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Bis(mercaptoimidazolyl)borates and the control of nuclearity in cadmium thiolate complexes

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Abstract

Bis(mercaptoimidazolyl)borate cadmium(II) thiolate complexes of empirical formula (Bm^{Me})CdSR (R = Ph, *p*-Tol, C_6F_5) have been readily prepared from the new bromo derivative (Bm^{Me})CdBr and the corresponding thallium(I) thiolates Tl(SR). The new complexes have been characterized analytically and spectroscopically and, in the case of the *para*-thiocresolate derivative (Bm^{Me})CdS-*p*-C_6H_4Me, by X-ray diffraction. While the closely related tris(mercaptoimidazolyl)borate cadmium phenylthiolate complex ($Tm^{p\text{-Tol}}$)CdSPh is mononuclear, (Bm^{Me})CdS-*p*-C_6H_4Me exhibits in the solid state a dimeric structure in which each five-coordinate cadmium atom displays a trigonal bipyramidal geometry.

Keywords: Thallium; Cadmium; Thiolates; Bis(mercaptoimidazolyl)borate complexes; Crystal structures

1. Introduction

The coordination chemistry of metal thiolate complexes is dominated by the formation of complex molecular aggregates or polymeric species [1], applications of which range from the preparation of semiconductor quantum dots to the design of model compounds for the active sites in metalloenzymes. In particular, unusual optoelectronic properties have recently been uncovered for many highly structured cadmium thiolates as well as for thiolate-capped cadmium sulfide (CdS) nanoparticles [2]. Interesting cadmium thiolate clusters have also been prepared [3] to probe the stereochemistry of metallothioneins (MTs), a fascinating family of low-molecular weight (6–7 kDa) cysteine-rich proteins involved in the storage and transport of metal ions, especially those with a d^{10} electron configuration [e.g., Cu(I), Zn(II), Cd(II)] [4].

In contrast to the structural diversity that characterizes polynuclear cadmium thiolate compounds, mononuclear species, including trigonal planar $[Cd(SR)_3]^-$ and tetrahedral $[Cd(SR)_4]^{2-}$ and $Cd(SR)_2L_2$ derivatives, are more scarce [5]. In this vein, we have recently used the tris(mercaptoimidazolyl)borate ligand system [6] to prepare novel cadmium monothiolate species of the form ($Tm^{p\text{-Tol}}$)CdSR (R = Bz, Ph, *p*-Tol, C_6F_5) (Fig. 1) [7].

Continuing our investigation into the synthesis of well-defined cadmium thiolate complexes in a sulfur-rich environment, we report herein a complementary study on cadmium thiolate derivatives using the related bis(mercaptoimidazolyl)borates (Fig. 2) [8] as supporting ligands. While contrasting both ligand systems and their ability to control and hinder the assembly of cadmium thiolate complexes with extended structures, we envisioned that the presence of different sulfur-donor functionalities at a single metal center in the target molecules will also be an attractive feature for future reactivity studies.

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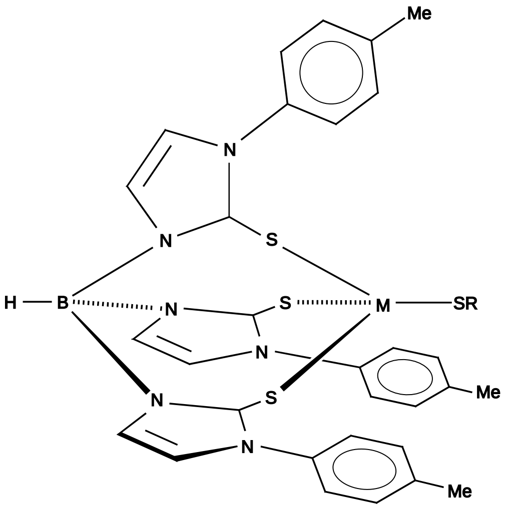

Fig. 1. The mononuclear tris(mercaptoimidazolyl)borate cadmium thiolates ($(Tm^R)CdSR$).

