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New Metal Complex Systems as Electrode Active Components of Ion Selective Electrode Membranes

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Abstract—New donor-acceptor 3*d*-transition metal complexes were synthesized and the cobalt and nickel complexes were studied by X-ray diffraction; CIF files CCDC no. 1516693 (**III**(Ni)) and 1516694 (**III**(Co)). The crystal structure details of the reactants were discussed. The proposed compounds were tested as the active components of ion selective electrode membranes for determination of thiocyanate ions. The selectivity of the SCN-SE with metal complex-based membranes depends on the ligand structure and the central metal ion type. The proposed electrode is suitable for determination of thiocyanate ions in the presence of sulfate, chloride, nitrate, nitrite, bromide, and iodide ions.

Keywords: donor–acceptor 3*d*-transition metal complexes, *N*-4-pyridylbenzamide, *N*-(5-quinolinyl)-3,5-dinitrobenzamide, active components of ion selective electrode (ISE) membranes, thiocyanate-selective electrodes

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INTRODUCTION

Cobalt(II), nickel(II), and zinc(II) complexes $ML_2(An)_2(H_2O)_n$ (L = *N*-(4-pyridinyl)benzamide, *N*-(5-quinolinyl)3,5-dinitrobenzamide, *N*-(4-pyridinyl)3,5-dinitrobenzamide, *N*-(5-quinolinyl)benzamide, $n = 2, 4$) were synthesized from aqua complexes containing the benzamide or dinitrobenzamide acceptor moiety and N-heterocycle (pyridine or quinoline) residues as donor components. Depending on the conditions of complexation (temperature, reaction time, solvent), it is possible to obtain complexes of different composition $ML_2(NO_3)_2(H_2O)_n(L'')_m$ either containing a solvent molecule (L'') or, in some cases, anhydrous [1–6].

The known metal complexes with a similar structure such as $Co[(NPBA)_2(OAc)_2(H_2O)_2]$ (NPBA = *N*-(4-pyridinyl)benzamide) [7, 8] proved to be applicable as sensors for colorimetric measurements; however, they have not been studied as active components of electrochemical sensors.

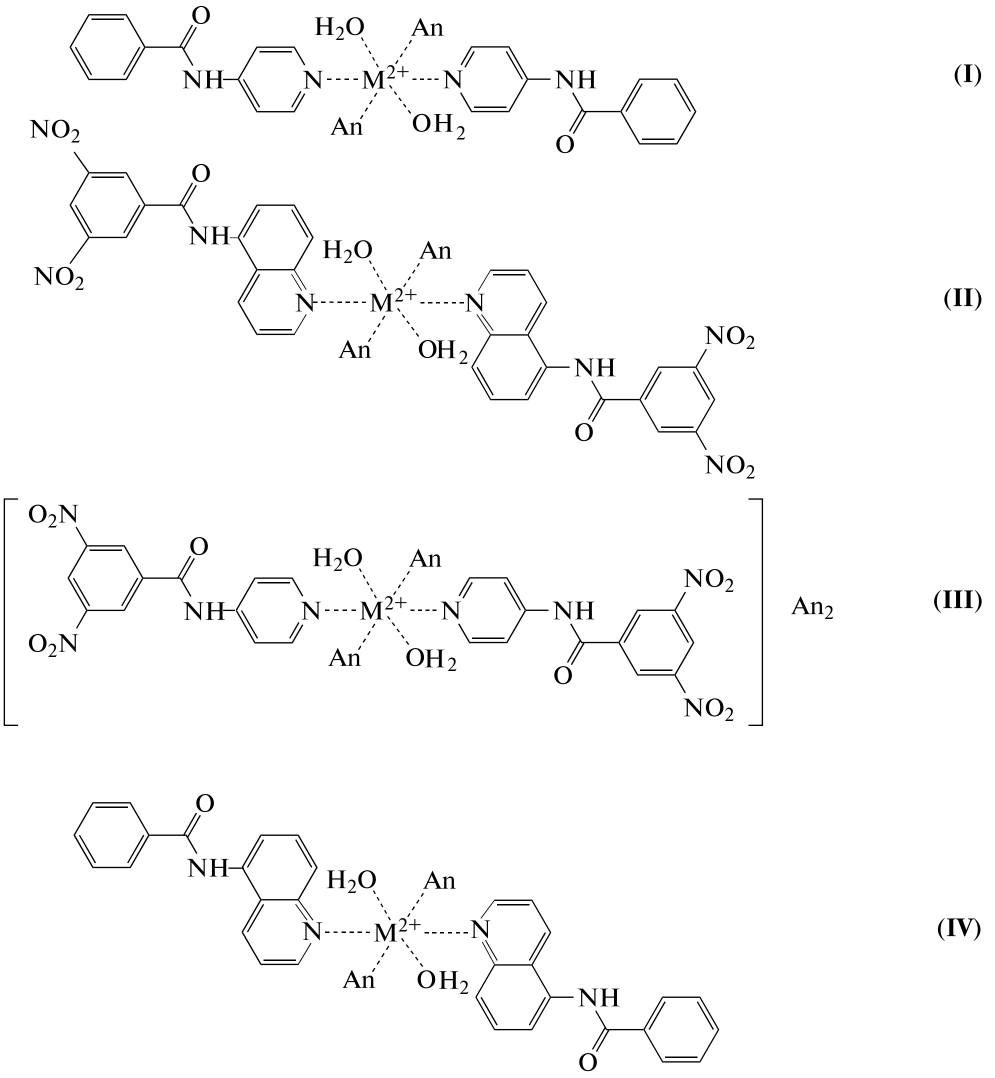
At the laboratory of electrochemical methods of analysis of the Division of Analytical Chemistry, Moscow State University, the metal complexes that we prepared were used as active components of ion selective electrode PVC-membranes for determination of nitrate and iodide ions in aqueous solutions [9–11].

