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Yuliia DAVYDENKO, PhD (Chem.)
ORCID ID: 0000-0003-0223-0363
e-mail: y.davydenko@knu.ua
Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

SYNTHESIS AND CHARACTERIZATION OF COORDINATION COMPOUNDS OF TRANSITION METALS BASED ON 5-METHYL-3-(TRIFLUOROMETHYL)-1H-PYRAZOLE

Background. *The design of coordination compounds using pyrazole-based ligands is of fundamental importance in contemporary materials chemistry due to their versatile coordination modes and diverse applications. Introducing trifluoromethyl groups onto such ligands is a powerful strategy to modulate the electronic and steric properties of the resulting metal complexes, significantly influencing their acidity, stability, and reactivity. In this context, 5-methyl-3-(trifluoromethyl)-1H-pyrazole stands out as a particularly promising ligand whose coordination chemistry with transition metals remains surprisingly underexplored. Despite its potential, a systematic investigation into the synthesis, structural diversity, and properties of its coordination compounds is largely absent from recent literature. This gap presents a missed opportunity, as the unique electronic profile of this ligand could unlock new functionalities in molecular materials. To address this, we present a comprehensive study on the synthesis and characterization of a new family of coordination compounds of first-row transition metals (Mn, Co, Ni, Cu, Zn) with the 5-methyl-3-(trifluoromethyl)-1H-pyrazole ligand. This work aims to systematically explore its coordination landscape, providing fundamental insights for the future design of advanced functional materials.*

Methods. *In this work, the coordination compounds with transition metals were obtained using the 5-methyl-3-(trifluoromethyl)-1H-pyrazole ligand. A variety of techniques were used to identify and characterize the complexes and the ligand, including infrared, UV/Vis, and NMR spectroscopy, as well as microanalyses.*

Results. *The interaction of 3d metals such as Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with 5-methyl-3-(trifluoromethyl)-1H-pyrazole in non-aqueous solutions was found to be solvent-dependent. In a solvent environment CH_3CN and CH_3OH ($M(Ac)_2{\cdot}4H_2O$–L–CH_3OH/CH_3CN systems) at M:L ratios of 1:1 and 1:2, products with the composition $M(Ac)_2{\cdot}2L$ were formed. Meanwhile, in dimethylformamide ($M(Ac)_2{\cdot}4H_2O$–L–DMF systems) under the same ratios, the complex $Mn(Ac)_2{\cdot}L{\cdot}DMF$, which incorporated a solvent molecule, was isolated.*

Conclusions. *An organic ligand, 5-methyl-3-(trifluoromethyl)-1H-pyrazole, was synthesized. The interaction of 3d metals (M = Mn, Co, Ni, Cu, Zn) $M(Ac)_2{\cdot}xH_2O$ with 5-methyl-3-(trifluoromethyl)-1H-pyrazole in non-aqueous (CH_3CN, CH_3OH and DMF) solutions was investigated. Methods for the synthesis of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) compounds with 5-methyl-3-(trifluoromethyl)-1H-pyrazole were developed. Based on the data of elemental analysis and methods of IR, NMR, and electronic spectroscopy, the composition and structure of the obtained complexes have been proposed. It has been shown that in the obtained complexes: the most typical method of coordination of the pyrazole cycle is realized: monodentate - through the pyridine nitrogen atom; the formation of two types of mononuclear Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes is observed: $M(Ac)_2{\cdot}2L$ and $M(Ac)_2{\cdot}L{\cdot}DMF$; in the obtained complexes $M(Ac)_2{\cdot}2L$ and $M(Ac)_2{\cdot}L{\cdot}DMF$ complexes, a six-coordinate environment of the central atom is realized due to four oxygen atoms from bidentate chelate coordinated acetate groups and two nitrogen atoms from molecules of a non-deprotonated ligand.*

Keywords: *5-methyl-3-(trifluoromethyl)-1H-pyrazole, complexes, 3d metals, ^{1}H NMR spectroscopy, IR spectroscopy.*

Background

The design and synthesis of coordination compounds using nitrogen-containing heterocyclic ligands are of fundamental importance in contemporary inorganic and materials chemistry. Among these, pyrazole-based ligands have been extensively employed to construct a diverse range of metal complexes with fascinating structural topologies and functional properties (Davydenko et al., 2024). The versatility of the pyrazole core, with its two adjacent nitrogen atoms, allows for various coordination modes-acting as a monodentate ligand (Davydenko et al., 2023; Vynohradov et al., 2022), a bridging unit to form polynuclear clusters (Davydenko, 2012; 2022; 2024; 2025;), or as a component of more complex chelating systems (Mezei et al., 2007; Pandolfo et al., 2017). This adaptability has led to the development of coordination compounds with remarkable applications in catalysis (Annes et al., 2022; Titi et al., 2023), magnetism (Li et al., 2023; Wang et al., 2023), luminescent sensing (Sun et al., 2023; Zhang et al., 2024), and the construction of metal-organic frameworks (MOFs) (Roy et al., 2023).

The strategic introduction of fluorine atoms or trifluoromethyl groups onto organic ligands has emerged as a powerful tool to modulate the electronic and steric properties of the resulting metal complexes. The strong electron-withdrawing nature of the CF_3 group can significantly influence the acidity of the N-H proton of the pyrazole ring, the donor ability of the nitrogen atoms, and the overall stability and reactivity of the coordination compounds. Furthermore, the presence of fluorine can enhance the volatility, thermal stability, and solubility of the complexes in non-polar solvents, and can lead to unique solid-state packing through non-covalent interactions. In this context, 5-methyl-3-(trifluoromethyl)-1H-pyrazole stands out as a particularly promising ligand. The CF_3 group is expected to significantly lower the pKa of the pyrazole proton, thereby facilitating deprotonation and the formation of pyrazolate-based complexes. Moreover, the electronic and steric effects of CF_3 substituents are anticipated to impart unique characteristics to the resulting coordination compounds, potentially leading to novel properties.

Despite the considerable potential of 5-methyl-3-(trifluoromethyl)-1H-pyrazole as a ligand, a survey of recent literature reveals that the coordination chemistry of this ligand with a broad range of transition metals remains surprisingly underexplored. Foundational studies have demonstrated the ability of fluorinated pyrazoles to form stable complexes (Fustero et al., 2014; Mykhailiuk, 2020), and recent research has touched upon related systems for applications such as photoswitching (Park et al., 2020; Kieffer et al., 2022; Kolarski et al., 2020) and catalysis with other fluorinated ligands (Sánchez-Cantú et al., 2018; Titi et al., 2023). However, a systematic investigation into the synthesis, structural diversity, and functional properties of coordination compounds based on 5-methyl-3-(trifluoromethyl)-1H-pyrazole in the last 5 years is largely absent. This represents a significant gap in the field, as the unique electronic profile of this ligand could unlock new

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opportunities in the design of functional molecular materials. For instance, the electron-poor nature of the pyrazolate ring could influence the magnetic exchange interactions in polynuclear complexes or tune the redox potentials of catalytically active metal centers.

