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The layered compound poly[μ_2-4,4′-bipyridyl-di-μ_2-chlorido-mercury(II)]

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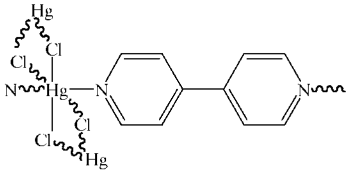
The title compound, $[HgCl_2(C_{10}H_8N_2)]_n$, features two-dimensional $[HgCl_2(4,4'\text{-bipy})]_n$ neutral networks (4,4′-bipy is 4,4′-bipyridine), based on an octahedral Hg atom coordinated by four μ_2-Cl atoms and two μ_2-4,4′-bipy ligands in *trans* positions, yielding a $HgCl_4N_2$ octahedron. The structure has *mmm* symmetry about the Hg atoms, with most of the atoms on at least one mirror plane, but the unsubstituted C atoms of the 4,4′-bipy rings are disordered across a mirror plane. Photoluminescent investigations reveal that the title compound displays a strong emission in the green region, which probably originates from a ligand-to-ligand charge-transfer transition.

Comment

Being an important class of inorganic–organic hybrid materials, metal halide–bipy systems (bipy is bipyridine) have attracted increasing attention in recent years, not only for their intrinsic aesthetic appeal, but also for their various potential applications. 4,4′-Bipy is a common linear synthon used in supramolecular syntheses. Many structures of metal halide–bipy materials have been reported (Figgis *et al.*, 1983; Hu *et al.*, 2003; Lu *et al.*, 1998). However, group 12 (IIB) metal halide–bipy materials are relatively rare. We describe here the synthesis and characterization of $[HgCl_2(4,4'\text{-bipy})]_n$, (I).



(I)

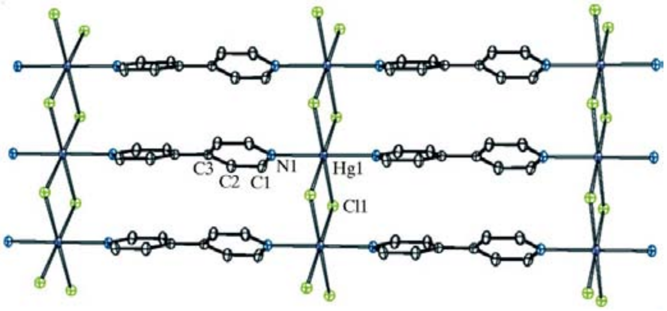


Figure 1
The layered structure of the title compound, showing the atom labels for the asymmetric unit and only one of the possible orientations of the disordered 4,4′-bipy rings. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

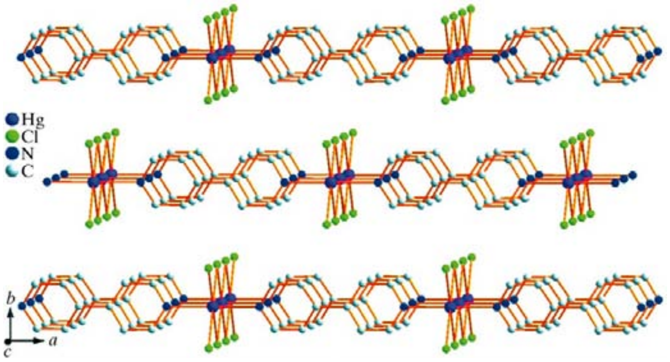


Figure 2
The packing of (I), showing the stacks of layers. H atoms have been omitted for clarity.

X-ray diffraction analysis reveals that the title compound features two-dimensional $[HgCl_2(4,4'\text{-bipy})]_n$ neutral networks, as shown in Fig. 1. The structure has high symmetry, with most of the atoms (except for atoms C1 and C2) lying on at least one mirror plane. The divalent Hg^{II} metal center, which is on an *mmm* site, has a slightly distorted octahedral coordination with four μ_2-Cl atoms and two bridging 4,4′-bipy ligands in *trans* positions, yielding edge-shared $HgCl_4N_2$ octahedra (Table 1). Each 4,4′-bipy ligand also has crystallographic *mmm* symmetry about its mid-point. The unsubstituted C atoms of the 4,4′-bipy rings, *viz*. C1 and C2, sit slightly off a mirror plane and so are disordered about it. Thus, the 4,4′-bipy ligand is twisted with an angle between the planes of the rings of 33.69 (19)°. The $HgCl_4N_2$ octahedra are interconnected *via* two μ_2-Cl atoms, forming a linear inorganic chain running along the [001] direction. These chains are bridged by μ_2-4,4′-bipy ligands to form inorganic–organic hybrid two-dimensional layers, which lie parallel to the (010) plane (Fig. 1). The atoms in adjacent layers are offset from one another by one-half of the length of the *a* axis. In this way, the layers stack in an –*ABAB*– mode along the *b* axis to yield the three-dimensional structure (Fig. 2).

