PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 22 (2003) 1077–1083

POLYHEDRON

www.elsevier.com/locate/poly

Bis(2-pyridylthio)methane complexes of cadmium(II) halides

Almudena Amoedo-Portela [a], Rosa Carballo [a], José S. Casas [b],
Emilia García-Martínez [a,*], Angeles Sánchez-González [b], José Sordo [b,*],
Ezequiel M. Vázquez-López [a]

[a] *Departamento de Química Inorgánica, Universidade de Vigo, 36200 Vigo, Galicia, Spain*
[b] *Departamento de Química Inorgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Galicia, Spain*

Received 12 November 2002; accepted 23 January 2003

Abstract

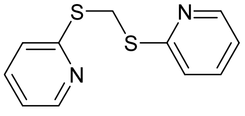
The complexes $[Cd_2Cl_4(bpytm)]$ (**1**), $[CdBr_2(bpytm)]$ (**2**), $[Cd_2Br_4(bpytm)]$ (**3**) and $[CdI_2(bpytm)]$ (**4**) [bpytm = bis(2-pyridylthio)methane] were prepared and characterized by elemental chemical analysis, by IR, Raman and ^1H and ^{13}C NMR spectroscopy, and in the cases of **2** and **4** by X-ray diffractometry. In **2** and **4** the ligand is *N*,*N′*-bidentate, forming an eight-membered chelate ring.

Keywords: Bis(2-pyridylthio)methane; Cadmium(II) complexes; Eight-membered chelate rings; X-ray diffraction; Cadmium(II) halides; NMR spectroscopy

---

1. Introduction

The synthesis and study of flexible N,S-donor ligands able to bridge between metal atoms to give macromolecular compounds or to chelate them to give discrete molecules is attractive as a route to new materials and because it can assist understanding of the interactions of metal ions with molecules present in living systems [1]. Bis(2-pyridylthio)methane {bpytm, $[(pyS)_2CH_2]$} is just such a ligand, the twisted structure given it by its –S–CH$_2$–S– bridge enabling it to adopt a variety of different coordination modes, some of which have previously been described by us [2–4]. For example, in $[ZnCl_2(bpytm)]\cdot H_2O$, $[ZnBr_2(bpytm)]$ and $[ZnI_2(bpytm)]$ it is *N*,*N′*-bidentate, forming an eight-membered chelate ring with a distorted boat-chair conformation; in $[Hg_2Cl_4(bpytm)]$, it is *N*,*N′*-bis-monodentate, bridging between two Hg atoms; and in $[HgBr_2(bpytm)]$ it is N-monodentate.



In order to investigate whether the coordination mode differences between the zinc compounds and mercury compounds described above are associated with the relative softness of Group 12 metals or with their different coordination number ranges, and since a search of the Cambridge Structural Database [5] found only one stable complex of CdX_2 with a chelate ring of eight or more atoms and an N-donor ligand [6], we decided to prepare cadmium(II) chloride, bromide and iodide complexes of bpytm. This paper describes syntheses of $[Cd_2X_4(bpytm)]$ (X = Cl and Br), for which structural characterization was not possible, and of $[CdX_2(bpytm)]$ (X = Br and I), which X-ray crystallography showed to have structures similar to those of their zinc analogues.

2. Experimental

2-Mercaptopyridine (99% pure, from Aldrich), $CdCl_2\cdot 2.5H_2O$ (98%, from Aldrich), $CdBr_2\cdot 4H_2O$

---

* Corresponding authors. Tel.: +34-986-812615; fax: +34-986-812556.
E-mail address: emgarcia@uvigo.es (E. García-Martínez).

0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00094-9

(97%, from Riedel de Haën), CdI_2 (99%, from Fluka), methanol, dichloromethane and absolute ethanol (from Panreac) and NaOH (98%, from Scharlau) were all used as supplied.

Analytical data were obtained with a Fisons Instruments EA-1108 CHN-O apparatus. Melting points (m.p.) were determined on a Gallenkamp MBF-595 apparatus and are uncorrected. Mass spectra were recorded on a VG Autospec Micromass under FAB conditions using 3-nitrobenzyl alcohol as matrix. Vibrational spectra were recorded on a Bruker model IFS-66V apparatus, the IR spectra from samples in KBr pellets (4000–400 cm^{-1}) or Nujol mulls between polyethylene sheets (400–100 cm^{-1}) and the Raman spectra using an FRA 106 Raman accessory. ^1H (300.13 MHz) and ^{13}C (75.47 MHz) NMR spectra of 0.1 M solutions in dmso-d_6 were recorded on a Bruker AMX 300 spectrometer; chemical shifts are referred to internal Me_4Si.

The ligand bis(2-pyridylthio)methane (bpytm) was prepared from 2-mercaptopyridine, sodium hydroxide and dichloromethane by a previously reported method [3].