Herein, we present a comprehensive study on the synthesis and characterization of a new family of coordination compounds of first-row transition metals (Mn, Co, Ni, Cu, Zn) with the 5-methyl-3-(trifluoromethyl)-1H-pyrazole ligand.

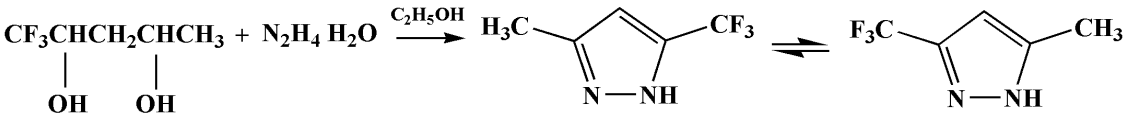
This work aims to systematically explore the coordination landscape of 5-methyl-3-(trifluoromethyl)-1H-pyrazole, providing fundamental insights that will pave the way for the future design of advanced functional materials based on this versatile building block.

Methods

All chemicals and solvents were commercial products of reagent grade and used without further purification. Microanalyses were performed with a Perkin-Elmer 2400 CHN. IR spectra (KBr pellets) were recorded with a Perkin–Elmer Spectrum BX FT-IR in the range of 400–4000 cm^{-1}. Absorbance UV/Vis spectra were registered with a Varian Cary 50 spectrometer in the range of 200–1000 nm at room temperature. ^1H NMR spectra were recorded on a Bruker AC-400 spectrometer (400 MHz) at room temperature.

Results

The synthesis of 5-methyl-3-(trifluoromethyl)-1H-pyrazole (L). The synthesis of 5-methyl-3-(trifluoromethyl)-1H-pyrazole was carried out according to the following scheme 1. 12.95 g (0.084 mol) of 1,1,1-trifluoro-2,4-pentadiol in 110 mL of ethanol was added dropwise, with constant stirring, 4.1 mL (4.2 g; 0.084 mol) of hydrazine hydrate. The reaction mixture was stirred for 3 hours while cooling on an ice bath. After complete addition of the hydrazine hydrate solution, the reaction mixture was left overnight. The solvents were completely distilled off on a rotary evaporator. The product was obtained in the form of light yellow crystals, which are highly soluble in DMF, acetonitrile, and methanol.



Scheme 1. Synthesis of 5-methyl-3-(trifluoromethyl)-1H-pyrazole

The yield of the product was 77 %. ^1H NMR (DMSO-d_6) δ: 2.30 (s., 3H; CH_3), 6.22 (s., 1H; pz-CH), 13.07 (br. s., 1H; NH). Elemental analysis: calculated (%): C 40.01; H 3.36; N 18.66. Found: C 40.04; H 3.35; N 18.70. IR (KBr disk, cm^{-1}, selected bands): 3194s, 3120s, 2890s, 2814m, 2562w, 1587s, 1504s, 1254s, 1159s.

The general method of the synthesis of the coordination compounds. The synthesis of coordination compounds with 5-methyl-3-(trifluoromethyl)-1H-pyrazole (L) was performed with $M(CH_3COO)_2 \cdot xH_2O$ of different 3d-metals (scheme 2).

$M(CH_3COO)_2\ xH_2O$ – L – Solv (O_2).
L – 5-methyl-3-(trifluoromethyl)-1H-pyrazole.
M = Mn, Zn, Cu, Co, Ni.
Solv – CH_3CN, DMF, CH_3OH.

Scheme 2. Synthesis of the coordination compounds

The synthesis of coordination compounds was carried out in a flat-bottomed reactor with a volume of 25 mL. A pre-dissolved salt (0.001 mol; 0.002 mol) was added to the reactor, to which a pre-dissolved ligand (0.001 mol; 0.002 mol) was slowly added dropwise. Metal : ligand ratios of both 1:1 and 1:2 were used. The amount of solvent was varied between 2 and 9 ml, depending on the nature of the solvent and the solubility of the reagents. The reaction mixture was stirred on a magnetic stirrer for 15 minutes at a temperature of 21–60 ºC until the complete conversion of the starting reagents. When an insoluble reaction product was formed, it was filtered off and dried in air. If a product in the form of a solution was formed, it was left to crystallize slowly in air at room temperature. The composition of the products obtained from the interaction of 5-methyl-3-(trifluoromethyl)-1H-pyrazole with non-aqueous solutions of 3d-metal acetates (Mn, Zn, Cu, Co, and Ni) and the elemental analysis data are presented in tabl. 1.

Discussion and conclusions

Thus, as a result of the interaction between 5-methyl-3-(trifluoromethyl)-1H-pyrazole and non-aqueous solutions of 3d-metal acetates (Mn, Zn, Cu, Co, Ni), different products were obtained. Specifically, in $M(Ac)_2 \cdot 4H_2O$–L–CH_3OH/CH_3CN systems with M:L ratios of 1:1 and 1:2, compounds with the composition $M(Ac)_2 \cdot 2L$ were formed (fig. 1, a). In contrast, in the systems with dimethylformamide ($M(Ac)_2 \cdot 4H_2O$–L–DMF) at similar ratios, $Mn(Ac)_2 \cdot L \cdot DMF$ was obtained (fig. 1, b), where the solvent became part of the complex. These conclusions are based on data from elemental analysis, IR, UV/Vis, and NMR spectroscopy.

NMR spectroscopy. ^1H NMR spectra of the ligand (^1H NMR (DMSO-d_6) δ: 2.30 (s., 3H; CH_3), 6.22 (s., 1H; pz-CH), 13.07 (br. s., 1H; NH)) (fig. 2), as a reference sample, and compound obtained as a result of synthesis $Zn(Ac)_2 \cdot 2H_2O$-L-Solv (fig. 3), demonstrate the fact of complex formation. ^1H NMR spectrum of the complex (DMSO-d_6) indicates the presence of the peaks are observed at δ: 2.30 and 3.10 (two singlets corresponding to three hydrogen atoms from two metal groups, two singlets at δ: 6.24 and 6.26 from two 1H pyrazole nuclei and a broadened singlet at 13.07 from the 1H group NH (fig. 3), which indicates the formation of a mixture of two zinc complexes. This is associated with a change in the position of the CH_3 and CF_3 substituents in the 3rd and 5th positions of the pyrazole nucleus.

