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Bis(acetonitrile-*N*)(1,4,8,12-tetraazacyclopentadecane)nickel(II) Bis(triiodide) and (1,4,8,12-Tetraazacyclopentadecane)palladium(II) Bis(triiodide)

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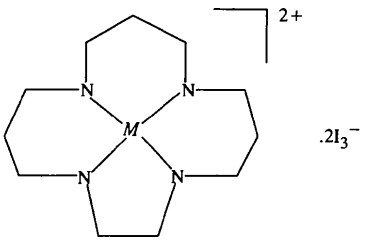
Abstract

In the first title compound, $[Ni(C_2H_3N)_2(C_{11}H_{26}N_4)](I_3)_2$, the Ni^{II} centre is coordinated octahedrally: all four N-donor atoms of the macrocyclic ligand occupy an equatorial plane and the coordination is completed by two axial acetonitrile ligands. Each N—H group forms a contact of 2.97–3.11 Å to one I atom of an I_3^- anion. One of these anions participates in long I···I contacts of 4.008 (3) Å to form infinite chains of symmetry-related anions. In the second title compound, $[Pd(C_{11}H_{26}N_4)](I_3)_2$, each Pd^{II} centre is coordinated in an equatorial plane by four N-donor atoms from the macrocyclic ligand and axially by a terminal iodine from each of two I_3^- anions at 3.525 (4) Å. The same I atom forms an I···I contact of 4.094 (3) Å such that cations and pairs of anions alternate within one-dimensional zigzag chains.

Comment

We have been studying the interactions of diiodine with both free homoleptic S-donor macrocyclic ligands (Blake, Cristiani *et al.*, 1997; Blake, Li *et al.*, 1997) and their metal complexes (Blake *et al.*, 1995, 1996; Blake, Gould *et al.*, 1998). In the latter, various polyiodide counter anions are observed, often as extended polyiodide arrays such as spirals, belts, ribbons, chains, sheets and cages (Blake, Gould *et al.*, 1998). Where short I···I contacts are absent, we have seen lattices formed *via* S···I contacts (Blake, Lippolis *et al.*, 1998). In this paper, we examine the structures of the bis(acetonitrile)-nickel(II), (1), and palladium(II), (2), title complexes, in which the macrocyclic ligand contains N- rather than S-donor atoms. Although the neutral nickel(II) complexes $Ni([15]aneN_4)Cl_2$ and $Ni([15]aneN_4)(NCS)_2$ ([15]aneN$_4$ is 1,4,8,12-tetraazacyclopentadecane) have been reported (Ito *et al.*, 1984), there is no previous report of any salt of the $[Pd([15]aneN_4)]^{2+}$ cation (Allen *et al.*, 1991).



(1) M=Ni(MeCN)$_2$
(2) M=Pd

In (1), the Ni^{II} centre is in an octahedral environment (Fig. 1): all four N-donor atoms of the macrocyclic ligand coordinate, with Ni—N distances in the range 2.098 (5)–2.193 (7) Å, in an equatorial plane from which the metal is displaced by 0.024 (3) Å in the direction of N2*S*. The coordination is completed by two axial acetonitrile ligands at 2.124 (5) and 2.060 (6) Å. The acute N1—Ni—N4 angle of 83.3 (2)° occurs within the unique five-membered chelate ring, while other N—Ni—N angles lie in the range 87.22 (19)–94.6 (2)°. The I_3^- anion is symmetric and therefore gives only one ν(I—I) band in the Raman spectrum (see below). Each N—H group has a contact with an I atom of a different I_3^- anion at 2.97–3.11 Å (based on hydrogen

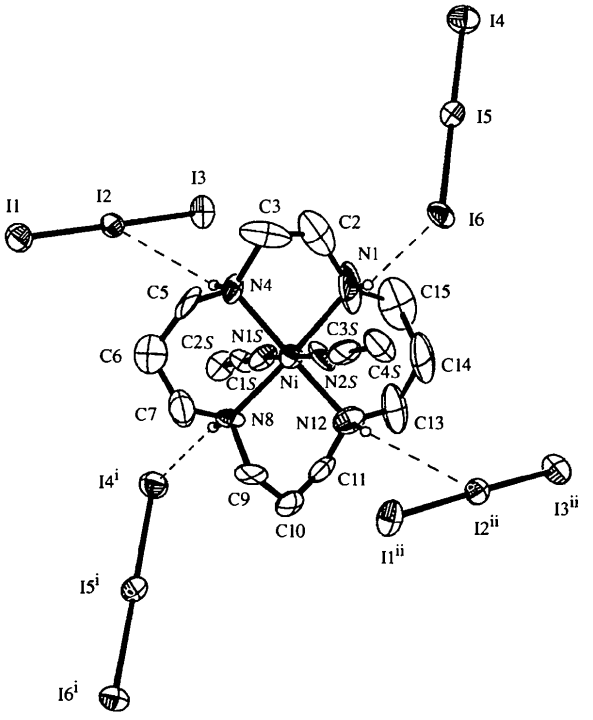


Fig. 1. A view with atom-numbering scheme of a single cation of (1) and its surrounding environment of iodides. Displacement ellipsoids enclose 50% probability surfaces. H atoms other than those bound to N atoms and the minor disorder component I6′ have been omitted for clarity. Symmetry codes: (i) $x-\frac{1}{2}, \frac{1}{2}-y, z-\frac{1}{2}$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, \frac{1}{2}+z$.

