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Polyhedron 22 (2003) 1645–1652

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The X-ray crystallographic structures, spectral and magnetic properties of nickel(II), copper(II) and cobalt(II) complexes with tetra(3-*iso*-propylpyrazol-1-yl)borate

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Received 6 January 2003; accepted 26 March 2003

Abstract

Tetra(3-*iso*-propylpyrazol-1-yl)borate ligand (L) forms mono-ligand LMX and bis-ligand L_2M complexes (where M = Ni(II), and Cu(II), and $X = Cl^-$ or NO_3^-) depending on the stoichiometry of the synthesis, while a polynuclear $(NCS)_2Co(L)Co(L)Co(NCS)_2$ complex is obtained when excess of cobalt(II) thiocyanate is used. The L coordinates to metal ions in a κ^3 fashion in LNiCl, $LNi(NO_3)(5\text{-}^iPrpzH)$ and $LCuCl(5\text{-}^iPrpzH)$, whereas a κ^2 binding mode was found in L_2Ni and in unique $(NCS)_2Co(L)Co(L)Co(NCS)_2$, in which L bridges two metal ions.

Keywords: Cobalt; Nickel; Copper; Tetra(3-*iso*-propylpyrazolyl)borate; Structures; Magnetism

1. Introduction

The complexes of hydrotris(pyrazolyl)borate have become a very well recognized area of transition metal ion chemistry [1]. The coordination chemistry of tetra(pyrazolyl)borates $[B(pz')_4]^-$, which are obtainable by the condensation of borohydride with an excess of the corresponding pyrazole (pz′H), is relatively less explored. The $[B(pz')_4]^-$ ligands provide usually three or two N(2-pz) donor atoms to metal ion centers in their complexes, depending on the metal ion, its oxidation state and additional ligands. Barely nine bis-ligand homoleptic complexes of $[B(pz')_4]$ of first-row transition metal ions have been characterized structurally: $[B(pz)_4]_2M$ (where $M = Fe^{2+}$, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) $[B(3\text{-cPrpz})_4]_2Fe$, $[B(3\text{-Mepz})_4]_2Cu$ and $[B(3\text{-}^iPrpz)_4]_2Co$, in which $[B(pz')_4]^-$ ligands were bound in a κ^3 manner, except the latter complex, where the ligands were bound in a κ^2 fashion [2–6]. Structures of many mono-ligand heteroleptic complexes are also known, in which the hapticity of tetrapyrazolylborate depends on the kind of metal ion, oxidation state and the ancillary ligands L in their $[B(pz')_4]ML_n$ complexes. For instance, the κ^3 coordination was found in $[B(pz)_4]M(CO)_3$, where M = Cr or Mn [7] and in $[B(3\text{-Mepz})_4]Cu(PR_3)$, [8] while the unsubstituted $[B(pz)_4]^-$ ligand coordinated κ^2 in a series of $[B(pz)_4]Cu(L')$ complexes [9,10]. Here we have described the coordination properties of the $[B(3\text{-}^iPrpz)_4]^-$ ligand bearing an intermediate size 3-*iso*-propyl substituent, for which a series of first-row transition metal ion complexes of variable stoichiometry were obtained, depending on the synthetic procedure.

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0277-5387/03/$ - see front matter
doi:10.1016/S0277-5387(03)00331-0

2. Experimental

2.1. Syntheses and analytical data

2.1.1. General syntheses

3(5)-*Iso*-propylpyrazole (3-^{i}PrpzH), sodium tetra(3-*iso*-propylpyrazol-1-yl)borate NaL and bis-[tetra(3-*iso*-propylpyrazolyl)borate]cobalt(II) (CoL_2) were synthesized by known procedures [6].

2.1.2. Cu(L)(5-^{i}PrpzH)Cl (**1**)

A solution of NaL (0.150 g, 0.319 mmol) in THF (10 cm^3) was added dropwise into the 0.2 M $CuCl_2$(aq) (30 cm^3). The mixture was extracted with dichloromethane (2×20 cm^3) and the solvents were distilled off under reduced pressure from the organic phase. The red crystals of **1** (0.146 g, 0.223 mmol, 70% yield) were obtained by recrystallization from benzene and subjected to X-ray crystallographic measurement.

2.1.3. Ni(L)Cl (**2**)

A solution of NaL (0.150 g, 0.319 mmol) in THF (10 cm^3) was added dropwise into 0.2 M $NiCl_2$(aq) (30 cm^3). The mixture was extracted with dichloromethane ($2 \times$ 20 cm^3) and the solvents were distilled off under reduced pressure from the organic phase. Analytically pure **2** was obtained by crystallization from THF-hexane (0.165 g, 0.305 mmol, 95% yield). One of the cube-shaped, red crystals was analyzed crystallographically.

