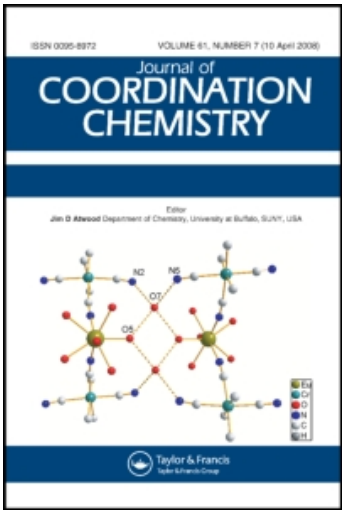

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

STUDIES OF TRINUCLEAR CADMIUM CLUSTER COMPLEXES. SYNTHESES AND CRYSTAL STRUCTURES OF $[NMe_4][Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_7]\cdot C_5H_{12}$ AND $[Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_6(HSC_6H_2Pr^i_3\text{-}2,4,6)]\cdot CH_3OH\cdot 7H_2O$

Kaluo Tang[a]; Xianglin Jin[a]; Aiqun Li[a]; Shoujun Li[a]; Zhifen Li[a]; Youqi Tang[a]
[a] Institute of Physical Chemistry, Peking University, Beijing, P. R. China

To cite this Article Tang, Kaluo , Jin, Xianglin , Li, Aiqun , Li, Shoujun , Li, Zhifen and Tang, Youqi(1994) 'STUDIES OF TRINUCLEAR CADMIUM CLUSTER COMPLEXES. SYNTHESES AND CRYSTAL STRUCTURES OF $[NMe_4][Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_7]\cdot C_5H_{12}$ AND $[Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_6(HSC_6H_2Pr^i_3\text{-}2,4,6)]\cdot CH_3OH\cdot 7H_2O$', Journal of Coordination Chemistry, 31: 4, 305 — 320
To link to this Article: DOI: 10.1080/00958979408024224
URL: http://dx.doi.org/10.1080/00958979408024224

J. Coord. Chem., 1994, Vol 31, pp. 305–320
Reprints available directly from the publisher
Photocopying permitted by license only

STUDIES OF TRINUCLEAR CADMIUM CLUSTER COMPLEXES. SYNTHESES AND CRYSTAL STRUCTURES OF $[NMe_4][Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_7]\cdot C_5H_{12}$ AND $[Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_6(HSC_6H_2Pr^i_3\text{-}2,4,6)]\cdot CH_3OH\cdot 7H_2O$

KALUO TANG,* XIANGLIN JIN, AIQUN LI, SHOUJUN LI, ZHIFEN LI and YOUQI TANG

Institute of Physical Chemistry, Peking University, Beijing 100871, P. R. China

(Received June 14, 1993; in final form December 3, 1993)

By the reaction of a sterically hindered arenethiol, 2,4,6-$Pr^i_3C_6H_2SH$, with $Cd(NO_3)_2\cdot 4H_2O$ under different conditions, the colourless salt of trinuclear cadmium cluster anion complex $[NMe_4][Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_7]\cdot C_5H_{12}$ (1) and the uncharged trinuclear cadmium complex $[Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_6(HSC_6H_2Pr^i_3\text{-}2,4,6)]\cdot CH_3OH\cdot 7H_2O$ (2) have been synthesized. These have in turn been structurally characterized. Crystals of (1) are monoclinic, space group $P2_1/n$ with a = 19.629(6), b = 25.608(9), c = 25.450(9)Å, β = 107.54(3)°, V = 12203(7)Å^3, Z = 4, R = 0.076 for 3839 observed reflections. Crystals of (2) are triclinic, space group $P\bar{1}$ with a = 19.792(10), b = 20.508(12), c = 33.97(2)Å, α = 85.81(5), β = 86.77(5), γ = 85.12(4)°, V = 13686(14)Å^3, Z = 4, R = 0.0921 for 8327 observed reflections. The core of the cluster anion of (1) $[Cd_3(SC_6H_2Pr^i_3\text{-}2,4,6)_7]^-$ is formed by a defect cubane unit with three cadmium and four sulphur atoms at its vertices. Each cadmium atom exhibits tetrahedral coodrination with one terminal sulphur, two doubly bridging sulphur and one triply bridging sulphur atoms. In complex (2), three cadmium atoms are coordinated by six thiolate (RS^-) and one thiol (RSH) ligands. Two of three cadmium atoms have tetrahedral coordination and one is trigonal planar.

KEYWORDS: Cadmium, trinuclear cluster, X-ray structure, 2,4,6-triisopropylthiophenol, synthesis

INTRODUCTION

Considerable current interest has been devoted to the chemistry and structures of cadmium and zinc complexes with sulfur-containing ligands, in view of their significance in bioinorganic chemistry. The crystal structure determination of Cd and Zn metallothionens (MTs) has proved that there are two metal clusters $[M_3(Cys\text{-}S)_9]^{3-}$ and $[M_4(Cys\text{-}S)_{11}]^{4-}$ in MTs.[1] Several crystal structures of Cd^{II}-SR cluster complexes have been reported: $[Cd_4(SC_6H_5)_{10}]^{2-}$,[2] $Cd_4(SC_6H_4Me\text{-}4)_8$,[3] $Cd_8(SC_6H_4Br\text{-}4)_{16}\cdot(DMF)_3$,[3] $Cd_7(SC_6H_4Me\text{-}2)_{14}\cdot(DMF)_2$,[4] $[S_4Cd_{10}(SPh)_{16}]^{4-}$,[5] $[S_4Cd_{17}(SPh)_{28}]^{2-}$,[6] *etc.* Also, some mono- and dimeric Cd thiolates with high steric hindrance are known: $[PPh_4][Cd(SC_6H_2Pr^i_3)_3]$,[7] $[Cd(SC_6H_2Pr^i_3)_2(1\text{-}Me\text{-}imid)]$[8] and

* Author for correspondence.

$Cd_2(SC_6H_2Bu^t_3)_4$.[9] However, no report on trinuclear Cd^{II}-SR species has been found. We have synthesized the first anionic trinuclear Cd^{II}-SR complex $[NMe_4][Cd_3(SC_6H_2Pr^i_3)_7]\cdot C_5H_{12}$ (1) and determined its crystal structure, which has been reported as a communication.[10] By use of the same ligand, in a different ratio of metal to ligand and in the absence of quaternary ammonium salt, a novel uncharged trinuclear cadmium complex $[Cd_3(C_6H_2Pr^i_3S)_6(C_6H_2Pr^i_3SH)]\cdot CH_3OH\cdot 7H_2O$ (2) has been synthesized. In this paper we present the syntheses and crystal structures of the two trinuclear Cd complexes in detail and make a comparison between them.

EXPERIMENTAL

The synthetic procedures were carried out under a nitrogen atmosphere by using standard Schlenk techniques. Infrared spectra were recorded from KBr discs on a Perkin-Elmer 983G spectrometer. ^{113}Cd NMR spectra were recorded on Varian XL-200 spectrometer operating at the ^{113}Cd frequency of 44.32 MHz for solutions of a sample at natural abundance in $CDCl_3$ at 298 ± 2°K. Chemical shifts are referenced to a saturated solution of $Cd(NO_3)_2\cdot 4H_2O$ in D_2O.

Preparation of Complex (1)

A solution of $Cd(NO_3)_2\cdot 4H_2O$ (308 mg, 1 mmol) in 3 cm^3 of methanol was added dropwise to a solution of 2,4,6-triisopropylthiophenol[11] (770 mg, 3.2 mmol) and Et_3N (0.49 cm^3, 3.5 mmol) in 4.5 cm^3 of methanol in the presence of Me_4NCl (134 mg, 1.2 mmol). The mixture was stirred for 12 h at room temperature. The white precipitate formed was filtered and washed with MeOH. Recrystallization of the crude product from pentane-benzene (2:1) gave large colourless crystals, m.p. 270–272°C. The crystals are not stable in air, losing solvent pentane molecules. I.r. (KBr)): 3037 w, 2945 vs, 2864 s, 1615 w, 1596 w, 1558 w, 1480 m, 1459 s, 1422 m, 1379 m, 1358 m, 1307 m, 1258 w, 1243 w, 1164 w, 1153 w, 1101 m, 1056 m, 1029 m, 943 m, 920 w, 874 m, 815 w, 755 w, 637 w, 521 w, 466 w, 403 w, 297 w, 246 w, 230 w cm^{-1}.

