

# Encapsulation of nitrate by a self-assembled tetranickel(II) complex†

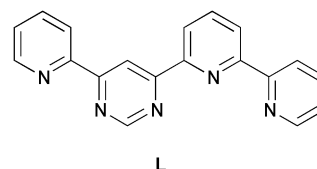
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Received (in Montpellier, France) 30th January 2002, Accepted 8th March 2002

First published as an Advance Article on the web 18th April 2002

Reaction of nickel(II) nitrate with the ditopic ligand 4-[6-(2-pyridyl)-2-pyridyl]-6-(2-pyridyl)pyrimidine (**L**) leads to a self-assembled tetranuclear  $[2 \times 2]$  grid complex, which encapsulates  $\text{NO}_3^-$  with short van der Waals contact distances.



Metal-directed self-assembly is emerging as one of the most promising approaches to the generation of container-like molecules with a wide variety of cavity sizes and shapes. Structurally characterized polynuclear complexes of this type that can trap an inorganic anion in the central cavity by electrostatic attractions are rare. Examples include a “molecular square” assembled from four nickel(II) ions and tetrazine derived ligands with a tetrafluoroborate guest,<sup>1</sup> molecular  $\text{Pd}^{\text{II}}/\text{Pt}^{\text{II}}$  triangles containing  $\text{ClO}_4^-$  or  $\text{PF}_6^-$ ,<sup>2</sup> and a grid-like  $\text{Fe}^{\text{II}}_2\text{Ru}^{\text{II}}_2$  complex of a 4,6-bis(2,2'-bipyridyl)pyrimidine ligand that encloses chloride in its central cavity.<sup>3</sup> We have also demonstrated the usefulness of polynuclear metal complexes as ionophores for the construction of anion-selective electrodes.<sup>4</sup>

The selective recognition of and selective chemosensors for nitrate are of particular interest since this ion is implicated in groundwater contamination and present in high concentration in certain waste waters. Most reported receptors for nitrate are based on H-bonding interactions.<sup>5</sup> Funnel-shaped tri- and hexanuclear  $\text{Pd}^{\text{II}}/\text{Pt}^{\text{II}}$  complexes that incorporate nitrate at the bottom of the funnel by very weak coordinative bonds, but at the same time enclose larger ions such as  $\text{PF}_6^-$  and  $\text{ClO}_4^-$ ,<sup>6</sup> have been structurally characterized. A metal-assembled molecular container that sharply discriminates nitrate from larger anions should encapsulate the anion more extensively with short van der Waals contact distances.

Here we describe a tetranickel(II)  $[2 \times 2]$  grid complex that is a “tight-fit” receptor for nitrate.

The tendency of 4,6-bis(2,2'-bipyridyl)pyrimidine type ligands to form tetranuclear  $[2 \times 2]$  grid complexes with octahedral metal ions is well-documented.<sup>7</sup> We have recently described the synthesis and characterisation of a related ligand **L** having one tpy- and one bpy-like coordination site.<sup>8</sup>

Reaction of **L** with  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (1 : 1) in an acetone–water mixture at room temperature resulted in formation of a precipitate, which was recrystallized from DMSO by addition of a solution of  $\text{NaClO}_4$  in acetone. The brown crystals had the composition  $[\text{Ni}_4\text{L}_4(\text{DMSO})_2(\text{H}_2\text{O})_2](\text{NO}_3)(\text{ClO}_4)_7 \cdot 4\text{DMSO} \cdot 6\text{H}_2\text{O}$  (**1**).

