PERGAMON

Polyhedron 21 (2002) 1795–1807

POLYHEDRON

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Syntheses and structures of mono-thiocyanate complexes of cadmium(II) and lead(II) containing bulky nitrogen based polydentate ligands

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Received 14 January 2002; accepted 13 May 2002

Abstract

The reaction of $[Cd_2(thf)_5](BF_4)_4$ with two equiv. of $Tl[HB(3\text{-}Bu^tpz)_3]$ (pz = pyrazolyl ring) produces the intermediate $\{[HB(3\text{-}Bu^tpz_3]Cd\}[BF_4]$ that reacts with potassium thiocyanate to yield $[HB(3\text{-}Bu^tpz)_3]Cd(NCS)$ (**1**). The solid state structure shows that the sterically demanding 3-*tert*-butyl groups enforce the formation of a tetrahedral, monomeric complex, the first four-coordinate cadmium(II)-thiocyanate complex to be structurally characterized. The decomposition of this compound produced $[(Bu^tHpz)_2Cd(NCS)_2]_n$ (**2**) as shown by X-ray crystallography. It was not possible to form a lead(II) complex analogous to **1**, but using less sterically demanding ligands allowed the preparation of $\{[HB(3,5\text{-}Me_2pz)_3]Pb(\mu\text{-}NCS)\}_2$ (**3**), and $\{[HB(pz)_3]Pb(\mu\text{-}NCS)\}_n$ (**4**). The former has a dimeric structure with both μ-NCS-*S*,*N* and μ-NCS-*S*,*S* bridging SCN^- ligands and the latter has a infinite 2-D layered array in which three nonequiv. $\{[HB(pz)_3]Pb\}^+$ groups sandwich a layer of SCN^- ligands. Using neutral 2,6-pyridyl-diimine ligands (pydim) having bulky 2,6-dimethylphenyl substituents, parallel complexes of both metals were prepared. The cadmium complex, $[(pydim)Cd\ (NCS)]_2[BF_4]_2$ (**5**) is dimeric with normal μ-NCS-*S*,*N* bridging groups. The structure of the lead(II) analog, $[(pydim)Pb(NCS)][BF_4]$ (**6**) is monomeric with an N-bound, isothiocyanate ligand and a four-coordinate lead(II). The structure of **6** is very different from **5**, presumably because of the stereoactive lone pair on lead(II). © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Tris(pyrazolyl)borate and 2,6-pyridyl-diimine ligands; Thiocyanate; Cadmium(II); Lead(II)

1. Introduction

We have been using the versatile tris(pyrazolyl)borate [1] and tris(pyrazolyl)methane ligands to prepare monomeric complexes of cadmium(II) and lead(II) in which the coordination sphere about the metal can be controlled by choice of substituent on the pyrazolyl rings of the ligands [2]. We wish to compare complexes of the two metals that have the same ligand set to determine the stereochemical impact of the lone pair of electrons on lead(II), a lone pair not present on cadmium(II) [3].

We have expanded this chemistry to include the ambidentate thiocyanate ligand. A variety of thiocyanate complexes of these two metals have been prepared, mainly with neutrally charged nitrogen based co-ligands and the thiocyanate ligand has been shown to bond in a variety of different fashions [4–7]. In most cases the cadmium(II) and lead(II) complexes are neutral containing two thiocyanate ligands with at least one of them bridging two metals [8–11].

Reported here are the synthesis and structural characterization of monothiocyanate complexes of these two metals supported by the bulky anionic $[HB(3\text{-}Bu^tpz)_3]^-$ (pz = pyrazolyl ring) and neutral 2,6-pyridyl-diimine (pydim) ligands shown in Scheme 1.

Ligands bearing bulky substituents were chosen in an attempt to prepare low coordination number complexes

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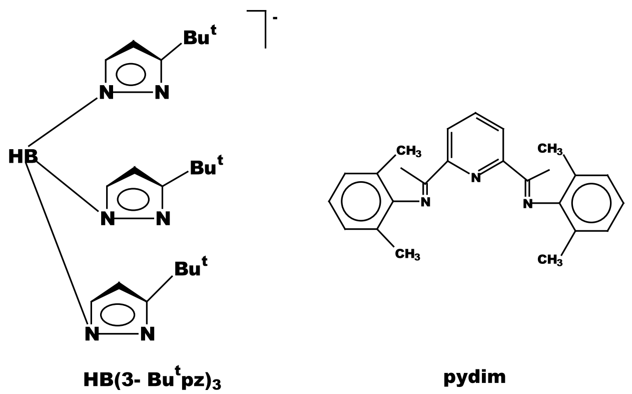
PII: S0277-5387(02)01058-6



Scheme 1.

with terminal thiocyanate ligands. The planar bonding substituted pyridine ligand pydim was chosen to contrast the tripodal, facial coordination of pyrazolylborate ligands [12]. We also report the syntheses of two lead thiocyanate complexes of less bulky tris(pyrazolyl)borate ligands. Specifically, the syntheses and solid state structure determinations of the following will be discussed: [HB(3-Bu^{t}pz)$_3$]Cd(NCS), [(Bu^{t}Hpz)$_2$Cd(μ-NCS-*N*,*S*)$_2$]$_n$, {[HB(3,5-Me$_2$pz)$_3$]Pb(μ-NCS)}$_2$, {[HB(pz)$_3$]Pb-(μ-NCS)}$_n$, [(pydim)Cd(μ-NCS,*N*,*S*)]$_2$[BF$_4$]$_2$, and [(pydim)Pb(NCS)][BF$_4$]. In the two complexes that are monomeric, the terminal thiocyanate ligands are N-bound.

2. Experimental

2.1. General procedure

All operations were carried out under a nitrogen atmosphere using standard Schlenk techniques and a Vacuum Atmospheres HE-493 dry box. All solvents were dried, degassed, and distilled prior to use. The ^{1}H NMR spectra were recorded on a Varian AM300 or AM400 spectrometer using a broad-band probe. Proton chemical shifts are reported in ppm versus internal Me$_4$Si. Mass spectral data were recorded on a VG 70SQ mass spectrometer. Clusters assigned to specific ions show appropriate isotopic patterns as calculated for the atoms present. Infrared spectra were recorded on a Perkin–Elmer 781 spectophotometer. Anhydrous CdCl$_2$ and KSCN were purchased from Aldrich Chemicals. The compounds 2,6-bis[(2,6-dimethylphenylimino)-methyl] pyridine (pydim), 2,6-bis[1-(2,6-dimethylphenyliimno)ethyl]pyridine (pydimMe$_2$) [14], K[HB(pz)$_3$] [1c], K[HB(3,5-Me$_2$pz)$_3$] [1d], Tl[HB(Bu^{t}pz)$_3$] [1g], [Cd$_2$(thf)$_5$][BF$_4$]$_4$ [2b] and [HB(pz)$_3$]PbCl [3a] were prepared according to published methods.

Note! Cadmium and lead compounds and their wastes are extremely toxic and must be handled carefully!!

2.2. {[HB(3-Bu^{t}pz)$_3$]Cd(II)}[BF$_4$]

[Cd$_2$(thf)$_5$][BF$_4$]$_4$ (0.43 g, 0.50 mmol) and Tl[(HB(3-Bu^{t}pz)$_3$] (0.58 g, 1.0 mmol) were dissolved in thf (20 ml) and allowed to stir for 2 h at ambient temperature. The mixture was filtered and the filtrate was evaporated to leave a white solid (0.25 g, 0.43 mmol, 43%); m.p. = 98–103 °C. ^{1}H NMR (acetone-*d*$_6$) δ: 7.68, 6.11 (d, d; 3, 3; $J = 2.2$ Hz; 4,5-H pz); 1.38 (27, s, Bu^t). FAB$^+$ MS: *m*/*z* Calc. for {[HB(3-Bu^{t}pz)$_3$]^{113}Cd}$^+$: 495.1966. Found: 495.1980.

2.3. [HB(3-Bu^{t}pz)$_3$]Cd(NCS) (**1**)

[Cd$_2$(thf)$_5$](BF$_4$)$_4$ (0.43 g, 0.50 mmol) and Tl[HB(3-Bu^{t}pz)$_3$] (0.58 g, 1.0 mmol) were charged into a round bottom Schlenk flask and thf (35 ml) was added to the flask via syringe. A white precipitate immediately formed, the mixture was allowed to stir for 2 h at room temperature (r.t.) and then filtered. The volatiles were removed in vacuo leaving a white solid. This solid and KSCN (0.080 g, 1.0 mmol) were dissolved in thf (20 ml). Immediately, a white precipitate formed, this mixture was allowed to stir for 3 h at r.t. then filtered. The solvent was removed in vacuo to leave a white solid (0.10 g, 0.17 mmol, 17%); m.p. = 135–142 °C. X-ray quality crystals were obtained from hot (50°)/cold(0°) toluene. ^{1}H NMR (acetone-*d*$_6$) δ: 7.78, 6.22 (3, 3; d, d; $J = 2.2$ Hz; 4,5-H pz); 1.39 (27, s, Bu^t). IR (νC≡N, Nujol mull, cm^{-1}): 2103. MS, direct ionization: *m*/*z* for *M*$^+$ Calc. for {[HB(3-Bu^{t}pz)$_3$]^{113}CdNCS}, 549.1732. Found: 549.1739.

2.4. [(3-Bu^{t}Hpz)$_2$Cd(μ-NCS-*S*,*N*)$_2$]$_n$ (**2**)

X-ray quality crystals were obtained from an attempted crystallization, from a layered solution of acetone and hexane, of the product produced in the [HB(3-Bu^{t}pz)$_3$]Cd(NCS) preparation. ^{1}H NMR (acetone-*d*$_6$), δ: 7.51 (2, br, 5-H pz); 6.09 (2, br, 4-H pz); 1.35 (18, s, Bu^t).