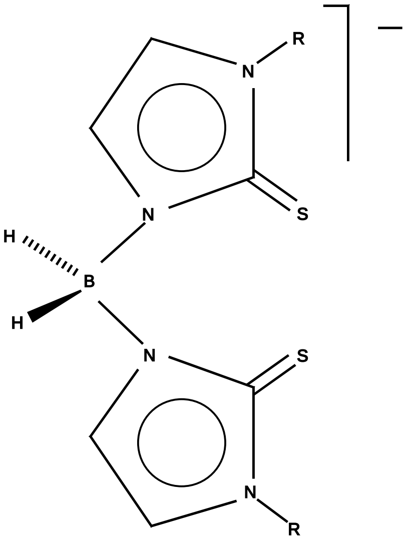

Fig. 2. The bis(mercaptoimidazolyl)borate ligand system (Bm^R).

2. Results and discussion

2.1. Bis(mercaptoimidazolyl)borate cadmium bromide

The hitherto unknown bis(mercaptoimidazolyl)borate complex $(Bm^{Me})CdBr$, which we considered would be a suitable starting material for further reactions, was readily obtained from cadmium(II) bromide and the sodium salt of the ligand in dichloromethane, as illustrated in Eq. (1),

$$CdBr_2 + Na(Bm^{Me}) \underset{-NaBr}{\overset{CH_2Cl_2}{\rightarrow}} (Bm^{Me})CdBr \tag{1}$$

and isolated in pure form and almost quantitative yield (ca. 95%) after the appropriate work-up. It is an air- and moisture-stable white solid, only slightly soluble in acetonitrile, chloroform, and dichloromethane but more so in dimethyl sulfoxide (DMSO). Surprisingly, repeated attempts to obtain the chloro or iodo analogues $(Bm^{Me})CdX$ ($X = Cl$, I) using a variety of reaction conditions consistently resulted in the formation of the known homoleptic derivative $Cd(Bm^{Me})_2$ [9], even if substoichiometric amounts of $[Bm^{Me}]^-$ were used. While we have not been able to obtain single crystals of $(Bm^{Me})CdBr$ suitable for an X-ray diffraction study, we believe that its structure may be analogous to that of $(Bm^{Me})ZnI$ [8,10], i.e., approximately trigonal planar and with the bonding at cadmium supplemented by a weak $Cd\cdots H–B$ interaction. In support of this proposal, we note that spectroscopic data (IR, NMR) for $(Bm^{Me})ZnI$ and $(Bm^{Me})CdBr$ are very similar.

2.2. Bis(mercaptoimidazolyl)borate cadmium thiolates

Following the methodology we applied to synthesize the aforementioned $(Tm^{p\text{-}Tol})CdSR$ complexes [7], bis (mercaptoimidazolyl)borate cadmium(II) thiolate derivatives of general formula $(Bm^{Me})CdSR$ (R = Ph, p-Tol, C_6F_5) were cleanly isolated in ca. 40–60% yield from the metathesis reactions of equimolar amounts of $(Bm^{Me})CdBr$ and the corresponding thallium(I) thiolates Tl(SR), as illustrated in Eq. (2).

$$(Bm^{Me})CdBr + Tl(SR) \underset{\substack{R=Ph,p\text{-}Tol,C_6F_5\\ -TlBr}}{\overset{CH_2Cl_2\text{ or }MeCN}{\rightarrow}} (Bm^{Me})CdSR \tag{2}$$

The three new complexes are white, air-stable solids, insoluble in benzene or methanol but soluble in polar aprotic solvents such as acetone and DMSO. In addition, the thiophenoxide and *para*-thiocresolate derivatives are soluble in dichloromethane and the pentafluorophenyl compound is soluble in tetrahydrofuran (THF). In general, the $(Bm^{Me})CdSR$ complexes exhibit lower solubilities than their corresponding $(Tm^{p\text{-}Tol})CdSR$ relatives. They were all characterized by a combination of analytical and spectroscopic methods, including elemental analyses (CHN) and IR and NMR spectroscopies. The solid-state IR spectra of the three thiolate complexes display single $\nu_{B–H}$ absorptions of medium intensity at ca. 2390 cm^{-1}, values which are shifted some 15 cm^{-1} to lower frequencies than those in $(Tm^{p\text{-}Tol})CdSR$. ^1H NMR data for the $(Bm^{Me})CdSR$ series, excluding the signals of the aryl substituents, are virtually identical to those in $(Bm^{Me})CdBr$ and show the expected small downfield shifts (ca. 0.2 ppm) relative to those in free $Na(Bm^{Me})$ [9]. Although the ^{13}C NMR spectra of $(Bm^{Me})CdSR$ are also similar to that of $(Bm^{Me})CdBr$, the resonances for the imidazolyl carbon atoms and the thione (C=S) groups tend to be moderately shielded (ca. 1–4 ppm) relative to the corresponding values observed in the $(Tm^{p\text{-}Tol})CdSR$ derivatives.

