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Hexakis(imidazole-*N*³)nickel(II) Carbonate Pentahydrate

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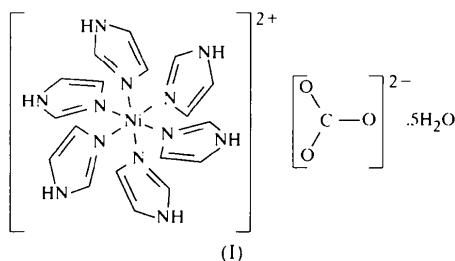
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Abstract

The crystal structure of the title complex, $[\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6]\text{CO}_3 \cdot 5\text{H}_2\text{O}$, which is isostructural with the Cd, Co and Ru analogues, is built up from cationic and anionic sheets parallel to the basal plane of the hexagonal unit cell. The former contain the $[\text{Ni}(\text{C}_3\text{H}_4\text{N}_2)_6]^{2+}$ cations and the latter the CO_3^{2-} anions together with the hydration water molecules. These are disordered on both sides of the $P6_3/m$ mirror plane, which thus exists in an average sense only. The sheets are linked by an extensive hydrogen-bonding system involving the non-coordinated NH imidazole groups, the hydration water molecules and the O atoms of the carbonate anions. The latter are acceptors of nine simultaneous strong hydrogen bonds.

Comment

Carbonate salts of octahedral hexakis(imidazole)-metal(II) cations, $[\text{M}(\text{Him})_6]^{2+}$, where Him is imidazole, are of interest as model complexes for the coordination sphere of metalloenzyme active sites. X-ray crystal structures have been reported for the series of complexes $[\text{M}(\text{Him})_6]\text{CO}_3 \cdot 5\text{H}_2\text{O}$, with $M = \text{Co}$ (Strandberg & Lundberg, 1971), Cd (Antti *et al.*, 1972) and Ru (Anderson & Beauchamp, 1995). We report here another member of the isostructural series, namely, $[\text{Ni}(\text{Him})_6]\text{CO}_3 \cdot 5\text{H}_2\text{O}$, (I).



The molecular diagram and the atomic numbering scheme used are shown in Fig. 1. The Ni^{2+} cation is coordinated by six equivalent monodentate imidazole ligands, forming an $[\text{Ni}(\text{Him})_6]^{2+}$ group which displays $\bar{3}$ symmetry, with Ni lying on a symmetry centre and with a single independent imidazole ligand generating the whole cation environment. In spite of differences in cationic size, the MN_6 polyhedra in the series show similar geometries, with slight departures from a perfect octahedral arrangement, as measured by the N—M—N angle subtended at the cationic site, *viz.* 89.8 (Co; mean value from the two independent entries 89.4/90.3, resulting from refinement in non-centrosymmetric $P6_3$), 89.6(1) (Cd), 90.3(1) (Ru) and 90.1(1)° (Ni; this work).

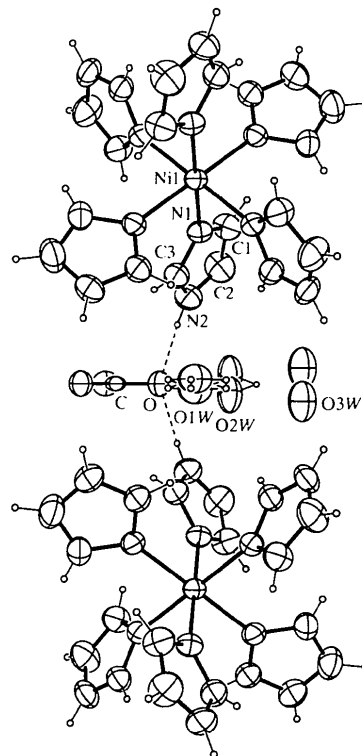


Fig. 1. A partial view of the structure of (I), showing the atom labelling and a simplified representation of contacts between layers. Interactions within layers are not shown. Displacement ellipsoids are drawn at the 50% probability level.