This objective of this study was to evaluate the electrode activity of PVC membranes based on donor-acceptor complexes of 3*d* transition metals, $M^{2+}(L)_2(An^-)_2(H_2O)_n$ (**I**–**IV**; Scheme 1), for determination of thiocyanate ions and to compare the crystal structures of some compounds studied by X-ray diffraction: **III**(Co), **III**(Ni), and **V**(Ni).

For quantification of toxic thiocyanate ions, which can occur in waste and surface waters and appear in the human body, by ion measurements [12, 13], electrode systems with solid membranes based on mixtures of Ag_2S and AgX (X = halogen) are often used. Electrodes with crystalline membranes based on an $AgSCN–Ag_2S$ mixture can also be employed. However, the thiocyanate determination is markedly interfered with by Br^-, I^-, S^{2-}, and CN^- ions and the limit of detection (c_{min}) is ~10^{-5} mol/L [14].

The moderate selectivity to the accompanying halides and pseudo-halides and insufficiently low limit of detection promoted the search for new electrode-active compounds. Broad opportunities for this search are provided by the use of polymeric PVC membranes characterized by a wider range in which the Nernst equation holds and a lower limit of detection than crystalline membranes (c_{min} ~ 10^{-6}–10^{-7} mol/L). There are known SCN-SE of this type based on organic reagents such as polyiminopyridines [15], crown ethers [16], calixarenes [17], and polyamines [18] and metal complexes containing cobalt [19], rhodium [20], manganese [21–23], zinc [24–26], mercury [27, 28], copper [29–31], iron [32], cadmium [33], and nickel [34–37] in various combinations with these reagents. The ISE operation is considerably affected by both the nature of the complexing metal and ligand structure.

Thus, the synthesis of new ligands for metal complexes and elucidation of the effect of these compounds on the characteristics of polymeric membrane-based electrodes is a promising task.



I: M = Co, Ni; L = *N*-(4-pyridinyl)benzamide; An = NO_3^-, OAc^-; $n = 0, 2$

II: M = Co, Ni, L = *N*-(5-quinolinyl)3,5-dinitrobenzamide; An = NO_3^-, OAc^-; $n = 0, 2$

III: M = Co, Ni, L = *N*-(4-pyridinyl)3,5-dinitrobenzamide; An = NO_3^-, OAc^-; $n = 0, 2, 4$

IV: M = Co, Ni, L = *N*-(5-quinolinyl)benzamide; An = Cl^-, NO_3^-, OAc^-; $n = 0, 2$.