Table 1
Selected bond lengths (Å) and bond angles (°) for $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$\mathrm{C_6H_4Me}$

Bond lengths	
Cd(1)–S(1)	2.5258(6)
Cd(1)–S(2)	2.4868(6)
Cd(1)–S(3)	2.5403(5)
Cd(1)–S(3A)	2.6442(6)
Cd(1)···H(1B)	2.44(3)
Bond angles	
S(1)–Cd(1)–S(2)	113.01(2)
S(1)–Cd(1)–S(3)	113.99(2)
S(1)–Cd(1)–S(3A)	91.59(2)
S(2)–Cd(1)–S(3)	126.72(2)
S(2)–Cd(1)–S(3A)	108.88(2)
S(3)–Cd(1)–S(3A)	93.48(2)
Cd(1)–S(3)–Cd(1A)	86.52(2)
S(1)–Cd(1)···H(1B)	84.7
S(2)–Cd(1)···H(1B)	75.3
S(3)–Cd(1)···H(1B)	85.5
S(3A)–Cd(1)···H(1B)	175.3

2.3. Molecular structure of $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$\mathrm{C_6H_4Me}$

The molecular structure of $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$\mathrm{C_6H_4Me}$ was determined by X-ray diffraction using crystals obtained by diffusion of diethyl ether into a dichloromethane solution of the complex. Selected bond lengths and angles are presented in Table 1. Each of the cadmium atoms in the centrosymmetric dimer (Fig. 3) is coordinated to two bridging thiolates and the two thione groups and one of the B–H bonds of a $[\mathrm{Bm^{Me}}]^-$ ligand, so that their geometries can be aptly described as being slightly distorted trigonal bipyramidal. In this regard, we note that: (i) the S(3A)–Cd(1)···H(1B) angle is almost linear (175.3°) and therefore S(3A) and H(1B) can be regarded as the axial atoms, (ii) the sum of angles in the equatorial plane formed by S(1), S(2), and S(3) is ca. 354°, and (iii) the average angle between axial and equatorial ligands is 89.9°, even if the individual S(3A)–Cd(1)–S and S–Cd(1)···H(1B) angles are moderately obtuse (91.6°–108.9°) or acute (75.3°–85.5°), respectively. Furthermore, a trigonality index (τ) of 0.81, which approaches the value for an ideal trigonal bipyramid, can be calculated for each cadmium center. [2] Significantly, a search of the Cambridge Structural Database (CSD version 5.24, November 2002) [11] revealed that $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$\mathrm{C_6H_4Me}$ is the first structurally characterized five-coordinated cadmium complex having a $[\mathrm{CdS_4H}]$ core.

The two Cd–S bond lengths to the $[\mathrm{Bm^{Me}}]^-$ ligand in $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$\mathrm{C_6H_4Me}$, 2.4868(6) and 2.5258(6) Å, are very close to those in $(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdSPh}$ [2.477(5)–2.529(5) Å] and are also within the range of values (ca. 2.48–2.60 Å) observed for such bonds in the limited number of cadmium(II) complexes with related ligands that have been structurally characterized [7,9,12–16] (Table 2). Although the Cd–S bond distances to the two bridging thiolate ligands in $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$\mathrm{C_6H_4Me}$ differ by ca. 0.1 Å, their *anti* configuration and the overall metrical parameters of the planar $\mathrm{Cd_2S_2}$ unit are nevertheless comparable to those in other dinuclear cadmium complexes containing bridging thiolate ligands, including neutral $\mathrm{L_2Cd(\mu\text{-}SR)_2CdL_2}$ (L = bipy, phen) [17] and dianionic $[\mathrm{Cd_2(SR)_6}]^{2-}$ [18]. With regards to the Cd···H–B interactions, the Cd···H distances [2.44(3) Å] are somewhat shorter than those observed in $\mathrm{Cd(pzBm^{Me})_2}$ (2.55 and 2.58 Å) [12], $\mathrm{Cd(Bm^{Me})_2}$ (2.58 Å) [9], or $\mathrm{Cd(Bm^{tBu})_2}$ (2.49 and 2.73 Å) [9] but considerably longer than those in the only other two compounds displaying such 3-center-2-electron bonds that are listed in the CSD, namely $[\mathrm{Tp^{Me_2}}]\mathrm{Cd(BH_4)}$ (1.97 and 2.13 Å)