2.1. Synthesis of the compounds

2.1.1. [Cd_2Cl_4(bpytm)] (**1**)

A solution of bpytm (0.110 g, 0.48 mmol) in 2 ml of 1:1 ethanol/dichloromethane was added dropwise to a solution of $CdCl_2 \cdot 2.5H_2O$ (0.113 g, 0.48 mmol) in 2 ml of the same solvent. The resulting white suspension was refluxed for 2 h and then stirred for 1 week, after which the product so obtained was filtered out and dried in vacuo. Yield 52%. M.p. 251 °C. *Anal.* Found: C, 21.7; H, 1.7; N, 4.7; S, 11.2%. $C_{11}H_{10}N_2S_2Cl_4Cd_2$ requires: C, 22.0; H, 1.7; N, 4.7; S, 10.7%. The main signals in the FAB spectrum are at *m/e* (ion, intensity): 234 ([bpytm], 4.5%), 235 ([Hbpytm], 100%), 383 ([CdCl(bpytm)], 2.0%), 419 ([$CdCl_2$(Hbpytm)], 19.8%). IR (Raman) data (cm^{-1}): 1583s, 1559m, 1459s (1587m, 1563s), ν(ring); 1203m, ω(CH, CH_2); 1163m, 1127s (1159m, 1129m), δ(C–H); 1017m (1017s), ν(ring); 769s, 724m (725m), γ(C–H); 643w (646m), δ(ring). ^1H NMR (δ in ppm): 4.97 (s, 2H, C(1)H_2), 7.14 (dd, 2H, H-5), 7.31 (dd, 2H, H-3), 7.65 (td, 2H, H-4), 8.48 (dt, 2H, H-6). ^{13}C NMR (δ in ppm): 30.0 C(1), 120.5 C(5), 122.5 C(3), 137.2 C(4), 149.8 C(6), 157.0 C(2).

2.1.2. [$CdBr_2$(bpytm)] (**2**)

A solution of $CdBr_2 \cdot 4H_2O$ (0.0734 g, 0.213 mmol) in 5 ml of ethanol was added dropwise to a solution of bpytm (0.100 g, 0.426 mmol) in 8 ml of the same solvent. The resulting white suspension was refluxed for 6 h and then stirred for 5 days, after which the crystalline product so obtained was filtered out and dried in vacuo. Crystals suitable for X-ray diffraction were obtained from the filtrate by slow evaporation. Yield 49%. M.p. 203 °C. *Anal.* Found: C, 26.0; H, 2.0; N, 5.5; S, 12.6%. $C_{11}H_{10}N_2S_2Br_2Cd$ requires: C, 26.1; H, 2.0; N, 5.4; S, 12.6%. The main signals in the FAB spectrum are at *m/e* (ion, intensity): 235 ([Hbpytm], 55.9%), 427 ([CdBr(bpytm)], 11.1%). IR (Raman) data (cm^{-1}): 1581s, 1560m, 1454s (1582m, 1560m, 1454w), ν(ring); 1214m, ω(CH, CH_2); 1158m, 1125m (1158m, 1126s), δ(C–H); 1017m (1016s), ν(ring); 777s, 721w, γ(C–H); 640m (641m), δ(ring); 192s, 179s (175s), ν(Cd–Br). ^1H NMR (δ in ppm): 4.98 (s, 2H, C(1)H_2), 7.15 (ddt, 2H, H-5), 7.31 (ddt, 2H, H-3), 7.66 (tdd, 2H, H-4), 8.48 (ddd, 2H, H-6). ^{13}C NMR (δ in ppm): 29.9 C(1), 120.4 C(5), 122.4 C(3), 137.1 C(4), 149.7 C(6), 157.0 C(2).

2.1.3. [Cd_2Br_4(bpytm)] (**3**)

A solution of bpytm (0.198 g, 0.84 mmol) in 13 ml of 2:3 ethanol/dichloromethane was added dropwise to a solution of $CdBr_2 \cdot 4H_2O$ (0.291 g, 0.84 mmol) in 10 ml of 1:1 ethanol/dichloromethane. The resulting white suspension was refluxed for 3 h and then stirred for 1 day, after which the product so obtained was filtered out and dried in vacuo. Crystals suitable for X-ray diffraction that in the event were identified as **2** were obtained by slow evaporation of an ethanol/dichloromethane solution of a crystalline solid obtained by slow evaporation of the filtrate. Yield 79%. M.p. 221 °C. *Anal.* Found: C, 17.1; H, 1.3; N, 3.6; S, 8.2%. $C_{11}H_{10}N_2S_2Br_4Cd_2$ requires: C, 17.0; H, 1.3; N, 3.6; S, 8.2%. The main signals in the FAB spectrum are at *m/e* (ion, intensity): 235 ([Hbpytm], 26.5%), 427 ([CdBr(bpytm)], 4.4%), 419 ([$CdBr_2$], 4.5%). IR (Raman) data (cm^{-1}): 1582s, 1558m, 1458s (1586m, 1562s, 1460m), ν(ring); 1203m, ω(CH, CH_2); 1160m, 1126s (1162m, 1128m), δ(C–H); 1015m (1015s), ν(ring); 768s, 724m (725m), γ(C–H); 642m (646m), δ(ring). ^1H NMR (δ in ppm): 4.98 (s, 2H, C(1)H_2), 7.14 (ddd, 2H, H-5), 7.31 (dt, 2H, H-3), 7.65 (td, 2H, H-4), 8.48 (ddd, 2H, H-6). ^{13}C NMR (δ in ppm): 30.0 C(1), 120.4 C(2), 122.4 C(3), 137.1 C(4), 149.7 C(6), 157.0 C(2).