2.1.4. Ni(L)(NO_3)(5-^{i}PrpzH) (**3**)

A solution of NaL (0.212 g, 0.451 mmol) in THF (10 cm^3) was added dropwise into 0.2 M $Ni(NO_3)_2$(aq) (30 cm^3). The mixture was extracted with dichloromethane (2×20 cm^3) and the solvents were distilled off under reduced pressure from the organic phase. Analytically pure **3** was obtained by crystallization from hexane (0.142 g, 0.209 mmol, 46% yield) as blue crystals and analyzed crystallographically.

2.1.5. $Ni(L)_2$ (**4**)

An aqueous solution of nickel(II) nitrate (0.52 g of $Ni(NO_3)_2 \cdot 6H_2O$, 1.753 mmol in 20 cm^3 H_2O) was added dropwise into a solution of NaL (1.649 g, 3.507 mmol) in THF (30 cm^3) with vigorous stirring. The solution turned reddish-violet. Volatiles were removed under reduced pressure, the solid residue was dissolved in hot hexane, the solution was then passed through a short column packed with Celite and left at room temperature. After 2-h reddish-pink crystals of **1** deposited (0.435 g, 0.912 mmol, 52% yield). One of the crystals was subjected to X-ray crystallographic measurement.

2.1.6. CuL_2 (**5**)

An aqueous solution of copper(II) nitrate (0.2176 g $Cu(NO_3)_2 \cdot 3H_2O$, 0.901 mmol in 20 cm^3 H_2O) was added dropwise to a solution of NaL (0.802 g, 1.704 mmol) in THF (10 cm^3). The deep-red solution was extracted with methylene chloride (100 cm^3), the organic phase was washed twice with water (100 cm^3), the solvents were removed under reduced pressure and the solid residue was vacuum dried. Fine red crystals of **5** were collected upon crystallization from hexane (0.550 g, 0.574 mmol, 67.4% yield).

2.1.7. $[(NCS)_2Co(L)]_2Co \cdot THF$ (**6**)

A solution of CoL_2 (0.150 g, 0.157 mmol) in benzene (15 cm^3) was added dropwise to 100 cm^3 0.5 M solution of cobalt(II) nitrate and 2 M potassium thiocyanate in water (20 cm^3). The blue solution was extracted with methylene chloride (100 cm^3), washed once with water (50 cm^3), the solvents were stripped out under reduced pressure and a solid residue was vacuum dried. 0.197 g of violet needle-shaped crystals were collected upon crystallization from THF-heptane solvents (0.156 mmol, 99% yield).

2.2. Analytical data

1: $C_{30}H_{46}N_{10}BClCu$ (656.57): Calc. C 54.88, H 7.06, N 21.33; Found: C 54.96, H 7.15, N 21.57. UV–Vis: λ (nm) (ε (mol^{-1} dm^3 cm^{-1})): 258 (3.40×10^3), 295 (sh, 1.56×10^3), 374 (1.95×10^3), 716 (66), 979 (113).

2: $C_{24}H_{36}N_8BClNi$ (541.58) C 53.23, H 6.70, N 20.99; Found: C 53.36, H 7.09, N 20.70. UV–Vis: λ (nm) (ε (mol^{-1} dm^3 cm^{-1})): 477 (430), 799 (119), 891 (132). $\mu =$ 3.10 B.M.

3: $C_{30}H_{46}N_{11}O_3BNi$ (678.30) C 53.12, H 6.83, N 22.71; Found: C 53.30, H 6.69, N 22.49. UV–Vis: λ (nm) (ε (mol^{-1} dm^3 cm^{-1})): 377 (40), 598 (16), 987 (13). $\mu = 3.13$ B.M.

4: $C_{48}H_{72}N_{16}B_2Ni$ (953.52): Calc. C 60.46, H 7.61, N 23.50; Found: C 60.21, H 7.78, N 23.17. UV–Vis: λ (nm) (ε (mol^{-1} dm^3 cm^{-1})): 464 (94), 531 (209), 744 (54), 866 (25). $\mu = 3.12$ B.M.

5: $C_{48}H_{72}N_{16}B_2Cu$ (958.38): Calc. C 60.16, H 7.57, N 23.38; Found: C 60.10, H 7.56, N 23.04. UV–Vis: λ (nm) (ε (mol^{-1} dm^3 cm^{-1})): 382 (1.57×10^3), 420 (1.34×10^3), 481 (832).

6: $C_{56}H_{80}N_{20}OB_2S_4Co_3$ (1376.07): Calc. C 48.88, H 5.86, N 20.36, S 9.32; Found: C 48.79, H 6.01, N 20.30, S 9.70. UV–Vis: λ (nm) (ε (mol^{-1} dm^3 cm^{-1})): 542 (1.28×10^3), 587 (1.57×10^3), 638 (2.49×10^3).

2.3. Methods and instruments

Elemental analyses were performed with a Perkin–Elmer 2400 CHN analyzer. The ^1H NMR spectra were recorded with a Bruker AMX300 spectrometer operating in the quadrature mode at 300 MHz. The residual peaks of solvents were used as internal standards. The FT IR spectra were recorded in KBr pellets on a

Perkin–Elmer 1725X instrument. The UV–Vis experiments were performed with an HP 8453 diode-array spectrophotometer in dichloromethane. The magnetic susceptibility was measured as a function of temperature within the 2–300 K range using a Quantum Design SQUID Magnetometer (type MPMS-5). The values of magnetic moment were calculated after considering the appropriate diamagnetic corrections.

