

Synthesis and crystal structure of a triangular nickel(II) complex with the shortest imine-based rigid ligand

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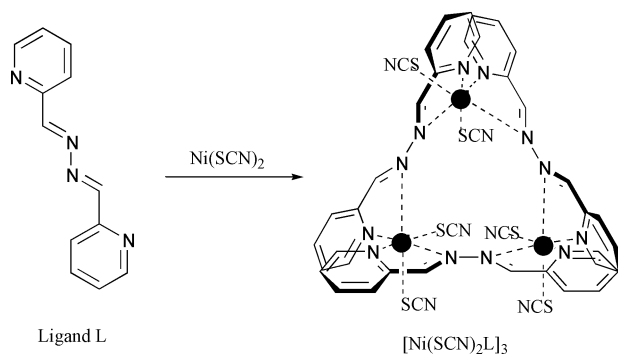
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A novel triangular complex $[\text{Ni}(\text{SCN})_2\text{L}]_3$ was generated via self-assembly from $\text{Ni}(\text{SCN})_2$ and the readily prepared imine-based ligand L, $(\text{C}_5\text{H}_4\text{N})\text{-CH=N-N=CH-(C}_5\text{H}_4\text{N)}$, by appropriately adjusting the coordination conditions of the metal center.

Transition metal-directed self-assembly has become a powerful methodology for the construction of different supramolecular architectures^{1–5} with unusual and interesting properties. In order to design species presenting specific structural and functional features, it is of great importance to establish the rules by which control of the self-assembly process can be achieved through chemical programming of suitable components and assembling algorithms.

In sharp contrast to the numerous examples of supramolecular architectures reported, the number of metal-containing molecular triangles is “surprisingly small”,⁶ mainly due to the rarity of suitable building blocks with proper turning angles. A triangle with a 60° turning angle at the metal does not exist due to the impossibility of generating such an angle in a metal fragment with a commonly occurring coordination number. Virtually all molecular triangles with metal entities at the corners display 80–90° angles.⁷ Among them, only several triangles assembled from oligo-bidentate ligands have been reported,^{6c,8} in which the metal entities at the corners are all in tetrahedral coordination geometries. We reasoned that if the *cis*-positions of the octahedral geometry were occupied by two strongly coordinating thiocyanates, the four empty positions should be coordinated by two bis-bidentate ligands and such a conformation of the metal center is more suitable for the construction of a triangular complex. Herein, we incorporate the bis-bidentate ligand L, $(\text{C}_5\text{H}_4\text{N})\text{-CH=N-N=CH-(C}_5\text{H}_4\text{N)}$, with $\text{Ni}(\text{SCN})_2$ to create a triangular architecture with the metal centers in *cis*-octahedral coordination geometries. To the best of our knowledge, no molecular triangles using metal ions with an octahedral coordination geometry as the corners have been documented in the literature.

Ligand L was obtained in a high yield by simply mixing hydrazine hydrate and 2-pyridinecarboxaldehyde in a methanol solution.⁹ Reaction of L with $\text{Ni}(\text{SCN})_2$ (molar ratio = 1 : 1) in a methanol–acetonitrile solution gave the corresponding Ni(II) trimer in high yield (Scheme 1). † Elemental analysis revealed



the formation of a complex of the form $[\text{ML}(\text{SCN})_2]_3$. ESI-MS in acetonitrile–methanol solution showed one strong peak corresponding to $[\text{Ni}_3\text{L}_3(\text{SCN})_3]^{3+}$ ($m/z = 326.1$), which is consistent with the formation of a triangular structure. The single-crystal X-ray structural analysis ‡ (Fig. 1) shows a triangular