2.5. {[HB(3,5-Me$_2$pz)$_3$]Pb(μ-NCS)}$_2$ (**3**)

PbCl$_2$ (0.25 g, 0.90 mmol) was dissolved in H$_2$O (15 ml) and added to a thf (15 ml) solution of K[HB(3,5-Me$_2$pz)$_3$] (0.30 g, 0.90 mmol). The mixture was stirred for 0.5 h at which time a white precipitate was formed. The mixture was filtered to leave a white solid. KSCN (0.050 g, 0.50 mmol) was added to the filtrate. This solution was allowed to stir for 6 h at r.t. A white precipitate formed and the mixture was filtered. The solvent was removed in vacuo to leave a white solid, (0.16 g, 31%); m.p. = 296–301 °C (dec). X-ray quality crystals were obtained from a layered solution of CH$_2$Cl$_2$ and hexane. ^{1}H NMR (CDCl$_3$) δ: 5.81 (s, 3, 4-H pz); 2.44 (s, 9, CH_3); 2.30 (s, 9, CH_3). IR: (νC≡N, Nujol mull, cm^{-1}): 2060 and 2020. ES^+/MS: Calc. for $\{[HB(3,5\text{-}Me_2pz)_3]^{207}Pb\}^+$, 505.1770. Found: 505.1776. Calc. for $C_{32}H_{44}B_2N_{14}Pb_2S_2$: C, 34.17; H, 3.94. Found: C, 33.85; H, 4.55%.

2.6. $\{[HB(pz)_3]Pb(\mu\text{-}NCS)\}_n$ (**4**)

$[HB(pz)_3]PbCl$ (0.13 g, 0.30 mmol) was dissolved in thf (10 ml) and KSCN (0.030 g, 0.30 mmol) added to this solution. A white precipitate formed as this mixture was stirred for 6 h at r.t. and the solution was filtered. The solvent was removed in vacuo to leave a white solid, (0.080 g, 57%); m.p. = 222–225 °C. Suitable crystals were obtained from a layered solution of CH_2Cl_2 and hexane. ^1H NMR (acetone-d_6) δ: 7.76, 7.53 (3, 3; s, br; 3,5-H pz); 6.12 (3, s, 4-H pz) IR: (νC≡N, Nujol mull, cm^{-1}): 2084, 2045, 2030, 2004. FAB^+ MS: *m*/*z* Calc. for $\{[HB(pz)_3]^{207}Pb\}^+$, 419.0805. Found: 419.0796.

2.7. $[(pydim)Cd(\mu\text{-}NCS\text{-}S,N)]_2[BF_4]_2$ (**5**)

$[Cd_2(thf)_5](BF_4)_4$ (0.24 g, 0.25 mmol) and pydim (0.18 g, 0.50 mmol) were charged into a round bottom Schlenk flask and thf (20 ml) was added via syringe. The mixture was allowed to stir for 1 h at r.t. and the solvent was removed to leave a yellow solid. This solid (0.15 g) and KSCN (0.050 g, 0.50 mmol) were dissolved in thf (20 ml) and allowed to stir for 3 h at r.t. This mixture was filtered and the volatiles were removed in vacuo to leave a yellow solid (0.18 g, 55%); m.p. = 260–262 °C (dec). Crystals suitable for X-ray analysis were grown from a layered solution of CH_2Cl_2 and hexane. ^1H NMR (acetone-d_6), δ: 9.03 (2, s, H-imino); 8.81 (1, m, 4-H py); 8.56 (2, d, $J = 7.8$, 3,5-H py); 7.14 (6, m, 3,4,5-H ph); 2.26 (12, s, CH_3). IR (νC≡N, Nujol mull, cm^{-1}): 2110, 2079. FAB^+ MS: *m*/*z* Calc. for $[(pydim)^{113}Cd]^+$ 509.0674. Found: 509.0668.

2.8. $[(pydimMe_2)Pb(NCS)][BF_4]$ (**6**)

$Pb(acac)_2$ (0.10 g, 0.25 mmol) was suspended in thf (10 ml). The mixture was treated with 54% $HBF_4\cdot Et_2O$ (0.10 ml, 0.50 mmol) and was allowed to stir for 30 min followed by addition of a thf (10 ml) solution of the $pydimMe_2$ ligand (0.090 g, 0.25 mmol) by cannula transfer. The yellow reaction mixture was heated to 70 °C for 1 h. A solution of KSCN (0.040 g, 0.41 mmol) in thf (10 ml) was added to the reaction mixture and allowed to stir for 12 h at r.t. The mixture was filtered and the solvent evaporated to dryness providing a yellow powder (0.14 g, 0.18 mmol, 72%); m.p. = 224–227 °C. Crystals suitable for X-ray analysis were grown from a layered solution of CH_2Cl_2 and hexane. ^1H NMR (acetone-d_6), δ: 8.91 (3, br, 3,4,5-H py); 7.20 (6, br, 3,4,5-H ph); 2.60 (6, s, (CH_3-imino), 2.24 (12, s, CH_3). IR (νC≡N, Nujol mull, cm^{-1}): 2040 br. FAB^+ MS: Calc. for $[(pydimMe_2)^{207}Pb]^+$ 635.1725. Found: 635.1744.

2.9. X-ray crystal determination for **1**, **2**, **3**, **4**, **5** and **6**

Crystal, data collection, and refinement parameters are collected in Table 1. Colorless crystals of **1**, **2**, **3** and **4** and small yellow crystals of **5** and **6** were epoxied onto the end of a thin glass fiber. X-ray intensity data were measured using a Bruker SMART APEX CCD-based diffractometer system using Mo Kα radiation ($\lambda = 0.71073$ Å). All unit cells were initially determined based on reflections harvested from a set of three scans measured in orthogonal wedges of reciprocal space. Subsequently, a hemisphere of data was collected with a scan width of 0.3° in ω and an exposure time of 60 s per frame. The first 50 frames were re-collected at the end of data set to monitor crystal decay. The structures were solved by a combination of direct methods and difference Fourier syntheses, and refined by full-matrix least-squares against F^2, using the SHELXTL software package. The final unit cell constants are based upon the refinement of the XYZ centroids. In all structures, hydrogen atoms were placed in calculated positions and refined using a riding model and an empirical absorption correction based on the multiple measurement of equivalent reflections was applied with the program SADABS.

Systematic absences in the data for **1** were consistent with the space groups *Pnma* and $Pna2_1$. After several unsuccessful initial trials in the centrosymmetric space group *Pnma*, the non-centrosymmetric space group $Pna2_1$ was chosen and confirmed by the successful solution and refinement of the structure. Upon successful solution in $Pna2_1$, a check for missing symmetry was performed with the ADDSYM routine in PLATON, which verified the space group choice with a refined absolute structure (Flack) parameter of −0.003(19). All non-hydrogen atoms were refined with anisotropic displacement parameters including the toluene solvent molecule present in the cell. Crystals of **2** were determined to belong to the monoclinic crystal system. Systematic absences in the diffraction data determined that the space group was $P2_1/n$. Compound **3**, $\{[HB(3,5\text{-}Me_2pz)_3]Pb(\mu\text{-}NCS)\}_2\cdot 1.5CH_2Cl_2$, crystallizes in the orthorhombic crystal system. Examination of the systematic absences in the data set indicated the space groups *Pnma* or $Pna2_1$. A good solution and refinement was obtained in the space group *Pnma*, revealing two $\{[HB(3,5\text{-}Me_2pz)_3]Pb\}^+$ cations related by mirror symmetry, and bridged by 2 inequiv. SCN^- groups. One SCN^- lies in the mirror plane; the second SCN^- is roughly perpendicular to the intervening plane, with the central carbon (C2) in the mirror plane. Due to the incompatibility of the SCN^- anion with a horizontal

Table 1
Crystallographic data for $[HB(3\text{-}Bu^tpz)_3]Cd(NCS)\cdot C_6H_5CH_3$ (**1**), $[(3\text{-}Bu^tHpz)_2Cd(\mu\text{-}NCS\text{-}N,S)_2]_n$ (**2**), $\{[HB(3,5\text{-}Me_2pz)_3]Pb(\mu\text{-}NCS)\}_2\cdot 1.5CH_2Cl_2$ (**3**), $\{[HB(pz)_3]Pb(\mu\text{-}NCS)\}_n$ (**4**), $[(pydim)Cd(\mu\text{-}NCS\text{-}N,S)]_2[BF_4]_2$ (**5**), and $[(pydimMe_2)Pb(NCS)][BF_4]\cdot 2CH_2Cl_2$ (**6**)

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{29}H_{42}BCdN_7S$	$C_{16}H_{22}CdN_6S_2$	$C_{33.50}H_{47}B_2Cl_3N_{14}Pb_2S_2$	$C_{10}H_{10}BN_7PbS$	$C_{48}H_{46}B_2Cd_2F_8S_2$	$C_{27}H_{29}BCl_2F_4N_4PbS$
Formula weight (g mol^{-1})	643.97	474.92	1252.32	478.31	1197.47	806.50
Temperature (K)	293(2)	298(2)	293(2)	173(2)	173(2)	293(2)
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	triclinic
Space group	$Pna2_1$	$P2_1/n$	$Pnma$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	19.684(3)	6.0016(2)	13.971(3)	15.0687(9)	14.884(3)	13.177(4)
b (Å)	16.029(2)	10.2759(3)	22.218(4)	23.3079(14)	11.465(2)	14.677(4)
c (Å)	10.3224(15)	17.4673(5)	14.969(3)	13.4082(8)	15.911(3)	18.478(6)
α (°)	90	90	90	90	90	103.762(6)
β (°)	90	92.2898(16)	90	116.0440(10)	107.843(4)	95.980(6)
γ (°)	90	90	90	90	90	110.748(6)
Volume (Å^3)	3256.9(8)	1076.38(6)	4646.5(14)	4231.0(4)	2584.4(9)	3175.4(17)
Z	4	2	4	12	2	4
Density (Mg m^{-3})	1.313	1.45	1.790	2.253	1.539	1.687
$F(000)$	1336	480	2412	2664	8556	1568
Crystal size (mm)	0.30 × 0.24 × 0.14	0.10 × 0.10 × 0.5	0.40 × 0.11 × 0.03	0.20 × 0.16 × 0.01	0.40 × 0.40 × 0.04	0.42 × 0.30 × 0.10
Final R indices $[I > 2\sigma(I)]$ [a]	$R_1 = 0.0318$, $R_2 = 0.0654$	$R_1 = 0.0549$, $wR_2 = 0.1200$	$R_1 = 0.0340$, $wR_2 = 0.0677$	$R_1 = 0.0507$, $wR_2 = 0.1206$	$R_1 = 0.0549$, $wR_2 = 0.1200$	$R_1 = 0.0408$, $wR_2 = 0.0927$

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where P is $[2F_c^2+\max(F_o^2, 0)]/3$.