IR spectroscopy. In the comparative analysis of the IR spectra of the synthesized complexes and ligand, the main attention was paid to the absorption bands corresponding to the oscillations of the functional groups of the ligand (IR (KBr disk, cm^{-1}, selected bands): 3194s, 3120s, 2890s, 2814m, 2562w, 1587s, 1504s, 1254s, 1159s). In the IR spectra of synthesized compounds of general composition $M(Ac)_2 \cdot 2L$ and $M(Ac)_2 \cdot L \cdot DMF$, absorption bands are observed in the region of 3300–3200 cm^{-1}, which is characteristic of valence vibrations of the NH group and indicates the presence of unprotonated molecules of the ligand 5-methyl-3-(trifluoromethyl)-1H-pyrazole. The following bands indicate the presence of acetate groups: ν_{as}(C=O) = 1510–1520 cm^{-1}, ν_s(C-O) = 1450–1460 cm^{-1} (fig. 4, 5). In $M(Ac)_2 \cdot L \cdot DMF$ complexes, the presence of a narrow intense absorption band at 1640 cm^{-1} attributed to the valence vibrations of the CO group indicates the coordination of dimethylformamide molecules (fig. 6).

Table 1

The original system	M:L:Solv	Composition of the extracted product	C, % calc./exp.	H, % calc./exp.	N, % calc./exp.
$Mn(Ac)_2{\times}4H_2O$-L- CH_3CN	1 : 1: 9mL	$M(Ac)_2{\times}2L$	34,78/34,52	2,89/2,86	10,14/10,08
$Mn(Ac)_2{\times}4H_2O$-L- CH_3OH	1 : 1: 9mL	$M(Ac)_2{\times}2L$	34,78/35,12	2,89/2,83	10,14/10,04
$Mn(Ac)_2{\times}4H_2O$-L- DMF	1 : 1: 9mL	$M(Ac)_2{\times}L{\times}DMF$	35,82/35,23	3,88/3,83	12,53/12,31
$Mn(Ac)_2{\times}4H_2O$-L- CH_3CN	1 : 2: 11mL	$M(Ac)_2{\times}2L$	34,78/34,17	2,89/2,84	10,14/9,87
$Mn(Ac)_2{\times}4H_2O$-L- CH_3OH	1 : 2: 11mL	$M(Ac)_2{\times}2L$	34,78/34,56	2,89/2,87	10,14/10,02
$Mn(Ac)_2{\times}4H_2O$-L- DMF	1 : 2: 11mL	$M(Ac)_2{\times}L{\times}DMF$	35,82/34,89	3,88/3,81	12,53/12,20
$Zn(Ac)_2{\times}2H_2O$- L- CH_3OH	1 : 1: 9mL	$M(Ac)_2{\times}2L$	33,56/33,13	2,79/2,64	9,79/9,55
$Zn(Ac)_2{\times}2H_2O$-L- CH_3CN	1 : 1: 9mL	$M(Ac)_2{\times}2L$	33,56/33,28	2,79/2,58	9,79/9,12
$Zn(Ac)_2{\times}2H_2O$-L- DMF	1 : 1: 9mL	$M(Ac)_2{\times}L{\times}DMF$	34,78/34,34	3,76/3,59	12,17/11,49
$Zn(Ac)_2{\times}2H_2O$-L- CH_3CN	1 : 2: 11mL	$M(Ac)_2{\times}2L$	33,56/33,12	2,79/2,66	9,79/9,47
$Zn(Ac)_2{\times}2H_2O$- L- CH_3OH	1 : 2: 11mL	$M(Ac)_2{\times}2L$	33,56/33,43	2,79/2,54	9,79/9,52
$Zn(Ac)_2{\times}2H_2O$-L- DMF	1 : 2: 11mL	$M(Ac)_2{\times}L{\times}DMF$	34,78/33,28	3,76/3,22	12,17/12,01
$Cu(Ac)_2{\times}H_2O$-L-CH_3CN	1 : 1: 9mL	$M(Ac)_2{\times}2L$	33,74/32,98	2,81/2,56	9,84/9,51
$Cu(Ac)_2{\times}H_2O$-L-CH_3OH	1 : 1: 9mL	$M(Ac)_2{\times}2L$	33,74/33,15	2,81/2,67	9,84/9,26
$Cu(Ac)_2{\times}H_2O$-L-DMF	1 : 1: 9mL	$M(Ac)_2{\times}L{\times}DMF$	34,93/34,58	3,78/3,41	12,22/12,00
$Cu(Ac)_2{\times}H_2O$-L-CH_3CN	1 : 2: 11mL	$M(Ac)_2{\times}2L$	33,74/33,46	2,81/2,48	9,84/9,56
$Cu(Ac)_2{\times}H_2O$-L-CH_3OH	1 : 2: 11mL	$M(Ac)_2{\times}2L$	33,74/33,27	2,81/2,56	9,84/9,49
$Cu(Ac)_2{\times}H_2O$-L-DMF	1 : 2: 11mL	$M(Ac)_2{\times}L{\times}DMF$	34,93/34,26	3,78/3,63	12,22/11,98
$Co(Ac)_2{\times}4H_2O$-L-CH_3CN	1 : 1: 9mL	$M(Ac)_2{\times}2L$	34,28/33,98	2,85/2,78	10,00/9.68
$Co(Ac)_2{\times}4H_2O$-L-CH_3OH	1 : 1: 9mL	$M(Ac)_2{\times}2L$	34,28/33.82	2,85/2,81	10,00/9,74
$Co(Ac)_2{\times}4H_2O$-L-DMF	1 : 1: 9mL	$M(Ac)_2{\times}L{\times}DMF$	35,39/34,91	3,83/3,76	12,38/12,23
$Co(Ac)_2{\times}4H_2O$-L- CH_3CN	1 : 2: 11mL	$M(Ac)_2{\times}2L$	34,28/34,02	2,85/2,74	10,00/9,84
$Co(Ac)_2{\times}4H_2O$-L- CH_3OH	1 : 2: 11mL	$M(Ac)_2{\times}2L$	34,28/33,83	2,85/2,68	10,00/9,76
$Co(Ac)_2{\times}4H_2O$-L- DMF	1 : 2: 11mL	$M(Ac)_2{\times}L{\times}DMF$	35,39/33,78	3,83/3,71	12,38/12,23
$Ni(Ac)_2{\times}4H_2O$-L- CH_3CN	1 : 1: 9mL	$M(Ac)_2{\times}2L$	34,28/33,96	2,85/2,78	10,00/9,79
$Ni(Ac)_2{\times}4H_2O$-L- CH_3OH	1 : 1: 9mL	$M(Ac)_2{\times}2L$	34,28/33,81	2,85/2,81	10,00/9,68
$Ni(Ac)_2{\times}4H_2O$-L- DMF	1 : 1: 9mL	$M(Ac)_2{\times}L{\times}DMF$	35,39/34,99	3,83/3,69	12,38/12,02
$Ni(Ac)_2{\times}4H_2O$-L- CH_3CN	1 : 2: 11mL	$M(Ac)_2{\times}2L$	34,28/33,46	2,85/2,71	10,00/9,82
$Ni(Ac)_2{\times}4H_2O$-L- CH_3OH	1 : 2: 11mL	$M(Ac)_2{\times}2L$	34,28/33,96	2,85/2,76	10,00/9,74
$Ni(Ac)_2{\times}4H_2O$-L- DMF	1 : 2: 11mL	$M(Ac)_2{\times}L{\times}DMF$	35,39/34,59	3,83/3,69	12,38/12,18