Crystal data are given in Table 1, together with refinement details. All measurements of crystals were performed at low temperature using an Oxford Cryosystem device on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated Mo Kα radiation. Crystals were positioned at 65 mm from the CCD camera. Six hundred and twelve frames were measured at 0.75° intervals with a counting time of 15–20 s. Accurate cell parameters were determined and refined by a least-squares fit of 2700–4200 of the strongest reflections. The data were corrected for Lorentz and polarization effects. No absorption correction was applied. Data reduction and analysis were carried out with the Oxford Diffraction (Poland) Sp: z o.o (formerly Kuma Diffraction Wrocław, Poland) programs. All structures were solved by direct methods (program SHELXS-97 [11]) and refined by the full-matrix least-squares method on all F^2 data using the SHELXL-97 [12] programs. Non-hydrogen atoms were refined with anisotropic displacement parameters; hydrogen atoms were included from the geometry of molecules and $\Delta\rho$ maps; they were refined with isotropic displacement parameters in **3**, and in the remaining structures the H atom parameters were fixed.

3. Results and discussion

Tetra(pyrazolyl)borates are advantageous over tris(pyrazolyl)borates due to their stability in highly oxidative conditions. Therefore they were extensively used as ligands for oxenoid complexes of rhenium at high oxidation state [13–17]. Generally, two or three nitrogen atoms of tetra(pyrazolyl)borates are involved in donation to metal ions. Extraneous nitrogen of a fourth pyrazolyl residue can serve as an additional donor with formation of polynuclear species, which were never observed before. We have attempted to explore this possibility using the $[B(3\text{-}^{i}Prpz)_4]^-$ anion (L). Thus, the series of mono-ligand and bis-ligand complexes of L with copper(II), nickel(II) and cobalt(II) were obtained, and in one case the formation of a trinuclear species was found. Mononuclear complexes were characterized structurally by means of X-ray

Table 1
Crystal data and structure refinement

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{30}H_{46}N_{10}BClCu$	$C_{24}H_{36}BN_8ClNi$	$C_{30}H_{46}BN_{11}O_3Ni$	$C_{48}H_{72}B_2N_{16}Ni$
Formula weight	656.57	541.58	678.30	953.54
T (K)	100(2)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P\bar{1}$	$C2/c$
a (Å)	11.701(2)	10.837(2)	10.4665(11)	18.958(5)
b (Å)	18.069(4)	13.955(3)	11.9906(12)	15.388(5)
c (Å)	17.433(6)	17.937(4)	13.7685(14)	19.770(4)
α (°)	90	90	88.002(8)	90
β (°)	111.96(2)	90	85.034(9)	111.75(3)
γ (°)	90	90	90	79.178(9)
V (Å^3)	3418.4(15)	2712.6(9)	1690.5(3)	5357(2)
Z	4	4	2	4
D_{calc} (Mg m^{-3})	1.276	1.326	1.333	1.182
μ (mm^{-1})	0.753	0.842	0.623	0.410
$F(0\,0\,0)$	1388	1144	720	2040
Crystal size (mm)	0.18 × 0.14 × 0.13	0.19 × 0.16 × 0.14	0.22 × 0.20 × 0.16	0.18 × 0.16 × 0.11
θ Range for data collection (°)	3.38–28.42	3.47–28.35	3.41–28.54	3.36–28.55
Ranges	$-10 \le h \le 15$, $-23 \le k \le 23$, $-22 \le l \le 22$	$-14 \le h \le 11$, $-18 \le k \le 17$, $-23 \le l \le 23$	$-9 \le h \le 14$, $-15 \le k \le 15$, $-18 \le l \le 18$	$-24 \le h \le 25$, $-19 \le k \le 20$, $-25 \le l \le 25$
Reflections collected	23 385	18 762	11 773	18 271
Independent reflections (R_{int})	7910 (0.0403)	6345 (0.0376)	7430 (0.0283)	6275 (0.0436)
Data/parameters	7910/398	6345/324	7430/595	6275/310
GOF (F^2)	1.066	0.989	1.077	1.037
Final R_1/wR_2 indices ($I > 2\sigma(I)$)	0.0472/0.1014	0.0314/0.0554	0.0353/0.0844	0.0486/0.0949
Largest difference peak/hole (e Å^{-3})	1.158/−0.473	0.271/−0.307	0.325/−0.463	0.327/−0.426

crystallography. The magnetic properties and spectral studies are reported here in detail.