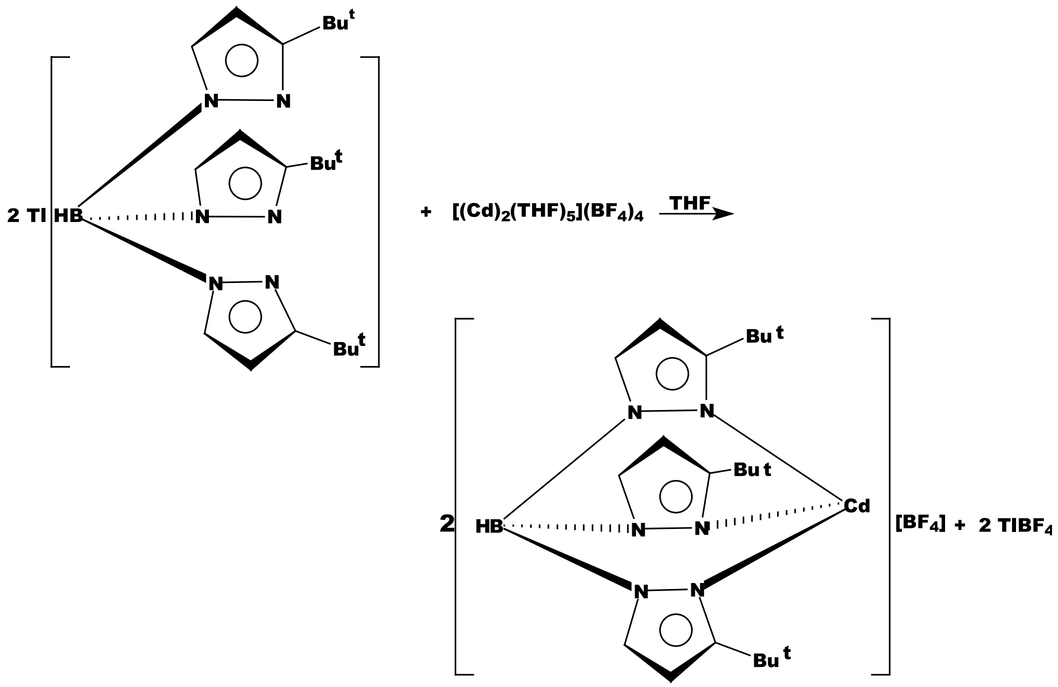
mirror plane, this arrangement results in this perpendicular SCN^- apparently half-occupying two orientations related through the mirror plane, with similar S–C and C–N distances. However, removing the mirror plane relating the two halves of the molecule and refining the structure in $Pna2_1$ yielded the same disorder, as well as chemically unreasonable $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand geometry and large correlations between atoms related by symmetry in $Pnma$. Further attempts to remove the disorder by reducing the symmetry even further to monoclinic or triclinic symmetry gave identical results. Therefore, $Pnma$ was selected as the correct space group. The similar S2–C2 and C2–N2 distances within the perpendicular SCN^- are an artifact of the disorder. While the displacement ellipsoid of C2 shows elongation along the bond directions, no satisfactory model with C2 off the mirror plane could be found. A total of 1.5 methylene chloride molecules disordered over three positions were located and refined with the aid of three geometrical restraints. Compound **4** crystallizes in the space group $P2_1/c$ as determined from the systematic absences in the intensity data. The asymmetric unit contains three crystallographically inequivalent $\{[HB(pz)_3]Pb\}^+$ cations and three SCN^- counterions and all atoms are on general positions. Crystals of **5** were determined to belong to the monoclinic crystal system. Systematic absences in the diffraction data determined that the space group was $P2_1/c$. Compound **6** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of two $[Pb(C_{25}H_{27}N_3)]^{2+}$ cations, two SCN^- and two BF_4^- counterions, and two CH_2Cl_2 molecules. Comparison of identical reflections measured at the beginning and at the end of the data collection showed an average loss of intensity of 4.1%; a linear decay correction was applied.

All computations were made using SHELXTL NT 5.10 and SADABS software (G. Sheldrick, Bruker AXS, Madison, WI).

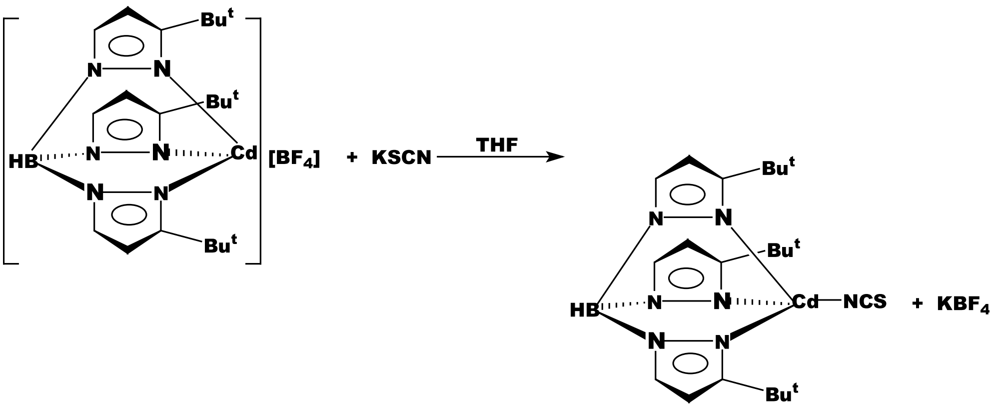
3. Results and discussion

3.1. tris(pyrazolyl)borate chemistry

The direct reaction of $CdCl_2$ with 1 equiv. of $Tl[HB(3\text{-}Bu^tpz)_3]$ and KSCN did not produce the desired $[HB(3\text{-}Bu^tpz)_3]Cd(NCS)$ (**1**) complex. The complex was produced in a two step procedure, starting with the reactive compound $[Cd_2(thf)_5](BF_4)_4$ [2b]. Mixing this compound with two equiv. of $Tl[HB(3\text{-}Bu^tpz)_3]$ produces the intermediate $\{[HB(3\text{-}Bu^tpz)_3]Cd\}[BF_4]$.



This intermediate reacts with potassium thiocyanate to yield [HB(3-Bu^{t}pz)$_3$]Cd(NCS) (**1**).



1

Complex **1** is air stable and is soluble in most common solvents. Infrared analysis shows a strong band at 2103 cm^{-1}, indicating the presence of a N-bound, terminal isothiocyante ligand. Reported CN stretching frequencies for terminal cadmium(II) isothiocyanate are in the range of 2059–2108 cm^{-1} [4b,5].

This arrangement was confirmed by a single crystal X-ray analysis. An ORTEP drawing is shown in Fig. 1 and selected bond angles and distances are shown in Table 2. The cadmium(II) site has a N$_4$ coordination arrangement in a pseudotetrahedral geometry. The chelate rings restrict the intraligand N–Cd–N angles to an average of 88.6°, with interligand N–Cd–N bond angles averaging 126.2°. The Cd–N–C bond angle of the isothiocyanate ligand is significantly bent at 150.7(3)° and the N–C–S bond angle is nearly linear at 178.9(4)°. The Cd–NCS bond distance is 2.107(3) Å, on the short end of the published ranges of analogous

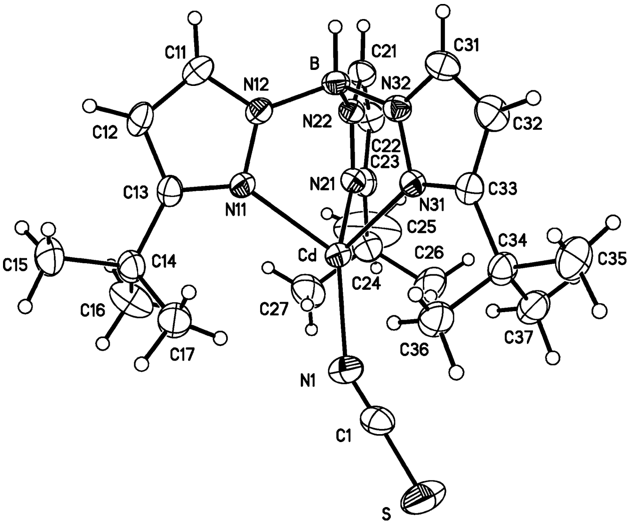


Fig. 1. ORTEP diagram of $[\mathrm{HB}(3\text{-}\mathrm{Bu}^t\mathrm{pz})_3]\mathrm{Cd(NCS)}$ (50% ellipsoids).