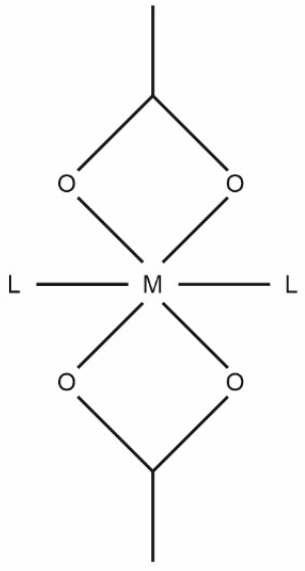


Fig. 1, a. Scheme of the proposed structure for the obtained complexes $M(Ac)_2{\cdot}2L$

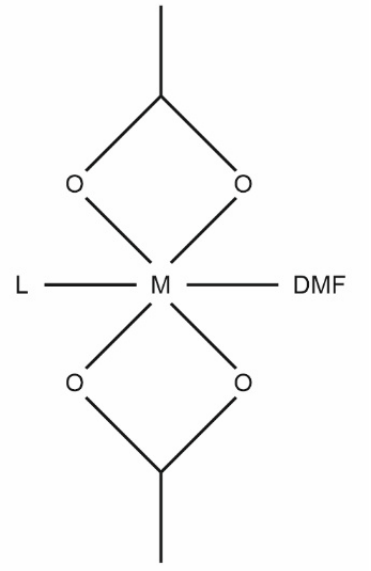


Fig. 1, b. Scheme of the proposed structure for the obtained complexes $M(Ac)_2{\cdot}L{\cdot}DMF$

