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Magnesium iodide–4,4′-bipyridine–water (1/3/4) and strontium iodide–4,4′-bipyridine–propan-1-ol (1/2.5/2)

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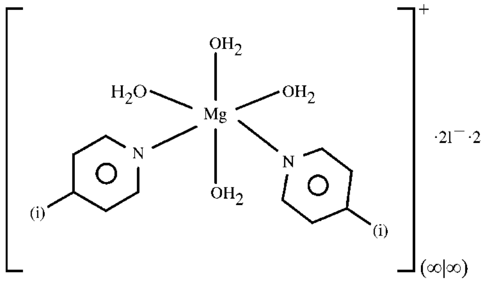
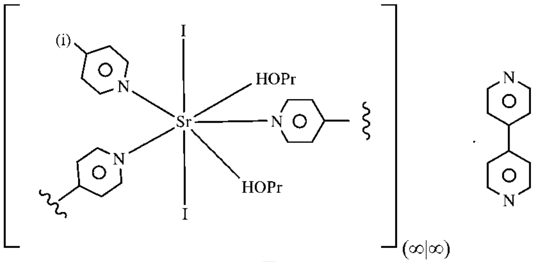
Both of the title compounds, *catena*-poly[[[tetraaquamagnesium(I)]-μ-4,4′-bipyridine-κ^2N:N'] diiodide bis(4,4′-bipyridine) solvate], $\{[Mg(C_{10}H_8N_2)(H_2O)_4]I_2\cdot 2C_{10}H_8N_2\}_n$, (I), and *catena*-poly[[[μ-4,4′-bipyridine-bis[diiodobis(propan-1-ol)strontium(I)]]-di-μ-4,4′-bipyridine-κ^4N:N'] bis(4,4′-bipyridine) solvate], $\{[Sr_2I_4(C_{10}H_8N_2)_3(C_3H_8O)_4]\cdot 2C_{10}H_8N_2\}_n$, (II), are one-dimensional polymers which are single- and double-stranded, respectively, the metal atoms being linked by the 4,4′-bipyridine moieties. The Mg complex, (I), is [*cis*-$\{(H_2O)_4Mg(N\text{-}4,4'\text{-bipyridine-}N')_{(2/2)}\}]_{(\infty|\infty)}I_2\cdot$4,4′-bipyridine and Mg has a six-coordinate quasi-octahedral coordination environment. The Sr complex, (II), is isomorphous with its previously defined Ba counterpart [Kepert, Waters & White (1996). *Aust. J. Chem.* **49**, 117–135], being [(propan-1-ol)$_2$-$I_2Sr(N\text{-}4,4'\text{-bipyridine-}N')_{(3/2)}]_{(\infty|\infty)}\cdot$4,4′-bipyridine, with the I atoms *trans*-axial in a seven-coordinate pentagonal–bipyramidal Sr environment.

Comment

In the course of extended studies undertaken some years ago concerning the synthesis and structural characterization of nitrogen base adducts of simple group 2 salts with simple nitrogen base ligands, a hitherto largely unexplored fundamental field, we investigated derivatives formed between the metal halides and the inherently bridging bidentate ligand 4,4′-bipyridine, in the expectation that unusual polymeric arrays might be obtained (Kepert *et al.*, 1996). In doing so, the metal iodides were dissolved with the ligand in 1:2 millimolar stoichiometry in a few millilitres of alcoholic solvent (propan-1-ol for the heavier metals, methanol for the lighter) under anaerobic conditions, *i.e.* specifically excluding moisture. At the time, a crystalline deposit was obtained only of a barium complex, which proved to be an adduct of stoichiometry BaI_2–4,4′-bipyridine–propan-1-ol (1/2.5/2), a novel polymer in which seven-coordinate Ba atoms of pentagonal–bipyramidal stereochemistry (environment: $BaI_2N_3O_2$), comprising two axial I atoms, three pyridyl N atoms (from different ligands) and two propan-1-ol O atoms, were linked into a one-dimensional double-stranded polymer. After standing for some years, two parallel vials containing magnesium iodide with the ligand in methanol, and strontium iodide with the ligand in propan-1-ol, deposited significant quantities of colourless well formed crystals, *viz.* the title complexes, (I) and (II), respectively. The Sr complex, (II), proved to be a counterpart of the previously described Ba adduct, while the Mg complex, (I), is an adduct of the form MgI_2–4,4′-bipyridine–water (1/3/4), presumably consequent upon the slow admission of water from the surroundings over an extended period and/or some presence in the initial mixture. In both complexes, coordinated bridging 4,4′-bipyridine moieties are found, so that polymers result. In both compounds, uncoordinated 4,4′-bipyridine moieties are also found, which are prone to stack or interleave interstitially, being (quasi-)planar but not inflexibly so.


