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Reactions of Disubstituted Cyanamide Ligands in 3*d*-Metal Complexes

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Abstract—Structural features and reactivity of the *N*,*N*-disubstituted cyanamide ligands in the complexes of late 3*d* metals are discussed. The results obtained by author's research group within the recent four years are analyzed in comparison. The reactivity of the cyanamide and nitrile ligands in the presence of the 3*d*-metal salts is comparatively examined. The reaction behavior of substituted cyanamides in the presence of 3*d*-metals is compared with that of coordinated cyanamides in the complexes of transition metals of the 4*d* and 5*d* series (platinum, palladium).

Keywords: 3*d* metals, disubstituted cyanamides, ligands, reactivity, nucleophilic addition, cycloaddition

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INTRODUCTION

Reactions of organic compounds involving metal complexes represent a broad area of synthetic chemistry and provide ways to the preparation of diverse organic, coordination, and organometallic compounds. In particular, the metal compounds are successfully used for the activation of the –C≡N nitrile group of organic compounds with respect to nucleophilic and electrophilic addition and 1,3-dipolar cycloaddition [1]. NCR nitrile activation involving the metal complexes remains topical and is considered regularly in reviews [1–8].

A special class of compounds with the –C≡N group is presented by disubstituted cyanamides $NCNR_2$, the coordination chemistry of which has actively been studied in the recent two decades [9, 10]. In the disubstituted cyanamides, the lone electron pair of the nitrogen atom of the NR_2 amide group is conjugated with electrons of the π system of the C≡N bond, which affords the properties of $NCNR_2$. In particular, coordinated cyanamides $NCNR_2$ differ in reactivity, reaction rate, and composition and structure of the products compared to the "traditional" nitrile ligands NCR (R = Alk, Ar) [9]. The structural features and reaction behavior of the metal complexes with ligands $NCNR_2$ and NCR were compared in the review [9]. It should be mentioned that such kinetically inert metallocenters as platinum(II, IV) and palladium(II) were used for the activation of disubstituted cyanamides in the most part of the works considered [9]. New studies in the field of coordination chemistry of disubstituted cyanamides using a broader range of metals, including those of the 3*d* series, appeared since the review [9] has been published.

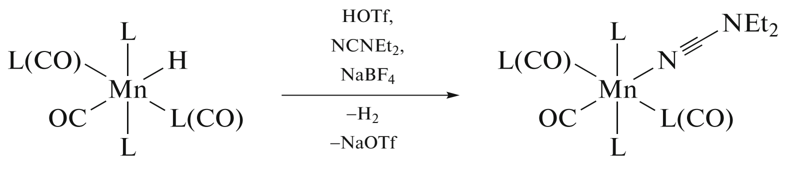
The purpose of this review is to generalize the recent results of research in the area of coordination chemistry of disubstituted cyanamides using 3*d*-metal complexes and to establish similarities and differences with the chemistry of the dialkyl cyanamide complexes of platinum and palladium.

The structures of the 3*d*-metal complexes with $NCNR_2$ are analyzed and the reactions of activated cyanamides with respect to the addition of nucleophiles (water, methanol, oximes, amidoximes, hydroxyguanidine, and hydrazines) and 1,3-dipoles (ketonitrones) are generalized in the review.

SYNTHESIS AND STRUCTURAL FEATURES OF 3*d*-METAL COMPLEXES WITH DISUBSTITUTED CYANAMIDES

The metal complexes with disubstituted cyanamides are known for almost all metals of the 3*d* series, including Ti(IV), Cr(0), Mn(I), Fe(II), Fe(III), Co(II), Co(III), Ni(0), Ni(II), Cu(I), Cu(II), and Zn(II) [9]. In many cases, only the empirical compositions were established for these compounds, whereas the structures of the complexes remained unproved. The synthesis and structural features of the transition metal complexes with dialkyl cyanamides have been studied in more detail in the recent works (see references cited in the review [9]). In this review, we consider the recent studies of author's and other research groups that were not cited in the review [9] devoted to the coordination chemistry of dialkyl cyanamides.

The manganese(I) complexes [Mn($NCNEt_2$)-$(CO)_n$$\{PPh(OEt)_2\}_{5-n}$]($BF_4$) ($n$ = 1 (**1**), 2 (**2**), 3 (**3**)) were synthesized [11] in 72–85% yields (Scheme 1) by the reactions of the corresponding hydride complexes [MnH$(CO)_n$$\{PPh(OEt)_2\}_{5-n}$] with trifluoromethanesulfonic acid (HOTf) (CH_2Cl_2, −196°C) followed by the addition of a fourfold excess of $NCNEt_2$ (room temperature (rt), 3 h) and salt $NaBF_4$. The IR spectra of compounds **1**–**3** exhibit the ν(CN) absorption bands at 2250–2260 cm^{-1} shifted to the high-frequency range by 30–40 cm^{-1} relative to the absorption band of uncoordinated $NCNEt_2$. The structure of complex **2** was determined by X-ray diffraction analysis [11]. The metallocenter in complex **2** exists in the octahedral environment, the CN bond length in the $NCNEt_2$ ligand (1.133(4) Å) is typical of that of the CN triple bond, and the MnNC angle (175°) slightly deviates from the linear angle.

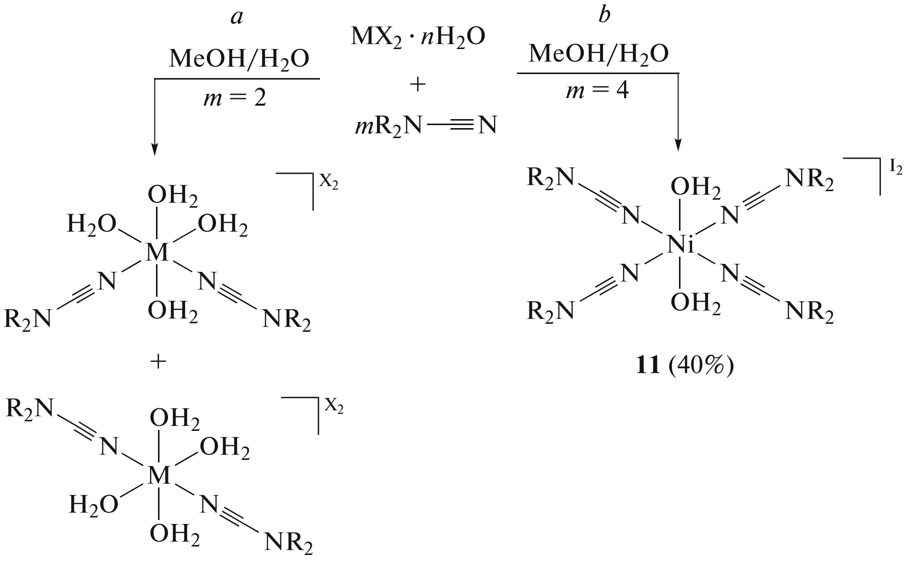


1–**3** (72–85%)

Scheme 1.

Complex [Fe$(NCNEt_2)_2$$\{P(OEt)_3\}_4$]$(BF_4)_2$ (**4**) (75%) was synthesized by the reaction of anhydrous salt $FeCl_2$ with a fivefold excess of $P(OEt)_3$ (EtOH, reflux 90 min) followed by the addition of a fivefold excess of $NCNEt_2$ (rt, 3 h) and a 2.5-fold excess of $NaBF_4$ [12]. The IR spectrum of complex **4** demonstrates an absorption band at 2265 cm^{-1} assigned to ν(CN) of the $NCNEt_2$ ligand.

The cobalt(II) complexes *trans*-[Co$(H_2O)_4$-$(NCNMe_2)_2$]X_2 · $2H_2O$ (X = Cl (**5**), Br (**6**)) were obtained by the reactions of cobalt salts $CoX_2 \cdot 6H_2O$ (X = Cl, Br) with dimethyl cyanamide in methanol followed by the evaporation of the reaction mixture in air (rt, 98% yield; Scheme 2*a*) [13]. In the IR spectra of compounds **5** and **6**, the ν(CN) absorption band lies in a range of 2260–2275 cm^{-1} (by 40–55 cm^{-1} higher than that for unbound $NCNMe_2$), indicating the electrophilic activation of coordinated $NCNMe_2$ [9]. It is shown on the basis of the X-ray diffraction analysis [9] for compounds **5** and **6** that the cationic complexes have an octahedral geometry with the *trans*-arrangement of the cyanamide ligands and the parameters of the $NCNR_2$ ligand (for example, the CN bond length equal to 1.148(6) and 1.160(3) Å) close to those in other dialkyl cyanamide complexes.



11 (40%)

M = Co: **5**–**6** (98%)
M = Ni: **7**–**10** (92–94%)

Scheme 2.