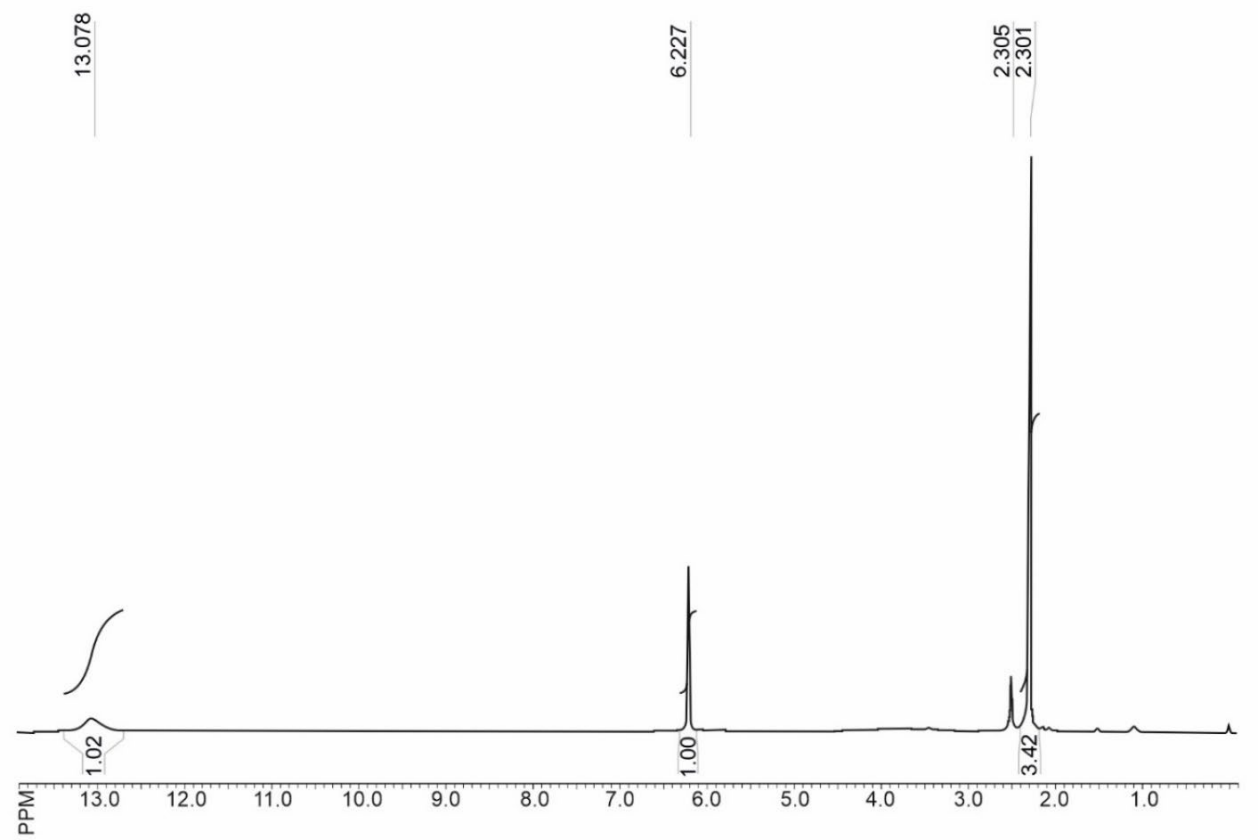


Fig. 2. ^{1}H NMR of 5-methyl-3-(trifluoromethyl)-1H-pyrazole

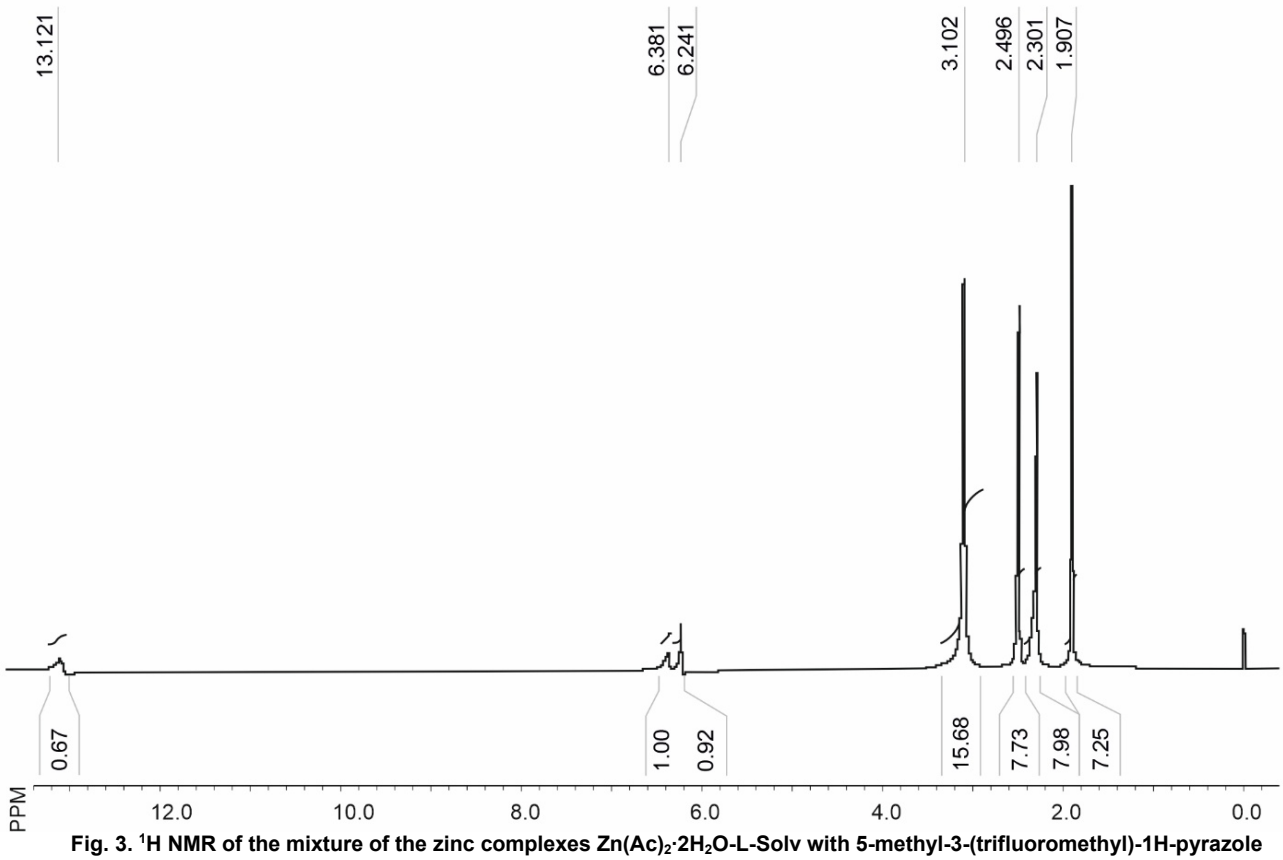


Fig. 3. ^{1}H NMR of the mixture of the zinc complexes $Zn(Ac)_2 \cdot 2H_2O$-L-Solv with 5-methyl-3-(trifluoromethyl)-1H-pyrazole

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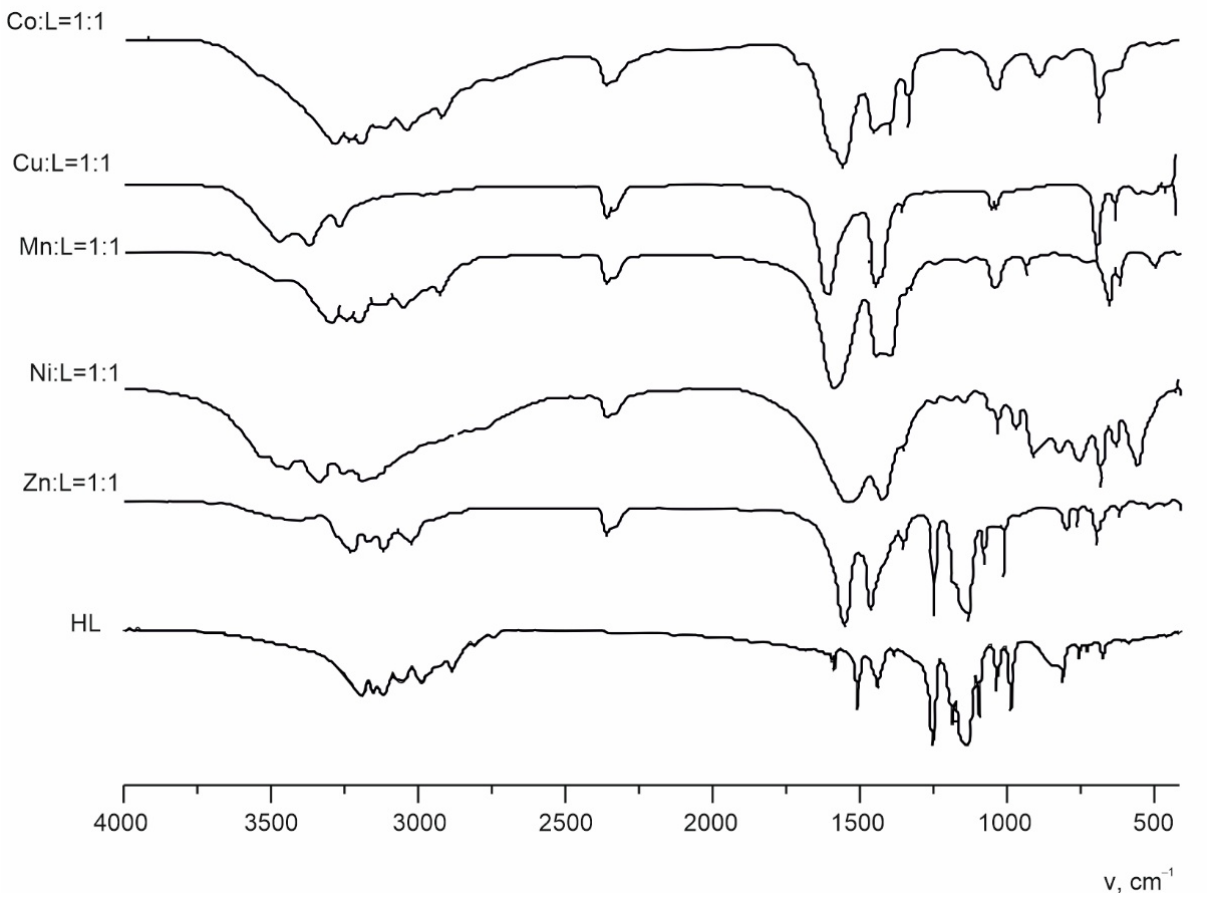

Fig. 4. IR spectra of the complexes $M(Ac)_2 \cdot 2L$ in the systems $M(Ac)_2 \cdot 4H_2O$-L-CH_3OH / CH_3CN at a ratio of M:L = 1:1

