Five-co-ordinate Cadmium(II) in [Bis(2-dimethylaminoethyl)methylamine]di-isothiocyanatocadmium(II)

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The crystal structure of the title compound has been determined from three dimensional *X*-ray data. Crystals are monoclinic, space group $P2_1/c$, with $Z = 4$ in a unit cell of dimensions: $a = 13.75(2)$, $b = 7.68(1)$, $c = 16.23(3)$ Å, $\beta = 97.0(3)°$. The structure was solved by the heavy-atom method and refined by least-squares techniques to R 0.033 for 2 370 observed reflections measured by diffractometer. The molecular geometry is close to square-pyramidal with the basal positions occupied by the amine [Cu–N(prim) 2.34, Cu–N(sec) 2.37 Å] and thiocyanate nitrogen (Cd–N 2.21 Å) atoms; the apical position is filled by the nitrogen of the second thiocyanate group (Cu–N 2.18 Å).

MOLECULAR complexes of the Cd^{II} cation are most frequently six-co-ordinate; the reported four-, five-, and seven-co-ordinate ones seem to suggest that their co-ordination number is determined by either size of donor atoms, or steric hindrance of the ligands, or a combination of both. The known tetrahedral structures, which contain CdS_4,[1] CdS_2Cl_2,[2] or $CdCl_2P_2$ groups,[3] and some five-co-ordinate structures, where $[CdCl_5]^{3-}$ (ref. 4), and CdS_5 groups[5] are present, are examples of the first effect. The second effect is the cause of five-co-ordination in $[Cd(tren)I]^+$ [6] and in μ-[terpyridylcadmio(II)]-pentacarbonylmanganese(II),[7] while a combination of both effects is present in the remaining five-co-ordinate complexes.[8] Seven-co-ordination is present in some complexes with nitrogen or oxygen as donor atoms;[9] moreover, the oxygen atoms happen to be in compact ligands, *i.e.* in chelating agents as nitrate and acetate groups in which intraligand distances are constrained to be very short.

The crystal structure of the title compound was undertaken to establish its stereochemistry; in fact, although conductivity measurements show all the ligands to be bonded to the metal,[10] there is no experimental evidence concerning co-ordination around the cation; seven-co-ordination is most improbable because of steric hindrance, but we were unable to decide from molecular models between a five- or six-co-ordinate species, the latter involving a bridged thiocyanate. Presumably, the form which exists is a result of a balance between the higher strains induced in the crowded ligand by an octahedral structure, and the tendency of the cation to be six-co-ordinate.

EXPERIMENTAL

The compound was prepared according to ref. 10, as colourless prismatic crystals by evaporation of a concentrated methyl alcohol solution, containing a few drops of water.

Crystal Data.—$C_{11}H_{23}N_5CdS_2$, $M = 401{\cdot}868$, Monoclinic, $a = 13.75(2)$, $b = 7.68(1)$, $c = 16.23(2)$ Å, $\beta = 97.0(3)°$, $U = 1\,701.11$ Å^3, D_m (flotation) $= 1.52$ g cm^{-3}, $Z = 4$, $D_c = 1.57$ g cm^{-3}, $F(000) = 816$. Space group $P2_1/c$ from systematic absences. Mo-K_α radiation, $\lambda = 0.710\,7$ Å; $\mu(Mo\text{-}K_\alpha) = 15.38$ cm^{-1}. Unit-cell parameters and their estimated standard deviations were determined by a least-squares fit to 12 values of θ, χ, ϕ, accurately measured by use of a very narrow counter aperture.

Intensity Measurements.—A crystal $0.02 \times 0.033 \times 0.073$ cm was mounted on a Siemens automatic single-crystal AED diffractometer, with the b axis nearly coincident with the polar ϕ axis of the goniostat. A total of 2 725 independent intensities up to $2\theta \leqslant 48°$ was recorded, by use of

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the θ—2θ scan method, by a procedure similar to that described previously.[11] The values of I and $\sigma(I)$, extrapolated to a unit scan-time, were corrected for Lorentz-polarization effects but not for absorption or extinction. Of 2 725 reflections, 355 having $I/\sigma(I) < 3$ were considered unobserved and were not used in the analysis.