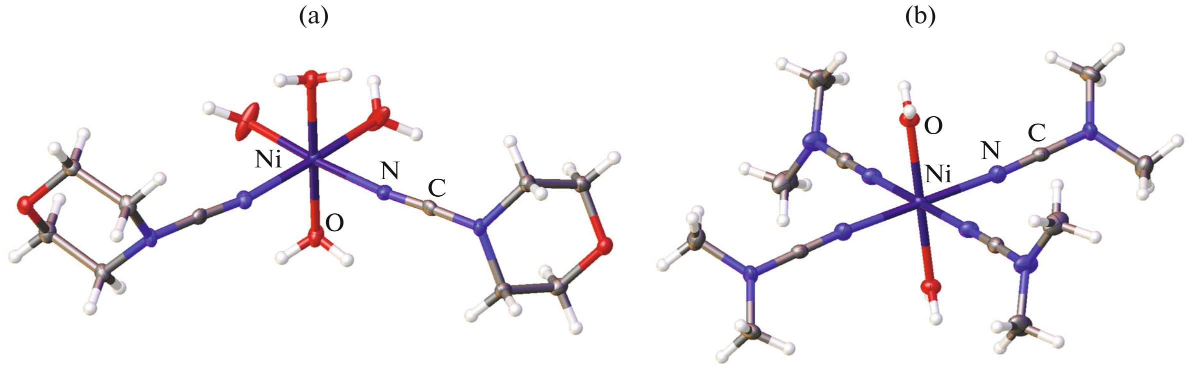
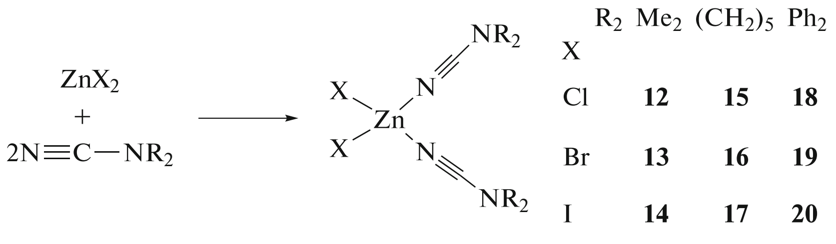


Fig. 1. Molecular structures of complexes (a) **10** and (b) **11** (anions and molecules of crystallization water are omitted).

The reactions of nickel salts $NiX_2 \cdot nH_2O$ (X = Cl and Br; $n = 0$ and 3, respectively) with dialkyl cyanamides $NCNR_2$ (R_2 = Me_2, $(CH_2)_2O(CH_2)_2$) in a molar ratio of 1 : 2 in undried methanol (rt) followed by the slow evaporation of the reaction mixture in air (rt, 24 h) results in the formation of complexes *cis*- and *trans*-$[Ni(H_2O)_4(NCNR_2)_2]X_2$ (X/R_2 = Cl/Me_2 (**7**), Br/Me_2 (**8**), $Cl/(CH_2)_2O(CH_2)_2$ (**9**), $Br/(CH_2)_2O(CH_2)_2$ (**10**); 92–94%) (Scheme 2*a*) [14]. The reaction of salt $NiI_2 \cdot 6H_2O$ with $NCNMe_2$ in a molar ratio of 1 : 4 and the slow evaporation of the mixture (rt, 24 h) make it possible to obtain compound *trans*-(O,O)-$[Ni(H_2O)_2(NCNR_2)_4]I_2$ (**11**) (Scheme 2*b*). The change in the molar ratio of the reactants to 1 : 2 does not result in the formation of the corresponding bis(dialkyl cyanamide) complex, but a mixture of compound **11** and the starting nickel salt is formed. The X-ray diffraction studies of the nickel(II) complexes with cyanamides **7–11** (Fig. 1) allowed one to establish that bis(cyanamide) complexes **7–10** were formed as *cis*- (**9** · $2H_2O$, **10** · $2H_2O$) and *trans*-isomers (**7** · $2H_2O$, **8** · $2H_2O$, **9** · $4H_2O$) containing crystallization water. In complex **11**, two molecules of coordinated water are in the *trans*-position. The CN bond in compounds **7–11** (1.148(3)–1.156(7) Å) and the NiNC angle (166°–171°) are characteristic for coordinated cyanamides. The IR data indicate the moderate electrophilic activation of the coordinated cyanamides and demonstrate the ν(CN) absorbance at 2260–2280 cm^{-1}, i.e., in a higher-frequency range compared to uncoordinated $NCNR_2$ (2210–2220 cm^{-1}).

The zinc(II) complexes with disubstituted cyanamides $[ZnX_2(NCNR_2)_2]$ (X = Cl, Br, I; R_2 = Me_2, $(CH_2)_5$, Ph_2 (**12–20**); 75–94%) were obtained by the reaction of the corresponding zinc salt ZnX_2 with cyanamide $NCNR_2$ (2 equiv mol) in CH_2Cl_2 (rt, 2 h) [15] (Scheme 3).



12–20 (75–94%)

Scheme 3.

These compounds are relatively stable in air and are completely characterized by physicochemical methods. The position of the ν(CN) absorption band (2240–2260 cm^{-1} for the complexes, 2210–2220 cm^{-1} for unbound $NCNR_2$) in the IR spectra of the complexes demonstrates the moderate electrophilic activation of coordinated cyanamide. It is found by the X-ray diffraction analysis for complexes **12–14**, **19**, and **20** [15] that the compounds have slightly distorted tetrahedral geometry and the CN bond length (1.145(3)–1.185(9) Å) is comparable with that for other complexes of disubstituted cyanamides. The ZnNC angle varies in a range of 159°–176°, which is

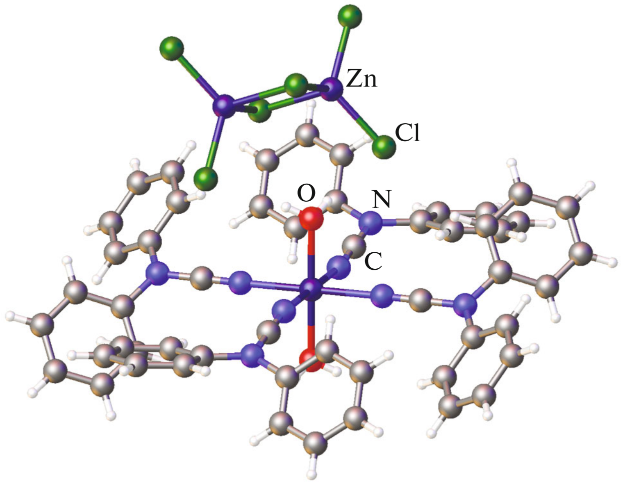
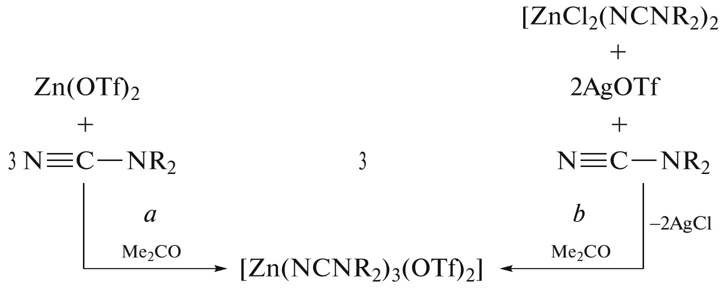


Fig. 2. Molecular structure of complex **21**.

determined by the steric hindrance of the R_2 substituents in the ligand.

The slow evaporation (2 weeks) of solutions of complexes **18** and **19** in undried CH_2Cl_2 results in the formation of crystals of ionic compounds $[Zn(NCNPh_2)_4(H_2O)_2][Zn_2(\mu\text{-}X)_2X_4]$ (X = Cl (**21**), Br (**22**); Fig. 2), whose structures were determined by X-ray diffraction analysis [15]. The occurrence of this reaction indicates a sufficiently high kinetic lability of the zinc compounds, and the driving force of the reaction can be a low solubility of the ionic complexes formed by the "large cation–large anion" pair.

Zinc complexes $[Zn(OTf)_2(NCNR_2)_3]$ (OTf = CF_3SO_3, $R_2 = Me_2$ (**23**), $(CH_2)_5$ (**24**)) containing no halogen were obtained in good yields (83–85%) by the reaction of salt $Zn(OTf)_2$ with $NCNR_2$ (3 equiv mol) in acetone (rt, argon) (Scheme 4*a*). These compounds were alternatively obtained in 76–79% yields in the exchange reaction between $[ZnCl_2(NCNR_2)_2]$ and AgOTf (2 equiv mol) in the presence of $NCNR_2$ (2 equiv mol) in acetone (rt, 2 h, argon) (Scheme 4*b*).



23–24 (76–85%)

Scheme 4.

The data of mass spectrometry (many fragmentation ions of diverse composition) and IR spectroscopy (the appearance of the ν(CN) absorption band at 2220 cm^{-1} from free cyanamide) indicate a noticeable kinetic lability of compounds **23** and **24** toward the ligand exchange. In fact, attempts to obtain crystals of these complexes by the slow evaporation of solutions gave compounds with different compositions: $[Zn(NCNMe_2)_3(H_2O)_2](OTf)_2$ (**23a**, crystallization from the reaction mixture when obtaining compound **23**, acetone, rt) and $[Zn(NCNMe_2)_2(OTf)_2]_n$ (**23b**, evaporation of a solution of complex **23** in CH_2Cl_2, rt; Fig. 3). Complex **23a** is an ionic compound, whose cation is formed by the zinc complex with the trigonal bipyramidal geometry. Complex **23b** is a polymer formed by one-dimensional chains in which the zinc atoms in the octahedral environment are linked to each other by the bridging ligands $CF_3SO_3^-$. Another specific feature of these complexes is an appreciable

