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Synthesis of mixed-ligand copper(II) complexes containing bis(pyrazol-1-yl)methane ligands

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Abstract

Complexes of copper(II) nitrate and chloride with several bis(pyrazol-1-yl)methane derivatives have been prepared and characterized by spectroscopic (IR, UV–Vis) and electrochemical (solution conductivity measurements, cyclic voltammetry) techniques. The complexes react with bidentate (2,2'-bipyridyl and acetylacetone) and monodentate (triphenylphosphine, 1*H*-benzimidazole, 1*H*-benzotriazole, 3,5-dimethyl-1*H*-pyrazole) ligands forming mixed-ligand complexes.

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1. Introduction

Bis(pyrazol-1-yl)methane (L^1 , Fig. 1) and its derivatives are bidentate chelating ligands forming complexes with most transition metal ions and some main-group elements [1]. The coordination properties of bis(pyrazol-1-yl)methanes may be varied in a rather wide range by introducing substituents into the pyrazole rings. Hence, the donor ability of the ligands is determined by the presence of electron-withdrawing or electron-donating functional groups, and steric factors altered by the introduction of bulky alkyl groups into the rings and the methylene bridge between them.

Several copper(II) complexes of bis(pyrazol-1-yl)methane derivatives are known so far. In 1979 Jan Reedijk et al. reported the preparation of bis(3,5-dimethylpyrazol-1-yl)methane (L^2) complexes with copper(II) halides and nitrate [2]. These authors found CuBr₂ to react with L^2 (molar ratio 1:2) in ethanol to give the Cu(L^2)₂Br₂ complex, while in the case of copper(II) chloride an adduct Cu₃(L^2)₄-Cl₆ · EtOH of undetermined structure was obtained [2]. Copper(II) nitrate also forms a complex with a metal to

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ligand ratio M:L = 1:2. According to IR- and UV–Vis spectroscopic data, the Cu^{2+} ion in this complex is octahedrally surrounded, and both of the nitrate ions are monodentate [2].

Complexes of L^1 and L^2 ligands with copper(II) chloride and nitrate of 1:1 composition were also reported [3]. IRspectroscopy suggests the nitrate ions to be monodentate, so the Cu²⁺ ions in these complexes are tetrahedral.

The reactivity of bis(pyrazol-1-yl)methane complexes with transition metals towards other ligands is scarcely investigated. Mesubi [4] reported the reactions of the 2,2bis(pyrazol-1-yl)propane complex Cu(L³)Cl₂ with pseudohalides in aqueous solution leading to the substitution of chloride ions with the formation of Cu(L³)X₂ (X = SCN⁻, CNO⁻, N₃⁻) complexes. A similar reaction with PF₆⁻ and BPh₄⁻ anions yields [Cu(L³)₂Cl]PF₆ and [Cu(L³)₂Cl]BPh₄ species [4].

Displacement of the L³ ligand from the coordination sphere was observed when the complex $Cu(L^3)Cl_2$ was reacted with bidentate anions (acetylacetone, dialkyldithiocarbamate, bis(pyrazol-1-yl)borate and tris(pyrazol-1-yl)borate) [4]. The first example of a 3*d*-transition metal mixed-ligand complex $Zn(L^4)(Q^-)_2$, containing bis-(3,4,5-trimethylpyrazol-1-yl)methane (L⁴) and anionic 1phenyl-3-methyl-4-benzoyl-5-pyrazolone enolate (Q⁻) was

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Fig. 1. Bis(pyrazol-1-yl)methane derivatives.

prepared by Pettinari et al. [5]. It was noted that in the case of the complexes of CdI_2 and $HgCl_2$ displacement of the L⁴ ligand is observed under analogous conditions. Nevertheless, L⁴ reacts with mercury(II) acetate in the presence of saccharine (*o*-sulfobenzoic acid imide, SacH) in aqueous solution with the formation of a mixed-ligand complex $Hg(L^4)(Sac^-)_2$ [5].

The same authors [5] also report that ligand L^4 is displaced from the complexes $Zn(L^4)X_2$ ($X = Cl^-$, Br^-) and $Cd(L^4)Br_2$ upon their reaction with various monodentate ligands (pyrazole, *N*-methylimidazole, 4-phenylimidazole) and 2,2'-bipyridyl. Similarly, when $Hg(L^5)Cl_2$ was reacted with triphenylphosphine (PPh₃) and 2,2'-bipyridyl (bipy), only $Hg(PPh_3)_2Cl_2$ and $Hg(bipy)Cl_2$ compounds were isolated [6].

A considerable quantity of 3*d*-transition-metal mixedligand complexes with bis(pyrazol-1-yl)methane derivatives involves copper(I) ions. Thus, $[Cu(NO_3)(PPh_3)_2]$ reacts with L¹ [7] or L⁵ [8] to form mixed-ligand adducts $[Cu(L)-(PPh_3)_2](NO_3)$ (L = L¹, L⁵). It is interesting to note that the same reaction was observed even in the case of strongly electron-deficient bis(4-nitropyrazol-1-yl)methane [7]. Similarly, complexes containing other counter-ions, namely $[Cu(L)(PPh_3)X]$ (L = L¹, L²; X = Cl⁻, Br⁻) [8], $[Cu(L)-(PPh_3)_2](ClO_4)$ (L = L¹, L², L⁵) [9], $[Cu(L^2)(PPh_3)](ClO_4)$ [10] and $[Cu(L^1)(MeCN)_n](ClO_4)$ (n = 1, 2) [11] have been reported.

A binuclear mixed-ligand copper(I) complex with a bridging bidentate heterocyclic ligand, $[Cu_2(L^2)_2(MeCN)_2-(\mu-Prz)](ClO_4)_2$, was prepared by the reaction of $[Cu(L^2)-(MeCN)](ClO_4)$ with pyrazine (Prz) in dichloromethane solution [10].

As it is seen from the literature, no copper(II) mixedligand complexes containing bis(pyrazol-1-yl)methane derivatives together with any other organic ligands are known.