Solution and Refinement of the Structure.—The positions of the cadmium and two sulphur atoms were determined from a three-dimensional Patterson synthesis; two successive three-dimensional Fourier maps gave the positions of all non-hydrogen atoms. The R factor, obtained by use of the overall temperature and scale factors derived from a Wilson plot, was 0.20 for 2 370 observed reflections. Both positional and isotropic thermal parameters were then refined by full-matrix least-squares method; the quantity minimized was $\Sigma w(\Delta F)^2$, where $w = 4F_o^2[\sigma^2(F_o^2) + (0.12 F_o^2)^2]$.[12] Three cycles of refinement reduced R to 0.07. A three-dimensional difference-Fourier synthesis calculated at this point showed the positions of all but one of the hydrogen atoms at distances in the range 0.80—1.01 Å from the pertinent carbon atoms. Their contribution to F_c lowered R to 0.062. Six more cycles of block-diagonal least-squares, by use of a program written by Shiono, with anisotropic thermal parameters reduced R to 0.033 and R' to 0.053 [$R' = \Sigma w(\Delta F)^2/\Sigma(wF_o)^2$] for the 2 370 observed reflections. The value of the goodness of fit, S, was 0.82 $\{S = [\Sigma w(\Delta F)^2/(m - n)]^{\frac{1}{2}}$, where m is the number of Δ values and n the number of variables$\}$. The final R for all measured reflections was 0.041. Atomic scattering factors were interpolated from values given in ref. 13 for non-hydrogen atoms and from ref. 14 for hydrogen. Final atomic parameters, with estimated standard deviations, are given in Table 1. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21520 (14 pp., 1 microfiche).*

TABLE 1

Atomic co-ordinates and anisotropic temperature factors * (× 10^4), with standard deviations in parentheses

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	2 587(0)	4 422(1)	5 433(0)	37(0)	108(1)	29(0)	5(0)	6(0)	2(0)
S(1)	4 958(2)	828(3)	7 102(2)	57(2)	172(4)	44(1)	18(2)	1(1)	28(2)
S(2)	−111(2)	1 295(4)	6 324(2)	54(2)	223(6)	70(2)	11(2)	24(1)	32(2)
N(1)	3 883(6)	3 189(11)	6 088(6)	62(5)	184(15)	56(4)	39(7)	−5(4)	15(7)
N(2)	1 415(6)	2 474(11)	5 505(6)	60(5)	171(15)	64(5)	−29(7)	19(4)	−5(7)
N(3)	2 649(5)	4 103(8)	4 001(4)	37(4)	127(11)	30(3)	8(5)	1(3)	−11(4)
N(4)	3 186(4)	7 174(8)	5 058(4)	36(3)	102(10)	31(3)	4(5)	0(2)	−4(4)
N(5)	1 906(5)	6 341(9)	6 319(4)	37(4)	149(12)	29(3)	11(5)	5(2)	0(5)
C(1)	4 319(6)	2 210(10)	6 518(5)	42(5)	124(14)	33(3)	2(6)	3(3)	0(5)
C(2)	777(6)	1 985(10)	5 848(6)	47(5)	124(15)	43(4)	5(7)	1(3)	0(6)
C(3)	1 660(8)	4 209(12)	3 543(7)	47(6)	220(21)	44(5)	−6(8)	−10(4)	−10(7)
C(4)	3 093(7)	2 453(13)	3 826(6)	64(6)	162(17)	50(5)	11(9)	9(4)	−25(7)
C(5)	3 256(7)	5 541(10)	3 754(5)	45(5)	170(17)	28(3)	3(7)	13(3)	−4(5)
C(6)	3 014(6)	7 249(10)	4 133(5)	49(5)	124(14)	31(3)	3(7)	9(3)	18(5)
C(7)	4 240(6)	7 347(12)	5 338(6)	31(4)	190(17)	46(4)	−10(7)	0(3)	−6(7)
C(8)	2 629(6)	8 516(11)	5 451(5)	52(5)	103(15)	44(4)	7(6)	4(4)	−12(6)
C(9)	2 465(6)	7 981(10)	6 306(5)	47(5)	136(15)	36(4)	6(7)	1(3)	−18(6)
C(10)	852(7)	6 612(14)	6 033(7)	37(5)	221(21)	66(6)	13(8)	2(4)	−2(9)
C(11)	2 004(10)	5 657(14)	7 167(7)	86(9)	244(25)	35(4)	−3(10)	15(5)	0(7)

