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2-tert-Butyl-5-(2-pyridyl)-2H-tetrazole as a chelating

ligand in the direct synthesis of novel Cu(II) and

Anastasiya P. Mosalkova,^a Sergei V. Voitekhovich,*^a Alexander S. Lyakhov,^a Ludmila S. Ivashkevich,^a Jochen Lach,^b Berthold Kersting,^b Pavel N. Gaponik^a and

For the first time, a representative of the 2,5-disubstituted tetrazoles, namely, 2-*tert*-butyl-5-(2-pyridyl)-2*H*-tetrazole (**L**), has been found to participate in oxidative dissolution of copper powder in homometalic systems $Cu^0-L-NH_4X-DMSO$ (X = Cl, SCN, ClO₄) and heterobimetallic ones $Cu^0-Mn(OAc)_2-L-NH_4OAc-$ Solv (Solv = DMSO, DMF), providing the formation of molecular homometallic complexes [CuL₂Cl₂] (**1**), [CuL₂(SCN)₂] (**2**), and [CuL₂(H₂O)](ClO₄)₂ (**3**), heterobimetallic complex [Cu₂MnL₂(OAc)₆] (**4**) from DMF solution and its mixture with complex [Cu₂MnL₂(OAc)₆]·2DMSO (**5**) from DMSO solution. Free ligand **L** and complexes **1–4** were characterized by elemental analysis, IR spectroscopy, thermal and X-ray single crystal analyses, whereas complex **5** was characterized by X-ray analysis only. Compounds **1–3** are mononuclear complexes, with chelating coordination mode of L *via* the tetrazole ring N4 and pyridine ring N7 atoms. Heterobimetallic complexes **4** and **5** possess trinuclear structures, with a linear Cu–Mn–Cu arrangement of the metal atoms, linked by the acetate anions; each copper(II) atom is decorated by a

chelating unit of L via the tetrazole ring N1 and pyridine ring N7 atoms in complex 4, and via the N4, N7

atoms in complex 5. Temperature-dependent magnetic susceptibility measurements of complex 4

revealed a weak antiferromagnetic coupling between the paramagnetic copper(II) and manganese(II) ions ($U = -2.5 \text{ cm}^{-1}$, $g_{CII} = 2.25$ and $g_{Mn} = 2.01$), with magnetic exchange through the acetato bridges.

heterobimetallic Cu(II)/Mn(II) complexest

Oleg A. Ivashkevich^a

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Introduction

Tetrazoles, containing six-membered nitrogen heterocyclic substituents, are promising multifunctional ligands, with the N atoms of both rings being able to bind to metal atoms.^{1–5} This allows formation of diverse coordination frameworks, resulting in coordination compounds with different structural motifs and important applications in the areas of single molecule magnetism,^{5–8} sensors,⁹ storage,¹⁰ nonlinear optics,^{11,12} light-emitting^{13–15} and dielectric devices.¹⁶ Among such ligands, the anionic forms of 5-(2-pyridyl)-, 5-(pyrimidyl)- and 5-(pyrazinyl)-tetrazoles (Scheme 1, **A**) have been mainly investigated. They have been found to act as chelating agents as well as linkers, assembling chelating motifs in unusual polymeric structures.^{1–16}

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have been investigated to a lesser extent. Only a few complexes with 1- and 2-substituted 5-(2-pyridyl)tetrazoles (Scheme 1, **B** and **C**) have been structurally characterized until now,^{17–23} and some spectroscopic assumptions concerning the structures of such complexes have been made.^{24,25} More intensive investigations in this area are retarded by the absence of convenient methods for synthesis of such tetrazole ligands.

The most common pathway for obtaining high-nuclearity transition-metal complexes as well as polymeric complexes of various dimensionalities with NH-tetrazoles and *N*-substituted ones is based on the self-assembly of ligands together with the

^aResearch Institute for Physical Chemical Problems, Belarusian State University, Leningradskaya 14, 220030 Minsk, Belarus. E-mail: azole@tut.by;

Fax: +375 17 2264696; Tel: +375 17 2095198

^bInstitut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany. E-mail: b.kersting@uni-leipzig.de

transition-metal salts.¹ Among the factors to affect the synthetic process (the ligand, the counterion, the solvent, and the reaction conditions etc.), the modification of reaction conditions is presently the most attractive approach to producing novel topologies and intriguing frameworks. It has long been known that coordination compounds can be prepared easily through the so-called "direct synthesis of coordination compounds" - a one-pot oxidative dissolution of a metal powder or metal oxide with a complex-forming agent in non-aqueous solution in air.²⁶ It has been shown that metal oxidation and complexation were conditioned by proton- and/or anion-donating reagents and air oxygen. Thus, this approach is very promising since the formation of new compounds with unexpected stoichiometry, diverse dimensionality and properties starts from easily available materials under usual conditions with good repeatability and high yield.²⁷⁻²⁹ Moreover, this straightforward approach has been extended to the preparation of heterobi- and trimetallic systems that are of current interest owing to their unique electronic, electrochemical, magnetic, catalytic and biological properties.^{30–33}

Recently, to explore the possibilities of a "direct synthesis" approach for the preparation of tetrazole-containing complexes of transition metals, we have tested a number of 5-substituted tetrazoles as both proton- and anion-donating agents, and 1-substituted tetrazoles in the presence of proton-donating substances in the oxidative dissolution of metal powder. A series of novel 5-R-tetrazolato-bridged Zn(π), Cu(π) and the first Cu(π)/Zn(π) heterobimetallic complexes, as well as complexes of Co(π) and Cu(π) based on 1-substituted tetrazoles, have been isolated and structurally characterized.^{34–37}

Considering this approach in combination with our earlier synthetic and structural investigations of metal complexes with 5-substituted tetrazoles^{34,35,38–40} and their *N*-derivatives,^{36,37,41–43} we were interested to clear up the behavior of potentially chelating 2-*tert*-butyl-5-(2-pyridyl)-2*H*-tetrazole (L) in oxidative dissolution of copper powder in homometalic systems Cu⁰–L–NH₄X–DMSO (X = Cl, SCN, ClO₄) and heterobimetallic ones Cu⁰–Mn(OAc)₂–L–NH₄OAc–Solv (Solv = DMSO or DMF), where ammonium salts were used as both protonand anion-donating agents. Herein, we report a facile route for the synthesis of L, its molecular and crystal structure, and present the crystal structures, spectroscopic, thermal and magnetic properties of new homometallic complexes [CuL₂Cl₂] (1), [CuL₂(SCN)₂] (2), [CuL₂(H₂O)](ClO₄)₂ (3), and heterobimetallic ones [Cu₂MnL₂(OAc)₆] (4) and [Cu₂MnL₂(OAc)₆]·2DMSO (5).