at calculated positions), with N—H···I angles ranging from 140 to 161°. One of these anions forms long I···I contacts of 4.008 (3) Å to form infinite chains of symmetry-related anions running along the **c** direction.

In (2), the palladium occupies a crystallographic inversion centre (Fig. 2) and as a consequence there is disorder in the 15-membered ring such that the unique N—CH_2—CH_2—N linkage is disordered with the N—CH_2—CH_2—CH_2—N linkage opposite (see below for details). The metal is coordinated in a square plane by all four aza donors of the [15]aneN_4, with Pd—N distances of 2.060 (11) and 2.084 (10) Å, and all the chelate rings exhibiting N—Pd—N angles of 90.0 (4)°; this regularity in the angles may derive partly from the disorder present in the cation. The coordination is completed by two contacts of 3.525 (4) Å to an iodine (I1) in two symmetry-related triiodide anions. These anions are asymmetric, as indicated by the two ν(I—I) bands in the Raman spectrum (see below), with the atoms forming the contact to the metal having longer intra-ion bonds [I1—I2 2.953 (3) *versus* I2—I3 2.871 (3) Å]. Each I1 atom also forms a contact of 4.094 (3) Å to an I1 related to it by an inversion centre and the Pd···I and I···I contacts result in the packing arrangement seen in Fig. 2, where cations are linked by bridges composed of pairs of linked triiodides to give one-dimensional zigzag chains running parallel to the *a* axis. There are no other I···I contacts below the relevant van der Waals sum of 4.2 Å.

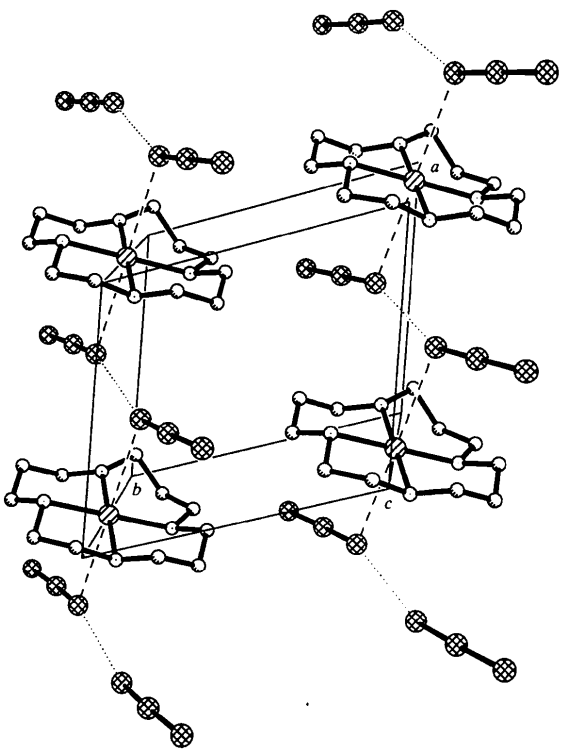


Fig. 2. A view of the packing arrangement in (2), showing $[Pd([15]aneN_4)]^{2+}$ cations linked by bridges composed of pairs of linked triiodides to give one-dimensional chains parallel to **a**. The atom-numbering scheme for (2) is the same as that for (1).

Experimental

A mixture of [15]aneN_4 (30 mg, 0.14 mmol) with $Ni(BF_4)_2 \cdot 6H_2O$ (32.5 mg, 0.14 mmol) or $[Pd(CH_3CN)_4](BF_4)$ (62.2 mg, 0.14 mmol) in CH_3CN (4 ml) was stirred at room temperature for 1 h. A solution of diiodine (106.7 mg, 0.42 mmol) in CH_3CN (3 ml) was then added and the resulting mixture stirred for a further 30 min. Dark-red crystals were formed after slow evaporation of the solvent. Yields: 52.5 mg (33.6%) for (1) and 55.5 mg (36.6%) for (2). Found (calculated for $C_{15}H_{32}N_6NiI_6$): C 15.98 (16.13), H 2.90 (2.88)%; found (calculated for $C_{11}H_{26}N_4PdI_6$): C 12.30 (12.21), H 2.38 (2.42)%. FT–Raman spectrum (500–50 cm^{-1}): ν(I—I) 111 cm^{-1} for (1); 135, 107 cm^{-1} for (2).

