plex, exemplified by $Fe(CO)_3$(diene) complexes. Indeed, equilibria between 1,4-η^2- and η^4-diene complexes have been observed by NMR for $(C_8H_8)M(C_4H_6)$ (M = Ti, Zr, Hf)[2] and $(C_5H_5)_2Zr$(diene).[3]

The hydrogen atoms of the C_4H_6 ligand have been located. The anti hydrogens attached to C1 and C4 are displaced away from Hf (ca. 0.6 Å out of the C1, C2, C3, C4 plane); the syn hydrogens are nearly in the butadiene plane. The hydrogen atoms attached to C2 and C3 are displaced ca. 0.3 Å toward Hf. Similar parameters have been observed in the structure of $Mn(C_4H_6)_2(CO)$[22] in which the hydrogen atoms have been located.

Each of the butadiene ligands has one Hf-terminal carbon distance that is 0.03 Å shorter than the other, a small but significant difference. This appears to be a trans effect as each short Hf-C distance occurs on the end of the diene trans to the dmpe phosphorus. The internal butadiene carbon-metal distances are unaffected.

The bite angle of the dmpe ligand, 72.0°, is somewhat smaller than the typical range, 75-85°,[23] a consequence of the long Hf-P distances. The conformation of the dmpe chelate ring is similar to other examples.[24]

Acknowledgment. The technical assistance of M. Cushing and suggestions of T. Tulip are gratefully acknowledged.

Registry No. **1**, 60300-64-3; **2**, 78791-10-3; **3**, 78791-11-4; **4**, 78791-12-5; **5**, 78791-13-6; **6**, 71328-76-2; **7**, 78791-14-7; **8**, 56315-41-4; **9**, 51733-16-5; ethylene, 74-85-1; $TiCl_4 \cdot 2THF$, 31011-57-1; $ZrCl_4 \cdot 2THF$, 21959-01-3; $[Zr(n\text{-}C_4H_6)dmpe]_2(dmpe)$, 69878-77-9; $NbCl_4(dmpe)_2$, 61202-65-1.

Supplementary Material Available: Listings of hydrogen atom positions and isotropic temperature factors (Table V) and structure factor amplitudes (Table VI) (37 pages). Ordering information is given on any current masthead page.

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Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and the Département de Chimie, Université de Montréal, Montréal, Québec H3C 3V1, Canada

Preparation and Spectral Characterization of Cadmium(II) Thiocyanate Complexes of Tricyclohexyl-, Triphenyl- and Tri-*m*-tolylphosphines and the Crystal and Molecular Structure of the Tri-*m*-tolylphosphine Complex

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The complexes $Cd(SCN)_2PR_3$, where R = cyclohexyl, phenyl, or *m*-tolyl, have been isolated from the reaction of $Cd(SCN)_2$ with the phosphine. Phosphorus-31 NMR, infrared, and Raman spectra of the complexes have been examined, and the structure of the tri-*m*-tolylphosphine complex has been determined by a single-crystal X-ray diffraction study. No satellites due to $^{111}Cd/^{113}Cd-^{31}P$ spin-spin couplings are observed in the ^{31}P NMR spectra even at 183 K. The vibrational spectra of the complexes are consistent with a polymeric structure involving bridging thiocyanates and five-coordinate cadmium. The crystals of the *m*-tolyl compound $Cd(SCN)_2(P(C_7H_7)_3)$ belong to the monoclinic space group $P2_1/c$, with a = 10.866 (7) Å, b = 10.203 (3) Å, c = 20.077 (6) Å, β = 101.14 (4)°, and Z = 4. The structure was solved by the heavy-atom method and refined by least-squares procedures on 1965 nonzero reflections. The final R factor was 0.038. Infinite chains of five-coordinated Cd atoms and bridging SCN groups extend along the b direction in the crystal. The metal shows a distorted trigonal-bipyramid geometry with the equatorial positions being occupied by the phosphine (Cd-P = 2.584 (2) Å), an S-bonded SCN group (Cd-S = 2.595 (2) Å), and the N end of a symmetry-equivalent SCN group (Cd-N = 2.256 (6) Å). The remaining SCN group bridges axial positions along the chain by forming weaker bonds (Cd-S = 2.792 (2) Å, Cd-N = 2.297 (6) Å). The unusual distribution of soft S atoms and hard N atoms in both the axial and equatorial positions undoubtedly results from the intermediate softness of cadmium, since the strongly bonding equatorial sites are filled only by soft P and S atoms in the similar mercury complexes.