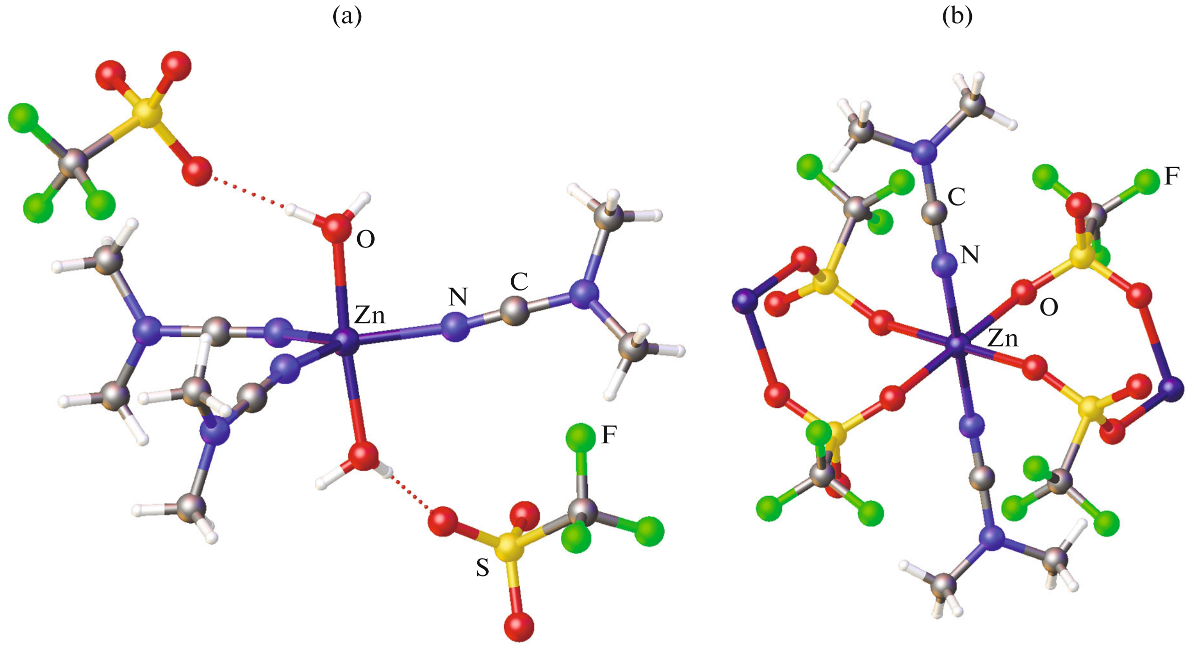


Fig. 3. Molecular structures of complexes (a) **23a** and (b) **23b** (fragment, b).

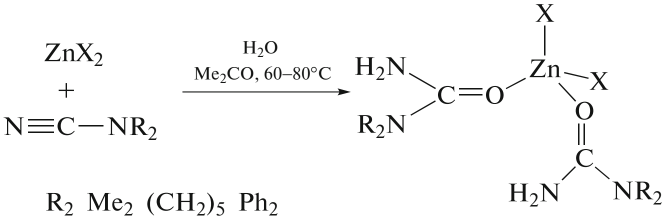
deviation of the ZnNC angle from linear one (143°–167° for **23a** and 159° for **23b**).

Thus, the 3*d*-metal complexes with disubstituted cyanamides can be obtained by the reactions of $NCNR_2$ with transition metal salts and due to the ligand exchange. As a rule, the 3*d*-metal complexes are kinetically labile and can form several species easily transforming into each other (*cis*/*trans*-isomers for the nickel(II) complexes, neutral and ionic halogen-containing zinc(II) complexes). The lability of the complexes is also determined by the ligand environment. The zinc(II) halide complexes $[ZnX_2(NCNR_2)_2]$ are fairly stable in the solid phase and in solutions, whereas the compounds with the triflate anion $[Zn(OTf)_2(NCNR_2)_3]$ are rapidly transformed in solutions into other zinc compounds with cyanamide ligands. The coordination to the metallocenter results in the shift by 30–50 cm^{-1} of the ν(CN) absorption band in the IR spectra relative to the cyanamide unbound to the metallocenter, which is comparable with the corresponding values for the platinum(II) and palladium(II) complexes [9]. This indicates the electrophilic activation of the nitrile group when coordinating to the metals in the positive oxidation states. The CN bond length of coordinated cyanamides is comparable with that of the nitrile ligands, and the CN bond is triple. The MNC angle can vary in wide ranges (143°–180°) and is determined by the geometric parameters of the complex and steric hindrance of the ligands.

REACTIONS OF CYANAMIDE LIGANDS WITH NUCLEOPHILES

The most part of the earlier described [9] examples of reactions of the disubstituted cyanamide ligands with nucleophiles is related to the chemistry of platinum(II, IV). This metallocenter provides the electrophilic activation of $NCNR_2$ sufficient for the reactions with water, oximes, amidoximes, amidines, and guanidines under mild conditions [9]. In all cases, the coordinated products of coupling of dialkyl cyanamides with a nucleophile were obtained. In this section, we consider the recent examples of the reactions of $NCNR_2$ with nucleophiles in the presence of kinetically more labile metallocenters of the 3*d* metals: iron(II), nickel(II), and zinc(II). These metallocenters electrophilically activate dialkyl cyanamides toward the reactions with water, methanol, oximes, amidoximes, hydroxyguanidine, and hydrazines. The higher (compared to platinum) lability of the metallocenters provides the diversity of the reaction products and the possibility of forming uncoordinated compounds.

Reactions with water and methanol. Disubstituted cyanamides coordinated to 3*d* metals react with water under fairly mild conditions. For instance, in the presence of zinc salts ZnX_2 (X = Cl, Br, I), compounds $NCNR_2$ (R_2 = Me_2, C_5H_{10}, Ph_2) in a mole ratio of 2 : 1 react with water (40-fold excess) in acetone (R_2 = Me_2, C_5H_{10}, 60°C, 3 days; R_2 = Ph_2, 80°C, 24 h) to form the corresponding complexes with O-coordinated substituted urea $[ZnX_2\{OC(NH_2)NR_2\}_2]$ (**24**–**32**, 57–81% yield) (Scheme 5) [15].



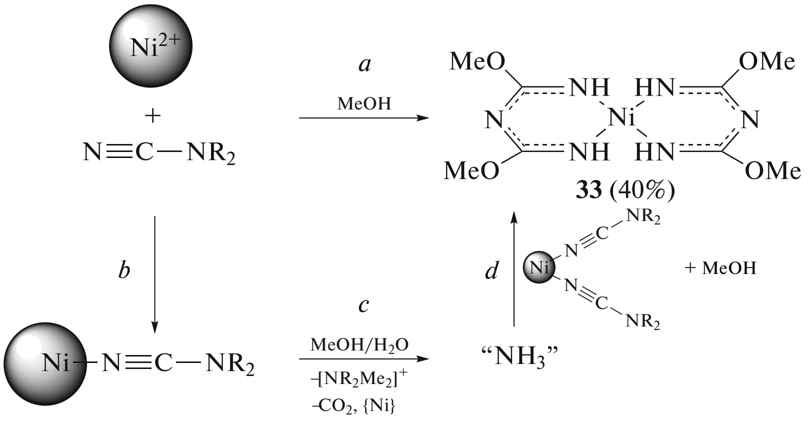
24–32 (57–81%)

X \ R₂	Me₂	(CH₂)₅	Ph₂
Cl	**24**	**27**	**30**
Br	**25**	**28**	**31**
I	**26**	**29**	**32**

Scheme 5.

The control experiment on studying the reactions of disubstituted cyanamides with water in the absence of a zinc salt, under the same conditions (acetone, 60°C, 3 days), did not afford ureas. Thus, the hydration of cyanamides is promoted by zinc(II). It should be mentioned that several examples of zinc(II)-catalyzed hydration to the corresponding carboxamides $O{=}C(NH_2)R$ occurring in the Zn(II)–R'R"C=NOH [16, 17] and Zn(II)–$OC(NH_2)R'$ [18] systems are known for traditional nitriles NCR (R = Alk, Ar). In the case described above, the hydration of disubstituted cyanamides needs no cocatalyst (oxime or amide), and the reaction is metal-promoted rather than catalyzed and results in the formation of coordinated coupling products.

Complex $[Ni\{NH{=}C(OMe)NC(OMe){=}NH\}_2]$ (**33**, 40%) (Scheme 6) was isolated from the reactions of dialkyl cyanamides $NCNR_2$ (R_2 = Me_2, C_4H_8O) and nickel salt $NiCl_2$ in undried methanol (rt, 3 days or 50°C, 1 day) [19].



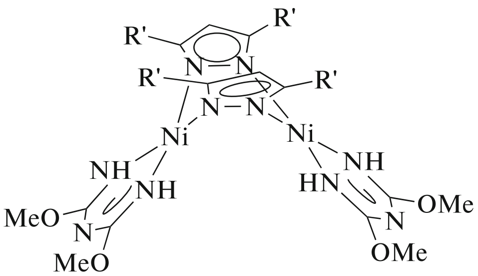
33 (40%)

Scheme 6.

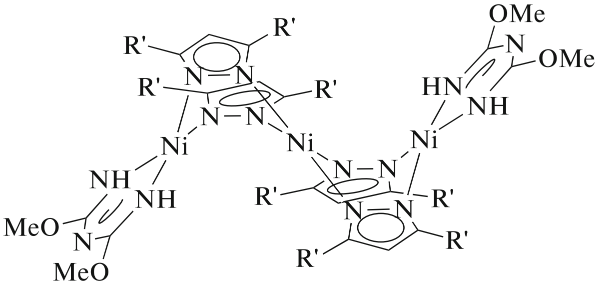
Compound **33** is the product of the multistep methanolysis–hydrolysis reaction of the disubstituted cyanamide ligands. It was shown that no hydrolytic coupling product was formed upon the replacement of methanol by other alcohols (EtOH, *iso*-PrOH). The probable mechanism was proposed for the formation of complex $[Ni\{NH{=}C(OMe)NC(OMe){=}NH\}_2]$ on the basis of the literature data and analysis of the reaction coproducts [19]. The cyanamide ligand is cleaved first under the action of a methanol–water mixture to form ammonia (Scheme 6*b*, 6*c*). In this reaction, methanol acts as a methylating agent and also promotes the substitution of amide groups NR_2 by OMe in one of the steps (Scheme 6*d*). The more pronounced alkylating ability of methanol compared to other alcohols explains the sensitivity of the reaction to the choice of the solvent. Ammonia formed upon cyanamide cleavage interacts with the dialkyl cyanamide ligands to form the product of coupling of two ligands **33** (Scheme 6*d*).