2.1.4. [CdI_2(bpytm)] (**4**)

A solution of bpytm (0.189 g, 0.81 mmol) in 8 ml of 1:1 ethanol/dichloromethane was added dropwise to a solution of CdI_2 (0.296 g, 0.81 mmol) in 8 ml of the same solvent. The resulting yellow solution was refluxed for 2 h and then stirred for 1 day, after which the solvent was evaporated until there appeared a white solid, which was filtered out and dried in vacuo. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanol/chloroform solution of the dry white solid. Yield 63%. M.p. 173 °C. *Anal.* Found: C, 22.3; H, 1.7; N, 4.7; S, 10.5%. $C_{11}H_{10}N_2S_2I_2Cd$ requires: C, 22.0; H, 1.7; N, 4.7; S, 10.7%. The main signals in the FAB spectrum are at *m/e* (ion, intensity): 234 ([bpytm], 3.4%), 235 ([Hbpytm], 78.3%), 475 ([CdI(bpytm)], 13.3%). IR

(Raman) data (cm^{-1}): 1581s, 1560m, 1454s (1581m, 1559m), ν(ring); 1212s, ω(CH, CH$_2$); 1156m, 1125m (1156m, 1124m), δ(C–H); 1016s (1015s), ν(ring); 773s, 721w, γ(C–H); 639m (639s), δ(C–H); 162s, 151s (147m), ν(Cd–I). ^{1}H NMR (δ in ppm): 4.98 (s, 2H, C(1)H$_2$), 7.15 (ddd, 2H, H-5), 7.31 (dt, 2H, H-3), 7.66 (td, 2H, H-4), 8.48 (ddd, 2H, H-6). ^{13}C NMR (δ in ppm): 29.9 C(1), 120.4 C(5), 122.4 C(3), 137.0 C(4), 149.7 C(6), 157.0 C(2).

2.2. *X-ray data collection and reduction*

The X-ray diffraction patterns of the complexes were recorded at room temperature on a Bruker Smart CCD apparatus [7] using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), and were corrected with SADABS [8]. Crystal data and details of the structure refinement are given in Table 1. Structure solution (by direct methods for **2** and by the Patterson method for **4**) revealed the positions of all the non-hydrogen atoms. The structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for non-hydrogen atoms [9]. Hydrogen atoms were located in calculated positions and were refined using a riding model (HFIX 43 for aromatic H and HFIX 23 for methylene H). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* [10] and graphics were produced using the programs ORTEP III [11] and PLATON [12].

Table 1
Crystal structure refinement data for the compounds studied by X-ray diffraction

Compound	[CdBr$_2$(bpytm)] (**2**)	[CdI$_2$(bpytm)] (**4**)
Chemical formula	$C_{11}H_{10}Br_2N_2S_2Cd$	$C_{11}H_{10}I_2N_2S_2Cd$
Formula weight	506.56	600.54
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
Unit cell dimensions		
a (Å)	7.524(2)	7.6988(1)
b (Å)	16.134(3)	16.7689(1)
c (Å)	13.519(4)	13.6283(1)
β (°)	98.73(2)	98.4697(5)
V (Å^3)	1622.1(7)	1740.23(3)
Z	4	4
D_{calc} (Mg m^{-3})	2.074	2.292
Absorption coefficient (mm^{-1})	6.514	5.028
F(0 0 0)	960	1104
Crystal size (mm)	0.30 × 0.10 × 0.05	0.55 × 0.40 × 0.10
Range (°)	2.52–28.39	2.43–28.30
Index ranges	$-4 \leqslant h \leqslant 9$, $-21 \leqslant k \leqslant 20$, $-18 \leqslant l \leqslant 17$	$-10 \leqslant h \leqslant 10$, $-22 \leqslant k \leqslant 22$, $-9 \leqslant l \leqslant 18$
Reflections collected/unique	5476/1994 [$R_{int} = 0.0349$]	5896/2161 [$R_{int} = 0.0775$]
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0294$, $wR_2 = 0.0648$	$R_1 = 0.0557$, $wR_2 = 0.1379$
R indices (all data)	$R_1 = 0.0437$, $wR_2 = 0.0688$	$R_1 = 0.0606$, $wR_2 = 0.1405$
Goodness-of-fit on F^2	0.967	0.972
Max./min. transmission factors	1.000000/0.480298	1.000000/ 0.256335