Preparation of Complex (2)

A solution of $Cd(NO_3)_2\cdot 4H_2O$ (313 mg, 1.015 mmol) in 3 cm^3 of MeOH was added to a solution of 2,4,6-triisopropylthiophenol (480 mg, 2.03 mmol) and Et_3N (0.28 cm^3, 2.03 mmol) in 4 cm^3 of MeOH. The colourless reaction solution was stirred at room temperature for 13 h, then sealed and stored in a refrigerator (0 – 10°C). Colourless crystals with a columnar habit formed over seven days. The crystals effloresce in air, losing solvent molecules, m.p 234–235°C. I.r. (KBr): 3448 w, 3040 w, 2954 s, 2864 m, 2720 w, 1594 w, 1588 w, 1456 s, 1420 s, 1381 s, 1357 s, 1308 m, 1261 w, 1165 w, 1100 w, 1056 w, 1029 w, 874 w, 834 w, 753 w, 646 w, 297 w, 248 w, 246 w, 231 w cm^{-1}. ^{113}Cd NMR chemical shifts (ppm) are 496 (2Cd), 712 (1Cd), ratio of peak area is 2.3:1.

X-ray Crystal Structural Determinations of Complexes (1) and (2)

The crystal data for complexes (1) and (2) are summarized in Table 1, together with some experimental details. The diffraction intensities were collected at room temperature on a Siemens R3 diffractometer with MoK_α radiation (λ = 0.71073Å). The crystals of complexes (1) and (2) were sealed in glass capillaries with mother liquor. No absorption correction was applied. The SHELXTL PLUS program was used to solve and refine the structures and all calculations were completed on a MicroVAXII computer. Both structures were solved by direct methods. Block-diagonal refinement of all positional parameters, anisotropic thermal parameters for cadmium and sulphur atoms, and isotropic thermal parameters for other non-hydrogen atoms was applied for the two complexes. The hydrogen atoms were placed in their geometrically calculated positions and included in final structure factor calculations with isotropic thermal parameters. Atomic co-ordinates for the non-hydrogen atoms of complexes (1) and (2) are reported in Table 2 and 3; selected bond lengths and angles are given in Tables 4 and 5, respectively.

RESULTS AND DISCUSSION

The crystal structure determinations indicated that the complex (1) consists of a $[Me_4N]^+$ cation and an anionic trinuclear cadmium cluster coordinated by seven

Table 1 Summary of crystal data and experimental details for complexes (1) and (2)

	(1)	(2)
Formula	$C_{114}H_{185}Cd_3NS_7$	$C_{106}H_{180}Cd_3O_8S_7$
M	2131.39	2144.27
Colour habit	Colourless block	Colourless column
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
a/Å	19.629 (6)	19.792 (10)
b/Å	25.608 (9)	20.508 (12)
c/Å	25.450 (9)	33.97 (2)
α/°		85.81 (5)
β/°	107.54 (3)	86.77 (5)
γ/°		85.12 (4)
V/Å[a]	12203 (7)	13686 (14)
Z	4	4
Dc/g cm^{-a}	1.18	1.04
μ (MoK_α)/mm^{-1}	0.671	0.602
F(000)/e	4528	4544
Crystal dimensions/mm	0.5 × 0.4 × 0.4	0.4 × 0.5 × 0.6
Scan mode	2θ	2θ
Scan rate/°min^{-1}	4.51–29.3	4.51–23.9
Scan range/°	3.0 < 2θ < 35.0	3.0 < 2θ < 35.0
No. of reflections measured	7635	17304
No. of observed [$F > 6.0\ \sigma\ (F)$]	3839	8327
Weighting scheme	unit	$W^{-1} = \sigma^2(F) + 0.0001F^2$
R	0.076	0.0921
R_w	0.076	0.0906
Goodness-of-fit	1.54	3.75
Largest difference peak/e Å^{-3}	0.93	0.55

Table 2 Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement coefficient is ($Å^2 \times 10^3$) of non-hydrogen atoms for complex (1)

	x/a	y/b	z/c	U(*eq*)
Cd (1)	7747 (1)	960 (1)	5455 (1)	61 (1)
Cd (2)	7506 (1)	839 (1)	6960 (1)	67 (1)
Cd (3)	8567 (1)	2012 (1)	6534 (1)	70 (1)
S (1)	7210 (4)	1569 (3)	6153 (3)	55 (3)
S (2)	7707 (4)	272 (3)	6166 (3)	70 (4)
S (3)	8813 (4)	1574 (3)	5709 (3)	57 (3)
S (4)	8666 (5)	1312 (4)	7272 (3)	129 (5)
S (5)	6691 (4)	413 (3)	7371 (3)	83 (4)
S (6)	6973 (4)	707 (3)	4542 (3)	72 (4)
S (7)	3962 (4)	2106 (3)	1634 (3)	81 (4)
C (11)	6330 (14)	1892 (11)	5942 (10)	55 (8)
C (12)	6261 (16)	2416 (12)	6144 (11)	72 (9)
C (13)	5586 (16)	2631 (12)	5996 (11)	74 (9)
C (14)	5020 (15)	2366 (12)	5700 (11)	76 (9)
C (15)	5076 (15)	1654 (11)	5483 (10)	75 (9)
C (16)	5749 (14)	1628 (10)	5603 (10)	53 (8)
C (17)	6904 (16)	2721 (9)	6479 (12)	87 (10)
C (18)	4342 (16)	2696 (14)	5625 (13)	166 (16)
C (19)	5794 (15)	1082 (11)	5381 (11)	77 (9)
C (171)	6886 (14)	3321 (6)	6405 (11)	93 (10)
C (172)	7094 (14)	2585 (11)	7092 (10)	104 (10)
C (181)	3676 (19)	2406 (14)	5924 (15)	225 (18)
C (182)	3834 (23)	2533 (20)	5065 (15)	380 (29)
C (191)	5299 (15)	1016 (11)	4809 (11)	104 (11)
C (192)	5679 (15)	679 (11)	5769 (11)	108 (11)
C (21)	8325 (13)	−247 (10)	6362 (9)	58 (8)
C (22)	8976 (15)	−251 (11)	6275 (10)	61 (8)
C (23)	9424 (17)	−691 (12)	6423 (11)	89 (10)
C (24)	9217 (17)	−1144 (12)	6667 (12)	91 (11)
C (25)	8517 (15)	−1122 (12)	6710 (11)	87 (10)
C (26)	8092 (15)	−683 (11)	6589 (11)	66 (9)
C (27)	9236 (14)	198 (11)	5989 (10)	68 (9)
C (28)	9758 (19)	−1591 (13)	6880 (15)	157 (14)
C (29)	7380 (14)	−722 (11)	6707 (10)	74 (10)
C (271)	9033 (14)	117 (11)	5397 (9)	91 (10)
C (272)	10071 (14)	303 (11)	6234 (11)	113 (11)
C (281)	9453 (18)	−2065 (13)	6694 (14)	333 (24)
C (282)	10100 (20)	−1586 (15)	7432 (14)	212 (16)
C (291)	7384 (14)	−1016 (10)	7231 (10)	106 (10)
C (292)	6803 (14)	−939 (12)	6201 (10)	162 (12)
C (31)	8830 (14)	2007 (10)	5157 (10)	63 (8)
C (32)	8213 (15)	2263 (10)	4842 (11)	67 (8)
C (33)	8280 (16)	2558 (11)	4385 (11)	84 (10)
C (34)	8915 (16)	2587 (10)	4256 (10)	74 (9)
C (35)	9479 (15)	2347 (10)	4548 (11)	74 (9)
C (36)	9475 (15)	2035 (11)	5011 (11)	65 (9)
C (37)	7523 (13)	2285 (10)	4986 (10)	61 (8)
C (38)	8960 (18)	2888 (10)	3742 (11)	111 (12)
C (39)	10143 (15)	1773 (11)	5364 (11)	81 (10)
C (371)	7467 (14)	2808 (10)	5245 (10)	99 (9)
C (372)	6838 (13)	2182 (10)	4517 (10)	106 (9)
C (381)	8528 (15)	2678 (12)	3212 (11)	142 (12)
C (382)	8811 (18)	3467 (11)	3806 (13)	160 (14)
C (391)	10455 (18)	1434 (13)	5054 (14)	163 (15)
C (392)	10685 (18)	2133 (14)	5644 (14)	193 (16)

