(4,4′-Bipyridine)mercury(II) Coordination Polymers, Syntheses, and Structures

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Mercury(II) complexes with 4,4′-bipyridine (4,4′-bipy) ligand were synthesized and characterized by elemental analysis, and IR, ^{1}H- and ^{13}C-NMR spectroscopy. The structures of the complexes $[Hg_3(4,4'\text{-bipy})_2(CH_3COO)_2(SCN)_4]_n$ (**1**), $[Hg_5(4,4'\text{-bipy})_5(SCN)_{10}]_n$ (**2**), $[Hg_2(4,4'\text{-bipy})_2(CH_3COO)_2]_n(ClO_4)_{2n}$ (**3**), and $[Hg(4,4'\text{-bipy})I_2]_n$ (**4**) were determined by X-ray crystallography. The single-crystal X-ray data show that **2** and **4** are one-dimensional zigzag polymers with four-coordinate Hg-atoms, whereas **1** is a one-dimensional helical chain with two four-coordinate and one six-coordinate Hg-atom. Complex **3** is a two-dimensional polymer with a five-coordinate Hg-atom. These results show the capacity of the Hg-ion to act as a soft acid that is capable to form compounds with coordination numbers four, five, and six and consequently to produce different forms of coordination polymers, containing one- and two-dimensional networks.

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1. Introduction. – Over the last few years, there has been much interest in trying to design and build 1D, 2D, and 3D polymeric networks from mononuclear metal building blocks and linear N,N′-donor spacers such as 4,4′-bipyridine (4,4′-bipy) [1–14]. So far, extended systems of a variety of metals have been characterized providing very interesting information about supramolecular isomerism.

In contrast, reports on coordination polymers of transition-metal ions or of mean-group metal ions such as mercury(II) are disproportionately sparse when compared with that of other metals. Typically, Hg^{II} complexes with spacer ligands such as 4,4′-bipy have been rarely described until recently, probably because of the low solubility of these complexes resulting in unsuccessful isolating of suitable single crystals. In the present work, we used a new method (branch-tube method) by which single crystals of adducts were formed from the 4,4′-bipy ligand and Hg^{II} ions with different counter-ions, *i.e.*, $[Hg_3(4,4'\text{-bipy})_2(MeCOO)_2(SCN)_4]_n$ (**1**), $[Hg_5(4,4'\text{-bipy})_5(SCN)_{10}]_n$ (**2**), $[Hg_2(4,4'\text{-bipy})_2(CH_3COO)_2]_n(ClO_4)_{2n}$ (**3**), and $[Hg(4,4'\text{-bipy})I_2]_n$ (**4**) were synthesized and isolated.

Experimental. – *General.* M.p.: *Electrothermal 9100* apparatus; uncorrected. IR Spectra: nujol mulls; *Perkin-Elmer 597* and *Nicolet 510P* spectrophotometers; $\tilde{\nu}$ in cm^{-1}. Microanalyses: *Heraeus CHNO-Rapid* analyzer.

Bis(acetato)bis(4,4′-bipyridine)tetrakis(thiocyanato-κS)trimercury Polymer ($[Hg_3(4,4'\text{-bipy})_2(CH_3COO)_2(SCN)_{4n}]$; **1**). Ligand 4,4′-bipy (0.156 g, 1 mmol) was placed in one arm of the branched tube, and a mixture of mercury(II) acetate (0.160 g, 0.5 mmol) and mercury(II) thiocyanate (0.159 g, 0.5 mmol) was placed in the other arm. MeOH was carefully added to fill both arms, the tube sealed, and the salt-containing arm immersed in a bath at 60° while the other was at r.t. (see *Fig. 1*). After 12 days, white crystals had deposited in the cooler arm which were filtered off, washed with acetone and Et_2O, and air-dried: 0.213 g (45%) of **1**. M.p. 160°. IR (KBr; selected signals): 620*s*, 798*s*, 1212*m*, 1390v*s*, 1573v*s*, 2093v*s*, 3050*w*. ^{1}H-NMR ((D$_6$)DMSO): 1.98 (*s*, 2 MeCOO); 7.90–8.00 (*m*, 8 H, H–C(2,2′), H–C(6, 6′)); 9.50–9.65 (*m*, 8 H, H–C(3,3′), H–C(5,5′)). ^{13}C{^{1}H}-NMR ((D$_6$)DMSO): 21.3 (*Me*COO); 123.5 (C(4,4′)); 146.6 (C(3,3′), C(5,5′)); 151.5 (C(2,2′), C(6,6′)); 174.9 (Me*C*OO). Anal calc. for $C_{60}H_{40}N_{10}O_4S_4Hg_3$: C 32.11, H 2.11, N 9.85; found: C 32.50, H 2.20, N 9.70.

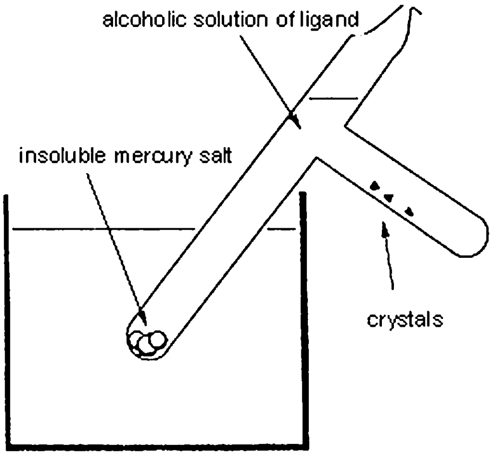

Fig. 1

Pentakis(4,4′-bipyridine)tetrakis(thiocyanato-κS)pentamercury Polymer ([Hg_5(4,4′-bipy)$_5$(SCN)$_{10}$]; **2**). As described for **1**, with 4,4′-bipy (0.156 g, 1 mmol) in one arm and mercury(II) thiocyanate (0.318 g, 1 mmol) in the other arm, for 15 days: 0.190 g (40%) of **2**. Colorless crystals. M.p. 187.5°. IR (KBr; selected signals): 622*s*, 804*s*, 1212*m*, 1390*s*, 1588v*s*, 2095v*s*, 3050*w*. ^{1}H-NMR ((D$_6$)DMSO): 8.10–8.20 (*m*, 4 H, H–C(2,2′), H–C(6,6′)); 8.90–9.00 (*m*, 4 H, H–C(3,3′), H–C(5,5′)). ^{13}C{^{1}H}-NMR ((D$_6$)DMSO): 123.5 (C(4,4′)); 146.6 (C(3,3′), C(5,5′)); 151.5 (C(2,2′), C(6,6′)). Anal calc. for $C_{60}H_{40}Hg_5N_{20}S_{10}$: C 30.44, H 1.69, N 11.84; found: C 30.10, H 1.20, N 11.70.