3. Results and discussion

The ligand bpytm reacted with CdX$_2$ (X = Cl, Br and I) in ethanol or ethanol/dichloromethane to give the neutral species [Cd$_2$Cl$_4$(bpytm)] (**1**), [CdBr$_2$(bpytm)] (**2**), [Cd$_2$Br$_4$(bpytm)] (**3**) and [CdI$_2$(bpytm)] (**4**) in 52, 49, 79 and 63% yield, respectively. To obtain the 1:1 adduct (**2**) a 1:2 cadmium:ligand mole ratio was necessary, and with CdCl$_2$ even this ratio afforded the 2:1 adduct.

Figs. 1 and 2 show ORTEP III [11] views of the compounds of which crystals suitable for X-ray diffraction were obtained, **2** and **4**, respectively, together with the atomic numbering schemes. Details of the coordination spheres around the cadmium atom are given in Table 2, and bond lengths and angles in the bpytm moieties in Table 3.

The structures of these two complexes are isotypic and consist of neutral molecules of composition [CdX$_2$(C$_{11}$H$_{10}$S$_2$N$_2$)] (X = Br, I) with the Cd atom lying on a twofold axis (e position in Wyckoff notation) and the two 2-thiopyridyl groups related by a symmetry operation (see Table 2). The Cd atom is coordinated by two halide ions and by the two pyridyl N atoms of the bpytm ligand in a distorted tetrahedral configuration. The *N*,*N′*-bidentate ligand creates an eight-membered CdN$_2$C$_2$S$_2$C chelate ring that, probably due to steric requirements, adopts a distorted boat-chair conformation that widens the N–Cd–N bite angle from the ideal tetrahedral angle, 109.44°, to 122.0(2)° or 123.15(13)°.

The Cd–N distances are similar to those found in the CCDC [5] for tetrahedral CdX$_2$ adducts and are essentially unaffected by the difference in size between the bromine and iodine atoms, being 2.301(2) Å in **2** and 2.295(4) Å in **4**. This constancy may be due to the flexibility of bpytm.

The bpytm moieties of **2** and **4** are very similar. Each pyridine ring is planar, with no atom deviating more than 0.006 Å from the six-atom least-squares plane. The pseudotetrahedral coordination results in the angles between the pyridine planes, 57.80(0.10)° in [CdBr$_2$(bpytm)] and 59.95(0.19)° in [CdI$_2$(bpytm)], being narrower than the 67.67(0.09)° found in the free ligand. The geometry of the pyridine rings is unexceptional: for example, the average C–C and C–N bond lengths are 1.37 and 1.34 Å respectively, in agreement with similar averages found in other complexes of this ligand [3,4].

The Cd–S distances, 3.2670(11) Å in **2** and 3.2701(16) Å in **4**, are close to those previously found in the