Scheme 1.

EXPERIMENTAL

The synthesis of metal complexes was performed as described in our previous study [1] using commercially available 4-aminopyridine, 5-aminoquinoline, and 3,5-dinitrobenzoic acid. The hexahydrates of Co(II) and Ni(II) nitrates were used as received. 3,5-Dinitrobenzoyl chloride was prepared by refluxing the initial acid with thionyl chloride with the addition of 2 or 3 drops of DMF as the catalyst; the crude product was crystallized from a minimum volume of hot toluene and dried [1–5].

The structures of the products were confirmed by IR spectra, which were recorded on an IR 200 Fourier Transform IR spectrometer (Thermo-Nikolet). In some cases, internal reflection spectroscopy was used to avoid undesirable absorption in the region of 3400 cm^{-1} (OH stretching vibrations).

The reactions were monitored and the purity of compounds was determined by TLC on Silufol UV-254 plates with a toluene–acetone mixture (1 : 1) as the eluent.

MALDI mass spectra were measured on an Autoflex II Bruker instrument (FWHM resolution of 18000). The samples were deposited on polished steel substrates. The spectra were recorded in the positive and negative ion modes.

The ^1H NMR spectra of solutions in CD_3OD were recorded in a Bruker Avance 400 DPX spectrometer (400 MHz) with TMS as an internal standard.

The X-ray diffraction study of **III**(Ni) (An = NO_3^-) was carried out on a Bruker Apex DUO CCD automated diffractometer ($\lambda(\mathrm{Cu}K_\alpha)$ = 1.54178 Å, $2\theta < 144°$), that of **III**(Co) (An = NO_3^-) was performed on a Bruker Smart Apex II CCD automated diffractometer ($\lambda(\mathrm{Mo}K_\alpha)$ = 0.71073 Å, $2\theta < 60°$). The empirical absorption corrections and systematic error corrections for both structures were applied using the SADABS program package. The structures were solved by the direct method and refined by full-matrix least squares on F^2_{hkl} with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms attached to carbon atoms were placed into calculated positions and included in the refinement in the riding model with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2\ U_{\mathrm{eq}}(\mathrm{C})$, and the hydrogens of coordinated water molecules were found from difference Fourier maps and refined in the isotropic approximation.

Crystallographic parameters and final *R* factors for **III**(Ni) ($C_{24}H_{24}NiO_{20}N_{10}$, $M = 831.24$): at $T = 120$ K, light green crystals, monoclinic, space group $P2_1/c$, $a = 8.56210(10)$, $b = 14.8957(2)$, $c = 12.2736(2)$ Å, $\beta = 91.7390(10)°$, $V = 1564.64(4)$ Å^3, $Z = 2$ ($Z' = 0.5$), ρ(calcd.) = 1.764 g/cm^3, $R_1 = 0.0290$ (for 2806 reflections with $I > 2\sigma(I)$ out of 3043 unique reflections), $wR_2 = 0.0763$, GOOF = 1.049; for **III**(Co) ($C_{24}H_{24}CoO_{20}N_{10}$, $M = 831.46$): at $T = 120$ K, brown crystals, monoclinic, space group $P2_1/c$, $a = 8.6104(4)$, $b = 14.9748(7)$, $c = 12.2327(5)$ Å, $\beta = 91.6150(10)°$, $V = 1576.65(12)$ Å^3, $Z = 2$ ($Z' = 0.5$), ρ(calcd.) = 1.751 g/cm^3, $R_1 = 0.0319$ (for 3777 reflections with $I > 2\sigma(I)$ out of 4591 unique reflections), $wR_2 = 0.0808$, GOOF = 1.044.

The structure solution and refinement were carried out using the SHELX program package, version 2014/7 [38]. The structures are deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1516693 (**III**(Ni)) and no. 1516694 (**III**(Co)); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

Membrane preparation. Polyvinyl chloride (PVC) of C-70 brand and *o*-nitrophenyl octyl ether (Fluka) plasticizer in 1 : 2 ratio and electrode active compounds (EAC), namely, metal complexes **I**–**IV** (2 wt %), were dissolved in tetrahydrofuran (THF) (Khimmed), sonicated for 10 min, and left for complete evaporation of the solvent. In the preparation of the membrane with a lipophilic additive, the ionic liquid 1,3-dihexadecylimidazolium nitrate (0.5 wt %) was also added.

