A Nonanuclear Ni^{II} Cluster with a 1,2,4-Triazolo[4,3-*a*]pyrimidine Derivative

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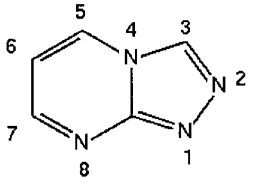
This article describes the nickel cluster compound [Ni_9-$\mathbf{L}_8(OH)_6(NH_3)_4(H_2O)_8](NO_3)_4\cdot 8H_2O$, where **L** represents the anionic form of the ligand 7,8-dihydro-1,2,4-triazolo[4,3-*a*]-pyrimidin-7-one. The structure of the cation of this compound is rather complicated, involving nine metal atoms, eight bridging organic ligands, bridging hydroxyl groups, and terminal ammonia and water molecules. The central nickel atom lies on a crystallographic inversion centre, while the other eight define two disorted "cubane-like" [$Ni_4(OH)_3]^{5+}$ subclusters. Each subcluster is linked to the central atom by three triple bridging organic ligands. Additional **L** ligands bridge two external metal atoms in each subcluster. The variation with temperature of the magnetic susceptibility of the compound indicates the presence of both ferromagnetic and antiferromagnetic interactions; the latter is predominant.

Introduction

The condensation of a 1,2,4-triazole ring and another of a pyrimidine molecule may give rise to four different families of heterocyclic, bicyclic compounds. Among these, the thermodynamically more stable, and hence the most studied ones, are 1,2,4-triazolo[1,5-*a*]pyrimidines, which bind to metal atoms in a number of different ways to give rise to different structural motifs.[1] More bonding possibilities arise if the positions of the nitrogen atoms in the heterocycle are interchanged, defining the isomeric families 1,2,4-triazolo[1,5-*c*]pyrimidines,[2] 1,2,4-triazolo[4,3-*a*]pyrimidines,[3] and 1,2,4-triazolo[4,3-*c*]pyrimidines.[4] These are far less thermodynamically stable, and isomerisation processes (Dimroth rearrangement) are possible on heating, possibly catalysed by acidic or basic pH conditions,[5] so working with any of these families is potentially more difficult.

Our research group has just started to explore the coordination possibilities of one of these families, namely the 1,2,4-triazolo[4,3-*a*]pyrimidines, which differ from the 1,5-*a* derivatives in the position of one of the nitrogen atoms of the triazole ring, which is separated as far as possible from the pyrimidine ring, is subject to less steric hindrance, and is contiguous to the other external imidazole nitrogen atom. The skeleton of this family of compounds, as well as the numbering scheme used for identifying their atoms, is shown in Scheme 1.



Scheme 1.

The first metal complex of one of these derivatives (with an exocyclic oxo group in position 7) is a silver dimer recently published by us.[6] In this complex the ligand bridges the metal atoms through the two nitrogen atoms of the triazole ring. Following this research line, we have started to explore the behaviour of this ligand towards metal atoms of the first transition series. We used a pH high enough to deprotonate the nitrogen atom of the pyrimidine ring, which usually carries the acidic proton (N8), so that it could become a new binding site, and we have been successful in obtaining a crystalline solid with nickel(II) in ammonia aqueous solution. The solid is a nonanuclear cluster, and the metal atoms are bridged by organic ligands and hydroxyl groups, which transmit both ferromagnetic and antiferromagnetic interactions.

Results and Discussion

The main feature of the crystal structure of the title compound is the presence of centrosymmetric clusters built from nine nickel atoms, eight **L** ligands, six hydroxo groups, four ammonia molecules and eight water molecules. Discrete clusters with nine metal atoms are not very frequently observed, nevertheless, a number of nonanuclear nickel compounds have been described with different bridging li-