Structurally similar complexes with the triazapentadiene ligand $[Ni\{NH{=}C(R)NC(R){=}NH\}_2]$ were obtained earlier due to the hydrolytic coupling of nitriles NCR that occurred in methanol in the presence of the nickel(II) salts and acetamidoxime [20–22]. The reaction involving dialkyl cyanamides $NCNAlk_2$ does not require the $Me_2C=NOH$ cocatalyst and is accompanied, in addition to the formation of the triazacyclopentadiene fragment {N=CNC=N}, by the cleavage of the $NC-NR_2$ bond to form ligand NH=C(OMe)NC(OMe)=NH [19].

The formation of the bi- and trinuclear nickel complexes with the terminal triazapentadienate ligands and bridging azolate ligands was demonstrated for more complicated $NiCl_2-NCNR_2-HPzR'_2-MeOH$ systems ($R_2 = Me_2$, C_4H_8O; $HPzR'_2$ are 3,5-disubstituted pyrazoles; R' = Me, Ph, and indazole): $[Ni_2(PzR'_2)_2$-{NH=C(OMe)NC(OMe)=NH}$_2$] (R' = Me (**34**), Ph (**35**)) and $[Ni_3(PzR'_2)_4${NH=C(OMe)NC-(OMe)=NH}$_2$] (R' = Me (**36**), PzR'_2 = Ind (**37**)) (Scheme 7) [19].



34, **35**

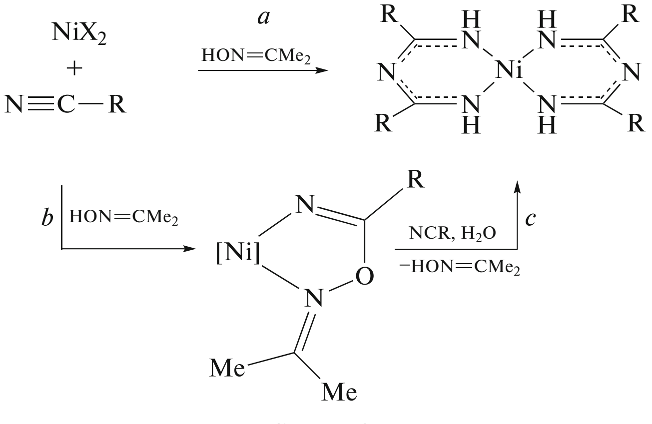


36, **37**

Scheme 7.

No nucleophilic addition of azoles (as HN nucleophiles) to the dialkyl cyanamide ligands is observed in these systems, but the nickel(II)-promoted solvolytic coupling of cyanamide ligands involving methanol occurs with the formation of ligand NH=C(OMe)NC(OMe)=NH. Substituted azoles undergo deprotonation and act as bridging ligands in the formation of bi- and trinuclear complexes **34–37**.

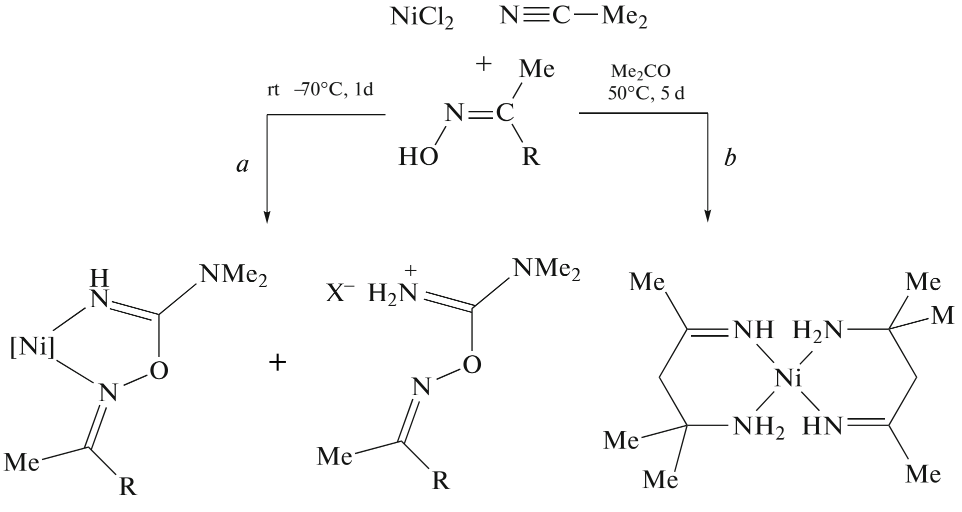
Reactions with oximes. It has previously been established that in the $Ni(II)-Me_2C=NOH$ system in undried methanol nitriles NCR undergo hydrolytic coupling to form complexes $[Ni\{NH=C(R)NHC(R)=NH\}_2]^{2+}$. Acetoxime acts as a catalyst of the process, and the reaction does not occur in the absence of acetoxime [20–22]. It is assumed that the catalytic role of oxime consists in the nucleophilic attack to nitrile activated by coordination to nickel(II) accompanied by the formation of the coupling product $\{NH=C(R)-ON=CMe_2\}Ni$ as an intermediate, which was not detected (Scheme 8).



Scheme 8.

The formation of the intermediate cross-coupling product was indicated by the results of the works on the synthesis of the nickel complexes containing the polydentate imino ligands (cross-coupling products of nitriles and bidentate oximes in the presence of the nickel(II) salts) [23–25] and the works on studying the formation of the platinum(II, IV) imino complexes {NH=C(R)ON=CR'R"}Pt due to the reactions of the nitrile complexes (NCR)Pt (R = Alk, Ar) with mono- and bidentate oximes HON=CR'R'' (R' = H, Alk; R' = H, Alk, Ar, C(Alk)=NOH) [26–31].

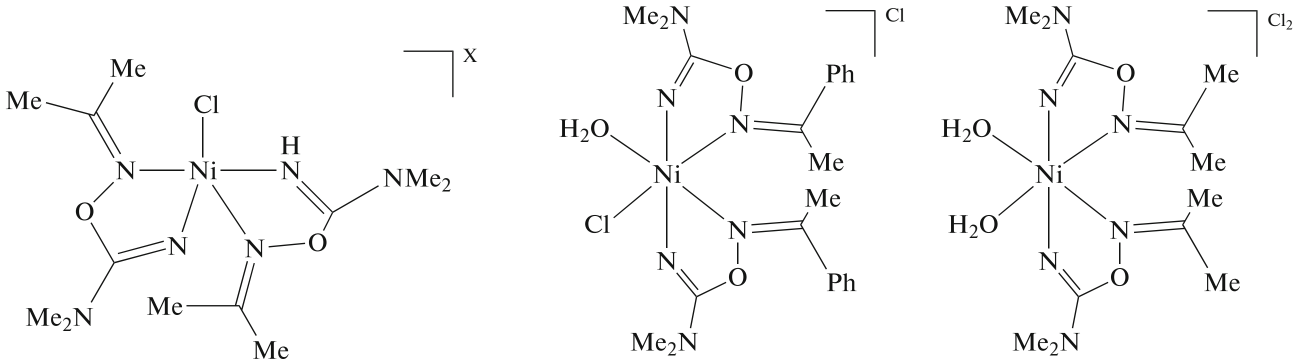
We studied the reactions of dimethyl cyanamide $NCNMe_2$ with ketoximes HON=C(Me)R (R = Me, Ph) in the presence of nickel chloride (acetone or Me-*iso*-BuCO, rt or 50–70°C, 24 h) and isolated the addition products as complexes with the bidentate coordinated imino ligand $\{\underline{N}H{=}C(NMe_2){-}O\underline{N}{=}C(Me)R\}Ni^{II}$ (**38**–**41**, <5–82%) (Scheme 9*a*, 10) and salts $[NH_2{=}C(NMe_2)ON{=}C(Me)R]X$ (X = Cl, R = Ph (**42**), <5%; X = $1/2NiCl_4$, R = Me (**43**), 70%) (Scheme 9*a*) [32].



38–**41** (<5–70%) **42**–**43** (<5–83%) **44** (30%)

Scheme 9.

The structure of nickel complexes **38–42** are presented in Scheme 10.



X = Cl, **38** (40%)
X = $1/2NiCl_2$, **39** (<5%)

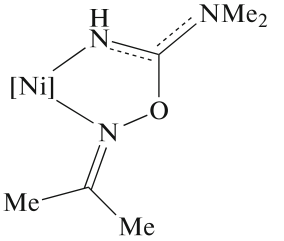
40 (82%)

41 (44%)

Scheme 10.

The relatively high kinetic lability of the nickel(II) complexes and coordination nonrigidity resulted in the formation of structurally different compounds **36–41** (Scheme 10) with a change in the reaction conditions. For example, after keeping the $NiCl_2$–$NCNMe_2$–HON=CMe(R) system in acetone at room temperature for 24 h, the crystals of salts **42** (R = Ph) and **43** (R = Me) were isolated, whereas complex **38** (R = Me) or **40** (R = Ph), respectively, was formed if the same reaction was carried out at 50°C. Product **41** was obtained from the $NiCl_2$–$NCNMe_2$–$HON{=}CMe_2$ system using Me-*iso*-BuCO as a solvent (50°C, 4 days).