The  $\text{C}_2$  symmetric tetranuclear complex cation contains two crystallographically independent nickel ions. The four nitrogen atoms of two different molecules of **L**, and two oxygen atoms of *cis*-orientated DMSO and  $\text{H}_2\text{O}$  molecules, respectively, constitute the coordination environment of Ni(1). Angles and distances of the Ni(1) polyhedron are consistent with a distorted octahedral coordination (see Table 1). Ni(2) is coordinated by six nitrogen atoms of the tridentate sites of two molecules of **L**. The linear and angular variations around Ni(2) are more pronounced  $[1.983(4)–2.136(4) \text{ \AA}$  and  $78.29(17)–104.59(17)^\circ$ ; Table 1]. Four nickel atoms are arranged at the corners of an almost ideal square  $[\text{Ni}(1) \cdots \text{Ni}(2) 6.170 \text{ \AA}$ ,  $\text{Ni}(1) \cdots \text{Ni}(2a) 6.235 \text{ \AA}$ ,  $\text{Ni}(1) \cdots \text{Ni}(2) \cdots \text{Ni}(1a) = 88.4^\circ$ ,  $\text{Ni}(2) \cdots \text{Ni}(1) \cdots \text{Ni}(2a) 91.6^\circ$ ; deviations from the mean plane average to  $0.0414 \text{ \AA}$ .

A  $\text{NO}_3^-$  anion is trapped in the central cavity of **1**, which is hydrophobic since formed by heterocyclic aromatic rings of the ligands. The molecular plane of  $\text{NO}_3^-$  is coplanar to one ligand pair and perpendicular to the second [Fig. 1(b)]. The close fit of nitrate is confirmed by several short van der Waals contacts of nitrate oxygens with the host:  $\text{O}(4) \cdots \text{C}(25) 2.814 \text{ \AA}$ ,  $\text{O}(4a) \cdots \text{C}(27) 2.812 \text{ \AA}$ ,  $\text{O}(4) \cdots \text{C}(7) 2.714 \text{ \AA}$ ,  $\text{O}(3) \cdots \text{C}(7) 3.101 \text{ \AA}$ . Isotropic thermal displacement parameters of nitrate N and O atoms are smaller than those of most C and N atoms of **L**.

Literature values for the sum of O and  $\text{sp}^2$  C van der Waals radii are on the order of  $3.1 \text{ \AA}$ .<sup>9</sup> It is obvious (Fig. 1) that the mobility of nitrate within the cage is highly restricted since the two pairs of **L** are not coplanar (interplane angles are  $38.2^\circ$  and  $33.4^\circ$ ) but display a roof-shaped arrangement. Binding of even slightly larger anions should be disfavoured since anion host contacts would be unfavourably short. Anion binding studies in solution, such as by NMR spectroscopy, were complicated by the paramagnetism of  $\text{Ni}^{\text{II}}$  and by the limited stability of the tetranuclear complex (it was not possible to detect the intact complex by electrospray or MALDI mass spectrometry). Attempts to crystallize complexes from **L** and nickel(II) chloride, acetate and perchlorate failed.

Both variation of metal ion (size) and ligand structure allow a fine tuning of cavity size in this type of complexes. In a related tetranuclear  $\text{Fe}^{\text{II}}_2\text{Ru}^{\text{II}}_2$  grid complex with a 4,6-bis(2,2'-bipyridyl)pyrimidine ligand, a chloride ion was trapped in the central cavity.<sup>3</sup> In this case, both anion and cavity are smaller. The average  $\text{M} \cdots \text{M}$  distance is  $6.11 \text{ \AA}$  compared with an  $\text{Ni} \cdots \text{Ni}$  distance of  $6.20 \text{ \AA}$  in **1**. We could also crystallize a Co(II) complex  $[\text{Co}_4\text{L}_4(\text{DMF})_4](\text{NO}_3)(\text{ClO}_4)_7$  with encapsulated nitrate; the structure is similar to that of **1** but was not included due to disorder problems. The  $\text{Co} \cdots \text{Co}$  distances

† Dedicated to Prof. Dr Gottfried Huttner on the occasion of his 65th birthday.

