

Syntheses and crystal structures of divalent complexes with a new hexadentate ligand derived from 1,4,7-triazacyclononane ‡

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Mononuclear complexes [Ni(lbptcn)][ClO₄]₂, [Cu(lbptcn)][ClO₄]₂ and [Fe(lbptcn)][ClO₄]₂ with a new hexadentate ligand 1-(6-methyl-2-pyridylmethyl)-4,7-bis(2-pyridylmethyl)-1,4,7-triazacyclononane (lbptcn) having unequivalent pendant arms have been prepared and characterized by electronic spectroscopy and X-ray crystallography.

Triazamacrocyclic ligands containing pendant arms on each nitrogen atom form very stable complexes with various transition-metal ions.^{1–3} It has been reported that 1,4,7-tris(2-pyridylmethyl)-1,4,7-triazacyclononane (tptcn) and 1,5,9-tris(2-pyridylmethyl)-1,5,9-triazacyclododecane (tptcd) with three equivalent '2-pyridylmethyl' pendant groups give a low-spin and a high-spin iron(II) complex, respectively, and that the difference in the spin-states is related to the flexibility of the macrocyclic main frame.⁴ In another approach to control the spin-states of iron(II) complexes, we prepared 1-(6-methyl-2-pyridylmethyl)-4,7-bis(2-pyridylmethyl)-1,4,7-triazacyclononane (lbptcn) in which one of the pendant arms of tptcn is replaced by a bulky '6-methyl-2-pyridylmethyl' group. In this communication, the syntheses and structural properties of the divalent transition-metal complexes, [Ni(lbptcn)][ClO₄]₂ **1**, [Cu(lbptcn)][ClO₄]₂ **2** and [Fe(lbptcn)][ClO₄]₂ **3** are presented.

The compounds were obtained as follows. The ligand lbptcn was prepared as its Li complex [Li(lbptcn)]ClO₄: 1-(6-methyl-2-pyridylmethyl)-1,4,7-triazacyclononane was prepared as an oil by the reaction of 1,4,7-triazatricyclo[2.2.2.1]decane⁵ with 1-chloromethyl-6-methyl-2-pyridine in tetrahydrofuran (thf), followed by succeeding deprotection reactions under alkaline conditions. Under vigorous stirring 2-chloromethylpyridine hydrochloride (3.3 g, 20 mmol) in water (25 cm³) was added dropwise to a mixture of the resulting oil (2.3 g, 10 mmol) in dichloromethane (25 cm³), aqueous NaOH (1.6 g in 15 cm³) and tetraethylammonium chloride (0.04 g, 0.2 mmol). The reaction mixture was stirred vigorously for 5 d at room temperature. The separated organic phase was dried over Na₂SO₄. The solvent was removed under vacuum. The resulting oil was extracted with boiling light petroleum (b.p. 30–70 °C) (50 cm³) and the extract was concentrated to 10 cm³. To this solution, LiClO₄ (1.6 g, 10 mmol) in thf (50 cm³) was added. The white crystals were collected by suction and recrystallized from CHCl₃–thf. Yield 2.2 g (42%) (Found: C, 56.90; H, 5.95; N, 15.70. C₂₅H₃₂ClLiN₆O₄ requires C, 57.40; H, 6.15; N, 16.05%). *m/z*

(FAB) 423 ([Li(lbptcn)]⁺). Complex **1**: a methanol solution (5 cm³) of Ni(ClO₄)₂·6H₂O (0.073 g, 0.2 mmol) was added to a solution of [Li(lbptcn)]ClO₄ (0.104 g, 0.2 mmol) in methanol (5 cm³). The mixture was stirred for 10 min. The precipitated violet crystals were collected by suction and recrystallized from acetonitrile–ethanol. Yield 0.110 g (82%) (Found: C, 44.50; H, 4.75; N, 12.45. C₂₅H₃₂Cl₂N₆NiO₈ requires C, 44.55; H, 4.80; N, 12.45%). *m/z* (FAB) 573 {[Ni(lbptcn)ClO₄]⁺}. Complex **2**: this complex was prepared in the same way as that of **1** using CuCl₂·2H₂O (0.034 g, 0.2 mmol). The complex was obtained as blue crystals. Yield 0.106 g (78%) (Found: C, 44.15; H, 4.55; N, 12.30. C₂₅H₃₂Cl₂CuN₆O₈ requires C, 44.20; H, 4.75; N, 12.40%). *m/z* (FAB) 578 {[Cu(lbptcn)ClO₄]⁺}. Complex **3**: this complex was prepared in the same way as that of **1** using Fe(ClO₄)₂·6H₂O (0.073 g, 0.2 mmol). The complex was obtained as dark brown crystals. Yield 0.094 g (70%) (Found: C, 44.70; H, 4.65; N, 12.50%. C₂₅H₃₂Cl₂FeN₆O₈ requires C, 44.70; H, 4.80; N, 12.50%). *m/z* (FAB) 571 {[Fe(lbptcn)ClO₄]⁺}.