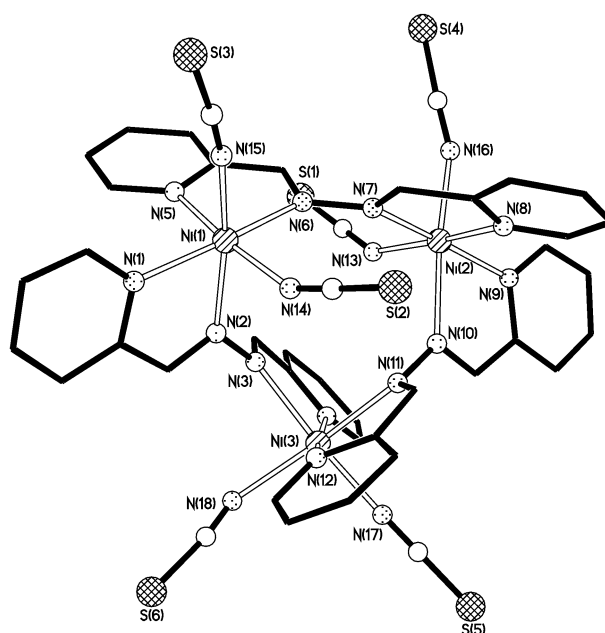


Fig. 1 Molecular structure of $[\text{Ni}_3\text{L}_3(\text{SCN})_6]$. Selected bond lengths (Å): Ni(1)–N(1), 2.082(8); Ni(1)–N(2), 2.168(8); Ni(1)–N(5), 2.097(7); Ni(1)–N(6), 2.101(7); Ni(1)–N(14), 2.013(7); Ni(1)–N(15), 2.013(7); Ni(2)–N(7), 2.130(7); Ni(2)–N(8), 2.047(7); Ni(2)–N(9), 2.046(9); Ni(2)–N(10), 2.178(9); Ni(2)–N(13), 2.035(7); Ni(2)–N(16), 2.014(8); Ni(3)–N(3), 2.114(8); Ni(3)–N(4), 2.074(9); Ni(3)–N(11), 2.147(9); Ni(3)–N(12), 2.074(9); Ni(3)–N(17), 1.981(8); Ni(3)–N(18), 2.178(11).

structure with the ligands linking the three metal centers overlapping in a progressive manner: in each ligand, one pyridyl-imine binding unit lies above, whilst the other pyridyl-imine binding unit lies below the averaged plane of the molecule. The average distance between the three metal centers is *ca.* 4.95 Å. Each metal center has a distorted *cis*-octahedral geometry to permit the triangular arrangement. The dihedral angles between the two pyridyl-imine binding sites coordinated to one nickel center are 75.6, 84.2 and 86.6°, respectively. The Ni–N (pyridyl) distances in the range of 2.046(9)–2.097(7) Å and Ni–N (CH=N) distances in the range of 2.101(7)–2.178(9) Å. The SCN groups point outwards giving the molecule an outer diameter of 13 Å and a height of 9 Å. The shortest distance between the center of the triangle and the atoms of the ligands is *ca.* 2.0 Å, indicating that the cavity at the center of the triangle is too small to include any guests. Coordination to the metal center causes internuclear twisting between the pyridyl-imine units with twist angles for two pyridyl-imine sites in one ligand of 53.7, 76.4 and 89.2°, respectively. It is apparent that

the C=N–N=C bond allows a substantial degree of rotation, which is important for creating this triangle and thus provides opportunities for the construction of other supramolecular architectures. To test the structural purity of this complex, powder X-ray diffraction analysis was undertaken. As shown in Fig. 2, the powder X-ray diffraction pattern of the triangular