Bis(acetato)bis(4,4′-bipyridine)dimercury(2+) Diperchlorate Polymer ([Hg_2(4,4′-bipy)$_2$-($CH_3COO)_2]_n(ClO_4)_{2n}$; **3**). *Caution!* Perchlorate salts are potentially explosive and heating must be avoided. We use small quantities, and the synthesis is carried out at the mmol scale. As described for **1**, with 4,4′-bipy (0.156 g, 1 mmol) in one arm and the mixture of mercury(II) acetate (0.200 g, 1 mmol) and sodium perchlorate (0.246 g, 2 mmol) in the other arm for 7 days: 0.229 g (45%) of **3**. Yellow crystals. M.p. 323°. IR (KBr; selected signals): 621*s*, 828*s*, 1108v*s*, 1216*m*, 1399*s*, 1553v*s*, 1590v*s*, 2950*w*, 3105*w*. ^{1}H-NMR ((D$_6$)DMSO): 2.00 (*s*, MeCOO); 8.20–8.30 (*m*, 4 H, H–C(2,2′), H–C(6,6′)); 9.00–9.15 (*m*, H–C(3,3′), H–C(5,5′)). ^{13}C{^{1}H}-NMR ((D$_6$)DMSO): 21.32 (*Me*COO); 123.5 (C(4,4′)); 146.7 (C(3,3′), C(5,5′)); 151.5 (C(2,2′), C(6,6′)); 174.9 (Me*C*OO).

(4,4′-Bipyridine)diiodomercury Polymer ([Hg(4,4′-bipy)I_2]; **4**). As described for **1**, with 4,4′-bipy (0.156 g, 1 mmol) in one arm and mercury(II) acetate (0.200 g, 1 mmol) and potassium iodide (0.332 g, 2 mmol) in the other arm for 12 days: 0.244 g (40%) of **4**. Yellow crystals. M.p. 273°. IR (KBr; selected signals): 617*s*, 798v*s*, 1059*s*, 1209*m*, 1587v*s*, 3010*w*. ^{1}H-NMR ((D$_6$)DMSO): 8.00–8.15 (*m*, 4 H, H–C(2,2′), H–C(6,6′)); 9.05–9.15 (*m*, 4 H, H–C(3,3′), H–C(5,5′)). ^{13}C{^{1}H}-NMR ((D$_6$)DMSO): 123.5 (C(4,4′)); 146.6 (C(3,3′), C(5,5′)); 151.5 (C(2,2′), C(6,6′)). Anal. calc. for $C_{10}H_8HgI_2N_2$: C 19.65, H 1.31, N 4.58; found: C 19.10, H 1.20, N 4.70.

X-Ray Structure Analyses. Crystal data and details of structural determination of compounds **1**–**4** are given in the *Tables 1* and *2*. The single-crystal X-ray diffraction analyses were carried out with a *Bruker-*

Table 1. *Crystal Data and Details of Structural Determination of Compounds* **1** *and* **2**

	1	**2**
Formula	$C_{38}H_{30}Hg_3N_{10}O_4S_4$	$C_{60}H_{40}Hg_5N_{20}S_{10}$
M_r	1420.73	2364.67
Crystal color, shape	colorless, block	colorless, block
Crystal size/mm	0.356 × 0.380 × 0.507	0.158 × 0.260 × 0.345
Space group	triclinic/P-1	orthorhombic/$Pna2_1$
a/Å	8.8839(9)	11.0392(9)
b/Å	10.5144(12)	44.0375(36)
c/Å	12.2546(13)	14.5481(12)
α/°	69.990(2)	90
β/°	86.425(2)	90
γ/°	84.026(2)	90
V/Å^3	1069.31(9)	7072.4(1)
Z	1	4
D/Mg/cm^{-3}	2.206	2.221
T/K	295 ± 2	295 ± 2
μ/mm^{-1}	10.989	11.166
F(000)	664	4400
2θ range/°	53.0	51.0
Measured reflections	6004	36195
Unique reflections	4335	12291
Observed reflections	2987	5440
Number of variables	269	821
R_1 and wR_2 ($I > 2\sigma(I)$)	0.0747, 0.1715	0.0859, 0.2013
R_1 and wR_2 (all data)	0.955, 0.1813	0.1399, 0.2214
Goodness of fit (g.o.f.)	0.925	0.822
Data completeness	97.7%	100.0%

CCDC area detector system. The intensity data were collected by means of graphite-monochromated Mo−K_α radiation (λ 0.71073 Å). Accurate unit-cell parameters and an orientation matrix for data collection were obtained from least-squares refinement. The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2. The positions of H-atoms were idealized and included in the calculations of the structure factors as fixed contributions. Each H-atom was assigned an isotopic thermal parameter. Corrections for the *Lorentz* and polarization effects as well as the empirical correction for absorption using the SADABS programs were applied. All structural calculations were carried out with a *PDP-11/23+* computer and the SDP-PLUS program package [15][16]. CCDC-240093 (**1**), -240092 (**2**), -231499 (**3**), and -231500 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* www.ccdc.cam.ac.uk/data_request/cif.

Discussion. – *Syntheses.* The reaction between the 4,4′-bpy ligand and mercury(II) iodid, mercury(II) thiocyanate, or mixtures of mercury(II) acetate and sodium perchlorate as well as mercury(II) acetate and mercury(II) thiocyanate nitrate by diffusion along a thermal gradient in MeOH solution, according to the branched-tube method (see *Fig. 1*), provided crystalline material analyzing as $[Hg_3(4,4'\text{-bipy})_2(CH_3COO)_2(SCN)_4]_n$ (**1**), $[Hg_5(4,4'\text{-bipy})_5(SCN)_{10}]_n$ (**2**), $[Hg_2(4,4'\text{-bipy})_2(CH_3COO)_2]_n(ClO_4)_{2n}$ (**3**), and $[Hg(4,4'\text{-bipy})I_2]_n$ (4), respectively. Their NMR spectra were compatible with these structures (see *Exper. Part*).

