

## Hexaaquanickel(II) disulfato(1,4,8,11-tetraazacyclotetradecane)nickelate(II) dihydrate

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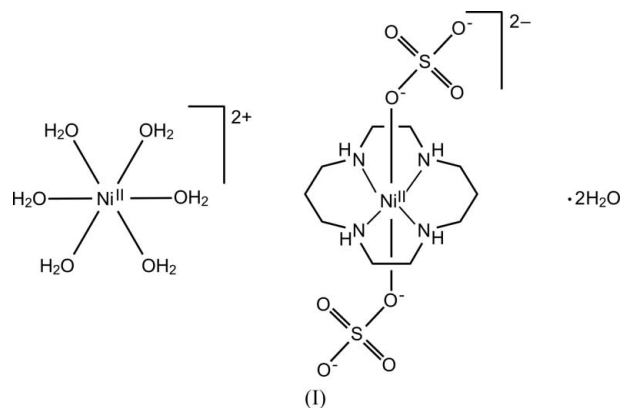
The title compound,  $[\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{SO}_4)_2(\text{C}_{10}\text{H}_{24}\text{N}_4)] \cdot 2\text{H}_2\text{O}$ , is an unusual compound in that it is composed of a hexaaqua complex, formally a dication, and a mixed-donor complex (four N and two O atoms), formally a dianion, with substantial charge separation between the two nickel centres (6.536 Å). The homoleptic dication complex consists of the weaker-field ligands, whilst the dianion retains the coordination of all the higher-field donors. Both nickel ions are located at centres of symmetry. This rare compound is placed in the context of previously reported structures which emphasizes its peculiarity.

## Comment

Macrocyclic complexes of transition metals are a common sight in the coordination chemistry landscape, being chemically distinct from related noncyclic chelates. The versatile and useful ligand cyclam (1,4,8,11-tetraazacyclotetradecane) has been extensively studied because of its employment with many different metals and across a range of applications including enzyme modelling, metal ion extraction, medicine and a broad range of catalysis. Reflecting such interest, at the time of writing there are 374 cyclam structures and 1694 cyclam derivatives [with a cyclam backbone, but additional functional groups (including further cyclam units) attached at any point on the ring] in the Cambridge Structural Database (CSD; Allen, 2002; updates to November 2009); of these, 514 contain Ni.

The structure reported here, (I), however, is notably distinct from the plethora of reported structures because of the presence of two nickel centres in very different chemical environments: one (Ni1) is coordinated by a tetraaza macrocycle and two mutually *trans* sulfate groups, and the second (Ni2) is found in a homoleptic hexaaqua environment. What makes this complex remarkable is the substantial charge

separation between two quite distant Ni centres: while Ni2 carries only weak-field water ligands, the Ni1 atom retains the coordination of the higher-field-strength cyclam as well as both the dianionic  $\text{SO}_4^{2-}$  groups.



Examination of the proton affinity of the ligands, a useful proxy for  $\sigma$ -donor ability (Senn *et al.*, 2000), emphasizes the curiosity of this arrangement. Water has a proton affinity of 691 kJ mol<sup>-1</sup> (Hunter & Lias, 2010) and whilst we do not have an exact value for the proton affinity of cyclam, related amine compounds all have values between 900 and 1000 kJ mol<sup>-1</sup> (Hunter & Lias, 2010). The sulfate anion has a proton affinity above 1800 kJ mol<sup>-1</sup> (House & Kemper, 1987). It would seem reasonable that a balanced distribution of the available ligand-donated electron density across each Ni<sup>II</sup> centre would provide for stabilization of both, but rather we see the weaker  $\sigma$ -donor ligands (the six water ligands) coordinate to one Ni while the more powerful donors congregate on the other. This leaves the former complex with an overall charge of 2+, and the latter with a charge of 2-, giving the coordination compound  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}[\text{Ni}(\text{cyclam})(\text{SO}_4)_2]^{2-}$  (plus the two waters of crystallization).