Introduction

Tertiary phosphine complexes of cadmium(II) and mercury(II) halides were first reported[1c] 40 years ago. During the last decade, phosphine complexes of a variety of mercury(II) salts such as pseudohalides,[2-11] nitrate,[2,12-14] perchlorate,[2,15] and carboxylates[16-18] have been extensively investigated. However, very little has hitherto been known about phosphine complexes of cadmium(II) derivatives other than the halides. A recent study[16,19] showed that cadmium(II) halides and thiocyanate form 1:1 complexes with tri-*tert*-butylphosphine.

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Table I. Analytical Data, Melting Points, and ^{31}P NMR Chemical Shifts[a]

compd	mp, °C	% C found	% C calcd	% H found	% H calcd	% N found	% N calcd	δ
$Cd(SCN)_2P(Cy)_3$	185	46.73	47.19	6.65	6.55	5.01	5.05	30.0
$Cd(SCN)_2P(Ph)_3$	150	49.13	48.93	3.13	3.09	5.70	5.60	−5.6
$Cd(SCN)_2P(m\text{-}MeC_6H_4)_3$	148	51.79	51.83	3.88	3.98	5.03	5.26	−5.7

[a] In CH_2Cl_2 containing 10% acetone-d_6 at ambient temperature.

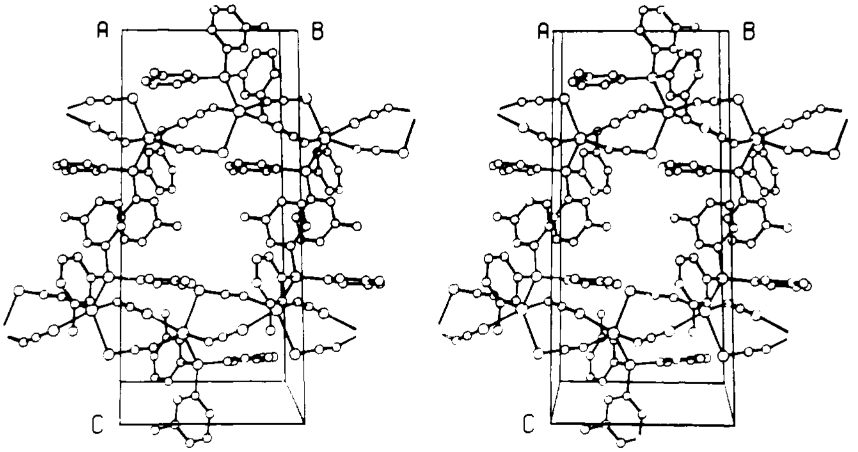

Figure 1. Stereoview of the unit cell of $Cd(SCN)_2P(m\text{-}MeC_6H_4)_3$. The atoms can be identified by reference to Figure 2. Hydrogens are omitted for simplicity.

Since cadmium(II) halides are known to form 1:1 as well as 1:2 complexes with tricyclohexylphosphine,[5] which is sterically less demanding than tri-*tert*-butylphosphine, reactions of cadmium(II) thiocyanate with tricyclohexylphosphine, triphenylphosphine, tri-*m*-tolylphosphine, and tri-*o*-tolylphosphine, were investigated in the present work. The resulting complexes were characterized by elemental analyses and by ^{31}P NMR and vibrational spectral measurements. In view of unexpected solid structures[10,11] adopted by the mercury(II) thiocyanate complex $Hg(SCN)_2PPh_3$, the crystal structure of one of the cadmium(II) thiocyanate complexes, $Cd(SCN)_2P(m\text{-}MeC_6H_4)_3$, was also determined by a single-crystal X-ray diffraction study.

Results and Discussion

Synthesis. Reactions of cadmium(II) thiocyanate with tricyclohexylphosphine, triphenylphosphine, and tri-*m*-tolylphosphine in refluxing alcohol or acetone afforded stable 1:1 complexes. Repeated attempts to prepare complexes containing more than 1 mol of phosphine/mol of cadmium failed and gave only mixtures containing 1:1 complex and unreacted phosphine. No reaction occurred when cadmium(II) thiocyanate and tri-*o*-tolylphosphine were refluxed for up to 24 h.