Table 2. *Crystal Data and Details of Structural Determination of Compounds* **3** *and* **4**

	3	**4**
Formula	$C_{24}H_{22}Hg_2Cl_2N_4O_{12}$	$C_{10}H_8HgI_2N_2$
M_r	1030.54	610.57
Crystal color, shape	pale yellow, block	colorless, plate
Crystal size/mm	0.147 × 0.236 × 0.245	0.109 × 0.233 × 0.241
Space group	triclinic/P-1	monoclinic/$C2/c$
a/Å	9.0715(12)	16.789(3)
b/Å	9.8474(14)	5.5702(10)
c/Å	9.8659(14	16.506(3)
α/°	119.080(2)	90
β/°	98.713(3)	118.724(4)
γ/°	92.059(3)	90
V/Å^3	755.19(12)	1353.7(4)
Z	1	4
D/Mg/cm^{-3}	2.266	2.996
T/K	295 ± 2	295 ± 2
μ/mm^{-1}	10.397	15.903
F(000)	484	1072
2θ range/°	54.0	52.0
Measured reflections	4498	3517
Unique reflections	3213	1313
Observed reflections	2339	708
Number of variables	195	69
R_1 and wR_2 ($I > 2\sigma(I)$)	0.0698, 0.1654	0.0813, 0.1933
R_1 and wR_2 (all data)	0.0880, 0.1860	0.1218, 0.2105
Goodness of fit (g.o.f.)	0.930	0.881
Data completeness	97.2%	99.2%

Crystal Structure of $[Hg_3(4,4'\text{-bipy})_2(CH_3COO)_2(SCN)_4]_n$ (**1**). The structure determination of **1** by X-ray crystallography showed the complex in the solid state (*Fig. 2*) to be a polymeric species, *i.e.*, it is a 1D helical-chain polymer. The Hg-atoms are linked within a classical 'stair-polymer' array by O-, S- and N-atoms. There are two types of Hg-atoms, two in a four- and one in a six-coordinate HgO_2S_2N and HgO_4N_2 units, respectively (*Table 3*). The coordination polyhedron about the Hg-atoms with coordination number six is distorted octahedral, and the molecules have an inversion center and approximate D_{2h} symmetry. Each of these Hg-atoms is chelated by two bidentate acetato ligands, through their O-atoms, forming a four-member metallocycle, and two 4,4′-bipy ligands. The N-atoms of the two 4,4′-bipy ligands, the acetato atoms O(2) and O(2)i, and O(1) and O(1)i are mutually in *trans* positions (the angles N(1)–Hg(1)–N(1)i, O(1)–Hg(1)–O(1)i and O(2)–Hg(1)–O(2)i are 180°). The coordination polyhedron about the Hg-atoms with coordination number four is distorted tetrahedral and defined by two S-atoms from two thiocyanato, one O-atom from an acetato and one N-atom from a 4,4′-bipy ligand. It is worth noticing that there are two types of 4,4′-bipy ligands in complex **1**. One type is involved in the octahedral coordination polyhedron as monodentate ligand with a dangling pyridine group. The other type forms a bridge between two tetrahedral Hg^{II} centers by coordination *via* both N-

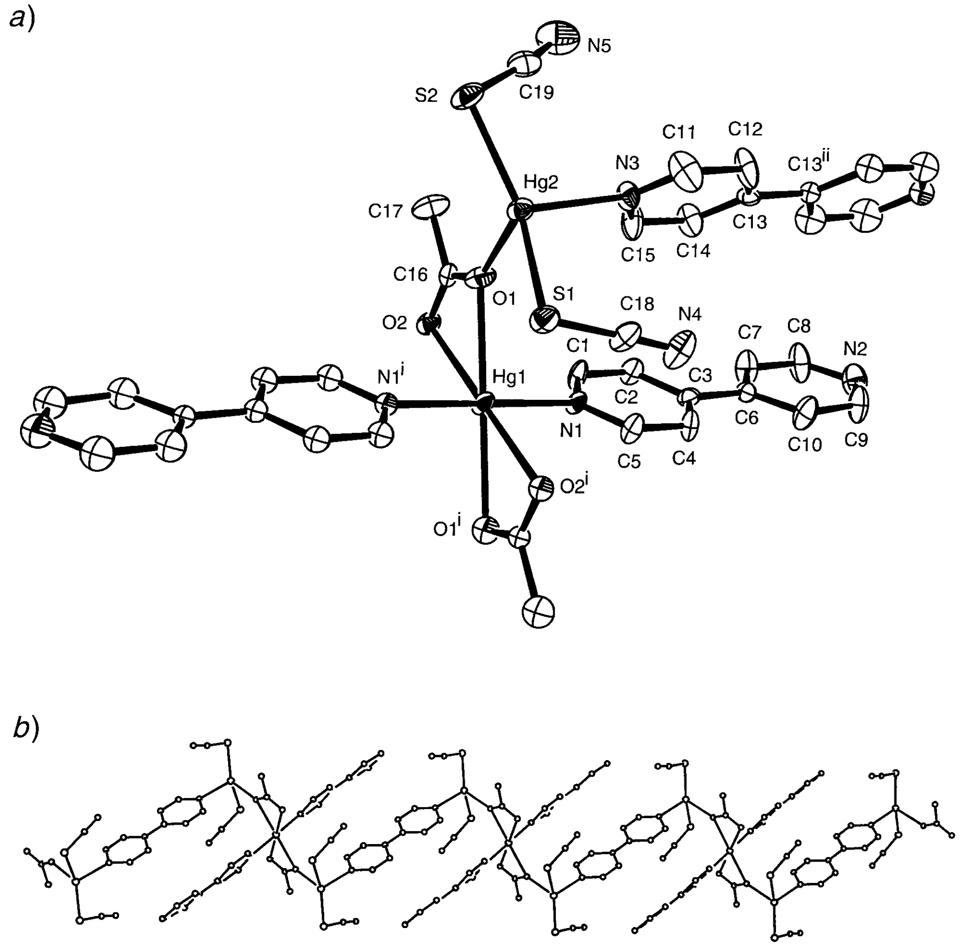

Fig. 2. a) *ORTEP View of compound* **1**; b) *1D network of* **1**. Symmetry codes: $i = -x, 2-y, 2-z$; $ii = 1-x, 2-y, 1-z$. Arbitrary numbering.

atoms, resulting in a novel one-dimensional organic-inorganic hybrid polymer involving simultaneously tetra- and hexa-coordinate Hg^{II} complex units.

