The Crystal Structure of Cadmium Ethylxanthate

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The crystal structure of cadmium ethylxanthate, $Cd(S_2COC_2H_5)_2$, is monoclinic with $a = 11\cdot289$ (0·010), $b = 5\cdot872$ (0·004), $c = 9\cdot057$ (0·002) Å, $\beta = 90\cdot28$ (0·05)°, and space group *Pa*. The unit cell contains two formula units. Intensity measurements of the X-ray reflexions were made using a counter diffractometer. A three-dimensional structure analysis was carried out with the final R value of 0·022. Absolute structure with reference to the external shape of the crystal was determined. Each cadmium atom is tetrahedrally coordinated to four sulphur atoms belonging to different xanthic groups. Each xanthic group bridges two cadmium atoms forming a two-dimensional network. The networks are piled up through van der Waals contact of the ethyl groups. Cd–S bond lengths are all longer than the sum of the covalent radii of cadmium and sulphur atoms. Two asymmetric xanthic radicals have almost the same configuration. The mean value of the four C–S bond lengths and that of the two C–O bond lengths show the partial double bond character of these bonds. Cd–S–C bond angles range from 97·8° to 107·5°.

Introduction

The crystal structures of zinc and cadmium salts of the same dithioacids, such as zinc and cadmium diethyl-dithiocarbamate (Bonamico, Mazzone, Vaciago & Zambonelli (1965) and Domenicano, Torelli, Vaciago & Zambonelli (1968) respectively) or zinc and cadmium diisopropyldithiophosphate (Lawton & Kokotailo, 1969) are isostructural. With xanthic radicals as ligands, however, the structural data of zinc and cadmium xanthates with the same ligand were not available. Zinc ethylxanthate (hereafter written as ZnEX) (Ikeda & Hagihara, 1966) and cadmium n-butyl-xanthate (Cdn-BX) (Rietveld & Maslen, 1965) show a closely similar structure. Except for the difference in the lengths of the *c* axis of Cdn-BX (25·7 Å, with space group $P2_1/a$) and the *a* axis of ZnEX (18·278 Å, with space group $P2_1/c$) which arises from the difference in the lengths of the alkyl groups of the ligand, the two structures are intrinsically the same. The CdEX crystal was, therefore, expected to be isostructural with that of ZnEX. Contrary to this expectation, a provisional X-ray study of the CdEX crystal showed unit-cell dimensions and diffraction symmetry quite different from those of the ZnEX crystal. A precise structure determination of the CdEX crystal was, therefore, undertaken by the use of a counter diffractometer in order to compare the structure with that of the ZnEX and Cdn-BX crystals.

Experimental

Crystal data

Cadmium ethylxanthate powder was precipitated by mixing aqueous solutions of cadmium acetate and potassium ethylxanthate slowly in a molar ratio of 1:2. The precipitate was filtered and dried in a vacuum desiccator. Crystals were obtained by slow evaporation of a methanol solution of the precipitate at room temperatures. From preliminary Weissenberg photographs the crystal was found to be monoclinic with the *a* axis as the prism axis. The reflexions, systematically absent for *h0l* with *h* odd, revealed the space group to be either the non-centric *Pa* or the centric *P2/a*. *Pa* was adopted because a statistical study indicated lack of centrosymmetry, and was subsequently confirmed by the solution of the structure. The cell dimensions were measured with a diffractometer of equi-inclination type READ 1 (Sakurai, Ito & Iimura, 1970) using Bond's method (Bond, 1960).

Cadmium ethylxanthate, $Cd(S_2COC_2H_5)_2$;
F.W. 354·80
Monoclinic prismatic along the *a* axis,
$a = 11\cdot289$ (0·010), $b = 5\cdot872$ (0·004), $c = 9\cdot057$ (0·002) Å,
$\beta = 90\cdot28$ (0·05)°, $V = 600\cdot4$ (0·7) Å^3.
$D_m = 1\cdot98$ g.cm^{-3} by flotation, $Z = 2$, $D_x = 2\cdot02$ g.cm^{-3}.
Space group *Pa*.
$\mu(\text{Mo } K\alpha) = 25\cdot08$ cm^{-1}.

Intensity measurements

The intensities were measured with the diffractometer READ-1 around the *a* (0 to 14th layers) and [120] (0 to 1st layers) axes. Graphite monochromated Mo $K\alpha$ radiation was used. The cross section of the crystal used for the *a*-axis setting was 0·15 × 0·16 mm. The crystal was rotated in the ω-scan mode with the scanning speed of 1° per minute. The diffracted X-rays were detected with a scintillation counter with a pulse height analyser. Deviations from linearity in the sensitivity of the counter were kept below 1% by the use of zirconium attenuators. For every twenty reflexions a standard reflexion was measured as a monitor. When the deviation of the intensity of the monitor reflexion was less than 1% before and after twenty measurements the intensity data were adopted.