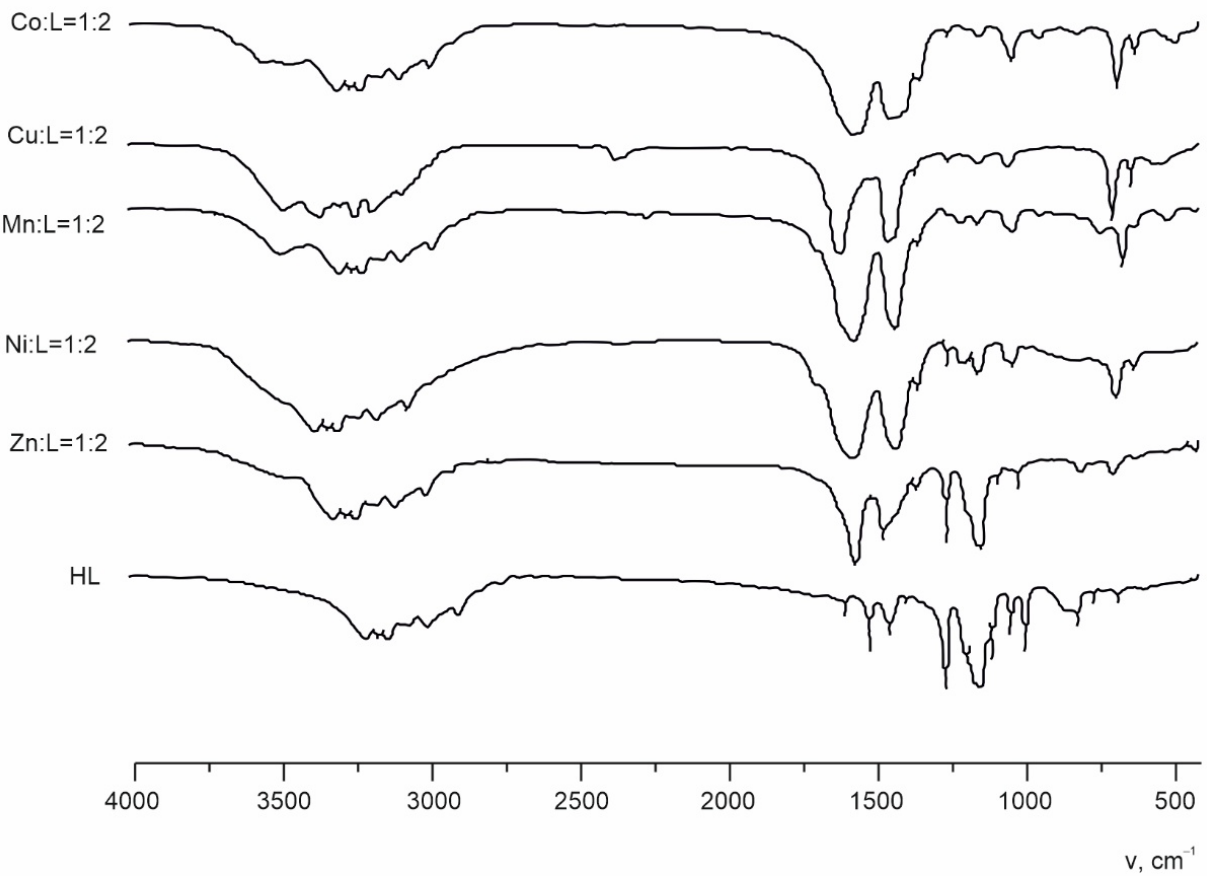

Fig. 5. IR spectra of the complexes $M(Ac)_2 \cdot 2L$ in the systems $M(Ac)_2 \cdot 4H_2O$-L- CH_3OH / CH_3CN at a ratio of M:L = 1:2

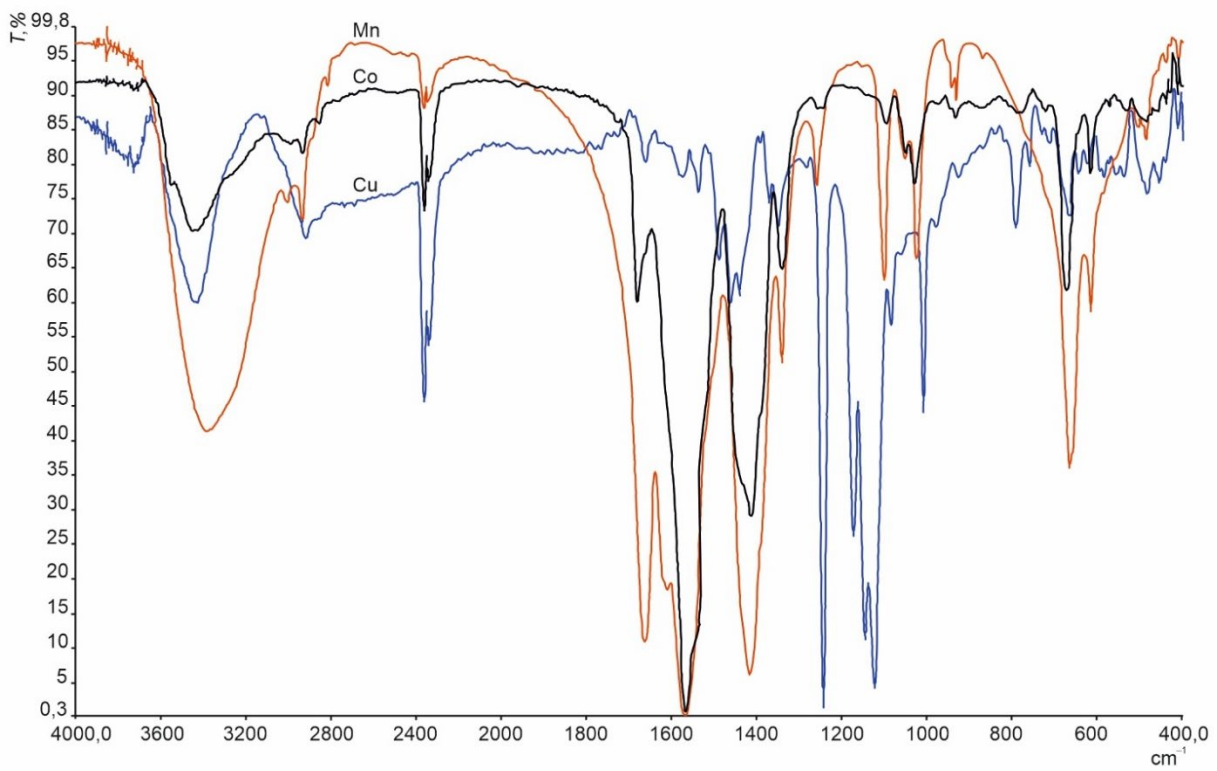

Fig. 6. IR spectra of the complexes $M(Ac)_2 \cdot L \cdot DMF$ in the systems $M(Ac)_2 \cdot 4H_2O$-L- DMF at a ratio of M:L = 1:1 and 1:2

UV-Vis spectroscopy. Diffuse reflection electron spectra were obtained for the synthesized compounds. Thus, the electronic spectrum of diffuse reflection for the copper powder sample of the obtained $Cu(Ac)_2 \cdot 2L$ complex (fig. 7) showed the presence of a broad absorption band in the 550–700 nm region, which is attributed to the d-d transition and is characteristic of Cu^{2+} complexes.