Experimental

General methods, equipment and chemicals used

5-(2-Pyridyl)-1*H*-tetrazole, used for the synthesis of 2-*tert*-butyl-5-(2-pyridyl)-2*H*-tetrazole, was prepared by the reaction of sodium azide with 2-cyanopyridine according to a common procedure.⁴⁴ Copper powder (particle size 13.2 \pm 1.1 μ m), other chemicals and solvents were of analytical grade and used as purchased without further purification. All synthetic procedures were carried out in vessels open to air. Elemental analyses (C, H, N, S) were performed on a VARIO EL-elemental analyzer. ¹H and ¹³C NMR spectra were recorded in (CD₃)₂SO on a Bruker Avance 500 spectrometer. The observed chemical shifts were referenced to solvent signals ($\delta_{\rm H}$ 2.50, $\delta_{\rm c}$ 39.43). Infrared spectra were recorded with a Nicolet Thermo Avatar 330 FT-IR system over the 400–4000 cm^{-1} range (SiC cavities), and with a Bruker Optik GmbH Vertex 70 over the 50-400 cm⁻¹ range (between two polyethylene plates). The TG and DSC curves were obtained with a NETZSCH STA429 thermoanalyzer in a dynamic nitrogen atmosphere (heating rate: 10 K min⁻¹, aluminum oxide, mass 5–6 mg and temperature range from room temperature up to 600 °C). Temperaturedependent magnetic susceptibility for a powder sample of 4 was measured between 2 and 330 K using a MPMS 7XL SQUID magnetometer (Quantum Design) in an applied external magnetic field of 500 G. The experimental susceptibility was corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

Quantum chemical calculations have been carried out within density functional theory with Becke's three parameter hybrid method employing the Lee–Yang–Parr correlation functional $(B3LYP)^{45}$ and 6-31+G(d,p) basis set. The solvent effect has been incorporated by using the polarizable continuum model.⁴⁶ The geometry of both *syn*-L and *anti*-L rotamers was fully optimized in the presence of solvent. For all structures the force constants have been calculated to verify whether the optimized structures were minima on the potential energy surface. All the calculations have been performed using the Gaussian 03 program.⁴⁷

Single crystal X-ray diffraction study

X-ray data were collected on a SMART APEX II diffractometer using graphite monochromated Mo-K α radiation (λ = 0.71073 Å). The reflection data were corrected on absorption. The structures were solved by direct methods with the program SIR2004⁴⁸ and refined on F^2 by full-matrix least squares technique with SHELXL-97.49 All non-hydrogen atoms were refined in anisotropic approximation. For complexes 1-5, the hydrogen atoms at carbon atoms were placed in calculated positions and refined using a "riding" model, with $U_{iso}(H) =$ $1.5U_{eq}(C)$ for the methyl groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for others. For compound L and water molecules in complex 3, the hydrogen atoms were localized from Fourier maps and refined isotropically. Molecular graphics was performed with the programs ORTEP-3 for Windows⁵⁰ and PLATON.⁵¹ X-ray powder diffraction data of polycrystalline compounds were used to control their purity. The patterns were recorded with a HZG 4A diffractometer (Carl Zeiss, Jena) using Cu-Kα radiation (Ni-filter) at 298 K.

Synthesis of 2-tert-butyl-5-(2-pyridyl)-2H-tetrazole (L)

tert-Butanol (1.3 mL, 14 mmol) was added dropwise with stirring to a suspension of 5-(2-pyridyl)-2*H*-tetrazole (2.06 g, 14 mmol) in aqueous 65% perchloric acid (5 mL). The solution obtained was kept at room temperature for 2 h and then

neutralized with 1 M NaOH to pH 7–8. The precipitate was filtered off, washed with cold water, and dried on air. Recrystallization from water solution gave colorless crystals L, suitable for X-ray analysis.

Yield: 2.37 g (83%). Melting point: 140–142 °C. Elemental analysis (%): found (calculated for $C_{10}H_{13}N_5$): C 59.00 (59.10); H 6.27 (6.245); N 34.35 (34.46). ¹H NMR (500 MHz, DMSO-d⁶) δ : 8.77 (1H, d, J = 7.6 Hz), 8.21 (1H, d, J = 7.6 Hz), 8.10 (1H, t, J = 7.6 Hz), 7.63 (1H, t, J = 7.6 Hz), 1.75 (9H, s, *t*-Bu) ppm; ¹³C NMR (100 MHz, DMSO-d⁶) δ : 162.9 (CN₄), 149.2, 145.5, 138.7, 125.5, 122.7, 64.4, 28.8 ppm. FT-IR (KBr): ν (cm⁻¹): 3091 (s), 3055 (s), 2987 (s), 2941 (m), 2913 (vw), 2879 (w), 1613 (s), 1592 (s), 1531 (m), 1473 (s), 1423 (s), 1371 (s), 1304 (s), 1251 (s), 1204 (s), 1164 (w), 1081 (vs, br), 1051 (w), 1011 (w), 983 (w), 938 (w), 917 (w), 802 (s), 755 (s), 724 (s), 644 (m), 621 (s), 588 (m), 520 (sh), 462 (w), 433 (m), 403 (s), 280 (s), 175 (m), 98 (s), 75 (s).

Synthesis of $[CuL_2Cl_2]$ (complex 1)

A mixture of copper powder (32 mg, 0.5 mmol), 2-*tert*-butyl-5-(2-pyridyl)-2*H*-tetrazole (203 mg, 1 mmol), ammonium chloride (54 mg, 1 mmol) and DMSO (5 mL) was heated at 70–80 °C with stirring for 70 min until total dissolution of copper. After cooling the solution to room temperature, greenish-blue fine polycrystalline complex **1** was precipitated. Filtered mother solution was allowed to stand for two days to give green crystals of **1** suitable for X-ray analysis.

Yield: 115 mg (43%). Elemental analysis (%): found (calculated for $C_{20}H_{26}Cl_2CuN_{10}$): C 44.20 (44.41); H 4.67 (4.84); N 25.75 (25.89). FT-IR (KBr): ν (cm⁻¹): 3072 (w), 3043 (w, sh), 2987 (s), 2942 (m), 2881 (w), 1608 (vs), 1574 (s), 1535 (m), 1445 (sh), 1402 (m), 1372 (vs), 1301 (vs), 1269 (m), 1239 (m), 1193 (sh), 1160 (m), 1107 (s), 1037 (vs, br), 981 (m), 943 (sh), 904 (m), 823 (s), 802 (vs), 758 (vs), 725 (vs), 650 (vs), 598 (vs), 518 (s), 438 (m), 410 (s), 353 (w), 275 (vs), 232 (m), 162 (m), 134 (vs), 76 (w).

Synthesis of [CuL₂(SCN)₂] (complex 2)

Complex 2 was prepared by analogy with complex 1, but using NH_4SCN (76 mg, 1 mmol) in place of NH_4Cl . Dissolution of copper powder was observed for 1 h. Green crystals of complex 2 suitable for X-ray analysis were obtained directly from the reaction mixture the next day.

Yield: 170 mg (58%). Elemental analysis (%): found (calculated for $C_{22}H_{26}CuN_{12}S_2$): C 44.90 (45.08); H 4.36 (4.47); N 28.54 (28.67); S 10.88 (10.94). FT-IR (KBr): ν (cm⁻¹): 3084 (m), 3053 (m), 2987 (s), 2937 (m, sh), 2877 (w), 2086 (vs), 1605 (vs), 1574 (s), 1533 (m), 1441 (vs), 1371 (vs), 1302 (m), 1266 (m), 1187 (sh), 1157 (m), 1100 (m), 1058 (s), 1045 (w), 1023 (w), 981 (w), 951 (m), 903 (w), 821 (s), 800 (s), 7569 (s), 724 (s), 6469s), 593 (s), 515 (m), 468 (m), 431 (m), 410 (m), 305 (s), 262 (s), 235 (s), 169 (s), 78 (m).