Two different structural supramolecular isomers can be generated by angular nodes of *cis*-configurated metal moieties [1], a 1D zigzag chain or a 1D helix. Zigzag-chain polymers are quite common and tend to pack efficiently, whereas the helix coordination polymers are rather rare [1]. The supramolecular structure of complex **1** belongs to the less common one-dimensional helical chain. There are weak intermolecular $Hg \cdots S$, $Hg \cdots N$, and $Hg \cdots Hg$ interactions within complex **1** which induce a distortion of the tetrahedral coordination spheres to distorted pseudo-octahedral geometries (*Fig. 3*). Also $\pi - \pi$ interactions occur between parallel aromatic rings belonging to adjacent chains of two molecules (*Fig. 3*), the centroid-centroid distance, shift angle, and interplanar angle of pyridine moieties being 3.81 Å, 20.45°, and 4.11°, respectively.

Table 3. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for* **1**. Arbitrary numbering (see *Fig. 2,a*)[a]).

Hg(1)–N(1)	2.210(9)	Hg(1)–O(1)	2.501(9)
Hg(2)–S(1)	2.413(4)	Hg(2)–S(2)	2.424(4)
Hg(2)–N(3)	2.442(11)	Hg(2)–O(1)	2.476(11)
Hg(1)–O(2)	2.608(9)		
N(1)–Hg(1)–N(1)^i	180.0	N(1)–Hg(1)–O(1)	91.0(3)
N(1)^i–Hg(1)–O(1)	89.0(4)	O(1)^i–Hg(1)–O(1)	180.0
N(1)–Hg(1)–O(2)^i	89.4(3)	N(1)–Hg(1)–O(2)	90.6(3)
O(1)^i–Hg(1)–O(2)	129.3(3)	O(1)–Hg(1)–O(2)	50.7(3)
O(2)^i–Hg(1)–O(2)	180.0	S(1)–Hg(2)–S(2)	155.2(1)
S(1)–Hg(2)–N(3)	100.1(3)	S(2)–Hg(2)–N(3)	101.3(3)
S(1)–Hg(2)–O(1)	88.7(2)	S(2)–Hg(2)–O(1)	104.9(2)
N(3)–Hg(2)–O(1)	86.9(4)		

[a]) Symmetry code: $i = -x, 2 - y, 2 - z$.

Crystal Structure of $[Hg_5(4,4'\text{-bipy})_5(SCN)_{10}]_n$ (**2**). The crystal structure of complex **2** consists of one-dimensional polymer units of $[Hg_5(4,4'\text{-bipy})_5(SCN)_{10}]$. The N-atoms of the 4,4′-bipy ligands are bridging two different Hg-atoms, and the thiocyanato ligands are coordinated to Hg *via* their S-atoms but are not bridging (*Fig. 4*; *Table 4*). The coordination number of the Hg-atoms is four, involving two 4,4′-bipy and two thiocyanato ligands, and the environment is a distorted tetrahedron. The bridging by 4,4′-bipy produces one-dimensional polymeric units in the solid state. Since the inversion center is not located in the middle of the single C–C bonds between two pyridine moieties of the 4,4′-bipy ligands, the aromatic rings are not coplanar. The two 4,4′-bipy and two thiocyanato ligands are mutually in *cis* position at each metal center, thus generating angular nodes of metal moieties. The supramolecular structure of complex **2** is of the 1D zigzag-chain type [1] (*Fig. 5*).

Crystal Structure of $[Hg_2(4,4'\text{-bipy})_2(CH_3COO)_2]_n(ClO_4)_{2n}$ (**3**). The molecular structure of complex **3** consists of a $[Hg(4,4'\text{-bipy})(CH_3COO)]^+$ cation and ClO_4^- anion (*Fig. 6*). The cationic complex is polynuclear, with each 4,4′-bipy ligand bridging two different Hg-atoms thus creating a chain structure. The two O-atoms of the acetato ligand are coordinated to the same Hg-atom in a bidendate chelating fashion. But one of the chelating O-atoms of the acetato ligand is linked to two different Hg-atoms of adjacent chains yielding 1D infinite chains that run parallel to the *a* axis, and thus a 2D coordination polymer as shown in *Fig. 7*. The coordination around the Hg-atom is a distorted trigonal bipyramide (*Table 5*). Since the inversion center is located at the middle of the C(4)–C(4′) bond (systematic numbering), the aromatic rings of 4,4′-bipy are coplanar. The supramolecular structure of the two-dimensional metal-organic polymer **3** is of the brick-wall type (*Fig. 7*) [1].

Crystal Structure of $[Hg(4,4'\text{-bipy})I_2]_n$ (**4**). The crystal structure of **4** consists of one-dimensional polymer units of $[Hg(4,4'\text{-bipy})I_2]$. The 4,4′-bipy ligand bridges two different Hg-atoms producing a one-dimensional polymer chain, and two I-atoms not involved in bridges are coordinated to each Hg-atom, the Hg–N distance being 2.478 (17) Å and the Hg–I distance 2.6429 (18) Å (*Fig. 8*; *Table 6*). The coordination number in this complex is four. Since the inversion center is located at the middle of the C(4)–C(4′) bond (systematic numbering) of the 4,4′-bipy ligand, the aromatic

