Contribution from Istituto Chimico,
Università di Cagliari, 09100 Cagliari, Italy

Unusual Mode of Coordination of Bis(2-aminoethyl)amine in *catena*-Bis[μ-bis(2-aminoethyl)amine]-bis(μ-thiocyanato)-bis(isothiocyanato)dicadmium(II)[1]

M. CANNAS,* G. CARTA, A. CRISTINI, and G. MARONGIU

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Crystals of the title compound are triclinic, space group $P1$, with $Z = 2$ (Cd(ben)(SCN)$_2$) (ben = bis(2-aminoethyl)amine) in a unit cell of dimensions $a = 12.46$ (2), $b = 9.07$ (1), $c = 7.52$ (1) Å; $\alpha = 121.8$ (3), $\beta = 123.4$ (3), $\gamma = 83.9$ (3)°. The structure was solved by the heavy-atom method and refined by least-squares techniques to $R = 0.031$ for 1350 observed reflections measured by diffractometer. Each of the two crystallographically independent "ben" molecules is bonded by two nitrogen atoms to the same cation and by the remaining one to the nearest cation, giving rise to a polymeric structure. The two independent cations both have octahedral structure: one has the coordination sites occupied by four amine nitrogen atoms and by two sulfur atoms of bridging thiocyanates; in the other the coordination sites are occupied by two amine nitrogen atoms and by four nitrogen atoms of the thiocyanate groups.

Introduction

Recently we studied the crystal structures of some complexes of the type CuL(SCN)$_2$ and CuL(NCS)(ClO$_4$), with L = triethylenetetramine, bis(ethylenediamine), bis(1,3-diaminopropane), bis(2-aminoethyl)amine (ben), or bis(2-aminopropyl)amine;[2a] the aim of our studies was to examine the factors which affect the bonding mode of the thiocyanate group in copper(II) polyamine complexes. The structural results in these compounds and in others reported in the literature[2a] seem to suggest that in copper(II) complexes S_{SCN} bonding is favored by short covalent Cu–N σ bonds (average value 2.00 Å), in agreement with the HSAB theory;[2b] in fact, if σ donation is rather strong, the fractional charge $\delta+$ on the metal is reduced and it becomes soft and favors sulfur-bonded thiocyanate.

According to this theory S bonding should be favored in Cd(II) complexes of the same type, since this cation is considered softer than Cu(II). The structure of bis(ethylenediamine)cadmium(II) bis(isothiocyanate)[3] is however in contrast with this expectation, and we have therefore extended the structure analysis to a series of cadmium(II) complexes in order to gain further structural information about the bonding mode of the thiocyanate group.

Collection of the Diffraction Data

Colorless crystals of Cd(ben)(SCN)$_2$ were provided by Dr. G. Ponticelli[4] of this institute. The crystal selected for the x-ray diffraction study was a small prism of dimensions 0.007 × 0.016 × 0.023 cm. It was mounted on a glass fiber along the longest dimension (c direction). Preliminary hk(0–3) Weissenberg photographs and a c axis oscillation photograph yielded approximate unit-cell dimensions, revealed only $C_i(\bar{1})$ Laue symmetry, and showed no systematic absences. The triclinic space groups $P1$ (No. 1) or $P\bar{1}$ (No. 2) are therefore indicated. The crystal was transferred to a Siemens AED automatic single-crystal diffractometer equipped with a scintillation counter and pulse height analyzer. Intensity data were collected by use of zirconium-filtered Mo Kα radiation.

The setting angles 2θ, χ, ϕ of 17 high-angle reflections, measured with a narrow counter aperture, were used in a least-squares refinement of cell and orientation parameters. The resulting cell parameters and their estimated standard deviations are $a = 12.46$ (2), $b = 9.07$ (1), $c = 7.52$ (1) Å; $\alpha = 121.8$ (3), $\beta = 123.4$ (3), $\gamma = 83.9$ (3)°. The unit-cell volume is 581.7 Å^3. The experimental density, 1.91 (2) g/cm^3, measured by flotation in a CCl$_4$/CH$_2$I$_2$ mixture is consistent with the value of 1.89 g/cm^3 calculated for mol wt 331.73 and $Z = 2$ (Cd(ben)(SCN)$_2$).