Synthesis of [CuL₂(H₂O)](ClO₄)₂ (complex 3)

Complex 3 was prepared by analogy with complex 1, but using NH_4ClO_4 (120 mg, 1 mmol) in place of NH_4Cl . Dissolution of

Yield: 200 mg (58%). Elemental analysis (%): found (calculated for $C_{20}H_{28}Cl_2CuN_{10}O_9$): C 34.76 (34.97); H 4.05 (4.11); N 20.30 (20.39). FT-IR (KBr): ν (cm⁻¹): 3391 (br), 3119 (sh), 3055 (m), 3021 (w), 2989 (m), 2952 (w), 2886 (w), 1623 (m). 1567 (m), 1462 (s), 1380 (m), 1305 (m), 1285 (m), 1237 (m), 1207 (m), 1180 (m), 1107 (vs), 1041 (vs), 980 (w), 924 (m), 818 (m), 796 (s), 758 (s), 724 (s), 645 (m), 621 (vs), 594 (m), 513 (m), 460 (vw), 422 (s), 353 (s), 275 (vs), 232 (m), 162 (m), 134 (s), 76 (w).

Synthesis of [Cu₂MnL₂(OAc)₆] (complex 4)

A mixture of copper powder (56 mg, 0.9 mmol), $Mn(OAc)_2$ · 4H₂O (220 mg, 0.9 mmol), 2-*tert*-butyl-5-(2-pyridyl)-2*H*-tetrazole (370 mg, 1.8 mmol), ammonium acetate (270 mg, 3.6 mmol) and DMF (5 mL) was heated at 70–80 °C under stirring for 30 min until total dissolution of copper powder. Blue crystals of complex 4 suitable for X-ray diffraction were obtained directly from the reaction mixture the next day.

Yield: 265 mg (62.5%, based on Cu⁰). Elemental analysis (%): found (calculated for $C_{32}H_{44}Cu_2MnN_{10}O_{12}$): C 40.54 (40.77); H 4.43 (4.70); N 15.08 (14.86). FT-IR (KBr): ν (cm⁻¹): 3107 (m), 3077 (w), 3050 (vw), 2985 (s), 2938 (m), 2880 (vw), 1595 (vs, sh), 1476 (w), 1410 (vs, sh), 1340 (w), 1304 (m), 1274 (w), 1252 (w), 1201 (m), 1174 (m), 1103 (m), 1041 (s), 1015 (w), 979 (vw), 934 (m), 903 (w), 822 (m), 798 (s), 755 (s), 727 (s), 668 (vs), 616 (m), 592 (w), 523 (m), 489 (w), 457 (w), 430 (m), 409 (w), 332 (s), 271 (m), 178 (s), 70 (m).

Synthesis of [Cu₂MnL₂(OAc)₆]·2DMSO (complex 5)

Blue crystals of complex 5 suitable for X-ray analysis were separated off from the mixture of complexes 4 and 5 obtained according to the procedure described above for complex 4 using DMSO instead of DMF.

Results

Synthesis of ligand and complexes

2-*tert*-Butyl-5-(2-pyridyl)-2*H*-tetrazole was obtained in 83% yield by alkylation of 5-(2-pyridyl)-1*H*-tetrazole with *tert*-butyl alcohol in 65% aqueous perchloric acid. *t*-BuOH–HClO₄ was chosen for alkylation in connection with our recent success in adjusting the regioselectivity of *N*-functionalization of azoles using this system. In particular, it is an efficient tool for introducing a lipophilic *tert*-butyl group into the N2 position of the tetrazole cycle.^{52,53} The regioselectivity of alkylation of 5-R-tetrazoles is explained by protonation of latter on the N4 atom, resulting in formation of 5-R-1*H*-tetrazol-4-ium cations, in which only equivalent N2 and N3 atoms are accessible for attack by carbenium cations generated from the alkylation agents, like olefins and alcohols.⁵⁴ The same mechanism can be proposed for *tert*-butylation of 5-(2-pyridyl)-1*H*-tetrazole. In this case, however, primary protonation on the pyridine

N atom⁵⁵ should be taken into account as well. Therefore, the 2-(1H-tetrazol-4-ium-5-yl)pyridinium dication can act as an alkylation substrate in highly acidic mediums (Scheme 2).

The obtained compound was attributed to 2,5-disubstituted tetrazoles based on ¹³C NMR chemical shifts of the tetrazole ring C5 atom, in accordance with the data on the related tetrazoles.^{17,24,25} X-ray analysis of single crystals, grown from water solution of the compound, confirmed the formation of L and showed that the molecules were in the anti conformation in the solid (Scheme 2). However, due to possible rotation of both heterocycles around the exocyclic C-C bond, the syn conformation of L is also possible. Conformational changes can be caused by specific interactions of the molecules with solvents of different polarity and protic abilities under recrystallization or complexation conditions. Quantum chemical calculations of the total energy of both rotamers in DMSO and DMF show almost equal total energies of conformers in both solvents. The total energy of *syn*-L is about 1 kJ mol^{-1} lower than that of anti-L. As a result, not only anti, but also syn conformation of the ligand molecule were realized in complexes synthesized in this work (see below).



Scheme 2 *tert*-Butylation of 5-(2-pyridyl)-1*H*-tetrazole and formation of rotameric forms of 2-*tert*-butyl-5-(2-pyridyl)-2*H*-tetrazole.

Direct synthesis of complexes 1–5 have been carried out in systems Cu^0 –L–NH₄X–DMSO (X = Cl, SCN, ClO₄) and Cu^0 – Mn(OAc)₂–L–NH₄OAc–Solv (Solv = DMSO or DMF), where ammonium salts were used as both proton- and anion-donating agents. The interaction of copper powder with L and ammonium salts in DMSO, using a molar ratio of $Cu : L : NH_4X =$ 1 : 2 : 2, gave compounds [CuL₂X₂] (complex 1, X = Cl; complex 2, X = SCN) and [CuL₂(H₂O)](ClO₄)₂ (complex 3, X = ClO₄). It should be noted that complexes 2 and 3 can be also prepared from DMF solutions.

Heterobimetallic compound $[Cu_2MnL_2(OAc)_6]$ (complex 4) has been synthesized by the reaction of L, copper powder, manganese(II) acetate and ammonium acetate in DMF, with a molar ratio of the components $Cu:Mn(OAc)_2:L:NH_4OAc =$ 1:1:2:4 in open air. The use of DMSO instead of DMF results in a mixture (~1:1) of complex 4 and its solvated analogue $[Cu_2MnL_2(OAc)_6]:2DMSO$ (complex 5). It should be noted that ligand L in complexes 4 and 5 exists in different rotameric forms, namely *syn* and *anti*, respectively (see Scheme 2).

The complexes **1–4** have been isolated directly from the reaction mixtures as crystalline products. Their moderate yields of 40–60% are due to their high solubility in the solvents used (DMSO or DMF). At the same time, these complexes are soluble in water, ethyl alcohol, and acetonitrile. They have been characterized by elemental analysis, IR spectroscopy, thermal and X-ray analyses. Complex **5**, obtained in a mixture with complex **4**, has been characterized by X-ray analysis only.

Crystal structures of L and complexes 1-5

Crystal data, data collection, and refinement details for the structures reported are summarized in Table 1.