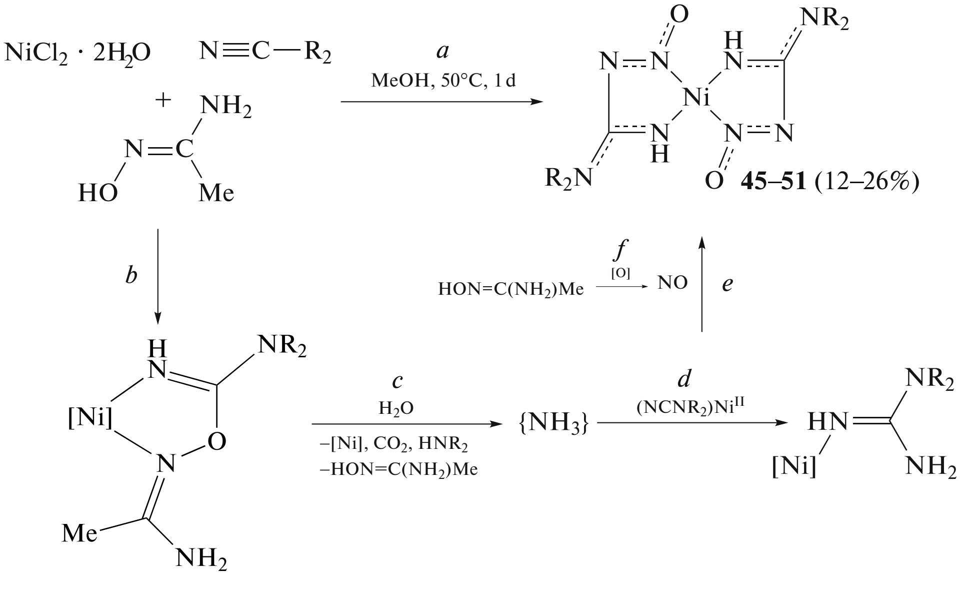
The observed difference in the reaction products of the Ni(II)–ketoxime system with dimethyl cyanamide and traditional nitriles NCR (R = Alk, Ar) can be explained from the viewpoint of stability of the coupling products {N̲H=C(R)ON̲=C(R')R''}Ni^{II} (R = NMe_2 or Alk, Ar). In the dimethyl cyanamide derivative, the conjugation of the lone electron pair of the NR_2 amide group with π electrons of the NC fragment results in the stabilization of the nucleophilic addition product, unlike the derivatives of traditional nitriles [32] (Scheme 11).



Scheme 11.

A more prolonged keeping of the $NiCl_2$–$NCNMe_2$–HON=CMe(R) reaction mixture (R = Me, Ph) in acetone (50°C, 2–5 days) leads to the formation of the known complex $[Ni\{NH=C(Me)CH_2CMe_2NH_2\}_2]Cl_2$ (**44**, 30%) [33], which is the product of condensation of acetone with ammonia in the coordination sphere of nickel(II). Ammonia can also be formed due to the hydrolytic cleavage of dimethyl cyanamide in the Ni(II)–ketoxime system that occurs in undried acetone via the intermediate product {N̲H=C(NMe_2)ON̲=C-(Me)R}Ni^{II}. This reaction also confirms the hypothesis that the hydrolytic cleavage of nitriles NCR in the presence of Ni(II)–ketoxime serves as a source of ammonia necessary for the formation of the coupling products $[Ni\{NH=C(R)NHC(R)=NH\}_2]^{2+}$ (Scheme 9*b*) [20].

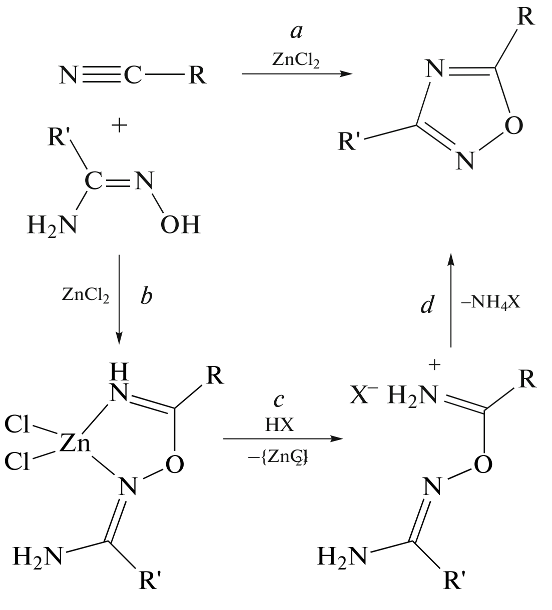
Reactions with amidoximes and hydroxyguanidine. The reactions of disubstituted cyanamides with acetamidoxime in the presence of nickel chloride in methanol were studied. It is shown that the reactions afford nitrosoguanidine complexes $[Ni\{NH=C(NR_2)NN(O)\}_2]$ (R_2 = Me_2 (**45**), $(CH_2)_4O$ (**46**), $(CH_2)_4$ (**47**), $(CH_2)_5$ (**48**), (Me)Ph (**49**), Ph_2 (**50**), and $(p\text{-}MeC_6H_4)_2$ (**51**) (12–26%) [34] (Scheme 12*a*).



Scheme 12.

These products are assumed [34] to be a result of the multistep nickel(II)-promoted reaction of disubstituted cyanamides in the first step including the formation of the product of coupling of amidoxime and cyanamides {$NH=C(NR_2)ON=C(NH_2)Me$}Ni^{II} (Scheme 12*b*). The coupling products were detected in the reaction mixture by IR spectroscopy and mass spectrometry but were not isolated as individual compounds, probably, because of the coordination lability of the nickel(II) complexes. These complexes can serve as intermediate products in the hydrolytic cleavage of $NCNR_2$ to ammonia (Scheme 12*c*), as in the case of the reaction of dimethyl cyanamide with the Ni(II)–ketoxime system (see section Reactions with oximes). Ammonia is necessary for the formation of the guanidine complex due to the coupling with coordinated cyanamide (Scheme 12*d*). Acetamidoxime present in the system can serve as a source of NO (Scheme 12*f*), which in the last step of the reaction reacts with the guanidine ligand to form coordinated nitrosoguanidine (Scheme 12*e*). A similar N-nitrosation reaction was described earlier for the iron complexes with the amidinate ligands [35].

The reactions of amidoximes $HON{=}C(NH_2)R'$ with nitriles NCR (R = Alk, Ar) in the presence of a catalytic amount of the zinc salts are used for the preparation of 1,2,4-oxadiazoles, heterocycles applied in various areas, under mild conditions [36]. The detailed study of the reactions of zinc chloride with amidoximes $HON{=}C(NH_2)R'$ (R' = Me, Ph) and nitriles or cyanamides NCR (R = Et, Ph, NMe_2, $N(CH_2)_4O$, NHC(O)Ph) made it possible to establish the main steps of the process [37–39]. The zinc-promoted coupling of nitrile and amidoxime to form the complex with the imino ligand $[ZnCl_2\{NH{=}C(R)ON{=}C(NH^2)R'\}_2]$ (R' = Me, R = Ph (**52**), NMe_2 (**53**), $N(CH_2)_4O$ (**54**), NHC(O)Ph (**55**); R' = Ph, R = Et (**56**), Ph (**57**), NMe_2 (**58**), $N(CH_2)_4O$ (**59**), NHC(O)Ph (**60**); 75–96%) occurs in the first step (Scheme 13*b*).