Intensity data for reflections in the hemisphere defined by $\pm h,\pm k,l$ and $2\theta \leq 52°$ were collected by the θ–2θ scan technique. The scan range was from 0.65° below to 0.75° above the 2θ value calculated for $\lambda = 0.71069$ Å, the scan rate being 2.5°/min. Stationary-background counts were recorded at the two extremes of the scan for a time equal to the scan time. The takeoff angle was 4.5°. The receiving aperture (2.0 mm in diameter) was set 6.0 cm from the crystal.

The stability of the entire assembly (i.e., x-ray beam, crystal, electronics) was monitored by measuring three reflections after every 200 reflections; their intensities remained essentially constant throughout, showing only the deviations from the mean predicted from counting statistics.

A total of 1741 independent reflections were recorded; their intensities were assigned standard deviations equal to $N_T^{1/2}$, where N_T = peak + background counts. The values of I and $\sigma(I)$ were corrected for Lorentz–polarization effects. No absorption or extinction corrections were applied. Ninety-six reflections had a negative net intensity count and were reset to zero; 1350 obey the condition $F_o > 2\sigma(F_o)$ and were used in subsequent calculations.

Solution and Refinement of the Structure

The positions of Cd(1) and S(1) atoms were determined from a three-dimensional Patterson synthesis; the successive three-dimensional Fourier map was calculated as centrosymmetric $P\bar{1}$, and it showed a rather high peak, later identified as S(4), in a position which is sterically impossible in this space group. The positions of cadmium, sulfur, and a few other light atoms determined from this synthesis were used in the next calculation performed in $P1$ and the Fourier map gave the positions of all nonhydrogen atoms. The R factor, obtained by use of the overall temperature and scale factors derived from a Wilson plot, was 0.18. Refinement of the structure was carried out by block-diagonal least-squares techniques. Throughout the refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$; the weights were taken as $4F_o^2/[\sigma^2(F_o^2) + (0.12F_o^2)^2]$. Atomic scattering factors for Cd, S, N, and C were taken from Cromer and Waber;[5] that for hydrogen was from Stewart, Davidson, and Simpson.[6]

Five cycles of isotropic refinement of the nonhydrogen atom parameters gave $R = \sum(|F_o - F_c|)/\sum F_o = 0.08$. Refinement was terminated after six cycles of anisotropic refinement including the contribution of the hydrogen atoms held fixed at calculated positions ($B = 4.0$ Å^2). The final R factor is 0.031 for 1350 refined reflections and 0.049 for 1741 measured ones. The translation of the coordination polyhedra of about $^1/_2a$ weakens the reflections with $h = 2n + 1$; the agreement for this group of reflections is therefore poorer ($R = 0.06$).

The difference electron density map calculated from the final structure factors with no hydrogen contribution showed peaks ranging from 0.7 to 0.9 e/Å^3 in height and at distances from 0.7 to 1.1 Å from the pertinent nitrogen and carbon atoms. A few other peaks of comparable height were found close to cadmium atoms and scattered throughout the cell. Final structural parameters are given in Table I; Table II (supplementary material) shows observed and calculated structure factors.

Description of the Structure

As shown in the projections of the crystal structure (Figures 1 and 2) each of the two crystallographically independent molecules of the terdendate amine "ben" chelates with two nitrogen atoms to Cd(1) and bonds the two closest Cd(2)'s

Table I. Atomic Coordinates and Anisotropic Temperature Factors[a] ($\times 10^4$) with Standard Deviations in Parentheses