3.1. Synthesis of complexes

The copper and nickel complexes bearing one L (mono-ligand complexes) were synthesized upon addition of a solution of sodium tetra(3-*iso*-propylpyrazolyl)borate (NaL in THF) to an aqueous solution of copper(II) chloride, nickel(II) chloride or nickel(II) nitrate followed by extraction of the neutral complexes into dichloromethane. In this way the analytically pure pentacoordinate Cu(L)(5-^{i}PrpzH)Cl (**1**), tetracoordinate Ni(L)Cl (**2**) and hexacoordinate Ni(L)(NO_3)(5-^{i}PrpzH) (**3**) were obtained in good yield and their structures were determined crystallographically. The same synthetic procedure aimed at the Co(L)(NCS) complex resulted unexpectedly in formation of the complex analyzed as $Co_3L_2(NCS)_4$ THF. The same compound was obtained with the modified procedure starting from CoL_2 and aqueous cobalt(II) thiocyanate. On the other hand, the bis-ligand complexes: Ni$(L)_2$ (**4**) and Cu$(L)_2$ (**5**) were obtained upon addition of aqueous metal(II) nitrates into a nearly twofold excess of NaL, followed by extraction of **4** and **5** into organic solvent. The structure of **4** was elucidated crystallographically. The syntheses of **1** and **3** were accompanied by a partial hydrolysis of the tetra(pyrazolyl)borate ligand leading to the coordination of the released pyrazole into metal centers in **1** and **3**.

*3.2. Structures of **1**–**4** in the solid state*

The copper(II) metal ion in **1** is surrounded by three nitrogen donors from L, an additional nitrogen atom from 5-*iso*-propylpyrazole and a chloride anion. The molecular structure of **1** is shown in Fig. 1. The central metal ion is placed in the plane with the chloride anion, N(2) and N(4) of L, while N(6) and N(9) of 5-^{i}PrpzH are in nearly axial positions. Thus, the copper ion is arranged in a distorted trigonal bipyramidal geometry. The same coordination mode of L was found in **2** (Fig. 2). The chloride anion completes the coordination sphere of the tetracoordinate central nickel(II) ion. The mean Ni–N(L) distance in **2** is 1.98 Å. Analogically, L is coordinated in a κ^3 fashion in hexacoordinate **3**, in which κ^2 coordinated nitrate anion and a nitrogen atom from 5-*iso*-propylpyrazole serve as additional donors (Fig. 3). Here the mean Ni–N(L) distance is 2.05 Å. In the bis-ligand complex (**4**) the central nickel(II) ion is in a tetrahedral surrounding provided by four nitrogen donors from two κ^2 coordinated ligands (Fig. 4).

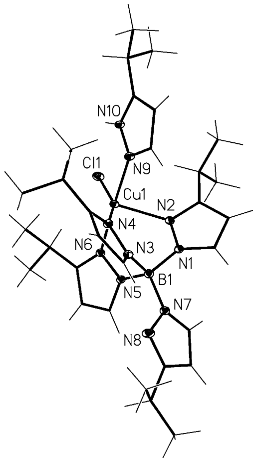

Fig. 1. Molecular structure of **1** with crystallographic numbering. Selected bond lengths (Å) and angles (°): Cu(1)–N(6), 2.0095(19); Cu(1)–N(9), 2.014(2); Cu(1)–N(4), 2.052(2); Cu(1)–N(2), 2.200(2); Cu(1)–Cl(1), 2.2940(8); N(6)–Cu(1)–N(9), 172.42(8); N(6)–Cu(1)–N(4), 84.36(8); N(9)–Cu(1)–N(4), 88.26(8); N(6)–Cu(1)–N(2), 88.05(8); N(9)–Cu(1)–N(2), 90.92(8); N(4)–Cu(1)–N(2), 95.13(8); N(6)–Cu(1)–Cl(1), 97.91(6); N(9)–Cu(1)–Cl(1), 89.53(6); N(4)–Cu(1)–Cl(1), 156.00(6); N(2)–Cu(1)–Cl(1), 108.80(5); N(7)–B(1)–N(1), 109.8(2); N(7)–B(1)–N(3), 112.4(2); N(1)–B(1)–N(3), 109.5(2); N(7)–B(1)–N(5), 108.7(2); N(1)–B(1)–N(5), 109.69(19); N(3)–B(1)–N(5), 106.6(2).

The comparison of metric parameters for known complexes of L shows that: (i) the mean M–N(L) distance for tetracoordinate complexes is 0.07–0.13 Å shorter than that for penta- and hexacoordinate ones, (ii) the boron-centered and metal ion-centered bite angles of a κ^3 bound ligand are smaller for tetracoordinate **2** in comparison with those in penta- or hexacoordinate **1** and **3** (columns 5 and 6, respectively in Table 2), (iii) the deviations from tetrahedral geometry around the boron atom in L (column 7 in Table 2) depends on the coordination mode of L and within the series of nickel(II) complexes the ligand is the most relaxed in **4**, where L is bound κ^2 in a tetracoordinate complex,