The Ni1–N distances [Ni1–N1 = 2.0691 (13) Å and Ni1–N2 = 2.0743 (13) Å] of the cyclam complex show the typical strong bonds of high-spin Ni<sup>II</sup>(cyclam) complexes (Donnelly & Zimmer, 1999), whilst the flexibility of the ring structure

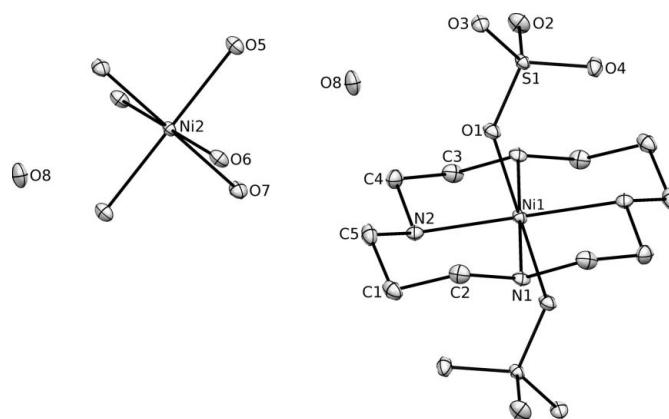


Figure 1

Displacement ellipsoid (50% probability) representation of the crystal structure of  $[\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{SO}_4)_2(\text{cyclam})] \cdot 2\text{H}_2\text{O}$ . H atoms have been omitted for clarity.

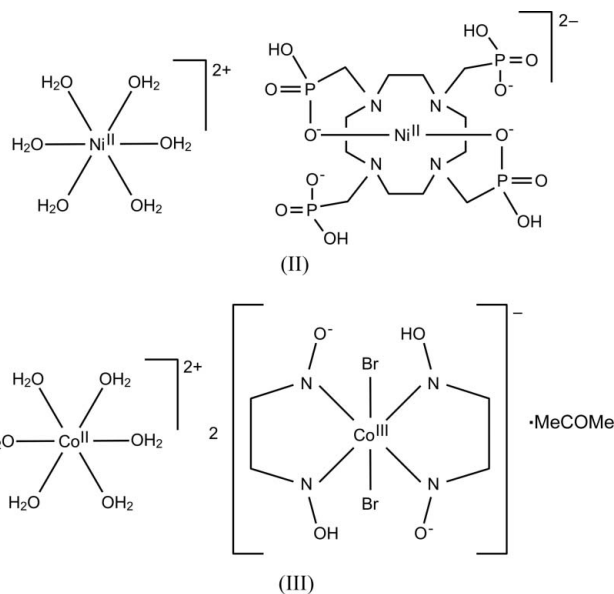
allows Ni1 to sit at the centre (planar by symmetry) of four N atoms. The cyclam ring is in the lowest energy configuration, *trans* type III [according to the scheme of Bosnich *et al.* (1965)], which is also the most common (Donnelly & Zimmer, 1999). The Ni1–O1 distance [2.1522 (10) Å] involving the sulfate ligands is longer than those found in anhydrous NiSO<sub>4</sub> (2.020–2.118 Å; *T* = 293 K; Wildner, 1990), whose range is also representative for such bonds in organometallic complexes, though longer examples are occasionally found {*e.g.* [N-(3-aminopropyl)-1,3-propanediamine]diaqua(sulfato-*O*)nickel(II) monohydrate, with Ni–OSO<sub>3</sub> = 2.171 (2) Å; Mukherjee *et al.* (1995)}. In the hexaaqua subunit, the Ni2–O distances [Ni2–O5 = 2.0451 (11) Å, Ni2–O6 = 2.0701 (12) Å and Ni2–O7 = 2.0837 (12) Å] agree very closely with those found in the hexaaqua complex [Ni(H<sub>2</sub>O)<sub>6</sub>]SO<sub>4</sub> (2.0096–2.0852 Å; *T* = 300 K; Rousseau *et al.*, 2000).

There is substantial hydrogen bonding within the crystal structure. The strongest instances are found between the water H atoms and the terminal O atoms of the SO<sub>4</sub><sup>2-</sup> ligands (O2, O3 and O4), such that altogether each SO<sub>4</sub><sup>2-</sup> ligand is stabilized by six strong hydrogen bonds [distances in the range 1.91 (2)–2.08 (2) Å]. Two of these hydrogen bonds arise from the solvent water molecules, and four from the Ni-complexed waters. The SO<sub>4</sub><sup>2-</sup> ligands are further stabilized by weaker hydrogen bonding between the amine H atoms of cyclam (H5 and H10) and O2 and O4, respectively [2.377 (17) and 2.229 (18) Å]. The orientation of the SO<sub>4</sub><sup>2-</sup> ligands is noticeably influenced by these latter hydrogen bonds, with the S1–O2 and S1–O4 bonds being almost parallel to the plane of the four N atoms, increasing their proximity to H5 and H10, whilst S1–O3 is substantially angled away. The appreciable stabilization afforded by these hydrogen bonds likely enables the formation of the formally ionic 2+/2- complexes, as due to the considerable Ni1...Ni2 distance (the shortest Ni1...Ni2 distance is 6.536 Å, found between adjacent asymmetric units), we infer the Madelung energy must be small.