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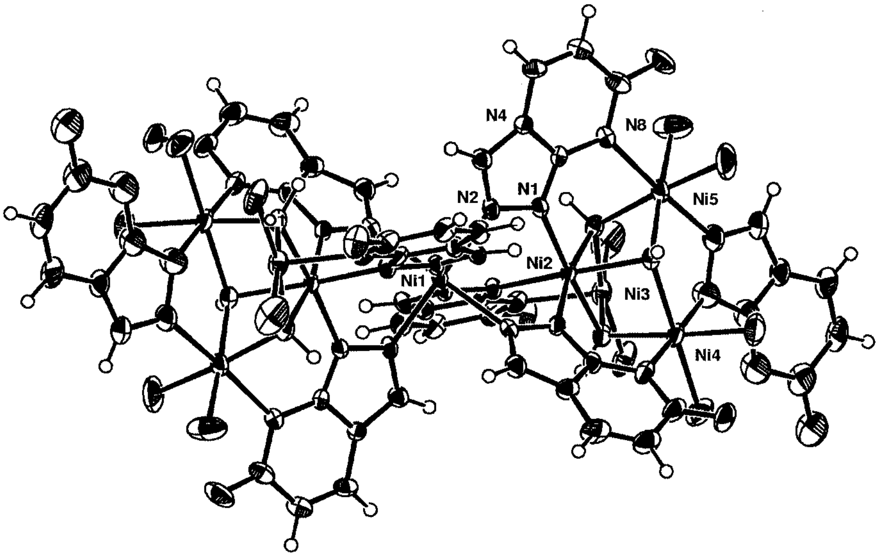

Figure 1. Molecular structure of the $[Ni_9L_8(OH)_6(NH_3)_4(H_2O)_8]^{4+}$ cluster according to X-ray analysis. Both halves are related by a crystallographic inversion centre. Non-hydrogen atoms are represented by ellipsoids at the 50% probability level. Only the metal atoms on one side of the central metal atom, and the nitrogen atoms of one of the organic ligands have been labelled for clarity.

gands and different topologies,[7,8] some of them involving hydroxo groups.[9,10]

Two crystallographically independent clusters are present in the unit cell, but they are chemically equivalent and subsequently will be described jointly. The quality of the crystal data is not high enough for a very accurate structural determination and, in fact, some ambiguity remains in the assignment of the water and ammonia molecules. Additionally, some of the nitrate counteranions and interstitial water molecules are poorly defined and have been introduced into the structural model with partial occupancy (see Exp. Sect.).

A view of one of these clusters is shown in Figure 1. The nickel atom placed at the centre of the cluster (Ni1) lies on a crystallographic inversion centre, and is octahedrally coordinated to by the nitrogen atom in position 2 of the six different **L** moieties. The environment of this atom has approximate D_{3d} symmetry, and the Ni1···N2 distances are in the range of 2.07–2.11 Å.

On each side of this central atom, a $Ni_4(OH)_3$ subcluster is placed. Nickel and oxygen atoms in this subcluster form a cubane-like backbone with one of the vertices missing. Each hydroxyl group bridges three nickel atoms, one of these (Ni2) is close to the centre of the cluster (distance Ni1···Ni2, 3.65–3.66 Å) and is linked to the three hydroxyl groups, whereas the other three (Ni3, Ni4 and Ni5, which we will refer to as the "external" nickel atoms from here onward) are linked to only two hydroxyl groups each. The "cubane" is heavily distorted with the external metal atoms, which are adjacent to the empty vertex,separated outwards from their ideal positions. This is reflected in the bond angles around the hydroxyl oxygen atoms, which are in the 92.0–96.0° range if Ni2 is considered, and in the 113.9–125.5° range if it is not. The distortion of the "cubane" is also seen in the intermetallic distances, 2.97–3.03 Å for Ni2···Ni(external), and 3.36···3.64 Å for Ni(external)···Ni(external). Nickel···oxygen distances (the edges of the cube) are in the range of 2.04–2.08 Å for Ni2–OH, and 2.00–2.06 Å for Ni(external)–OH bonds.

Several examples of structures containing Ni_4O_4 "cubane-like" clusters can be found in the bibliography; in most of them, the oxygen atoms belong to methoxy groups,[11] or to more complex organic molecules,[12] but surprisingly, very few have bridging hydroxo groups.[13] The Ni–O distances in these species are around 2.0–2.1 Å, and the cubes are usually quite distorted with angles above and below 90° around the oxygen and nickel atoms, respectively; the actual degree of distortion clearly is conditioned by the presence of other ligands. On the other hand, the only examples of "incomplete" Ni_4O_3 cubanes that we have found are those linked by extra oxygen bridges to other metal atoms, thus they are just portions of more complex Ni–O skeletons.[14]

The six organic ligands coordinated to the central metal atom join it to both cubane-like subclusters (three ligands to each), and act as triple bridges through the nitrogen atoms at positions 2, 1 and 8: N2 is linked to Ni1 as previously said, N1 is linked to Ni2 and N8 is linked to Ni3, Ni4 or Ni5. Atom Ni2 is then coordinated to the three hydroxyl oxygen atoms, and the N1 atom of the three organic ligands in an approximate C_{3v} environment.