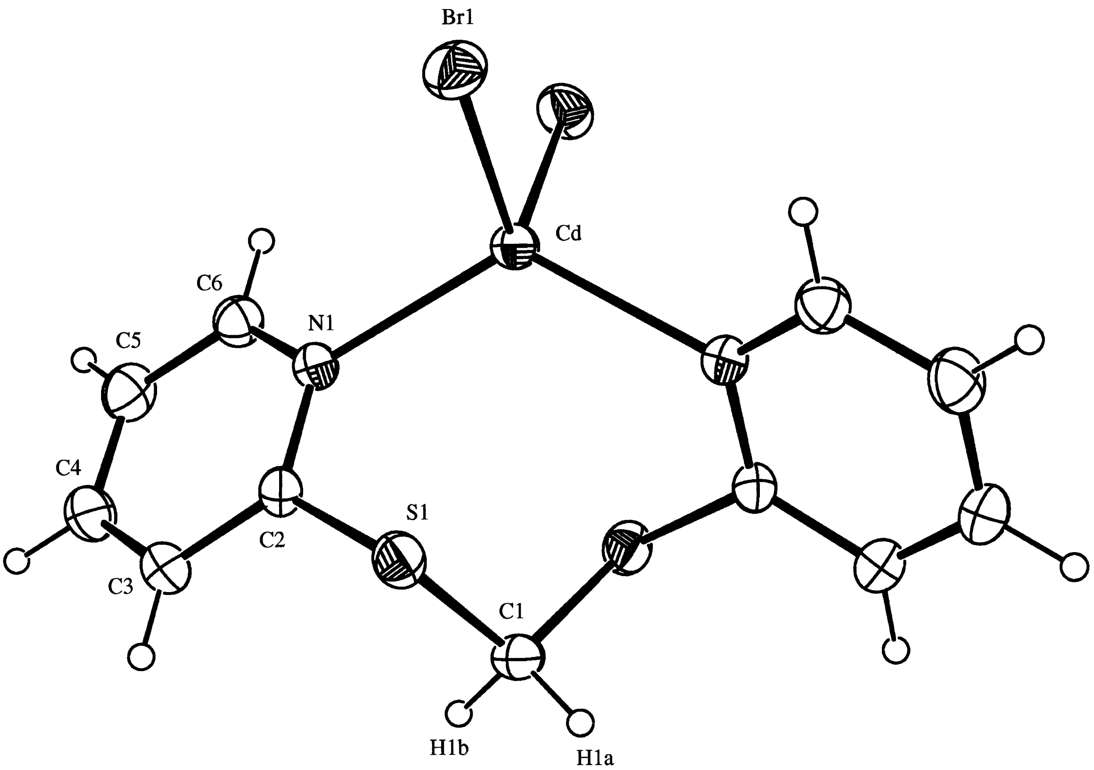


Fig. 1. ORTEP plot of [$CdBr_2$(bpytm)] (**2**).

similar ZnX_2 complexes [3,4]. These values, although shorter than the sum of the Van der Waals radii (3.40 Å), are significantly longer than the calculated single bond length (2.40 Å), and show the Cd–S interaction to be very weak. A shorter distance [$Hg\cdots S = 3.193(4)$ Å] was found in [$HgBr_2$(bpytm)] [3], in which bpytm has a different coordination mode.

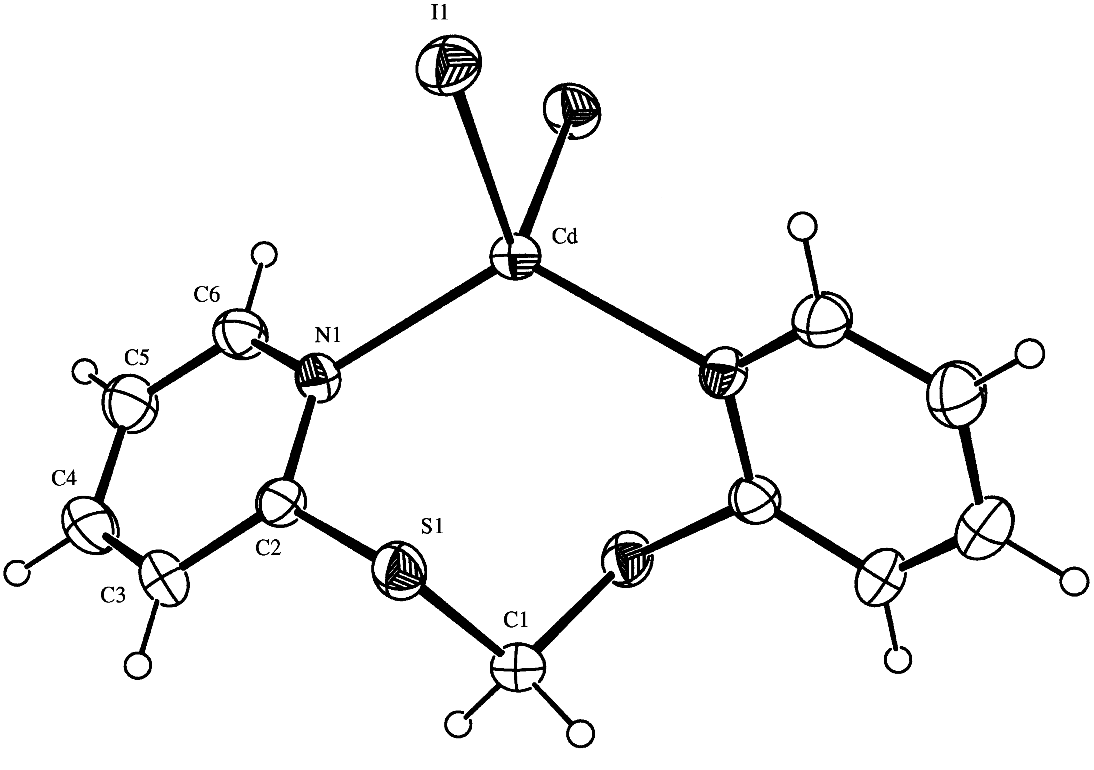


Fig. 2. ORTEP plot of [CdI_2(bpytm)] (**4**).