Mercury(II) thiocyanate forms 1:1 as well as 1:2 complexes with triphenylphosphine[10,11] and tricyclohexylphosphine[5] and a 1:1 complex with the bulkier tri-*o*-tolylphosphine.[6] Cadmium(II) halide complexes of tricyclohexylphosphine (1:2) have also been reported.[5] Thus, the failure to isolate 1:2 cadmium(II) thiocyanate complexes of tricyclohexyl-, triphenyl-, and tri-*m*-tolylphosphines and its lack of complex formation with tri-*o*-tolylphosphine are not due to steric reasons. Differences in the coordination behavior of cadmium(II) and mercury(II) thiocyanates toward phosphine ligands are best explained in terms of the differences in the preferences of the two metals for the hard N and the soft P or S donor sites.[20] Cadmium(II), unlike mercury(II), is indicated to prefer the hard N donor site to the soft S or P donor sites, whereas the opposite is true for mercury(II), which is undoubtedly a soft acid.[20] Evidence for the preference of cadmium(II) for the hard donors is also provided by the differences in the solid-state structures of cadmium(II)[21] and mercury(II)[22] thiocyanates. In cadmium(II) thiocyanate[21] each cadmium has two relatively strong Cd–N bonds and four weaker Cd–S bonds, but the reverse is found for mercury(II) thiocyanate.[22] Formation of both the 1:1 and 1:2 complexes of cadmium(II) thiocyanate with pyridines[23,24] and pyridine *N*-oxides[25] is also consistent with the greater preference of cadmium(II) for the hard N or O donors.

The cadmium(II) thiocyanate complexes prepared in this work are air-stable white solids that are only sparingly soluble in polar organic solvents such as acetone and dichloromethane and are insoluble in hydrocarbon solvents. The tri-*m*-tolylphosphine complex was obtained in a crystalline form suitable for structure determination by X-ray diffraction. Attempts to crystallize the other two complexes did not succeed due to their poor solubility. The low solubility of the complexes also precluded determination of their molecular weights. Phosphorus-31 NMR spectra of the complexes were measured in dichloromethane (containing 10% acetone-d_6) by extended signal accumulation in the Fourier-transform mode. The spectra at ambient temperatures as well as at 183 K showed only a single peak downfield from free phosphine. Failure to observe the satellites due to the ^{111}Cd/^{113}Cd–^{31}P spin–spin couplings is in marked contrast with the solution behavior of $Cd(SCN)_2P(t\text{-}Bu)_3$[19] for which satellites due to couplings are observed at ambient temperatures. The NMR chemical shifts for the complexes are given in Table I along with their analytical data.

Crystal Structure of $Cd(SCN)_2P(m\text{-}MeC_6H_4)_3$. The refined coordinates are listed in Table II, and the unit cell is represented in Figure 1. The structure consists of helical chains

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Table II. Refined Coordinates ($\times10^4$; Cd $\times10^5$, H $\times10^3$)