Bond lengths and angles at the Ni atom (Table 2) are very similar to those reported for $[\text{Ni}(\text{Him})_6](\text{NO}_3)_2$, (II) [2.128(2) Å and 91.73(6)°; Santoro *et al.*, 1969; Finney *et al.*, 1981]. The imidazole rings are planar in both structures, with maximum deviations of 0.004(4) Å in (I) and 0.006(3) Å in (II). The most significant difference between the two coordination spheres is observed in the rotation of the Him groups around the N—Ni vector, away from the NiN_4 coordination plane, this rotation being 7.8(1)° in (I) and 21.8(1)° in (II).

When viewed parallel to the basal planes, the crystal structure appears as a stacking of broad cationic sheets of [Ni(Him)₆]²⁺ units, disposed parallel to (001) at heights $z \sim 0$ and $\frac{1}{2}$, while the CO₃²⁻ anions, as well as the hydration water molecules, are located midway between them and define densely woven hydrogen-bonded two-dimensional nets parallel to the former, at heights $z \sim \frac{1}{4}$ and $\frac{3}{4}$. The link between different types of sheets is provided by two strong hydrogen bonds that each carbonate O atom accepts from two non-coordinating NH groups, one on each side of the mirror plane. At the same time, when the packing is viewed along the unique axis, this same pair of interactions, together with those generated by the threefold axis at the Ni atom, define trigonal bipyramidal-type assemblies, Ni(Him)₃··(CO₃)₃··(Him)₃Ni, with a span of $c/2 = 10.54$ Å between the Ni atoms acting as vertices, and with O1W located at the interstitial centre and O2W near the middle of the basal edge. In this description, cohesion along z is provided by the sharing of bipyramidal apices (Ni atoms), while that in the xy plane is given by the sharing of corners (CO₃ groups), as well as by a strong threefold O3W··H2W—O2W contact.

The complex hydrogen-bonding scheme is summarized in Table 3 and shown schematically in Fig. 2. All the H atoms involved were found in the ΔF synthesis; this was probably due to the clamping effect the interaction had on the H-atom positions. Those attached to O3W, disordered around a threefold axis and sterically restrained from making such contacts, could not be located.

It is perhaps worth emphasizing that O1W cannot donate three protons at a time, as the rotationally averaged picture in Fig. 2 might suggest; only two positions out of three can be occupied simultaneously

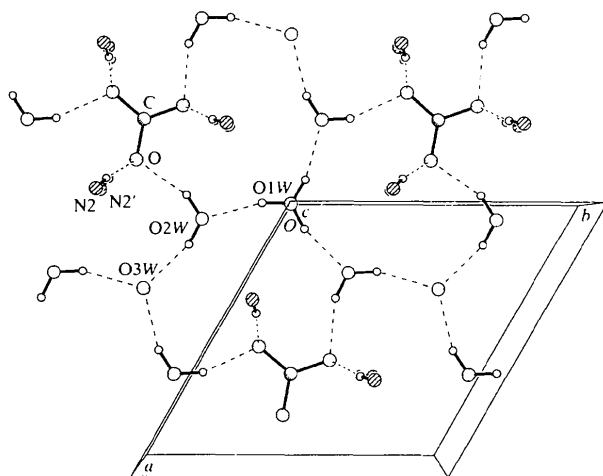


Fig. 2. View of the $z = \frac{1}{4}$ plane, showing the hydrogen-bonding scheme. For clarity, [Ni(Him)₆]²⁺ ions have been represented schematically by the N—H groups involved in the interaction.

by H atoms. On the other hand, the fact that O2W is not affected by this kind of disorder means that all the depicted hydrogen bonds involving H2WA and H2WB are real. Within this picture, O1W ends up donating two bonds, O2W donates two and receives $\frac{3}{2}$, and O3W receives three. As a result, the carbonate ion ends up acting as a hydrogen-bond acceptor of nine strong O··H contacts in the range 1.89–1.93 Å. Only three such examples could be traced in the literature beyond the four members of the present series; these are guanidinium carbonate (CO₃²⁻ acceptor of ten O··H contacts in the range 1.86–2.33 Å; Adams & Small, 1974), di(biguanidinium) carbonate (CO₃²⁻ acceptor of ten O··H contacts in the range 1.84–2.29 Å; Pinkerton & Schwarzenbach, 1978) and guanidinium bicarbonate (CHO₃⁻ acceptor of seven O··H contacts in the range 1.61–2.29 Å; Baldwin *et al.*, 1986).