A search of the CSD returns 15 structures where one Ni is coordinated to cyclam or a derivative, whilst another Ni has no bonds to any form of cyclam. Seven of these involve the second Ni atom in the low-spin environment of four cyano ligands. Another five of these structures have the second Ni bound by four S atoms in a square-planar fashion, and the remaining three structures have mixed N/O donors. None show the second Ni bound by six O donors, as in the compound presented here. Additionally, nine of the 15 structures show molecular crystals (molecules held together into a crystal structure by weaker interactions between molecules, *e.g.* hydrogen bonds and van der Waals forces), as here, and six one-dimensional chains.

Searching for structures containing any transition metals where one metal atom is coordinated to six water molecules, while a second metal atom (of the same element as the first) is attached at least to four N atoms, returns 22 structures. Eleven of these are disregarded as they do not have a metal centre with the relevant mixed-donor functionality of (I) (*i.e.* four N atoms plus a different donor atom bound to the same metal). Another five are simply aquated [M(phen)<sub>2</sub>] complexes (phen

is 1,10-phenanthroline) together with an additional hexaaqua complex of the same metal [*i.e.* [M(phen)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][M(H<sub>2</sub>O)<sub>6</sub>], M = Mn, Co, Ni, Zn] and of little interest. Another structure is discounted here due to its complexity, *i.e.* its unit cell contains 13 Co, 12 of which are bound by a single mixed N/O donor macromolecule. Four of the remaining five of the 22 structures have metal centres with four N donors and two O donors, but all of the O-donor ligands are chelates with N and O functionality. The most interesting of these, *viz.* hexaaquanickel(II) [1,4,7,10-tetrakis(methylenephosphonic acid)-1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*,*O,O'*]nickel(II) (CSD refcode SAHPOH; Kong *et al.*, 2004), (II), is discussed below, along with the final structure from this search, *viz.* hexaaquacobalt(II) bis[dibromidobis(ethanedial dioximato)cobaltate(III)] acetone solvate (CSD refcode BIYTUY; Egharevba *et al.*, 1982), (III), which does bear some similarity to the title compound.



SAHPOH [see (II) in scheme] is a compound with a striking superficial similarity to (I). It has a directly analogous hexaaqua metal centre and a similar (albeit with *cis* rather than *trans* geometry) [12]aneN<sub>4</sub> ring derivatized with N-pendant methylenephosphonate groups, where two phosphonate groups act as O donors corresponding to the sulfate groups of (I). However, the crucial difference between (I) and this compound is the hexadentate nature of the single mixed-donor ligand. This tethering of the phosphonates to the [12]aneN<sub>4</sub> ring gives them considerably greater tendency to coordinate to the same Ni as the [12]aneN<sub>4</sub> rather than to another metal centre by cause of the chelate effect. This is an important difference from (I), where the free sulfate groups can potentially coordinate to a noncyclam-connected metal centre but in fact do not.

BIYTUY [see (III) in scheme] is a tricobalt compound akin to (I) in having two distinct metal environments, *viz.* a hexaaqua metal complex and a dibromobis(glyoximate)cobalt unit. Besides the change in metal, there are, however, three significant differences from (I). The first is that each individual

ligand bears a single negative charge, for a total ligand charge of 4−, where the title compound bears this 4− charge (formally) on just the two  $\text{SO}_4^{2-}$  ligands. More significantly, the ratio of the two different Co complexes is 1:2, requiring a  $\text{Co}^{\text{III}}$  complex,  $[\text{CoBr}_2(\text{gH}^-)_2]^-$  ( $\text{gH}^-$  is glyoximate), to ensure charge neutrality. This triply charged metal centre is naturally more attractive to  $\text{Br}^-$  ligands than a doubly charged centre would be with the same bis-glyoximate ligands. Finally, the  $\text{C}=\text{N}$  functionality of the glyoximate ligands is capable of much stronger  $\pi$ -interactions with the transition metal than the secondary amines of (I).