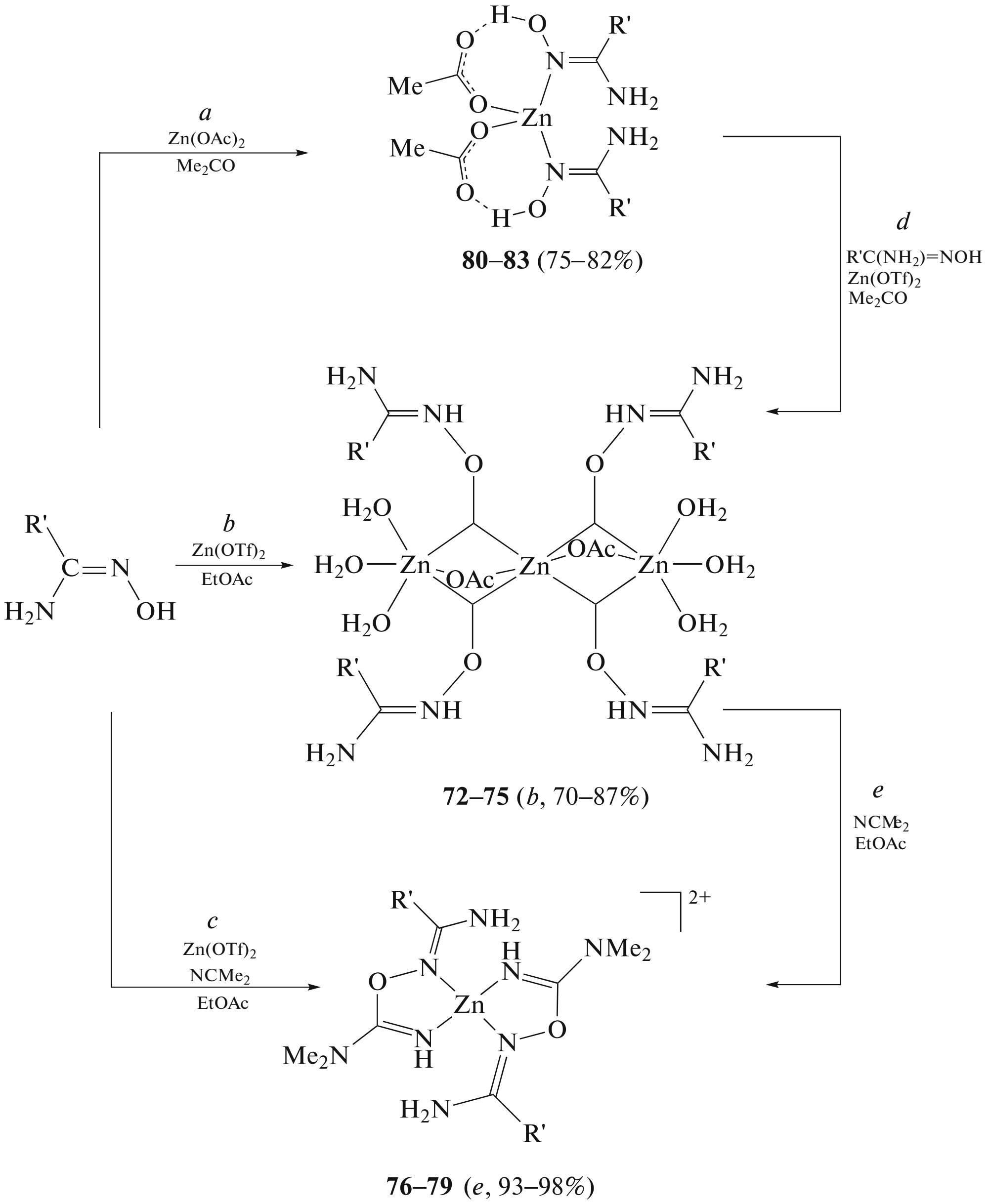
52–60 (75–96%) **61–71** (79–99%)

Scheme 13.

The addition of p-$MeC_6H_4SO_3H$ (1 equiv mol) to a solution of complexes **52–60** results in the protonation and decoordination of the imino ligand in the form of salt $[NH_2{=}C(R)ON{=}C(NH_2)R'](p\text{-}MeC_6H_4SO_3)$ (R' = Me; R = NMe_2 (**61**), $N(CH_2)_4O$ (**62**), NHC(O)Ph (**63**), R' = Ph, R = Ph (**64**), NMe_2 (**65**), $N(CH_2)_4O$ (**66**), NHC(O)Ph (**67**); 79–99%) (Scheme 13*c*). It should be mentioned that the derivatives of cyanamides (R = NMe_2, NC_4H_8O, NHC(O)Ph) and traditional nitriles (R = Et, Ph) differ in stability. The salts of imidoylamidoximes (R = Et, Ph) are unstable and were not isolated (except for **64**) as individual compounds because of their high reactivity, while the salts of carbimidoylamidoximes **61–63** and **65–67** (R = NMe_2, NC_4H_8O, NHC(O)Ph) were isolated in the solid state and completely characterized. The difference in stability can be explained from the viewpoint of electronic effects of substituent R. The cyanamide derivatives contain the guanidinium-like fragment $[NH_2{=}C(NR^1R^2)OR^3]^+$ stable due to the positive charge delocalization. It was shown later that the iminium salts $[NH_2{=}C(R)ON{=}C(NH_2)R'](p\text{-}MeC_6H_4SO_3)$ (R_2 = Me_2, R' = $PhCH_2$ (**68**) and p-BrC_6H_4 (**69**); R_2 = C_5H_{10}, R' = $PhCH_2$ (**70**) and p-BrC_6H_4 (**71**); 81–92%) can be synthesized directly from $ZnCl_2$, cyanamide, and amidoxime if the reaction was carried out in two steps (Scheme 13*b*, 13*c*) [38].

Salts $[NH_2{=}C(R)ON{=}C(NH_2)R'](p\text{-}MeC_6H_4SO_3)$ are transformed into the corresponding 1,2,4-oxadiazoles (Scheme 13*d*) [37, 38]. In this case, the ring closure of the derivatives with R = Et and Ph takes place already at the moment of formation of salts from the corresponding zinc complexes (R = Et, 5 min, rt; Ph, 1 h, rt), whereas a longer time (R = NHC(O)Ph, 5 h, rt or 1 h, 65°C) or heating (R = NMe_2, NC_4H_8O, 48 h, 6°C) is required for the transformation of the cyanamide derivatives. The selectivity of the reaction depends on the choice of the solvent. For the nitrile derivatives, the highest yields of the heterocycles were obtained when ring closure was carried out in DMSO (R = Et, 80–90%) and MeOH (R = Ph, 80%). For the cyanamide derivatives, the yields are approximately comparable (30–90%) in all the systems used: DMSO, MeOH, and $MeOH/H_2O$. In addition to the heterocycles, the corresponding amidoximes $HON{=}C(NH_2)R'$ and acetamides $NH_2C({=}O)R$ (R = Et, Ph) or mono- ($NH_2C({=}O)NHR'$) and disubstituted ($NH_2C({=}O)R$) ureas (R = NMe_2, NC_4H_8O, NHC(O)Ph) are formed in the side reactions, which results in a decrease in the yields of 1,2,4-oxadiazoles [37].

The reactions of the trinuclear zinc complexes $[Zn_3(\mu\text{-}OAc)_2\{\mu\text{-}ON(H){=}C(R')NH_2\}_4(H_2O)_6](OTf)_4$ (R' = Me (**72**), *tert*-Bu (**73**), Ph (**74**), and o-ClC_6H_4 (**75**)) containing the O-bridging amidoxime ligands in the aminonitrone form with dimethyl cyanamide $NCNMe_2$ were shown [39] to easily afford the coupling products $[Zn\{\underline{N}H{=}C(NMe_2)O\underline{N}{=}C(NH_2)R'\}_2](OTf)_2$ (R' = Me (**76**), *tert*-Bu (**77**), Ph (**78**), o-ClC_6H_4 (**79**); EtOAc, 3 h, rt, 93–98%) (Scheme 14*d*).



80–83 (75–82%)

72–75 (*b*, 70–87%)

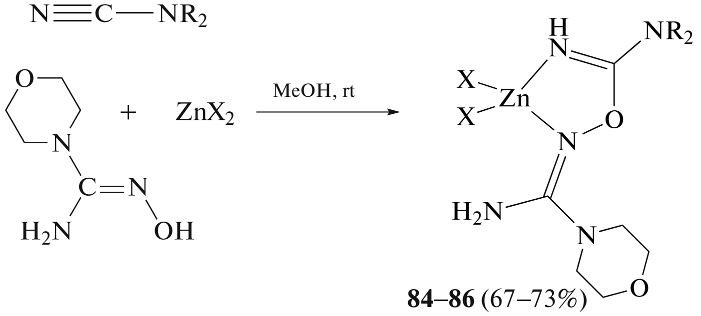
76–79 (*e*, 93–98%)

Scheme 14.

At the same time, the reactions of $NCNMe_2$ with the zinc complexes containing N-coordinated amidoximes $[Zn(OAc)_2\{HON=C(NH_2)R'\}_2]$ (R' = Me (**80**), *tert*-Bu (**81**), Ph (**82**), *o*-ClC_6H_4 (**83**) (Me_2CO, 24 h, rt) afford no coupling products. Complexes **80**–**83** can be transformed into trinuclear compounds **72**–**75** in the reaction with $Zn(OTf)_2$ (2 equiv mol) and $HON=C(NH_2)R'$ (2 equiv) (Me_2CO, 5 min, 50°C) (Scheme 14*d*). The trinuclear products are formed by the reaction of amidoxime $HON=C(NH_2)R'$ with $Zn(OTf)_2$ in a molar ratio of 4 : 3 in undried EtOAc (30 min, reflux) (Scheme 14*b*). In spite of the fact that acetates in the form of salts or complexes are not introduced into the system in the last reaction, the solvent EtOAc can serve as a source of the OAc^- ion in the product due to the metal-promoted hydrolytic cleavage.

The data on studying these reactions allow one to assume that O-coordinated amidoxime in the aminonitrone form in the oligonuclear zinc complex can be the active form of the nucleophile in the zinc(II)-promoted reactions of amidoximes with cyanamides. The same assumption is confirmed by the results of the previous works on studying the mechanism of amidoxime addition to the nitrilium group in the boron clusters [40]. The reaction of $Zn(OTf)_2$ with $HON=C(NH_2)R'$ and $NCNMe_2$ (molar ratio 1 : 2 : 2, EtOAc, 3 h, rt) leading to the formation of complexes containing the coupling products (76–82%) is assumed to proceed via the formation of trinuclear complexes **72–75** as intermediates (Scheme 14*c*).

Cyanamides $NCNR_2$ (R = Me, Et) were found to react with hydroxyguanidine $HON{=}C(NH_2)NC_4H_8O$ in the presence of zinc salts ZnX_2 (X = Cl, Br, I) with the formation of complexes $[ZnX_2\{NH{=}C(NR_2)\text{-}ON{=}C(NH_2)NC_4H_8O\}]$ (R/X = Me/Cl (**84**), Et/Cl (**85**), Me/Br (**86**); 67–73%; the derivatives with R/X = Et/Br, Me/I, and Et/I were not isolated as individual compounds) (MeOH, 2 min, rt) (Scheme 15) [41].