Table 2 Continued

	x/a	y/b	z/c	U(*eq*)
C (41)	9232 (15)	1275 (12)	7974 (11)	74 (9)
C (42)	9670 (14)	847 (10)	8138 (10)	74 (8)
C (43)	10122 (13)	838 (10)	8678 (10)	76 (8)
C (44)	10149 (16)	1223 (13)	9066 (12)	100 (11)
C (45)	9671 (15)	1644 (12)	8874 (12)	108 (10)
C (46)	9218 (16)	1685 (12)	8336 (12)	74 (10)
C (47)	9676 (13)	381 (11)	7754 (12)	112 (11)
C (48)	10681 (18)	1195 (16)	9657 (12)	158 (14)
C (49)	8718 (18)	2167 (14)	8217 (15)	136 (13)
C (471)	9236 (14)	-38 (11)	7845 (11)	112 (11)
C (472)	10451 (13)	220 (13)	7804 (12)	150 (14)
C (481)	11386 (26)	963 (18)	9716 (18)	197 (19)
C (482)	10303 (19)	855 (13)	9985 (15)	207 (16)
C (491)	8036 (16)	2041 (13)	8346 (13)	190 (14)
C (492)	9071 (18)	2639 (13)	8466 (13)	163 (15)
C (51)	6606 (16)	769 (11)	7952 (12)	82 (10)
C (52)	7080 (18)	674 (12)	8447 (14)	104 (11)
C (53)	7025 (20)	948 (14)	8914 (16)	157 (14)
C (54)	6477 (25)	1295 (17)	8897 (17)	195 (17)
C (55)	5931 (17)	1350 (12)	8348 (12)	115 (11)
C (56)	5993 (17)	1096 (12)	7864 (13)	96 (11)
C (57)	7755 (15)	336 (11)	8568 (12)	94 (10)
C (58)	6274 (21)	1645 (15)	9323 (15)	205 (17)
C (59)	5444 (16)	1193 (13)	7352 (13)	104 (11)
C (571)	8431 (15)	492 (12)	9012 (11)	157 (12)
C (572)	7547 (17)	-203 (12)	8699 (12)	161 (13)
C (581)	6900 (20)	2012 (16)	9586 (16)	289 (23)
C (582)	6012 (20)	1267 (1%)	9686 (14)	263 (19)
C (591)	5571 (17)	1634 (12)	7082 (13)	157 (14)
C (592)	4700 (16)	1192 (13)	7366 (13)	170 (14)
C (61)	7388 (13)	265 (10)	4170 (10)	60 (8)
C (62)	7724 (13)	493 (10)	3811 (10)	65 (8)
C (63)	7874 (13)	129 (11)	3451 (10)	84 (9)
C (64)	7726 (14)	-385 (11)	3415 (10)	75 (9)
C (65)	7491 (13)	-601 (11)	3828 (10)	87 (9)
C (66)	7317 (14)	-273 (11)	4227 (11)	75 (9)
C (67)	7956 (14)	1039 (10)	3819 (11)	85 (9)
C (68)	7925 (19)	-740 (12)	2993 (12)	131 (13)
C (69)	7084 (14)	-519 (11)	4677 (11)	84 (9)
C (671)	8683 (16)	1106 (13)	3793 (12)	163 (13)
C (672)	7482 (17)	1385 (13)	3417 (13)	194 (15)
C (681)	7487 (19)	-559 (15)	2465 (14)	243 (18)
C (682)	7720 (17)	-1265 (12)	3033 (13)	177 (14)
C (691)	7506 (15)	-973 (11)	4948 (11)	129 (11)
C (692)	6299 (15)	-659 (12)	4491 (12)	143 (12)
C (71)	9840 (15)	2985 (11)	6766 (11)	79 (9)
C (72)	9942 (17)	3369 (12)	6394 (12)	96 (10)
C (73)	10615 (18)	3477 (12)	6395 (13)	131 (11)
C (74)	11183 (17)	3235 (13)	6742 (13)	115 (11)
C (75)	11112 (16)	2853 (12)	7107 (11)	114 (10)
C (76)	10420 (16)	2730 (11)	7118 (11)	76 (9)
C (77)	9283 (19)	3547 (13)	5969 (14)	141 (14)
C (78)	11927 (19)	3375 (13)	6697 (16)	211 (18)
C (79)	10350 (15)	2270 (11)	7498 (11)	100 (10)
C (771)	9090 (22)	4108 (13)	6076 (17)	336 (23)
C (772)	9279 (16)	3525 (12)	5399 (11)	149 (12)

Table 2 Continued

	x/a	y/b	z/c	U(*eq*)
C (781)	12187 (20)	3939 (12)	6845 (15)	250 (20)
C (782)	12301 (20)	2958 (14)	6449 (15)	280 (21)
C (791)	10457 (14)	1785 (10)	7238 (10)	124 (10)
C (792)	10912 (13)	2321 (11)	8066 (10)	118 (10)
C (81)	5171 (18)	294 (13)	3361 (13)	197 (18)
C (82)	5260 (21)	1153 (12)	3172 (15)	261 (25)
C (83)	4601 (17)	615 (14)	2508 (13)	212 (19)
C (84)	5610 (17)	534 (16)	2787 (16)	257 (27)
C (85)	1440 (44)	-785 (33)	9235 (32)	411 (43)
C (86)	2066 (59)	-366 (45)	9346 (40)	418 (57)
C (87)	2356 (69)	-35 (43)	9197 (47)	541 (71)
C (88)	3053 (71)	70 (42)	9378 (42)	473 (60)
C (89)	3904 (67)	36 (49)	9299 (43)	466 (79)
N	5216 (10)	649 (8)	2957 (6)	155 (11)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Atomic co-ordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) of non-hydrogen atoms for complex (2)

	x/a	y/*b*	z/*c*	U(*eq*)
Cd (1)	6856 (1)	3319 (1)	3825 (1)	102 (1)
Cd (2)	7313 (1)	2328 (1)	4806 (1)	97 (1)
Cd (3)	6909 (10	1328 (1)	3833 (1)	113 (1)
S (1)	7632 (4)	1274 (4)	4414 (2)	91 (4)
C (101)	7629 (17)	473 (15)	4643 (9)	93 (11)
C (102)	7061 (17)	285 (17)	4901 (10)	122 (13)
C (103)	7133 (19)	-349 (18)	5109 (10)	142 (14)
C (104)	7753 (23)	-780 (20)	5111 (12)	159 (16)
C (105)	8256 (19)	-570 (20)	4842 (12)	140 (14)
C (106)	8266 (17)	46 (18)	4610 (10)	107 (12)
C (107)	6358 (16)	693 (15)	4915 (10)	107 (11)
C (108)	6201 (17)	887 (17)	5346 (11)	141 (14)
C (109)	5825 (17)	271 (16)	4757 (10)	132 (13)
C (110)	7706 (21)	-1407 (22)	5403 (13)	194 (18)
C (111)	8168 (22)	-1307 (22)	5742 (13)	226 (21)
C (112)	8097 (23)	-1927 (22)	5157 (14)	233 (21)
C (113)	8866 (15)	256 (15)	4344 (10)	109 (12)
C (114)	9561 (14)	-36 (15)	4505 (9)	114 (12)
C (115)	8724 (16)	-33 (16)	3938 (10)	134 (13)
S (2)	6239 (4)	2549 (4)	4376 (3)	88 (4)
C (121)	5425 (14)	2893 (14)	4542 (8)	70 (9)
C (122)	4849 (17)	2574 (16)	4464 (9)	95 (11)
C (123)	4173 (18)	2833 (18)	4568 (10)	116 (13)
C (124)	4132 (19)	3418 (20)	4740 (11)	132 (14)
C (125)	4691 (22)	3741 (18)	4825 (10)	142 (14)
C (126)	5376 (17)	3491 (17)	4733 (9)	111 (12)
C (127)	4921 (15)	1912 (16)	4265 (10)	109 (12)
C (128)	4348 (15)	1462 (15)	4411 (9)	127 (13)
C (129)	4922 (16)	2063 (16)	3820 (10)	131 (13)
C (130)	3429 (19)	3769 (19)	4861 (11)	174 (16)
C (131)	2929 (20)	3340 (20)	5082 (12)	198 (18)