The plasticized membranes formed as films and cut-out as circles 10 mm in diameter were attached by a special tip and a coupling nut to a cylindrical Teflon electrode body, which was filled with a 1×10^{-4} M solution of KCl. A silver wire coated by a silver chloride layer served as the internal reference electrode. An ESSR 10103 silver chloride electrode filled with a 3 M solution of KCl was used as the external reference electrode. Prior to investigation of electrode properties, the membrane PVC electrodes were preconditioned in a 0.1–0.01 M solution of KSCN for at least 5–7 days.

Preparation of solutions. The initial 1×10^{-1} M solutions of KSCN for studying the electrode characteristics were prepared by dissolving weight portions of reagent grade and analytical grade dry substances in distilled water. More dilute working solutions (1×10^{-2}–1×10^{-6} M) were prepared by successive dilution. Solutions containing foreign anions for investigating the potentiometric selectivity were prepared by dissolving weight portions of the corresponding reagent grade and analytical grade alkali metal salts in water.

Potentiometric measurements were carried out on an Expert 001 ion meter (Russia) and on a HI 2211 HANNA pH/ORP-meter (Germany). The potential was recorded with not more than 1 mV/min drift.

The potentiometric selectivity coefficients ($k_{i/j}^{\mathrm{pot}}$) were determined by the method of separate solutions, with concentrations of the target and foreign ions being 1×10^{-2} mol/L.

The calculation was performed by the formula:

$$gk_{i/j}^{\mathrm{pot}} = \frac{Z_i}{S}\left(E_j - E_i\right) + \left(1 - \frac{Z_i}{Z_j}\right)\log a_i,$$

where E_i, E_j are the electrode potentials measured in solutions of the target and foreign ions (mV), Z_i and Z_j are ion charges, a_i is the target ion activity in the solution, S is the slope of the electrode function for a singly charged ion [3].

The effect of pH was studied by measuring the electrode potential in a 1×10^{-3} M solution of KSCN (30 mL); pH was decreased by adding a dilute solution of H_2SO_4 and increased by adding solid LiOH.

Table 1. Effect of the nature of the complexing ion on the electrode characteristics of PVC-membranes based on reagent **I** in KSCN solutions

Central ion	Slope of the electrode function, mV/decade	Linearity range, mol/L	Limit of detection, mol/L
Co^{2+}	50	5×10^{-5}–0.1	8.7×10^{-6}
Ni^{2+}	39	1×10^{-4}–0.1	2.0×10^{-5}
Zn^{2+}	37	1×10^{-3}–0.1	3.3×10^{-4}

RESULTS AND DISCUSSION

In order to elucidate the effect of the metal nature on the electrode properties of membranes based on proposed compounds, we studied the electrode characteristics of PVC membranes based on EAC **I** containing various complexing ions (M = Co^{2+}, Ni^{2+}, Zn^{2+}) in solutions of potassium thiocyanate (Table 1).

A comparison of the obtained results showed that the highest electrode response of 53 mV/decade, an extended linearity range of 5×10^{-5}–0.1 mol/L, and a low limit of detection of 5.6×10^{-6} mol/L were characteristic of the cobalt-containing reagent **I** (Table 1). For the membranes with nickel(II)- and zinc(II)-based EAC, the slope of the ISE electrode function did not correspond to the theoretical value and the limit of detection was much higher.

It follows from X-ray diffraction data for the crystalline forms of tetraaqua-bis[4-(3,5-dinitrobenzamido)pyridine]cobalt(II) nitrate (**III**(Co)) and tetraaqua-bis[4-(3,5-dinitrobenza-mido)pyridine]nickel(II) nitrate (**III**(Ni)) that the synthesized complexes, similar in the structure to reported complexes [7, 8], have a different solvation shell structure, because the metal atom in them is surrounded by four H_2O molecules rather than by two molecules, while the NO_3^- counterions occur in the outer sphere, but are not directly bound to the metal atom as in [7, 8] (Fig. 1). In the structures that we studied by X-ray diffraction, the hydrogen atoms of coordinated water molecules (O(1*wA*) and O(2*wA*)) form an extensive hydrogen bond network with nitrate anions and carbonyl oxygen atoms (O(5) and O(5*A*)). The hydrogen atom of the N(1) and N(1*A*) amide moiety also forms a hydrogen bond with the nitrate anion.