(I)


(II)

In complex (I), one half of the 1/3/4 MgI_2–4,4′-bipyridine–water formula unit comprises the asymmetric unit of the structure, the Mg atom being disposed on a crystallographic 2 axis, while the mid-point of the central bond of the coordinated 4,4′-bipyridine ligand lies at a crystallographic centre of symmetry, with the two C_5N rings necessarily parallel and essentially coplanar, and the Mg atom deviating by 0.234 (6) and 0.199 (14) Å. The lattice 4,4′-bipyridine moiety is fully crystallographically independent. The Mg atom environment is six-coordinate and quasi-octahedral in stereochemistry. Symmetry-related 4,4′-bipyridine moieties lie *cis* in the coordination sphere, bonded through their N atoms and bridging to inversion-related Mg atoms to generate an infinite one-dimensional zigzag polymeric cation along the crystallographic *c* axis (Fig. 2).

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Coordination distances to the Mg atom (Table 1) are unremarkable and are comparable with values reported for similar bonds in complexes containing pyridine bases and aqua ligands (*e.g.* Waters & White, 1996), there being no significant difference in the two Mg—OH_2 distances indicative of any significant difference in the *trans* effects of the two ligand types.

Although the polymer of (I) is one-dimensional, its profile is extended in the second dimension (*b*) by its zigzag aspect, with the overall array having a planar core disposed in the *bc* face of the cell (Fig. 2*b*) and the dihedral angle of the C_5N ligand plane to that face being 51.0 (1)°. One H atom from each water molecule is involved in a strong hydrogen bond projecting out of the plane to the same nearby iodide ion (Table 2), and these interactions are perhaps responsible for the considerable deviations of the angles about the Mg atom from orthogonality. Whereas the coordinated ligand is essentially planar, the uncoordinated moiety is twisted about its central bond, the dihedral angle between the two C_5N planes (χ^2 = 20 and 1) being 33.8 (2)°.

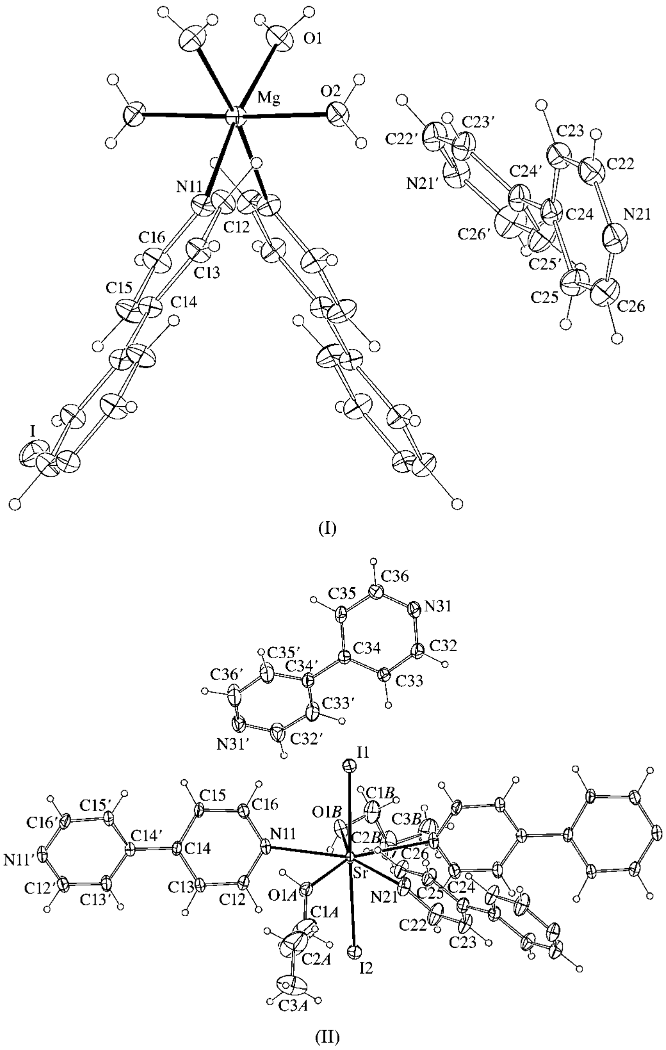

Figure 1
(*a*) The numbering scheme and coordination around the Mg atom for (I). (*b*) The numbering scheme and coordination around the Sr atom for (II). Displacement ellipsoids are drawn at the 20% probability level in this and other figures and H atoms are shown with arbitrary radii of 0.1 Å.