The crystal structures for the complex dications of **1** and **2** are illustrated in Figs. 1 and 2. In complex **1**, the ligand coordinates to the Ni^{II} ion through six nitrogen atoms, forming a distorted octahedral geometry with an elongated N(2)–Ni–N(6) axis. The axial Ni–N(6) bond length [2.199(6) Å] is considerably longer than the other axial Ni–N(2) bond [2.117(6) Å]. The Ni–N (equatorial) bond distances are in the range of 2.058(5)–2.090(6) Å much shorter than the axial Ni–N(6) bond. The Ni–N (amine) bond distances are similar to those found for other nickel(II) complexes with 1,4,7-triazacyclononane analogs.^{3,7} It is clear that the 6-methyl-2-pyridylmethyl pendant arm reduces the donor strength of N(6) due to the steric repulsion of the bulky methyl group attached to the pyridine ring.⁸

The copper(II) ion in **2** is well described as having a square-pyramidal configuration with N(1), N(3), N(4) and N(5) in the equatorial plane and an apical Cu–N(2) distance of 2.287(5) Å. The Cu···N(6) distance of 2.465(6) Å is too long to be considered as a chemical bond, however, the existence of a weak interaction with the Cu^{II} center might be suggested. The Cu–N(2) distance to the apical nitrogen is also remarkably long, 2.287(5) Å, especially as this nitrogen atom is one of the donor atoms from the 1,4,7-triazacyclononane ring. In this respect the

§ Crystal data and data collection parameters. Complex **1**: C₂₅H₃₂Cl₂N₆NiO₈, *M* = 674.17, triclinic, *a* = 11.235(5), *b* = 12.831(2), *c* = 10.953(2) Å, α = 97.27(1), β = 110.55(2), γ = 95.50(3)°, *U* = 1430.1(7) Å³, space group *P*1̄ (no. 2), *Z* = 2, *T* = 296 ± 1 K, μ(Mo–Kα) = 9.25 cm^{−1}, transmission factors 0.91–1.00, 6914 reflections measured, 3415 unique reflections with *I* > 3.00σ(*I*), final value for *R* = 0.068. Complex **2**: C₂₅H₃₂Cl₂CuN₆O₈, *M* = 679.02, triclinic, *a* = 10.47(1), *b* = 16.433(6), *c* = 9.723(4) Å, α = 92.20(3), β = 114.40(5), γ = 107.93(6)°, *U* = 1422(2) Å³, space group *P*1̄ (no. 2), *Z* = 2, *T* = 296 ± 1 K, μ(Mo–Kα) = 10.15 cm^{−1}, transmission factors 0.91–1.00, 6907 reflections measured, 3283 unique reflections with *I* > 3.00σ(*I*), final value for *R* = 0.052. CCDC reference number 186/905.

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‡ Non-SI units employed: μ_B ≈ 9.274 × 10^{−24} J T^{−1}, G = 10^{−4} T.

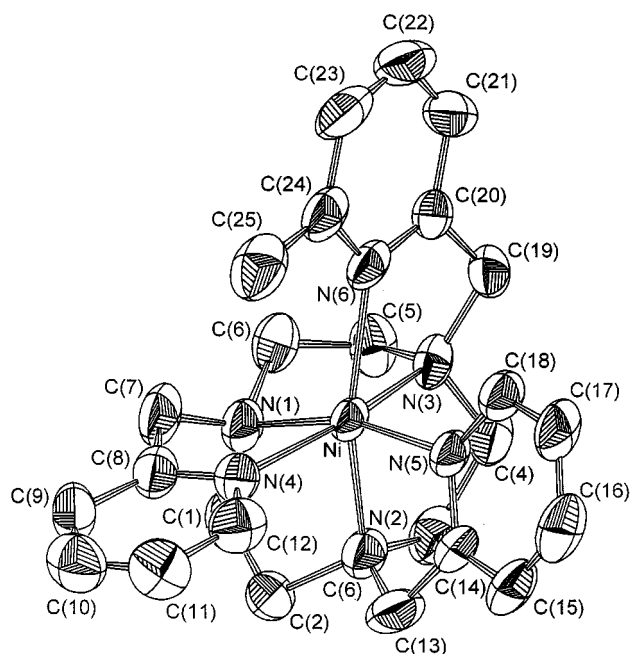


Fig. 1 An ORTEP⁶ drawing for the complex cation of **1**. Selected bond distances (Å) and angles (°): Ni–N(1) 2.090(6), Ni–N(2) 2.117(6), Ni–N(3) 2.082(6), Ni–N(4) 2.089(6), Ni–N(5) 2.058(5), Ni–N(6) 2.199(6); N(1)–Ni–N(3) 83.9(2), N(1)–Ni–N(4) 80.1(2), N(3)–Ni–N(5) 99.4(2), N(4)–Ni–N(5) 96.0(2), N(2)–Ni–N(6) 163.3(2). Deviations from the least-square plane N(1)–N(3)–N(4)–N(5) (Å): Ni –0.1694, N(2) 1.9385, N(6) –2.3240