Experimental

To a water-ethanol solution (1:1, 100 ml) of imidazole (0.300 g, 4.4 mmol) at room temperature was added basic nickel carbonate, NiCO₃·2Ni(OH)₂·4H₂O (0.100 g, 0.2 mmol). After stirring for 10 h, a greenish solution formed, which was filtered to remove traces of solids and allowed to stand at room temperature. After a week, green crystals were collected by vacuum filtration and dried in air (yield: 0.30 g, 80%). Analysis calculated (found) for C₁₉H₃₃N₁₂NiO₈: C 36.90 (36.80), H 5.50 (5.55), N 27.20% (27.50%). IR (KBr disc, cm⁻¹): 3131 (*vs*), 3036 (*s*), 2926 (*s*), 2851 (*s*), 2718 (*m*), 1545 (*s*), 1495 (*s*), 1458 (*vs*), 1393 (*vs*; CO₃²⁻), 1325 (*s*), 1256 (*m*), 1096 (*m*), 1071 (*s*), 939 (*s*), 916 (*m*), 844 (*m*), 752 (*s*), 667 (*s*) and 621 (*m*); IR (CsI, nujol mull, cm⁻¹): 260 (*s*) and 227 (*m*) (Ni—N). The compound is thermally stable at room temperature and thermogravimetric analysis shows that five water molecules are lost in one stage in the range 310–426 K, in accordance with the microanalysis and X-ray data. The reactants (Fluka) were used without further purification. The elemental analyses (C, H, N) were performed on a Carlo Erba EA 1108 instrument, the IR spectra were recorded with a Nicolet 510P FT-IR spectrophotometer and the thermogravimetric analysis was recorded on a Mettler TG-50 thermal analyser under an atmosphere of oxygen at a heating rate of 5 K min⁻¹.

Crystal data

[Ni(C₃H₄N₂)₆]CO₃·5H₂O

$M_r = 617.28$

Hexagonal

$P6_3/m$

$a = 9.0124(11)$ Å

$c = 21.080(6)$ Å

$V = 1482.8(5)$ Å³

$Z = 2$

$D_x = 1.38$ Mg m⁻³

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 7.5$ – 12.5°

$\mu = 0.72$ mm⁻¹

$T = 293(2)$ K

Hexagonal plate

$0.15 \times 0.15 \times 0.08$ mm

Pale green

Data collection

Siemens R3m diffractometer
 $\omega/2\theta$ scans

594 reflections with
 $I > 2\sigma(I)$

Absorption correction:	$R_{\text{int}} = 0.045$
ψ scans (XEMP in	$\theta_{\text{max}} = 25.05^\circ$
SHELXTL/PC; Sheldrick,	$h = -10 \rightarrow 8$
1994)	$k = 0 \rightarrow 10$
$T_{\text{min}} = 0.89$, $T_{\text{max}} = 0.95$	$l = 0 \rightarrow 25$
2852 measured reflections	2 standard reflections
911 independent reflections	every 98 reflections
	intensity decay: <2%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.01$
$R[F^2 > 2\sigma(F^2)] = 0.038$	$\Delta\rho_{\text{max}} = 0.34 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.112$	$\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{\AA}^{-3}$
$S = 1.02$	Extinction correction: none
911 reflections	Scattering factors from
82 parameters	International Tables for
H atoms; see below	Crystallography (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.044P)^2$	
+ 0.067P]	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

	x	y	z	U_{eq}
Ni1	0	0	0	0.0339 (2)
C1	-0.2867 (3)	0.0779 (4)	-0.04808 (14)	0.0530 (7)
C2	-0.3971 (4)	0.0458 (4)	-0.09709 (16)	0.0651 (9)
C3	-0.2531 (3)	-0.0850 (3)	-0.11282 (12)	0.0454 (7)
N1	-0.1949 (2)	-0.0043 (3)	-0.05812 (9)	0.0388 (5)
N2	-0.3740 (3)	-0.0580 (3)	-0.13743 (12)	0.0524 (7)
C	-2/3	-1/3	-1/4	0.0281 (13)
O	-0.5603 (3)	-0.1731 (3)	-1/4	0.0496 (7)
O1W†	0	0	-0.2438 (8)	0.071 (2)
O2W†	-0.6681 (5)	0.0607 (4)	-0.2357 (3)	0.079 (2)
O3W†	-1/3	1/3	-0.2279 (4)	0.085 (4)

† Site occupancy = 0.50.