atom	*x*	*y*	*z*
Cd	10750 (5)	15576 (5)	28826 (2)
P	2671 (2)	655 (2)	3813 (1)
S1	2571 (2)	3521 (2)	2517 (1)
S2	1327 (2)	603 (2)	1824 (1)
N1	591 (6)	5205 (6)	2054 (3)
N2	125 (6)	−1786 (6)	1878 (3)
C1	1404 (6)	4501 (7)	2247 (3)
C2	614 (7)	−814 (7)	1862 (3)
C11	4131 (6)	1559 (7)	3901 (3)
C12	4720 (6)	1617 (8)	3394 (3)
C13	5803 (6)	2332 (8)	3404 (4)
C14	6286 (7)	3010 (8)	3940 (4)
C15	5711 (7)	2979 (8)	4438 (4)
C16	4640 (6)	2252 (8)	4419 (3)
C17	6414 (8)	2386 (11)	2852 (4)
C21	2089 (6)	834 (7)	4522 (3)
C22	1233 (7)	1819 (7)	4564 (3)
C23	728 (7)	2018 (7)	5085 (3)
C24	1107 (7)	1169 (8)	5569 (3)
C25	1962 (8)	184 (8)	5547 (3)
C26	2449 (7)	17 (8)	5026 (3)
C27	−222 (10)	3076 (10)	5111 (4)
C31	3064 (6)	−1046 (7)	3769 (3)
C32	4316 (6)	−1509 (7)	3881 (3)
C33	4586 (7)	−2829 (7)	3853 (3)
C34	3601 (8)	−3680 (7)	3719 (4)
C35	2361 (7)	−3279 (8)	3602 (4)
C36	2108 (7)	−1970 (8)	3623 (4)
C37	5937 (8)	−3296 (10)	3952 (5)
H12	438 (5)	118 (5)	307 (2)
H14	695 (5)	346 (6)	396 (3)
H15	612 (6)	361 (6)	478 (3)
H16	422 (5)	228 (6)	479 (3)
H22	94 (4)	239 (5)	427 (2)
H24	81 (7)	128 (8)	591 (3)
H25	201 (7)	−26 (8)	590 (3)
H26	306 (6)	−71 (7)	501 (3)
H32	498 (5)	−88 (5)	400 (2)
H34	375 (5)	−454 (6)	368 (2)
H35	175 (5)	−396 (5)	348 (2)
H36	137 (5)	−169 (6)	351 (2)
H171	642 (9)	325 (10)	272 (4)
H172	603 (8)	168 (9)	261 (4)
H173	725 (10)	221 (11)	299 (4)
H271	−84 (12)	321 (13)	473 (6)
H272	12 (13)	377 (13)	513 (6)
H273	−52 (13)	315 (13)	540 (6)
H371	612 (10)	−328 (11)	365 (5)
H372	605 (10)	−420 (11)	409 (5)
H373	653 (10)	−290 (10)	428 (5)

running along 2_1 axes in the *b* direction. The building blocks are trigonal bipyramids linked by pairs of bridging SCN groups.

The environment of Cd is shown in Figure 2. Selected interatomic distances and bond angles are given in Table III. The phosphine occupies an equatorial position of the distorted trigonal bipyramid. The Cd–P distance (2.584 (2) Å) is slightly shorter than observed in the tetrahedral $CdCl_2(PPh_3)_2$ molecule (2.63 Å),[26] where steric hindrance between the bulky phosphines is likely to be more severe. The bond length observed here is much longer than the Hg–P distances (2.43 Å) found in analogous five-coordinate $Hg(SCN)_2PPh_3$ compounds,[10,11] in spite of the similar sizes of Cd and Hg.[27] This probably reflects the lower affinity of harder Cd for the soft phosphine.

The binding of SCN in $Cd(SCN)_2P(m\text{-}MeC_6H_4)_3$ is also consistent with a greater affinity of Cd for hard N than for soft S. The Cd–N bonds are definitely stronger than the Cd–S bonds (Table III), while the reverse was observed with soft Hg. Crystal structures of the $Cd(SCN)_2$ complexes reported so far show six-coordination for cadmium.[28-30] The Cd–N distances in these structures seem to depend on the type of donors in the coordination sphere: when a large number of S atoms are present, like in $Cd(SCN)_2$ itself,[21] the observed Cd–N distance is ~2.25 Å. For a coordination sphere containing only N donors, as found in $Cd(NCS)_2(en)_2$,[28] the Cd–N distances increase to 2.40 Å. The remaining known structures[29] are consistent with this trend, except for $Cd(NSC)_2(urea)_2$ for which the Cd–N distances of 2.00 Å seem to be anomalous.[30] Our equatorial Cd–N2 distance 2.256 (6) Å) is consistent with the aforementioned trend. The axial Cd–N1 bond (2.297 (6) Å) is slightly longer as usually found in trigonal-bipyramid species of d^{10} ions.[41] The equatorial Cd–S2 bond length (2.595 (2) Å) is on the low side of the range found for other bridging Cd–SCN compounds of known structure (2.60–2.93 Å),[21,28-30] while the axial Cd–S1 bond is in the middle of that range. Thus, S2–C2–N2 bridges only equatorial positions and it is bonded through both of its ends to a greater extent than S1–C1–N1, which links only axial sites. The resulting ligand distribution around Cd is somewhat

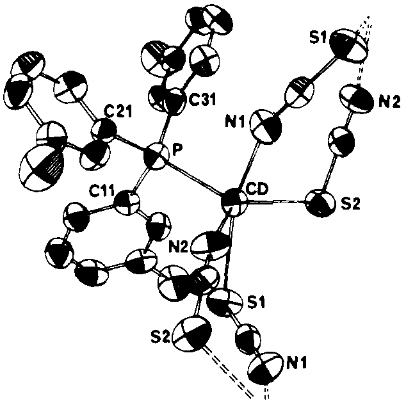

Figure 2. Environment of Cd in $Cd(SCN)_2P(m\text{-}MeC_6H_4)_3$. The ellipsoids correspond to 50% probability. Hydrogens are omitted for simplicity.