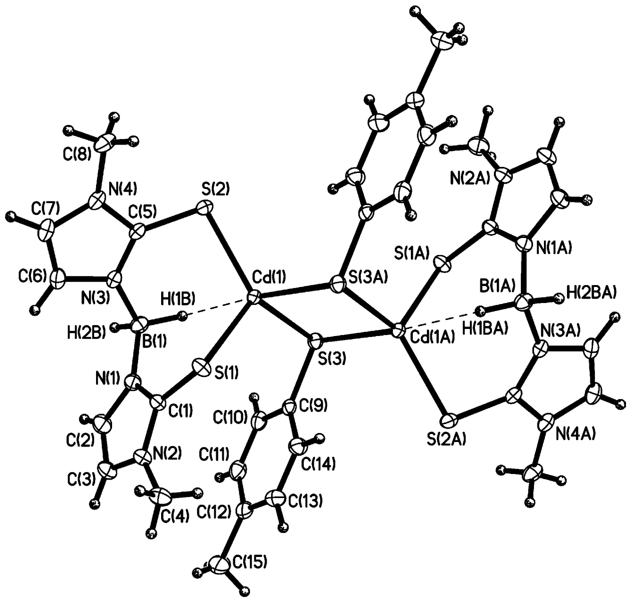

Fig. 3. Molecular structure of $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$\mathrm{C_6H_4Me}$ with thermal ellipsoids shown at the 30% probability level (a molecule of $\mathrm{CH_2Cl_2}$ present in the crystal lattice is not shown).

Table 2
Structurally characterized cadmium(II) complexes of poly(mercaptoimidazolyl)borate and related ligands

Complex	*d*(Cd–$\mathrm{S_{thione}}$) (Å)	Reference
$\mathrm{Cd(pzBm^{Me})_2}$	2.5259(7)–2.5723(7)	[12]
$(\mathrm{Tm^{Bz}})\mathrm{CdBr}$	2.5154(9)–2.5693(9)	[13]
$(\mathrm{Tm}^{p\text{-Tol}})\mathrm{CdSPh}$	2.477(5)–2.529(5)	[7]
$(\mathrm{Tm^{Me}})\mathrm{CdBr}$	2.5154(9)–2.5693(9)	[14]
$(\mathrm{Tm^{tBu}})\mathrm{CdBr}$	2.5363(8)–2.5548(8)	[15]
$\mathrm{Cd(Bm^{Me})_2}$	2.509(2)–2.572(2)	[9]
$\mathrm{Cd(Bm^{tBu})_2}$	2.5356(8)–2.5954(8)	[9]
$(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$\mathrm{C_6H_4Me}$	2.4868(6) & 2.5258(6)	this work
$(\mathrm{Tm^{tBu}})\mathrm{CdSC_6F_5}$	2.5371(4)–2.5558(5)	[16]

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[2] The trigonality index $\tau = (\beta - \alpha)/60$, where β and α are the largest and second-largest interligand angles, has been used to estimate the degree of structural distortion from the ideal square pyramidal ($\tau = 0$) and trigonal bipyramidal ($\tau = 1$) geometries in five-coordinate complexes. See Ref. [23].

[19] and the anionic cadmaborane $[Cd(B_9H_{13})_2]^{2-}$ (2.213–2.314 Å) [20].

3. Conclusions

We have demonstrated that the bis(mercaptoimidazolyl)borate ligand system has a lower tendency relative to the tris(mercaptoimidazolyl)borates to stabilize mononuclear cadmium thiolate complexes. As such, whereas $(Tm^{p\text{-}Tol})CdSPh$ and $(Tm^{tBu})CdSC_6F_5$ are mononuclear and tetrahedral, the less sterically demanding ligand $[Bm^{Me}]^-$ leads instead to the formation of dinuclear complexes such as $[(Bm^{Me})Cd(\mu\text{-S-}p\text{-}C_6H_4Me)]_2$, in which two thiolates bridge trigonal bipyramidal metal centers. Interestingly, the fact that both Bm^R and Tm^R ligands in these types of compounds effectively exhibit tridentate coordination modes (κ^3-*S,S,H* vs. κ^3-*S,S,S*, respectively) is a reflection of the increased proclivity in the former to partake in M···H–B interactions.