The interactions of various natures are expected to weaken metal–anion bonds and increase the lability of the anion involved in the ion exchange at the membrane–aqueous solution interface.

Furthermore, the results of X-ray diffraction demonstrated that the metal–ligand bond in the Co complex is longer than that with Ni; hence, it is less strong, which may facilitate ion exchange near the coordination sphere.

Hence, according to the results of potentiometric measurements and X-ray diffraction data for metal complexes, it is expedient to study the electrode characteristics only for membranes with various cobalt-containing ligands.

The logarithms of the potentiometric selectivity coefficients to thiocyanate ions in the presence of some anions ($-\log K_{SCN/X^-}$) were calculated for the ISE based on cobalt-containing membrane (**I**); the resulting values are summarized in Table 2. No interfering effect of the foreign ions on the SCN-selective electrode potential was found; however, in the presence of iodide and salicylate ions, the potentiometric

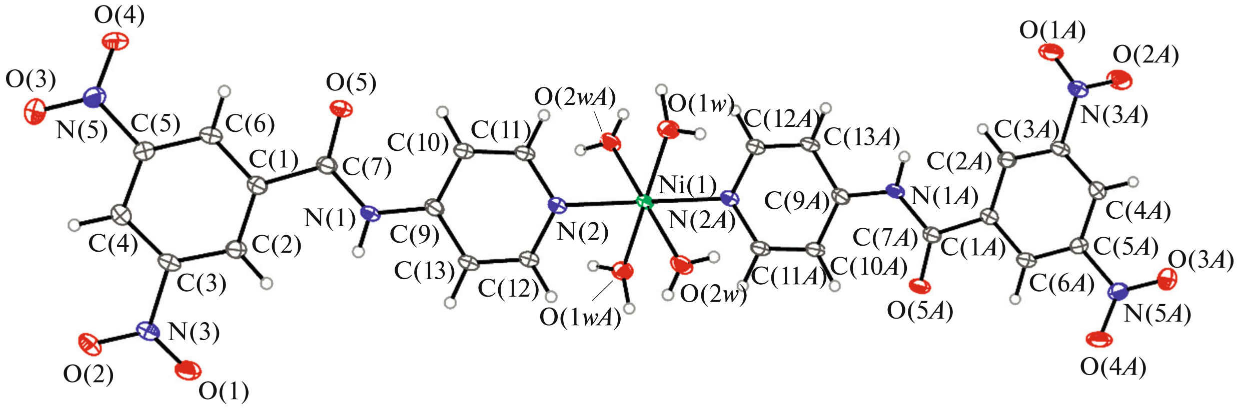


Fig. 1. General view of the cation of tetraaqua-bis[4-(3,5-dinitrobenzamido)pyridine]nickel(II) nitrate complex (**III**).

Table 2. Effect of foreign ions on the potentiometric response of SCN-SE based on reagent **I**

Ion (X^-)	$-\log K_{SCN/X^-}$
SO_4^{2-}	2.74
F^-	2.54
Cl^-	2.57
CH_3COOH^-	2.74
Br^-	2.59
NO_2^-	2.71
NO_3^-	2.15
I^-	1.06
$C_6H_5COO^-$	2.36
$C_6H_4OHCOO^-$	1.08

selectivity coefficients were an order of magnitude lower than in the presence of other ions.

The effect of the ligand structure on functioning of SCN electrodes was elucidated by investigating the electrode properties of PVC membrane electrodes also on the basis of cobalt reagents **II**–**IV**. Table 3 presents the key characteristics of all of the studied SCN-ISE.

A comparison of experimental results showed that the slope of the electrode function and the limit of detection for PVC-ISE in potassium thiocyanate solutions depend on the structure of ligands in the metal complexes. The lowest electrode response (34.8 mV/decade) and the highest limit of detection (6.1×10^{-4} mol/L) were inherent in compound **IV** devoid of terminal nitro groups.