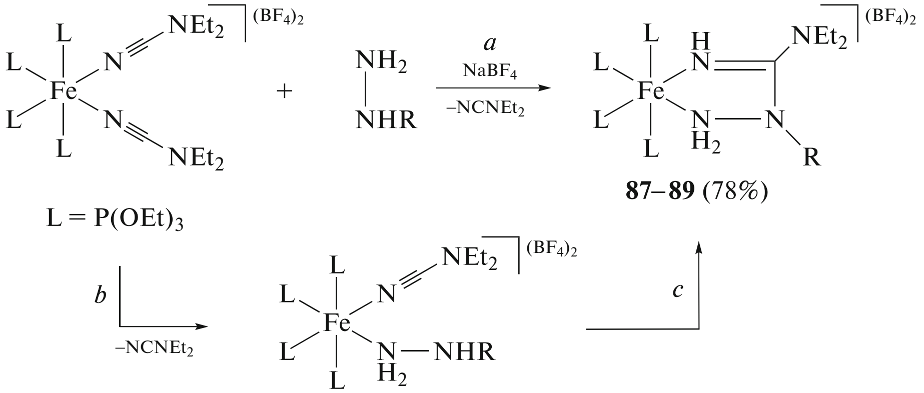


84–86 (67–73%)

Scheme 15.

A comparison of the conditions of this reaction and the reaction with amidoximes $HON{=}C(NH_2)R'$ considered above indicates a higher reactivity of hydroxyguanidine compared to that of amidoximes, which is due to the presence in the $HON{=}C(NH_2)NC_4H_8O$ molecule of two donor substituents NH_2 and NR'_2 enhancing nucleophilicity as a result of the donation of the electron density. It was also shown that the coupling products $[ZnX_2\{NH{=}C(NR_2)ONC(NH_2)\text{-}NC_4H_8O\}]$ were unstable in solutions but were stabilized in the solid state in the form of solvates $[ZnX_2\{NH{=}C(NR_2)\text{-}ONC(NH_2)NC_4H_8O\}] \cdot MeOH$ (**84–86**).

Reactions with hydrazines. The reactions of the iron complex $[Fe(NCNEt_2)_2\{P(OEt)_3\}_4](BF_4)_2$ (**4**) with hydrazines NH_2NHR (R = H, Me, Ph) (CH_2Cl_2, −196°C, then 4 h at rt) to form coordinated hydrazinecarboxyimidamides in the compositions of complexes $[Fe\{\underline{N}H{=}C(NEt_2)NR\underline{N}H_2\}\{P(OEt)_3\}_4](BF_4)_2$ (R = H (**87**), Me (**88**), Ph (**89**); 78%) (Scheme 16*a*) were carried out [12].



87–89 (78%)

Scheme 16.

It is assumed [12] that the reaction proceeds via the substitution of one diethyl cyanamide ligand followed by the intramolecular nucleophilic attack of the atom of the NHR group to the carbon atom of the nitrile group (Scheme 16*b*, 16*c*). This reaction mechanism is favored by the regioselectivity of the process, and the formation of the product of the attack by the NH_2 group would be preferable in the case of the intermolecular reaction.

It should be mentioned that the reactions of iron complex **4** with amines H_2NR (R = *n*-Pr, *iso*-Pr) do not lead to the formation of the addition products at the nitrile group of ligand $NCNEt_2$, and the substitution products $[Fe(NCNEt_2)(H_2NR)\{P(OEt)_3\}_4](BF_4)_2$ are formed in the reaction [42].

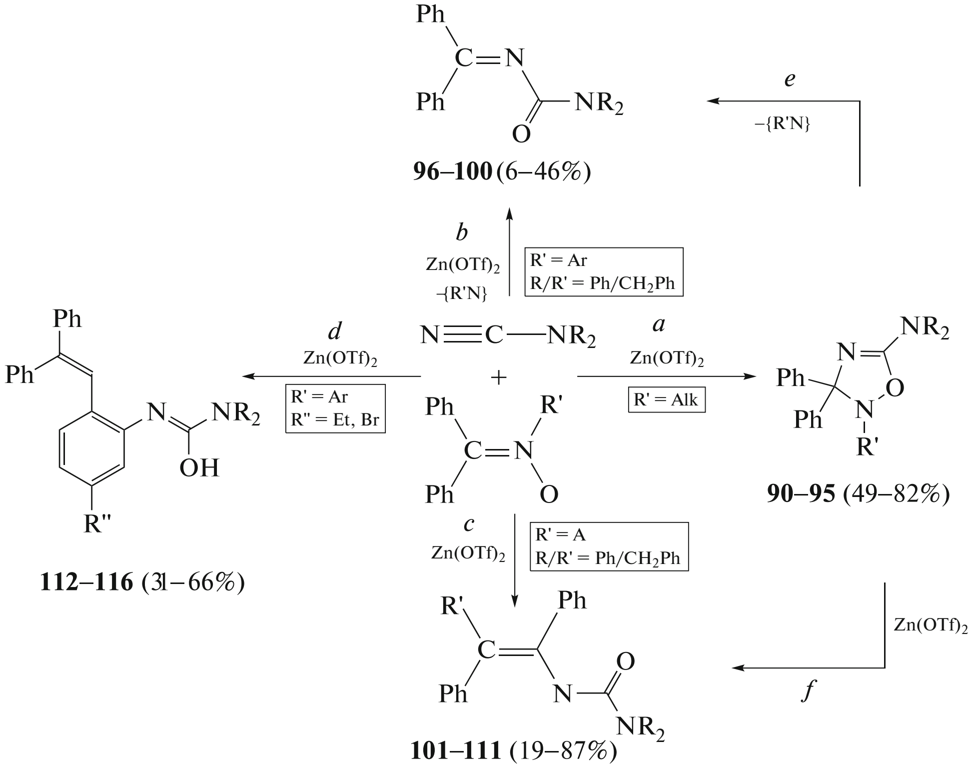
Thus, the 3*d* metals activate disubstituted cyanamides with respect to the reactions with various OH- and NH-nucleophiles. These reactions always afford both coordinated or metal-unbound coupling products and the products of multistep transformations of cyanamides. This is a distinction between the reactions involving the

3*d* metals and the reactions with the platinum(II, IV) dialkyl cyanamide complexes. In the latter case, the coupling products are always coordinated to the metal center. The products of the coupling of $NCNR_2$ with nucleophiles, unlike similar derivatives of nitriles NCR, are stabilized due to the conjugation system involving the lone electron pair of the amide group and can be isolated as stable compounds in the form of complexes or iminium salts.

REACTIONS OF CYANAMIDES WITH 1,3-DIPOLES

The metal-promoted reactions of disubstituted cyanamides with 1,3-dipoles are being actively studied in the recent two decades. It is found in the recent works that the coordination of $NCNR_2$ to the metallocenter activates these compounds toward the reactions with nitrones [43–45], oxazoline-*N*-oxides [46, 47], imidazoline-*N*-oxides [48], and nitrile oxides [49]. The reactivity of coordinated cyanamides $NCNR_2$ in the reactions with such dipoles as nitrones is comparable with that of ligand PhCN and appreciably exceeds the reactivity of coordinated EtCN [43, 44]. It should be mentioned that the majority of the metal-promoted reactions of disubstituted cyanamides with 1,3-dipoles was carried out using the kinetically fairly inert platinum(II) [43, 44, 46–48] and palladium(II) [45, 49] complexes. In all cases, the coordinated heterocycles in the composition of the metal complexes were obtained by the cycloaddition to disubstituted cyanamides. Some heterocycles were isolated in the free state due to the additional decoordination step [43, 44, 46, 49].

The use of the kinetically more labile 3*d* metals, zinc(II) and copper(I), for the promotion of cycloaddition to disubstituted cyanamides was described [50, 51]. The reactions of disubstituted cyanamides $NCNR_2$ (R_2 = Me_2, Et_2, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$, Ph_2) with ketonitrones $Ph_2C{=}N^+(O^-)R'$ (R' = Me, $PhCH_2$, Ph, 4-BrC_6H_4, 4-EtC_6H_4) in the presence of zinc salt $Zn(OTf)_2$ were studied. Zinc(II) was established to promote the reactions, whereas no interaction is observed in the absence of the zinc(II) salt [50]. The reaction direction is determined by the nature of substituent R' in ketonitrone: 2,3-dihydro-1,2,4-oxadiazoles (R_2/R' = Me_2/Me (**90**), Et_2/Me (**91**), $(CH_2)_5$/Me (**92**), $O(CH_2)_4$/Me (**93**), Ph_2/Me (**94**), and $Me_2/PhCH_2$ (**95**); 49–82%) (1 equiv mol $Zn(OTf)_2$, CH_2Cl_2, rt, 5 h–2 days) are the reaction products (Scheme 17*a*) for the *N*-alkyl-substituted dipoles (R' = Me, $PhCH_2$; except for the pair of reactants with R_2/R' = $Ph_2/PhCH_2$), and mixtures of open-chain products **96**–**116** (0.5 equiv mol $Zn(OTf)_2$, CH_2Cl_2, rt, 30–60 min) (Scheme 17*b*–17*d*) were obtained for the *N*-aryl-substituted dipoles and the pair with R_2/R' = $Ph_2/PhCH_2$ (product **101** is formed). In the case of using the reactants with R_2/R' = $Ph_2/PhCH_2$, the formation of open-chain products **100** (46%) and **101** (48%) (Scheme 17*b*, 17*c*) was observed instead of the expected heterocycle.