4. Experimental

4.1. General considerations

All reactions were performed in the air, solvents were purified and degassed by standard procedures, and all commercially available reagents were used as received. $Na(Bm^{Me})$ was prepared as recently published [9] and the thallium(I) thiolates Tl(SR) were obtained using a modification of the procedure reported for the synthesis of thallium(I) phenoxides [21] by reacting Tl(OEt) with a slight excess of the corresponding thiols in pentane; the bright yellow (R = Ph, *p*-Tol) or off-white ($R = C_6F_5$) solids were isolated in 90–95% yield and stored under dry nitrogen in a glove box. ^1H and ^{13}C NMR spectra were obtained on a Varian Gemini (300 MHz) FT spectrometer. Chemical shifts (δ) are reported in parts per million relative to $SiMe_4$ ($\delta = 0$ ppm) and were referenced internally with respect to the solvent resonances (^1H δ 2.49 for d_5-DMSO; ^{13}C δ 39.5 for d_6-DMSO); coupling constants are given in hertz (Hz). IR spectra were recorded as KBr pellets on a Thermo Mattson Satellite 3000 FT-IR spectrophotometer and are reported in cm^{-1}; relative intensities of the absorptions are indicated in parentheses (vs = very strong, s = strong, m = medium, w = weak). Elemental analyses were determined by Atlantic Microlab, Inc. (Norcross, GA).

4.2. Synthesis of $(Bm^{Me})CdBr$

A white suspension of $CdBr_2$ (2.08 g, 7.63 mmol) and $Na(Bm^{Me})$ (2.00 g, 7.63 mmol) in CH_2Cl_2 (40 mL) was stirred for 2 h and concentrated under reduced pressure to ca. 20 mL. The white solid was isolated by filtration, washed with H_2O (2 × 20 mL) and Et_2O (2 × 20 mL), and dried in vacuo for 19 h (3.19 g, 97%). m.p. = 254 °C (dec). NMR data (in d_6-DMSO): ^1H δ 3.53 (s, 6H, CH_3), 7.05 (s, 2H, imidazole *H*), 7.25 (s, 2H, imidazole *H*), H_2B not located; ^{13}C δ 34.8 (q, $^1J_{C\text{–}H} = 141$, 2C, CH_3), 120.5 (d, $^1J_{C\text{–}H} = 197$, 2C, imidazole *C*), 123.4 (d, $^1J_{C\text{–}H} = 197$, 2C, imidazole *C*), 153.7 (s, 2C, *C*=S). IR data (cm^{-1}): 3161 (w), 3144 (m), 3114 (m), 3088 (w), 2944 (w), 2421 (m), 2366 (m), 2230 (w), 2072 (w), 1561 (s), 1460 (vs), 1419 (w), 1408 (m), 1384 (vs), 1333 (w), 1306 (w), 1217 (m), 1194 (vs), 1163 (s), 1121 (vs), 1036 (w), 1015 (w), 975 (w), 874 (m), 748 (s), 734 (m), 724 (s), 696 (m), 674 (w), 644 (w), 594 (w), 509 (w), 495 (w), 469 (w), 454 (w). *Anal.* Calc. for $C_8H_{12}BBrCdN_4S_2$: C, 22.3; H, 2.8; N, 13.0. Found: C, 22.0; H, 2.7; N, 13.0%.