In this contribution we report the preparation of complexes of L^1 , L^2 ligands and novel bis(4-iodopyrazol-1-yl)methane (L^6) and bis(3,5-dimethyl-4-iodopyrazol-1-yl)methane (L^7) ligands with copper(II) nitrate and chloride. The reactivity of the complexes obtained with various mono- and bidentate ligands is investigated.

2. Experimental

2.1. Syntheses

Commercial reagents and solvents were used as received. Bis(pyrazol-1-yl) methane (L¹) was prepared as previously described [12]. Briefly, 5.00 g (73.5 mmol) of 1H-pyrazole were dissolved in 30 ml of DMSO, and 16.46 g (294.0 mmol) of finely powdered KOH were added. The suspension was vigorously stirred for 1 h at 60 °C, and 6.40 g (2.6 ml, 36.8 mmol) of dibromomethane in 20 ml of DMSO were added dropwise over 30 min. Stirring at 60 °C was continued for an additional 4 h, and the reaction mixture was poured into 300 ml of water and extracted with chloroform (6×30 ml). The extract was washed with water $(2 \times 20 \text{ ml})$ and dried over anhydrous calcium chloride. Removal of the solvent produced 4.45 g (yield 82%) of solid product. M.p. 107-107.5 °C (benzene-hexane, 1:1, lit. m.p. 108 °C [13]). Anal. Calc. for C₇H₈N₄: C, 56.74; H, 5.44; N, 37.81. Found: C, 56.36; H, 5.67; N, 38.05%. ¹H NMR spectrum corresponds to literature data [14]. IR bands, cm⁻¹: 1610, 1510, 1450 (v_{ring} – pyrazole ring stretching vibrations); 1355 (βCH – in-plane C–H bending vibrations); 1045 (pyrazole ring breathing); 940, 740 (δ_{C-H}). UV–Vis bands (EtOH), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 222 (8860), 203 (sh).

Bis(3,5-*dimethylpyrazol-1-yl*)*methane* (L²) was prepared similarly. Yield 92%, m.p. 105–105.5 °C (benzene–hexane, 1:1, lit. m.p. 105 °C [13]). *Anal.* Calc. for C₁₁H₁₆N₄: C, 64.68; H, 7.89; N, 27.43. Found: C, 63.88; H, 8.03; N, 26.82%. ¹H NMR spectrum corresponds to literature data [14]. IR bands, cm⁻¹: 1550, 1450 (v_{ring}); 1345 (βCH); 1125; 1020 (pyrazole ring breathing); 955, 765, 700. UV–Vis bands (EtOH), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 222 (6790), 206 (5900).

Bis(4-iodopyrazol-1-yl) methane (L⁶) was prepared as previously described [15]. Briefly, a suspension of 3.50 g (23.6 mmol) of L^1 , 4.80 g (18.9 mmol) of powdered iodine, 1.65 g (9.4 mmol) of HIO₃ in 30 ml of glacial acetic acid and 3 ml 30% aqueous H₂SO₄ was vigorously stirred for 15 min at 70 °C until the reaction mixture became colorless. The mixture was then poured into 250 ml of water, the precipitate formed was filtered, washed with H₂O, and dried to yield 9.25 g (98%) of compound L^6 . M.p. 165-165.5 °C (benzene-hexane, 4:1), Anal. Calc. for C₇H₆N₄I₂: C, 21.02; H, 1.51; N, 14.01. Found: C, 21.47; H, 1.93; N, 13.99%. ¹H NMR (CDCl₃): δ, ppm: 6.15 (s, 2H, CH₂), 7.49 (s, 2H, H³), 7.62 (s, 2H, H⁵). IR bands, cm⁻¹: 1520 (v_{ring}); 1395 (β CH); 1310; 1000 (pyrazole ring breathing). UV–Vis bands (EtOH), λ_{max} , nm (ε , $dm^3 cm^{-1} mol^{-1}$): 238 (8410), 202 (8410).

Bis(3,5-dimethyl-4-iodopyrazol-1-yl)methane (L^7) was prepared similarly. Yield 94%, m.p. 183–184 °C (EtOH). *Anal.* Calc. for C₁₁H₁₄N₄I₂: C, 29.27; H, 3.09; N, 12.28. Found: C, 29.34; H, 3.04; N, 12.08%. ¹H NMR (CDCl₃): δ, ppm: 2.12 (s, 6H, 3-CH₃), 2.40 (s, 6H, 5-CH₃), 6.08 (s, 2H, CH₂). IR bands, cm⁻¹: 1525, 1460 (ν_{ring}); 1370; 1335 (βCH); 1050 (pyrazole ring breathing). UV–Vis bands (EtOH), λ_{max}, nm (ε, dm³ cm⁻¹ mol⁻¹): 238 (6790), 204 (6560).

2.1.1. Bis(pyrazol-1-yl)methanedinitratocopper(II) monohydrate (1)

A solution of 0.752 g (4.0 mmol) of L¹ in 6 ml of acetone was added to a solution of 0.592 g (4.0 mmol) of Cu(NO₃)₂ · 3H₂O in 3 ml of the same solvent. The immediately formed light-blue precipitate was filtered after 30 min, thoroughly washed with acetone and dried in vacuo at 40 °C. The yield of compound **1** was 0.800 g (57%).

Complexes 2–5, 7, 9, 10 were obtained similarly, whilst a 2:1 ligand to metal ratio was used in case of compounds 6 and 8.

2.1.2. Bis(pyrazol-1-yl)methane-2,2'-bipyridylnitratocopper(II) nitrate (11)

A solution of 0.078 g (0.5 mmol) 2,2'-bipyridyl in 1 ml of acetone was added to a warmed-up (40 °C) solution of 0.168 g (0.5 mmol) of the complex $[Cu(L^1)(O_2NO)_2] \cdot H_2O$ (1) in 15 ml of acetone. The precipitated light-blue crystals of compound **11** (yield 0.170 g, 69%) were filtered, washed with acetone and dried in vacuo.