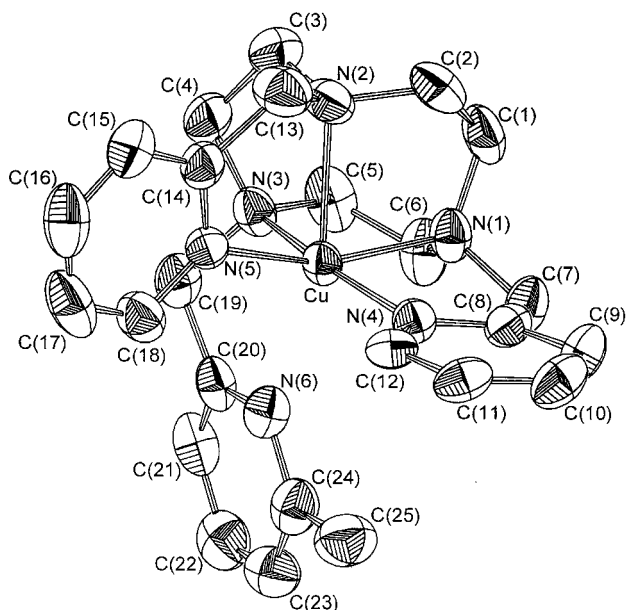


Fig. 2 An ORTEP drawing for the complex cation of **2**. Selected bond distances (Å) and angles (°): Cu–N(1) 2.052(5), Cu–N(2) 2.287(5), Cu–N(3) 2.061(5), Cu–N(4) 2.020(5), Cu–N(5) 2.047(5), Cu...N(6) 2.465(6); N(1)–Cu–N(3) 85.0(2), N(1)–Cu–N(5) 80.9(2), N(3)–Cu–N(5) 98.3(2), N(4)–Cu–N(5) 94.9(2). Deviations from the least-square plane N(1)–N(3)–N(4)–N(5) (Å): Cu –0.1396, N(2) 2.0974, N(6) –2.5589

structure is quite similar to the structure of $[\text{Pd}(\text{tptcn})]^{2+}$ where the Pd^{II} ion has the expected square-planar co-ordination.²

X-Ray structural analysis for complex **3** is in progress.⁹ According to the preliminary results for **3**, the complex cations

in **1** and **3** can be regarded as isostructural. Therefore, it is assumed that the ligand-field splitting of **3** is less than that of $[\text{Fe}(\text{tptcn})][\text{ClO}_4]_2$. Actually, the spin equilibrium behavior with a T_c value of ca. 200 K was observed in the magnetic measurement for complex **3** (80–309 K). In the temperature range 80–200 K, magnetic moments are nearly constant (ca. $0.5 \mu_B$) and the dominant state is low-spin over this range. Above 200 K, the magnetic moments gradually increase with temperature. The limit of the observation was $1.24 \mu_B$ at 309 K, but the moments seem to increase above this temperature. Further details about the spin equilibria system for complex **3** will be discussed with the structural information in a later publication.⁹

The electronic spectra of the nickel(II) complexes can be used to estimate the ligand-field parameter for the corresponding iron(II) complexes in spin-equilibria systems. The UV/VIS electronic absorption spectrum of complex **1** shows four band maxima at λ/nm (H_2O) 264 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 11 151), 534 (17), 830 (32) and 891 (30) with shoulders at 270 and 280. The band arising from the ${}^3\text{T}_{2g}$ term splits into two bands (${}^3\text{B}_{2g}$ and ${}^3\text{E}_g$) caused by the axial distortion. These bands are located between those of $[\text{Ni}(\text{tptcn})]^{2+}$ (818 nm) and $[\text{Ni}(\text{tptcd})]^{2+}$ (930 nm)¹⁰ suggesting an intermediate ligand-field strength. Thus, the lbptcn ligand can give the appropriate ligand-field splitting for the Fe^{II} spin-equilibrium system.

The frozen-glass ESR spectrum of complex **2** is consistent with the solid-state structure suggesting that this geometry is retained in solution. The spectrum can be fitted to two g values $g_z = 2.243$, $g_{xy} = 2.057$ showing that the geometry is close to axial and with the unpaired electron in a $d_{x^2-y^2}$ symmetrical orbital. Superhyperfine splitting patterns (nine lines) are observed both at the low-field g_z hyperfine component ($A_z = 9.5$ G) and in the g_{xy} region ($A_{xy} = 12.0$ G). The observation of nine lines shows that four nearly equivalent nitrogen atoms are bound to the copper center.

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