Table 3 Continued

	x/a	y/*b*	z/*c*	U(*eq*)
C (132)	3150 (18)	4218 (18)	4520 (11)	161 (15)
C (133)	5980 (17)	3895 (18)	4812 (11)	138 (14)
C (134)	5971 (18)	3852 (18)	5248 (12)	158 (15)
C (135)	5885 (17)	4589 (18)	4595 (10)	141 (14)
S (3)	6732 (4)	2351 (4)	3411 (3)	106 (5)
C (141)	7169 (20)	2316 (15)	2904 (11)	118 (12)
C (142)	7901 (22)	2296 (17)	2905 (13)	143 (14)
C (143)	8157 (21)	2299 (20)	2511 (16)	172 (17)
C (144)	7810 (27)	2301 (20)	2146 (14)	185 (18)
C (145)	7098 (21)	2288 (16)	2255 (12)	124 (13)
C (146)	6733 (20)	2286 (17)	2599 (13)	133 (14)
C (147)	8343 (18)	2319 (17)	3253 (11)	133 (13)
C (148)	8740 (17)	1638 (18)	3275 (10)	144 (14)
C (149)	8751 (17)	2921 (17)	3217 (10)	147 (14)
C (150)	8088 (22)	2326 (22)	1701 (14)	203 (19)
C (151)	8016 (23)	3049 (22)	1563 (13)	226 (21)
C (152)	8060 (24)	1616 (23)	1599 (14)	244 (23)
C (153)	5956 (21)	2402 (22)	2713 (12)	182 (17)
C (154)	5621 (24)	2903 (23)	2411 (14)	264 (24)
C (155)	5706 (25)	1783 (23)	2571 (15)	259 (24)
S (4)	7880 (4)	3049 (5)	4263 (3)	116 (5)
C (161)	8657 (15)	3404 (17)	4314 (8)	84 (10)
C (162)	9231 (19)	2955 (18)	4404 (9)	121 (12)
C (163)	9873 (18)	3259 (19)	4473 (10)	127 (13)
C (164)	9904 (18)	3938 (20)	4439 (10)	131 (13)
C (165)	9320 (19)	4365 (16)	4315 (9)	120 (12)
C (166)	8717 (17)	4063 (18)	4267 (9)	100 (11)
C (167)	9250 (14)	2209 (16)	4425 (9)	97 (11)
C (168)	9872 (15)	1932 (16)	4166 (9)	131 (13)
C (169)	9227 (15)	1965 (15)	4864 (10)	122 (12)
C (170)	10566 (19)	4282 (18)	4500 (11)	170 (16)
C (171)	11111 (19)	3974 (18)	4213 (11)	171 (16)
C (172)	10723 (19)	4071 (19)	4930 (11)	186 (17)
C (173)	8107 (17)	4535 (17)	4120 (10)	127 (13)
C (174)	8324 (20)	5061 (20)	3805 (12)	186 (17)
C (175)	7819 (18)	4873 (18)	4487 (10)	162 (15)
S (5)	7212 (50	2411 (5)	5512 (3)	131 (5)
C (181)	8047 (17)	2375 (18)	5690 (9)	105 (12)
C (182)	8393 (20)	1718 (18)	5817 (10)	128 (13)
C (183)	9032 (20)	1686 (19)	5948 (10)	125 (13)
C (184)	9293 (21)	2273 (25)	5975 (11)	143 (15)
C (185)	9072 (22)	2908 (22)	5865 (11)	157 (16)
C (186)	8393 (22)	2944 (20)	5720 (11)	148 (15)
C (187)	8049 (18)	1096 (18)	5757 (11)	134 (13)
C (188)	8584 (19)	573 (19)	5608 (11)	163 (15)
C (189)	7663 (19)	943 (18)	6162 (12)	172 (16)
C (190)	10049 (22)	2140 (26)	6066 (16)	265 (24)
C (191)	10672 (27)	2314 (26)	5810 (15)	281 (26)
C (192)	10162 (28)	2235 (28)	6493 (16)	298 (29)
C (193)	8041 (20)	3607 (20)	5554 (12)	167 (16)
C (194)	8572 (21)	4085 (21)	5411 (13)	219 (20)
C (195)	7700 (23)	3906 (22)	5919 (15)	224 (21)
S (6)	6617 (5)	4449 (5)	3575 (3)	136 (6)
C (201)	6193 (21)	4472 (16)	3111 (12)	132 (13)
C (202)	6604 (22)	4556 (19)	2769 (15)	162 (16)

Table 3 Continued

	x/a	y/*b*	z/*c*	U(*eq*)
C (203)	6248 (24)	4635 (18)	2414 (12)	156 (15)
C (204)	5520 (26)	4636 (20)	2415 (15)	176 (17)
C (205)	5164 (23)	4611 (22)	2800 (18)	201 (20)
C (206)	5464 (22)	4484 (18)	3158 (14)	153 (15)
C (207)	7400 (21)	4475 (21)	2728 (12)	179 (17)
C (208)	7718 (23)	4049 (22)	2400 (14)	238 (22)
C (209)	7621 (23)	5178 (22)	2719 (14)	235 (21)
C (210)	5134 (25)	4724 (24)	2023 (14)	237 (22)
C (211)	4914 (25)	5464 (24)	1967 (15)	261 (24)
C (212)	5505 (23)	4448 (22)	1653 (14)	231 (21)
C (213)	5071 (23)	4379 (23)	3569 (14)	190 (18)
C (214)	4515 (25)	4945 (23)	3575 (15)	265 (24)
C (215)	4701 (25)	3763 (25)	3528 (14)	244 (23)
S (7)	6607 (6)	238 (5)	3714 (3)	155 (6)
C (221)	6404 (24)	199 (17)	3203 (12)	131 (14)
C (222)	6900 (24)	137 (21)	2926 (17)	183 (18)
C (223)	6705 (26)	38 (20)	2550 (14)	182 (18)
C (224)	5963 (29)	−2 (20)	2495 (15)	183 (18)
C (225)	5457 (19)	78 (17)	2799 (13)	146 (15)
C (226)	5703 (22)	189 (16)	3187 (12)	129 (13)
C (227)	7659 (23)	183 (21)	3001 (13)	197 (19)
C (228)	7946 (21)	499 (21)	2613 (13)	202 (19)
C (229)	7896 (22)	−547 (21)	3050 (13)	215 (20)
C (230)	5494 (34)	100 (36)	2141 (15)	545 (67)
C (231)	5944 (28)	201 (29)	1766 (18)	300 (28)
C (232)	5694 (31)	−579 (30)	1990 (19)	308 (30)
C (233)	5133 (19)	198 (21)	3507 (12)	167 (16)
C (234)	5029 (23)	−501 (25)	3704 (14)	232 (21)
C (235)	4459 (20)	494 (20)	3350 (12)	202 (18)
Cd (1)′	2255 (1)	1776 (1)	1237 (1)	104 (1)
Cd (2)′	2675 (1)	2752 (1)	248 (1)	103 (1)
Cd (3)′	1931 (1)	3782 (1)	1237 (1)	115 (1)
S (2)′	1582 (4)	2469 (4)	687 (3)	97 (4)
C (241)	896 (17)	2052 (18)	529 (9)	103 (11)
C (242)	234 (19)	2386 (17)	574 (9)	118 (12)
C (243)	−359 (17)	2070 (21)	490 (11)	140 (15)
C (244)	−180 (22)	1491 (23)	349 (12)	149 (15)
C (245)	422 (22)	1096 (18)	277 (10)	142 (14)
C (246)	996 (19)	1410 (19)	386 (10)	120 (13)
C (247)	120 (17)	3056 (17)	750 (11)	136 (14)
C (248)	−514 (18)	3464 (18)	581 (11)	179 (17)
C (249)	102 (18)	2978 (18)	1198 (12)	163 (16)
C (250)	−743 (24)	1061 (25)	247 (15)	289 (27)
C (251)	−1307 (25)	1350 (23)	−17 (14)	252 (23)
C (252)	−1104 (22)	652 (22)	570 (13)	210 (20)
C (253)	1725 (20)	1091 (19)	297 (12)	148 (15)
C (254)	1852 (19)	1097 (19)	−151 (13)	179 (17)
C (255)	1687 (19)	379 (21)	496 (12)	175 (16)
S (1)′	2706 (4)	3812 (4)	634 (3)	98 (4)
C (261)	2616 (19)	4633 (16)	375 (9)	104 (12)
C (262)	3109 (17)	5061 (20)	410 (10)	119 (13)
C (263)	3073 (17)	5675 (19)	202 (11)	118 (13)
C (264)	2557 (28)	5863 (24)	−45 (14)	199 (20)
C (265)	2037 (19)	5418 (21)	−60 (10)	137 (14)
C (266)	2039 (19)	4771 (19)	146 (11)	124 (13)