Table 2
Selected bond lengths and angles in the environment of the metal in the compounds

Compound	[CdBr$_2$(bpytm)] (**2**)	[CdI$_2$(bpytm)] (**4**)
Bond lengths		
Cd–N(1)	2.301(2)	2.295(4)
Cd–X(1)	2.5767(7)	2.7447(5)
Cd–S(1)	3.2670(10)	3.2701(16)
Bond angles		
N(1)$^{\#1}$–Cd–N(1)	123.15(13)	122.0(2)
N(1)$^{\#1}$–Cd–X(1)	101.31(7)	110.07(11)
N(1)–Cd–X(1)	109.82(6)	102.01(11)
X(1)$^{\#1}$–Cd–X(1)	111.59(3)	110.67(3)
N(1)$^{\#1}$–Cd–S(1)	75.51(6)	74.71(12)
N(1)–Cd–S(1)	53.94(7)	53.78(11)
X(1)$^{\#1}$–Cd–S(1)	146.63(2)	99.29(3)
X(1)–Cd–S(1)	98.95(3)	147.31(3)

Symmetry transformations used to generate equivalent atoms $^{\#1} = -x, y, 1/2-z$ for compound **2** and $^{\#1} = 2-x, y, 3/2-z$ for compound **4**.

Table 3
Selected bond lengths and angles in the bpytm moieties of the complexes

Compound	[CdBr$_2$(bpytm)] (**2**)	[CdI$_2$(bpytm)] (**4**)
Bond lengths		
N(1)–C(6)	1.337(4)	1.339(7)
N(1)–C(2)	1.352(4)	1.354(7)
S(1)–C(2)	1.778(3)	1.774(6)
S(1)–C(1)	1.822(3)	1.816(5)
C(2)–C(3)	1.382(4)	1.381(8)
C(3)–C(4)	1.381(5)	1.377(10)
C(4)–C(5)	1.373(5)	1.381(10)
C(5)–C(6)	1.386(5)	1.377(9)
Bond angles		
C(2)–S(1)–C(1)	97.66(11)	97.5(2)
C(6)–N(1)–C(2)	118.1(3)	117.5(5)
S(1)$^{\#1}$–C(1)–S(1)	115.9(2)	116.2(5)
N(1)–C(2)–C(3)	122.1(3)	122.7(5)
N(1)–C(2)–S(1)	116.2(2)	116.1(4)
C(3)–C(2)–S(1)	121.6(3)	121.3(5)
C(4)–C(3)–C(2)	119.1(3)	118.8(6)
C(5)–C(4)–C(3)	119.0(3)	119.1(6)
C(4)–C(5)–C(6)	119.0(3)	118.9(6)
N(1)–C(6)–C(5)	122.6(3)	123.0(6)
Torsion angles		
C(2)–S(1)–C(1)–S(1)$^{\#1}$	71.56(10)	71.5(2)
C(6)–N(1)–C(2)–S(1)	177.7(2)	177.3(4)
C(1)–S(1)–C(2)–N(1)	−90.9(3)	−89.6(5)
C(1)–S(1)–C(2)–C(3)	87.9(3)	89.1(6)
S(1)–C(2)–C(3)–C(4)	−178.1(3)	−176.9(5)

Symmetry transformations used to generate equivalent atoms $^{\#1} = -x, y, 1/2-z$ for compound **2** and $^{\#1} = 2-x, y, 3/2-z$ for compound **4**.

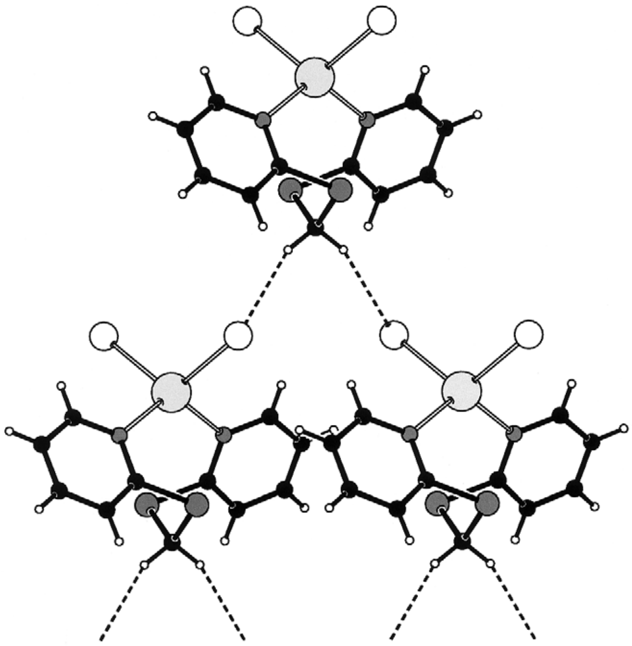


Fig. 3. PLATON plot of [CdBr$_2$(bpytm)] (**2**), showing the intermolecular hydrogen bonds.