A search for the type  $[\text{TM}(\text{O})_6][\text{TM}(\text{SO})_2(\text{N})_4]$ , *i.e.* any transition metal (TM) compound such that one TM is bound to six O and another TM of the same element is bound to four N donors and two O—S groups (O donor, with S free to have any other connections), returned no results. Placed in the context of previously reported structures, this confirms that the title compound is an intriguing and rare structure for transition metal complexes.

## Experimental

Crystals of (I) were obtained as a by-product during the synthesis of  $\text{Ni}(\text{cyclam})(\text{SO}_4)$  (Churchard *et al.*, 2010). Prolonged exposure (several days) to atmospheric water resulted in hydration of the anhydrous solution and precipitation of violet crystals of (I).

### Crystal data

$[\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{SO}_4)_2(\text{C}_{10}\text{H}_{24}\text{N}_4)] \cdot 2\text{H}_2\text{O}$	$\beta = 99.869 (8)^\circ$
$M_r = 654.00$	$\gamma = 91.640 (7)^\circ$
Triclinic, $P\bar{1}$	$V = 621.59 (9) \text{ \AA}^3$
$a = 8.0997 (7) \text{ \AA}$	$Z = 1$
$b = 8.4360 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 9.3521 (9) \text{ \AA}$	$\mu = 1.76 \text{ mm}^{-1}$
$\alpha = 98.558 (7)^\circ$	$T = 100 \text{ K}$
	$0.10 \times 0.10 \times 0.05 \text{ mm}$

### Data collection

Kuma KM-4 CCD diffractometer	<i>SCALE3 ABSPACK</i> scaling algorithm]
Absorption correction: multi-scan [ <i>CrysAlis RED</i> (Oxford Diffraction, 2004); empirical absorption correction using spherical harmonics, implemented in	$T_{\min} = 0.844$ , $T_{\max} = 0.917$
	10420 measured reflections
	2438 independent reflections
	2010 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.018$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.040$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
$S = 0.95$	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$
2438 reflections	
197 parameters	

H atoms, except those on C atoms, were located from difference maps and refined isotropically. Other H atoms were placed in calculated positions and refined within the riding model. The C—H distances were constrained to  $0.99 \text{ \AA}$ , with  $U_{\text{iso}}(\text{H})$  values of  $1.2U_{\text{eq}}(\text{C})$ .

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{N1---H5}\cdots\text{O2}^{\text{i}}$	0.834 (16)	2.377 (17)	3.1555 (18)	155.6 (14)
$\text{N2---H10}\cdots\text{O4}$	0.875 (18)	2.229 (18)	3.0594 (17)	158.4 (15)
$\text{O5---H13}\cdots\text{O8}^{\text{ii}}$	0.79 (2)	1.93 (2)	2.6873 (19)	162 (2)
$\text{O5---H14}\cdots\text{O3}^{\text{iii}}$	0.79 (2)	1.91 (2)	2.6941 (17)	170.7 (19)
$\text{O6---H15}\cdots\text{O2}^{\text{iv}}$	0.77 (2)	1.93 (2)	2.6891 (18)	169 (2)
$\text{O6---H16}\cdots\text{O3}^{\text{iii}}$	0.80 (2)	2.08 (2)	2.8332 (17)	157.4 (19)
$\text{O7---H17}\cdots\text{O4}^{\text{iii}}$	0.76 (2)	1.99 (2)	2.7448 (17)	177 (2)
$\text{O7---H18}\cdots\text{O8}^{\text{v}}$	0.86 (2)	1.98 (2)	2.7972 (19)	159 (2)
$\text{O8---H19}\cdots\text{O3}^{\text{i}}$	0.73 (2)	2.06 (2)	2.7811 (18)	172 (2)
$\text{O8---H20}\cdots\text{O2}^{\text{iii}}$	0.83 (2)	1.91 (2)	2.7035 (19)	160 (2)

Symmetry codes: (i)  $-x + 1, -y, -z + 2$ ; (ii)  $x - 1, y, z$ ; (iii)  $x, y, z - 1$ ; (iv)  $-x + 1, -y + 1, -z + 2$ ; (v)  $-x + 1, -y + 1, -z + 1$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *Mercury*.

The X-ray structure was determined in the Crystallographic Unit of the Physical Chemistry Laboratory at the Chemistry Department of the University of Warsaw.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3137). Services for accessing these data are described at the back of the journal.

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