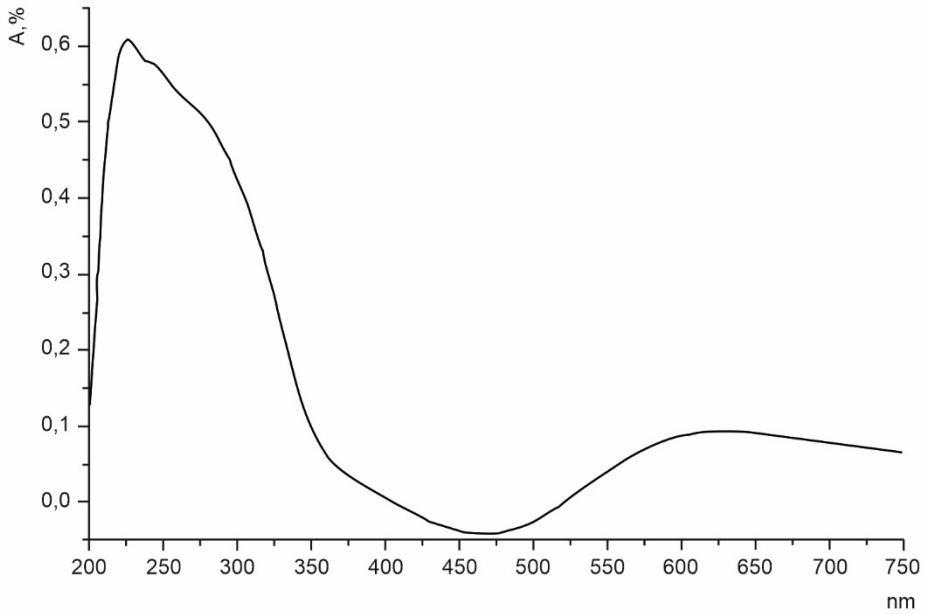

Fig. 7. Electronic spectrum of diffuse reflection for the complex $Cu(Ac)_2 \cdot 2L$

The theoretical data for octahedral cobalt complexes are 400–500 nm (chromophore CoO6–CoN6), while for tetrahedral complexes it is 600–700 nm (chromophore CoN4), the results obtained confirm the tetrahedral structure of the complex.

In the case of the cobalt (II) complex, a diffuse reflection electron spectrum was obtained, which showed a maximum absorption in the region of 12000 cm^{-1}, indicating an octahedral coordination environment of the metal ion. Literature data for octahedral complexes indicate a transition from the {CoO6} chromophore ~ 12000 cm^{-1} to the {CoN6} chromophore ~ 17000 cm^{-1}, and a transition from the {CoO6} chromophore (~ 12455 cm^{-1}) to {Co4N2} (~ 14770 cm^{-1}) (fig. 8).

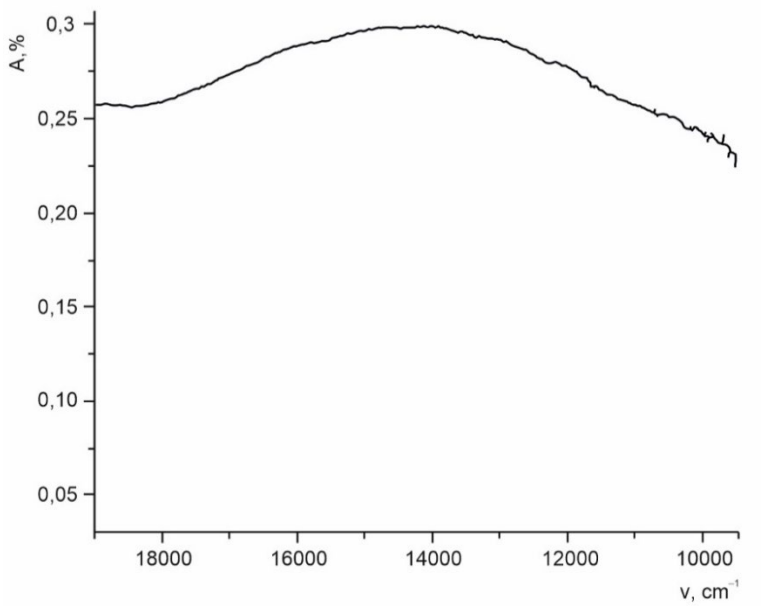

Fig. 8. Electronic spectrum of diffuse reflection for the complex $Co(Ac)_2 \cdot 2L$

Therefore, it can be concluded that cobalt is in an octahedral nitrogen-oxygen donor environment.

The similarity in the structure of manganese and nickel complexes is evidenced by their diffuse reflection electron spectra. The presence of a broad band in the 450–550 nm region, which is attributed to the d-d transition and is characteristic of manganese and nickel complexes. The bands in the 250 nm and 300 nm regions are attributed to charge transfer from the ligand to the metal (fig. 9).

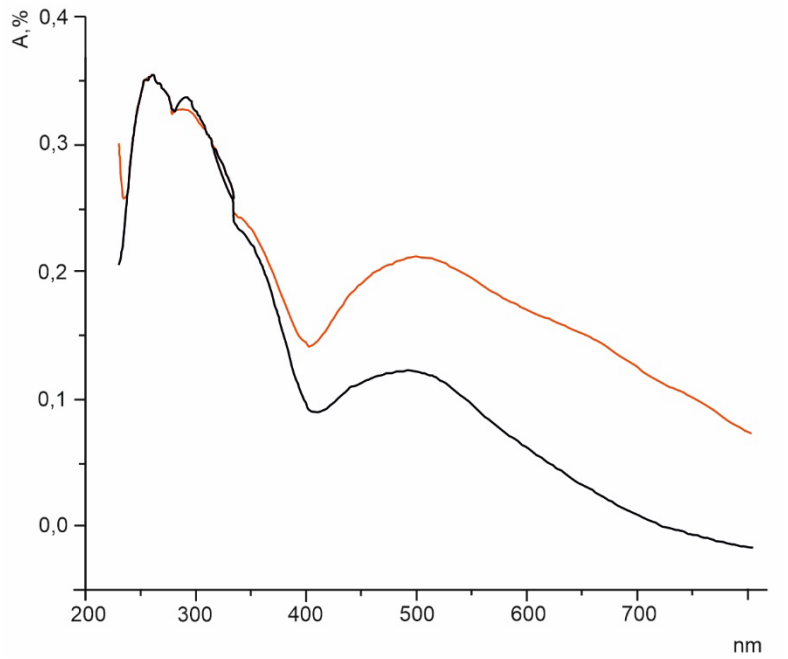

Fig. 9. Electronic diffuse reflection spectra for $Mn(Ac)_2 \cdot 2L$ (top) and $Ni(Ac)_2 \cdot 2L$ (bottom) complexes