Table 1	Main crystal	data and	structure	refinement	details for	L and	complexes	1–5
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	L	Complex 1	Complex 2	Complex 3	Complex 4	Complex 5
Formula	$C_{10}H_{13}N_5$	C ₂₀ H ₂₆ Cl ₂ CuN ₁₀	C22H26CuN12S2	C20H28Cl2CuN10O9	C32H44Cu2MnN10O12	C36H56Cu2MnN10O14S2
Formula weight	203.25	540.95	586.21	686.96	942.79	1099.05
<i>T</i> /K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_{1}/c$	Рс	$P2_{1}/c$	C2/c	$P\bar{1}$	PĪ
Crystal size/mm	$0.40 \times 0.20 \times 0.20$	$0.25 \times 0.25 \times 0.12$	$0.30 \times 0.20 \times 0.20$	0.20 imes 0.20 imes 0.02	0.19 imes 0.15 imes 0.05	0.25 imes 0.25 imes 0.52
a/Å	9.8402(6)	10.2378(8)	10.2627(4)	26.510(2)	8.5655(4)	8.34040(10)
b/Å	10.5972(6)	8.6284(7)	9.3012(4)	6.9403(6)	9.9404(5)	8.63110(10)
c/Å	11.2157(7)	14.6102(12)	15.2346(8)	15.2164(13)	12.7777(7)	17.2045(2)
$\alpha/^{\circ}$	90	90	90	90	81.761(2)	93.7780(10)
β/°	116.8140(10)	110.1260(10)	109.8770(10)	95.384(2)	75.090(2)	93.0760(10)
γ/°	90	90	90	90	70.822(2)	98.7330(10)
$V/\text{\AA}^3$	1043.80(11)	1211.80(17)	1367.59(11)	2787.2(4)	990.91(9)	1218.93(2)
Ζ	4	2	2	4	1	1
$D_{\rm c}/{\rm g~cm^{-3}}$	1.293	1.483	1.424	1.637	1.580	1.497
μ/mm^{-1}	0.085	1.152	0.987	1.044	1.449	1.275
Reflections	2392	5393	2687	3191	4525	5592
Restraints	0	2	36	0	0	21
Parameters	188	305	203	198	265	311
$R_1/WR_2 \left[I > 2\sigma(I)\right]$	0.0359/0.0905	0.0314/0.0848	0.0230/0.0655	0.0345/0.0764	0.0233/0.0571	0.0217/0.0603
R_1/WR_2 [all data]	0.0428/0.0959	0.0328/0.0860	0.0246/0.0667	0.0583/0.0851	0.0290/0.0605	0.0232/0.0613
Goodness-of-fit	1.012	1.035	1.010	1.014	0.999	1.020

 ^{a}V = volume of the unit cell; Z = number of formula units in unit cell; D_{c} = calculated density; μ = linear absorption coefficient; R_{1} and wR_{2} are discrepancy factors.

2-tert-Butyl-5-(2-pyridyl)-2H-tetrazole (L). The compound crystallizes in the monoclinic space group $P2_1/c$, with four molecules in the unit cell. The asymmetric unit of L comprises one molecule, showing anti conformation (Scheme 2, Fig. 1). In the molecule, the tetrazole and pyridine rings are inclined at 21.30(5)°. Bond lengths and valence angles in the molecule are in the expected ranges [Cambridge structural Database (CSD), version 5.33, November 2011]. In the tetrazole ring, formally single bond N4-C5 of 1.3537(13) Å is the longest bond, while the remaining ones lie in a narrow range of 1.3263(13)-1.3326(13) Å. In the pyridine ring, C-C bonds are in a narrow range of 1.3868(15)-1.3914(14) Å, and the two N-C bonds are close in length [1.3419(14) and 1.3456(13) Å]. The bridge bond C5-C6 is 1.4758(14) Å. Intermolecular non-classic hydrogen bonds C11-H11···N7^{*a*} [symmetry code: (*a*) x, -y-1/2, z + 1/2; hydrogen bond geometry: $C11 \cdots N7^a = 3.3890(14)$ Å, C11-H11…N7^{*a*} = 138.0(10)°] between the pyridine H and N atoms of neighbouring molecules form polymeric chains running along the c axis (Fig. 2). Only van der Waals interactions are between the chains.

[CuL₂Cl₂] (complex 1). The compound 1 crystallizes in the monoclinic space group *Pc* and presents a molecular complex.



Fig. 1 The molecular structure of **L**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary radii.



Fig. 2 Crystal packing of **L** viewed along the *b* axis. Dashed lines indicate hydrogen bonds.



Fig. 3 Complex molecule of **1**, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary radii.

The asymmetric unit is composed of one complex molecule (one Cu and two Cl atoms, and two ligands L). In complex 1, ligand molecules L show *anti* conformation (Fig. 3).

The copper environment contains a planar arrangement of two chelating ligands L, coordinated *via* the tetrazole ring N41 (N42) and pyridine ring N71 (N72) nitrogen atoms. Two chlorine atoms complete the coordination environment to a distorted octahedron, with distances Cu1–N41 = 2.422(2), Cu1–N42 = 2.493(2), Cu1–N71 = 1.993(2), Cu1–N72 = 2.005(2), Cu1–Cl1 = 2.3253(7), and Cu1–Cl2 = 2.3234(7) Å. As seen, the tetrazole ring nitrogen atoms are more distant from the copper atom compared with the pyridine nitrogen atoms. Most of coordination angles around the copper atom are very close to 90° or 180°, except for the angles N42–Cu1–N72 = 76.52(8)°, N42–Cu1–N71 = 103.46(8)°, N41–Cu1–N71 = 77.72(8)° and N41–Cu1–N72 = 102.30(8)°.

In both molecules of L, the structural units composed of the pyridine and tetrazole rings are considerably flattened as compared with that in free ligand L. So, the least squares planes of the tetrazole ring N11/C51 and the pyridine ring C61/C111 are inclined at 4.97(15)°; for the rings N12/C52 and C62/C112, the angle between the planes is of 3.56(15)°. In the tetrazole and pyridine rings, the bonds lengths and valence angles are usual.

Intermolecular non-classic hydrogen bonds C92–H92…Cl1^{*b*} [symmetry code: (*b*) *x*, –*y*, *z* – 1/2; hydrogen bond geometry: C92…Cl1^{*b*} = 3.682(3) Å, C92–H92…Cl1^{*b*} = 164°] between the pyridine ring hydrogen atom and the chlorine atom of neighbouring complex molecules form polymeric chains running along the *c* axis (Fig. 4).

 $[CuL_2(SCN)_2]$ (complex 2). Compound 2, crystallizing in the monoclinic space group $P2_1/c$, presents a molecular complex (Fig. 5). The complex molecule has C_i symmetry imposed by position of the copper atom lying on inversion centre. The ligand molecule L shows *anti* conformation.



Fig. 4 Crystal packing of **1**, viewed along the *b* axis. Dashed lines show hydrogen bonds. The *tert*-butyl groups are omitted for clarity.



Fig. 5 Complex molecule of **2**, with the atom-numbering scheme for the asymmetric unit and displacement ellipsoids at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary radii. For the disordered *tert*-butyl group, only the atoms being in sites of higher occupancy are shown.