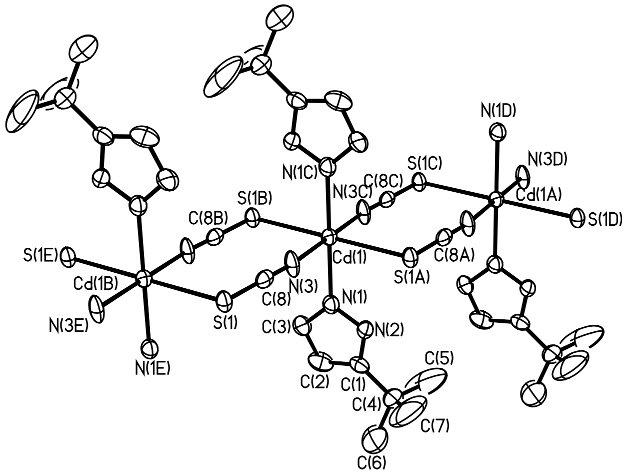


Fig. 2. ORTEP diagram of $[(3\text{-}\mathrm{Bu}^t\mathrm{Hpz})\mathrm{Cd}(\mu\text{-NCS-}N,S)]_n$ (50% ellipsoids).

Table 2
Selected bond distances (Å) and bond angles (°) for $[\mathrm{HB}(3\text{-}\mathrm{Bu}^t\mathrm{pz})_3]\mathrm{Cd(NCS)}$ (**1**)

Bond distances			
Cd−N(1)	2.107(3)	N(21)−N(22)	1.360(3)
Cd−N(11)	2.2234(19)	N(31)−N(32)	1.364(4)
Cd−N(21)	2.219(2)	N(1)−C(1)	1.093(4)
Cd−N(31)	2.2302(18)	C(1)−S	1.612(4)
N(11)−N(12)	1.364(3)		
Bond angles			
N(1)−Cd−N(11)	128.87(12)	N(11)−Cd−N(21)	87.82(11)
N(1)−Cd−N(21)	126.57(11)	N(21)−Cd−N(31)	90.10(12)
N(1)−Cd−N(31)	123.22(13)	C(1)−N(1)−Cd	150.7(3)
N(11)−Cd−N(31)	87.97(7)	N(1)−C(1)−S	178.9(4)

Table 3
Selected bond distances (Å) and bond angles (°) for $[(3\text{-}\mathrm{Bu}^t\mathrm{Hpz})\mathrm{Cd}(\mu\text{-NCS-}N,S)]_n$ (**2**)

Bond distances			
Cd(1)−N(1)	2.286(9)	N(3)−C(8)	1.131(13)
Cd(1)−N(3)	2.309(10)	C(8)−S(1)	1.650(13)
Cd(1)−S(1A)	2.762(2)		
Bond angles			
N(1)−Cd(1)−N(1C)	180.0(4)	N(3)−Cd(1)−S(1B)	88.4(2)
N(1)−Cd(1)−S(1A)	92.4(2)	N(3)−Cd(1)−N(3C)	180.0(4)
N(1)−Cd(1)−S(1B)	87.5(2)	S(1A)−Cd(1)−S(1B)	180.0(9)
N(3)−Cd(1)−N(1)	88.5(4)	Cd(1)−N(1)−C(3)	132.1(8)
N(3)−Cd(1)−N(1C)	91.5(4)	Cd(1)−S(1)−C(8)	101.6(3)
N(3)−Cd(1)−(S1A)	91.5(4)	N(3)−C(8)−S(1)	177.5(9)

distances for terminal CdNCS groups [4,5,13]. The Cd−N bond distances for the $[\mathrm{HB}(3\text{-}\mathrm{Bu}^t\mathrm{pz})_3]^-$ ligand are all very similar and average 2.22 Å.

As expected, the sterically demanding 3-*tert*-butyl groups enforce the formation of a tetrahedral, monomeric complex, the first 4-coordinate cadmium(II)-thiocyanate complex to be structurally characterized. In contrast, many cadmium(II)-thiocyanate complexes form intricate networks with bridging thiocyante ligands coordinated to cadmium forming polymeric chains, 2-D sheets and 3-D extended lattices [4,7,14–16].

In our first attempt to crystallize compound **1** from a layered solution of acetone and hexane, the compound we obtained was a decomposition product that was shown by X-ray crystallography to be a polymer, $[(3\text{-}\mathrm{Bu}^t\mathrm{Hpz})_2\mathrm{Cd}(\mu\text{-NCS})_2]_n$ (**2**). Fig. 2 shows the ORTEP diagram and bond distances and angles are shown in Table 3. The cadmium(II) is six-coordinate, bonding to two *tert*-butyl pyrazole rings located in the axial positions and four doubly bridging thiocyanate ligands in equatorial positions forming a $\mathrm{CdN_4S_2}$ octahedral arrangement. The cadmium(II) is located on an inversion center. The two pyrazole groups coordinate to cadmium with a Cd−N bond distance of 2.286(9) Å, while the N-coordinated SCN^- groups have a Cd−N distance 0.02 Å longer at 2.309(10) Å. The Cd−S distance is normal at 2.762(2) Å. The SCN^- groups are nearly linear at 177.5(9)°. The atoms of the doubly bridging $(\mu\text{-NCS-}N,S)^-$ groups and the two cadmium(II) form an eight member ring that closely resembles that observed in $[\mathrm{Cd(NCS)_2(CH_3C_5H_4N)_2}]_n$ [17], $\mathrm{Cd(NCS)_2\{(C_6H_5CH_2)_2NH\}_2}$ [18], and $[\mathrm{Cd(NCS)_2(isonicotinamide)_2}]$ [19].

Multiple attempts were made to synthesize the tetrahedral lead(II) compound analogous to **1** with the bulky $[\mathrm{HB}(3\text{-}\mathrm{Bu}^t\mathrm{pz})_3]^-$ ligand, but this complex could not be prepared. The tetrahedral enforcer character of this ligand apparently prevents the formation of a four-coordinate lead(II) complex with a stereochemically active lone pair. The failure to prepare the lead(II) analog of **1** clearly shows the influence of the lone pair.

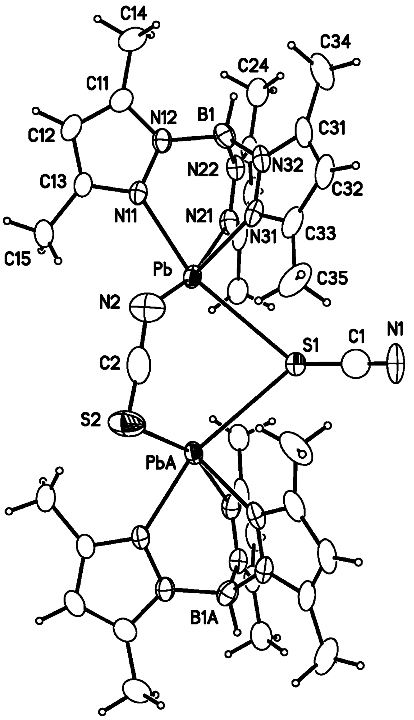
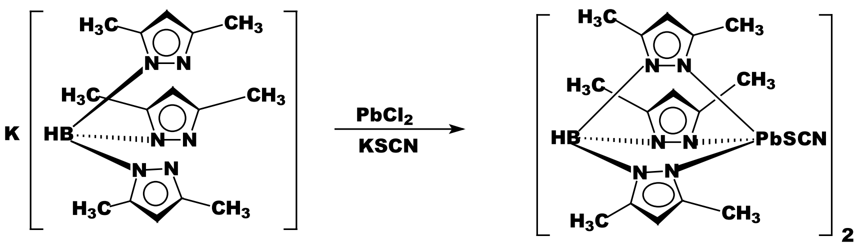


Fig. 3. ORTEP diagram of $\{[HB(3,5\text{-}Me_2pz)_3]Pb(\mu\text{-}NCS)\}_2$ (50% ellipsoids).

In contrast, two new lead(II) compounds with less sterically hindered ligands were prepared. The reaction of equimolar amounts of $PbCl_2$, $K[HB(3,5\text{-}Me_2pz)_3]$ and KSCN in thf yields $\{[HB(3,5\text{-}Me_2pz)_3]Pb(\mu\text{-}NCS)\}_2$ (**3**).



3

This compound is air-stable and soluble in halocarbons, thf, and slightly soluble in aromatic solvents. It has CN stretching frequencies at 2060 and 2020 cm^{-1} indicating bridging SCN^- groups.

Fig. 3 shows the ORTEP diagram of the cation in **3** and selected bond distances and angles are shown in Table 4. The solid state structure of **3** is dimeric with an unusual structure containing both μ-NCS-*S*,*N* and μ-NCS-*S*,*S* bridging SCN^- ligands. The μ-NCS-*S*,*S* ligand is in the mirror plane located between the two metal centers and bridges them through sulfur with relatively long Pb–S bond distance of 3.3277(16) Å [4c,11,20]. The other is in a normal bridging μ-NCS-*S*,*N* bonding one metal through nitrogen and the other through sulfur, but due to the incompatibility of this orientation of the SCN^- anion with a horizontal mirror plane, this perpendicular SCN^- half-occupies two orientations related through the mirror plane. The Cd–N bond distances for the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand are all similar with a range of 2.381(5)–2.436(5) (average 2.40 Å). Overall, the structure about each lead(II) can be considered octahedral with three sites occupied by nitrogen donor atoms from the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand with N–Pb–N bond angles restricted by the chelate rings to an average of 77.4°. The sulfur of the symmetrically bridged SCN^- occupies a fourth site while the N and S from the disordered SCN^- share the fifth site.