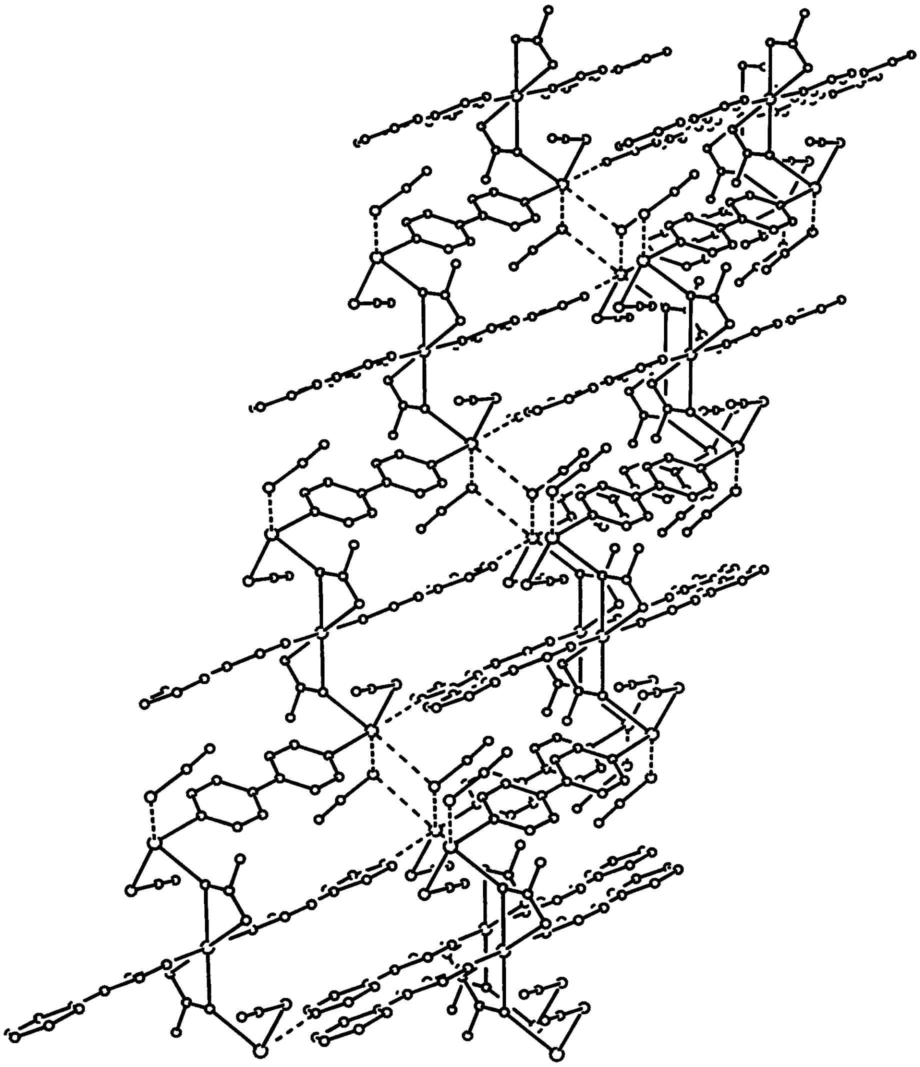

Fig. 3 *π–π Stacking and weak* Hg···S *interactions in the crystal packing of* **1**

rings are coplanar. The two 4,4′-bipy and two I ligands are mutually *cis*-positioned, the angle N(1)–Hg(1)–N(1′) being 96.3(8)° and the angle I(1)–Hg(1)–I(2) being 149.75(13)°, generating angular nodes of metal moieties and a supramolecular structure of the 1D zigzag-chain type (*Fig. 9*).

Recently, the $[Pb(4,4'\text{-bipy})I_2]_n$ complex has been reported [17]. This complex is a 2D polymer and constructed from $[PbI_2]$ units bridged by 4,4′-bipyridine. These infinite chains build edge-sharing distorted PbI_4N_2 octahedrons running parallel to the *c* axis. Complex **4** shows, as a strikingly similar feature to that of the $[Pb(4,4'\text{-bipy})I_2]_n$ complex, π–π stacking [18–19] interactions between parallel aromatic rings belonging to

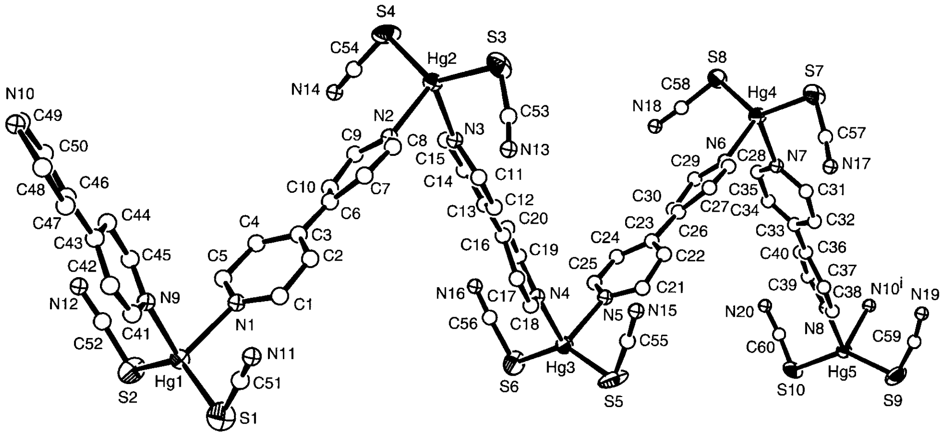

Fig. 4. *ORTEP View of compound* **2**. Arbitrary numbering.