An additional triazolopyrimidine ligand is present on each side of the cluster bridging two of the "external" metal atoms (namely Ni4 and Ni5) through the two nitrogen atoms of the triazole ring (N1 to Ni4 and N2 to Ni5). The coordination environments of the three external nickel atoms are completed by two water or ammonia molecules: those attached to Ni3 have been assigned as ammonia, and those attached to Ni4 and Ni5 as water, although these as-

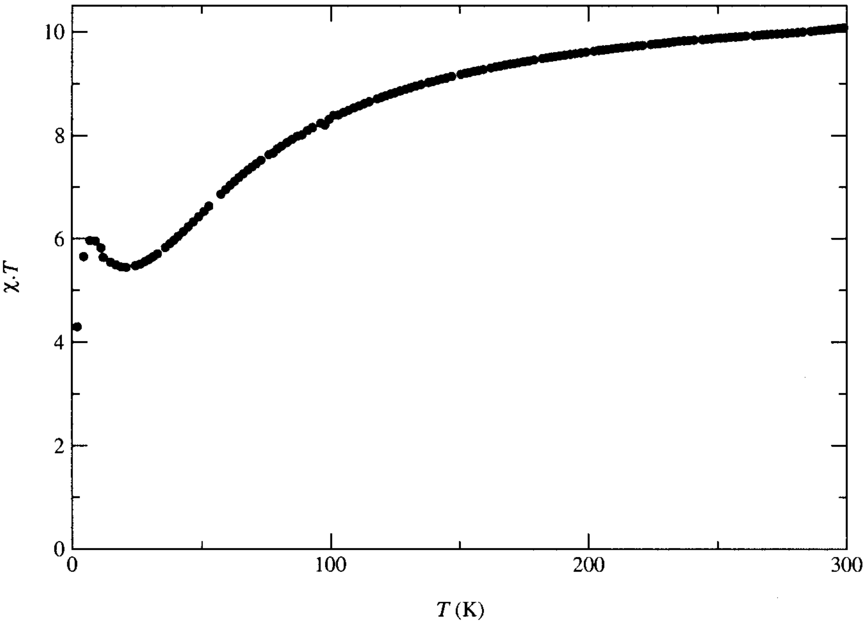

Figure 2. Variation with temperature of the magnetic susceptibility of the title compound, represented as a χT vs. T curve (χ in emu per mol of clusters).

signments are far from being certain (see Exp. Sect.). An octahedral environment is completed in this way for Ni4 and Ni5, whereas a not very frequently observed square-pyramidal environment is found for Ni3. For this atom, the sixth position is not available since the above-mentioned organic ligand attached to Ni4 and Ni5 is orientated in that direction preventing either water or ammonia from occupying that position.

If a comparison is made between the geometries of all the organic ligands in the title compound and those in the previously mentioned silver dimeric complex,[6] in which the ligand is in the neutral form, the most noticeable differences are the lengthening of the C7–O7 bond (from 1.221 to 1.24–1.30 Å) and, probably more significantly, the closing of the C7–N8–C8 angle (from 122.0 to 116–117°), a consequence of the N8 deprotonation. This is true for both triple bridging and double bridging ligands, supporting the idea that all are anionic. The non-coordinated N8 atom of the double bridging ligand forms an intramolecular hydrogen bond with one of the water molecules attached to Ni4 [distances 2.743(9) and 2.862(11) Å].

The magnetic susceptibility of the compound has been measured in the 2–300 K temperature range. The results are shown in Figure 2, in the form of a χT vs. T plot. The product χT steadily decreases with T reaching a minimum at 20 K. It then increases reaching a maximum at 8 K before decreasing sharply at very low temperature. This behaviour indicates that both ferromagnetic and antiferromagnetic interactions are taking place, the latter being predominant. The decrease at very low T may be attributed to antiferromagnetic intermolecular interactions. After normalising the χT value where $T \to \infty$ to 1, the normalised values at different temperatures are 0.89 (300 K), 0.48 (minimum at 19 K), 0.53 (maximum at 8 K), and 0.38 (at 2 K, the lowest temperature used).