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cd(1)	2500 (0)	5000 (0)	5 000 (0)	2.08 (1)	2.70 (2)	2.63 (2)	0.81 (3)	2.16 (3)	3.28 (3)
Cd(2)	7484 (2)	4951 (2)	4 937 (3)	2.04 (1)	3.38 (2)	2.21 (2)	1.49 (3)	2.36 (3)	3.45 (3)
S(1)	2482 (2)	2925 (4)	390 (6)	1.90 (9)	4.13 (12)	2.27 (12)	0.49 (16)	2.32 (17)	2.60 (18)
S(2)	2453 (3)	7253 (4)	9 292 (6)	2.04 (9)	4.05 (12)	3.18 (13)	0.91 (16)	2.84 (18)	3.38 (20)
S(3)	5544 (3)	1156 (4)	−4 267 (6)	2.71 (10)	4.60 (13)	2.30 (13)	1.05 (18)	2.64 (18)	3.26 (20)
S(4)	9461 (3)	8913 (4)	14 054 (6)	3.08 (11)	4.67 (14)	2.11 (13)	1.09 (20)	2.75 (20)	3.03 (21)
N(1)	5239 (9)	3710 (14)	2 925 (20)	2.35 (36)	6.59 (53)	3.87 (54)	4.12 (73)	4.15 (73)	6.21 (87)
N(2)	9781 (10)	6080 (13)	7 044 (22)	3.31 (38)	4.02 (42)	4.75 (56)	0.09 (63)	4.93 (74)	5.12 (79)
N(3)	7261 (8)	2940 (10)	909 (16)	3.47 (37)	2.82 (32)	1.44 (36)	2.14 (54)	2.35 (60)	3.10 (54)
N(4)	7800 (9)	7269 (12)	8 656 (18)	3.83 (42)	4.57 (41)	3.14 (46)	5.20 (67)	5.29 (73)	6.16 (71)
N(5)	2859 (9)	2671 (11)	5 517 (20)	2.94 (37)	2.97 (34)	4.89 (52)	2.06 (57)	4.26 (71)	5.64 (70)
N(6)	230 (7)	3296 (9)	2 435 (15)	1.85 (28)	2.11 (27)	1.57 (34)	0.63 (44)	1.54 (49)	2.53 (48)
N(7)	8146 (7)	3033 (10)	6 133 (16)	1.37 (26)	3.31 (33)	1.98 (35)	0.29 (46)	1.01 (50)	3.27 (55)
N(8)	2270 (7)	7308 (10)	4 433 (17)	1.50 (27)	3.55 (33)	3.59 (43)	2.91 (49)	3.13 (55)	5.92 (62)
N(9)	4725 (9)	6657 (11)	7 491 (18)	3.03 (35)	2.84 (33)	3.13 (42)	3.00 (55)	4.10 (64)	3.11 (59)
N(10)	6932 (9)	7125 (11)	3 790 (17)	3.73 (38)	2.91 (32)	1.88 (40)	0.67 (55)	3.73 (65)	2.80 (56)
C(1)	4129 (9)	3421 (12)	1 883 (20)	1.91 (36)	2.67 (37)	2.84 (50)	0.75 (59)	2.53 (70)	2.36 (68)
C(2)	907 (11)	6563 (13)	7 983 (22)	3.49 (46)	2.37 (37)	3.01 (55)	0.59 (66)	3.43 (82)	2.48 (71)
C(3)	6468 (9)	2116 (14)	−1 225 (20)	1.70 (36)	4.19 (47)	1.73 (46)	1.02 (63)	1.35 (65)	3.59 (73)
C(4)	8436 (10)	7829 (12)	10 844 (21)	3.83 (45)	2.48 (35)	3.27 (50)	4.20 (64)	6.37 (80)	4.97 (69)
C(5)	1507 (12)	1263 (15)	3 254 (28)	3.76 (52)	3.41 (47)	6.38 (75)	3.94 (81)	5.50 (106)	7.53 (99)
C(6)	375 (10)	1984 (11)	3 004 (20)	3.18 (39)	1.59 (29)	2.59 (48)	1.38 (54)	3.41 (71)	3.29 (58)
C(7)	9432 (8)	2357 (11)	9 461 (17)	1.12 (29)	2.42 (34)	1.46 (41)	1.44 (51)	0.21 (55)	1.79 (58)
C(8)	9082 (9)	3758 (12)	8 925 (18)	1.85 (33)	2.66 (36)	1.38 (42)	−0.01 (56)	0.54 (59)	2.28 (60)
C(9)	4654 (10)	7841 (15)	6 554 (25)	1.51 (35)	4.65 (51)	4.44 (63)	1.50 (67)	2.58 (75)	6.01 (91)
C(10)	3472 (9)	8789 (12)	6 470 (21)	2.21 (37)	2.31 (36)	3.11 (53)	0.32 (58)	1.99 (71)	3.57 (68)
C(11)	5512 (10)	7613 (12)	228 (20)	2.92 (40)	2.80 (38)	1.81 (45)	0.41 (61)	2.95 (70)	2.70 (65)
C(12)	5858 (13)	6270 (14)	1 053 (23)	5.34 (61)	3.36 (46)	2.58 (56)	−0.71 (82)	2.78 (94)	4.72 (81)

[a] The anisotropic temperature factor is of the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + B_{12}hka^*b^* + B_{13}hla^*c^* + B_{23}klb^*c^*)]$.