The electrodes based on compound **I** possess somewhat better characteristics: the slope of the electrode function is 50.0 mV/decade, which is, however, lower than the theoretical value, and the limit of detection is 8.7×10^{-6} mol/L.

For electrodes based on active components **II** and **III**, electrode responses close to theoretical ones were obtained, 55.5 and 60.9 mV/decade, respectively, the lowest limit of detection being observed for the membrane based on **II** (4.9×10^{-6} mol/L).

A comparison of the structures of reagents used in membranes as electrode-active components with the determined electrode characteristics in thiocyanate solutions shows that the best response and the lowest limit of detection are inherent in the membrane based on the ligand with several terminal nitro groups and quinoline as the donor moiety.

An important characteristic of the electrode behavior of the membrane is the pH range in which the potential is invariable. SCN-SE potential measurements in solutions of thiocyanate ions at various pH showed that the structure of the EAC ligand affects the stability of the electrode potential in thiocyanate solutions. Figure 2 shows the potentials of the SCN electrode based on cobalt-containing metal complexes **II** and **III** plotted vs. the solution acidity. It was found that the electrode potential for the membrane based on **III** does not change in acid media as pH increases from 2 to 4. In the pH range above 4, the electrode potential loses stability and first increases and then (at pH > 6) substantially decreases.

Conversely, the potential of the SCN electrode with the membrane based on compound **II**, which differs from **III** by the presence of quinoline moiety in the ligand, barely depends on the medium acidity. It changes only slightly as pH increases from 2 to 10. While evaluating the differences in the structures of these two metal complexes present in the membrane, it is noteworthy that according to X-ray diffraction data, quinoline-containing structures are prone to intermolecular stacking interactions and hydrogen bonding, which may affect in different ways the behavior of the membranes based on them upon variation of the acidity.

Thus, the best electrode characteristics and the largest pH range of functioning are inherent in the SCN-SE based on the cobalt-containing complex **II**.

Since the best characteristics were found for the membrane electrodes based on **II** and **III**, the selectiv-

Table 3. Effect of the EAC ligand on the PVC-ISE characteristics based on cobalt reagents **I**–**IV** in KSCN solution

EAC	Slope of the electrode function, mV/decade	Linearity range, mol/L	c_{min}, mol/L
I	50.0	1×10^{-1}–5×10^{-5}	8.7×10^{-6}
II	54.5	1×10^{-1}–1×10^{-5}	4.9×10^{-6}
III	60.9	1×10^{-1}–1×10^{-4}	8.8×10^{-5}
IV	34.8	1×10^{-1}–1×10^{-3}	6.1×10^{-4}

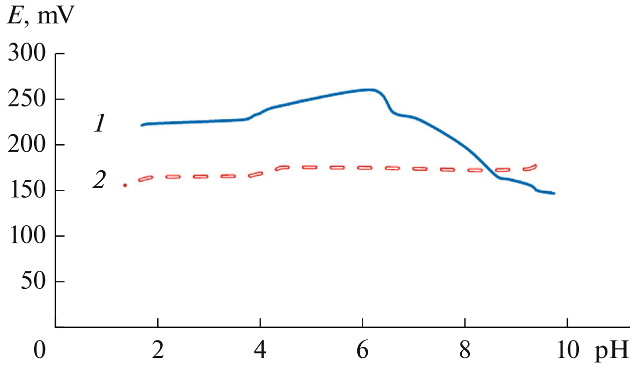


Fig. 2. Effect of pH on the potentials of thiocyanate SE membrane electrodes based on (*2*) **II** and (*1*) **III** in KSCN solutions.

ity of these electrodes in the presence of some anions was studied (Table 4).

Note that the found selectivity coefficients are rather low for both electrodes; however, in most cases, the electrode based on cobalt reagent **II** with a ligand containing terminal nitro groups and a quinoline donor moiety was more selective.

Relying on the above data, all the tested SCN electrodes exhibited non-Hofmeister type selectivity. This suggests that some stronger and more complex interactions occur between the membrane active component and the target ion than anion exchange processes based only on electrostatic interactions. Examples of such interactions include donor-acceptor or stacking interactions including intermolecular hydrogen bonding in the ligand. In turn, the thiocyanate ion can also be incorporated in this intricate and flexible system of interactions at various stages of passage through the membrane, which should increase the ISE selectivity.