Table 4
Selected bond distances (Å) and bond angles (°) for $\{[HB(3,5\text{-}Me_2pz)_3]Pb(\mu\text{-}NCS)\}_2$ (**3**)

Bond distances			
Pb–S(1)	3.3277(16)	PbA–S(2)	3.326(5)
Pb–N(2)	2.540(14)	S(1)–C(1)	1.673(11)
Pb–N(11)	2.386(4)	S(2)–C(2)	1.394(5)
Pb–N(21)	2.436(5)	C(1)–N(1)	1.079(11)
Pb–N(31)	2.381(5)	C(2)–N(2)	1.378(15)
Pb···Pb(A)	4.2361(9)		
Bond angles			
N(11)–Pb–N(2)	89.2(4)	N(2)–Pb–S(1)	105.2(3)
N(21)–Pb–N(2)	162.5(4)	C(2)–N(2)–Pb	124.2(10)
N(31)–Pb–N(2)	89.6(4)	C(1)–S(1)–Pb	121.3(2)
N(11)–Pb–N(21)	76.30(15)	C(1)–S(1)–Pb(A)	121.3(2)
N(11)–Pb–N(31)	77.79(14)	C(2)–S(2)–Pb(A)	85.5(4)
N(21)–Pb–N(31)	78.08(15)	Pb–S(1)–Pb(A)	79.06(5)
N(11)–Pb–S(1)	161.79(11)	S(2)–Pb(A)–S(1)	109.98(9)
N(21)–Pb–S(1)	87.50(11)	N(1)–C(1)–S(1)	180.0(9)
N(31)–Pb–S(1)	90.93(10)	N(2)–C(2)–S(2)	176.9(11)

The remaining octahedral site is generally attributed to a stereoactive lone pair on the lead(II) center. In

Table 5
Selected bond distances (Å) and bond angles (°) for $[HB(pz)_3]Pb(\mu\text{-}NCS)]_n$ (**4**)

Bond distances			
Pb(1)–N(111)	2.486(10)	Pb(3)–N(331)	2.410(11)
Pb(1)–N(121)	2.494(11)	Pb(3)–N(311)	2.421(11)
Pb(1)–N(131)	2.524(10)	Pb(3)–N(321)	2.455(10)
Pb(1)–N(1)	2.793(13)	Pb(3)–N(3)	2.802(12)
Pb(1)–N(2)	2.798(13)	Pb(3)–S(3A)	3.251(4)
Pb(1)–S(1)A	3.134(4)	C(1)–N(1)	1.178(18)
Pb(2)–N(211)	2.508(10)	S(1)–C(1)	1.588(16)
Pb(2)–N(221)	2.448(9)	C(2)–N(2)	1.108(16)
Pb(2)–N(231)	2.460(10)	S(2)–C(2)	1.650(16)
Pb(2)–S(1)	3.015(4)	C(3)–N(3)	1.137(15)
S(3)–C(3)	1.644(13)		
Bond angles			
N(111)–Pb(1)–N(121)	73.0(3)	N(211)–Pb(2)–N(221)	78.8(3)
N(111)–Pb(1)–N(131)	78.6(3)	N(211)–Pb(2)–N(231)	75.9(3)
N(121)–Pb(1)–N(131)	74.7(3)	N(221)–Pb(2)–N(231)	74.8(3)
N(111)–Pb(1)–N(1)	84.1(4)	N(211)–Pb(2)–S(1)	157.6(2)
N(121)–Pb(1)–N(1)	145.2(4)	N(221)–Pb(2)–S(1)	97.2(2)
N(131)–Pb(1)–N(1)	126.6(4)	N(231)–Pb(2)–S(1)	81.8(3)
N(111)–Pb(1)–N(2)	97.5(3)	N(311)–Pb(3)–N(321)	75.3(3)
N(121)–Pb(1)–N(2)	78.5(3)	N(311)–Pb(3)–N(331)	77.6(4)
N(131)–Pb(1)–N(2)	152.9(3)	N(321)–Pb(3)–N(331)	78.5(3)
N(111)–Pb(1)–S(1A)	160.4(3)	N(311)–Pb(3)–S(3A)	88.9(2)
N(121)–Pb(1)–S(1A)	94.9(3)	N(321)–Pb(3)–S(3A)	162.0(2)
N(131)–Pb(1)–S(1A)	83.3(2)	N(331)–Pb(3)–S(3A)	90.0(3)
N(1)–Pb(1)–S(1A)	113.3(3)	N(311)–Pb(3)–N(3)	87.6(3)
N(2)–Pb(1)–S(1A)	95.1(2)	N(321)–Pb(3)–N(3)	94.2(3)
Pb(1)–S(1A)–Pb(2A)	152.24(14)	N(331)–Pb(3)–N(3)	164.6(4)

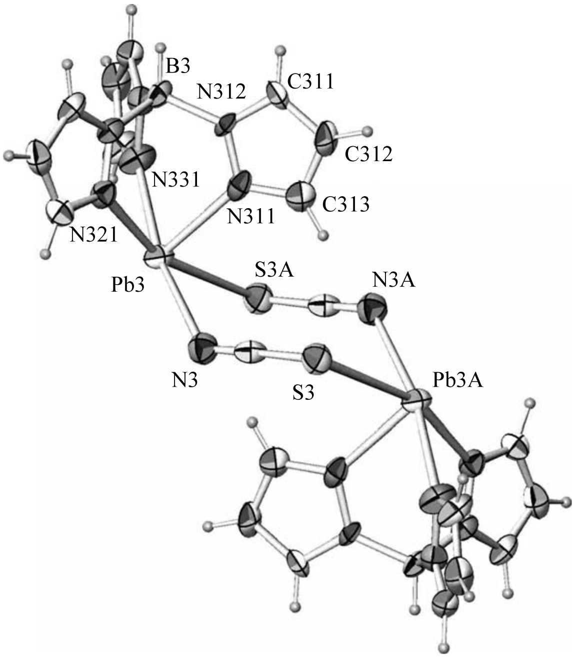


Fig. 5. $\{[HB(pz)_3]Pb(3)(\mu\text{-}NCS\text{-}N,S)\}_2$ units in $\{[HB(pz)_3]Pb(\mu\text{-}NCS)\}_n$.

general, it is well known that in higher coordinate lead structures, bonds adjacent to the presumed location of the lead(II) lone pair are longer than bonds remote from the lone pair [21]. The structure of **3** is very unique in that the Pb–N bonds of the $[HB(3,5\text{-}Me_2pz)_3]^-$ ligand adjacent to the open site are only 0.03 Å longer, on average, than the *trans* Pb–N bond. For comparison, the three Pb–N bonds adjacent to the open site in the distorted structure of $[HB(pz)_3]_2Pb$ are 0.24 Å longer, on average, than the *trans* Pb–N bonds [3a]. In addition, the nitrogen atom of the SCN^- ligand in the mirror plane has long range interactions at 3.161(5) Å with both lead(II) centers of an adjacent dimeric unit in the area of this open, sixth site, an unlikely interaction if substantial electron density from the lone pair on lead(II) were present. These results support calculations that indicate that in distorted structures of lead(II) the amount of mixing of the p orbital into the lone pair orbital is small [3g].

The reaction of $[HB(pz)_3]PbCl$ and KSCN in equimolar amounts in thf yields $\{[HB(pz)_3]Pb(\mu\text{-}NCS)\}_n$ (**4**).

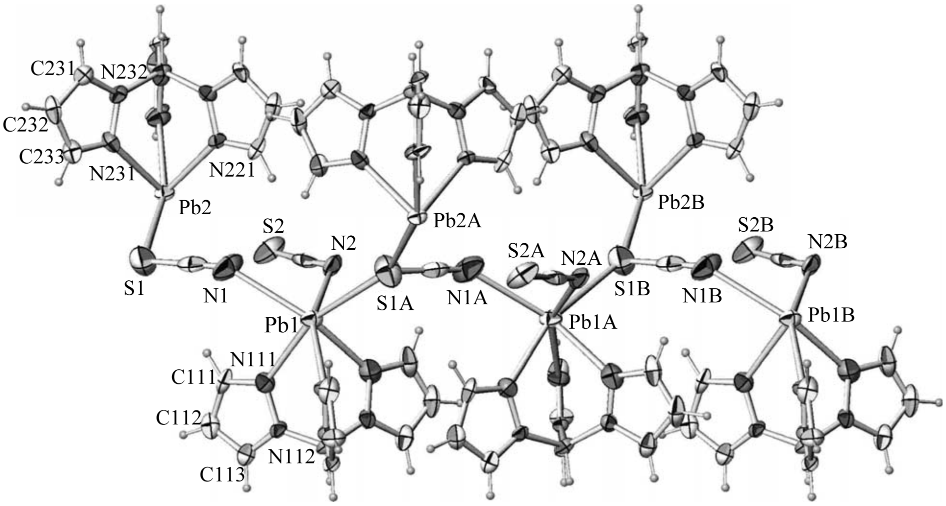


Fig. 4. Diagram of the polymer chain formed by Pb(1) and Pb(2) in $\{[HB(pz)_3]Pb(\mu\text{-}NCS)\}_n$.