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**Table 1** Bond lengths (Å) and angles (°) for  $[\text{Ni}_4\text{L}_4(\text{DMSO})_2(\text{H}_2\text{O})_2](\text{NO}_3)(\text{ClO}_4)_7 \cdot 4\text{DMSO} \cdot 6\text{H}_2\text{O}$  (**1**)

Ni(1)–O(1)	2.042(4)
Ni(1)–N(6)	2.064(5)
Ni(1)–O(2)	2.074(4)
Ni(1)–N(1)	2.074(5)
Ni(1)–N(2)	2.093(4)
Ni(1)–N(7)	2.103(4)
Ni(2)–N(4)	1.983(4)
Ni(2)–N(9a)	1.985(4)
Ni(2)–N(10a)	2.078(4)
Ni(2)–N(5)	2.094(5)
Ni(2)–N(3)	2.113(4)
Ni(2)–N(8a)	2.136(4)
O(1)–Ni(1)–N(6)	88.69(17)
O(1)–Ni(1)–O(2)	87.92(18)
N(6)–Ni(1)–O(2)	91.81(18)
O(1)–Ni(1)–N(1)	95.09(17)
N(6)–Ni(1)–N(1)	173.79(17)
O(2)–Ni(1)–N(1)	93.24(19)
O(1)–Ni(1)–N(2)	89.55(17)
N(6)–Ni(1)–N(2)	96.87(17)
O(2)–Ni(1)–N(2)	170.90(17)
N(1)–Ni(1)–N(2)	78.27(17)
O(1)–Ni(1)–N(7)	167.25(16)
N(6)–Ni(1)–N(7)	79.07(16)
O(2)–Ni(1)–N(7)	88.92(17)
N(1)–Ni(1)–N(7)	97.42(16)
N(2)–Ni(1)–N(7)	95.38(15)
N(4)–Ni(2)–N(9a)	174.92(17)
N(4)–Ni(2)–N(10a)	104.59(17)
N(9a)–Ni(2)–N(10a)	79.91(17)
N(4)–Ni(2)–N(5)	79.6(2)
N(9a)–Ni(2)–N(5)	102.75(19)
N(10a)–Ni(2)–N(5)	92.5(2)
N(4)–Ni(2)–N(3)	78.29(17)
N(9a)–Ni(2)–N(3)	99.57(16)
N(10a)–Ni(2)–N(3)	89.47(17)
N(5)–Ni(2)–N(3)	157.59(18)
N(4)–Ni(2)–N(8a)	97.28(15)
N(9a)–Ni(2)–N(8a)	78.15(16)
N(10a)–Ni(2)–N(8a)	158.02(16)
N(5)–Ni(2)–N(8a)	93.49(18)
N(3)–Ni(2)–N(8a)	92.92(16)

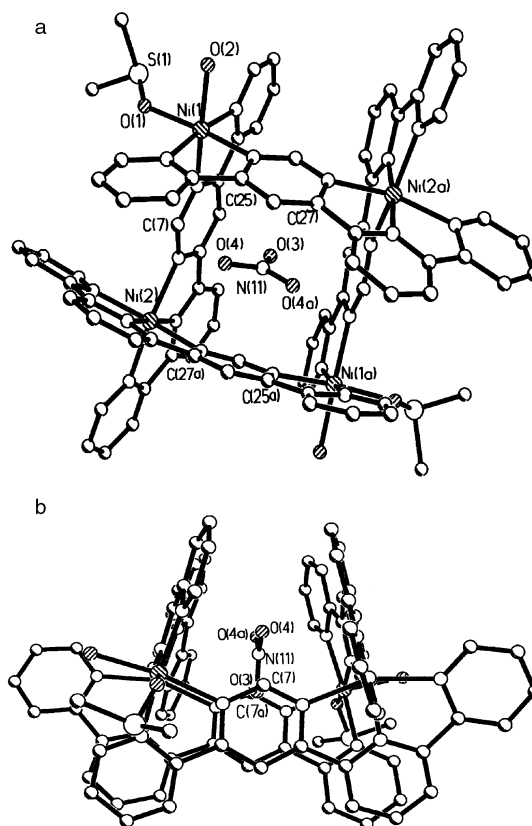
average to 6.25 Å. This is significantly shorter than in a related tetracobalt(II) complex of a 4,6-bis(2,2'-bipyridyl)pyrimidine ligand (6.49 Å).<sup>7a,e</sup> Expansion of the cage is an effect of the additional pyridyl donor of the ligand in the latter system, which distorts the coordination sphere and increases the distance of the two pyrimidine-bridged Co ions. Additionally, the presence of a methyl substituent at pyrimidine-C2 may contribute to the larger metal-metal separation.