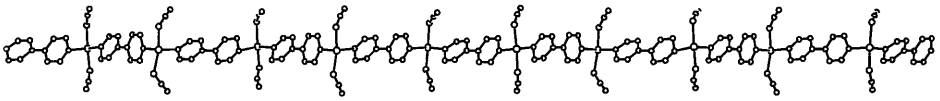

Fig. 5. *View of the one-dimensional chain of* **2**

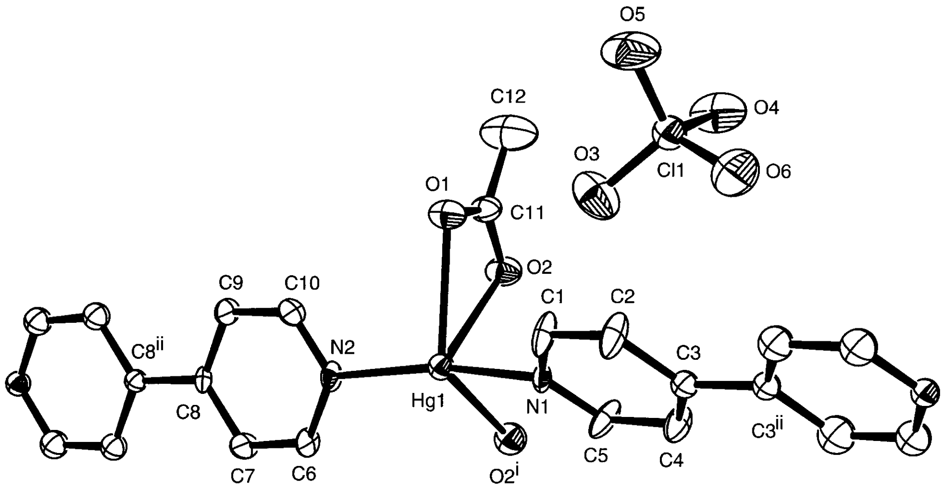

Fig. 6. *ORTEP View of compound* **3**. Symmetry codes: $i=2-x, 1-y, 1-z$; $ii=3-x, 2-y, 2-z$. Arbitrary numbering.

adjacent chains of two molecules, as shown in *Fig. 10*. The mean molecular planes of the aromatic rings separated by a distance of *ca.* 3.5 Å, close to that of the planes in graphite, and the centroid-centroid distance, shift angle, and interplanar angle of the pyridine moieties are 3.77 Å, 18.83°, and 5.71°, respectively.

Table 4. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for* **2**. Arbitrary numbering (see *Fig. 4*)[a]).

Hg(1)–N(1)	2.38(2)	Hg(1)–N(9)	2.34(2)
Hg(1)–S(1)	2.387(12)	Hg(1)–S(2)	2.414 (8)
Hg(2)–N(3)	2.37(2)	Hg(2)–N(2)	2.373(19)
Hg(2)–S(4)	2.392(9)	Hg(2)–S(3)	2.427(8)
Hg(3)–N(4)	2.34(2)	Hg(3)–N(5)	2.39(2)
Hg(3)–S(5)	2.387(11)	Hg(3)–S(6)	2.398(9)
Hg(4)–N(6)	2.33(2)	Hg(4)–N(7)	2.36(2)
Hg(4)–S(8)	2.393(8)	Hg(4)–S(7)	2.436(8)
Hg(5)–N(8)	2.40(2)	Hg(5)–S(10)	2.391(8)
Hg(5)–S(9)	2.403(11)	Hg(5)–N(10)^{i}	2.42(2)
N(9)–Hg(1)–N(1)	90.9(8)	N(9)–Hg(1)–S(1)	105.0(6)
N(1)–Hg(1)–S(1)	108.2(7)	N(9)–Hg(1)–S(2)	112.1(5)
N(1)–Hg(1)–S(2)	101.8(6)	S(1)–Hg(1)–S(2)	131.4(4)
N(3)–Hg(2)–N(2)	87.4(8)	N(3)–Hg(2)–S(4)	106.3(6)
N(2)–Hg(2)–S(4)	111.7(6)	N(3)–Hg(2)–S(3)	105.5(7)
N(2)–Hg(2)–S(3)	106.7(5)	S(4)–Hg(2)–S(3)	130.5(4)
N(4)–Hg(3)–N(5)	95.0(8)	N(4)–Hg(3)–S(5)	100.2(6)
N(5)–Hg(3)–S(5)	103.0(7)	N(4)–Hg(3)–S(6)	109.5(7)
N(5)–Hg(3)–S(6)	103.0(7)	S(5)–Hg(3)–S(6)	138.4(4)
N(6)–Hg(4)–N(7)	88.9(8)	N(6)–Hg(4)–S(8)	115.1(6)
N(7)–Hg(4)–S(8)	103.3(6)	N(6)–Hg(4)–S(7)	106.1(6)
N(7)–Hg(4)–S(7)	107.8(7)	S(8)–Hg(4)–S(7)	128.1(4)
N(8)–Hg(5)–S(10)	108.5(6)	N(8)–Hg(5)–S(9)	99.9(7)
S(10)–Hg(5)–S(9)	139.5(4)	N(8)–Hg(5)–N(10)^{i}	92.7(8)
S(10)–Hg(5)–N(10)^{i}	104.3(6)	S(9)–Hg(5)–N(10)^{i}	102.7(7)

[a]) Symmetry code: $i = 1.5 - x, 0.5 + y, -2.5 + z$.

Table 5. *Selected Bond Lengths* [Å] *and Bond angles* [°] *for* **3**. Arbitrary numbering (see *Fig. 6*)[a]).

Hg(1)–N(1)	2.133(12)	Hg(1)–N(2)	2.162(12)
Hg(1)–O(2)	2.473(13)	Hg(1)–O(1)	2.548(12)
Hg(1)–O(2)^{i}	2.618(12)		
N(1)–Hg(1)–N(2)	166.2(5)	N(1)–Hg(1)–O(2)	96.1(5)
N(2)–Hg(1)–O(2)	97.7(5)	N(1)–Hg(1)–O(1)	90.4(5)
N(2)–Hg(1)–O(1)	98.8(5)	O(2)–Hg(1)–O(1)	50.6(4)
N(1)–Hg(1)–O(2)^{i}	93.9(5)	N(2)–Hg(1)–O(2)^{i}	90.1(5)
O(2)–Hg(1)–O(2)^{i}	70.2(5)	O(1)–Hg(1)–O(2)^{i}	120.7(4)

[a]) Symmetry code: $i = 2 - x, 1 - y, 1 - z$.

Table 6. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for* **4**. Arbitrary numbering (see *Fig. 8*)[a]).

Hg(1)–N(1)	2.482(17)	Hg(1)–I(1)	2.642(2)
N(1)–Hg(1)–N(1)^{i}	96.3(8)	N(1)–Hg(1)–I(1)^{i}	100.2(5)
N(1)–Hg(1)–I(1)	99.8(5)	I(1)–Hg(1)–I(1)^{i}	149.8(1)

[a]) Symmetry code: $i = 1 - x, y, 1.5 - z$.