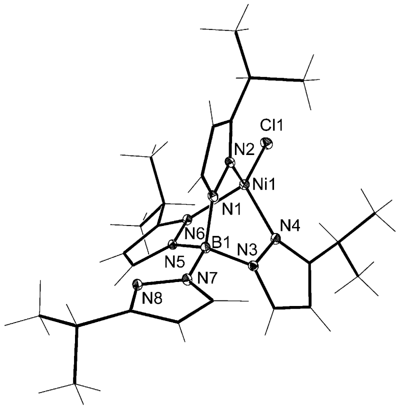

Fig. 2. Molecular structure of **2** with crystallographic numbering. Selected bond lengths (Å) and angles (°): Ni(1)–N(4), 1.9644(15); Ni(1)–N(2), 1.9748(15); Ni(1)–N(6), 2.0156(16); Ni(1)–Cl(1), 2.1709(6); N(4)–Ni(1)–N(2), 91.95(7); N(4)–Ni(1)–N(6), 89.81(6); N(2)–Ni(1)–N(6), 93.02(6); N(4)–Ni(1)–Cl(1), 126.51(5); N(2)–Ni(1)–Cl(1), 124.01(5); N(6)–Ni(1)–Cl(1), 121.81(5); N(7)–B(1)–N(5), 113.69(16); N(7)–B(1)–N(1), 108.45(16); N(5)–B(1)–N(1), 108.26(16); N(7)–B(1)–N(3), 110.42(17); N(5)–B(1)–N(3), 107.39(16); N(1)–B(1)–N(3), 108.51(16).

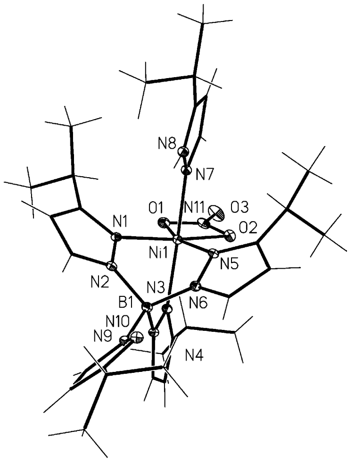

Fig. 3. Molecular structure of **3** with crystallographic numbering. Selected bond lengths (Å) and angles (°): Ni(1)–N(1), 2.0294(14); Ni(1)–N(5), 2.0694(14); Ni(1)–N(7), 2.0947(14); Ni(1)–N(3), 2.0972(14); Ni(1)–O(2), 2.1138(13); Ni(1)–O(1), 2.1330(13); N(1)–Ni(1)–N(5), 92.11(6); N(1)–Ni(1)–N(7), 90.25(6); N(5)–Ni(1)–N(7), 90.07(6); N(1)–Ni(1)–N(3), 87.12(6);N(5)–Ni(1)–N(3), 88.20(6); N(7)–Ni(1)–N(3), 176.79(5); N(1)–Ni(1)–O(2), 166.52(5); N(5)–Ni(1)–O(2), 101.08(5); N(7)–Ni(1)–O(2), 87.00(5); N(3)–Ni(1)–O(2), 95.98(5); N(1)–Ni(1)–O(1), 105.50(5); N(5)–Ni(1)–O(1), 161.86(5); N(7)–Ni(1)–O(1), 85.61(5); N(3)–Ni(1)–O(1), 96.85(5); O(2)–Ni(1)–O(1), 61.14(5); N(9)–B(1)–N(6), 113.84(14); N(9)–B(1)–N(4), 110.60(14); N(6)–B(1)–N(4), 107.57(14); N(9)–B(1)–N(2), 107.15(14); N(6)–B(1)–N(2), 108.86(14); N(4)–B(1)–N(2), 108.72(14).

while a considerable deviation takes place for κ^3 bound L in hexacoordinate **3**. On the other hand, a large distortion from tetrahedral geometry in the cobalt(II) analogue of **4** indicates that the phenomenon is also dependent on crystal packing.

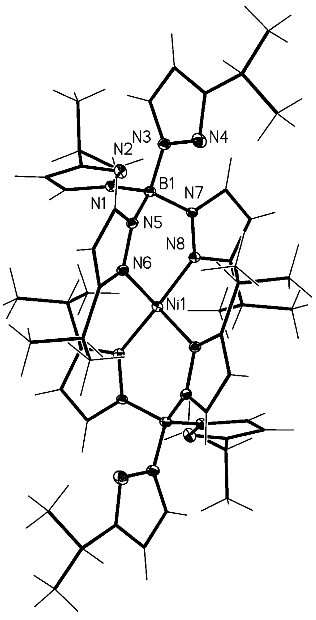

Fig. 4. Molecular structure of **4** with crystallographic numbering. Selected bond lengths (Å) and angles (°): Ni(1)–N(8), 1.9440(16); Ni(1)–N(6), 1.9845(16); N(6)–Ni(1)–N(8), 97.12(7);N(6)–Ni(1)–N(8)′, 109.68(7); N(6)–Ni(1)–N(6)′, 98.62(9); N(8)–Ni(1)–N(8)′, 138.62(9); N(3)–B(1)–N(1), 110.73(16); N(3)–B(1)–N(7), 107.79(16); N(1)–B(1)–N(7), 109.40(16); N(3)–B(1)–N(5), 108.79(16); N(1)–B(1)–N(5), 108.32(16); N(7)–B(1)–N(5), 111.82(16).