	x/a	y/b	z/c		x/a	y/b	z/c
H(31)	1 719	3 885	2 998	H(71)	4 447	8 587	5 155
H(32)	1 514	3 266	3 630	H(73)	4 623	6 403	5 119
H(33)	1 315	5 208	3 739	H(82)	3 058	9 639	5 591
H(43)	2 689	1 497	3 985	H(81)	2 028	8 665	5 137
H(42)	3 255	2 433	3 276	H(92)	3 127	7 911	6 697
H(41)	3 548	2 220	4 154	H(91)	2 004	8 867	6 526
H(51)	3 261	5 477	3 070	H(102)	853	6 907	5 513
H(52)	3 865	5 069	3 798	H(101)	567	5 396	5 948
H(62)	3 413	8 282	3 905	H(111)	1 720	6 560	7 429
H(61)	2 329	7 389	4 040	H(112)	1 842	4 729	7 108
H(72)	4 316	7 238	5 840	H(113)	2 697	5 000	7 243

* In the form: $\exp -(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$.

DISCUSSION

The crystal structure consists of discrete five-co-ordinate $[Cu(Me_5den)(NCS)_2]$ molecules, as shown by the projection along the b axis (Figure 1). Bond angles and distances are given in Table 2. The molecular geometry (Figure 2) is distorted square-pyramidal with the amine nitrogen atoms co-ordinated on the base and the thiocyanate nitrogen atoms in the remaining positions. The metal is displaced by 0.64 Å from the least-squares basal plane towards the apex (Table 3). The values of Cd–N(amine) bond distances are close to those found in octahedral dichlorobis(thiocarbohydrazide-*N*,*S*)cadmium (2.34 Å)[15] and bis(hydrazinecarboxylato-*N'*,*O*)-cadmium (2.40 and 2.38 Å).[16]

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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All the remaining bond lengths and angles have values close to those expected, the greatest differences between corresponding values in the two chelated rings and thiocyanate groups being only 0.017 Å and 1.5°. The only exception to this regularity, which emphasises the accuracy of the analysis, are the differences between the Cd–N(1) and Cd–N(2) distances (0.034 Å) and Cd–N(1)–C(1) and Cd–N(2)–C(2) angles (9.3°). This emphasizes that the basal and apical positions of the polyhedron, which are occupied by the two thiocyanate groups, are not equivalent as was also found in tris(thiourea)cadmium sulphate [8b] and in the tris(*O*-ethyl dithiocarbonato)cadmate(II) anion.[5] The ligand is almost symmetric with respect to a plane through Cd, N(4), N(1) and its general features resemble closely those of Co(Me_5den)Cl_2.[17] A comparison of the two structures shows that non-bonded repulsions are smaller in the cadmium than in the cobalt compound as a consequence of the lengthening of Cd–N bonds and of the presence of less bulky isothiocyanate nitrogen atoms. This fact, according to conclusions drawn from a comparison of the analogous [Co(Me_5den)Cl_2] and [Co(Et_4den)Cl_2], should favour a trigonal-bipyramidal configuration of the co-ordination polyhedron; bond distances and angles show, however, that it is much closer to a square-pyramid. This geometry has been found in other five-co-ordinate cadmium(II) complexes,[5,8b,8d] where it is influenced by the ligand; in the remaining cases [4,6,7,8a] it is trigonal-bipyramidal.

TABLE 2

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) Distances

Cd–N(1)	2.178(12)	N(3)–C(4)	1.450(12)
Cd–N(2)	2.212(9)	N(3)–C(5)	1.469(11)
Cd–N(3)	2.349(8)	C(5)–C(6)	1.503(12)
Cd–N(4)	2.375(7)	C(6)–N(4)	1.492(11)
Cd–N(5)	2.334(9)	N(4)–C(7)	1.471(11)
N(1)–C(1)	1.144(12)	N(4)–C(8)	1.475(11)
N(2)–C(2)	1.158(13)	C(8)–C(9)	1.490(13)
S(1)–C(1)	1.611(10)	C(9)–N(5)	1.478(11)
S(2)–C(2)	1.612(11)	N(5)–C(10)	1.481(12)
N(3)–C(3)	1.470(14)	N(5)–C(11)	1.464(13)