Compounds 12–14 were prepared similarly from copper complexes 2 or 3 and bidentate ligands (2,2'-bipyridyl or acetylacetone) in a 1:1 ratio. Mixed-ligand complexes 15– 18 were obtained upon mixing one equivalent of complex 2 with two equivalents of the corresponding monodentate ligand in ethanol (compound 15), acetone (complexes 16, 17) or isopropyl alcohol (compound 18).

2.2. Analytical data

2.2.1. Bis(pyrazol-1-yl)methanedinitratocopper(II) monohydrate (1)

Cu(L¹)(NO₃)₂ · H₂O. Yield 57%; m.p. 207 °C; molar conductivity $\lambda = 27.5 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ (acetone). *Anal*. Calc. for C₇H₁₀CuN₆O₇: C, 23.77; H, 2.85; N, 23.76. Found: C, 24.04; H, 2.86; N, 24.10%. IR bands, cm⁻¹: 3400br (v_{O-H} , H₂O); 2354, 2167 ($v_1 + v_3$ of NO₃⁻); 1788, 1757 ($v_1 + v_4$ of NO₃⁻); 1618 (δ_{O-H} , H₂O); 1514 (v_{ring}); 1464 (v_3 mode of NO₃⁻); 1398 (v_{ring}); 1321 (βCH); 1285 (v_3 mode of NO₃⁻); 1045 (pyrazole ring breathing); 1017 (v_1 mode of NO₃⁻); 809 (v_2 mode of NO₃⁻); 760, 729 (v_4 mode of NO₃⁻). UV– Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 935 (sh), 685 (120), 338 (sh), 256 (sh), 219 (16580). Cyclic voltammetry, $E_{1/2} = -214 \text{ mV}$, $\Delta E = 182 \text{ mV}$.

2.2.2. Bis(3,5-dimethylpyrazol-1-yl)methanedinitratocopper(II) (2)

Cu(L²)(NO₃)₂. Yield 93%; m.p. 230–231 °C; $\lambda = 19.1 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ (acetone). *Anal*. Calc. for C₁₁H₁₆Cu-N₆O₆: C, 33.72; H, 4.12; N, 21.45. Found: C, 34.20; H, 4.45; N, 20.98%. IR bands, cm⁻¹: 1540 (ν_{ring}); 1500

(v₃ mode of NO₃⁻); 1455 (v_{ring}); 1370 (βCH); 1280 (v₃ mode of NO₃⁻); 1040 (pyrazole ring breathing); 995 (v₁ mode of NO₃⁻); 820 (v₂ mode of NO₃⁻); 730, 690 (v₄ mode of NO₃⁻). UV-Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 935 (sh); 685 (120); 338 (sh); 256 (sh); 219 (16580). $E_{1/2} = -137$ mV, $\Delta E = 112$ mV.

2.2.3. Bis(4-iodopyrazol-1-yl)methanedinitratocopper(II) (3)

Cu(L⁶)(NO₃)₂. Yield 77%; m.p. 229–230 °C. *Anal.* Calc. for C₇H₆CuI₂N₆O₆: C, 14.31; H, 1.03; N, 14.30. Found: C, 14.77; H, 1.30; N, 14.00%. IR bands, cm⁻¹: 1742, 1703 ($v_1 + v_4$ of NO₃⁻); 1521 (v_{ring}); 1454 (v_3 mode of NO₃⁻); 1433 (v_{ring}); 1329 (β CH); 1293 (v_3 mode of NO₃⁻); 1032 (pyrazole ring breathing); 1003 (v_1 mode of NO₃⁻); 827 (v_2 mode of NO₃⁻); 782, 735 (v_4 mode of NO₃⁻).

2.2.4. Bis(3,5-dimethyl-4-iodopyrazol-1-yl)methanedinitratocopper(II) dihydrate (4)

Cu(L⁷)(NO₃)₂ · 2H₂O. Yield 94%; m.p. 222–223 °C; $\lambda = 14.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (acetone). *Anal.* Calc. for C₁₁H₁₈-CuI₂N₆O₈: C, 19.44; H, 2.67; N, 12.37. Found: C, 19.82; H, 2.95; N, 12.09%. IR bands, cm⁻¹: 3400br ($v_{\text{O-H}}$, H₂O); 1620 ($\delta_{\text{O-H}}$, H₂O); 1520 (v_3 mode of NO₃⁻); 1470 (v_{ring}); 1370 (β CH); 1265 (v_3 mode of NO₃⁻); 1070 (pyrazole ring breathing); 1000 (v_1 mode of NO₃⁻); 835 (v_2 mode of NO₃⁻); 725, 700 (v_4 mode of NO₃⁻). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 1030 (sh); 722 (50.0); 342 (sh); 234 (13860); 204 (27650). $E_{1/2} = -176 \text{ mV}$, $\Delta E = 183 \text{ mV}$.

2.2.5. Bis(pyrazol-1-yl)methanedichlorocopper(II) (5)

Cu(L¹)Cl₂. Yield 93%; m.p. 266–267 °C (lit. m.p. 264– 265 [3]); $\lambda = 15.0 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ (acetone). *Anal.* Calc. for C₇H₈Cl₂CuN₄: C, 29.75; H, 2.85; N, 19.82. Found: C, 29.55; H, 2.60; N, 20.10%. IR bands, cm⁻¹: 1500 (ν_{ring}); 1260 (β CH); 1050 (pyrazole ring breathing). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 940 (sh); 765 (73); 334 (sh); 260 (sh); 215 (11630). $E_{1/2} = -169 \ mV$, $\Delta E = 128 \ mV$.