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ni1—N1	2.126 (2)	C3—N1	1.323 (3)
C1—C2	1.361 (4)	C3—N2	1.334 (4)
C1—N1	1.376 (4)	C—O	1.273 (2)
C2—N2	1.355 (4)		
N1'—Ni1—N1	90.10 (7)	N1—C3—N2	112.0 (3)
C2—C1—N1	109.9 (3)	C3—N1—C1	104.5 (2)
N2—C2—C1	106.0 (3)	C3—N2—C2	107.6 (2)

Symmetry code: (i) $-y, x - y, z$.

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)

Atom labels in parentheses refer to the second member in a disordered pair across the mirror plane.

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N2—H2A \cdots O	0.86 (1)	1.93 (1)	2.790 (3)	172.8 (2)
O2W—H2WA \cdots O	0.92 (1)	1.89 (1)	2.742 (6)	151.1 (3)
O1W—H1W \cdots O2W'	0.91 (2)	1.95 (2)	2.764 (4)	147.2 (8)
O1W—H1W \cdots (O2W'')	0.91 (2)	1.91 (2)	2.792 (5)	160.7 (8)
O2W—H2WB \cdots O3W	0.92 (2)	1.99 (2)	2.785 (3)	142.6 (4)
O2W—H2WB \cdots (O3W''')	0.92 (2)	1.99 (2)	2.883 (4)	161.1 (3)

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 + x, y, -\frac{1}{2} - z$; (iii) $x, y, -\frac{1}{2} - z$.

A major problem in the isostructural series of $[M(\text{Him})_6]\text{CO}_3 \cdot 5\text{H}_2\text{O}$ complexes has been the determination of the correct

space group. The Co complex, for example, was solved and refined in a rather low-precision study (final $R = 0.088$) in non-centrosymmetric $P6_3$, although it is clearly isostructural with the Cd and Ru analogues which are reported to crystallize in centrosymmetric $P6_3/m$. The latter, in turn, are only centrosymmetric in an average sense, since the abnormally prolate displacement ellipsoids of some water molecules which were bisected by the mirror plane, could only be fixed by splitting them up into two half-occupied disordered positions slightly shifted along z . Being aware of these problems, we tried several models in the course of refinement, *viz.* non-centrosymmetric $P6_3$, a variant of $P6_3$ where centrosymmetric constraints were imposed on the Ni coordination polyhedron while leaving the water molecules free, and centrosymmetric $P6_3/m$. No convincing evidence was found, either in the R factors or in the s.u.'s or displacement ellipsoids, which supported any eventual superiority of the lower symmetry refinements. Thus, $P6_3/m$ was finally chosen, with the ten hydration water molecules expected in the structure distributed with six of them in a site of type h (O2W), two in a site of type a (O1W) and the remaining two in a site of type c (O3W). Besides the obvious rotational disorder which the latter positions implied for O1W and O3W, least-squares refinement of all three O atoms resulted (as with the isostructural homologues) in displacement ellipsoids abnormally prolated along the z direction. This fact in turn confirmed the existence of extra disorder along the unique hexagonal axis, with two images with halved occupancies (due to the mirror requirement) symmetrically displaced at each side of the plane. In contrast to the other reported homologues, in this case, the effect was also perceptible for O1W, though to a lesser degree than for O2W and O3W. The results obtained made it clear that even though $P6_3/m$ offered the most suitable description available for this isostructural series, this was in an 'average' sense only. The proposed model refined satisfactorily, and a ΔF synthesis showed all the H atoms quite clearly, except for those corresponding to O3W, which could not be confidently found. H atoms relevant for the packing description were refined with restrained N—H and O—H distances and isotropic displacement factors; those attached to C were idealized and allowed to ride. The final ΔF map showed no relevant peaks above a fairly featureless background, with extremes of 0.34 and $-0.19 \text{ e } \text{\AA}^{-3}$.