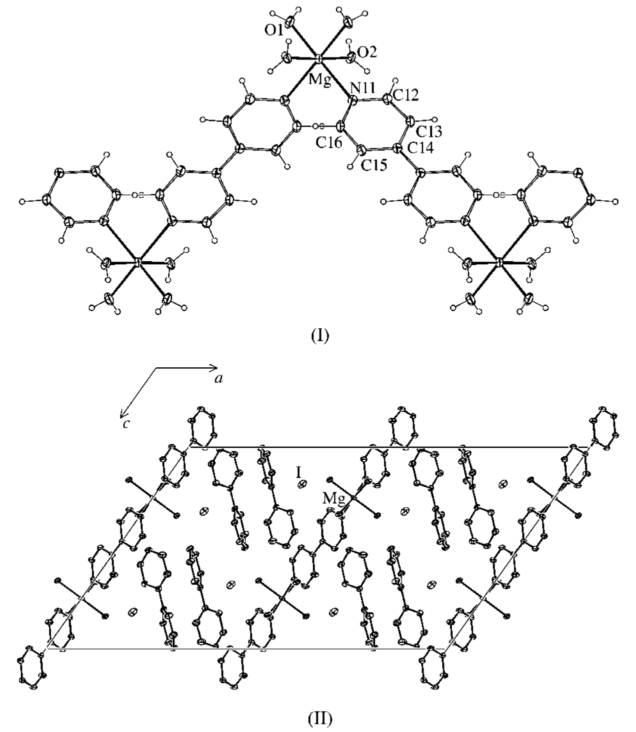

Figure 2
(*a*) A strand of the polymeric cation of the magnesium complex, (I), projected normal to its plane (*bc*) and with its axis, parallel to crystallographic *c*, horizontal in the page. (*b*) The unit-cell contents of (I) projected down *b*, showing the disposition of anions and lattice 4,4′-bipyridine moieties between the polymer planes, which lie about the *bc* face of the cell.

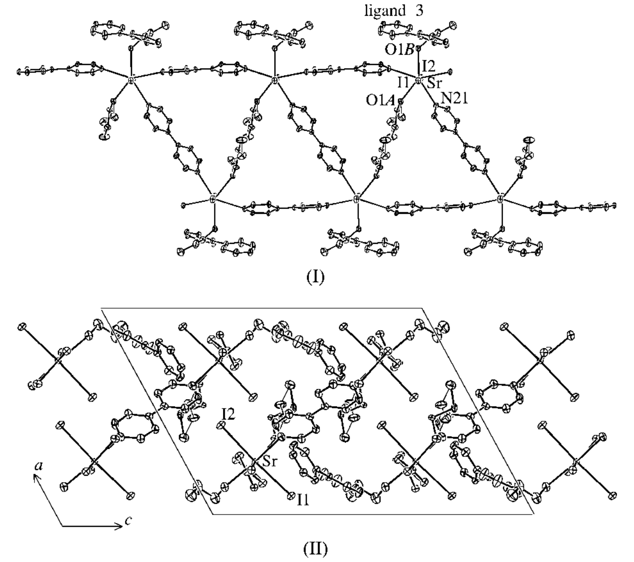

Figure 3
(*a*) The double-stranded array of (II), generated by the unit *b* translation together with inversion (*b* horizontal in the page). (*b*) Unit-cell projection of (II) down the polymer *b* axis, showing its extent and disposition across the cell diagonal.