*3.3. Spectral and magnetic properties of **1–6***

The FIR spectra of **1**–**5** were compared with that of NaL in order to identify stretching vibration M–N absorption bands. IR spectra of complexes **1**–**5** are almost superimposable with that of NaL in the region of 736–420 cm^{-1}, while additional bands are observed in the 410–200 cm^{-1} region for **1**–**5** (Table 3). A medium intensity band centered at 372–402 cm^{-1} observed for both bis-ligand (**4**, **5**, and L_2Co) and mono-ligand **1**–**3** complexes allows for unambiguous identification of the band as ν(M–N(pyrazolyl)). The higher wavenumber of the band in the case of **4** is consistent with a shorter Ni–N in **4** (1.96 Å) in comparison with the Co–N distance in L_2Co (1.98 Å). Following the trend, the Cu–N distance in **5** is probably the longest among L_2M complexes. The position of the ν(M–N) stretching vibration for complexes **1**–**3** is in accordance with this conclusion. The band is observed at 402 cm^{-1} for tetracoordinate **2** (Ni–N distance is 1.98 Å) while it is centered at 397 cm^{-1} for pentacoordinate **1** (Cu–N distance is 2.09 Å). The hexacoordinate **3** does not follow the trend; in this case three stretching vibrations at lower wavenumbers are observed in accordance with the structural parameters (three distinct Ni–N(pyrazole) distances are observed in the structure of **3**, see caption of Fig. 3). Additionally, in the case of **3** two bands at 342 and 336 cm^{-1} have been attributed to ν(M–O(nitrate)), while ν(M–Cl) bands occur at 364 and 351 cm^{-1} for **1** and **2**, respectively. In the case of **3** the presence of a strong band at 944 cm^{-1}, which is absent in any other complexes and in NaL, was attributed to one of the N–O vibrations in the coordinated nitrate.

The magnetic susceptibility measurements indicate clearly that nickel(II) ions are the in the high-spin state in all studied complexes (**2**–**4**). In accordance with these results the *d–d* bands in the electronic spectrum of tetrahedral **4** are assigned to spin-allowed $^{3}T_{2}(P)\leftarrow{}^{3}T_{1}(F)$ (18 830 cm^{-1}), $^{3}A_{2}(P)\leftarrow{}^{3}T_{1}(F)$ (13 440 cm^{-1}) and $^{3}T_{2}(F)\leftarrow{}^{3}T_{1}(F)$ (11 550 cm^{-1}) transitions and a spin-forbidden $^{1}G\leftarrow{}^{3}T_{1}(F)$ one at 21 552 cm^{-1} [19]. The positions of spin-allowed *d–d* transitions for the nickel(II) metal ion in nearly C_{3v} symmetrical **2** are significantly altered in comparison with **4** due to replacement of one nitrogen donor with a chloride one and red shifted $^{3}T_{2}(F)\leftarrow{}^{3}T_{1}(F)$ and $^{3}A_{2}(P)\leftarrow{}^{3}T_{1}(F)$ bands are observed at 10 190 and 12 520 cm^{-1}, respectively, while the $^{3}A_{2}(P)\leftarrow{}^{3}T_{1}(F)$ transition band is observed at 20 960 cm^{-1}. Three low-intensity *d–d* transitions in the spectrum of hexacoordinate **3** were attributed to $^{3}T_{2}\leftarrow{}^{3}A_{2}$, $^{3}T_{1}(F)\leftarrow{}^{3}A_{2}$ and $^{3}T_{1}(P)\leftarrow{}^{3}A_{2}$ at 10 130, 16 720 and 26 520 cm^{-1}, respectively [19]. The

Table 2
Metric parameters for 1–4 (from crystallographic data)

Compound	Coordination number	Coordination mode of L	Mean M–N(L) (Å)	α [a] (°)	β [b] (°)	θ [c] (°)
1	5	κ^3	2.09	94.0	170.2	1.25
2	4	κ^3	1.98	89.0	162.8	1.67
3	6	κ^3	2.05	93.7	170.0	1.78
4	4	κ^2	1.96			1.18
CoL_2 [d]	4	κ^2	1.98			1.70

[a] Boron-centered and metal ion-centered bite angles calculated as in Ref. [18].

[b] Boron-centered and metal ion-centered bite angles calculated as in Ref. [18].

[c] The distorion from tetragonal geometry calculated as a mean deviation of N(pz)–B–N(pz) bond from tetrahedral angle: $(\Sigma_1^6|(NBN)^\circ - 105.28^\circ|)/6$.

[d] From Ref. [6].

spectrum remained unaltered upon addition of excess of 3(5)-*iso*-propylpyrazole, which indicated that the spectrum recorded for the solution of **3** in dichloromethane originated from hexacoordinate **3**.

