Crystal and Molecular Structure of a Novel Mixed-spin Binuclear Nickel(II) Complex with *N,N',N'',N'''*-Tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane†

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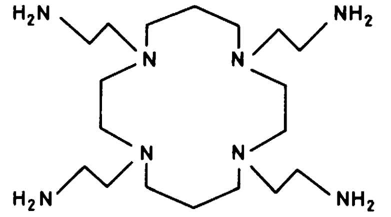
The crystal structure of $[Ni_2(taec)Cl]Cl_3{\cdot}H_2O$ was determined by the single-crystal *X*-ray diffraction method, where taec is *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane. The $[Ni_2(taec)Cl]^{3+}$ cation has a novel binuclear structure in which one of the nickel ions is co-ordinated by a square-planar N_4 donor set and the other by a distorted square-pyramidal N_4Cl donor set.

We have recently reported the synthesis and characterization of a series of binuclear metal (Cu^{II}, Ni^{II}, and Co^{II}) complexes of an octadentate ligand, *N,N',N'',N'''*-tetrakis(2-aminoethyl)-1,4,8,11-tetra-azacyclotetradecane (taec).[1–3] Among these complexes, the nickel(II) complex, $Ni_2(taec)Cl_4{\cdot}H_2O$, is interesting, since it was assumed to be a mixed-spin binuclear complex containing a low-spin Ni^{II} and a high-spin Ni^{II} on the basis of the spectral and magnetic data. Although some mixed-spin nickel(II) binuclear complexes have been reported, all of them have a binucleating ligand with inequivalent co-ordination sites.[4–6] Therefore, if our assumption is correct, the present complex is a novel type of mixed-spin complex having a symmetric binucleating ligand. Thus, in this study, we have carried out the *X*-ray analysis of $Ni_2(taec)Cl_4{\cdot}H_2O$ in order to elucidate the structure.



taec

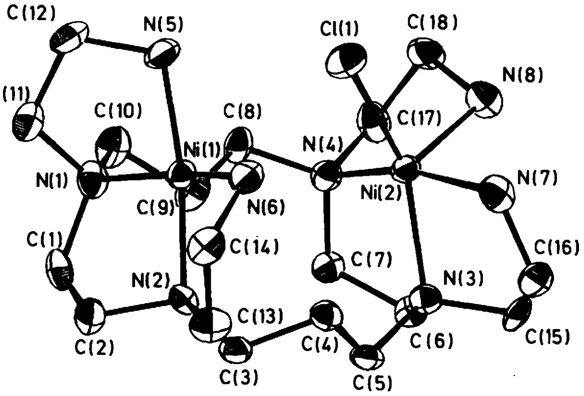


Figure. A perspective view of the $[Ni_2(taec)Cl]^{3+}$ cation

Table 1. Molecular dimensions in the metal co-ordination spheres of $[Ni_2(taec)Cl]Cl_3{\cdot}H_2O$; distances in Å, angles in °

Ni(1)–N(1)	1.907(7)	Ni(2)–N(3)	2.096(6)
Ni(1)–N(2)	1.978(6)	Ni(2)–N(4)	2.183(6)
Ni(1)–N(5)	1.903(7)	Ni(2)–N(7)	2.121(7)
Ni(1)–N(6)	1.931(7)	Ni(2)–N(8)	2.014(7)
		Ni(2)–Cl(1)	2.289(2)
N(1)–Ni(1)–N(2)	90.3(3)	N(4)–Ni(2)–N(8)	84.1(3)
N(1)–Ni(1)–N(5)	86.6(3)	N(7)–Ni(2)–N(8)	96.0(3)
N(2)–Ni(1)–N(6)	85.1(3)	Cl(1)–Ni(2)–N(3)	151.1(2)
N(5)–Ni(1)–N(6)	95.7(3)	Cl(1)–Ni(2)–N(4)	103.8(2)
N(3)–Ni(2)–N(4)	83.7(2)	Cl(1)–Ni(2)–N(7)	91.7(2)
N(3)–Ni(2)–N(7)	81.5(2)	Cl(1)–Ni(2)–N(8)	99.3(2)

Results and Discussion

The crystal consists of binuclear complex cations, $[Ni_2(taec)Cl]^{3+}$, chloride ions, and water molecules of crystallization. A perspective view of $[Ni_2(taec)Cl]^{3+}$ is shown in the Figure. Molecular dimensions are listed in Table 1. The taec ligand incorporates two nickel ions with a separation Ni(1) ··· Ni(2) of 4.427(1) Å. Two co-ordination modes are known for the taec ligand: one is the *trans* III form[7] concerning the cyclam (1,4,8,11-tetra-azacyclotetradecane) ring (chair form) as found for $Cu_2(taec)(ClO_4)_4$ and the other is the *trans* I form (boat form)[7] as found for $Cu_2(taec)Br(ClO_4)_3$.[1,2] In the case of $Ni_2(taec)Cl_4{\cdot}H_2O$, taec assumes the latter form, though the co-ordination environments of the two nickel ions are inequivalent. One of the nickel ions, Ni(1), has a square-planar co-ordination, with two nitrogen atoms of the cyclam moiety and two nitrogen atoms of the pendant 2-aminoethyl groups, whereas the other, Ni(2), has a square-pyramidal co-ordination, with the remaining four nitrogen atoms of taec and the chloride ion in the apical position. The Ni(1)–N bond lengths [1.903(7)—1.978(6) Å] are typical of those found in low-spin, square-planar nickel(II) complexes with N_4 macrocyclic ligands.[8] The Ni(2)–N bond lengths [2.014(7)—