2.2.6. Bis {bis(pyrazol-1-yl)methane}copper(II) dichloride dihydrate (6)

Cu(L¹)₂Cl₂ · 2H₂O. Yield 90%; m.p. 180–182 °C; $\lambda = 11.7 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (acetone). *Anal.* Calc. for C₁₄H₂₀-Cl₂CuN₈O₂: C, 36.02; H, 4.32; N, 24.00. Found: C, 36.03; H, 4.16; N, 23.60%. IR bands, cm⁻¹: 3400br (v_{O-H}, H₂O); 1630 (δ_{O-H} , H₂O); 1500, 1450 (v_{ring}); 1390 (β CH); 1045 (pyrazole ring breathing). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 1040 (sh); 765 (82); 337 (sh); 319 (163); 268 (2175); 220 (12120). $E_{1/2} = -111 \text{ mV}$, $\Delta E = 45 \text{ mV}$.

2.2.7. Bis(3,5-dimethylpyrazol-1-yl)methane-

dichlorocopper(II) (7)

Cu(L²)Cl₂. Yield 78%; m.p. 200–202 °C; $\lambda = 52.3 \ \Omega^{-1}$ cm² mol⁻¹ (acetone). *Anal*. Calc. for C₁₁H₁₆Cl₂CuN₄: C, 39.00; H, 4.76; N, 16.54. Found: C, 38.60; H, 4.78; N,

16.90%. IR bands, cm⁻¹: 1540 (ν_{ring}); 1260 (βCH); 1015 (pyrazole ring breathing). UV–Vis bands (ethanol), λ_{max} , nm (ϵ , dm³ cm⁻¹ mol⁻¹): 950 (sh); 740 (102); 335 (sh); 268 (2433); 222 (10260). $E_{1/2} = -179$ mV, $\Delta E = 140$ mV.

2.2.8. Bis {bis(3,5-dimethylpyrazol-1-yl)methane}copper(II) dichloride dihydrate (8)

Cu(L²)₂Cl₂·2H₂O. Yield 73%; m.p. 174–175 °C; $\lambda = 52.1 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$ (acetone). *Anal.* Calc. for C₂₂H₃₆-Cl₂CuN₈O₂: C, 45.63; H, 6.27; N, 19.35. Found: C, 45.62; H, 5.86; N, 19.20%. IR bands, cm⁻¹: 3430br (v_{O-H}, H₂O); 1610 (δ_{O-H} , H₂O); 1550, 1460 (v_{ring}); 1370 (βCH); 1020 (pyrazole ring breathing). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 945 (sh); 715 (168); 351 (sh); 265 (sh); 225 (30950). $E_{1/2} = -202 \ \text{mV}$, $\Delta E = 140 \ \text{mV}$.

2.2.9. Bis(4-iodopyrazol-1-yl)methanedichlorocopper(II) (9)

Cu(L⁶)Cl₂. Yield 93%; m.p. 267–269 °C; $\lambda = 18.6 \ \Omega^{-1}$ cm² mol⁻¹ (acetone). *Anal.* Calc. for C₇H₈Cl₂CuI₂N₄: C, 15.73; H, 1.13; N, 10.48. Found: C, 15.80; H, 1.19; N, 10.90%. IR bands, cm⁻¹: 1500, 1430 (ν_{ring}); 1360 (β CH); 1005 (pyrazole ring breathing). UV–Vis bands (ethanol), λ_{max} , nm (ϵ , dm³ cm⁻¹ mol⁻¹): 870 (38.7); 228 (15800).

2.2.10. Bis(3,5-dimethyl-4-iodopyrazol-1-yl)methanedichlorocopper(II) dihydrate (10)

Cu(L⁷)Cl₂ · 2H₂O. Yield 88%; m.p. 229 °C; $\lambda = 22.7 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$ (acetone). *Anal.* Calc. for C₁₁H₁₈Cl₂CuI₂N₄O₂: C, 21.09; H, 2.90; N, 8.94. Found: C, 21.33; H, 3.10; N, 8.49%. IR bands, cm⁻¹: 3300br ($\nu_{\text{O-H}}$, H₂O); 1690 ($\delta_{\text{O-H}}$, H₂O); 1585, 1520, 1470 (ν_{ring}); 1345 (β CH); 1070 (pyrazole ring breathing). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 820 (67); 341 (sh); 238 (14460). $E_{1/2} = -180 \text{ mV}$, $\Delta E = 164 \text{ mV}$.

2.2.11. Bis(pyrazol-1-yl)methane-2,2'-bipyridylnitratocopper(II) nitrate (11)

Cu(L¹)(bipy)(NO₃)₂. Yield 69%; m.p. 194–196 °C; $\lambda = 52.6 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ (acetone). *Anal.* Calc. for C₁₇H₁₆Cu-N₈O₆: C, 41.51; H, 3.28; N, 22.78. Found: C, 41.90; H, 2.90; N, 22.30%. IR bands, cm⁻¹: 2371, 2278 ($v_1 + v_3$ of NO₃⁻); 1743, 1712 ($v_1 + v_3$ of NO₃⁻); 1610, 1601 (v_{ring} of pyridine); 1567 (v_{ring}); 1475 (v_3 mode of NO₃⁻); 1343 (βCH); 1279 (v_3 mode of NO₃⁻); 1160 (βCH of pyridine ring); 1032 (pyrazole ring breathing); 1016 (v_1 mode of NO₃⁻); 902 (γ CH – out-of-plane C–H bending vibrations of pyridine ring); 831, 812 (v_2 mode of NO₃⁻); 731, 705 (v_4 mode of NO₃⁻). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 880 (sh); 695 (65.3); 336 (sh); 312 (16270); 300 (17370); 242 (sh); 213 (32850). $E_{1/2} = -153 \text{ mV}$, $\Delta E = 121 \text{ mV}$.