Compound (1)

Crystal data

$[Ni(C_2H_3N)_2(C_{11}H_{26}N_4)](I_3)_2$
M_r = 1116.58
Monoclinic
Cc
a = 16.885 (6) Å
b = 18.689 (4) Å
c = 9.452 (3) Å
β = 94.05 (5)°
V = 2975.2 (13) $Å^3$
Z = 4
D_x = 2.493 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 18 reflections
θ = 13.5–20.1°
μ = 6.892 mm^{-1}
T = 150 K
Plate
0.58 × 0.33 × 0.15 mm
Dark red

Data collection

Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)
ω/θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
T_{min} = 0.103, T_{max} = 0.305
2631 measured reflections

2631 independent reflections
2413 reflections with $I > 2\sigma(I)$
θ_{max} = 25.07°
h = −20 → 20
k = 0 → 22
l = 0 → 11
3 standard reflections
frequency: 60 min
intensity variation: ±2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.095
S = 1.131
2631 reflections
266 parameters
H atoms: see below

Extinction correction: *SHELXL*96
Extinction coefficient: 0.000310 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 43.4P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.027$
$\Delta\rho_{max} = 1.37$ e Å^{-3} (0.92 Å from I3)
$\Delta\rho_{min} = -1.21$ e Å^{-3} (0.94 Å from I1)
Absolute structure: Flack (1983)
Flack parameter = 0.12 (12)

Table 1. *Selected geometric parameters (Å, °) for (1)*

Ni—N1	2.193 (7)	I1—I2	2.9125 (12)
Ni—N4	2.098 (5)	I2—I3	2.9203 (12)
Ni—N8	2.103 (4)	I4—I5	2.9235 (13)
Ni—N12	2.128 (6)	I5—I6	2.9178 (13)
Ni—N1*S*	2.124 (5)	I5—I6′	2.9358 (18)
Ni—N2*S*	2.060 (6)		
N1—Ni—N4	83.3 (2)	N8—Ni—N12	88.41 (18)
N1—Ni—N8	176.7 (2)	N8—Ni—N1*S*	87.22 (19)
N1—Ni—N12	94.6 (2)	N8—Ni—N2*S*	93.0 (2)
N1—Ni—N1*S*	91.4 (2)	N12—Ni—N1*S*	90.1 (2)
N1—Ni—N2*S*	88.4 (3)	N12—Ni—N2*S*	89.0 (2)
N4—Ni—N8	93.72 (18)	N1*S*—Ni—N2*S*	179.1 (3)
N4—Ni—N12	177.5 (2)	I1—I2—I3	177.595 (17)
N4—Ni—N1*S*	88.71 (19)	I4—I5—I6	179.50 (4)
N4—Ni—N2*S*	92.2 (2)	I4—I5—I6′	168.83 (3)

Compound (2)

Crystal data

$[Pd(C_{11}H_{26}N_4)](I_3)_2$
$M_r = 1082.2$
Triclinic
$P\bar{1}$
$a = 7.787$ (7) Å
$b = 9.173$ (9) Å
$c = 9.382$ (6) Å
$\alpha = 99.03$ (9)°
$\beta = 101.14$ (9)°
$\gamma = 107.43$ (10)°
$V = 610.6$ (9) Å^3
$Z = 1$
$D_x = 2.943$ Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 28 reflections
$\theta = 13.0$–$16.5°$
$\mu = 8.346$ mm^{-1}
$T = 150$ K
Lath
0.35 × 0.19 × 0.07 mm
Dark red

Data collection

Stoe Stadi-4 four-circle diffractometer with Oxford Cryosystems open-flow cryostat (Cosier & Glazer, 1986)
ω/θ scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{min} = 0.204$, $T_{max} = 0.392$
2146 measured reflections
2146 independent reflections
1863 reflections with $I > 2\sigma(I)$
$\theta_{max} = 25.09°$
$h = -9 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: 4.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.113$
$S = 1.154$
2146 reflections
100 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.032P)^2 + 11.04P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.51$ e Å^{-3} (0.83 Å from I1)
$\Delta\rho_{min} = -1.84$ e Å^{-3} (0.84 Å from I1)
Extinction correction: *SHELXL*96
Extinction coefficient: 0.0012 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 2. *Selected geometric parameters (Å, °) for (2)*

Pd—N1	2.060 (11)	I1—I2	2.953 (3)
Pd—N5	2.084 (10)	I2—I3	2.871 (3)
N1—Pd—N5	90.0 (4)	I1—I2—I3	176.85 (4)

