihydroperchlorate dihydrate ($2aH_2^{2+} \cdot 2ClO_4^- \cdot 2H_2O$) was synthesized from a solution of formazan **1a** in CH_2Cl_2 and nickel perchlorate hexahydrate as lustrous black prismatic crystals in 21% yield. The melting point was not measured and microanalysis was not carried out because the complex is dangerously explosive. ^{1}H NMR (DMSO-d$_6$, 20 °C), δ: 9.34 (br.s, 1 H, α'-H$_{Py}$); 8.79 (br.d, 1 H, α-H$_{Py}$, J = 4.6 Hz); 8.70 (br.s, 1 H, γ-H$_{Py}$); 7.93 (br.d, 1 H, β-H$_{Py}$, J = 7.3 Hz); 7.85 (br.d, 4 H, o-H$_{Ph}$, J = 7.5 Hz); 7.11—7.23 (m, 6 H, m-H$_{Ph}$, p-H$_{Ph}$).

Nickel(II) bis[3-(4-pyridyl)-1,5-diphenylformazanate] (2b) was synthesized from a solution of formazan **1b** in MeCN and nickel acetate tetrahydrate; the yield was 70%, a black-brown crystalline powder, m.p. 293 °C. Found (%): C, 65.15; H, 4.46; N, 21.00. $C_{36}H_{28}N_{10}Ni$. Calculated (%): C, 64.90; H, 4.53; N, 20.89. ^{1}H NMR (DMSO-d$_6$, 20 °C), δ: 8.71 (br.s, 2 H, α-H$_{Py}$); 8.00 (br.s, 2 H, β-H$_{Py}$); 7.76 (br.s, 4 H, o-H$_{Ph}$); 7.13 (br.s, 6 H, m-H$_{Ph}$, p-H$_{Ph}$).

Nickel(II) bis[5-(3-pyridyl)-1,3-diphenylformazanate] (2c) was synthesized from a solution of formazan **1c** in MeCN and nickel perchlorate hexahydrate as lustrous black crystals in 44% yield, m.p. >360 °C. Complex **2c** was synthesized analogously from nickel chloride hexahydrate as lustrous black crystals (76% yield) and from nickel acetate tetrahydrate as a black-brown powder (91% yield). Complex **2c** was also prepared from nickel nitrate hexahydrate and a solution of formazan **1c** in CH_2Cl_2 as lustrous black crystals in 61% yield. Found (%): C, 65.29; H, 4.47; N, 21.05. $C_{36}H_{28}N_{10}Ni$. Calculated (%): C, 65.55; H, 4.25; N, 21.24. ^{1}H NMR (DMSO-d$_6$, 50 °C), δ: 9.05 (s, 1 H, α'-H$_{Py}$); 8.26 (d, 1 H, α-H$_{Py}$, J = 3.9 Hz); 8.11 (d, 2 H, o-H$_{Ph(2)}$, J = 7.1 Hz); 8.03 (br.s, 1 H, γ-H$_{Py}$); 7.78 (d, 2 H, o-H$_{Ph(1)}$, J = 7.8 Hz); 7.61 (t, 2 H, m-H$_{Ph(2)}$, J = 7.7 Hz); 7.50 (t, 2 H, m-H$_{Ph(1)}$, J = 7.9 Hz); 7.10—7.24 (m, 3 H, p-H$_{Ph(2)}$, p-H$_{Ph(1)}$, β-H$_{Py}$).

Nickel(II) bis(1,3,5-triphenylformazanate) (2d) was synthesized from formazan **1d** in CH_2Cl_2 and nickel acetate tetrahydrate as black prismatic single crystals in 83% yield, m.p. >300 °C. Complex **2d** was also prepared from nickel chloride hexahydrate and a solution of formazan **1d** in MeCN as a finely crystalline powder in 40% yield. ^{1}H NMR (DMSO-d$_6$, 50 °C), δ: 8.11 (d, 2 H, o-H$_{Ph(2)}$, J = 8.0 Hz); 7.75 (d, 4 H, o-H$_{Ph(1)}$, J = 7.6 Hz); 7.60 (t, 2 H, m-H$_{Ph(2)}$, J = 7.5 Hz); 7.48 (t, 1 H, p-H$_{Ph(2)}$, J = 7.1 Hz); 7.17 (t, 4 H, m-H$_{Ph(1)}$, J = 7.3 Hz); 7.11 (t, 2 H, p-H$_{Ph(1)}$, J = 7.0 Hz).

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