2.2.12. Bis(3,5-dimethylpyrazol-1-yl)methane-2,2'bipyridylnitratocopper(II) nitrate (12)

Cu(L²)(bipy)(NO₃)₂. Yield 81%; m.p. 229–231 °C; $\lambda = 81.6 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$ (acetone). *Anal.* Calc. for C₂₁H₂₄-CuN₈O₆: C, 46.03; H, 4.41; N, 20.45. Found: C, 45.76;

H, 4.45; N, 20.93%. IR bands, cm⁻¹: 2392, 2283 ($v_1 + v_3$ of NO₃⁻); 1744, 1713 ($v_1 + v_4$ of NO₃⁻); 1601 (v_{ring} of pyridine); 1567 (v_{ring}); 1477 (v_3 mode of NO₃⁻); 1334 (βCH); 1288 (v_3 mode of NO₃⁻); 1159 (βCH of pyridine ring); 1041 (pyrazole ring breathing); 1018 (v_1 mode of NO₃⁻); 902 (γCH of pyridine ring); 833, 808 (v_2 mode of NO₃⁻); 732, 705 (v_4 mode of NO₃⁻). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 910 (sh); 685 (74.4); 341 (sh); 313 (12410); 302 (13060); 243 (sh); 210 (35740). $E_{1/2} =$ -190 mV, $\Delta E = 157$ mV.

2.2.13. Bis(4-iodopyrazol-1-yl)methane-2,2'-bipyridylnitratocopper(II) nitrate (13)

Cu(L⁶)(bipy)(NO₃)₂. Yield 46%; m.p. 203–206 °C; $\lambda = 76.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (acetone). Anal. Calc. for C₁₇-H₁₄CuI₂N₈O₆: C, 27.45; H, 1.90; N, 15.07. Found: C, 27.74; H, 2.07; N, 14.96%. IR bands, cm⁻¹: 2371, 2282 ($v_1 + v_3$ of NO₃⁻); 1743, 1716 ($v_1 + v_4$ of NO₃⁻); 1610, 1601 (v_{ring} of pyridine); 1567 (v_{ring}); 1497 (v_3 mode of NO₃⁻); 1445 (v_{ring}); 1331 (β CH); 1293 (v_3 mode of NO₃⁻); 1160 (β CH of pyridine ring); 1032 (pyrazole ring breathing); 1014 (v_1 mode of NO₃⁻); 734, 706 (v_4 mode of NO₃⁻). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 910 (sh); 705 (107); 336 (sh); 311 (26460); 308 (30370); 290 (sh); 232 (sh); 210 (53520). $E_{1/2} = -150 \text{ mV}, \Delta E = 127 \text{ mV}.$

2.2.14. Bis(3,5-dimethylpyrazol-1-yl)methaneacetylacetonatonitratocopper(II) (14)

Cu(L²)(acac)(NO₃). Yield 67%; m.p. 177–178 °C; $\lambda = 67.9 \ \Omega^{-1} \ cm^2 \ mol^{-1}$ (acetone). *Anal.* Calc. for C₁₆H₂₃-CuN₅O₅: C, 44.80; H, 5.40; N, 16.33. Found: C, 44.35; H, 5.12; N, 16.78%. IR bands, cm⁻¹: 2392, 2283 ($v_1 + v_3$ of NO₃⁻); 1744, 1709 ($v_1 + v_4$ of NO₃⁻); 1556 (v_{ring}); 1478 (v_3 mode of NO₃⁻); 1475 (v_{ring}); 1335 (βCH); 1288 (v_3 mode of NO₃⁻); 1041 (pyrazole ring breathing); 1018 (v_1 mode of NO₃⁻); 836, 807 (v_2 mode of NO₃⁻); 741, 704 (v_4 mode of NO₃⁻). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 1020 (sh); 680 (54.1); 340 (sh); 295 (5970); 245 (sh); 219 (sh). $E_{1/2} = -187 \ mV$, $\Delta E = 114 \ mV$.

2.2.15. Bis(3,5-dimethylpyrazol-1-yl)methanebis(triphenylphosphine)nitratocopper(II) nitrate (15)

Cu(L²)(PPh₃)₂(NO₃)₂. Yield 77%; m.p. 184–185 °C; $\lambda = 88.1 \ \Omega^{-1} \ \text{cm}^2 \ \text{mol}^{-1}$ (acetone). Anal. Calc. for C₄₇H₄₆Cu-N₆O₆P₂: C, 61.60; H, 5.06; N, 9.17. Found: C, 61.65; H, 5.07; N, 8.75%. IR bands, cm⁻¹: 1557 (v_{ring}); 1479 ($v_3 \ \text{mode}$ of NO₃⁻); 1465 (v_{ring}); 1435 ($v_{\text{C=C}}$); 1332 (β CH); 1281 ($v_3 \ \text{mode}$ of NO₃⁻); 1097; 1049 (pyrazole ring breathing); 1022 ($v_1 \ \text{mode}$ of NO₃⁻); 836, 810 ($v_2 \ \text{mode}$ of NO₃⁻); 743, 705 ($v_4 \ \text{mode}$ of NO₃⁻); 694 (δ -mode of PPh₃); 521 ($v_{\text{C-P}}$); 503 (y-mode of PPh₃). UV–Vis bands (methanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 700 (16.8); 340 (sh); 256 (sh); 215 (80910). $E_{1/2} = -171 \ \text{mV}$, $\Delta E = 145 \ \text{mV}$; $E_{1/2} = -829 \ \text{mV}$, $\Delta E = 244 \ \text{mV}$.

2.2.16. Bis(3,5-dimethylpyrazol-1-yl)methane-

bis{1H-benzimidazole}nitratocopper(II) nitrate (16)