In order to prevent the loss of diiodine by sublimation, it was necessary to coat the crystals in films of perfluoropolyether oil (Hoechst RS3000). An absorption correction was essential, but the optimum method (numerical by means of face indexing) was not practicable because we could neither identify the faces nor obtain reliable measurements of their distances from a common point within the crystal. It is clear from the results that the correction made is not completely adequate. Disorder was identified for one I atom, I6, in (1) and was modelled by allowing two alternative sites for this atom: the occupancies converged to 0.6384 (9) for I6 and 0.3616 (9) for I6′. Methyl H atoms were located from ΔF syntheses, others being introduced at geometrically calculated positions; thereafter these were refined using constraints or a riding model, respectively. Within the macrocyclic ring of (2), the ethyl linkage is disordered with one of the propyl linkages across an inversion centre; this disorder was modelled using partial occupancies for the C atoms involved and by restraining the C—C and C—N distances to 1.52 (1) and 1.47 (1) Å, respectively. The occupancies of the disorder components were found to be equal. The H atoms bonded to the N donor atoms were not included in the refinement model, but all others were introduced at geometrically calculated positions and thereafter refined using a riding model. In both structures, the major residual difference electron-density features lay close to I atoms.

For both compounds, data collection: *STADI*4 (Stoe & Cie, 1996*a*); cell refinement: *STADI*4; data reduction: *X-RED* (Stoe & Cie, 1996*b*); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*96 (Sheldrick, 1996); molecular graphics: *SHELXTL/PC* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*96.

We thank EPSRC for provision of a four-circle diffractometer and for a postdoctoral award (to W-SL), and The University of Nottingham for support (to VL).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1203). Services for accessing these data are described at the back of the journal.

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Polymeric μ,μ'-Pyrazine-*N*,*N*′-bis(*N*-salicylidene-*R*,*S*-alaninato)copper(II) Tetrahydrate†

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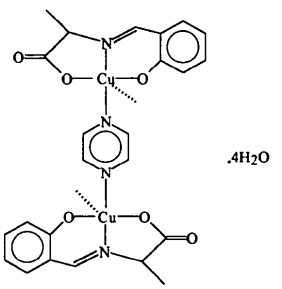
Abstract

The Cu^{II} atom in the title compound, $[Cu_2(C_{10}H_9NO_3)_2(C_4H_4N_2)].4H_2O$, adopts a square-pyramidal coordination with the three donor atoms of the *N*-salicylidene-*R*,*S*-alaninato Schiff base dianion and one N atom of the pyrazine ligand bound in the basal plane. The axial position is occupied by a phenolato O atom of a symmetry-related ligand at an apical distance of 2.396 (2) Å. The molecules are connected through the second N atom of the pyrazine to form binuclear copper units, and are further linked through the above-mentioned apical coordinations into chains parallel to [100]. The water molecules help to form a hydrogen-bonding network between the chains. All copper polyhedra and the molecular axis are oriented parallel.

Comment

Recently, we reported the monomeric structure of pyrazine(*N*-salicylidene-α-amino-2-methylpropanato)-copper(II) (Warda, 1997), in which the pyrazine ligand acts as a monodentate ligand. In this communication, we report the title structure, (I), which has a bidentate pyrazine ligand.



(I)

The Cu^{II} atoms adopt a (4+1) square-pyramidal geometry, with the three donor atoms of the tridentate Schiff base (TSB) *N*-salicylidene-*R*,*S*-alaninato dianion (ONO^{2-} chelator) and one N atom of the pyrazine ligand in the basal plane. All the equatorial copper distances are in the normal range.

The apical coordination site is occupied by the $O1^i$ atom of a neighbouring molecule, with a Cu—$O1^i$ distance of 2.396 (2) Å [symmetry code: (i) $1-x$, $1-y$, $-z$]. The apical distance is the most variable in this class of complex. The Cu atom is displaced from the basal plane by 0.136 (1) Å towards the apical ligand.

The pyrazine ring (pzn) lies on an inversion centre, oriented to the basal plane (O1, O2, N1, N2) at an angle of 30.4 (4)°; it acts as a bidentate ligand joining two CuTSB molecules to form pzn$(CuTSB)_2$, with a Cu—N2 distance of 2.053 (2) Å. The overall effect of the dual linkage of monomers (*via* pyrazine N and TSB O atoms) is to form chains parallel to [100] with composition $[pzn(CuTSB)_2]_\infty$.

The chains are stabilized through hydrogen bonding with water molecules. The H atoms of two O4 water molecules and two O5 build an eight-membered ring. Additionally, two O3 atoms of the ligands also build an eight-membered ring [O3···H52—O5—H51]$_2$ to form finally a two-dimensional network of $\{[pzn(CuTSB)_2].4H_2O\}_\infty$.

† Alternative name: poly[μ-pyrazine-*N*:*N*′-bis[μ-(*N*-salicylidene-*R*,*S*-alaninato-O^1,*N*,O^2:O^1)copper(II)]] tetrahydrate.