Similarly to **3**, the UV–Vis spectrum of **1** remained unchanged upon addition of excess of 3(5)-*iso*-propylpyrazole. It is composed of many bands, which could be expected for a pentacoordinate complex of low symmetry. The presence of three *d–d* transition bands for **5** indicates rather a trigonally distorted octahedral environment (C_2 symmetry) of the central metal ion than a tetragonally distorted octahedral one (four *d–d* transitions expected) [19].

The spectral and magnetic properties of **6** deserve separate comment. For **6** the single ν(NCS) at 2060 cm^{-1} showed that terminal thiocyanate occurs in this trinuclear complex. The ^1H NMR spectrum consists of eight resonances: two peaks of integral intensity corresponding to 6 protons at −24.6 and 4.9 ppm from methyl hydrogens of the 3-*iso*-propyl substituent, and six resonances of intensity 2H, corresponding to two 4-H(pz) and two 5-H(pz) at 66.8, 34.4, 30.2 and 14.4 ppm, and two resonances from C–H(^{i}Pr) at 9.6 and −69.0 ppm (Fig. 5(A)). Thus, it can be concluded that the L ligands form bridges between the middle and two terminal cobalt ions, while four thiocyanate anions are coordinated to the terminal metal centers as it is shown in the formula (Fig. 5(B)).

The UV–Vis spectrum of **6** showed a series of *d–d* bands within the 18 000–15 000 cm^{-1} region characteristic for high-spin cobalt(II) in a tetrahedral environment. There are three bands centered at 18 450, 17 040 and 15 670 cm^{-1} and two shoulders at about 17 540 and 15 080 cm^{-1} attributed to multiple $^4T_1(P) \leftarrow {}^4A_2$ transitions, while a weak and broad absorption band at about 10 000 cm^{-1} ($\varepsilon = 300$ mol^{-1} dm^3 cm^{-1}) is due to a $^4T_1(P) \leftarrow {}^4A_2$ transition. Moreover, in the ultraviolet part of the spectrum, a very strong L←M charge transfer band centered at about 30 000 cm^{-1} ($\varepsilon = 4 \times 10^4$ mol^{-1} dm^3 cm^{-1}) is consistent with the presence of terminal thiocyanate ligands [14]. The magnetic susceptibility measurements as a function of temperature indicated that all metal ions are in the high spin state (magnetic moment equal to 4.28 B.M. per cobalt ion at 293 K). From the temperature dependence of the magnetic susceptibility the zero-field splitting parameter D has been calculated [20]. The average value of D falls within the typical range for high-spin cobalt(II) complexes and equals −7.9 cm^{-1} (Fig. 5(C)).

Our attempts to synthesize mixed metal trinuclear species starting from L_2M (M = Co(II) or Cu(II)) and slightly excessive amounts of $M'(X)_2$ (M′ = Co(II),

Table 3
The positions of bands in FIR (column 2) and other characteristic bands (column 3) in IR spectra (in cm^{-1})

Compound	FIR bands (intensity, assignment)	Other bands
NaL	421(m); 354(w); 287(m); 237(w); 199(m); 135(w)	
1	424(m,L); 397(m,ν(Cu–N); 364(m); 340(w,L); 313(w,L); 292(m,L); 251(m); 213(w,L); 191(w,L); 175 (w,L); 140(w,L)	
2	433(m,L); 402(m,ν(Ni–N); 351(m); 341(w,L); 282(m,L); 248(m); 193(w,L); 169(w,L)	
3	425(m,L); 387(w,ν(Ni–N); 379(w,ν(Ni–N); 372(m,ν(Ni–N); 341(m); 336 (m); 312(w,L); 289(w,L); 269(w,L); 233(w,L); 214(m,L)	944 and 1572 $\nu_s + \nu_{as}$ (NO_3)
4	423(m,L); 403(m,ν(Ni–N); 368(w,L); 360(w,L); 340(w,L); 309(w,L); 292(m,L); 254(w,L); 200(w,L); 167(m,L); 138(w,L)	
5	423(m,L); 395(m,ν(Cu–N); 354(w,L); 340(w,L); 311(w,L); 292(w,L); 213(w,L); 194(w,L); 177(w,L); 140(w,L)	
L_2Co [6]	423(m,L); 397(m,ν(Co–N); 368(w,L); 343(w,L); 303(m,L); 250(w,L); 172(w,L)	
6		2060 ν(NCS)

L (column 2) denotes intraligand band.