Therefore, in this paper, an organic ligand 5-methyl-3-(trifluoromethyl)-1H-pyrazole, was synthesized. The compound was identified by elemental analysis, IR and ^1H NMR spectroscopy. The interaction of 3d metals such as Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) with 5-methyl-3-(trifluoromethyl)-1H-pyrazole was investigated. Methods for the synthesis of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) compounds with 5-methyl-3-(trifluoromethyl)-1H-pyrazole were developed. Based on the data of elemental analysis and methods of IR, NMR, and electronic spectroscopy, the composition and structure of the obtained complexes have been proposed. It has been shown that in the obtained complexes: the most typical method of coordination of the pyrazole cycle is realized: monodentate - through the pyridine nitrogen atom; the formation of two types of mononuclear Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes is observed: $M(Ac)_2 \cdot 2L$ and $M(Ac)_2 \cdot L \cdot DMF$; in the obtained complexes $M(Ac)_2 \cdot 2L$ and $M(Ac)_2 \cdot L \cdot DMF$ complexes, a six-coordinate environment of the central atom is realized due to four oxygen atoms from bidentate chelate coordinated acetate groups and two nitrogen atoms from molecules of a non-deprotonated ligand.

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Юлія ДАВИДЕНКО, канд. хім. наук
ORCID ID: 0000-0003-0223-0363
e-mail: y.davydenko@knu.ua
Київський національний університет імені Тараса Шевченка, Київ, Україна

СИНТЕЗ І ХАРАКТЕРИСТИКА КООРДИНАЦІЙНИХ СПОЛУК ПЕРЕХІДНИХ МЕТАЛІВ НА ОСНОВІ 5-МЕТИЛ-3-(ТРИФТОРМЕТИЛ)-1Н-ПІРАЗОЛУ

В с т у п . *Синтез координаційних сполук на основі піразолів є надзвичайно важливим у сучасній хімії, оскільки ці сполуки мають універсальні властивості та різноманітне практичне застосування в таких сферах: каталіз, матеріалознавство, оптоелектроніка та медицина. Введення трифторметильних груп у такі ліганди є потужною стратегією для модуляції електронних і стеричних властивостей комплексів, що значно впливає на їхню кислотність, стабільність і реакційну здатність. У цьому контексті 5-метил-3-(трифторметил)-1Н-піразол виділяється як особливо перспективний ліганд, координаційна хімія якого з перехідними металами залишається напрочуд недослідженою. Незважаючи на потенціал 5-метил-3-(трифторметил)-1Н-піразолу, систематичне дослідження синтезу, структурної різноманітності та властивостей його координаційних сполук в основному відсутнє в сучасній літературі. Ця прогалина є втраченою можливістю, оскільки унікальний електронний профіль цього ліганду може відкрити нові функціональні можливості в молекулярних матеріалах. Щоб розв'язати цю проблему, пропонується комплексне дослідження синтезу та характеристик нового сімейства координаційних сполук перехідних металів першого ряду (Mn, Co, Ni, Cu, Zn) з лігандом 5-метил-3-(трифторметил)-1Н-піразол. Ця робота має на меті систематично дослідити його координаційний ландшафт, надаючи фундаментальні знання для майбутнього проєктування передових функціональних матеріалів.*

М е т о д и . *Для ідентифікації отриманих сполук було використано різні методи, такі як: інфрачервона, електронна та ЯМР-спектроскопія. Усі матеріали були отримані з комерційних джерел без додаткового очищення. ІЧ-спектри синтезованих сполук записували на ІЧ-Фур'є-спектрометрі Perkin-Elmer BX (400–4000 см$^{-1}$) у таблетках KBr. Електронні спектри дифузного відбиття отриманих зразків в УФ і видимому діапазоні реєстрували на спектрометрі Varian Cary 50. Інтенсивність вимірювали відносно KBr. Розчинники очищали за стандартними методиками. Спектри ЯМР ^{1}H записували на спектрометрі Bruker AC-400.*

Р е з у л ь т а т и . *Взаємодія 5-метил-3-(трифторметил)-1Н-піразолу (L) з ацетатами 3d-металів (Mn, Zn, Cu, Co, Ni) у неводних розчинах виявилася залежною від розчинника. У середовищі розчинників CH_3CN і CH_3OH (системи $M(Ac)_2{\cdot}4H_2O$–L–CH_3OH/CH_3CN) при співвідношенні M:L 1:1 і 1:2 утворювалися продукти зі складом $M(Ac)_2{\cdot}2L$. Тим часом у диметилформаміді (системи $M(Ac)_2{\cdot}4H_2O$–L–DMF) за тих самих співвідношень були виділені комплекси $M(Ac)_2{\cdot}L{\cdot}DMF$, що містили молекулу розчинника. Склад сполук було підтверджено елементним аналізом, а також інфрачервоною, електронною та ЯМР-спектроскопією.*

Висновки. ***Синтезовано органічний ліганд, 5-метил-3-(трифторметил)-1Н-піразол. Сполука ідентифікувалась за допомогою елементного аналізу, ІЧ- та ^{1}Н ЯМР-спектроскопії. Було досліджено взаємодію 3d-металів, таких як Mn(II), Co(II), Ni(II), Cu(II) і Zn(II), з 5-метил-3-(трифторметил)-1Н-піразолом. Розроблено методи синтезу сполук Mn(II), Co(II), Ni(II), Cu(II) та Zn(II) з 5-метил-3-(трифторметил)-1Н-піразолом. На основі даних елементного аналізу й методів ІЧ, ЯМР та електронної спектроскопії запропоновано склад і будову отриманих комплексів. Було показано, що в отриманих комплексах: реалізовано найбільш типовий спосіб координації піразольного циклу: монодентатний – через піридиновий атом нітрогену; отримано два типи моноядерних комплексів Mn(II), Co(II), Ni(II), Cu(II) та Zn(II): $M(Ac)_2{\cdot}2L$ та $M(Ac)_2{\cdot}L{\cdot}DMF$; в отриманих комплексах $M(Ac)_2{\cdot}2L$ та $M(Ac)_2{\cdot}L{\cdot}DMF$ реалізується шестикоординаційне оточення центрального атома завдяки чотирьом атомам оксигену від бідентатно-хелатно координованих ацетатних груп і двох атомів нітрогену від молекул недепротонованого ліганду.***

Ключові слова: ***5-метил-3-(трифторметил)-1Н-піразол, комплекси, 3d-метали, ^{1}Н ЯМР-спектроскопія, ІЧ-спектроскопія.***

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