Table 3 Continued

	x/a	*y/b*	*z/c*	U(*eq*)
C (267)	3735 (16)	4853 (15)	662 (9)	110 (12)
C (268)	4415 (15)	5161 (14)	480 (9)	106 (11)
C (269)	3546 (16)	5143 (16)	1070 (9)	141 (14)
C (270)	2457 (22)	6536 (24)	−301 (14)	201 (19)
C (271)	2973 (24)	6410 (23)	−644 (14)	241 (23)
C (272)	2577 (25)	7106 (24)	−60 (15)	258 (25)
C (273)	1386 (17)	4373 (16)	145 (10)	123 (13)
C (274)	1368 (17)	4227 (16)	−291 (11)	142 (14)
C (275)	790 (15)	4797 (15)	342 (9)	122 (12)
S (3)′	1862 (4)	2746 (4)	1642 (3)	105 (5)
C (281)	2226 (18)	2788 (14)	2130 (10)	101 (11)
C (282)	2941 (19)	2847 (15)	2123 (11)	111 (12)
C (283)	3112 (18)	2852 (17)	2525 (13)	137 (14)
C (284)	2727 (26)	2848 (20)	2901 (14)	192 (18)
C (285)	2002 (21)	2877 (17)	2827 (12)	147 (15)
C (286)	1740 (17)	2816 (16)	2463 (12)	127 (13)
C (287)	3419 (18)	2815 (17)	1750 (11)	133 (13)
C (288)	3768 (18)	3454 (17)	1738 (11)	156 (15)
C (289)	3954 (17)	2238 (17)	1822 (10)	139 (14)
C (290)	3013 (23)	2850 (24)	3323 (14)	208 (20)
C (291)	2890 (22)	2192 (22)	3541 (13)	214 (20)
C (292)	2663 (29)	3492 (27)	3454 (17)	330 (32)
C (293)	994 (19)	2725 (20)	2359 (11)	162 (15)
C (294)	680 (22)	2218 (21)	2646 (13)	223 (20)
C (295)	606 (21)	3359 (20)	2476 (13)	218 (20)
S (4)′	3296 (4)	2050 (5)	779 (3)	128 (5)
C (301)	4189 (16)	1714 (18)	742 (8)	92 (11)
C (302)	4667 (19)	2181 (18)	659 (10)	120 (13)
C (303)	5341 (17)	1890 (19)	572 (10)	127 (13)
C (304)	5551 (19)	1208 (21)	614 (11)	144 (14)
C (305)	5016 (20)	789 (16)	754 (10)	123 (13)
C (306)	4354 (18)	1052 (19)	784 (9)	109 (12)
C (307)	4522 (15)	2921 (16)	605 (10)	101 (11)
C (308)	5021 (16)	3264 (16)	835 (9)	125 (13)
C (309)	4524 (15)	3144 (15)	163 (10)	122 (12)
C (310)	6291 (19)	902 (18)	537 (11)	154 (15)
C (311)	6518 (20)	1152 (19)	119 (11)	187 (17)
C (312)	6719 (21)	1131 (21)	858 (12)	212 (19)
C (313)	3781 (17)	579 (17)	918 (11)	123 (13)
C (314)	4016 (19)	117 (19)	1285 (12)	173 (16)
C (315)	3699 (19)	181 (20)	572 (12)	182 (17)
S (6)′	2177 (5)	654 (5)	1506 (3)	140 (6)
C (321)	1675 (20)	599 (15)	1968 (11)	111 (12)
C (322)	2094 (24)	569 (20)	2302 (15)	179 (17)
C (323)	1613 (24)	472 (18)	2656 (12)	161 (16)
C (324)	885 (24)	462 (18)	2678 (13)	156 (16)
C (325)	571 (20)	576 (19)	2306 (15)	165 (16)
C (326)	944 (21)	658 (16)	1942 (12)	134 (14)
C (327)	2876 (24)	619 (22)	2320 (13)	207 (20)
C (328)	2972 (20)	1087 (20)	2645 (12)	199 (18)
C (329)	3117 (24)	−111 (23)	2385 (14)	248 (23)
C (330)	458 (23)	373 (22)	3075 (13)	222 (21)
C (331)	763 (22)	693 (21)	3411 (13)	213 (20)
C (332)	429 (23)	−372 (22)	3165 (13)	228 (21)
C (333)	593 (21)	796 (20)	1543 (12)	179 (17)

Table 3 Continued

	x/a	y/*b*	z/*c*	U(*eq*)
C (334)	326 (21)	148 (20)	1464 (12)	204 (19)
C (335)	38 (21)	1354 (21)	1597 (13)	222 (20)
S (5)′	2693 (5)	2710 (5)	-463 (3)	142 (6)
C (341)	3576 (18)	2765 (22)	-657 (10)	123 (13)
C (342)	3966 (22)	2161 (22)	-659 (11)	140 (14)
C (343)	4663 (22)	2250 (21)	-837 (11)	153 (15)
C (344)	4886 (26)	2872 (29)	-976 (13)	189 (19)
C (345)	4457 (23)	3425 (20)	-934 (11)	148 (15)
C (346)	3751 (22)	3422 (22)	-766 (11)	145 (15)
C (347)	3791 (21)	1469 (24)	-500 (13)	193 (18)
C (348)	4406 (20)	1063 (19)	-335 (12)	183 (17)
C (349)	3527 (23)	1179 (22)	-856 (15)	227 (21)
C (350)	5645 (26)	3021 (26)	-1058 (16)	274 (25)
C (351)	6227 (27)	2759 (26)	-796 (16)	285 (26)
C (352)	5722 (24)	2816 (24)	-1483 (15)	247 (24)
C (353)	3273 (20)	4070 (21)	-760 (12)	155 (15)
C (354)	3697 (19)	4619 (19)	-625 (11)	167 (16)
C (355)	2914 (19)	4200 (19)	-1162 (12)	181 (17)
S (7)′	1434 (6)	4873 (5)	1357 (3)	182 (7)
C (361)	1046 (22)	4951 (16)	1858 (12)	128 (14)
C (362)	1495 (22)	5020 (18)	2155 (15)	154 (16)
C (363)	1158 (31)	5122 (23)	2549 (16)	220 (22)
C (364)	450 (30)	5135 (22)	2590 (16)	197 (19)
C (365)	75 (18)	5049 (17)	2271 (14)	141 (14)
C (366)	343 (25)	4911 (19)	1866 (14)	160 (16)
C (367)	2279 (23)	5018 (25)	2091 (13)	218 (21)
C (368)	2584 (21)	4640 (21)	2453 (13)	210 (19)
C (369)	2472 (22)	5737 (24)	1995 (13)	219 (20)
C (370)	-48 (28)	5343 (30)	2938 (16)	332 (35)
C (371)	427 (27)	5444 (27)	3262 (17)	289 (27)
C (372)	79 (29)	4676 (26)	3179 (17)	298 (28)
C (373)	-171 (25)	4870 (25)	1551 (14)	207 (20)
C (374)	-305 (24)	5559 (26)	1359 (14)	238 (22)
C (375)	-770 (28)	4535 (25)	1726 (15)	261 (25)
O (1)	3509 (30)	1270 (43)	5894 (26)	431 (59)
O (2)	8316 (23)	3452 (22)	8978 (13)	453 (21)
O (3)	4685 (29)	2258 (28)	5699 (17)	506 (33)
O (4)	8537 (29)	1363 (28)	7843 (17)	510 (33)
O (5)	3655 (31)	1883 (30)	6866 (18)	545 (36)
O (6)	3530 (38)	2696 (37)	8093 (23)	680 (50)
O (7)	4020 (31)	3619 (31)	6200 (19)	555 (38)
O (8)	688 (35)	1440 (34)	7767 (21)	628 (44)
O (9)	5921 (49)	2234 (47)	6437 (28)	843 (70)
O (10)	1789 (29)	909 (29)	8476 (17)	524 (35)
O (11)	34 (48)	1461 (47)	8955 (28)	565 (60)
O (12)	7819 (34)	1281 (33)	8691 (20)	611 (44)
O (13)	4198 (35)	3577 (35)	7117 (22)	634 (45)
O (14)	7846 (39)	2249 (38)	6988 (23)	700 (52)
O (15)	9155 (39)	3120 (38)	8096 (23)	691 (52)
O (16)	500 (43)	2608 (42)	9279 (25)	502 (52)
C (1)	2771 (30)	1323 (43)	6009 (25)	306 (48)
C (2)	8949 (33)	3332 (42)	9206 (23)	804 (63)

*Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4 Selected bond lengths (Å) and angles (°) for complex (1)

Cd(1)–S(1)	2.800 (8)	Cd(1)–S(2)	2.544 (8)
Cd(1)–S(3)	2.540 (7)	Cd(1)–S(6)	2.445 (6)
Cd(2)–S(1)	2.709 (7)	Cd(2)–S(2)	2.613 (8)
Cd(2)–S(4)	2.488 (9)	Cd(2)–S(5)	2.421 (9)
Cd(3)–S(1)	2.787 (7)	Cd(3)–S(3)	2.552 (8)
Cd(3)–S(4)	2.560 (10)	Cd(3)–S(7A)	2.434 (8)
S(1)–C(11)	1.844 (28)	S(2)–C(21)	1.767 (26)
S(3)–C(31)	1.796 (26)	S(4)–C(41)	1.801 (25)
S(5)–C(51)	1.788 (33)	S(6)–C(61)	1.813 (29)
S(7)–C(71A)	1.797 (32)		
S(1)–Cd(1)–C(2)	80.5 (2)	S(1)–Cd(1)–S(3)	86.1 (2)
S(2)–Cd(1)–S(3)	116.6 (2)	S(1)–Cd(1)–S(6)	120.5 (2)
S(2)–Cd(1)–S(6)	110.5 (2)	S(3)–Cd(1)–S(6)	129.1 (3)
S(1)–Cd(2)–S(2)	81.1 (2)	S(1)–Cd(2)–S(4)	82.7 (3)
S(2)–Cd(2)–S(4)	100.4 (3)	S(1)–Cd(2)–S(5)	128.4 (2)
S(2)–Cd(2)–S(5)	110.9 (3)	S(4)–Cd(2)–S(5)	137.9 (3)
S(1)–Cd(3)–S(3)	86.2 (2)	S(1)–Cd(3)–S(4)	79.8 (2)
S(3)–Cd(3)–S(4)	107.8 (3)	S(1)–Cd(3)–S(7A)	131.8 (3)
S(3)–Cd(3)–S(7A)	123.0 (3)	S(4)–Cd(3)–S(7A)	118.2 (3)
Cd(1)–S(1)–Cd(2)	93.5 (2)	Cd(1)–S(1)–Cd(3)	86.8 (2)
Cd(2)–S(1)–Cd(3)	93.0 (2)	Cd(1)–S(1)–C(11)	124.4 (9)
Cd(2)–S(1)–C(11)	119.9 (10)	Cd(3)–S(1)–C(11)	129.2 (9)
Cd(1)–S(2)–Cd(2)	102.2 (3)	Cd(1)–S(2)–C(21)	123.7 (10)
Cd(2)–S(2)–C(21)	116.8 (8)	Cd(1)–S(3)–Cd(3)	97.8 (3)
Cd(1)–S(3)–C(31)	113.0 (8)	Cd(3)–S(3)–C(31)	115.2 (9)
Cd(2)–S(4)–Cd(3)	104.3 (3)	Cd(2)–S(4)–C(41)	121.5 (11)
Cd(3)–S(4)–C(41)	130.8 (11)	Cd(2)–S(5)–C(51)	111.5 (11)
Cd(1)–S(6)–C(61)	114.7 (7)	Cd(3A)–S(7)–C(71A)	108.3 (10)

arenethiolate (RS^-) ligands $[Cd_3(SC_6H_2Pr^i_3)_7]^-$. The core and the structure of the anion are shown in Figures 1 and 2. Complex (2) consists of an uncharged trinuclear cadmium cluster surrounded by six arenethiolate (RS^-) and one arenethiol (RSH) ligands. In each asymmetric unit there are two molecules (A and B), whose structures are almost the same. The core and the structure of the molecule (A) of complex (2) are shown in Figures 3 and 4.

The principal structural differences between complexes (1) and (2) are summarized as follows:

(i) The anion of complex (1) contains a defect cubane-like Cd_3S_4 cage, composed of a Cd_3-triangle and a distorted S_4-tetrahedron. The cage closely approaches C_{3v} symmetry. The distances between the central S (1) atom and the three Cd atoms are similar (2.800, 2.787, 2.709Å, respectively). In contrast with complex (1), the Cd_3S_4 core of complex (2) does not present a defect cubane-like cage. One of the distances between the central S atom and three Cd atoms is much longer than other two [(S (2)–Cd (3) 3.356, S (2)–Cd (1) 2.670, S (2)–Cd (2) 2.637Å in molecule (A), S (2)′–Cd (3)′ 3.524, S (2)′–Cd (1)′ 2.618, S (2)′–Cd (2)′ 2.640Å in (B)].

(ii) In the anion of (1), there are three types of coordination in the seven thiolate ligands: three terminal, three doubly bridging and one triply bridging thiolates. However, in the uncharged complex (2) there are only two types of coordination in the six thiolate and one thiol ligands, three terminal, four doubly bridging. No triply bridging sulphur atom exists in the metal aggregates of MTs and in other cadmium thiolates. The mean values of the two types of Cd–S bond lengths in complexes (1)

Table 5 Selected bond lengths (Å) and angles (°) for complex (2)

Cd(1)–S(2)	2.670 (8)	Cd(1)–S(3)	2.550 (10)
Cd(1)–S(4)	2.581 (9)	Cd(1)–S(6)	2.426 (10)
Cd(2)–S(1)	2.634 (9)	Cd(2)–S(2)	2.637 (8)
Cd(2)–S(4)	2.548 (9)	Cd(2)–S(5)	2.413 (10)
Cd(3)–S(1)	2.496 (9)	Cd(3)–S(3)	2.461 (9)
Cd(3)–S(7)	2.429 (11)	S(1)–C(101)	1.766 (31)
S(2)–C(121)	1.780 (28)	S(3)–C(141)	1.888 (37)
S(4)–C(161)	1.779 (33)	S(5)–C(181)	1.785 (34)
S(6)–C(201)	1.825 (44)	S(7)–C(221)	1.814 (44)
Cd(1)′–S(2)′	2.618 (9)	Cd(1)′–S(3)′	2.545 (9)
Cd(1)′–S(4)′	2.587 (9)	Cd(1)′–S(6)′	2.427 (10)
Cd(2)′–S(2)′	2.640 (8)	Cd(2)′–S(1)′	2.627 (9)
Cd(2)′–S(4)′	2.531 (10)	Cd(2)′–S(5)′	2.420 (10)
Cd(3)′–S(1)′	2.490 (9)	Cd(3)′–S(3)′	2.457 (9)
Cd(3)′–S(7)′	2.420 (11)	S(2)′–C(241)	1.792 (37)
S(1)′–C(261)	1.841 (33)	S(3)′–C(281)	1.855 (35)
S(4)′–C(301)	1.842 (32)	S(6)′–C(321)	1.812 (38)
S(5)′–C(341)	1.840 (37)	S(7)′–C(361)	1.840 (42)
S(2)–Cd(1)–S(3)	81.5 (3)	S(2)–Cd(1)–S(4)	83.0 (3)
S(3)–Cd(1)–S(4)	109.2 (3)	S(2)–Cd(1)–S(6)	133.0 (3)
S(3)–Cd(1)–S(6)	122.6 (3)	S(4)–Cd(1)–S(6)	117.9 (3)
S(1)–Cd(2)–S(2)	87.2 (3)	S(1)–Cd(2)–S(4)	91.4 (3)
S(2)–Cd(2)–S(4)	84.3 (3)	S(1)–Cd(2)–S(5)	128.2 (3)
S(2)–Cd(2)–S(5)	120.7 (3)	S(4)–Cd(2)–S(5)	130.6 (3)
S(1)–Cd(3)–S(3)	120.8 (3)	S(1)–Cd(3)–S(7)	110.1 (3)
S(3)–Cd(3)–S(7)	128.4 (4)	Cd(2)–S(1)–Cd(3)	108.6 (3)
Cd(2)–S(1)–C(101)	122.4 (11)	Cd(3)–S(1)–C(101)	107.6 (11)
Cd(1)–S(2)–Cd(2)	94.1 (3)	Cd(1)–S(2)–C(121)	113.2 (10)
Cd(2)–S(2)–C(121)	125.7 (10)	Cd(1)–S(3)–Cd(3)	108.7 (3)
Cd(1)–S(3)–C(141)	120.1 (11)	Cd(3)–S(3)–C(141)	113.9 (10)
Cd(1)–S(4)–Cd(2)	98.5 (3)	Cd(1)–S(4)–C(161)	134.9 (11)
Cd(2)–S(4)–C(161)	123.8 (10)	Cd(2)–S(5)–C(181)	108.2 (11)
Cd(1)–S(6)–C(201)	109.6 (11)	Cd(3)–S(7)–C(221)	110.6 (12)
S(2)′–Cd(1)′–S(3)′	82.9 (3)	S(2)′–Cd(1)′–S(4)′	83.2 (3)
S(3)′–Cd(1)′–S(4)′	110.1 (3)	S(2)′–Cd(1)′–S(6)′	131.0 (3)
S(3)′–Cd(1)′–S(6)′	121.4 (3)	S(4)′–Cd(1)′–S(6)′	118.8 (3)
S(2)′–Cd(2)′–S(1)′	88.4 (3)	S(2)′–Cd(2)′–S(4)′	83.8 (3)
S(1)′–Cd(2)′–S(4)′	91.9 (3)	S(2)′–Cd(2)′–S(5)′	120.4 (3)
S(1)′–Cd(2)′–S(5)′	126.0 (3)	S(4)′–Cd(2)′–S(5)′	132.3 (3)
S(1)′–Cd(3)′–S(3)′	119.2 (3)	S(1)′–Cd(3)′–S(7)′	110.5 (3)
S(3)′–Cd(3)′–S(7)′	130.0 (4)	Cd(1)′–S(2)′–Cd(2)′	94.8 (3)
Cd(1)′–S(2)′–C(241)	112.2 (11)	Cd(2)′–S(2)′–C(241)	125.4 (10)
Cd(2)′–S(1)′–Cd(3)′	111.5 (3)	Cd(2)′–S(1)′–C(261)	120.8 (11)
Cd(3)′–S(1)′–C(261)	109.6 (11)	Cd(1)′–S(3)′–Cd(3)′	110.5 (3)
Cd(1)′–S(3)′–C(281)	118.4 (10)	Cd(3)′–S(3)′–C(281)	111.5 (10)
Cd(1)′–S(4)′–Cd(2)′	98.2 (3)	Cd(1)′–S(4)′–C(301)	134.1 (11)
Cd(2)′–S(4)′–C(301)	126.0 (10)	Cd(1)′–S(6)′–C(321)	112.8 (11)
Cd(2)′–S(5)′–C(341)	108.0 (12)	Cd(3)′–S(7)′–C(361)	114.2 (11)