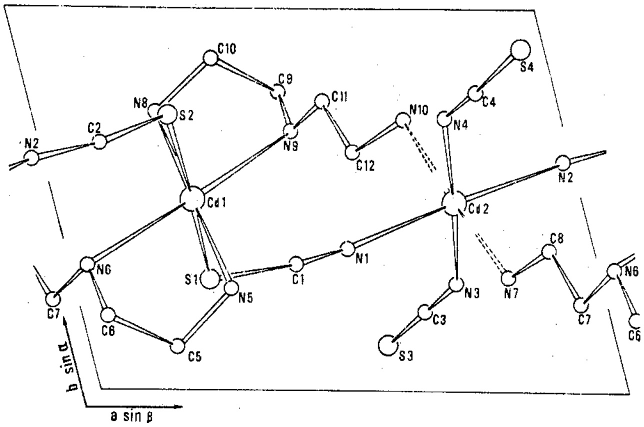

Figure 1. Projection of the crystal structure along the c axis. Dashed bonds refer to atoms translated by a c unit.

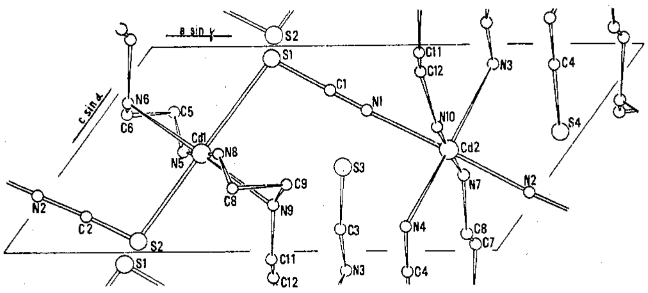

Figure 2. Projection of the crystal structure along the b axis.

with the nonchelating arm of the molecule.

The apical positions of the octahedron around Cd(1) are filled with the sulfur atoms of two thiocyanate groups bonded end-to-end to two adjacent Cd(2)'s; the coordination polyhedron around this last atom is formed by six nitrogen atoms—two from the nonchelating arms of two amine molecules, two from bridging thiocyanate, and two from the remaining monodentate thiocyanate groups.

Table III. Bond Distances (Å) with Standard Deviations in Parentheses[a]

Cd(1)–S(1)	2.93 (1)	Cd(2)–N(1)	2.36 (2)
Cd(1)–S(2)	2.80 (1)	Cd(2)–N(2)	2.38 (2)
Cd(1)–N(5)	2.30 (1)	Cd(2)–N(3)	2.44 (2)
Cd(1)–N(6)	2.42 (2)	Cd(2)–N(4)	2.27 (2)
Cd(1)–N(8)	2.31 (1)	Cd(2)–N(7)	2.25 (1)
Cd(1)–N(9)	2.38 (2)	Cd(2)–N(10)	2.44 (1)
S(1)–C(1)	1.67 (1)	N(1)–C(1)	1.12 (1)
S(2)–C(2)	1.61 (1)	N(2)–C(2)$^{\mathrm{I}}$	1.17 (2)
S(3)–C(3)	1.59 (2)	N(3)–C(3)	1.12 (2)
S(4)–C(4)	1.67 (2)	N(4)–C(4)	1.17 (2)
N(5)–C(5)	1.54 (2)	N(9)–C(11)$^{\mathrm{III}}$	1.42 (2)
N(6)–C(6)	1.43 (1)	N(10)–C(12)	1.46 (2)
N(6)–C(7)$^{\mathrm{II}}$	1.56 (2)	C(5)–C(6)	1.45 (2)
N(7)–C(8)	1.49 (2)	C(7)–C(8)	1.48 (1)
N(8)–C(10)	1.46 (2)	C(9)–C(10)	1.61 (1)
N(9)–C(9)	1.54 (2)	C(11)–C(12)	1.56 (2)

[a] I = $1 + x, y, z$; II = $-1 + x, y, -1 + z$; III = $x, y, 1 + z$.