Reflexions within the range $\sin\theta/\lambda \leq 0.5$ were explored and a total of 1903 independent reflexions, excluding the $h00$ reflexions, were obtained. Of these, 1688 reflexions with intensities larger than 2·5 times the standard deviations based on the counting statistics were taken as observed reflexions. These were corrected for Lorentz and polarization factors. No absorption ($\mu R = 0.20$) or extinction corrections were applied. The intensity data around the [120] axis were used for the inter-layer scaling. The intensities of the seven $h00$ ($h = 2,4,\ldots,14$) reflexions were measured from the 0-layer Weissenberg photograph of a b-axis oriented crystal, but they were not used in the calculations of the least squares refinement because of the difference in the accuracy of intensity measurements with the counter and the photographic methods.

Determination of the structure

From a three-dimensional Patterson function approximate coordinates of cadmium and sulphur atoms were found. All the thirteen non-hydrogen atoms in the asymmetric unit were located by a Fourier synthesis. The atomic coordinates and isotropic thermal param-

eters were then refined by three cycles of block-diagonal least-squares to an R value of 0·095. A further five cycles including anisotropic thermal parameters reduced the R value to 0·026. At this point a difference synthesis showed the positions of all the ten hydrogen atoms. These were then included in the refinement with isotropic thermal parameters. After five cycles the final R value was 0·022. The quantity $\sum w(kF_o - F_c)^2$ was minimized, where k is a scale factor. The weight w was chosen as 1 if $0 < F_o < 50$ and $(50/F_o)^2$ if $F_o \geq 50$.
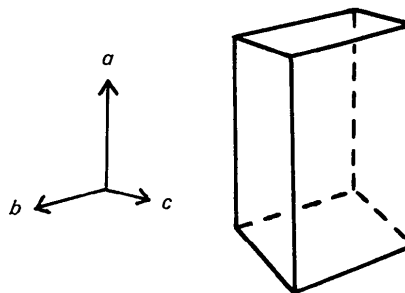
Fig. 1. External shape and crystal axes of a typical cadmium ethylxanthate crystal.

Table 1. *Atomic coordinates of the non-hydrogen atoms with standard deviations*

	x/a	y/b	z/c
Cd	0·50000 (6)	0·45111 (5)	0·50000 (8)
S(1)	0·72043 (10)	0·36398 (20)	0·44560 (14)
S(2)	0·87708 (11)	0·68391 (27)	0·27928 (16)
S(3)	0·53477 (11)	0·87401 (19)	0·54853 (15)
S(4)	0·40895 (14)	1·23609 (19)	0·71527 (15)
O(1)	0·6464 (3)	0·6455 (6)	0·2520 (4)
O(2)	0·3734 (3)	0·7980 (5)	0·7414 (3)
C(1)	0·7436 (4)	0·5738 (7)	0·3214 (5)
C(2)	0·6504 (5)	0·8388 (10)	0·1512 (6)
C(3)	0·5319 (6)	0·8479 (12)	0·0763 (7)
C(4)	0·4335 (4)	0·9597 (7)	0·6728 (5)
C(5)	0·2749 (5)	0·8560 (9)	0·8381 (6)
C(6)	0·2285 (6)	0·6373 (11)	0·9005 (7)

Table 3. *Atomic coordinates and isotropic thermal parameters of the hydrogen atoms with standard deviations*

	x/a	y/b	z/c	$B(\text{Å}^2)$
H(1)	0·671 (6)	0·971 (11)	0·209 (7)	2·5 (1·3)
H(2)	0·719 (6)	0·784 (12)	0·091 (7)	2·9 (1·5)
H(3)	0·522 (11)	0·978 (13)	0·019 (13)	5·2 (2·2)
H(4)	0·476 (6)	0·838 (12)	0·140 (7)	2·7 (1·4)
H(5)	0·508 (9)	0·716 (12)	0·013 (12)	5·1 (1·8)
H(6)	0·304 (7)	0·952 (12)	0·915 (7)	3·2 (1·6)
H(7)	0·210 (6)	0·931 (10)	0·778 (7)	2·2 (1·3)
H(8)	0·165 (7)	0·676 (12)	0·966 (8)	3·4 (1·6)
H(9)	0·303 (9)	0·553 (16)	0·966 (10)	6·3 (2·5)
H(10)	0·184 (11)	0·536 (18)	0·818 (12)	7·7 (2·9)

Table 2. *Thermal parameters of the non-hydrogen atoms with standard deviations*

The thermal parameters refer to the expression:

$$T = \exp\left[-10^{-4}.2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)\right]$$