and (2) are similar: Cd−S_{db} 2.550 (2.488–2.613)Å in (1), 2.560 (2.461–2.670)Å and 2.562 (2.457–2.640)Å in molecule (A) and (B) of (2), respectively; Cd−S_t 2.433 (2.421–2.445)Å in (1), 2.423 (2.413–2.429)Å and 2.422(2.420–2.427)Å in (A) and (B) of (2), respectively. The bond lengths of triply bridging Cd−Stb (Av. 2.765 (2.709–2.800)Å) are much longer than those of the other two types. Elongation of M−S distances is commonly observed when the coordination numbers of metal are

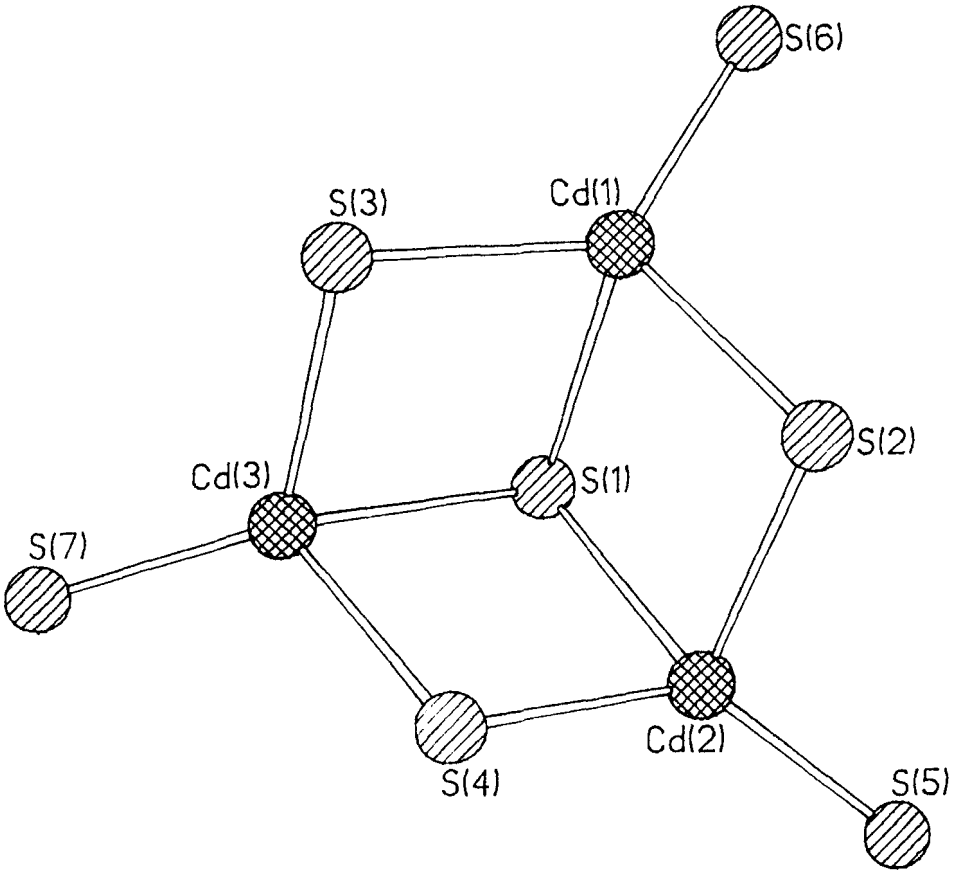

Figure 1 The structure of the Cd_3S_7 core of complex (1).

increased. The reason may be that the higher the coordination number, the lower the bond order.

(iii) A remarkable feature of (2) is that the three cadmium atoms have two coordination modes: two Cd atoms exhibit distorted tetrahedral coordination with one terminal sulphur and three doubly bridging sulphur atoms, while one Cd atom is trigonal planar with one terminal and two doubly bridging sulphur atoms. A ^{113}Cd NMR spectrum confirmed this. There are two peaks in the spectrum, with a ratio of approximately 2 to 1. In contrast, the three Cd atoms of (1) have only one coordination mode. Each Cd atom has one terminal, two doubly bridging and one triply bridging thiolate ligands forming a distorted tertrahedal CdS_4 unit. The mean bond length for tetrahedral coordination, $Cd-S_{tetr}$, is 2.574 (2.421–2.800)Å in (1), which is close to $Cd-S_{tetr}$ in (2) (2.555Å and 2.559Å in (A) and (B) respectively), and slightly longer than the mean bond length for trigonal coordination, $Cd-S_{tri}$, in (2) (2.462 and 2.456Å in (A) and (B), respectively).

(iv) It has been found in the difference Fourier map of complex (2) that near one sulfur atom (S (7) in (A), S (7)′ in (B)) is an oxygen atom of solvent CH_3OH (O (1)