The values of bond distances and angles are given in Tables III and IV together with esd's calculated from the parameters given in Table I; they however seem to be rather optimistic, and if we consider the difference of chemically equivalent C–C and C–N bonds from their mean values, it appears that they should be multiplied by a factor of about 3. After this correction some Cd–N and the two Cd–S bond distances are still significantly different. Some of them, as Cd(2)–N(4) (2.27 Å) and Cd(2)–N(7) (2.25 Å), are close to the sum of the pertinent covalent radii, while all of the others appear to be more or less elongated. Other distortions appear in the values of some bond angles, 119.1 and 119.2°, for Cd(1)–N(9)–C(11) and Cd(2)–N(7)–C(8), respectively, which are much higher than the expected tetrahedral value, and 140° for Cd(2)–N–C(NCS) which is much different from the value of 160–170°, as generally found.[2a]

In Table V are given the distances from selected least-squares planes of the atoms in the amine molecule; they show a marked puckering which is very close to that calculated when the values of M–N bonds are 2.30 Å.[7] The configurations are

Table IV. Bond Angles (deg) with Standard Deviations in Parentheses[a]

S(1)-Cd(1)-S(2)	174.1 (1)	Cd(1)-S(1)-C(1)	97.9 (7)
S(1)-Cd(1)-N(5)	90.7 (4)	Cd(1)-S(2)-C(2)	99.8 (7)
S(1)-Cd(1)-N(6)	89.5 (6)	Cd(2)-N(1)-C(1)	164.4 (9)
S(1)-Cd(1)-N(8)	86.2 (4)	Cd(2)-N(2)-C(2)$^{\mathrm{I}}$	176.7 (9)
S(1)-Cd(1)-N(9)	90.1 (6)	Cd(2)-N(3)-C(3)	139.7 (8)
S(2)-Cd(1)-N(5)	95.2 (4)	Cd(2)-N(4)-C(4)	140.0 (8)
S(2)-Cd(1)-N(6)	91.2 (6)	Cd(1)-N(5)-C(5)	102.1 (7)
S(2)-Cd(1)-N(8)	87.9 (4)	Cd(1)-N(6)-C(6)	103.9 (6)
S(2)-Cd(1)-N(9)	89.2 (6)	Cd(1)-N(6)-C(7)$^{\mathrm{II}}$	115.5 (7)
N(5)-Cd(1)-N(6)	79.1 (4)	C(6)-N(6)-C(7)	110.2 (9)
N(5)-Cd(1)-N(8)	175.5 (3)	Cd(2)-N(7)-C(8)	119.2 (7)
N(5)-Cd(1)-N(9)	100.9 (5)	Cd(1)-N(8)-C(10)	111.4 (7)
N(6)-Cd(1)-N(8)	104.2 (4)	Cd(1)-N(9)-C(9)	106.1 (7)
N(6)-Cd(1)-N(9)	179.6 (1)	Cd(1)-N(9)-C(11)$^{\mathrm{III}}$	119.1 (8)
N(8)-Cd(1)-N(9)	75.9 (4)	C(9)-N(9)-C(11)$^{\mathrm{III}}$	113.3 (9)
N(1)-Cd(2)-N(2)	176.5 (4)	Cd(2)-N(10)-C(12)	111.7 (7)
N(1)-Cd(2)-N(3)	91.7 (7)	S(1)-C(1)-N(1)	177.0 (10)
N(1)-Cd(2)-N(4)	94.2 (7)	S(2)$^{\mathrm{I}}$-C(2)$^{\mathrm{I}}$-N(2)	179.3 (23)
N(1)-Cd(2)-N(7)	90.8 (5)	S(3)-C(3)-N(3)	167.8 (10)
N(1)-Cd(2)-N(10)	93.3 (5)	S(4)-C(4)-N(4)	170.8 (9)
N(2)-Cd(2)-N(3)	88.7 (7)	N(5)-C(5)-C(6)	113.8 (10)
N(2)-Cd(2)-N(4)	86.1 (7)	N(6)-C(6)-C(5)	113.8 (9)
N(2)-Cd(2)-N(7)	85.8 (5)	N(6)-C(7)-C(8)	108.1 (8)
N(2)-Cd(2)-N(10)	90.1 (5)	N(7)-C(8)-C(7)	114.0 (9)
N(3)-Cd(2)-N(4)	168.5 (3)	N(9)-C(9)-C(10)	106.5 (8)
N(3)-Cd(2)-N(7)	93.1 (4)	N(8)-C(10)-C(9)	104.2 (8)
N(3)-Cd(2)-N(10)	86.9 (4)	N(9)-C(11)$^{\mathrm{III}}$-C(12)$^{\mathrm{III}}$	110.3 (9)
N(4)-Cd(2)-N(7)	96.8 (4)	N(10)-C(12)-C(11)	113.0 (9)
N(4)-Cd(2)-N(10)	82.9 (4)		
N(7)-Cd(2)-N(10)	175.9 (3)		

[a] I = 1 + *x*, *y*, *z*; II = −1 + *x*, *y*, −1 + *z*; III = *x*, *y*, 1 + *z*.