An elongated octahedral environment around the copper atom is formed by four nitrogen atoms of two ligands L, coordinated in a bidentate chelating mode, and two nitrogen atoms of two monodentate thiocyanate ligands. The Cu–N bonds of the tetrazole nitrogen atoms, lying in the axial positions [Cu1–N4(N4^c) = 2.3944 (12) Å], are considerably longer compared to those for the pyridine [Cu1–N7(N7^c) = 2.0540 (12) Å] and the thiocyanate [Cu1–N7S(N7S^c) = 1.9628 (13) Å] nitrogen atoms, occupying the equatorial sites [symmetry code: (*c*) –*x*, –*y*, –*z* + 1]. The coordination angles N4–Cu1–N7 and N4^{*c*}– Cu1–N7^{*c*} are of 76.60(4)° (as a consequence, the angles N4^{*c*}– Cu1–N7 and N4–Cu1–N7^{*c*} are of 103.40(4)°). All remaining coordination angles are very close to 90° or 180°.

In complex 2, the *tert*-butyl group of ligand L is disordered over two positions, with occupancies 0.622(9) and 0.378(9). The tetrazole and pyridine rings are practically co-planar in the molecule, with the dihedral angle of $0.12(8)^\circ$ between their least squares planes. There are no hydrogen bonds in the crystal structure of 2, and its crystal packing is defined by van-der-Waals interactions only.



Fig. 6 The cation $[CuL_2(H_2O)]^{2+}$ and perchlorate anion in the crystal structure of **3**. The atom-numbering scheme is given for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary radii.

 $[CuL_2(H_2O)](ClO_4)_2$ (complex 3). Compound 3 (monoclinic, the space group C2/c) is composed of complex cations $[CuL_2(H_2O)]^{2+}$ and perchlorate anions (Fig. 6). The ligand L is in the *anti* conformation.

The copper and water oxygen atoms lie on a two-fold axis, imposing C_2 symmetry on the cation. The copper atom coordinates four nitrogen atoms of two chelating ligands L and one water oxygen atom, forming a square pyramid. The basal bond lengths are Cu1–N4(N4^{*d*}) = 1.9928(19) Å for the tetrazole ring nitrogen atoms and Cu1–N7(N7^{*d*}) = 2.0377(18) Å for the pyridine ring nitrogen atoms [symmetry code: (*d*) 1 – *x*, *y*, 1/2 – *z*]. Water oxygen atom lies in the apical site, with bond lengths Cu1–O1W = 2.190(3) Å. The coordination angles O1W–Cu1–N4 (N4^{*d*}) and O1W–Cu1–N7(N7^{*d*}) take on the values 93.27(5)° and 94.61(5)°, respectively. The angle N4–Cu1–N7 (N4^{*d*}–Cu1–N7^{*d*}) of 80.78(7)° is considerably less than 90°, whereas the angle N4–Cu1–N7^{*d*} (N4^{*d*}–Cu1–N7) of 98.70(7)° is greater than 90°.

In ligand molecule L, the tetrazole and pyridine rings are close to co-planarity, with the dihedral angle of $1.80(1)^{\circ}$ between their least squares planes.

In the crystal structure of complex 3, intermolecular hydrogen bonds of perchlorate oxygen atoms with the pyridine ring H atoms, C10–H10····O4^{*e*} and C11–H11····O2^{*f*} [symmetry codes: (*e*) 1 – *x*, 1 – *y*, –*z*; (*f*) *x*, 1 – *y*, *z* – 1/2; hydrogen bonds geometry: C10–···O4^{*e*} = 3.304(3) Å, C10–H10····O4^{*e*} = 138°, C11····O2^{*f*} = 3.386(3) Å, C11–H11····O2^{*f*} = 159°], connect the anions and cations into polymeric chains running along the *c* axis. The chains are located around the planes *x* = 0 and *x* = 1/2.

Hydrogen bonds of water molecules with perchlorate anions, O1W–H1W···O2^{*g*} [symmetry code: (*g*) *x*, *y* – 1, *z*; hydrogen bond geometry: O1W···O2^{*g*} = 2.769(2) Å, O1W–H1W···O2^{*g*} = 173(3)°], combine the above chains in double-chains. An arrangement of the chains located around the plane x = 1/2 is



Fig. 7 An arrangement of hydrogen-bonded polymeric double-chains, located around the plane x = 1/2, in the crystal structure of complex **3**. The *tert*-butyl groups are omitted for clarity.

shown in Fig. 7. Intramolecular hydrogen bonds C8–H8···N3^{*h*} [symmetry code: (*h*) 1 – *x*, *y*, 1/2 – *z*; hydrogen bond geometry: C8···N3^{*h*} = 3.187(3) Å, C8–H8···N3^{*h*} = 143°] between the pyridine H atom and the tetrazole ring N atom, belonging to different ligands L of the same complex molecule, are additional in the chains.

 $[Cu_2MnL_2(OAc)_6]$ (complex 4). Heterobimetallic compound 4 crystallizes in the triclinic space group $P\overline{1}$ and presents a linear trinuclear complex, with the *syn*-rotamer of ligand L (Fig. 8). The complex molecule is centrosymmetric. All atoms of the asymmetric unit occupy general sites except for the manganese atom lying on the inversion centre. In the complex molecule, the copper and manganese atoms are separated by *ca*. 3.42 Å, being linked together *via* three acetato bridges.

The manganese atom adopts slightly elongated octahedral coordination of six oxygen atoms of six acetato anions, with equatorial bond lengths Mn1–O2(O2^{*i*}) = 2.1434(11) and Mn1–O3(O3^{*i*}) = 2.1559(11) Å, and with axial ones Mn1–O6(O6^{*i*}) = 2.2028(11) Å [symmetry code: (*i*) 1 – *x*, 2 – *y*, 1 – *z*]. In the octahedron, the angles between neighbouring Mn–O bonds lie in the range of 84.94(4)–95.06(4)°.

The Cu1 atom is surrounded by one chelating ligand L and three acetato anions. It would be considered as five-coordinated, with a square pyramidal environment, when taking into account the tetrazole ring N1 atom [Cu1–N1 = 2.4267(13) Å] lying in the apical position of the pyramid, and the pyridine N7, acetato O1, O4, and O5 atoms being in basal sites, with distances Cu1–N7 = 2.0458(13), Cu1–O1 = 1.9299(11), Cu1–O4 = 1.9521(11) and Cu1–O5 = 1.9652(11) Å. However, there are two long bonds with two acetato anions, Cu1–O3 = 2.8319(12) Å and



Fig. 8 Complex molecule of **4**, with the atom-numbering scheme for the asymmetric unit and displacement ellipsoids at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary radii. Dashed lines show semi-coordinated Cu–O bonds.

Cu1-O6 = 2.7920(13) Å, which can be considered as semicoordinated. They complete the copper environment to an octahedron with a bifurcated vertex (O3, O6). In the copper polyhedron, N1-Cu1-N7 = 76.76(5)°, O1-Cu1-N7 = 171.97(5)°, O4-Cu1-O5 = 172.13(5)°, and all remaining angles (except for those including the atoms O3 and O6) lie in the range 89.87(5)-94.95(4)°.

Both heterorings of ligand L show the usual bond lengths and valence angles. The tetrazole and pyridine rings are inclined at $10.86(11)^{\circ}$.