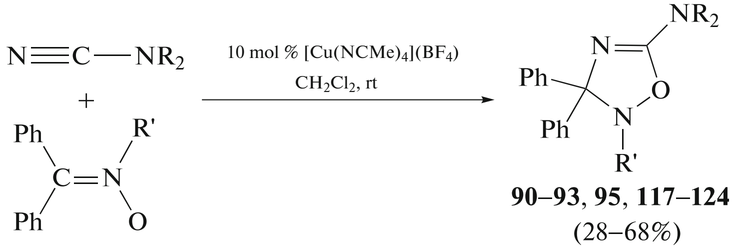
Scheme 17.

The zinc(II)-promoted reactions of cyanamides with nitrones $Ph_2C{=}N^+(O^-)R'$ (R' = Me, $PhCH_2$), which proceed as [2+3] cycloaddition, afford heterocycles **90–95** unbound to the metallocenter. This distinguishes the zinc(II) promoted reactions of $NCNR_2$ with ketonitrones from the reactions involving the platinum(II) and palladium(II) complexes. In the former case, the decoordination step is not required for the formation of the free heterocycle.

The formed heterocycles **90–95** were shown to be unstable and undergo transformations with ring opening to form methylideneurea (Scheme 17*e*) and carbamoylamidine (Scheme 17*f*), and the latter reaction is promoted by zinc(II).

Triaryl-substituted nitrones $Ph_2C{=}N^+(O^-)R'$ (R' = Ph, 4-BrC_6H_4, 4-EtC_6H_4) react with disubstituted cyanamides in the presence of $Zn(OTf)_2$ to form three different open-chain products in different ratios depending on substituent R': (Scheme 17*b*, R_2 = Me_2 (**96**), Et_2 (**97**), $(CH_2)_5$ (**98**), $O(CH_2)_4$ (**99**), Ph_2 (**100**); 6–38%), (Scheme 17*c*, R_2/R' = Me_2/Ph (**102**), Et_2/Ph (**103**), $(CH_2)_5$/Ph (**104**), $O(CH_2)_4$/Ph (**105**), Ph_2/Ph (**106**); Me_2/C_6H_4Br-4 (**107**), Et_2/C_6H_4Br-4 (**108**), $(CH_2)_5/C_6H_4Br$-4 (**109**), $O(CH_2)_4/C_6H_4Br$-4 (**110**), Ph_2/C_6H_4Br-4 (**111**); 19–66%) and (Scheme 17*d*, R_2/R' = $(CH_2)_5/C_6H_4Br$-4 (**112**), Ph_2/C_6H_4Br-4 (**113**), Me_2/C_6H_4Et-4 (**114**), $(CH_2)_5/C_6H_4Et$-4 (**115**), Ph_2/C_6H_4Et-4 (**116**); 31–66%). An appreciable amount of products **112–116** (31–66%) is formed for nitrones with R' = 4-BrC_6H_4 and 4-EtC_6H_4. For triphenyl-substituted nitrone, the major products are compounds **102–105** (57–87%). In the most part of reactions, products **96–100** are minor (6–16%) except for two systems with R_2 = Ph_2 (**100**) and R' = $PhCH_2$ (46%) and 4-EtC_6H_4 (38%). It is assumed that all these products are also formed via the [2+3] cycloaddition step, and the formed heterocycle undergoes ring opening at the N–O bond to form compounds **96–116**.

The reactions of disubstituted cyanamides $NCNR_2$ (R_2 = Me_2, Et_2, C_4H_8, $(CH_2)_5$, $O(CH_2)_4$, $(CH_2Ph)_2$, Me/Ph, tetrahydroisoquinolin-2-yl (C_9H_{10})) with ketonitrones $Ph_2C{=}N^+(O^-)R'$ (R' = Me, $PhCH_2$) were conducted in the catalytic variant using the copper(I) complex as a catalyst (10 mol % $[Cu(NCMe)_4](BF_4)$, CH_2Cl_2, 45°C, 2–48 h) (Scheme 18) [51]. Heterocycles **90–93**, **95**, and **117–124** ($(CH_2)_4$/Me (**117**), $(CH_2Ph)_2$/Me (**118**), (Me/Ph)/Me (**119**), $(CH_2)_4/PhCH_2$ (**120**), $(CH_2)_5/PhCH_2$ (**121**), $O(CH_2)_4/PhCH_2$ (**122**), $(CH_2Ph)_2/PhCH_2$ (**123**), $(Me/Ph)/PhCH_2$ (**124**)) were obtained in moderate yields (28–68%) in one step. It is shown for the model reaction of $NCNMe_2$–$Ph_2C{=}N^+(O^-)Me$ that, in the absence of the metal complex, the reaction does not occur even under more drastic conditions (toluene, 80°C, 3 h), whereas copper(I) provides higher yields of heterocycle **90** than copper(II) (cf.: 56% with 10 mol % $[Cu(NCMe)_4](BF_4)$ and 13% with 10 mol % $Cu(OTf)_2$) under the same conditions (CH_2Cl_2, 20–25°C, 2 h).



90–93, **95**, **117–124**
(28–68%)

Scheme 18.

Note that the order of reagent addition is important. The highest yields (68%; CH_2Cl_2, 45°C, 24 h) of the heterocycle were achieved when $NCNMe_2$ was added first to a solution of $[Cu(NCMe)_4](BF_4)$ and then $Ph_2C{=}N^+(Me)O^-$ was added. If nitrone was first added to a solution of the catalyst and then dimethyl cyanamide was added, then the yield of target heterocycle **90** was much lower (~10%). This can be explained by the competition of ketonitrone and $NCNMe_2$ for the coordination vacancy. The occurrence of cycloaddition is favored by the interaction of coordinated dialkyl cyanamide and the free dipole [52] and, therefore, the above indicated order of reagent addition is preferable. The data of theoretical calculations [52] are consistent with the experimental results and support the assignment of the cycloaddition to Group I according to Sustmann's classification [53, 54].

Thus, the 3*d* metals (copper(I) and zinc(II)) activate disubstituted cyanamides in the reactions with the 1,3-dipoles (ketonitrones). The degree of activation of $NCNR_2$ by coordination with these metallocenters is comparable with the activation provided by platinum(II) or palladium(II) in complexes $[MCl_2(NCNR_2)_2]$ (M = Pt, Pd). An advantage of the reactions of $NCNR_2$ with ketonitrones in the presence of the 3*d* metals is the possibility of the one-pot synthesis of 2,3-dihydro-1,2,4-oxadiazoles, and the character of the reactions is catalytic in the case of using copper(I).

To conclude, such 3*d* metals as manganese(I), iron(II), nickel(II), zinc(II), and copper(I) can coordinate disubstituted cyanamides via the nitrogen atom of the nitrile group. The complexes formed are appreciably labile with respect to isomerization and ligand substitution. The electrophilic activation of cyanamides $NCNR_2$ toward the reactions with water, methanol, oximes, amidoximes, hydroxyguanidine, and ketonitrones is observed for coordination. The degree of activation of $NCNR_2$ by the 3*d* metals is comparable with that when using platinum(II) and palladium(II) and results in the occurrence of the reactions under mild conditions. The use of kinetically more labile metallocenters provides the formation of various products, both coordinated and free. The uncoordinated products, 2,3-dihydro-1,2,4-oxadiazoles and iminium salts $[NH=C(NR_2)ON=C(NH_2)R']X$, are readily formed in the zinc(II)-promoted reactions of $NCNR_2$ with ketonitrones and amidoximes. The kinetic lability of nickel(II) leads to the cascade character of interaction of cyanamides with amidoximes and undried methanol to form the (nitrosoguanidine)Ni(II) and (triazapentadiene)Ni(II) complexes as a result of multistep reactions.

The reactions involving the 3*d* metals provide new convenient routes for the synthesis of heterocyclic compounds. For example, 5-aminosubstituted 2,3-dihydro-1,2,4-oxadiazoles form a poorly studied class of heterocycles [52]. They were synthesized by the copper(I)-catalyzed or zinc(II)-promoted reactions of disubstituted cyanamides with ketonitrones. These heterocycles have been synthesized previously using the two-step reactions promoted by platinum(II) and palladium(II) [43–45]. On the one hand, the use of more accessible 3*d* metals provides a simple and convenient way for preparation and serves for the development of the chemistry of these poorly studied compounds. On the other hand, the zinc(II)-promoted reactions of amidoximes with cyanamides afford iminium salts $[NH=C(NR_2)ON=C(NH_2)R']X$, which are readily transformed into 1,2,4-oxadiazoles [37] finding wide use in medicine and industry [36]. The metal-promoted reactions represent an alternative method for the preparation of these heterocyclic compounds.

The metal-promoted multicomponent reactions of cyanamides with nucleophiles, for example, the reactions of $NCNR_2$ with the nickel salts and azoles in methanol, make it possible to obtain oligonuclear compounds $[Ni_n(\mu\text{-azolate})_m\{NH=C(OMe)\text{-}NC(OMe)=NH\}_2]$ ($n = 2, 3$; $m = 2, 4$). The oligonuclear nickel compounds with the $\{Ni(azolate)_2\}$ fragment have actively been studied in the recent time as compounds of potential applied significance, for example, in the chemistry of anion recognition [55]. The reactions involving cyanamides are interesting as a simple convenient method for the synthesis of these compounds with specified nuclearity.

In spite of achievements in the area of coordination and synthetic organic chemistry of disubstituted cyanamides involving 3*d* metals, some aspects require further studying. It seems promising to carry out the reactions of cyanamides in the catalytic mode, and the further studies can be focused on the search for new catalytic systems for such reactions involving a wide range of nucleophiles and dipoles.

ACKNOWLEDGMENTS

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