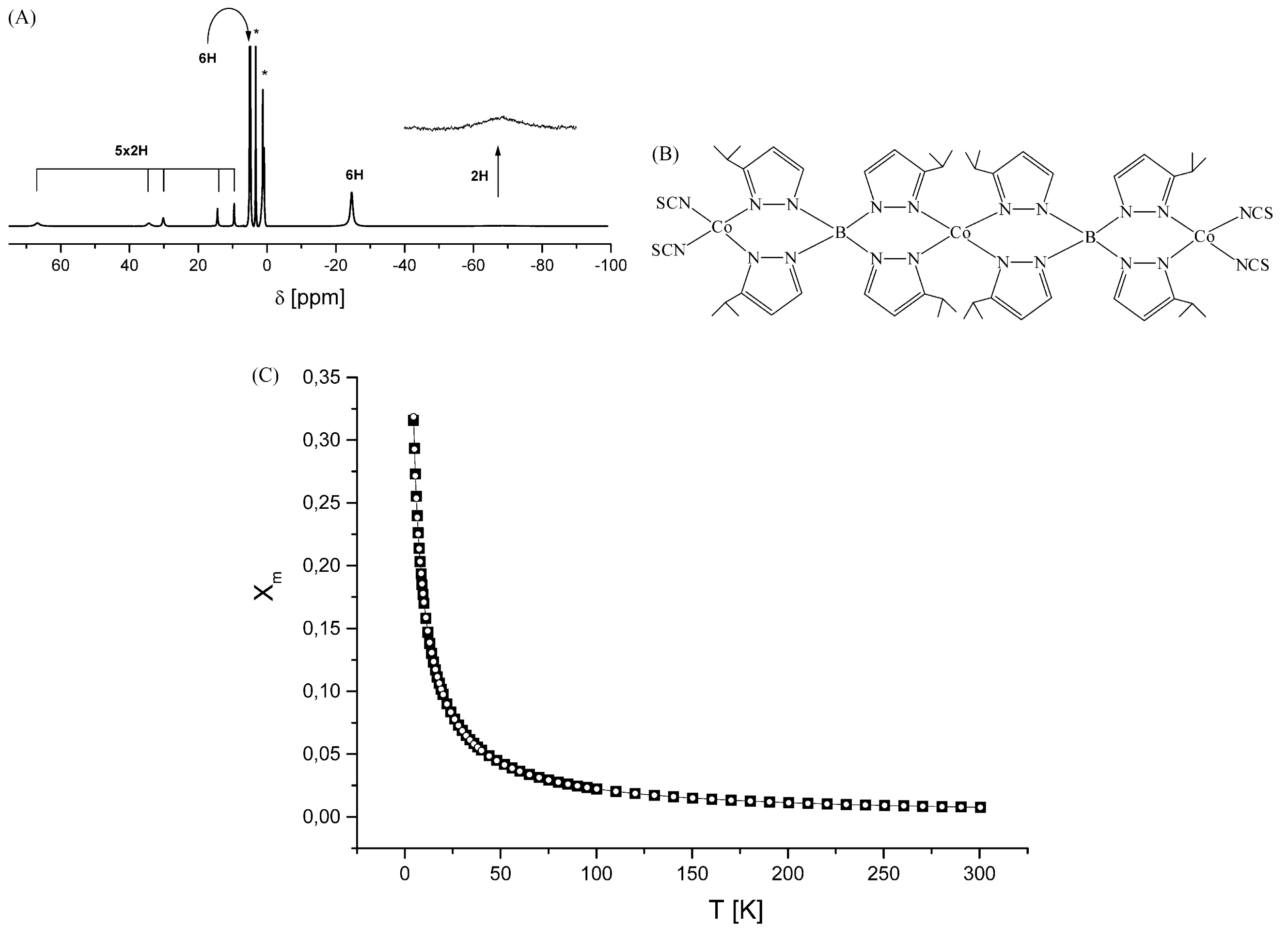

Fig. 5. (A) ^{1}H NMR spectrum of **6** in methanol-d_4 The residual peaks from the solvent are labelled with asterisks. (B) Schematic formula of **6**. (C) Magnetic susceptibility measurements data (black squares). The value of ZFS parameter $D = -7.9(1)$ cm^{-1}, $g_\perp = 2.835(2)$, and $g_\| = 2.010(2)$ have been fitted (open circles) according to the formulas given in [20] with $R = 0.1516 \times 10^{-4}$.

Cu(II) or Ni(II), and X = NCS$^-$ or Cl$^-$) in every case led to a simple ligand L exchange with formation of mixtures of LMX complexes, some of which were characterized here structurally as pure products obtained in separate synthetic pathways. Using the above mentioned procedure in some cases we were able to grow the crystals containing for instance **2** doped with LCuCl, as could be concluded from accordance of unit cell parameters obtained from crystallographic measurement and the EPR spectrum of a copper(II) center doped isostructurally into the lattice of **2**.

4. Supplementary material

Crystallographic data for the structures reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 199835 for compound **1**, CCDC No. 199836 for **2**, CCDC No. 199837 for **3** and CCDC No. 199838 for **4**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 UNION Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

Authors kindly acknowledge financial support from the State Committee for Scientific Research KBN (Grant PBZ-KBN 15/T09/99/01D—J. Kisała and S. Wołowiec and Grant number 3 T09A 05219—Z. Ciunik, T. Ruman and S. Wołowiec).

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