In complex 4, non-classic hydrogen bonds C10–H10···O5^{*j*} between the pyridine ring H and acetato O atoms of neighbouring complex molecules form polymeric chains extending along the *a* axis; hydrogen bonds C14–H14B···O4^{*k*} between the acetato anions, belonging to different complex molecules, link the chains into polymeric layers parallel with the *ab* plane (Fig. 9) [symmetry codes: (*j*) x + 1, *y*, *z*; (*k*) 2 - x, 1 - y, 1 - z; hydrogen bonds geometry: C10···O5^{*j*} = 3.412(2) Å, C10–H10···O5^{*j*} = 150°; C14···O4^{*k*} = 3.384(2) Å, C14–H14B···O4^{*k*} = 179°]. In the layer, each complex molecule is hydrogen-bonded to four others. Intramolecular hydrogen bonds C8–H8···O3 = 118°] between the pyridine H and acetato O atoms of a complex molecule are additional within the layer.

 $[Cu_2MnL_2(OAc)_6]$ -2DMSO (complex 5). Compound 5 crystallizes in the triclinic space group $P\bar{1}$ and presents a heterobimetallic trinuclear complex, co-crystallized with solvate DMSO molecules (Fig. 10). The ligand L exists as the *anti* rotamer, in contrast to complex 4. The manganese atom lies on the inversion centre, providing C_i symmetry of the complex molecule. All remaining atoms of the asymmetric unit occupy general positions. As in complex 4, the copper and manganese atoms are linked together *via* three acetato bridges and separated by *ca.* 3.44 Å. Coordination features of the manganese



Fig. 9 Crystal packing of complex **4**, viewed along the *c* axis. Dashed lines indicate hydrogen bonds. Hydrogen atoms not participating in hydrogen bonds and the *tert*-butyl groups are omitted for clarity.



Fig. 10 Complex molecule of **5** and solvate DMSO molecule. The atom-numbering scheme is given for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level, and the hydrogen atoms are shown as spheres of arbitrary radii. Dashed lines show semi-coordinated Cu–O bonds. For disordered DMSO molecule, only the atoms being in sites of higher occupancy are shown.

and copper atoms are close to those in complex **4**. A distorted octahedral coordination of the manganese atom shows the bond lengths Mn1–O2(O2^{*l*}) = 2.1252(9), Mn1–O3(O3^{*l*}) = 2.1731(9), and Mn1–O6(O6^{*l*}) = 2.1920(9) Å [symmetry code: (*l*) 2 – *x*, 2 – *y*, 1 – *z*]. The angles between neighbouring Mn–O bonds in the octahedron lie in the range of 85.30(4)–94.70(4)°. As in the case of complex **4**, the copper atom is seven-coordinated, with usual bonds Cu1–O4 = 1.9639(10), Cu1–O5 = 1.9526(10), Cu1–O1 = 1.9480(10), Cu1–N7 = 2.0652(11) Å, somewhat elongated

bond Cu1–N4 = 2.3486(11) Å, and two semi-coordinated long bonds Cu1–O3 = 2.7756(9) and Cu1–O6 = 2.7790(10) Å. These bonds form a distorted octahedron around the copper atom with a bifurcated vertex (O3, O6). In the copper polyhedron, N4– Cu1–N7 = 77.04(4)°, O1–Cu1–N4 = 101.74(4)°, O4–Cu1–O5 = 175.58(4)°, O1–Cu1–N7 = 177.31(4)°, and all remaining coordination angles lie in the range of 88.16(4)–93.79(4)° (the angles including the atoms O3 and O6 are excluded from the list).

In ligand L of complex 5, the tetrazole and pyridine rings are inclined at $6.03(7)^{\circ}$. The bonds lengths and valence angles in both heterocycles are usual. In solvate DMSO molecule, the sulphur and methyl H atoms are disordered over two positions, with occupancies 0.9789(14) and 0.0211(14).

In the crystal structure of complex 5, there are no direct hydrogen bonds between the complex molecules. They are linked together only by DMSO molecules, which play the role of bridges between the complex molecules due to hydrogen bonds. These are C18-H18B····O1^m, C19-H19A····O5ⁿ, and C19-H19E \cdots O4^m between solvate H and acetato O atoms, as well as the bond C10-H10...O7^o between the pyridine H and solvate O atoms [symmetry codes: (m) 1 - x, 2 - y, 1 - z; (n) 1 - x, 1 - y, 1 - z; (o) 2 - x, 1 - y, 1 - z; hydrogen bonds geometry: $C18\cdots O1^{m} = 3.338(2)$ Å, $C18-H18B\cdots O1^{m} = 151^{\circ}$, $C19\cdots O5^{n} =$ 3.449(2) Å, C19-H19A····O5ⁿ = 168°, C19····O4^m = 3.375(2) Å, C19-H19E····O4^m = 156°, C10····O7^o = 3.2926(18) Å, C10-H10...O7^o = 136°]. These non-classic hydrogen bonds form polymeric layers parallel with the ab plane. Intramolecular hydrogen bonds C8-H8--O6 [hydrogen bond geometry: C8····O6 = 3.1590(17) Å, C8-H8····O6 = 123°] between the pyridine H and acetato O atoms are additional in the layers.

FT-IR spectra of compound L and complexes 1-4

Vibrational spectra of free ligand L and complexes 1-4 were interpreted in accordance with the literature data on related compounds, in particular chelating pyridyl-containing azoles,⁵⁶ *N*-alkyltetrazoles and their metal complexes.⁵⁷ According to these data, coordination with metal ion leads to significant changes in the frequencies of the ν (C=N) bands of the pyridine and tetrazole rings, typically located in the region 1500-1450 cm⁻¹ in spectra of N-containing heterocyclic compounds.57,58 These vibrational bands of both heterocycles, found at 1471 cm^{-1} in the spectrum of L, are shifted to 1445, 1440, 1463 and 1410 cm^{-1} in the spectra of complexes 1, 2, 3 and 4, respectively. This is in accordance with chelating coordination of ligand molecules L in the complexes. It should be noted that in the spectrum of complex 4, the heterocyclic ν (C=N) band and the band of symmetric ν (CO) stretching vibrations of the carboxylato group of bridging acetato ligands (typically located at 1410 cm⁻¹)⁵⁹ are overlapping, and, as a result, only one broad intense band at 1410 cm⁻¹ is registered. This is responsible for a seeming considerable shift of the heterocyclic ν (C=N) band for complex 4 in comparison with 1-3.

In general, the spectra of complexes **1–4** in the region of stretching and stretching-deformation vibrations of the tetrazole and pyridine rings and the C–H bonds of the *tert*-butyl

substituent are almost identical with the spectrum of **L**. The shifts of C–H stretching bands of the pyridine ring by $10-20 \text{ cm}^{-1}$ to lower values on going from **L** (3090 and 3055 cm^{-1}) to its complexes can be attributed to involving the pyridine ring H atoms in hydrogen bonding.

The thiocyanate groups in complex 2 are revealed in the spectrum due to intense absorption at 2086 and 821 cm⁻¹ attributed to the asymmetric vibrations ν (C–N) and ν (C–S), respectively. The coordination of the thiocyanate groups in complex 2 is responsible for a strong band ν (Cu–N_{NCS}) at 305 cm⁻¹ in the far-IR region.⁵⁸ The uncoordinated perchlorate anions in complex 3 are identified by the strong bands at 1110 and 1040 cm⁻¹.⁵⁸ The very strong band ν (OH) at 3390 cm⁻¹ as well as the very weak band ν (Cu–O) at 460 cm⁻¹ found in the spectrum of complex 3 are typical of coordination of water molecules to a copper(II) atom.⁵⁸ In complex 4, weak bands ν (Mn–O_{acetate}) and ν (Cu–O_{acetate}) appear at 489 and 457 cm⁻¹, respectively.