Table V. Equations of Molecular Planes, Referred to *a*, *b*, and *c* Axes, with Deviations of Atoms from the Planes

Plane *a*: Cd(1), N(5), N(6)
Equation: $-7.288X + 0.264Y + 6.271Z = 1.446$
Dev from plane, Å: C(5), −0.47; C(6), 0.22

Plane B: Cd(1), N(8), N(9)
Equation: $-7.320X + 0.753Y + 6.037Z = 1.565$
Dev from plane, Å: C(9), −0.42; C(10), 0.46

Plane C: N(5), N(6), N(8), N(9)
Equation: $-7.302X + 0.510Y + 6.156Z = 1.472$
Dev from plane, Å: N(5), 0.03; N(6), −0.03; N(8), −0.03; N(9), 0.03; Cd(1), 0.04

k′ for the ring formed by Cd(1), N(5), N(6), C(5), C(6) and *k* for the other one.

The crystal structure is polymeric and can be described as an alternation of two pseudocentrosymmetric coordination polyhedra, with their axes almost parallel. Sulfur atoms, because of their dimensions, play an important role in the molecular packing; they form S---S contacts (≃3.88 Å) close to the sum of van der Waals radii (3.70 Å) and S---N contacts of about 3.4–3.5 Å which may be considered as hydrogen bonds.

Discussion

In the crystal structures determined up to now bis(2-aminoethyl)amine has always been found coordinated to one metal atom to form two five-membered chelate rings; this structure is the first example where this ligand forms only one ring and uses the nonchelating end to bond another metal atom. This result is rather surprising and only a few other examples are known where chelation, although expected, does not occur. Referring to amine ligands, there is the case of ethylenediamine (en) acting as a bridge in $[(\mathrm{Me_3enPt})_2\mathrm{en}]^{2+}$,[8] in $[(\mathrm{Me_3acacPt})_2\mathrm{en}]$,[9] and in $[\mathrm{Cd(en)Ni(CN)_4{\cdot}2C_6H_6}]$;[10] in all of these compounds chelation of ethylendiamine would require the cleavage either of Pt–C(methyl) or of Cd–N-(cyanide) bonds, which are however rather strong; in the second compound a bridging behavior of acetylacetonate could be thought possible, but it is unlikely because this ligand forms a ring stabilized by resonance. Two more examples are found in LiCl·2en and LiBr·2en[11] where one en molecule is chelated while the other is bridging; here the tetrahedral coordination of the cation opposes chelation, since it requires angles close to 109°, much higher than the bite angle of the ligand (≃85°).

Chelation is mainly an entropy effect, since it induces bond torsions and angle bendings which increase the enthalpy;[12] moreover in the case of two fused chelate rings further steric constraints are introduced, as shown by the overall heat of formation for some transition metal complexes with two molecules of ben, which is 3–4 kcal mol^{-1} lower than the corresponding values for the complexes with three molecules of en.[13] One could then expect that in the present structure the bridging behavior of the amine could result by an enthalpic contribution; the structural parameters show however that this type of bonding does not reduce angle bendings but even generates bond length distortions, which generally are not observed in ben complexes with discrete molecules. Evidently the formation of a polymeric network gives a contribution to the stabilization of the structure which exceeds all of these factors, and in our opinion it is allowed by particular conditions met by the structural parameters. As clearly shown in Figure 2, the structure consists of zigzag Cd(1)–SCN–Cd(2) chains, running along the *a* axis, which are held together by the nonchelating arm of the amine; this arm has the right length to make this possible: a shorter dimension would in fact require a crowding of the structure which, as it is, has a rather dense packing, and a longer dimension has a lower statistical probability for the formation of bridges.

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Registry No. Cd(ben)(SCN)$_2$, 60840-52-0.

Supplementary Material Available: Table II, listing structure factor amplitudes (8 pages). Ordering information is given on any current masthead copy.

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