The use of **1** or related complexes as ionophores for the development of anion sensors is an interesting perspective. Coordination of appropriate coligands to the free metal sites might be a straightforward approach to the functionalization of  $\text{L}_4\text{M}_4$  for specific applications (e.g., with lipophilic groups for incorporation into anion-selective liquid-membrane electrodes).<sup>4</sup>

## Experimental

### Synthesis

To a stirred solution of **L** (20 mg, 64 mmol) in acetone (5 mL) was added a solution of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (18 mg, 64 mmol) in water (5 mL). A precipitate formed, which was filtered, washed with acetone and dried. The complex crystallized from DMSO upon layering with a solution of  $\text{NaClO}_4$  in acetone to give  $[\text{Ni}_4\text{L}_4(\text{DMSO})_2(\text{H}_2\text{O})_2](\text{NO}_3)(\text{ClO}_4)_7 \cdot 4\text{DMSO} \cdot 6\text{H}_2\text{O}$ . Yield: 17.6 mg, 11%. Anal. calcd for  $\text{C}_{88}\text{H}_{104}\text{N}_{21}\text{S}_6\text{O}_{45}\text{Ni}_4\text{Cl}_7$ : H, 3.68; C, 37.07; N, 10.32; found: H, 3.73; C, 36.87; N, 10.56%.



**Fig. 1** Different views of the structure of the complex cation of **1** with enclosed nitrate ion [distances: N(11)–O(3) 1.240, N(11)–O(4) 1.263 Å]. H atoms are omitted for clarity.

### Crystallography

Unique sets and intensity data were collected at 173 K with a Bruker SMART diffractometer (Mo-K $\alpha$  radiation,  $\lambda = 0.71073$  Å, graphite monochromator,  $\omega$  scan). Empirical absorption corrections (multi-scans) were applied.<sup>10</sup> The structure was solved by direct methods (SHELXS86)<sup>11</sup> and refined by least-squares methods based on  $F^2$  with all measured reflections (SHELX97).<sup>12</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions.

$[\text{Ni}_4\text{L}_4(\text{DMSO})_2(\text{H}_2\text{O})_2](\text{NO}_3)(\text{ClO}_4)_7 \cdot 4\text{DMSO} \cdot 6\text{H}_2\text{O}$ :  $\text{C}_{88}\text{H}_{104}\text{N}_{21}\text{S}_6\text{O}_{45}\text{Ni}_4\text{Cl}_7$ ,  $M = 2851.28$ , brown needles, crystal size  $0.52 \times 0.24 \times 0.17$  mm; monoclinic, space group  $C2/c$ ;  $a = 27.3760(6)$ ,  $b = 12.7124(2)$ ,  $c = 34.4278(7)$  Å,  $\beta = 100.957(1)^\circ$ ,  $U = 11763.0(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.610$  g cm<sup>−3</sup>,  $\mu = 0.992$  mm<sup>−1</sup>,  $R_1 = 0.0858$  ( $I > 2\sigma$ ),  $wR_2 = 0.2806$  for all data.

CCDC reference number 169244. See <http://www.rsc.org/suppdata/nj/b2/b201132h/> for crystallographic data in CIF or other electronic format.

### Acknowledgements

This work was funded by the Deutsche Forschungsgemeinschaft (Gerhard Hess-Programm) and supported by the Fonds der Chemischen Industrie.

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