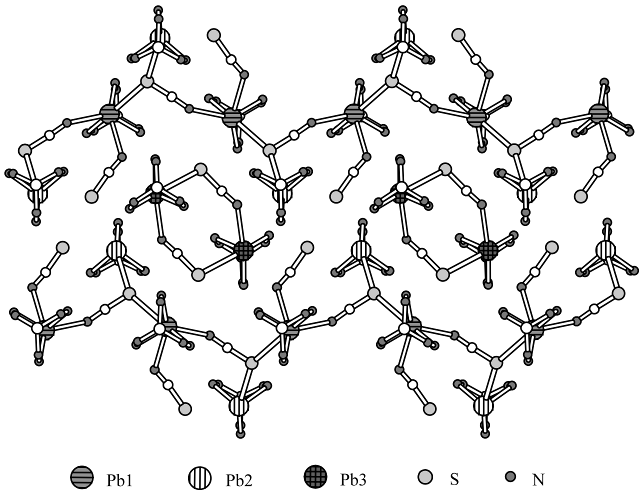
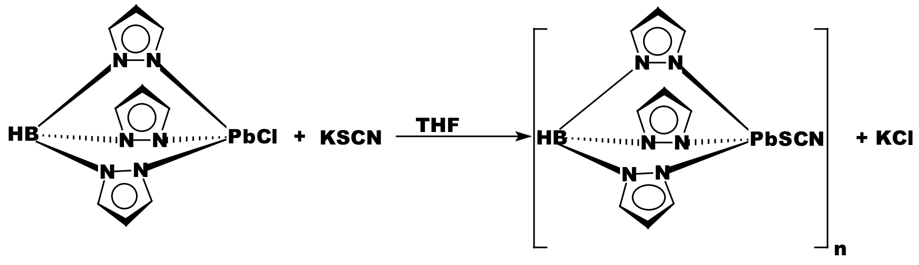


Fig. 6. Total arrangement of the three types of lead(II) in $\{[HB(pz)_3]Pb(\mu\text{-NCS})\}_n$ viewed perpendicular to the view in Figs. 4 and 5. Hydrogen atoms have been omitted for clarity.



4

This compound is air-stable and soluble in halocarbons, thf, and slightly soluble in some aromatic solvents. It has CN stretching frequencies at 2084, 2045, 2030, 2004 cm^{-1} indicating a complicated bridging arrangement of the SCN^- groups.

The solid state structure was solved crystallgraphically and selected bond distances and angles are shown in Table 5. The structure of this complex is a complicated infinite 2-D layered array in which $\{[HB(pz)_3]Pb\}^+$ groups sandwich a layer of SCN^- ligands with the lead(II) centers oriented toward them. There are three independent $\{[HB(pz)_3]Pb(NCS)\}^+$ units. As shown in the lower part of Fig. 4, $\{[HB(pz)_3]Pb(1)\}^+$ units form a chain connected by $(\mu\text{-SCN-}S,N)^-$ ligands. There is also a terminal N-bound SCN^- making Pb(1) six-coordinate. The bridging SCN^- groups are also linked through sulfur to the $\{[HB(pz)_3]Pb(2)\}^+$ units on the other side of the sandwich array. The $\{[HB(pz)_3]Pb(3)\}^+$ units are in a centrosymmetric dimeric arrangement with end-on bridging $(\mu\text{-SCN-}N,S)^-$ ligands forming eight member rings, Fig. 5, with the two lead units on each side of the sandwich array.

Shown in Fig. 6 is a combined view perpendicular to the view in Figs. 4 and 5. The $\{[HB(pz)_3]Pb(3)(NCS)\}_2$ units are surrounded by two of the infinite chains formed by Pb(1) and Pb(2). There are secondary interactions between the two units, most notably between the bridging N(3) of the dimeric Pb(3) units and Pb(2) at 2.996 Å. There are also π–π stacking interactions between the pyrazolyl groups attached to Pb(1) along the chain and between alternate Pb(2) and Pb(3) pyrazolyl groups attached parallel to this chain ranging from 3.50 to 3.69 Å. Typical interplanar distances for π–π interactions of aromatic groups range from 3.3 to 3.8 Å [22].

3.2. 2,6-bis(imino)pyridine chemistry

Using a method similar to the preparation of the tris(pyrazolyl)borate compound **1**, a new thiocyanate complex of the pydim ligand is prepared starting with

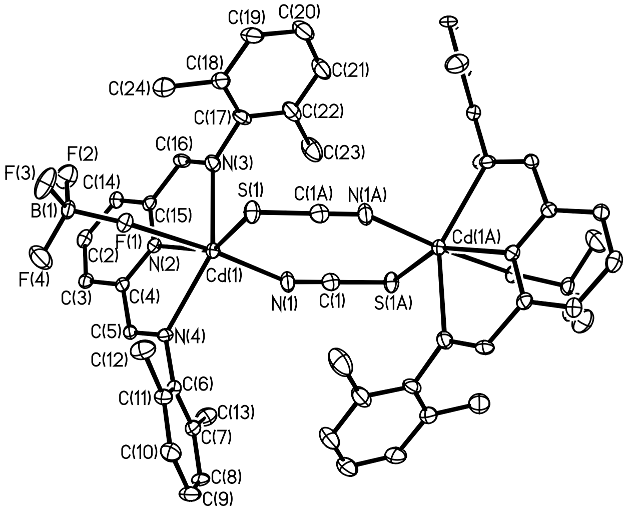
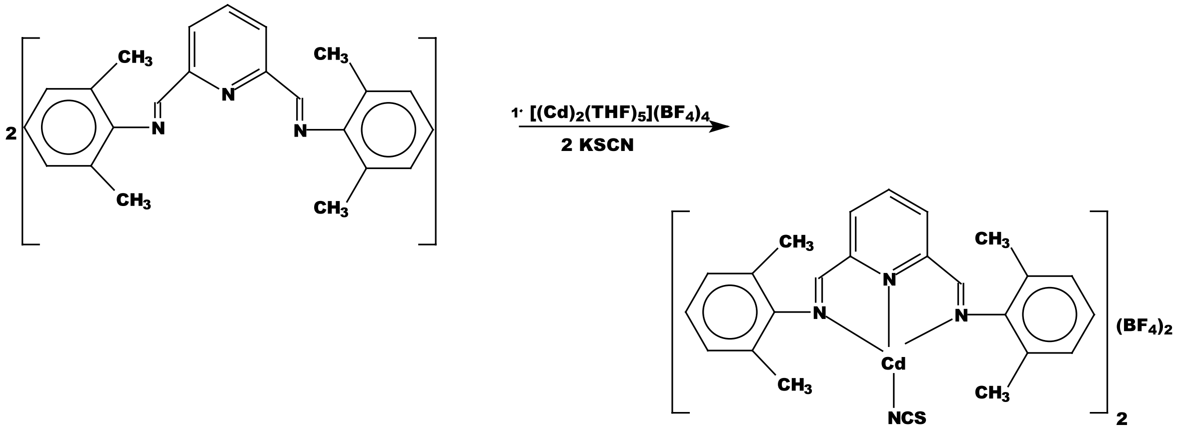


Fig. 7. ORTEP diagram of $[(pydim)Cd(\mu\text{-NCS-}N,S)]_2[BF_4]_2$ (50% ellipsoids)

Table 6
Selected bond distances (Å) and bond angles (°) for [(pydim)Cd(μ-NCS-*N*,*S*)]$_2$[BF$_4$]$_2$ (**5**)

Bond distances			
Cd(1)–N(1)	2.246(6)	N(1)–C(1)	1.155(8)
Cd(1)–N(2)	2.256(5)	C(1)–S(1)	1.667(7)
Cd(1)–N(3)	2.452(5)	Cd(1)–F(1)	2.544(4)
Cd(1)–N(4)	2.448(5)	Cd(1)–S(1)	2.5551(17)
Bond angles			
N(1)–Cd(1)–N(2)	108.92(19)	N(4)–Cd(1)–S(1)	123.55(12)
N(1)–Cd(1)–N(3)	100.4(2)	S(1)–Cd(1)–F(1)	78.0(9)
N(1)–Cd(1)–N(4)	94.51(19)	N(1)–Cd(1)–F(1)	171.71(18)
N(2)–Cd(1)–N(3)	69.6(17)	N(2)–Cd(1)–F(1)	77.07(15)
N(2)–Cd(1)–N(4)	70.63(17)	N(3)–Cd(1)–F(1)	86.95(15)
N(3)–Cd–N(4)	140.15(16)	N(4)–Cd(1)–F(1)	81.94(15)
N(1)–Cd(1)–S(1)	98.0(15)	N(1)–C(1)–S(1)	178.9(6)
N(2)–Cd(1)–S(1)	148.87(13)	Cd(1)–S(1)–C(1)	99.2(2)
N(3)–Cd(1)–S(1)	90.78(13)	Cd(1)–N(1)–C(1)	156.35(5)

[Cd$_2$(thf)$_5$][BF$_4$]$_4$. This starting material is treated first with the pydim ligand followed by potassium thiocyanate resulting in the formation of [(pydim)Cd(μ-NCS-*S*,*N*)]$_2$[BF$_4$]$_2$ (**5**).



5

This complex is air-stable in the solution and solid states. It is soluble in acetone, CH$_2$Cl$_2$, and chloroform. The infrared spectrum shows CN stretching frequencies of 2078 and 2110 cm^{-1}, indicating that the SCN$^-$ ligands are in bridging positions [5,11].