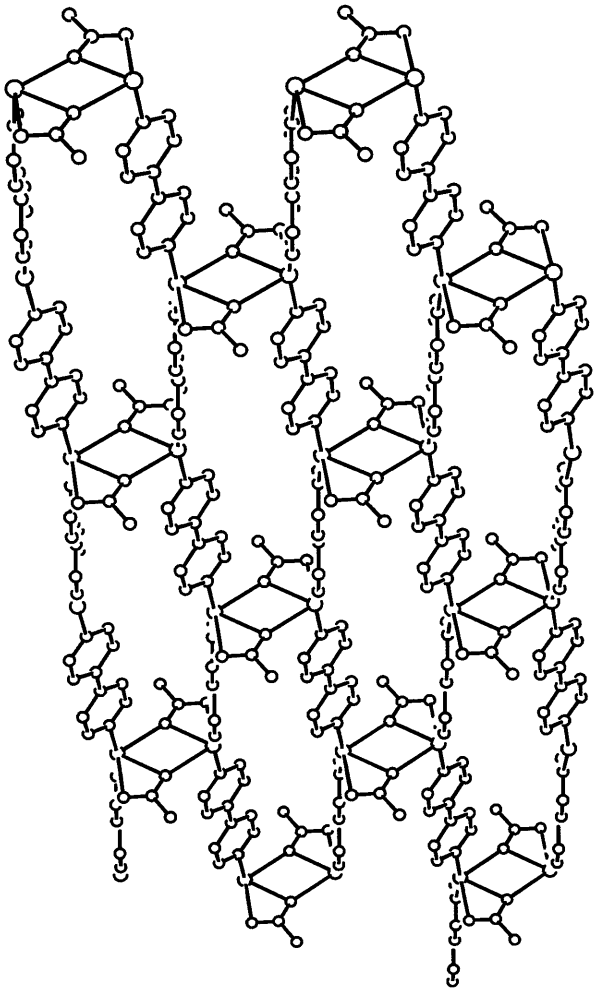

Fig. 7. *Two-dimensional network along [100] of* **3**

A simple model to describe the nature of π–π interactions has been developed by *Hunter et al.* [20]. This model predicts that face-to-face π-stacked interactions will be disfavored due to the dominance of π-π repulsion. It has been shown that electron-poor aromatic groups interact most strongly with electron-rich aromatic groups [21][22]. Hence, since the packing of **4** or $[Pb(4,4'bipy)I_2]_n$ includes equally or almost equally electron-deficient, or indeed electron-rich rings, it is expected that within these structures face-to-face π-stacked interactions are disfavored due to the dominance of π–π repulsion.

The other strikingly similar feature of **4** and $[Pb(4,4'\text{-bipy})I_2]$ [17] is the presence of C–H···I ($-1/2+x$, $1/2+y$, z and $1/2-x$, $-1/2+y$, $3/2-z$) interactions, the weak H-bonding between the H-atoms of the 4,4′-bipy ligand and the I-atoms belonging to

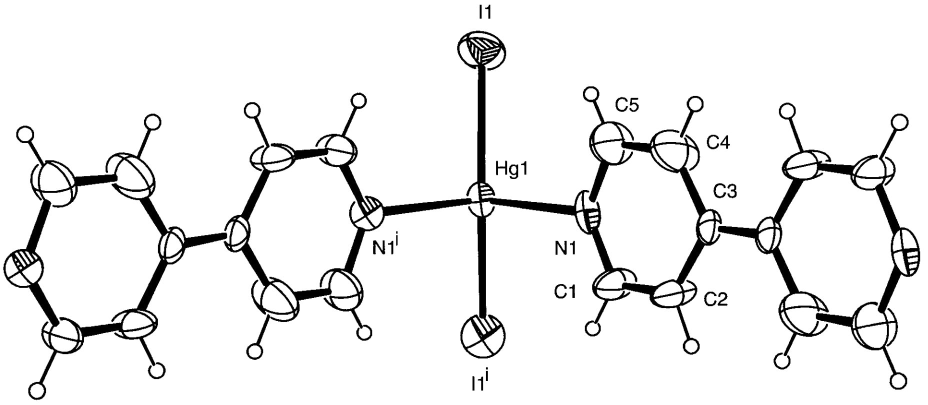

Fig. 8. *ORTEP View of compound* **4**. Symmetry codes: $i = 1-x, y, 1.5-z$. Arbitrary numbering.

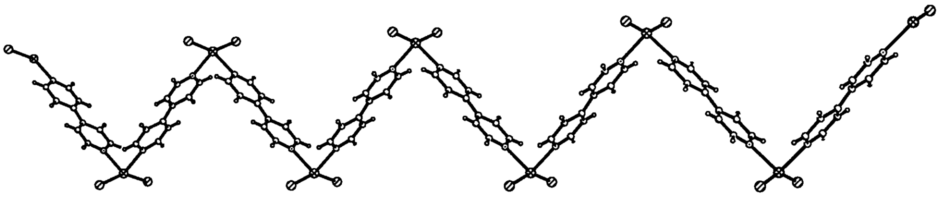

Fig. 9. *1D Zigzag network of* **4**

the adjacent chains of two molecules (*Fig. 10*). The distance C–H···I is 3.800 Å and the distance I···H *ca.* 3.120 Å. The CH···I distance in the [Pb(4,4′-bipy)I_2] complex was reported to be 3.99 Å.

Thus, the crystal structure of complex **4** may be controlled by two factors, the weak hydrogen bonding C–H···I and the π–π stacking. The question then arises whether the C–H···I interactions stretch the coordinate bonds to result in ligand stacking or whether the stacking interactions impose a positioning of the donor atoms to allow C–H···I interactions. Since the face-to-face π-stacked interaction model is disfavored (see above), the C–H···I interactions might be the dominant factor and thus induce the π–π stacking. Indeed, it is now recognized that C–H···I interactions such as O–H···O, C–H···O, C–H···π interactions [23] can also play a significant and predictable structure-determining role in the generation of polymeric structures.