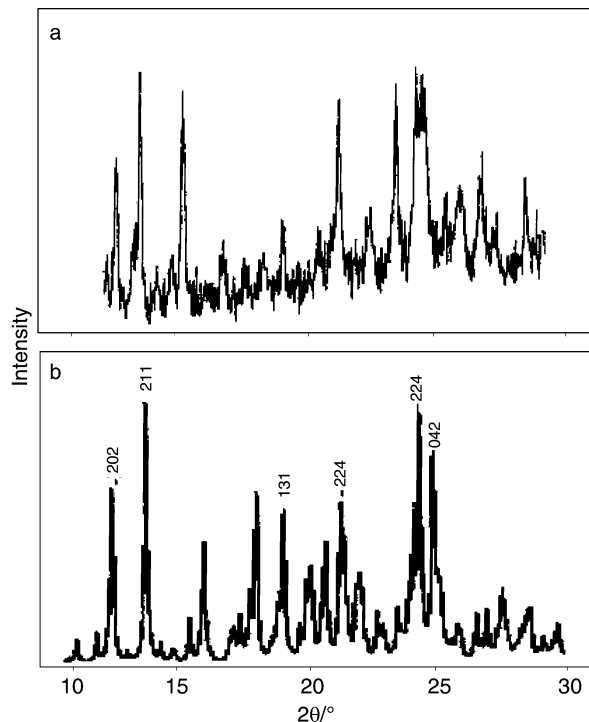


Fig. 2 (a) The powder X-ray diffraction pattern of the triangular complex. (b) The powder X-ray diffraction pattern calculated from the single-crystal data of the triangular complex.

nickel complex is quite similar to that calculated from the single crystal data. This observation demonstrates that the powder and single crystal structure data are isomorphous.

In the absence of SCN⁻ anions, interaction of one equivalent of ligand with one equivalent of Ni(BF₄)₂ in ethanol yields a triple helicate with the formula [Ni₂L₃][BF₄]₄.[‡] Crystal structure analysis[§] (Fig. 3) shows that each nickel center is bound to three pyridylimine units to attain a pseudo-octahedral coordination geometry with the pyridine nitrogen atoms situated *trans*

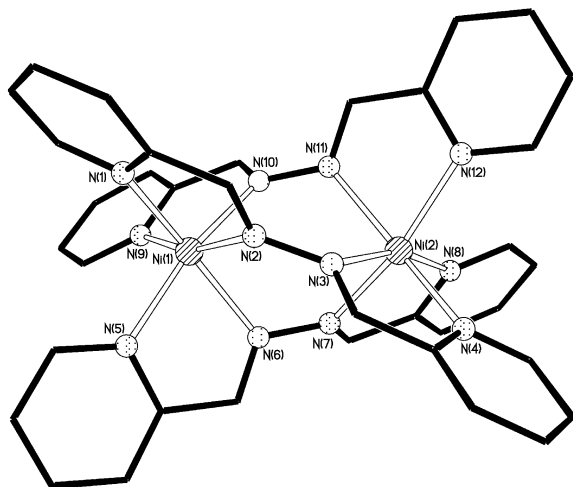


Fig. 3 Molecular structure of [Ni₂L₃(BF₄)₄]. Selected bond lengths (Å): Ni(1)–N(1), 2.093(4); Ni(1)–N(2), 2.078(4); Ni(1)–N(5), 2.072(4); Ni(1)–N(6), 2.083(4); Ni(1)–N(9), 2.078(4); Ni(1)–N(10), 2.078(4); Ni(2)–N(3), 2.077(4); Ni(2)–N(4), 2.089(4); Ni(2)–N(7), 2.089(4); Ni(2)–N(8), 2.090(4); Ni(2)–N(11), 2.079(4); Ni(2)–N(12), 2.097(4).

to the imine nitrogen atoms of another different ligand. The twist angles of two binding sites in one nickel center are *ca.* 79° on average. Each ligand bridges two nickel centers with the metal...metal separation being 3.78 Å and the bridging mode of each ligand facilitated by a twist angle of *ca.* 51° between two pyridylimine units.

In summary, we have assembled a discrete molecular triangle using a rigid ligand, L, by controlling the coordination conformation. It is clear that the *cis*-octahedral arrangement of the metal center for such a bis-bidentate ligand makes it suitable to act as the corner of a molecular triangle and the ability to accept various dihedral angles between the two pyridylimine fragments also plays an important role for the incorporation of metal ions into the present rigid helical triangular arrangement. An understanding of the factors controlling the assembly of different supramolecular architectures is essential in the field of metallosupramolecular chemistry and this communication reinforces the importance of the geometric coordination requirements of metallic ions and the ligand structure in controlling the outcome of assembly processes.