Intermolecular hydrogen bonds involving the methylene group [see Fig. 3, C(1)–H(1A)···Br(1)$^{\#2}$ = 0.97, 2.92, 3.843(3) Å, 158.8°; C(1)–H(1B)···Br(1)$^{\#3}$ = 0.97, 2.92, 3.843(3) Å, 158.8° ($^{\#2}x-1/2, y-1/2, z$; $^{\#3}1/2-x, y-1/2, 1/2-z$)] associate the molecules of **2** into sheets parallel to the *ab* plane, as shown in Fig. 4.

The vibrational spectra of the complexes exhibit the bands usually associated with coordinated bpytm [3]. Relative to the spectrum of the free ligand [IR (Raman) data (cm^{-1}): 1578s, 1554s, 1465m (1578s, 1557s, 1466w), ν(ring); 1214s, ω(CH, CH$_2$); 1143m, 1123m (1149m, 1125m), δ(C–H); 987m (987s), ν(ring); 754s, 740s, γ(C–H); 620m (616m), δ(ring)], the main changes affect the py ring vibrations at 987 and 620 cm^{-1}, although most of the other bands also shift to higher wavenumbers (the only bands shifting to lower wavenumbers are the ring stretching band at 1465 cm^{-1} and the δ(C–H) vibration at 740 cm^{-1}). In the far-IR spectra of the [CdX$_2$(bpytm)] complexes the two ν(Cd–X) bands that are expected in view of the local C_{2v} symmetry of the CdN$_2$X$_2$ kernel are close to those found in the spectra of similar complexes [13].

Our failure to achieve unequivocal identification of the bands of the [Cd$_2$X$_4$(bpytm)] complexes leaves their structures uncertain. In the absence of relevant data it seems likely that they are similar to [(HgCl$_2$)$_2$(bpytm)] [3], in which the ligand bridges between two metal atoms.

The absence of signals for the molecular ions in the FAB MS spectra of **1**–**4** is attributable to the fast fragmentation of these species even under FAB conditions.

As usual [14], coordination to the d^{10} Cd^{2+} ion shifts the ^{1}H NMR signals of the complexes down field from those of the free ligand by only 0.0–0.1 ppm [^{1}H NMR

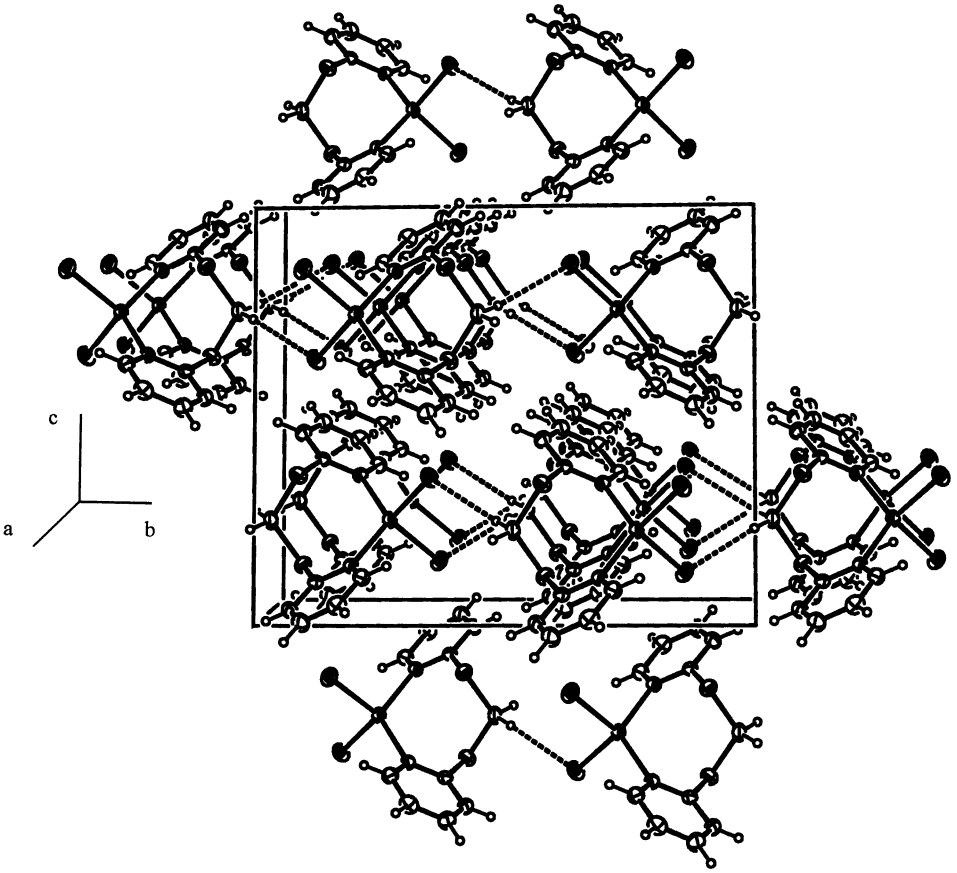


Fig. 4. Association of (**2**) into sheets parallel to *ab* plane.