4.3. Synthesis of $(Bm^{Me})CdSC_6H_5$

A pale yellow suspension of $(Bm^{Me})CdBr$ (0.30 g, 0.69 mmol) and $Tl(SC_6H_5)$ (0.22 g, 0.69 mmol) in CH_2Cl_2 (50 mL) was stirred for 1.5 h and filtered. The colorless filtrate was concentrated under reduced pressure to ca. 3 mL and addition of pentane (10 mL) resulted in the formation of a white solid, which was isolated by filtration and dried in vacuo for 19 h (0.19 g, 58%). m.p. = 252 °C (dec). NMR data (in d_6-DMSO): ^1H δ 3.51 (s, 6H, CH_3), 6.81 (t, $^3J_{H\text{–}H} = 7$, 1H, H_p), 6.90 (t, $^3J_{H\text{–}H} = 7$, 2H, H_m), 6.99 (s, 2H, imidazole *H*), 7.21 (s, 2H, imidazole *H*), 7.25 (d, $^3J_{H\text{–}H} = 7$, 2H, H_o), H_2B not located; ^{13}C δ 34.6 (q, $^1J_{C\text{–}H} = 141$, 2C, CH_3), 120.3 (dd, $^1J_{C\text{–}H} = 197$, $^2J_{C\text{–}H} = 12$, 2C, imidazole *C*), 121.6 (d, $^1J_{C\text{–}H} = 160$, 1C, C_p), 123.3 (dd, $^1J_{C\text{–}H} = 196$, $^2J_{C\text{–}H} = 10$, 2C, imidazole *C*), 127.4 (d, $^1J_{C\text{–}H} = 157$, 2C, C_o or C_m), 132.4 (d, $^1J_{C\text{–}H} = 159$, 2C, C_o or C_m), 143.6 (s, 1C, C_{ipso}), 154.0 (s, 2C, *C*=S). IR data (cm^{-1}): 3158 (w), 3121 (w), 3053(w), 2940 (w), 2383 (m), 2253 (w), 1561 (w), 1478 (m), 1458 (s), 1434 (s), 1416 (s), 1385 (vs), 1318 (w), 1303 (w), 1262 (w), 1193 (vs), 1153 (w), 1116 (s), 1094 (s), 1027 (m), 936 (w), 803 (w), 747 (m), 726 (s), 695 (vs), 523 (s), 503 (m). *Anal.* Calc. for $C_{14}H_{17}BCdN_4S_3$: C, 36.5; H, 3.7; N, 12.2. Found: C, 35.4; H, 3.7; N, 12.5%.

4.4. Synthesis of $(Bm^{Me})CdS\text{-}p\text{-}C_6H_4Me$

A white suspension of $(Bm^{Me})CdBr$ (0.40 g, 0.92 mmol) in acetonitrile (50 mL) was treated with $Tl(S\text{-}p\text{-}C_6H_4Me)$ (0.30 g, 0.92 mmol), resulting in the formation of a pale yellow suspension, which was stirred for 1 h and filtered. The solvent was removed under reduced pressure from the colorless filtrate to give a white solid, which was dried in vacuo for 3.5 h (0.18 g, 42%). m.p. = 172 °C (dec). NMR data (in d_6-DMSO): ^1H δ 2.12 (s, 3H, $C_6H_4CH_3$), 3.50 (s, 6H, CH_3), 6.70 (d, 2H, $^3J_{H\text{–}H} = 7$, $C_6H_4CH_3$), 6.99 (s, 2H, imidazole *H*), 7.11

Table 3
Crystallographic data for $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$C_6H_4Me \cdot CH_2Cl_2$

Formula	$C_{16}H_{21}BCdCl_2N_4S_3$
Formula weight	559.66
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
Temperature (K)	150(2)
Unit cell dimensions	
a (Å)	11.1657(7)
b (Å)	17.104(1)
c (Å)	11.9665(7)
β (°)	96.375(1)
V (Å^3)	2271.2(2)
Z	4
ρ (calculated) (g cm^{-3})	1.637
μ (Mo Kα) (mm^{-1})	1.482
$\theta_{\max}$ (°)	28.28
Number of data	5164 [$R_{\mathrm{int}} = 0.0148$]
Number of parameters	320
$R_1(I > 2\sigma(I))$[a]	0.0269
$wR_2(I > 2\sigma(I))$[a]	0.0681

[a] $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

(d, 2H, $^3J_{\mathrm{H-H}} = 7$, $C_6H_4CH_3$), 7.21 (s, 2H, imidazole *H*), H_2B not located; ^{13}C δ 20.2 (q, $^1J_{\mathrm{C-H}} = 126$, 1C, $C_6H_4CH_3$), 34.6 (q, $^1J_{\mathrm{C-H}} = 141$, 2C, CH_3), 120.1 (dd, $^1J_{\mathrm{C-H}} = 197$, $^2J_{\mathrm{C-H}} = 11$, 2C, imidazole *C*), 123.3 (dd, $^1J_{\mathrm{C-H}} = 195$, $^2J_{\mathrm{C-H}} = 10$, 2C, imidazole *C*), 127.9 (d, $^1J_{\mathrm{C-H}} = 155$, 2C, C_o or C_m), 129.7 (s, 1C, C_p), 132.2 (dd, $^1J_{\mathrm{C-H}} = 159$, $^2J_{\mathrm{C-H}} = 6$, 2C, C_o or C_m), 140.6 (s, 1C, C_{ipso}), 154.2 (s, 2C, $C{=}S$). IR data (cm^{-1}): 3127 (w), 2941 (w), 2395 (m), 1557 (m), 1488 (s), 1460 (s), 1414 (m), 1381 (vs), 1325 (w), 1301 (w), 1192 (vs), 1165 (m), 1119 (s), 1085 (m), 1040 (w), 1016 (w), 875 (w), 806 (m), 729 (s), 695 (m), 681 (m), 625 (w), 516 (w), 492 (m), 456 (w). *Anal.* Calc. for $C_{15}H_{19}BCdN_4S_3$: C, 38.0; H, 4.0; N, 11.8. Found: C, 38.0; H, 4.1; N, 11.6%.