It is noteworthy that group 12 (IIB) metal halide–bipy materials are relatively rare and, to our knowledge, only two halide–4,4′-bipy compounds have been reported, *viz*. HgI_2–4,4′-bipy (Niu *et al.*, 2003; Morsali & Zhu, 2006) and ZnI_2–4,4′-bipy (Fan & Wu, 2006). Both of these compounds exhibit a one-dimensional structure, in contrast to the two-dimensional structure of the title compound. For HgI_2–4,4′-bipy and ZnI_2–4,4′-bipy, each 4,4′-bipy ligand bridges two HgI_2 or ZnI_2 groups to form a one-dimensional zigzag single chain. In both

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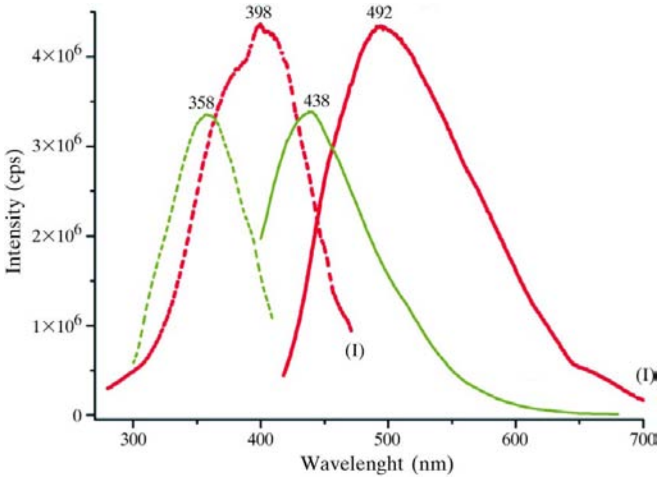

Figure 3
Solid-state emission and excitation spectra of (I) and pure 4,4′-bipyridine at room temperature. Solid lines: emission spectra; dashed lines: excitation spectra.

structures, the I atoms are terminally coordinated to the metal centers, while in the title compound the Cl atoms act as bridging atoms. For the title compound, the Hg atom is in an octahedral coordination environment, while in the two diiodide compounds, the metal atoms are in tetrahedral coordination environments.

The solid-state emission spectrum of the title compound was investigated at room temperature (Fig. 3). The fluorescence spectrum shows that the title compound exhibits a broad and strong emission with a maximum wavelength of 492 nm upon photo-excitation at 398 nm, which is red-shifted by 54 nm compared with that of pure 4,4′-bipy (Fig. 3). The emission of (I) can probably be assigned to the ligand-to-ligand charge-transfer transition from the highest occupied molecular orbital of the Cl atom to the lowest occupied molecular orbital of the 4,4′-bipy group. Thus, this compound may be a candidate in green-light luminescent materials.

Experimental

$HgCl_2$ (0.1 mmol, 27 mg), 4,4′-bipyridine (0.2 mmol, 31 mg), ethanol (1 ml) and distilled water (3 ml) were loaded into a Teflon-lined stainless steel autoclave (25 ml) and kept at 473 K for 3 d. After the mixture had been cooled slowly to room temperature at a rate of 8 K h^{-1}, colorless crystals suitable for X-ray analysis were obtained.

Crystal data

$[HgCl_2(C_{10}H_8N_2)]$
$M_r = 427.67$
Orthorhombic, *Cmmm*
$a = 11.6289$ (17) Å
$b = 12.179$ (2) Å
$c = 3.8538$ (7) Å
$V = 545.81$ (16) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 14.55$ mm^{-1}
$T = 293$ (2) K
0.16 × 0.09 × 0.05 mm

Data collection

Rigaku AFC-7*R* diffractometer
Absorption correction: ψ scan (*Psi* in *WinAFC*; Rigaku Corporation, 2002)
$T_{min} = 0.571$, $T_{max} = 1.000$ (expected range = 0.276–0.483)
338 measured reflections
323 independent reflections
323 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
30 standard reflections every 5 reflections intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.019$
$wR(F^2) = 0.045$
$S = 1.09$
323 reflections
35 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.90$ e Å^{-3}
$\Delta\rho_{min} = -1.11$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg1—N1	2.280 (4)	Hg1—Cl1	2.7549 (9)
Cl1^i—Hg1—Cl1	91.23 (4)		

Symmetry codes: (i) $-x, -y, -z+1$.

All H atoms were placed geometrically and refined using a riding model, with C—H distances of 0.93 Å and U_{iso}(H) values of $1.2U_{eq}$(C).

Data collection: *WinAFC* (Rigaku, 2002); cell refinement: *WinAFC*; data reduction: *CrystalStructure* (Rigaku, 2002); program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3048). Services for accessing these data are described at the back of the journal.

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