(*b*) Angles

N(1)–Cd–N(2)	103.8(4)	Cd–N(4)–C(6)	105.9(5)
N(1)–Cd–N(3)	108.2(2)	Cd–N(4)–C(7)	111.2(5)
N(1)–Cd–N(4)	102.9(3)	Cd–N(4)–C(8)	107.2(5)
N(1)–Cd–N(5)	109.9(4)	C(6)–N(4)–C(7)	109.7(8)
N(2)–Cd–N(3)	95.5(5)	C(7)–N(4)–C(8)	110.3(7)
N(2)–Cd–N(4)	153.3(3)	Cd–N(5)–C(9)	106.3(5)
N(2)–Cd–N(5)	92.6(4)	Cd–N(5)–C(10)	110.2(6)
N(3)–Cd–N(4)	77.5(3)	Cd–N(5)–C(11)	110.8(6)
N(3)–Cd–N(5)	137.8(3)	C(9)–N(5)–C(10)	111.5(7)
N(4)–Cd–N(5)	76.9(3)	C(9)–N(5)–C(11)	109.3(8)
Cd–N(1)–C(1)	156.9(8)	C(10)–N(5)–C(11)	109.7(9)
Cd–N(2)–C(2)	147.6(8)	N(1)–C(1)–S(1)	178.1(9)
Cd–N(3)–C(3)	110.6(7)	N(2)–C(2)–S(2)	179.8(8)
Cd–N(3)–C(4)	110.6(6)	N(3)–C(5)–C(6)	112.5(7)
Cd–N(3)–C(5)	106.3(6)	C(5)–C(6)–N(4)	111.2(7)
C(3)–N(3)–C(4)	109.6(7)	N(4)–C(8)–C(9)	110.9(7)
C(3)–N(3)–C(5)	110.7(7)	C(8)–C(9)–N(5)	112.8(7)
C(4)–N(3)–C(5)	109.7(7)		

TABLE 3

Equations of molecular planes, referred to *a*, *b*, and *c* axes, with deviations (Å) of atoms from the planes given in square brackets

Plane (*a*): N(2)—(5)

$$10.4320x - 3.2561y + 6.4667z = 4.1281$$

[Cd 0.64, S(1) 5.36, S(2) −0.58, N(1) 2.82, N(2) 0.10, N(3) −0.11, N(4) 0.13, N(5) −0.11, C(1) 3.87, C(2) −0.18, C(3) −1.48, C(4) 0.77, C(5) −0.11, C(6) −0.67, C(7) 1.35, C(8) −0.63, C(9) 0.08, C(10) −1.49, C(11) 0.76]

Plane (*b*): N(3)—(5)

$$-9.3862x + 4.0124y - 6.8803z = -3.5922$$

[Cd −0.80, C(3) 1.28, C(4) −0.96, C(5) 0.18, C(6) 0.83, C(7) −1.11, C(8) 0.79, C(9) 0.14, C(10) 1.29, C(11) −0.95]

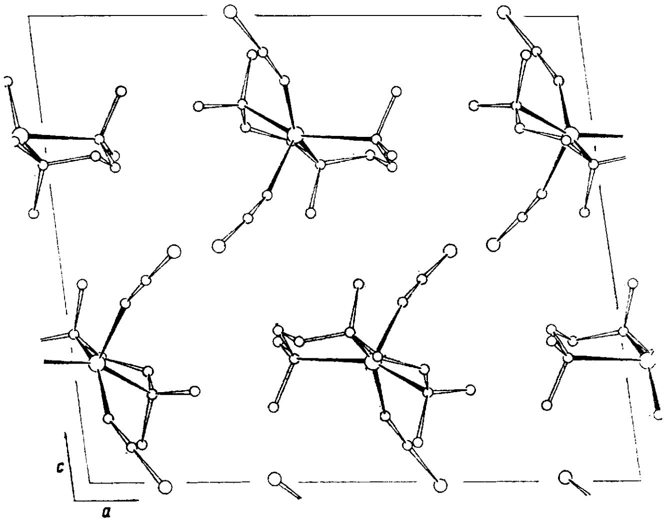

FIGURE 1 Projection of the structure along *b* axis

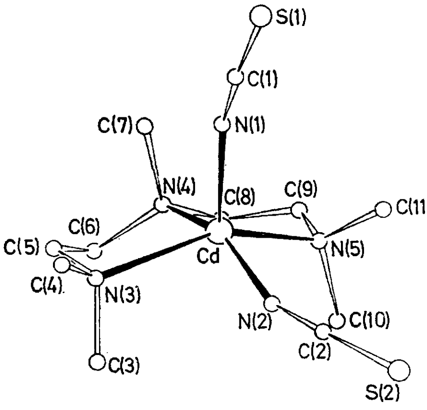

FIGURE 2 A view of the molecule of Cd(Me_5den)$(NCS)_2$

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