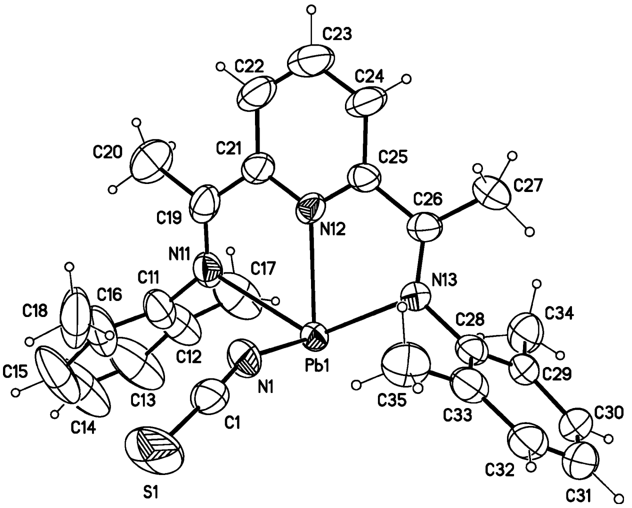
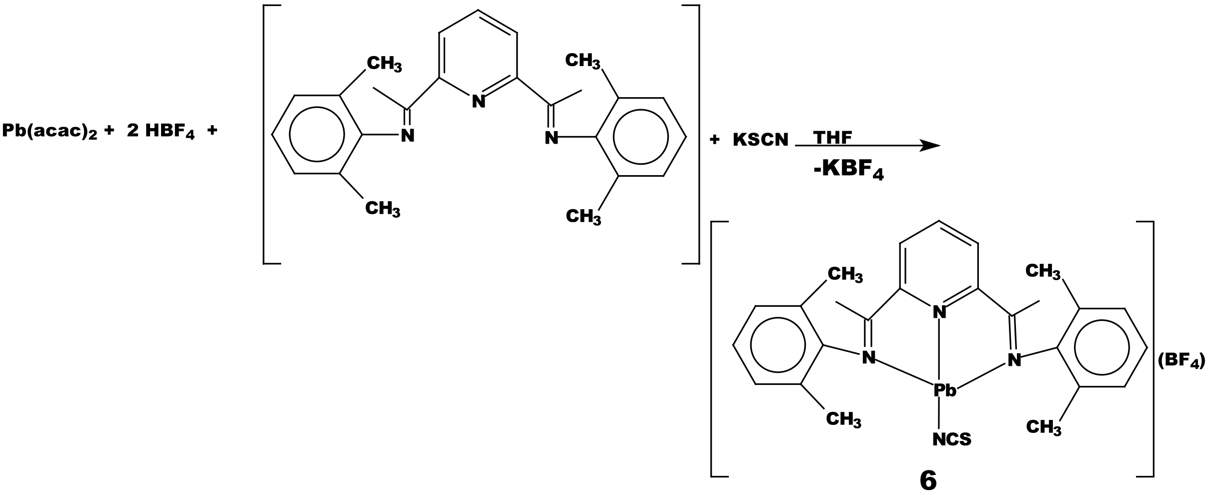


Fig. 8. ORTEP diagram of [(pydimMe$_2$)Pb(1)(NCS)][BF$_4$] (50% ellipsoids).

X-ray crystallography shows that the complex is a dimer. Fig. 7 shows an ORTEP drawing of **5**, and selected bond distances and angles are shown in Table 6. The environment about the cadmium(II) is best described as a distorted octahedron. It is strongly bonded by five donor atoms, with the two bridging thiocyanate groups making the overall structure a dimer. The three nitrogen atoms of the planar pyridine ligand occupy three sites in a meridional arrangement, but the intrinsic bite angle of the ligand coupled with the large size of the cadmium(II) force a significant distortion from an octahedral arrangement with the *trans* N–Cd–N bond angle of 140.15(16)°. The Cd–N(py) bond (2.256(5) Å) is significantly shorter than the Cd–N(imino) bonds (average 2.45 Å). The bridging SCN$^-$ groups form a N–Cd–S angle much greater than 90° at 123.55(12)° and the SCN$^-$ ligands are nearly linear at 178.9(6)°. The Cd–NCS bond distance is 2.246(6) Å and the Cd–SCN bond distance is 2.5551(17) Å, both typical for this bridging ligand forming an eight membered ring with the two cadmium(II) [10,14–16]. Within the ring, the Cd(1)–N(1)–C(1) bond angle of 156.35(5)° is much larger than the Cd(1)–S(1)–C(1) bond angle of 99.2(2)°. The sixth coordination site is occupied by a weak interaction from a fluorine of the BF_4^- group.

An analogous lead(II) isothiocyanide complex was synthesized using similar chemistry as outlined in the cadmium synthesis using the pydimMe_2 ligand. In this reaction, $Pb(acac)_2$ was treated with two equiv. of tetrafluorohydroboric acid followed by one equiv. of pydimMe_2 and KSCN to yield a tetra-coordinate lead(II) complex [(pydimMe_2)Pb(NCS)][BF_4] (**6**).



6

This moderately high melting solid compound is air-stable and soluble in halocarbons and acetone. The CN stretching frequency is a broad band centered at 2040 cm^{-1}.

The solid state structure was determined by X-ray crystallography. There are two independent cations in the structure, Fig. 8 shows an ORTEP drawing for one of those, Pb(1), and Table 7 shows the bond angles and distances for both. The primary structures of both cations are similar and are four-coordinate monomeric arrangements. The geometry about lead(II) is irregular, with the N-bound SCN^- ligand oriented basically perpendicular to the N_3Pb plane formed by the donor atoms of the pydimMe_2 ligand and lead(II). The planes of the phenyl rings are also oriented essentially orthogonal to this plane. The Pb–NCS bond distances are short, as would be expected for the low coordinate number for lead(II) of four, at 2.275(7) Å for Pb(1) and 2.333(7) Å for Pb(2). Published Pb–NCS bond distances range from 2.4 to 2.8 Å [11]. The Pb–N–C bond angles are 152.6(7)° and 156.0(7)° while the N–C–S bond angles are nearly linear. In contrast to the cadmium complex **5** and other structures of the pydim ligand [12b], the Cd–N(py) bond (2.466 (6) Å) for Pb(1) is actually longer than one of the Cd–N(imino) bond distances (2.456(6) Å) and only slightly shorter than the other (2.522(6) Å). While the Cd–N(py) bond distance (2.466(5) Å) for Pb(2) is shorter than the average of the Cd–N(imino) bond distances (2.54 Å), the difference is much less than the 0.2 Å distance commonly observed [12]. As expected for the larger size of lead(II) compared with cadmium(II), the three nitrogen atoms of the planar pyridine ligand form even smaller N–Pb–N bond angles with the *trans* N(11)–Pb(1)–N(13) bond angles of only 129.1(2)° for Pb1 and 129.6(2)° for Pb(2).

4. Conclusions

We have prepared and characterized several cadmium(II) and lead(II) thiocyanate complexes containing either tris(pyrazolyl)borate ligands or neutral 2,6-pyridyl-diimine ligands and one thiocyanate ligand per metal. Complex **1**, [HB(3-Bu^tpz)$_3$]Cd(NCS), is the first 4-coordinate cadmium(II) isothiocyanate complex to be structurally characterized and contains a short Cd–NCS bond distance (2.107(3) Å). An analogous complex of lead(II) could not be synthesized. It appears that the tetrahedral enforcer character of this ligand prevents the formation of a four-coordinate lead(II) complex with a stereochemically active lone pair and, apparently, a tetrahedral complex isostructural with **1** is energetically unfavorable. The use of less sterically demanding tris(pyrazolyl)borate ligands allowed the preparation

Table 7
Selected bond distances (Å) and bond angles (°) for [(pydim-Me$_2$)Pb(NCS)][BF$_4$] (**6**)

Bond distances (molecule 1)			
Pb(1)–N(1)	2.275(7)	N(11)–C(19)	1.269(11)
Pb(1)–N(11)	2.456(6)	N(12)–C(21)	1.342(9)
Pb(1)–N(12)	2.466(6)	N(12)–C(25)	1.330(9)
Pb(1)–N(13)	2.522(6)	N(13)–C(26)	1.275(8)
N(1)–C(1)	1.110(9)	N(13)–C(28)	1.436(9)
N(11)–C(11)	1.455(13)	C(1)–S(1)	1.623(9)
Bond angles			
N(1)–Pb(1)–N(11)	83.9(2)	C(1)–N(1)–Pb(1)	152.6(7)
N(1)–Pb(1)–N(12)	86.0(2)	C(11)–N(11)–Pb(1)	116.7(6)
N(1)–Pb(1)–N(13)	86.2(2)	C(19)–N(11)–Pb(1)	119.5(6)
N(11)–Pb(1)–N(12)	64.7(2)	C(21)–N(12)–Pb(1)	119.5(6)
N(11)–Pb(1)–N(13)	129.1(2)	C(25)–N(12)–Pb(1)	119.8(4)
N(12)–Pb(1)–N(13)	64.96(19)	C(26)–N(13)–Pb(1)	120.0(5)
C(28)–N(13)–Pb(1)	119.3(4)	N(1)–C(1)–S(1)	176.4(9)
Bond distances (molecule 2)			
Pb(2)–N(2)	2.333(7)	Pb(2)–N(22)	2.466(5)
Pb(2)–N(23)	2.509(5)	Pb(2)–N(21)	2.577(6)
C(2)–N(2)	1.150(9)	C(2)–S(2)	1.604(8)
C(41)–N(21)	1.432(10)	C(49)–N(21)	1.266(9)
C(51)–N(22)	1.345(9)	C(55)–N(22)	1.325(9)
C(56)–N(23)	1.291(8)	C(58)–N(23)	1.430(10)
Bond angles			
N(2)–Pb(2)–N(21)	90.8(2)	C(49)–N(21)–Pb(2)	119.9(5)
N(2)–Pb(2)–N(22)	91.2(2)	C(51)–N(22)–Pb(2)	119.5(6)
N(2)–Pb(2)–N(23)	85.8(2)	C(55)–N(22)–Pb(2)	118.6(5)
N(22)–Pb(2)–N(21)	64.0(2)	C(56)–N(23)–Pb(2)	118.7(5)
N(22)–Pb(2)–N(23)	65.8(2)	C(58)–N(23)–Pb(2)	121.3(5)
C(2)–N(2)–Pb(2)	156.0(7)	N(23)–Pb(2)–N(21)	129.6(2)
C(41)–N(21)–Pb(2)	119.7(4)	N(2)–C(2)–S(2)	178.0(7)

of two interesting new [tris(pyrazolyl)borate]Pb(NCS) complexes. The use of the 3,5-dimethyl substituted ligand produces {[HB(3,5-Me$_2$pz)$_3$]Pb(μ-NCS)}$_2$ that has a dimeric structure with both μ-NCS-*S*,*N* and μ-NCS-*S*,*S* bridging SCN$^-$ ligands. The parent ligand produces {[HB(pz)$_3$]Pb(μ-NCS)}$_n$, having an unusual infinite 2-D layered array in which three nonequiv. {[HB(pz)$_3$}Pb}$^+$ groups sandwich a layer of SCN$^-$ ligands, where the overall structure is supported by π–π stacking interaction.