Table III. Interatomic Distances and Bond Angles around Cadmium

	Distances (Å)		
Cd–S1	2.792 (2)	S1–C1	1.631 (7)
Cd–S2	2.595 (2)	C1–N1	1.152 (10)
Cd–P	2.584 (2)	S2–C2	1.649 (8)
Cd–N1^a	2.297 (6)	C2–N2	1.129 (10)
Cd–N2^b	2.256 (6)		
	Angles (Deg)		
S1–Cd–S2	80.83 (7)	Cd–S2–C2	98.7 (3)
S1–Cd–P	98.58 (6)	Cd–N1^a–C1^a	154.8 (6)
S1–Cd–N1^a	162.8 (2)	Cd–N2^b–C2^b	163.9 (6)
S1–Cd–N2^b	85.6 (2)	S1–C1–N1	179.1 (7)
S2–Cd–P	114.30 (7)	S2–C2–N2	178.8 (7)
S2–Cd–N1^a	92.9 (2)	Cd–P–C11	109.9 (2)
S2–Cd–N2^b	131.1 (2)	Cd–P–C21	111.2 (2)
P–Cd–N1^a	98.6 (2)	Cd–P–C31	115.6 (2)
P–Cd–N2^b	114.1 (2)	C11–P–C21	107.4 (3)
N1^a–Cd–N2^b	86.6 (2)	C11–P–C31	106.7 (3)
Cd–S1–C1	95.4 (3)	C21–P–C31	105.6 (3)

[a] $-x, -^1/_2 + y, ^1/_2 - z$. [b] $-x, ^1/_2 + y, ^1/_2 - z$.

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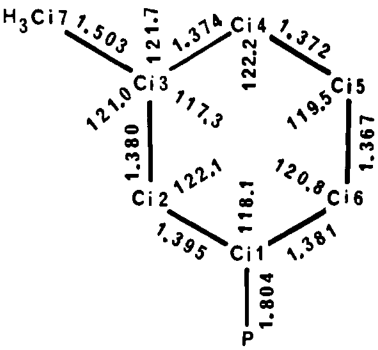

Figure 3. Geometry of the *m*-tolyl rings. The values have been averaged over the three independent rings. Individual bond lengths and angles are listed in Table VII (supplementary material). The esd's on individual results are as follows: P–C, 0.007 Å; C–C in ring, 0.009–0.011 Å; C–CH_3, 0.012–0.013 Å; C–C–C angles, 0.6–0.7°.

unusual. In the similar five-coordinate Hg complexes, the equatorial sites are filled by soft S and P donor atoms, while the hard N donors occupy the axial sites.[10,11] In the present case, the N as well as the S donors occupy both the equatorial and axial sites. Although crystal packing may contribute to the stabilization of this particular configuration, this behavior is undoubtedly related to the intermediate softness of Cd.

The angular distortions around Cd are probably due to solid-state effects. The three equatorial ligands are coplanar with Cd (sum of the angles at Cd = 359.5°), but the N2–Cd–S2 angle is 131.1 (2)°, that is, N2 and S2 are pulled apart in the direction of the chain. This distortion is distributed equally between the remaining angles in the plane (~114°). The lack of perpendicularity of the Cd–S1 bond to the equatorial plane is probably due to the constraints imposed by the polymeric structure.

The SCN ligands are linear within experimental errors. Although the two groups do not interact with the metal to the same extent, there are no significant differences between their S–C (average 1.640 Å) and C–N (average 1.14 Å) bond lengths, respectively. The Cd–S–C angles (95.4 (3), 98.7 (3)°) are in the usual range (85–105°).[31] The M–N–C angles have been reported to occur in a much wider range (150–177°), with which our Cd–N–C angles (154.8 (6), 163.9 (6)°) are consistent.