Cu(L²)(BImH)₂(NO₃)₂. Yield 84%; m.p. 312 °C; $\lambda = 55.6 \,\Omega^{-1} \,\mathrm{cm}^2 \,\mathrm{mol}^{-1}$ (ethanol). *Anal.* Calc. for C₂₅H₂₈CuN₁₀O₆: C, 47.81; H, 4.49; N, 22.30. Found: C, 47.50; H, 4.08; N, 22.11%. IR bands, cm⁻¹: 3380br ($\nu_{\text{N-H}}$ in BImH); 2388 ($\nu_1 + \nu_3$ of NO₃⁻); 1712 ($\nu_1 + \nu_4$ of NO₃⁻); 1624 ($\nu_{\text{C-C}}$); 1595, 1557 (ν_{ring}); 1479 (ν_3 mode of NO₃⁻); 1624 ($\nu_{\text{C-C}}$); 1595, 1557 (ν_{ring}); 1479 (ν_3 mode of NO₃⁻); 1641 (pyrazole ring breathing); 1012 (ν_1 mode of NO₃⁻); 1041 (pyrazole ring breathing); 1012 (ν_1 mode of NO₃⁻); 835, 808 (ν_2 mode of NO₃⁻); 748, 705 (ν_4 mode of NO₃⁻). UV–Vis bands (ethanol), λ_{max} , nm (ε , dm³ cm⁻¹ mol⁻¹): 1060 (sh); 670 (68.2); 339 (sh); 279 (14710); 273 (13320); 267 (sh); 250 (12720); 244 (13720); 213 (26440). $E_{1/2} = -171 \,\mathrm{mV}$, $\Delta E = 159 \,\mathrm{mV}$; $E_{1/2} = -509 \,\mathrm{mV}$, $\Delta E = 294 \,\mathrm{mV}$.

2.2.17. Bis(3,5-dimethylpyrazol-1-yl)methanebis{1H -benzotriazole}nitratocopper(II) nitrate (17)

Cu(L²)(BtaH)₂(NO₃)₂. Yield 43%; m.p. >330 °C. *Anal.* Calc. for C₂₃H₂₆CuN₁₂O₆: C, 43.84; H, 4.16; N, 26.68. Found: C, 43.86; H, 3.87; N, 27.00%. IR bands, cm⁻¹: 3380br (v_{N-H} in BtaH); 1763, 1720 ($v_1 + v_4$ of NO₃⁻); 1560 (v_{ring}); 1470 (v_3 mode of NO₃⁻); 1465 (v_{ring}); 1332 (β CH); 1283 (v_3 mode of NO₃⁻); 1195, 1153; 1049 (pyrazole ring breathing); 1011 (v_1 mode of NO₃⁻); 839, 830 (v_2 mode of NO₃⁻); 692 (v_4 mode of NO₃⁻).

2.2.18. Bis(3,5-dimethylpyrazol-1-yl)methanebis-

{3,5-dimethyl-1H-pyrazole}nitratocopper(II) nitrate (18) Cu(L²)(Me₂PyrH)₂(NO₃)₂. Yield 50%; m.p. 237–238 °C; $\lambda = 52.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ (ethanol). Anal. Calc. for C₂₁H₃₂-CuN₁₀O₆: C, 43.18; H, 5.52; N, 23.98. Found: C, 42.95; H, 5.70; N, 24.02%. IR bands, cm⁻¹: 3300br (v_{N-H} in Me₂-PyrH); 2393, 2283 (v₁ + v₃ of NO₃⁻); 1747, 1713 (v₁ + v₄ of NO₃⁻); 1557 (v_{ring}); 1479 (v₃ mode of NO₃⁻); 1467 (v_{ring}); 1333 (βCH); 1288 (v₃ mode of NO₃⁻); 1042 (pyrazole ring breathing); 1017 (v₁ mode of NO₃⁻); 835, 809 (v₂ mode of NO₃⁻); 733, 705 (v₄ mode of NO₃⁻). UV–Vis bands (ethanol), λ_{max} nm (ε, dm³ cm⁻¹ mol⁻¹): 1030 (sh); 685 (59.6); 340 (sh); 280 (sh); 215 (26150). $E_{1/2} = -193$ mV, $\Delta E =$ 162 mV; $E_{1/2} = -559$ mV; $E_{1/2} = -722$ mV, $\Delta E =$ 41 mV.

2.3. Physical measurements

Conductivities of solutions ($c = 1.0 \times 10^{-3} \text{ mol/dm}^3$ in acetone or ethanol) were measured in a temperature-controlled cell with stainless steel electrodes, cell constant $\varphi = 0.251 \text{ cm}^{-1}$.

Elemental analyses were carried out on a Carlo Erba analyzer.

IR spectra of solid samples as KBr pellets were recorded on Specord 71 IR (in the range of $4600-650 \text{ cm}^{-1}$) and Nicolet 5700 ($4000-400 \text{ cm}^{-1}$) spectrophotometers.

Electronic absorption spectra were registered on Perkin– Elmer 124 (in the range of 200–800 nm) and SF-26 (800– 1200 nm) spectrophotometers. NMR spectra were recorded on a Bruker AV300 instrument.

Cyclic voltammograms were obtained on a TA-4 voltammetric analyzer (Tomanalyt, Tomsk, Russia). The threeelectrode electrochemical cell consisted of a mercury-film working electrode and saturated Ag/AgCl reference and auxiliary electrodes. The concentration of the sample in the cell was 1.0×10^{-4} mol/dm³, and 0.1 mol/dm³ KCl was used as a supporting electrolyte. The potential was varied in the range 0 to -1.3 V at 50 mV s⁻¹ scan rate. Oxygen was removed from the solutions by bubbling nitrogen through immediately before any measurements. Formal potentials were calculated as $E_{1/2} = (E_{p.c.} + E_{p.a.})/2$.

3. Results and discussion

3.1. Synthesis of the ligands

Bis(pyrazol-1-yl)methanes L^1 and L^2 were first prepared by Trofimenko [14]. We have developed a new procedure for double alkylation of azoles via the reaction of 1*H*-pyrazole or 3,5-dimethyl-1*H*-pyrazole with dibromomethane in a superbasic medium (DMSO-KOH). Iodo-derivatives L^6 and L^7 were obtained by oxidative iodination of L^1 and L^2 by an I_2 -HIO₃-H₂SO₄ mixture in acetic acid.

3.2. Synthesis and characterization of bis(pyrazol-1-yl)methane complexes

The complexes were prepared by the reaction of the ligands with copper(II) nitrate or chloride in acetone solution. In the case of Cu(NO₃)₂, independent of the metal to ligand ratio used (1:1 or 1:2), complexes **1–4** of 1:1 composition were formed. The same feature was observed for the reaction of copper(II) chloride with the ligands L^6 and L^7 (complexes **9** and **10** were obtained). When CuCl₂ reacted with the ligands L^1 and L^2 , 1:1 complexes **5** and **7**, as well as 1:2 complexes **6** and **8** were isolated depending on the reagent ratio.