data for bpytm in dmso-d_6 (δ in ppm): 4.99 (s, 2H, $C(1)H_2$), 7.15 (ddd, 2H, H-5), 7.32 (dt, 2H, H-3), 7.66 (td, 2H, H-4), 8.49 (dd, 2H, H-6)]. This is attributed to the weak Lewis acidity of this ion. The trends in the ^{13}C NMR shifts are more or less the same: the spectra show six carbon signals very close to those of the free ligand [^{13}C NMR data for bpytm in dmso-d_6 (δ in ppm): 29.9 C(1), 120.4 C(5), 122.4 C(3), 137.0 C(4), 149.7 C(6), 157.0 C(2)]. In particular, the pyridyl C(6) signals do not show the downfield shifts normally observed in the spectra of complexes containing coordinated pyridyl groups [15,16]. These findings suggest the total dissociation of the complexes in dmso-d_6.

In conclusión, among the $[MX_2(bpytm)]$ complexes of Group 12 metals, bpytm is N,N'-bidentate in those of Zn (X = Cl, Br, I) [3,4] and Cd (X = Br, I) [this work], and N-monodentate in $[HgBr_2(bpytm)]$ [3]. Compounds of the form $[M_2X_4(bpytm)]$ have been synthesized for M = Cd (X = Cl, Br) and Hg (X = Cl), and are the only bpytm complexes of the chlorides $CdCl_2$ and $HgCl_2$.

4. Supplementary data

Crystallographic data for the structural analyses of **2** and **4** have been deposited with the Cambridge Crystallographic Data Centre as CCDC Nos. 193829 (for $[CdBr_2(bpytm)]$) and 193830 (for $[CdI_2(bpytm)]$). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Directorates General for Regional Policies (E.U.) and for Research of the Spanish Ministry of Science and Technology for financial support (ERDF programs) under project BQU2002-03543.

References

[1] E.B. Bouwman, W.L. Driessen, J. Reedijk, Coord. Chem. Rev. 104 (1990) 143.
[2] J.S. Casas, A. Castiñeiras, E. García-Martínez, P. Rodríguez-Rodríguez, U. Russo, A. Sánchez, A. Sánchez-González, J. Sordo, Appl. Organomet. Chem. 13 (1999) 69.
[3] A. Amoedo-Portela, R. Carballo, J.S. Casas, E. García-Martínez, C. Gómez Alonso, A. Sánchez-González, J. Sordo, E.M. Vázquez-López, Z. Anorg. Allg. Chem. 628 (2002) 939.

[4] A. Amoedo-Portela, R. Carballo, J.S. Casas, E. García-Martínez, A. Sánchez-González, J. Sordo, E.M. Vázquez-López, Main Group Met. Chem. 25 (2002) 311.

[5] F.H. Allen, O. Kennard, Chem. Design Automation News 8 (1993) 1.

[6] P. Ghosh, M. Wood, J.B. Bonano, T. Hascall, G. Parkin, Polyhedron 18 (1999) 1107.

[7] Siemens, SMART and SAINT. Area Detector Control and Integration Software, Siemens Analytical X-ray Instruments Inc, Madison, WI, 1995.

[8] G.M. Sheldrick, SADABS. Program for Absorption Correction, University of Göttingen, Germany, 1996.

[9] G.M. Sheldrick, SHELX-97. An Integrated System for Solving and Refining Crystal Structures from Diffraction Data, University of Göttingen, Germany, 1997.

[10] International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974. Present distributor: Kluwer Academic Publishers, Dordrecht.

[11] M.N. Burnett, C.K. Johnson, ORTEP III, ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.

[12] A.L Spek, PLATON, Utrecht University, The Netherlands, 2000. Available from http://www.cryst.chem-uu.nl/platon/.

[13] (a) C. Pettinari, F. Marchetti, A. Cingolani, S.I. Troyanov, A. Drozdov, J. Chem. Soc., Dalton Trans. (1998) 3335;
(b) A. Castiñeiras, C.F. Vidal, R. Bastida, A. Macias, W. Hiller, Polyhedron 7 (1988) 2503.

[14] C. Janiak, S. Deblon, H.P. Wu, M.J. Kolm, P. Klufers, H. Piotrowski, P. Mayer, Eur. J. Inorg. Chem. (1999) 1507.

[15] G. Minghetti, S. Stoccoro, M.A. Cinellu, A. Zucca, M. Manassero, M. Sansoni, J. Chem. Soc., Dalton Trans. (1998) 4119.

[16] C.J. Matthews, W. Clegg, S.L. Heath, N.C. Martin, M.N.S. Hill, J.C. Lockhart, Inorg. Chem. 37 (1998) 199.