4.5. Synthesis of $(\mathrm{Bm^{Me}})\mathrm{CdSC_6F_5}$

A white suspension of $(\mathrm{Bm^{Me}})$CdBr (0.27 g, 0.62 mmol) in acetonitrile (30 mL) was treated with $\mathrm{Tl(SC_6F_5)}$ (0.25 g, 0.62 mmol), resulting in the formation of a yellowish suspension, which was stirred for 2 h and filtered. The clear filtrate was concentrated under reduced pressure to ca. 15 mL, resulting in the formation of a white solid, which was isolated by filtration, washed with diethyl ether (10 mL), and dried in vacuo for 3 h (0.18 g, 53%). m.p. = 248 °C (dec). NMR data (in d_6-DMSO): ^{1}H δ 3.50 (s, 6H, CH_3), 6.93 (s, 2H, imidazole *H*), 7.20 (s, 2H, imidazole *H*), H_2B not located; ^{13}C δ 34.6 (q, $^1J_{\mathrm{C-H}} = 141$, 2C, CH_3), 120.3 (dd, $^1J_{\mathrm{C-H}} = 197$, $^2J_{\mathrm{C-H}} = 12$, 2C, imidazole *C*), 123.2 (dd, $^1J_{\mathrm{C-H}} = 197$, $^2J_{\mathrm{C-H}} = 12$, 2C, imidazole *C*), 135.4 (d, $^1J_{\mathrm{C-F}} = 250$, 1C, C_p), 136.5 (d, $^1J_{\mathrm{C-F}} = 252$, 2C, C_o or C_m), 146.9 (d, $^1J_{\mathrm{C-F}} = 234$, 2C, C_o or C_m), 153.9 (s, 2C, $C{=}S$), C_{ipso} not observed. IR data (cm^{-1}): 3160 (w), 3135 (w), 2948 (w), 2390 (m), 1557 (m), 1509 (vs), 1483 (vs), 1462 (s), 1416 (m), 1384 (s), 1328 (w), 1302 (w), 1196 (s), 1167 (m), 1118 (s), 1087 (m), 1011 (w), 973 (vs), 860 (vs), 739 (s), 696 (w), 682 (m), 518 (w), 499 (w), 456 (w). *Anal.* Calc. for $C_{14}H_{12}BCdF_5N_4S_3$: C, 30.5; H, 2.2; N, 10.2. Found: C, 30.4; H, 2.3; N, 10.1%.

4.6. X-ray structure determination

X-ray diffraction data were collected at 150 K on a Bruker diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å) and equipped with a SMART APEX CCD area detector. A summary of crystal data, data collection, and refinement parameters for $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$C_6H_4Me$ is given in Table 3. The space group was determined from systematic absence in the diffraction data. The structure was solved using direct methods, completed by subsequent difference Fourier syntheses, and refined by full-matrix least-squares procedures on F^2. All non-hydrogen atoms were refined with anisotropic displacement coefficients and the hydrogen atoms were located on the *F*-map and refined with isotropic thermal parameters. Besides the main molecule in the crystal structure there are two solvent CH_2Cl_2 molecules and the Cl atoms in one of them are disordered over two positions in a ratio 68/32. A correction for absorption was applied to the data set using SADABS ($T_{\min}/T_{\max} = 0.8967$). All software used and sources of scattering factors are contained in the SMART, SAINTPLUS, SADABS, and SHELXTL program libraries [22].

5. Supplementary data

Crystallographic data (excluding structure factors) for $(\mathrm{Bm^{Me}})\mathrm{CdS}$-*p*-$C_6H_4Me$ have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 212904. 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; www: http://www.ccdc.cam.ac.uk).

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