All of the coordination compounds obtained gave satisfactory elemental analysis and were characterized by molar conductivity, infra-red and electronic spectroscopy.

The complexes of copper(II) nitrate, 1, 2 and 4, are weak electrolytes in acetone, therefore both of the NO_3^- ions are bound to the central ion. The solubility of complex 3 was insufficient for conductivity measurements.

Bis(pyrazol-1-yl)alkanes are bidentate in most of their complexes, so the same coordination mode is to be expected for the investigated compounds with L^1 , L^2 , L^6 and L^7 . Bidentate coordination of bis(pyrazol-1-yl)methane derivatives in the prepared complexes can be assumed from the absence of the splitting of pyrazole ring vibrational bands in the IR spectra. This splitting should have occurred if only one of pyrazole rings in bis(pyrazol-1yl)methane ligand was coordinated to the copper(II) ion. The possibility of formation of polymeric complexes, in which metal ions are connected by bridging ligands, can be ruled out by sharp melting points of the compounds obtained. In the copper(II) nitrate complexes, the NO_3^- ions may be coordinated in a mono- or bidentate fashion. The coordination modes of nitrate ions can be established by means of IR spectroscopy [16–19].

Bands corresponding to all of the vibrational modes of the nitrate ion were detected in the IR spectra of complexes 1–4 (Table 1). Two intense bands in the 1455–1500 and 1265–1295 cm⁻¹ regions were assigned to stretching vibrations of N–O bonds in a NO₃⁻ ion (v_3) belonging to the C_{2v} symmetry group [17]. The bands of in-plane bending vibrations (v_4) appear at 690–735 and 725–780 cm⁻¹. Large splitting of these bands ($\Delta(v_3) > 160$ and $\Delta(v_4) > 25$ cm⁻¹) confirms the presence of bidentate nitrate ions in all of the four complexes. For monodentate coordination of NO₃⁻ the splitting of the v_3 band is not higher than 120 cm⁻¹ and that of v_4 is less than 20 cm⁻¹ [17]. Single bands around 820 cm⁻¹ (out-of-plane bending

Single bands around 820 cm^{-1} (out-of-plane bending vibrations v_2) as well as bands of medium intensity at about 1000 cm^{-1} (symmetric stretching vibrations v_1) were observed in IR spectra of complexes 1–4 [17]. The occurrence of the latter band gives further evidence for the nitrate ions coordination, since the vibrational transition v_1 in the

free NO_3^- is symmetry-forbidden, so this band does not appear in IR spectra or has a very minute intensity [16].

Furthermore, weak combination bands $(v_1 + v_4)$ and $(v_1 + v_3)$ with the splitting values $\Delta(v_1 + v_4)$ and $\Delta(v_1 + v_3)$ in accord with those expected for bidentate nitrate ion coordination [18] were detected in the spectra of the complexes **1** and **3**.

Therefore, in nitrate complexes 1–4 the bidentate organic ligands occupy two coordination places, also each of the nitrate ions occupies two places. Consequently, the copper(II) ions in these complexes are hexacoordinated. Locations of absorption bands in the region of d–d* transitions in the electronic spectra of the complexes (a shoulder in the 930–1030 nm area and a band around 685–720 nm) correspond very well to the literature values for octahedrally surrounded Cu^{2+} [20]. For example, the already mentioned [$Cu(L^2)_2(O_2NO)$](NO₃) exhibits an absorption at 694 nm with a shoulder at 1042 nm [2].

3.3. Preparation of mixed-ligand complexes

We have also studied the reactivity of the synthesized complexes towards various mono- and bidentate ligands,

Table I	Ta	ble	1
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Characteristic frequencies	of	nitrate	ion	vibrations
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Compound	Formula	<i>v</i> ₁	v_2	<i>v</i> ₃	$\Delta(v_3)$	v_4	$\Delta(v_4)$	$v_1 + v_4$	$\Delta(v_1 + v_4)$	$v_1 + v_3$	$\Delta(v_1 + v_3)$
1	$Cu(L^1)(NO_3)_2 \cdot H_2O$	1017	809	1464 1285	179	760 729	31	1788 1757	31	2354 2167	187
2	$Cu(L^2)(NO_3)_2$	1040	820	1500 1280	220	730 690	40				
3	$Cu(L^6)(NO_3)_2$	1003	827	1454 1293	161	782 735	47	1742 1703	39		
4	$Cu(L^7)(NO_3)_2 \cdot 2H_2O$	1000	835	1520 1265	255	725 700	25				
11	$Cu(L^1)(bipy)(NO_3)_2$	1016	831 812	1475 1279	196	731 705	26	1743 1712	31	2371 2278	93
12	Cu(L ²)(bipy)(NO ₃) ₂	1018	833 808	1477 1288	199	732 705	27	1744 1713	31	2392 2283	109
13	$Cu(L^6)(bipy)(NO_3)_2$	1014	831 812	1497 1293	204	734 706	28	1743 1716	27	2371 2282	89
14	Cu(L ²)(acac)(NO ₃)	1018	836 807	1478 1288	190	741 704	37	1744 1709	35	2392 2283	109
15	$Cu(L^2)(PPh_3)_2(NO_3)_2$	1022	836 810	1479 1281	198	743 705	38				
16	$Cu(L^2)(BImH)_2(NO_3)_2$	1012	835 808	1479 1290	189	748 705	43	1712		2388	
17	$Cu(L^2)(BtaH)_2(NO_3)_2$	1011	839 830	1470 1283	187	692		1763 1720	43		
18	$Cu(L^2)(Me_2PyrH)_2(NO_3)_2$	1017	835 809	1479 1288	191	733 705	28	1747 1713	34	2393 2283	110

namely 2,2'-bipyridyl (bipy), acetylacetone (Hacac), triphenylphosphine (PPh₃), benzimidazole (BImH), benzotriazole (BtaH) and 3,5-dimethylpyrazole (Me₂PyrH). These compounds represent four different types of ligands – phosphorus-containing, O,O-bidentate, N,N-bidentate and monodentate nitrogen-containing heterocycles, which are widely spread among important biologically active substances. Mixed-ligand complexes with such compounds may serve as models for metalloenzymes [21] and as building blocks for supramolecular systems [22].