The B_{eq} values are the equivalent isotropic temperature factors proposed by Hamilton (1959).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
Cd	306 (1)	278 (1)	448 (1)	−27 (2)	30 (1)	10 (2)	2·7
S(1)	272 (5)	351 (5)	528 (6)	27 (4)	7 (4)	120 (5)	3·0
S(2)	281 (5)	667 (9)	536 (7)	−95 (6)	8 (5)	199 (6)	3·9
S(3)	385 (6)	258 (5)	608 (7)	−58 (4)	210 (5)	−49 (5)	3·3
S(4)	647 (8)	240 (4)	503 (6)	28 (5)	213 (6)	1 (5)	3·7
O(1)	282 (15)	440 (17)	439 (16)	13 (14)	−14 (12)	126 (15)	3·1
O(2)	344 (15)	251 (13)	399 (15)	−6 (12)	55 (12)	−8 (12)	2·6
C(1)	249 (17)	315 (19)	333 (18)	−25 (15)	17 (14)	8 (16)	2·4
C(2)	519 (30)	469 (28)	502 (28)	42 (24)	−81 (23)	184 (24)	3·9
C(3)	578 (35)	698 (40)	604 (34)	129 (32)	−154 (29)	191 (32)	5·0
C(4)	325 (19)	216 (16)	359 (19)	−16 (15)	8 (15)	−3 (15)	2·4
C(5)	420 (25)	414 (24)	468 (25)	62 (21)	179 (20)	100 (21)	3·4
C(6)	542 (32)	529 (31)	655 (35)	−36 (27)	253 (27)	180 (28)	4·5

Table 4. *Observed and calculated structure factors*

F_o and F_c values are multiplied by a factor 10. F_o values of the $h00$ ($h = 2, 4, \ldots, 14$) reflexions are left blank, because they were measured photographically and were not included in the least-squares refinements.