Conclusions. – Four new Hg^{II} coordination polymers containing the 4,4′-bipy ligand are reported. Complexes $[Hg_5(4,4'\text{-bipy})_5(SCN)_{10}]_n$ (**2**) and $[Hg(4,4'\text{-bipy})I_2]_n$ (**4**) are one-dimensional zigzag polymers with four-coordinate Hg-atoms, whereas complex $[Hg_3(4,4'\text{-bipy})_2(CH_3COO)_2(SCN)_4]_n$ (**1**) is a one-dimensional helical chain polymer involving both tetra- and hexa-coordinate Hg^{II} ions, and complex $[Hg_2(4,4'\text{-bipy})_2(CH_3COO)_2]_n(ClO_4)_{2n}$ (**3**) is a two-dimensional polymer with five-coordinate Hg-atoms. The self-assembly of complex **1** represents the first one-dimensional helical-chain polymer involving both tetra- and hexa-coordinate Hg^{II} ions as tetrahedral and octahedral moieties linked by spacer ligand 4,4′-bipy and by acetate anions. The supramolecular struc-

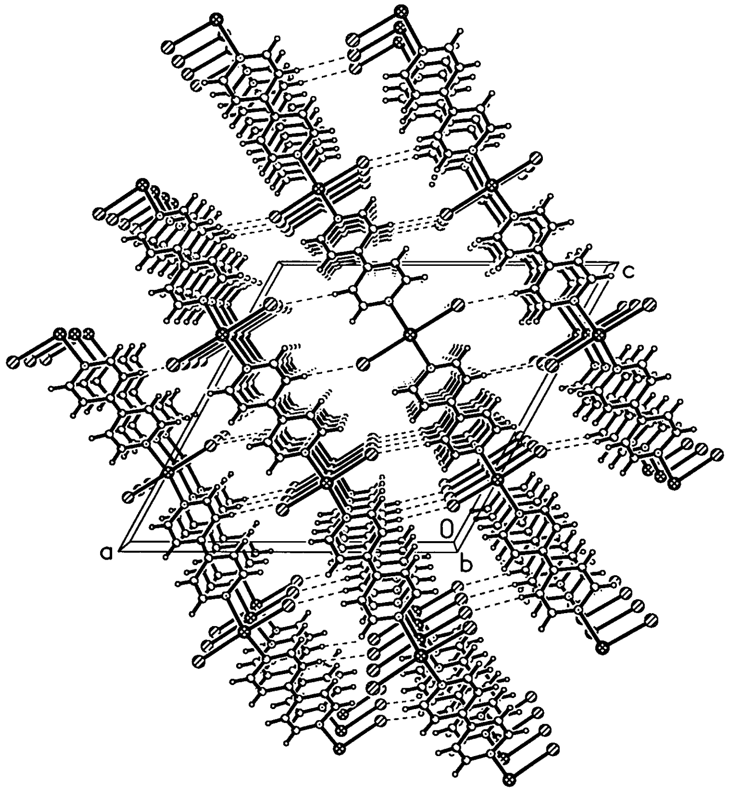

Fig. 10. *π–π Stacking and weak H-bonding,* i.e., *C–H···I interactions, in the crystal packing of* **4**

ture of **2** is a new form of conformational isomer. The structure of compound **3** is a new mixed-anion Hg^{II} complex with three ligands; two of the latter are bridging and thus produce a two-dimensional polymer. In complex **4**, weak H-bonding C–H···I interactions and π–π stacking occur, the C–H···I interactions being probably the most important factor and responsable for the π–π stacking. This study demonstrates the capacity of the Hg-ion to act as a soft acid that is capable to form compounds with coordination numbers four, five, and six, and consequently to adopt different forms of coordination polymers, containing one- and two-dimensional networks. The results also show that the polymeric structures of Hg^{II} complexes are strongly influenced by the counter ions. We anticipate that this property of the Hg^{2+} ion will result in a variety of new coordination polymers and supramolecular complexes with novel polymeric patterns and interesting physical properties.

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REFERENCES

[1] C. Janiak, *Dalton Trans.* **2003**, 2781.
[2] S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276.
[3] M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. Okeeffe, O. M. Yaghi, *Proc. Nat. Acad. Sci. U.S.A.* **2002**, *99*, 4900.
[4] S.-L. Zheng, X.-M. Chen, *Aust. J. Chem.* **2004**, *57*, 703.
[5] D. Maspoch, D. Ruiz-Molina, J. Veciana, *J. Mater. Chem.* **2004**, *14*, 2713.
[6] S. R. Batten, K. S. Murray, *Coord. Chem. Rev.* **2003**, *246*, 103.
[7] L. Carlucci, G. Ciani, D. Proserpio, *Coord. Chem. Rev.* **2003**, *246*, 247.
[8] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629.
[9] D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375.
[10] S. Kitagawa, R. Kitaura, S. Noro, *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.
[11] J. Manna, C. J. Kuehl, J. A. Whiteford, P. J. Stang, D. C. Muddiman, S. A. Hofstadler, R. D. Smith, *J. Am. Chem. Soc.* **1997**, *119*, 11911.
[12] P. J. Stang, B. Olenyuk, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 732.
[13] R. V. Slone, J. T. Hopp, *Inorg. Chem.* **1997**, *36,* 5422.
[14] A. Morsali, L.-G. Zhu, *Inorg. Chem. Commun.* **2004**, *7*, 1184.
[15] G. Ferguson, C. Glidewell, E. S. Lavender, *Acta Crystallogr., Sect. B* **1999**, *55*, 591.
[16] G. M. Sheldrick, 'SHLXTL-97', V5.10, 1997, Bruker AXS Inc., Madison, WI-53719, USA.
[17] Y. J. Shi, Y. Xu, Y. Zhang, B. Huang, D. R. Zhu, C. M. Jin, H. G. Zhu, Z. Yu, X. T. Chen, X. Z. You, *Chem. Lett.* **2001**, 678.
[18] N. N. Greenwood, A. Earnshaw, 'Chemistry of the Elements', Pergamon Press, Oxford, 1984, pp. 235–236.
[19] 'Molecular Complexes', Eds. R. Foster and Paul Elek, Scientific Books Ltd., London, 1973.
[20] C. A. Hunter, J. K. M. Sanders, *J. Am. Chem. Soc.* **1990**, *112*, 5525.
[21] J. C. Collings, K. P. Roscoe, E. G. Robins, A. S. Batsanov, L. M. Stimson, J. A. K. Howard, S. J. Clark, T. B. Marder, *New J. Chem.* **2002**, *26*, 1740.
[22] C. Janiak, *J. Chem. Soc., Dalton Trans.* **2000**, 3885.
[23] M. Brian, Z. J. Michael, *Chem. Rev.* **2001**, *101*, 1629.

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