The Sr complex, (II), is isomorphous with its Ba counterpart, previously recorded elsewhere (Kepert *et al.*, 1996). One full formula unit, devoid of crystallographic symmetry (but see below), comprises the asymmetric unit of the structure. The coordinated 4,4′-bipyridine complement comprises the two halves of different ligands 1, this ligand bridging to a unit translation-related metal atom along *b*, and one half of ligand 2, which lies with the mid-point of its central bond disposed at a crystallographic inversion centre. The two rings of the second ligand are necessarily parallel and quasi-coplanar, the metal atom deviating from the C_5N plane (χ^2 = 5.6) by 0.34 (1) Å. The two similar component planes (χ^2 = 6.5 and 0.4) of the first ligand lie twisted about the central bond with respect to each other, with an interplanar dihedral angle of 23.0 (4)° and with the associated Sr atoms considerably [0.81 (1) and 1.23 (3) Å] out of plane in each case. [The third uncoordinated ligand is crystallographically fully independent and is also similarly twisted, the interplanar dihedral angle being 33.7 (4)°.]

The metal atoms of (II) are seven-coordinate, the coordination environment approximating nicely to pentagonal–bipyramidal stereochemistry, with the I atoms occupying the *trans*-axial sites. Two of the five equatorial sites (not *cis*) are occupied by the propan-1-ol ligand O atoms, which thus define the orientation of the other three pyridine N atoms in the $I_2SrO_2N_3$ coordination sphere. As implied above, two of the N atoms come from the two independent rings of the symmetry-related ligands 1 which extend the resulting polymer in *b*; the other is from the independent half of ligand 2 which, by inversion, extends the polymer in the second dimension across the cell diagonal. The resulting planar array (Fig. 3*a*) comprises a double-stranded polymer running parallel to *b* (Fig. 3*b*).

The metal atom environment of (II) may be compared with that of its Ba counterpart, in which the Ba—I(1,2)/O(1*A*,*B*)/N(11,21,11′) distances are 3.382 (4), 3.403 (4), 2.69 (2), 2.74 (1), 2.85 (2), 2.94 (2) and 2.91 (2) Å, respectively. Thus, the differences between the Ba and Sr bond lengths for I, O and N donors are 0.13, 0.15, 0.14 Å, respectively, suggesting no outstanding differential between bond types.

Experimental

The title complexes were obtained as outlined in the *Comment*. Analysis for (I), found: C 43.7, H 4.0, N 8.4%; $C_{31}H_{36}I_2N_5O_2Sr$ requires: C 43.70, H 4.26, N 8.22%. Analysis for (II), found: C 44.2, H 3.7, N 10.3%; $C_{30}H_{32}I_2MgN_6O_4$ requires: C 44.01, H 3.94, N 10.26%.

Compound (I)

Crystal data

$[Mg(C_{10}H_8N_2)(H_2O)_4]I_2\cdot 2C_{10}H_8N_2$
M_r = 818.75
Monoclinic, $C2/c$
a = 27.574 (7) Å
b = 9.018 (4) Å
c = 16.974 (3) Å
β = 125.23 (2)°
V = 3448 (2) Å^3
Z = 4

D_x = 1.577 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8 reflections
θ = 18.1–23.8°
μ = 1.88 mm^{-1}
T = 298 (2) K
Block, colourless
0.35 × 0.33 × 0.32 mm

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

Mg—O1	2.056 (4)	Mg—O1^i	2.056 (4)
Mg—O2	2.052 (3)	Mg—O2^i	2.052 (3)
Mg—N11	2.226 (4)	Mg—N11^i	2.226 (4)
O1—Mg—O2	85.66 (12)	N11—Mg—O1^i	89.70 (13)
O1—Mg—N11	172.90 (14)	N11—Mg—O2^i	94.13 (13)
O1—Mg—O1^i	93.28 (15)	N11—Mg—N11^i	88.08 (14)
O1—Mg—O2^i	92.52 (13)	O1^i—Mg—O2^i	85.66 (13)
O1—Mg—N11^i	89.70 (13)	O1^i—Mg—N11^i	172.90 (14)
O2—Mg—N11	87.78 (12)	O2^i—Mg—N11^i	87.78 (12)
O2—Mg—O1^i	92.52 (13)	Mg—N11—C12	121.0 (3)
O2—Mg—O2^i	177.35 (14)	Mg—N11—C16	122.8 (2)
O2—Mg—N11^i	94.13 (13)		

Symmetry code: (i) $1-x, y, \frac{1}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1B⋯I^{ii}	0.76 (5)	2.88 (4)	3.601 (3)	161 (4)
O2—H2A⋯I^{ii}	0.75 (6)	2.71 (6)	3.466 (3)	178 (5)

Symmetry code: (ii) $1-x, 1+y, \frac{1}{2}-z$.