Data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991). Cell refinement: *P3/P4-PC Diffractometer Program*. Data reduction: *XDISK* in *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* in *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL97*, *PARST* (Nardelli, 1983) and the Cambridge Structural Database (Allen & Kennard, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1383). Services for accessing these data are described at the back of the journal.

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[CuL₂][ClO₄] and [AgL₂][BF₄], where L = 6,6'-Dibromo-2,2'-bipyridine

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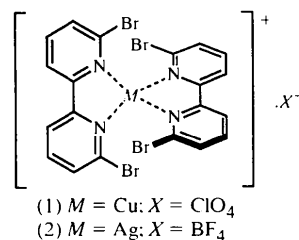
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Abstract

The complexes bis(6,6'-dibromo-2,2'-bipyridine-*N,N'*)copper(I) perchlorate, [Cu(C₁₀H₆Br₂N₂)₂][ClO₄], and bis(6,6'-dibromo-2,2'-bipyridine-*N,N'*)silver(I) tetrafluoroborate, [Ag(C₁₀H₆Br₂N₂)₂][BF₄], both contain four-coordinate pseudo-tetrahedral metal centres, in which the two bidentate chelating ligands are nearly mutually perpendicular; the average dihedral angle between the two MN₂ planes is 87.9° for *M* = Cu but only 75° for *M* = Ag, which reflects the lesser inter-ligand steric interactions in the silver(I) complex, arising from the greater metal–ligand bond distances. For both complexes, the crystal packing is dominated by intermolecular Br⋯Br interactions.

Comment

Four-coordinate mononuclear copper(I) complexes of the type Cu(*NN*)₂, where *NN* denotes a derivative of 2,2'-bipyridine or 1,10-phenanthroline, have been of interest for their photophysical and electrochemical properties, and in particular the relationship between these properties and the extent of distortion of the complexes away from *D*_{2d} symmetry (in which the two bidentate ligands are mutually perpendicular) towards *D*_{4h} (in which they are coplanar) (Cargill Thompson *et al.*, 1997; Müller *et al.*, 1996; Bardwell *et al.*, 1996; Geoffroy *et al.*, 1990; Federlin *et al.*, 1990). The pseudo-tetrahedral *D*_{2d} geometry can be favoured by attachment of bulky substituents (commonly aryl or alkyl) to the C atoms adjacent to the N donor atoms (*i.e.* C6 and C6' on a 2,2'-bipyridyl core, or C2 and C9 on a 1,10-phenanthroline core). Such substituents can favour pseudo-tetrahedral geometries by forming 'interlocked' structures with favourable inter-ligand interactions, and actively disfavour planar geometries for steric reasons. In contrast, complexes of this type with silver(I) are much rarer (Cargill Thompson *et al.*, 1997; Goodwin *et al.*, 1986). We describe here the crystal structures of the copper(I) and silver(I) complexes of 6,6'-dibromo-2,2'-bipyridine [(1) and (2), respectively], which should impose pseudo-tetrahedral geometry because of the bulky Br-atom substituents. These are the first crystal structures of complexes with this ligand to be reported.



Reaction of *L* with [Cu(MeCN)₄][PF₆] in methanol in a 2:1 ratio afforded [CuL₂][PF₆] as an orange solid; a small amount was converted to the perchlorate salt for crystallization, and X-ray quality crystals were grown from a dichloromethane/hexane mixture. The structure of [CuL₂][ClO₄] is rather unusual in that it contains three crystallographically independent formula units in the asymmetric unit. One of the independent complex cations is shown in Fig. 1; the other two are very similar. The atom-numbering scheme is the same for all three complex units, with the first digit (1, 2 or 3) denoting the complex unit. In all three complex cations, the Cu—N distances lie in the range 2.02–2.06 Å, with the usual distortion from regular tetrahedral geometry arising from the restricted bite angles of the chelating fragments (*ca* 80°). The dihedral angles between the two CuN₂ planes are 85.8 (2), 88.6 (2) and 89.4 (2)° for complex units 1, 2 and 3, respectively. The ligands are therefore virtually