The far-IR spectra of complexes **1–4** show low-frequency vibrations of ligand molecules L, as well as vibrations ν (Cu–N) at 232, 235, 321 and 332 cm⁻¹ for **1–4**, respectively, and ν (Cu–Cl) at 353 cm⁻¹ in the case of complex **1**.

Thermal properties

Thermal behaviour of L and complexes 1–4 is shown in Fig. 11. Compound L forms a stable melt at 141 °C. After heating up to 600 °C, it reveals mass loss of 58.8% and an exothermic peak at 262 °C. According to data on thermolysis of 2,5-disubstituted tetrazoles, decomposition of L proceeds probably through elimination of *tert*-butyl azide and formation of 2-cyanopyridine.⁶⁰

Decomposition of complexes 1 and 2 starts as an endothermic process at 236 and 215 °C, respectively, accompanied by a mass loss of 58.8 (1) and 69.8% (2), caused by partial (1) or total (2) desorption of ligand L. For complex 1, exothermic peak at 329 °C (mass loss 20.8%) indicates the transformation of intermediate destruction products of L. The solids, remaining after decomposition of complexes 1 and 2, revealed the compounds CuCl and CuS₂, respectively, as follows from XRD powder patterns.

Complex 3 shows an endothermic peak at 89 °C, with mass loss of 3.8%, which can be attributed to the removal of water molecules. After melting at 213 °C, a desolvate form of 3 decomposes explosively in an exothermic process (peaks at 256 and 295 °C, total mass loss 70.8%), corresponding to the destruction of ligands L, reduction of perchlorate anions and formation of CuO residue (confirmed by XRD powder data).

For complex 4, desorption of a molecular form of ligand L occurs as an endothermic process at 212 °C (mass loss 44.7%), analogous to the thermolysis of the heterobimetallic Cu(π)/Mn(π) acetato complex with 2,2'-bipyridine.⁶¹ The desorption is followed by destruction of acetato fragments of Cu₂Mn-(OAc)₆, passing through a three-step loss of acetato residues at 308, 344, and 385 °C, with mass loss of 12.6, 10.2 and 5.1%, respectively. According to XRD powder data, crystalline CuO and a spinel-like solid solution (Cu,Mn)Mn₂O₄ are solid



Fig. 11 TG/DSC/DTG curves of L and complexes 1-4.



Fig. 12 Temperature dependence of $\chi_M T$ for complex **4**. The solid line represents the best theoretical fits. The insert shows χ_M^{-1} vs. *T*.

products of thermal degradation of the complex. This shows that complex **4** might be suggested as a precursor of mixed-metal oxides systems for dedicated catalytic applications.⁶²

Magnetic properties of heterobimetallic complex 4

Fig. 12 shows the temperature dependence of the molar $\chi_M T$ product and the reverse magnetic susceptibility χ_M^{-1} for complex [Cu₂MnL₂(OAc)₆] over the 2–330 K temperature range, with an applied magnetic field of 500 G.

The value of $\chi_{\rm M}T$ at 330 K of 5.36 cm³ K mol⁻¹ (6.55 $\mu_{\rm B}$), being close to the spin only value of 5.12 cm³ K mol⁻¹ (6.40 $\mu_{\rm B}$) is expected for two magnetically isolated Cu(II) ions ($S_1 = S_3 =$ 1/2) and one high-spin Mn(II) ion ($S_2 = 5/2$) with g = 2.00. During cooling, $\chi_{\rm M}T$ decreases until near 60 K; below this temperature, the $\chi_{\rm M}T$ value decreases sharply to 1.65 cm³ K mol⁻¹ (3.63 $\mu_{\rm B}$) at 2 K, suggesting a net intramolecular antiferromagnetic exchange interaction. The magnetic susceptibility data in the temperature range 30–330 K obey the Curie–Weiss law expression⁶³ with a Curie constant of C = 5.32 cm³ K mol⁻¹ and a Weiss constant of $\theta = -10.3$ K, which further confirms an overall antiferromagnetic interaction between the acetatobridged Cu(II) and Mn(II) ions.

To estimate the magnitude of the exchange coupling in the trinuclear complex **4**, an isotropic Heisenberg–Hamiltonian with the addition of a Zeeman term (eqn (1)) was employed by using a full-matrix diagonalization approach.^{63,64}

$$\hat{H} = -J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3) + \mu_{\rm B} B[g_{\rm Cu}(\hat{S}_1 + \hat{S}_3) + g_{\rm Mn} \hat{S}_2]$$
(1)

In the model, the exchange coupling interaction between the terminal Cu(π) ions and the central Mn(π) ion were assumed to be predominant, therefore coupling between the two copper ions was neglected. Since the molecular structure revealed that the Mn(π) ($S_2 = 5/2$) ion lies on the inversion centre, the two Cu(π) ions ($S_1 = S_3 = 1/2$) can be considered identical. Hence, the magnetic exchange coupling constants $J_{12} = J_{23} = J$ were also assumed to be equivalent. A satisfactory fit of the experimental data, shown in Fig. 12 as solid lines, was possible over the full temperature range, yielding $J = -2.5 \text{ cm}^{-1}$, $g_{\text{Cu}} = 2.25$ and $g_{\text{Mn}} = 2.01$. Thus, each of the terminal copper(II) ions is weakly antiferromagnetic exchangecoupled to the central manganese(II) ion of the trinuclear complex 4.

Discussion

The synthesized monometallic complexes 1–3 are mononuclear, whereas heterobimetallic 4 and 5 show a trinuclear structure. In all the complexes, the ligand L is coordinated in a bidentate chelating mode *via* the pyridine nitrogen atom and the tetrazole ring N4 (complexes 1–3, 5) or N1 atom (complex 4). Coordination of ligand molecules L by metal atoms results in more planar geometry of the pyridine-tetrazole skeleton. So, the dihedral angle between two heterorings of 21.30(5)° in compound L decreases to 4.97(15)/3.56(15), 0.12(8), 1.80(1), 10.86(11), and 6.03(7)° in complexes 1–5, respectively. More planar geometry of the skeletons can be attributed to an influence of chelating coordination mode in the complexes.

In complexes 1–5, the ligands L are chelating ones relative to the copper atoms. Analysis of the chelate geometry (Table 2) shows that the bonds Cu–N_{Py} (Py = pyridine) with the pyridine nitrogen atoms are usual in all the complexes, with bond lengths lying in the range 1.993(2)–2.0652(11) Å; the exocyclic angles $\angle 5$ and $\angle 6$ do not differ to a great extent from an expected average value of 120°. However, another situation occurs for the coordinated tetrazole ring nitrogen atoms. Firstly, for all complexes 1–5, there is considerable deviation of exocyclic angles $\angle 1$ and $\angle 2$ from an expected average value of