Coordination of the phosphine does not affect the P–C bond lengths (average 1.804 Å), but it produces a significant increase in the C–P–C angles (average 106.6°) compared with the free ligand (average 101.7°).[32] The average C–C distance of 1.378 Å (Figure 3) is normal. A small effect of the substituents on the internal angles is detectable: the angles bearing P or CH_3 are 2–3° below 120°, and the deformation is distributed on the adjacent angles, which increase by ~2° to keep the ring planar. The phenyl rings are planar within 1σ (Table VIII, supplementary material). Some strain due to molecular packing is evidenced from the large distances (0.03–0.09 Å) from P to the planes of the rings. The methyl groups are also displaced, but to a lesser extent.

Table IV. Observed Infrared and Raman Frequencies due to the CN and CS Stretching and SCN Bending Vibrations[a]

	ν_{CN}		ν_{CS}	δ_{SCN}	
	IR	R	IR	IR	R
$Cd(SCN)_2P(Cy)_3$	2122 m	2122 s			468 w
	2111 s	2110 m		466 ms	464 w
$Cd(SCN)_2P(Ph)_3$	2128 m	2128 sh	758 w	465 ms	
	2115 s	2115 s		458 ms	
	2100 s	2098 w		450 w	
$Cd(SCN)_2P$-(*m*-$MeC_6H_4)_3$	2135 s	2135 m	768 sh	465 ms	465 sh
	2127 s	2127 s	760 w	462 sh	462 sh
	2092 vs	2093 s		458 sh	458 sh

[a] See footnote to Table V.

Table V. Observed Infrared and Raman Frequencies[a] in the 250–50-cm^{-1} Region

$Cd(SCN)_2$-$P(Cy)_3$	$Cd(SCN)_2P(Ph)_3$		$Cd(SCN)_2$-P(*m*-$MeC_6H_4)_3$		
IR	IR	R	IR	R	assignments
		242 m[b]		250 m[b]	
				228 sh[b]	
				222 sh[b]	
222 s	224 s	212 ms,b[b]	210 s	215 s[b]	νCd–N
		202 m[b]			
			194 m[b]	195 sh[b]	
		184 m[b]		190 m[b]	
172 sh[b]					
150 s,b	158 ms	156 m	160 ms	160 s	νCd–S (equatorial)
130 m	140 s	140 m	140 m	140 m	νCd–P
120 m	118 sh		121 ms	120 m	νCd–S (axial)
91 s	100 sh	97 s	100 m		δCd–N
		84 s		84 s	
				76 vs	
		60 s		64 vs[b]	
				50 vs[b]	

[a] In the solid state. [b] Bands due to the phosphine. Description of abbreviations: IR, infrared; R, Raman; m, medium; s, strong; sh, shoulder; v, very; w, weak, ν, stretching; δ, bending.

Vibrational Spectra. Infrared and Raman spectra of the complexes and the free phosphines were examined in the 4000–50-cm^{-1} region, in the solid state. CN and CS stretching and SCN bending frequencies for the complexes can be readily assigned by comparing their spectra with those of free phosphines. The data listed in Table IV show that the observed ν(CN), ν(CS), and δ(NCS) frequencies occur in the frequency ranges[31] suggested for the bridging thiocyanate ligand. Furthermore, the frequencies for the three complexes are not significantly different. Thus, the structures of the three compounds are indicated to be similar.

The infrared and Raman frequencies attributable to the vibrations involving metal–ligand bonds for the three complexes are observed below the 250-cm^{-1} region and are listed in Table V. The infrared spectra of all the three complexes show a strong band at ca. 215–210 cm^{-1}, a medium band at ca. 160–150 cm^{-1}, and three other medium to strong bands in the 140–90-cm^{-1} region. None of these bands can be attributed to the internal vibrations of the ligands. In this region, satisfactory Raman spectra could only be obtained for the triphenylphosphine and tri-*m*-tolylphosphine complexes. For both the complexes, the Raman bands in the region above 160 cm^{-1} are attributable to the internal vibrations of the phosphine. Although little has been known about the skeletal vibrations of the metal–thiocyanato complexes, cadmium–ligand stretching frequencies for all the three complexes can be assigned with reasonable certainty on the basis of the crystallographic data for the tri-*m*-tolylphosphine complex (vide supra). Apart from a Cd–P stretching frequency, the complex is expected to show two Cd–N and two Cd–S stretching frequencies in the infrared as well as in the Raman. The infrared bands at ca. 225–210 cm^{-1} and at ca. 160–150 cm^{-1} can, therefore, be assigned to the equatorial Cd–N and Cd–S stretching frequencies, respectively. The Cd–N stretching frequency due to the Cd–N axial bond is probably very similar to that due to the Cd–N equatorial bond, and the two frequencies are not well resolved. The failure to observe the Cd–N stretching frequency in the Raman spectrum is expli-