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 2. Atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	3 290(1)	3 422(1)	2 734(1)	C(4)	2 205(3)	4 312(5)	4 916(9)
Ni(2)	1 335(1)	3 262(1)	2 805(1)	C(5)	1 640(3)	4 894(5)	4 932(9)
Cl(1)	2 008(1)	2 204(2)	1 844(3)	C(6)	769(3)	5 090(5)	3 264(9)
Cl(2)	2 552(1)	2 191(2)	−2 665(3)	C(7)	1 096(3)	5 253(5)	1 754(8)
Cl(3)	254(1)	869(2)	3 865(4)	C(8)	1 764(3)	4 422(6)	−4(8)
Cl(4)	−664(1)	3 858(1)	2 757(3)	C(9)	2 315(4)	4 658(6)	885(10)
N(1)	3 388(3)	4 348(5)	1 163(8)	C(10)	2 892(4)	4 458(6)	35(9)
N(2)	3 300(3)	4 436(4)	4 301(7)	C(11)	3 920(4)	3 937(6)	378(10)
N(3)	1 114(3)	4 400(4)	4 242(7)	C(12)	3 798(4)	2 914(6)	−41(10)
N(4)	1 250(3)	4 324(4)	999(7)	C(13)	3 557(4)	4 028(6)	5 764(9)
N(5)	3 407(3)	2 491(5)	1 186(7)	C(14)	3 838(4)	3 080(6)	5 412(9)
N(6)	3 409(3)	2 566(4)	4 431(8)	C(15)	724(3)	3 963(6)	5 429(8)
N(7)	1 280(3)	2 504(5)	4 896(8)	C(16)	1 025(4)	3 100(6)	6 132(8)
N(8)	592(3)	2 718(5)	1 887(8)	C(17)	717(4)	3 998(6)	104(10)
C(1)	3 556(3)	5 272(5)	1 925(10)	C(18)	640(4)	2 934(6)	221(9)
C(2)	3 737(4)	5 092(6)	3 548(11)	O	−17(4)	1 257(7)	7 491(12)
C(3)	2 738(3)	4 958(5)	4 665(9)				

2.183(6) Å] are longer than any of the Ni(1)–N distances and fall in the range of those for high-spin nickel(II) complexes with N_4 macrocyclic ligands.[8] The Ni(2)–Cl(1) distance is 2.289(2) Å, and Cl(1) forms hydrogen bonds with the pendant amino groups [N(5)···Cl(1) 3.242(7), N(7)···Cl(1) 3.165(8), and N(8)···Cl(1) 3.284(7) Å]. These hydrogen bonds may contribute to the stabilization of the Ni(2)–Cl(1) bonding.

The unco-ordinated chloride ions, Cl(3) and Cl(4), are located in the vicinity of the pendant amino groups of taec by hydrogen bonding [N(7)···Cl(3) 3.390(7), N(8)···Cl(3) 3.216(8), N(8)···Cl(4) 3.349(7), and N(6) ($\frac{1}{2} + x$, $\frac{1}{2} - y$, z)···Cl(4) 3.249(7) Å]. The Cl(2) ion does not participate in any hydrogen bond, because the closest interatomic distance is C(12)···Cl(2) 3.775(9) Å. The water molecule is not co-ordinated to the nickel ion but is bound to Cl(3) by a hydrogen bond [O···Cl(3) 3.278(11) Å].

Thus, it has been revealed that $Ni_2(taec)Cl_4{\cdot}H_2O$ is a mixed-spin binuclear nickel(II) complex as was assumed from the spectral and magnetic data.

Experimental

Crystals were prepared as described in ref. 2.

Crystal Data.—$C_{18}H_{46}Cl_4N_8Ni_2O$, $M = 649.8$, orthorhombic, $a = 22.620(3)$, $b = 14.065(2)$, $c = 8.751(1)$ Å, $U = 2\,784(1)$ Å^3 (by least-squares refinement on diffractometer angles for 40 reflections in the range $20 < 2\theta < 30°$, $\lambda = 0.710\,73$ Å), space group $Pna2_1$, $D_m = 1.55$, $Z = 4$, $D_c = 1.55$ g cm^{-3}, $F(000) = 1\,368$. Green needles, dimensions 0.23 × 0.25 × 0.45 mm, μ(Mo-K_α) = 17.7 cm^{-1}.

Data Collection and Processing.—Rigaku AFC-5 diffractometer, ω—2θ mode with ω scan width = $1.40 + 0.50 \tan\theta$, ω scan speed 3.0° min^{-1}, graphite-monochromated Mo-K_α radiation; 5 961 unique reflections, of which 4 061 had $|F_o| > 3\sigma(|F_o|)$. No absorption correction was applied.

Structure Analysis and Refinement.—By direct method (Ni atoms) followed by normal heavy-atom procedures. Hydrogen atoms (except for those bound to the water oxygen atom) from difference map. Block-diagonal least squares with anisotropic thermal parameters for non-hydrogen atoms and isotropic for hydrogen atoms. Function minimized was $\Sigma w(|F_o| - k|F_c|)^2$, with $w = (11.9 + |F_o| + 0.007|F_o|^2)^{-1}$. Final R and R' values were 0.062, 0.086. All computations were performed on a HITAC M-680H computer of the Computer Centre of the Institute for Molecular Science using the UNICS-III programs.[9] The final atomic co-ordinates are given in Table 2.

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