Table 2 Chelate geometry (Å, °) in complexes 1–5^a

C

C

N

2



	Complex 1	Complex 2	Complex 3	Complex 4	Complex 5
u-N _{Py}	1.993(2), 2.005(2)	2.0540(12)	2.0377(18)	2.0458(13)	2.0652(11)
u-N _{Tz}	2.422(2), 2.493(2)	2.3944(12)	1.9928(19)	2.4267(13)	2.3486(11)
I _{Py} -Cu-N _{Tz}	77.72(8), 76.52(8)	76.60(4)	80.78(7)	76.76(5)	77.04(4)
1	150.55(18), 151.82(19)	148.04(10)	139.16(15)	152.39(10)	147.04(9)
2	103.31(15), 101.85(16)	105.52(9)	113.40(15)	104.36(10)	106.52(8)
.3 ^b	123.02(2), 123.4(2)	122.47(13)	118.4(2)	122.72(14)	121.88(11)
4^b	115.2(2), 116.7(2)	115.11(13)	111.85(19)	116.35(14)	115.29(11)
.5	120.67(17), 121.4(17)	120.30(10)	115.13(14)	119.16(11)	118.81(9)
.6	120.89(18), 119.91(18)	121.39(10)	127.14(15)	122.59(11)	122.61(9)

^{*a*} The schematic picture shows correspondence between the anglenumbering ($\angle 1 - \angle 6$) and the angles in the chelate ring. ^{*b*} For compound L, the angles $\angle 3$ and $\angle 4$ are 126.10(9) and 117.02(9)°, respectively.

ca. 127° (the angles $\angle 1$ and $\angle 2$ lie in the ranges *ca.* 139–152 and 102–113°, respectively). Secondly, all complexes, except for complex **3**, have elongated bonds Cu–N_{Tz} (Tz = tetrazole) lying in the range 2.3486(11)–2.493(2) Å, and high values of the angle $\angle 1$ and low values of the angle $\angle 2$. Thirdly, complex **3** reveals usual Cu–N_{Tz} bonds; the angles $\angle 1$ and $\angle 2$, having, respectively, lower and higher values in comparison with other complexes, differ to a lesser extent from the expected average value; the angles $\angle 3$ and $\angle 4$ have the lowest values among compounds **1–5**, **L**. It should be noted that all complexes **1–5** reveal rather low values of coordination angles N_{Py}–Cu–N_{Tz}, (the nitrogen atoms belong to the same ligand molecule), lying in the range 76.52(8)–80.78(7)°.

Based on these facts, the following conclusions can be made concerning the chelating coordination mode in the investigated compounds: (a) in molecular complexes 1, 2, 4, and 5, coordination bonds Cu–N_{Tz} are weaker than the bonds Cu–N_{Py}, and considerable deviation of exocyclic angles $\angle 1$ and $\angle 2$ from expected values takes place; (b) in complex 3, consisting of complex cations and perchlorate anions, the bonds Cu– N_{Tz} are stronger as compared with complexes 1, 2, 4, and 5, and some deformation of ligand L (*via* the angles $\angle 3$ and $\angle 4$) and some change in the exocyclic angles $\angle 1$, $\angle 2$, $\angle 5$ and $\angle 6$ occur. Probably, more information on chelate complexes with ligand L should be accumulated to explain specific coordination in complex 3 compared to others.

In heterobimetallic complexes 4 and 5, complex molecules show similar trinuclear structures, with acetato bridges between the copper and manganese atoms, and chelate ligands L coordinated only by the copper atoms. Another common feature of the complexes is that the copper atoms are seven-coordinated, with two long semi-coordinated Cu–O bonds completing a square pyramidal copper environment to distorted octahedron with a bifurcated vertex. In both compounds, the manganese atoms adopt the usual slightly distorted octahedral coordination, formed by the acetato O atoms.

Despite the similarity of complex molecules in compounds 4 and 5, they reveal considerable structural differences, consisting in different rotameric forms of ligand L in the compounds, namely *syn* in 4 and *anti* in 5. These forms correspond to different nitrogen atoms coordinated by the copper atoms in the chelate mode, namely N1 in complex 4 and N4 in complex 5. There is a difference in crystal packing of complexes 4 and 5, which takes place because of the presence of solvate DMSO molecules in crystals of complex 5. In this compound, in contrast to 4, there are no hydrogen bonds between the complex molecules, which are linked together only *via* the hydrogen bonds with DMSO molecules.

It should be noted that complex **4** presents the first example of coordination of 2,5-disubstituted tetrazole *via* the N1 tetrazole ring atom. The observed N1 coordination mode is rather unexpected, since quantum-chemical calculations of molecular electrostatic potential, charge distribution and energies of hydronation of nitrogen atoms in the molecule of 2-monosubstituted tetrazoles indicate that the N4 atom is the



Scheme 3 Carboxylato binding modes in $[M_3(\mu$ -RCOO)₆] type complexes (M = Mn, Cu).

most preferable coordination center in the tetrazole ring.⁶⁵ Moreover, in ligand molecules relatively bulk *tert*-butyl and 2-pyridyl substituents can hinder binding of the N1 atom with the copper atom. Notably, the Cu–N1 bond length of 2.4267(13) Å in complex 4 is shorter than those in copper(π) complexes of 2-monosubstituted tetrazoles, showing a rare (N1,N4)-bridging coordination mode [Cu–N1 bond lengths of 2.50–2.85 Å].^{65–67}

The analysis of crystal structures of complex **4** and analogous homometallic compounds with a $[Mn_3(\mu$ -RCOO)_6] core^{68–70} reveals the existence of two superexchange pathways controlling the overall magnetic behavior: (i) through a biatomic acetato O,O bridge (Scheme 3, *syn–syn* mode **D**), or (ii) *via* a monoatomic acetato O bridge (mode **E**). Moreover, a combined mode **F** can also contribute to the magnetic coupling.

 $[Mn_3(\mu$ -RCOO)₆] type compounds show weak antiferromagnetic coupling with J values lying in the range from -6.3 to -1.2 cm⁻¹ depending on the geometry of carboxylato bridges.⁶⁸⁻⁷⁰ In particular, the presence of a monoatomic bridge (mode E) reduces the M····M distance and increases the *I* value. Complex 4, being the first magnetically characterized linear trinuclear complex with two different 3d metal ions bridged by carboxylato moieties, also shows antiferromagnetic coupling. In contrast to monometallic trinuclear complexes, a significant shift of acetato bridged oxygen atoms away from the terminal copper(II) atom, which is accompanied by the formation of long semi-coordinated Cu-O bonds in complex 4, results in the asymmetric character of monoatomic acetato bridge and, therefore, in non-coupling between the Cu(II) and Mn(II) ions across the acetato binding modes E and F. By taking into account these facts, weak exchange coupling (I = -2.5 cm^{-1}) in complex 4 could be explained by acetato bridges in syn-syn coordination mode D only.

Conclusions

The first representative of the 2,5-disubstituted tetrazoles, 2-*tert*-butyl-5-(2-pyridyl)-2*H*-tetrazole, was involved in direct synthesis of coordination compounds using oxidative dissolution of copper powder in a non-aqueous solution of ammonium salts in open air. In accordance with our expectations, direct synthesis provided a facile and convenient tool toward novel Cu(π) and heterobimetallic Cu(π)/Mn(π) complexes with different nuclearity. Moreover, this approach has allowed us to realize the expected bidentate chelating mode of the ligand *via* the pyridine nitrogen atom and the tetrazole ring N4 atom, as well as unexpected one through the pyridine

nitrogen atom and the tetrazole ring N1 atom. The finding of monodentate coordination of the tetrazole ring through the N1 atom opens new routes in design of complexes based on 2-mono- and 2,5-disubstituted tetrazoles. Structural, thermal and magnetic properties of complexes reported here are encouragements for the further investigations of chelating tetrazoles as ligands in direct synthesis of heterometallic transition metal complexes for diverse applications.

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