We have found that the complexes of copper(II) nitrate 1–3 react with 2,2'-bipyridyl with the formation of mixedligand complexes 11–13, comprising of coordinated molecules of bis(pyrazol-1-yl)methane derivatives as well as those of 2,2'-bipyridyl. Moreover, complex 2 reacts with other above-mentioned compounds also forming mixedligand complexes 14–18. At the same time, copper(II) chloride complexes 5–10, as well as the nitrate complex 4 undergo a displacement of bis(pyrazol-1-yl)methanes from the coordination sphere yielding homoligand complexes. These complexes are identical by melting points and spectral characteristics to the compounds prepared under the same conditions using copper(II) chloride or nitrate instead of bis(pyrazol-1-yl)methane-copper(II) complexes.

Bands due to bis(pyrazol-1-yl)methane ligand vibrations as well as due to additional ligands were observed in the IR-spectra of the mixed-ligand complexes **11–18**. Strong bands in the area of 1550–1560 cm⁻¹ account for pyrazole ring stretching vibrations and bands at 1030–1050 cm⁻¹ correspond to ring breathing vibrations in bis(pyrazol-1yl)methane derivatives [23]. Absorption in the 1600 and 1610 cm⁻¹ regions of 2,2'-bipyridyl mixed-ligand complexes 11–13 spectra correspond to pyridine ring stretching vibrations [24,25]. Triphenylphosphine characteristic bands at 503 and 694 cm⁻¹ [26] were detected in the spectra of the PPh₃ derivative 15. Broad bands in the area of 3300– 3500 cm^{-1} corresponding to N–H stretching vibrations were detected in the spectra of the complexes 16–18, comprising of nitrogen-unsubstituted heterocycles. Strong broadening of these bands may be explained by intramolecular hydrogen-bonding with coordinated nitrate ions. The presence of these bands indicates that the heterocycles are coordinated in their neutral, not anionic forms.

Acetylacetonate and 2,2'-bipyridyl, as well as bis(pyrazol-1-yl)methane derivatives are certainly bidentate ligands. It can be assumed that the coordination sphere of the complexes **11–14** consists of two organic bidentate ligands and one nitrate ion is also coordinated in a bidentate fashion as follows from the IR data (see example in Fig. 2). The central copper(II) ion in these complexes is therefore hexacoordinated, and the second nitrate ion remains uncoordinated. This is consistent with the detection of two bands in the out-of-plane bending vibrations area ($800-830 \text{ cm}^{-1}$, Table 1). Presumably, one of them is related to bound NO₃⁻ ions and the other is due to the free nitrate ions. Apparently, the remaining bands of the free nitrate ions overlap with the bands of organic ligands and were not registered.

The same conclusions about hexacoordination of the copper(II) ion can be made for the complexes **15–18** containing two monodentate molecules of triphenylphosphine or nitrogen-containing heterocycle, one bidentate molecule of L^2 ligand and one bidentate nitrate-ion, while the second NO₃⁻ ion remains in the outer sphere (Fig. 3).



Fig. 2. Synthesis of bis(pyrazol-1-yl)methane-copper(II) mixed-ligand complexes with bidentate ligands.



Fig. 3. Synthesis of bis(pyrazol-1-yl)methane-copper(II) mixed-ligand complexes with monodentate ligands.

3.4. Cyclic voltammetry

We have also carried out a cyclic voltammetric study of the synthesized homo- and mixed-ligand coordination compounds. Complexes of copper(II) nitrate and chloride 1-10 as well as mixed-ligand complexes 11-18 undergo a quasi-reversible (or reversible in case of the complex 6) reduction on a mercury-film electrode in the range of potentials from -111 to -214 mV. Furthermore, cyclic voltammograms of several mixed-ligand complexes demonstrate additional peaks which are probably associated with the electrochemical activity of the organic ligands. Thus, the complex $[Cu(L^2)(PPh_3)_2(O_2NO)](NO_3)$ (15) undergoes a quasi-reversible reduction at a formal potential of -829 mV (relative to the saturated Ag/AgCl electrode) and the complex $[Cu(L^2)(BImH)_2(O_2NO)](NO_3)$ (16) is reduced at -509 mV. In the case of $[Cu(L^2)(Me_2PyrH)_2$ - (O_2NO) (NO₃) (18) an irreversible reduction wave at -559 mV and a reversible one at a formal potential of -722 mV were observed.

Many copper complexes can mimic metalloenzymes, superoxide dismutase (SOD) being one of them. Li et al. pointed out that in order to act as a SOD mimic, the copper complex should have a redox potential in the range -0.36...+0.69 V (vs. the saturated Ag/AgCl electrode) [27]. Furthermore, the higher the redox potential $E_{1/2}$ and the greater the reversibility of the electrode process (characterized by the $\Delta E = E_{p.a.} - E_{p.c.}$ value), the higher the antioxidant activity of a given complex. As is seen from our cyclic voltammetry data, all of the complexes meet the specified requirements, and the highest SOD-like activity should be expected for complexes **6**, **2**, **13**, **11** (in descending order of activity). A detailed study of the antioxidant properties of bis(pyrazol-1-yl)methane–copper(II) complexes will be reported elsewhere.

4. Conclusions

In summary, novel coordination compounds of copper(II) with bis(pyrazol-1-yl)methane derivatives are reported in this paper. The complexes synthesized reacted with a number of mono- and bidentate ligands yielding mixed-ligand complexes. No examples of bis(pyrazol-1-yl)methane

mixed-ligand complexes with these ligands have been reported previously.

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