It was possible to prepare parallel complexes of both metals using the bulky pydim ligands. However, for cadmium(II) the ligand was not bulky enough to prevent formation of dimeric **5**, [(pydim)Cd (μ-NCS-*N*,*S*)]$_2$[BF$_4$]$_2$, that has a conventional bridging mode where the two cadmium(II) and two (μ-NCS-*N*,*S*)$^-$ groups form an eight membered ring. It is interesting that compound **1** with a bulky tripodal ligand is monomeric, whereas **5** with a bulky tridentate planar ligand is dimeric. For lead(II), the monomeric complex **6**, [(pydimMe$_2$)Pb(NCS)][BF$_4$], formed in which the isothiocyanate ligand is N-bound and the lead(II) has the low coordination number of four. The structure of **6** is very different from **5**, presumably because of the stereoactive lone pair on lead(II).

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center, CCDC 177361–177366. Copies of the information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors thank the National Institute of Health (GM-26295 for D.L.R) and the National Science Foundation (CHE-0110493 for D.L.R) for support. The Bruker CCD Single Crystal Diffractometer (at the University of South Carolina) was purchased using funds provided by the NSF Instrumentation for Materials Research Program through Grant DMR: 9975623. The NSF (Grants CHE-8904942 and CHE-9601723) and NIH (Grant RR-02425) have supplied funds to support NMR equipment and the NIH (Grant RR-02849) has supplied funds to support mass spectrometry equipment at the University of South Carolina.

References

[1] (a) S. Trofimenko, Scorpionates—The Coordination Chemistry of Poly(pyrazolyl)borate Ligands, Imperial College Press, London, 1999;
(b) S. Trofimenko, Acc. Chem. Res. 4 (1971) 17;
(c) S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3170;
(d) S. Trofimenko, J. Am. Chem. Soc. 89 (1967) 6288;
(e) A.J. Shaver, Organomet. Chem. Lib. 3 (1976) 157;
(f) S. Trofimenko, Prog. Inorg. Chem. 34 (1988) 115;
(g) S. Trofimenko, Chem. Rev. 93 (1993) 943.

[2] (a) D.L. Reger, S.M. Myers, S.S. Mason, A.L. Rheingold, B.S. Haggerty, P.D. Ellis, Inorg. Chem. 34 (1995) 4996;
(b) D.L. Reger, J.E. Collins, S.M. Myers, A.L. Rheingold, L.M. Liable-Sands, Inorg. Chem. 35 (1996) 4904;
(c) D.L. Reger, S.S. Mason, A.L. Rheingold, Inorg. Chim. Acta 240 (1995) 669.

[3] (a) D.L. Reger, M.F. Huff, A.L. Rheingold, B.S. Haggerty, J. Am. Chem. Soc. 114 (1992) 579;
(b) D.L Reger, Synlett. (1992) 469.;
(c) D.L. Reger, T.D. Wright, C.A. Little, J.J.S. Lamba, M.D. Smith, Inorg. Chem. 40 (2001) 3810;
(d) D.L. Reger, Y. Ding, A.L. Rheingold, R.L. Ostrander, Inorg. Chem. 33 (1994) 4226;
(e) S.P. Constantine, H. Cox, P.B. Hitchcock, G.A. Lawless, Organometallics 19 (2000) 317 (and references therein);
(f) D.R. Armstrong, M.J. Duer, M.G. Davidson, D. Moncrieff, C.A. Russell, C. Stourton, A. Steiner, D. Stalke, D.S. Wright,

Organometallics 16 (1997) 3340;
(g) L. Shimoni-Livny, J.P. Glusker, C.W. Bock, Inorg. Chem. 37 (1998) 1853 (and reference therein).

[4] (a) C. Pariya, N.R. Chaudhuri, S. Seth, A. Das, Acta Crystallogr., Sect. C 52 (1996) 358;
(b) J. Dillen, T.H. Lentra, J.G. Haasnoot, J. Reedijk, Polyhedron 2 (1983) 195;
(c) D.J. Williams, D.L. VanDerveer, A. Lipscomb, R.L. Jones, Inorg. Chim. Acta 192 (1992) 51.

[5] (a) A. Diaz, M. Massaesi, G.J. Ponticelli, Inorg. Nucl. Chem. 37 (1975) 2469;
(b) R. Baggio, A. Frigerio, E.B. Halac, D. Vega, M.J. Perec, J. Chem. Soc., Dalton Trans. (1992) 549.

[6] L.M. Engelhardt, B.M. Furphy, J.M. Harrowfield, J.M. Patrick, B.W. Skelton, A.H. White, J. Chem. Soc., Dalton Trans. (1989) 595.

[7] (a) N. Mondal, M.K. Saha, S. Mitra, V.J. Gramlich, Chem. Soc., Dalton Trans (2000) 3218.;
(b) I.W. Nowell, Acta Crystallogr., Sect. B 35 (1979) 1891.

[8] A.E. Shvelashvili, M.A. Porai-Koshits, A.I. Kvitashvili, B.M. Shchedrin, L.P. Sarishvili, Zh. Strukt. Khim. 15 (1974) 315.

[9] L. Cavalca, M. Nardelli, G. Fava, Acta Crystallogr. 13 (1960) 125.

[10] (a) P.F. Rodesiler, R.W. Turner, N.G. Charles, A.H. Griffith, E.L. Amma, Inorg. Chem. 23 (1984) 999;
(b) H. Zhang, X. Wang, K. Zhang, B.K. Teo, Coord. Chem. Rev. 183 (1999) 157.

[11] (a) N.A. Bailey, D.E. Fenton, I.T. Jackson, R. Moody, L.R. Barbarin, J. Chem. Soc., Chem. Commun. (1983) 1463.;
(b) L.M. Engelhardt, J.M. Patrick, A.H. White, Aust. J. Chem. 42 (1989) 335;
(c) M.G.B. Drew, S.M. Nelson, Acta Crystallogr. 35 (1979) 1594;
(d) J.M. Harrowfield, H. Miyamae, B.W. Skelton, A.A. Soudi, A.H. White, Aust. J. Chem. 49 (1996) 1051;
(e) A.Y. Nazarenko, E.B. Rusanov, J. Coord. Chem. 34 (1995) 265;
(f) I.O. Cabral, M.F. Cabral, W.J. Cummins, G.B. Drew, A. Rodgers, S.M. Nelson, Inorg. Chim. Acta 30 (1978) L313.

[12] (a) B. Cetinkaya, E. Cetinkaya, M. Brookhart, P.S. White, J. Mol. Catal. 142 (1999) 101;
(b) G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastoianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Stromberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728;
(c) B.L. Small, M. Brookhard, Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.) 39 (1998) 213;
(d) P. Merrell, E. Alyea, L. Ecott, Inorg. Chim. Acta 59 (1982) 25;
(e) D.A. Edward, M.F. Mahon, W.R. Martina, K.C. Molloy, J. Chem. Soc., Dalton Trans. (1990) 3161.

[13] (a) S.M. Kuang, Z.Z. Zhang, B.M. Wu, T.C.W. Mak, J. Organomet. Chem. 540 (1997) 55;
(b) S.L. Li, Z.Z. Zhang, T.C.W. Mak, Inorg. Chim. Acta 268 (1998) 177;
(c) Chow, M.Y. Chen, X.M. Mak, T.C.W., J. Chem. Soc., Dalton Trans. (1993) 3413.

[14] M. Taniguchi, A. Ouchi, Bull. Chem. Soc. Jpn. 62 (1989) 424.

[15] M. Cannas, G. Carta, A. Cristini, G.J. Marongiu, Inorg. Chem. 16 (1977) 228.

[16] M. Cannas, G. Carta, A. Cristini, G.J. Marongiu, J. Chem. Soc., Dalton Trans. (1976) 210.

[17] M. Taniguchi, S. Mamoru, A. Ouchi, Bull. Chem. Soc. Jpn. 59 (1986) 2299.

[18] M. Taniguchi, S. Mamoru, A. Ouchi, Bull. Chem. Soc. Jpn. 60 (1987) 1192.

[19] G. Yang, H.G. Zhu, B.H. Liang, X.M. Chen, J. Chem. Soc., Dalton Trans. (2001) 580.

[20] (a) G.A. Bowmaker, J.M. Harrowfield, H. Miyamae, T.M. Shand, B.W. Skelton, A.A. Soudi, A.H. White, Aust. J. Chem. 49 (1996) 1081;
(b) G.A. Bowmaker, J.M. Harrowfield, H. Miyamae, T.M. Shand, B.W. Skelton, A.A. Soudi, A.H. White, Aust. J. Chem. 49 (1996) 1121;
(c) L.M. Engelhardt, B.M. Furphy, J.M. Harrowfield, J.M. Patrick, A.H. White, Inorg. Chem. 28 (1989) 1410.

[21] (a) P.G. Harrison, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Comprehensive Coordination Chemistry, vol. 3, Permagon, Oxford, 1987, p. 183;
(b) S.L. Lawton, G.T. Kokotailo, Inorg. Chem. 11 (1972) 363.

[22] C. Janiak, J. Chem. Soc., Dalton Trans (2000) 3885.