Table 4. Effect of the EAC nature on the selectivity of the SCN electrode

X^-	$-\log K_{SCN^-/X^-}$	
	membrane based on **II**	membrane based on **III**
SO_4^{2-}	3.85	3.00
CH_3COO^-	2.56	1.65
F^-	3.22	2.25
Cl^-	3.18	3.70
Br^-	2.54	2.10
NO_2^-	2.55	1.55
NO_3^-	1.86	1.60
I^-	0.59	0.70
$C_6H_5COO^-$	2.77	2.90
$C_6H_4OHCOO^-$	0.62	0.10

To study the effect of the ionogenic lipophilic additive on the electrode characteristics of SCN-ISE based on **II**, we prepared membranes additionally containing a hydrophobic component, an ionic liquid, for example, 1,3-dihexadecylimidazolium nitrate (Table 5). It was shown that the electrode response of this membrane is 55 mV/decade, the linearity range is 0.1–1 × 10^{-5} M KSCN, and the limit of detection is 5 × 10^{-6} mol/L, which almost coincides with membrane characteristics without an additive.

It was found that SCN-SE with addition of ionic liquid, which increases both the membrane polarity and hydrophobicity, is selective to the thiocyanate ion in the presence of foreign anions, but the selectivity coefficients are higher than those for the electrode without the additive. It can be concluded that the introduction of a lipophilic additive somewhat impairs the selectivity of the metal complex-based electrode towards the SCN ion. This may indicate that the SCN-SE selectivity cannot be improved by mere increase in the overall hydrophobicity of the membrane upon introduction of a lipophilic additive and that without the additive, the active component acts as a charged carrier.

Thus, as a result of this study, we developed a thiocyanate-selective PVC electrode based on cobalt-containing metal complex, Co(II)[(*N*-(5-quinolinyl)-3,5-dinitrobenzamide)$_2$(CH_3COO)$_2$(H_2O)$_2$], possessing a response in the thiocyanate ion concentration range of 1 × 10^{-1}–1 × 10^{-5} mol/L (c_{min} = 4.9 × 10^{-6} mol/L) and operating at pH 2–10.

Note also that we isolated and characterized the anhydrous Ni(II) complex, **V**(Ni), with the same ligand, but with a geometry fundamentally differing from that described in [8] (Fig. 3).

In anhydrous complex **V**(Ni), the coordination polyhedron of nickel is a highly distorted octahedron in which the pyridine nitrogen atoms of two ligand molecules occupy the axial positions (as in **III**(Ni)), while the other four coordination sites are occupied by the pyridine nitrogen atom of the third ligand, two oxygen atoms of one nitrate ion, and one oxygen atom of the second nitrate ion (Fig. 2). The amide hydrogen atoms in the crystal of **V**(Ni) are hydrogen-bonded to coordinated nitrate anions (N···O 2.849(3)–3.084(3) Å), while the oxygen atoms of the nitro groups are not involved in hydrogen bonding, like in the aqua complexes considered below. Table 6 summarizes the geometric parameters of the metal coordination polyhedra in **III**(Ni), **III**(Co), and **V**(Ni). Unfortunately, complex **V**(Ni) (M = Ni; *n* = 0) could not be used for membrane preparation because of its low solubility.

Thus, the patterns identified in the study of the key electrode characteristics of the PVC SCN-membrane are actually confirmed by X-ray diffraction studies of some donor-acceptor metal complex compounds based on cobalt and nickel ions.