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cable in terms of the low polarizability of the Cd–N bonds. The infrared and Raman bands at ca. 140 cm^{-1} for the triphenylphosphine and tri-*m*-tolylphosphine complexes and the 130-cm^{-1} infrared band for the tricyclohexylphosphine complex are assignable to the Cd–P stretching frequency by comparison with the infrared and Raman data for the cadmium(II) halide complexes of several tertiary phosphines.[33] The infrared and Raman bands at ca. 120 cm^{-1} can be assigned to the stretching of the axial Cd–S bond and those at ca. 100–90 cm^{-1} to the Cd–N bending. The assignments of the remaining Raman bands are not clear cut. The interpretation proposed in Table V is in good agreement with the assignments[34] for the infrared and Raman frequencies of $Cd(NCS)_2$. The assignment of the Cd–N stretching frequency is also consistent with the frequencies reported for the cadmium(II) nitrile complexes.[35]

A comparison of the data in Tables IV and V with the spectral data for $Cd(SCN)_2P(t\text{-}Bu)_3$ shows that the essential spectral features[19] for $Cd(SCN)_2P(t\text{-}Bu)_3$ are not markedly different from those reported herein. Thus, we now believe that $Cd(SCN)_2P(t\text{-}Bu)_3$ also has a polymeric five-coordinate structure in the solid state.

Experimental Section

Materials. Cadmium(II) thiocyanate was prepared from the metathetical reaction of barium(II) thiocyanate with reagent grade cadmium(II) sulfate. Barium(II) thiocyanate was prepared from the reaction of barium(II) hydroxide with ammonium thiocyanate; both the reactants were reagent grade. The hot aqueous solution of barium(II) thiocyanate was added dropwise, with stirring, to a hot aqueous solution of cadmium(II) sulfate. Precipitated barium sulfate was filtered off and the filtrate was evaporated to give cadmium(II) thiocyanate, which was recrystallized from ethanol. Tricyclohexylphosphine was used as received from Pressure Chemical Co. Triphenylphosphine (Eastman Kodak) and tri-*m*-tolylphosphine (Strem Chemical Co.) were recrystallized from hot ethanol. The purity of all the phosphines was checked by ^{31}P NMR measurements. Ethanol was dried by refluxing over magnesium and subsequently distilling under nitrogen. Other solvents were reagent grade.

Preparation of the Complexes. Tricyclohexylphosphine was handled in an atmosphere of *oxygen-free* dry nitrogen with use of a glovebox (Vacuum Atmospheres Corp.) and standard vacuum-line techniques. In a typical reaction, a solution of phosphine in ethanol was added dropwise, with stirring, to an alcoholic solution of cadmium(II) thiocyanate. The resulting mixture was refluxed for 3 h and then allowed to cool to room temperature. Upon removal of the solvent, a white residue was obtained, which was washed with hexane. The resulting solid was recrystallized from hot ethanol to give the 1:1 complex in about 80% yield.

Physical Measurements. Elemental analyses were performed by M-H-W Laboratories, Phoenix, Ariz. Melting points were determined with a Gallenkamp apparatus. Phosphorus-31 NMR spectra were measured in the Fourier-transform mode with a Bruker WP-60 spectrometer using 85% H_3PO_4 as external reference. Infrared spectra were measured with a Perkin-Elmer 180 double-beam spectrophotometer. Solid samples were prepared as mulls in Nujol and were placed between KRS-5 and polyethylene disks; spectra in solution were measured on saturated solutions in dichloromethane with use of 0.1-mm path length NaCl cells. Raman spectra were measured in the solid state with a Jarrell-Ash Raman spectrometer using the 5145-Å exciting line of an argon ion laser. Infrared and Raman frequencies are considered to be accurate within ±2 cm^{-1}.