Due to the low symmetry of the cluster, with five structurally different types of metal atoms, a large number of different coupling constants are expected (at least ten, even if those between atoms on different sides of the central metal atom are neglected). Deriving an expression for χ as a function of temperature from the resulting complex spin Hamiltonian, and fitting the many adjustable parameters to the experimental data, would be a very difficult task (if possible at all), so the values of the coupling constants have not been determined, and not even their signs (that indicate which pairs interact ferromagnetically and which antiferromagnetically) have been deduced.

The data above 50 K obey the Curie–Weiss law very well. The linear fitting of $1/\chi$ vs. T yields a value of –35.4(3) K for θ (somehow quantifying the strong antiferromagnetic interactions that prevail in this region), and an effective magnetic moment per nickel atom as $T \to \infty$ of 3.166(1) B.M. ($g = 2.24$).

Experimental Section

Reagents were obtained from standard commercial sources; organic reagents were of synthetic grade and inorganic reagents of analytical grade. The ligand 7,8-dihydro-1,2,4-triazolo[4,3-*a*]pyrimidin-7-one hemihydrate was synthesised as described previously.[6,15] Microanalysis of C, H and N were performed with a Fisons Instruments EA-1008 analyser. Magnetic susceptibility measurements were made with a SQUID MPMS-XL Quantum Design magnetometer, at the Universidad Complutense (Madrid), using a magnetic field of 1.00 T. Diamagnetic corrections were applied.

Synthesis of the Nickel Complex: Nickel chloride hexahydrate (0.238 g, 1 mmol) and 7,8-dihydro-1,2,4-triazolo[4,3-*a*]pyrimidin-7-one (LH) hemihydrate (0.145 g, 1 mmol) were dissolved in separate aliquots of 1 M aqueous ammonia (10 mL). Both solutions were mixed, and the resulting blue solution was left to stand so that the excess ammonia was eliminated. Deep blue crystals of the title compound, suitable for X-ray work, were obtained. Elemental analysis of $C_{40}H_{74}N_{40}Ni_9O_{42}$ $[Ni_9\mathbf{L}_8(OH)_6(NH_3)_4(H_2O)_8](NO_3)_4\cdot 8H_2O$ (2315.5): calcd. C 20.75, H 3.22, N 24.20; found C 20.7, H 3.5, N 24.2.

Crystallography: Data for a single crystal of the title complex (dimensions, $0.28\times0.15\times0.06$ mm) were collected at room temperature with a Bruker SMART APEX CCD system with Mo-K_α radiation (λ = 0.7107 Å). Data were corrected for absorption (multiscan, transmission range, 0.6667–0.8775). The structure was solved by Direct Methods. According to the elemental analysis data, four ammonia molecules are present per cluster, but the quality of the crystal data does not allow us to unambiguously distinguish between water and ammonia molecules. The Fourier peaks attached to the square-pyramidal Ni atom (Ni3) have been assigned as ammonia because of the coordination polyhedron of this atom, and because more favourable thermal parameters are obtained in this way, but of course, this assignment cannot be taken as granted (other assignments or possible disordered situations cannot be discarded). The structure was refined anisotropically (except for hydrogen atoms, disordered water molecules and two poorly defined nitrate anions) on F^2 using SHELXL-97.[16] Hydrogen atoms of the heterocycle and of the hydroxyl groups were placed at ideal positions, and those of the water and ammonia molecules were ignored. Isotropic thermal parameters for all H atoms were fixed to 1.2 times the equivalent isotropic thermal parameter of their parent atoms.

Crystal Data for $[Ni_9\mathbf{L}_8(OH)_6(NH_3)_4(H_2O)_8](NO_3)_4\cdot 8H_2O$: Triclinic, space group $P\bar{1}$, a = 11.0481(5), b = 18.2700(8), c = 21.3860(9) Å, α = 65.966(1) β = 83.287(1), γ = 86.043(1)°, V = 3914.4(3) Å^3, Z = 2, D_{calc} = 1.963 Mg/m^{-3}, μ = 2.237 mm^{-1}, 45862 reflections (17819 unique) collected (θ range 1.25–28.45°), wR_2 = 0.2454, $R[12041$ data with $I > 2\sigma(I)]$ = 0.0808.

CCDC-265692 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

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