Table 5. Effect of the lipophilic additive on the selectivity of SCN-SE based on **II**

X^-	$-\log K_{SCN^-/X^-}$	
	membrane based on **II**	membrane based on **II** with an additive
SO_4^{2-}	3.50	3.36
CH_3COO^-	2.56	3.20
F^-	3.22	3.02
Cl^-	3.18	2.78
Br^-	2.54	2.10
NO_2^-	2.55	2.33
NO_3^-	1.86	1.72
I^-	0.59	0.41
$C_6H_5COO^-$	2.77	2.51
$C_6H_4OHCOO^-$	0.62	0.50

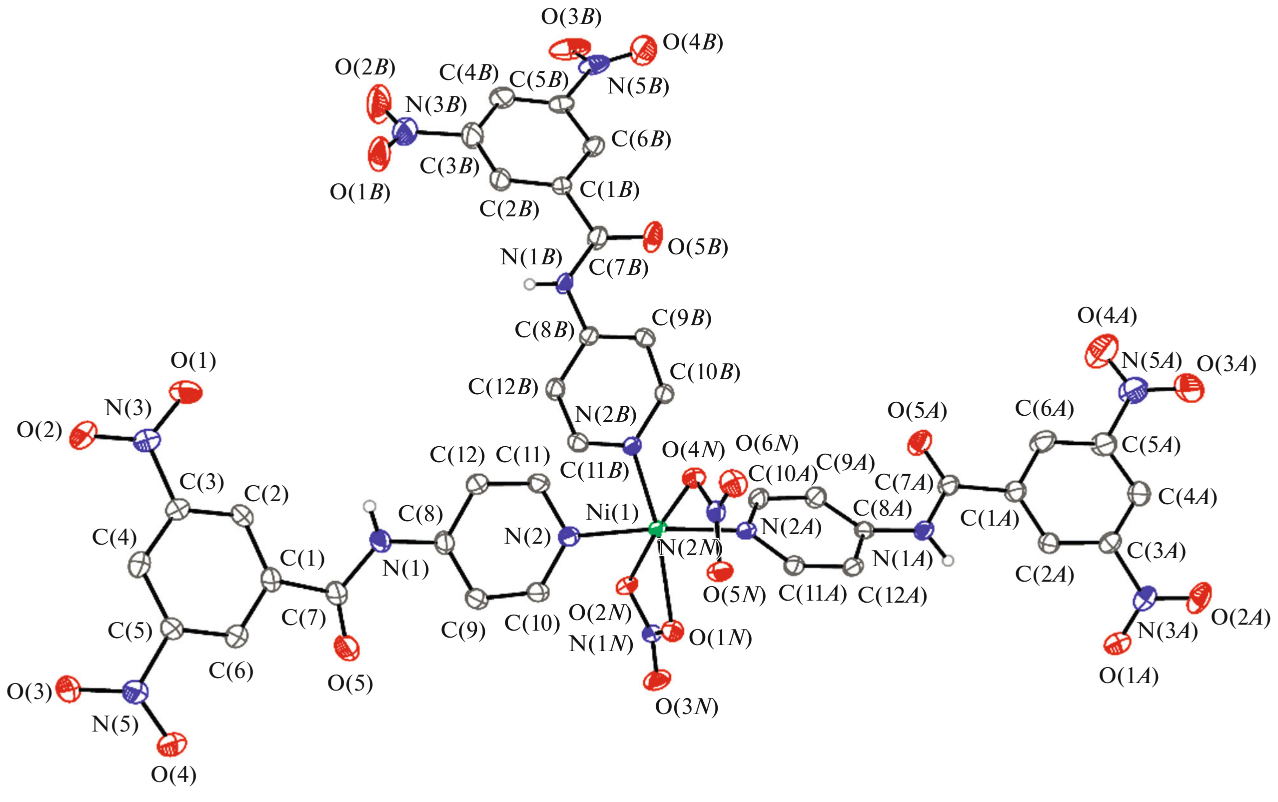


Fig. 3. General view of the tris[4-(3,5-dinitrobenzamido)pyridine]nickel(II) nitrate (**V**(Ni)) accordng to X-ray diffraction data.

Table 6. Geometric parameters of the coordination polyhedra of metal atoms in the complexes

Bond	**III**(Ni)	**III**(Co)	**V**(Ni)
M(1)–O(1*w*)	2.0702(11)	2.0888(11)	
M(1)–O(2*w*)	2.0785(12)	2.1109(11)	
M(1)–N(2)	2.0785(12)	2.1289(12)	2.084(2)
M(1)–N(2*w*)			2.090(2)
M(1)–N(2*B*)			2.055(2)
M(1)–O(1*N*)			2.2099(18)
M(1)–O(2*N*)			2.1353(18)
M(1)–O(4*N*)			2.0868(18)

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