Crystal Data: $C_{23}H_{21}CdS_2PN_2$, fw 532.9, monoclinic, space group $P2_1/c$, $a = 10.866$ (7) Å, $b = 10.203$ (3) Å, $c = 22.077$ (6) Å, $\beta = 101.14$ (4)°, $V = 2392.8$ Å^3, $d_c = 1.48$ g cm^{-3}, $Z = 4$ monomers per cell, λ(Mo K$\bar{\alpha}$) = 0.71068 Å (graphite monochromator), $t = 25$ °C, μ(Mo Kα) = 11.53 cm^{-1}.

Crystallographic Measurements and Structure Resolution. The crystal selected for data collection had dimensions 0.08 × 0.09 × 0.45 mm^3. It was mounted on an Enraf-Nonius CAD4 diffractometer, and the reduced cell was obtained by indexing 25 centered reflections. Metrically, this cell was *P*-monoclinic, and the Niggli parameters unambiguously showed that no higher Laue symmetry was present. As a check on cell dimensions and symmetry, each monoclinic axis was made to coincide with the *z* axis of the goniometer and an oscillation photograph was recorded on a Polaroid film placed behind the beam catcher, while a slow ω scan was performed ($\Delta\omega \geq 25°$, exposure time 30 min). The films showed the layer-line separation expected for their respective axes, and a top–bottom mirror symmetry was observed only for oscillation about *b*, as expected for a monoclinic cell. Among the various *P*-monoclinic space groups, $P2_1/c$ was selected from the systematic absences ($h0l$, $l \neq 2n$) noted after data collection.

The intensity data were collected with use of the $\omega/2\theta$ scan technique. A fixed slit of 4 × 4 mm^2 was used, and the scan range was $\omega = (0.80 + 0.35 \tan\theta)°$ extended 25% on either side for backgrounds. Scan speed between 10.06 and 0.67° min^{-1} was automatically selected to make $I/\sigma(I) = 100$, but a maximum scan time of 120 s was imposed. Prescans at 10 deg min^{-1} were done, and all reflections having $I/\sigma(I) < 1$ were labeled "weak" and not remeasured at low speed. Three standard reflections were used as a check on instrument and crystal stability and showed only random fluctuations. Crystal orientation was checked every 100 reflections by centering three reflections. No crystal recentering was necessary during data collection.

A total of 3836 hkl and $hk\bar{l}$ reflections in a sphere of $2\theta \leq 45°$ were measured. Net intensity I and esd $\sigma(I)$ were calculated as described previously.[36] A set of 1965 reflections with $I \geq 2.5\sigma(I)$ was retained for structure determination. No absorption correction was applied ($\mu R = 0.05$), but the data were corrected for Lp.

The structure was solved by the heavy-atom method and refined on F by full-matrix least squares. From a Patterson map, the four Cd atoms were found to occupy a general position. A Fourier map easily revealed the position of all nonhydrogen atoms. Isotropic refinement with unit weights converged to $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.069$. Refinement was continued using the block-diagonal approximation. Anisotropic temperature factors were refined for the nonhydrogen atoms. All hydrogen atoms were visible on the ΔF map, and they were isotropically refined. Individual weights based on counting statistics $w = 1/\sigma(F)^2$ were applied in the last least-squares cycles. Refinement converged to $R = 0.038$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.043$. The goodness-of-fit ratio was 1.53. The final ΔF map showed a maximum peak of 0.9 e Å^{-3} near cadmium.

The form factors used were those of Cromer and Waber,[37] except for hydrogen.[38] Anomalous dispersion terms f' and f'' were used for Cd.[39] The computer programs used were listed elsewhere.[40]

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Registry No. $Cd(SCN)_2P(m\text{-}MeC_6H_4)_3$, 78656-96-9; $Cd(SCN)_2PPh_3$, 78656-98-1; $Cd(SCN)_2PCy_3$, 78657-00-8.

Supplementary Material Available: Listings of structure and temperature factors as well as details on least-squares plane calculations and phenyl ring geometry (Tables VI–IX) (19 pages). Ordering information is given on any current masthead page.

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