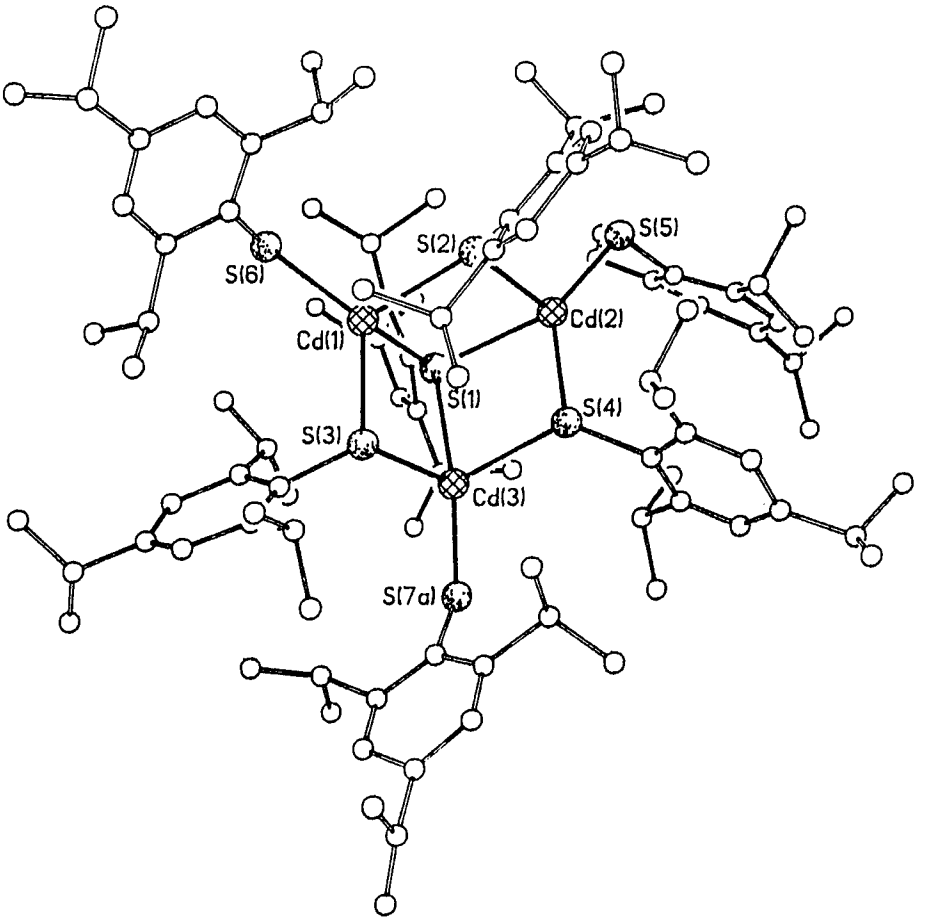

Figure 2 The structure of the $[Cd_3(SC_6H_2Pr^i_3)_7]^-$ anion in complex (1).

in (A), O (2) in (B)). The distances S (7) ··· 0 (1) and S (7)′ ··· O (2) are 3.298 and 3.605Å, respectively. The bond angles C (221)–S (7)–O (1) and C (361)–S (7)′–O (2) are 104.4° and 102.9°, respectively. It may be that there are weak hydrogen bonds (S–H···O) between S···O.[12] Complex (2) is neutral, that is, the ratio of Cd^{2+} to thiolates is 3:6. It is suggested that the ligands at S (7) and S (7)′ are thiol (RSH) instead of thiolate (RS^-). We wished to confirm this by ^1H NMR, but the SH peak is too weak compared with other H peaks (1:161). A ^{113}Cd NMR spectrum confirmed it indirectly. It is seldom that a thiol coordinates to a metal directly.

(v) In the anion of (1), there is one chair-like Cd_3 (μ–$S)_3$ ring. In complex (2) there are two six-membered rings Cd_3 (μ–$S)_3$; one is chair-like and the other is boat-like. A chair-like ring occurs in two aggregates (metal-cysteinate) in MTs and other Cd^{II}–SR cluster complexes, but the boat-like ring occurs neither in MTs nor in other cadmium thiolates.

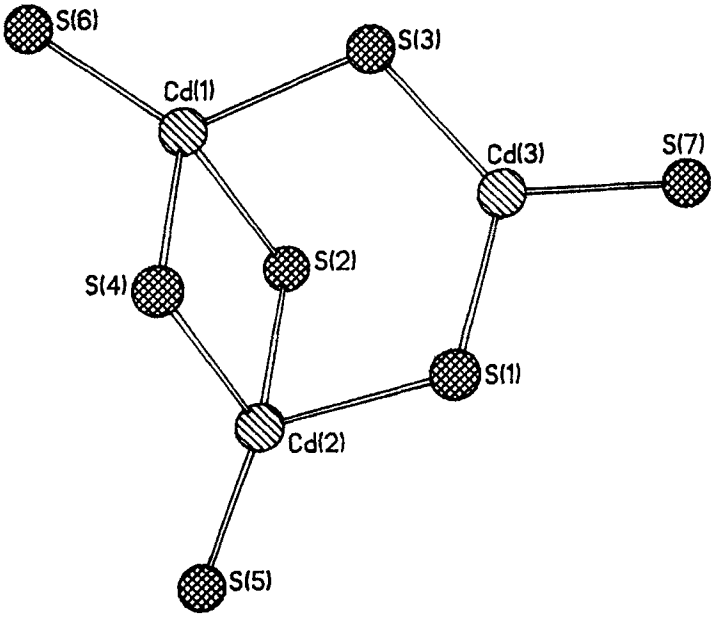

Figure 3 The Structure of the Cd_3S_7 core in molecule (A) of complex (2).

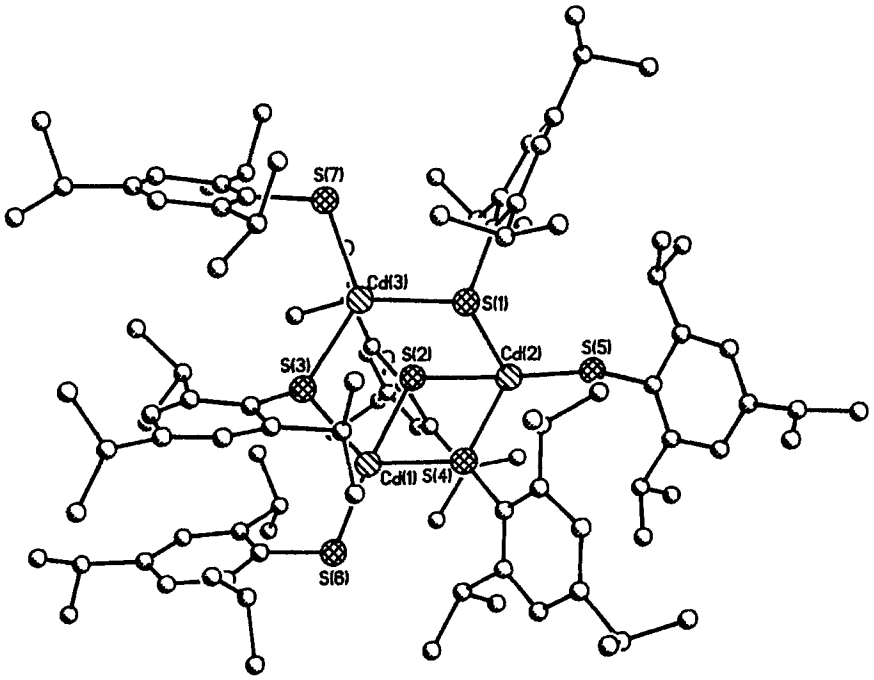

Figure 4 The structure of molecule (A) of complex (2).

Supplementary Material

Lists of anisotropic thermal parameters, bond lengths and angles, and tables of observed and calculated structure factors are available from K.T.

Acknowledgements

We wish to express our gratitude for financial support of this work by China's National Natural Science Foundation.

References

1. W.F. Furey, A.H. Robbins, L.L. Clancy, D.R. Winge, B.C. Wang and C.D. Stout, *Science*, **231**, 704 (1986).
2. K.S. Hagen and R.H. Holm, *Inorg. Chem.*, **22**, 3171 (1983).
3. I.G. Dance, R.G. Garbutt, D.C. Craig, M.L. Scudder and T.D. Bailey, *J. Chem. Soc., Chem. Commun.*, 1164 (1987).
4. I.G. Dance, R.G. Garbutt and M.L. Scudder, *Inorg. Chem.*, **29**, 1571 (1990).
5. A. Choy, D.C. Craig, I.G. Dance and M.L. Scudder, *J. Chem. Soc., Chem. Commun.*, 1246 (1982).
6. G.S.H. Lee, D.C. Craig, I. Ma., M.L. Scudder and I.G. Dance, *J. Am. Chem. Soc.*, **110**, 4863 (1988).
7. E.S. Gruff and S.A. Koch, *J. Am. Chem. Soc.*, **112**, 1245 (1990).
8. D.T. Corwin, E.S. Gruff and S.A. Koch, *J. Chem. Soc., Chem. Commun.*, 966 (1987).
9. M. Bochmann, K. Webb, M. Harman and M.B. Hursthouse, *Angew. Chem., Int. Ed. Engl.*, **29**, 638 (1990).
10. K. Tang, A. Li, X. Jin and Y. Tang, *J. Chem. Soc., Chem. Commun.*, 1590 (1991).
11. P.J. Blower and J.R. Dilworth, *J. Chem. Soc., Dalton Trans.*, 2639 (1985).
12. G.D. Zhou, "Inorganic Structure Chemistry," (Science Press, Beijing, 1982), p. 365.