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: Gaussian (*ABSORB* in *Xtal*3.5; Hall *et al.*, 1995)
T_{min} = 0.58, T_{max} = 0.63
5196 measured reflections
3955 independent reflections

2964 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.5°
$h = -31 \rightarrow 35$
$k = -11 \rightarrow 0$
$l = -22 \rightarrow 4$
8 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F
R = 0.040
wR = 0.052
S = 1.02
2964 reflections
260 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o)]$, where $\sigma(I) = [\sigma(I)_{meas} + 0.0004(I_{net})^2]^{1/2}$
$(\Delta/\sigma)_{max}$ = 0.049
$\Delta\rho_{max}$ = 1.06 e Å^{-3}
$\Delta\rho_{min}$ = −0.50 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 35 (4) × 10^3

Compound (II)

Crystal data

$[Sr_2I_4(C_{10}H_8N_2)_3(C_3H_8O)_4]\cdot 2C_{10}H_8N_2$
M_r = 1704.2
Monoclinic, $P2_1/c$
a = 15.365 (2) Å
b = 12.392 (2) Å
c = 20.979 (2) Å
β = 118.493 (8)°
V = 3510.6 (8) Å^3
Z = 2

D_x = 1.612 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8 reflections
θ = 16.7–18.5°
μ = 3.33 mm^{-1}
T = 298 (2) K
Prism, colourless
0.53 × 0.40 × 0.18 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\omega$ scans
Absorption correction: Gaussian (*ABSORB* in *Xtal*3.5; Hall *et al.*, 1995)
T_{min} = 0.33, T_{max} = 0.56
11 868 measured reflections
6161 independent reflections

4203 reflections with $I > 2\sigma(I)$
R_{int} = 0.025
θ_{max} = 25.0°
$h = -18 \rightarrow 18$
$k = -14 \rightarrow 0$
$l = -24 \rightarrow 21$
8 standard reflections
frequency: 60 min
intensity decay: none

Table 3
Selected geometric parameters (Å, °) for (II).

Sr—I1	3.2530 (11)	Sr—N11	2.729 (5)
Sr—I2	3.2801 (11)	Sr—N21	2.797 (5)
Sr—O1*A*	2.549 (4)	Sr—N11′$^{\rm iii}$	2.764 (5)
Sr—O1*B*	2.592 (4)		
I1—Sr—I2	176.07 (2)	O1*A*—Sr—O1*B*	140.38 (15)
I1—Sr—O1*A*	90.77 (16)	O1*A*—Sr—N11	70.08 (15)
I1—Sr—O1*B*	96.68 (16)	O1*A*—Sr—N21	70.34 (16)
I1—Sr—N11	88.27 (17)	O1*A*—Sr—N11′$^{\rm iii}$	139.79 (15)
I1—Sr—N21	88.06 (17)	O1*B*—Sr—N11	71.32 (15)
I1—Sr—N11′$^{\rm iii}$	86.74 (17)	O1*B*—Sr—N21	148.43 (16)
I2—Sr—O1*A*	87.76 (15)	O1*B*—Sr—N11′$^{\rm iii}$	79.64 (15)
I2—Sr—O1*B*	86.76 (16)	N11—Sr—N21	140.18 (16)
I2—Sr—N11	94.66 (17)	N11—Sr—N11′$^{\rm iii}$	149.72 (15)
I2—Sr—N21	88.01 (17)	N21—Sr—N11′$^{\rm iii}$	69.46 (16)
I2—Sr—N11′$^{\rm iii}$	92.03 (17)		

Symmetry code: (iii) $x, 1+y, z$.

Refinement

Refinement on F
$R = 0.044$
$wR = 0.05$
$S = 1.26$
4203 reflections
388 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o)]$, where $\sigma(I) = [\sigma(I)_{\rm meas} + 0.0004(I_{\rm net})^2]^{1/2}$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.87$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.55$ e Å^{-3}

The H atoms were located from difference Fourier maps and placed in idealized positions for those on C [C—H = 0.95 Å, $U_{\rm iso}$(H) = $1.25U_{\rm eq}$(CH) and $1.5U_{\rm eq}$(CH_3 and OH)], and were refined (in x, y, z and U) for (I) but not refined for (II). Atoms C1*A* and C2*A* of one propanol group of (II) were each modelled as disordered over two sites, C1*A*/C1*A*′ and C2*A*/C2*A*′, and assigned site-occupancy factors of 0.5 after initial trial refinement.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1418). Services for accessing these data are described at the back of the journal.

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