Acknowledgements

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Notes and references

[†] [NiL(SCN)₂]₃: To an absolute methanol solution (5 mL) of NiCl₂·6H₂O (0.07 g, 0.3 mmol) was added an absolute methanol solution (10 mL) of KSCN (0.06 g, 0.6 mmol). The solution was stirred for 10 min and the resulting KCl precipitate was then filtered off from the deep blue solution. The resultant solution was then added to an acetonitrile solution (15 mL) of L (0.06 g, 0.3 mmol) in a dropwise manner with heating. The filtrate was allowed to stand in air at room temperature for several days, yielding reddish yellow crystals (0.11 g, 0.09 mmol, yield 90%) which were dried over P₂O₅ in a vacuum. Anal. calc. for (C₄₂H₃₀S₆N₁₈Ni₃)(CH₃CN)₂: C, 44.6; H, 2.9; N, 22.6. Found: C, 44.5; H, 3.1; N, 22.4%. IR (KBr, cm⁻¹): ν = 3423.9m, 2082.0vs, 1627.6m, 1590.4m, 1567.1w, 1477.0m, 1441.1m, 1302.8m, 1219.5m, 1157.1w, 1105.1w, 1051.1w, 1019.4m, 776.0m.

[‡] [Ni₂L₃][BF₄]₄: The ligand L (0.13 g, 0.6 mmol) and Ni(BF₄)₂ (0.09 g, 0.4 mmol) were mixed in ethanol (25 mL), and after stirring for half an hour the red yellow solid (0.18 g, 0.16 mmol, yield 80%) obtained was filtered off, washed with ethanol (20 mL) and Et₂O (5 mL), and dried under vacuum. Anal. calc. for C₃₆H₃₀B₄F₁₆N₁₂Ni₂: C, 39.5; H, 2.8; N, 15.4. Found: C, 39.6; H, 2.9; N, 15.4%. IR (KBr, cm⁻¹): ν = 3385.0m, 3024.5w, 1625.9m, 1591.9m, 1564.9m, 1477.9m, 1447.4m, 1373.3m, 1303.2m, 1083.9s, 781.1m. Recrystallization of the complex from an acetonitrile solution, by diffusion of diethyl ether, afforded crystals suitable for X-ray crystallographic analysis.

[§] Crystal data for Ni₂L₃(SCN)₆: C₄₆H₃₆S₆N₂₀Ni₃, *M* = 1237.44, monoclinic, *P*2(1)/*n*, *a* = 16.671(5), *b* = 15.275(5), *c* = 22.405(6) Å, β = 101.00(2)°, *V* = 5601(3) Å³, *T* = 293(2) K, *Z* = 4, μ(Mo-Kα) = 1.275 mm⁻¹, 22705 reflections measured, 7312 independent reflections (*R*_{int} = 0.1623), *R* = 0.0726, *wR* = 0.1216 for 3343 observed reflections [*I* > 2σ(*I*)].

For Ni₂L₃(BF₄)₄: C₄₀H₃₆N₁₄Ni₂B₄F₁₆, *M* = 1177.49, monoclinic, *P*2(1)/*c*, *a* = 13.177(2), *b* = 20.579(3), *c* = 20.410(3) Å, β = 96.88(1)°, *V* = 5494.6(16) Å³, *T* = 293(2) K, *Z* = 4, μ(Mo-Kα) = 0.782 mm⁻¹, 27961 reflections measured, 9648 independent reflections (*R*_{int} = 0.079), *R* = 0.067, *wR* = 0.182 for 5889 observed reflections [*I* > 2σ(*I*)]. Intensities of the two complexes were collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using the SMART and SAINT programs.¹⁰ The structures were solved by direct methods and refined on *F*² using full-matrix least-squares methods and the SHELXTL program.¹¹ Non-hydrogen atoms were refined anisotropically and hydrogen atoms were localized in their calculated positions and refined using a riding model. CCDC reference numbers 172865 and 178249. See <http://www.rsc.org/suppdata/dt/b/1/b109526a/> for crystallographic data in CIF or other electronic format.

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