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  L  FO  FC        L  FO  FC        L  FO  FC        L  FO  FC        L   FO  FC       L   FU  FC       L   FU  FC        L   FO  FC        L   FO  FC        L   FO  FC        L   FO  FC        L  FO  FC
                   0  69  69                          3 130 128       -8 139 136       -6 533 535        8 119 120        1 324 320       -9 165 166        6  7  L          2 254 257
   0  0  L         1 209 206      -11 100  98         4 278 276       -7 198 198       -5 460 460        9  90  90        2 287 287       -8 216 219                          3 253 259
                   2 146 146      -10  79  85         5 271 272       -6 332 335       -4 629 638       10  51  51        3 364 365       -7 214 217       -4 156 167         4 174 176
 -12  83  72       3 199 198       -9  96  99                         -5 392 396      -311191126                         4 446 497       -6 182 182       -3 150 156         5 130 127
 -11  44  41       4 160 165       -8 189 194      -12  79  69        6 158 155       -214351508         4  5  L         5 395 397       -5 185 189       -2 133 128         6 119 109
 -10  75  85       5 197 203       -7 266 272      -11 134 136       10  54  51       -1 833 842                         6 197 196       -4 288 286       -1  82  86         7 129 117
  -9 202 212       6 135 138       -6 261 266      -10 172 175       11  53  48       -2 383 379        -9  41  31        7 139 139       -3 355 352        0 120 119         8  85  88
  -8 154 163       8 109 108       -5 186 190       -9 256 256                        -1 395 393        -8  80  78        8 143 138       -2 269 266        1 127 123
  -7  41  43       9 125 129       -4 160 155       -7 357 358         2  5  L        212591278         -6 116 114        9 142 145       -1 409 403        2  63  60         7  6  L
  -6 228 236      10 110 117       -3 365 363       -6 412 415                         3 640 632        -5  61  69       10 143 101        0 464 453        4  43  33
  -5 839 859      11  54  54       -2 498 491       -5 696 703       -8  54  47        2 354 346        -4  44  45       11  45  42        1 559 551                        -5 110 109
  -4 946 974                       -1 478 462       -4 846 861       -7  92  97        3 354 346        -3  71  70                         2 548 550         7  1  L         -4 156 158
  -3 676 698        0  5  L         0 238 232       -3 794 800       -5 108 109        5 207 205        -2  85  87         5  4  L         3 454 449                        -3 151 156
  -2 398 411                        1 230 225       -2 823 847       -4  44  23        3 383 379        -1  85  89                         4 517 518      -11  81  83        -2  98 108
 -111501277       -8  80  82        2 569 558       -1 582 586       -3  53  51        4 345 345                         0 108 108         5 445 444      -10 122 123        -1 163 173
  11551278        -7  78  78        3 559 549        0     768       -2 164 163        5 243 241         0  79  76      -10 104 101        6 386 393       -9  70  74         0 276 278
   2 401 412       -4 148 146        4 407 401      112411345        -1 260 261        6 219 224         9  37  47       -9 143 122        7 288 289       -8  57  43         1 260 261
   3 677 697       -3 176 177        5 289 280      213971465        0 120 117        7 200 196        10 128 128       -8 161 163        8 201 200       -7 149 146         2 236 240
   4 947 974       -2  76  83        6 299 295        3 625 637        2  50  42        8 184 180        11 141 137       -7 199 193        9 169 171       -6 143 145         3 214 219
   5 842 858       -1  92  95        7 331 325        6 636 636        3 149 146        9 159 166        12  83  82       -6 241 244       10 130 121       -5 136 137         4 210 208
   6 236 238        1  97  94        8 239 241        5 584 579        4  96  92       10 107 112                        -5 241 296       11  89  85        -4 133 135         5 176 173
   7  51  52        2  75  82        9 141 141        6 482 482        5  50  53       11  79  83         4  1  L        -4 329 338                         -3 359 364         6 126 119
   8 164 164        3 172 177       10  92  96        7 416 416        6  73  74                                         -3 243 248         6  2  L         -2 213 213
   9 209 212        4 142 147       11  99  95        8 248 251        9  49  41        3  4  L        -12  97  85        -2 345 350                         -1  52  51         7  7  L
  10  83  88        8  84  83                         9 261 267                                        -11 120 116       -1 383 386      -11  56  53                          0  49  46
  11  45  45                          1  4  L        10 175 177         2  6  L       -10 100  98       -10 138 134        0 378 380      -10 136 135         1 175 175        1 193 152
  12  72  71        0  6  L                          11  84  71                        -9 166 170        -9 134 132       -8  98  94        1 327 326       -9 162 163         2 271 270
                                   -11  68  71       12  79  77       -9 116 177       -8 208 203        -8 218 221       -6  63  55        2 272 273       -8 164 157         3  41  39
   0  1  L         -8  60  62      -10  81  79                        -8 146 150       -7 117 119        -7 345 352       -6  41  48        3 372 370       -7 153 159         4 238 241
                   -7  48  53       -9 144 134         2  1  L        -6 151 152       -6 398 400       -5  94  89        4 350 348       -6 197 202        5 157 159
 -12  75  74       -6 104 104       -8 187 193                        -5 301 303       -5 432 434       -4 349 345       -2  70  64        5 227 231       -6 176 175         6 193 194
 -11 101 102       -5 116 122       -7 253 256      -12  95  88       -4 403 413       -4 349 345       -3  94  89       -1 101  98        6 176 175       -5 348 353         7 101 100
 -10 152 150       -4  85  86       -6 278 284      -11 137 132        1  50  52       -3 393 395       -2  73  464       0  61  63        7 152 154       -4 403 402        8  77  71
  -9 186 187       -3  49  59       -5 255 262      -10 196 192        3 138 133       -2 218 220       -2 770 753        1 150 146        8 187 189       -3 406 408        9  93  99
  -8 248 266       -1 132 132       -4 431 434       -9 264 268        1 144 146       -1 300 296       -1 761 752        2  94  78        9 143 146       -2 352 350       10  77  73
  -7 290 306        0  56  50       -3 437 436       -8 275 281        2  92  96        0 538 533        0 677 663        3 111 109       10  81  73        1 437 436       11  51  44
  -6 355 369        1 132 135       -2 435 436       -7 320 325        5  72  79        1 566 566        1 631 614        4  80  81                         0 502 500
  -5 537 545        3  45  53       -1 454 450       -6 424 427        6  59  60        2 440 433        2 617 602        5  86  86         5  5  L         1 450 440         7  2  L
  -4 650 661        4  77  86        0 384 377       -5 297 294                         3 297 298        3 648 641        6  95  94                         2 355 346
  -3 550 555        5 118 125        1 485 479       -4 352 351         2  7  L         4 290 290        4 516 514        7  38  34        -9 125 121        3 328 320       -11  51  38
  -2 810 821        6 109 106        2 454 450       -3 328 518                         5 304 308        5 375 375                        -8 189 187        4 374 371       -10  88  86
  -1 969 997        7  46  51        3 286 289       -2 417 408       -6  70  69        6 303 305        6 369 372         4  7  L        -7 237 243        5 256 263       -9 174 176
   0 766 801        8  62  59        4 240 240       -1 647 629       -5 117 121        7 170 179        7 268 270                        -6 269 272        6 194 198       -8 202 202
   1 952 977                        5 317 321        0 262 254       -4 102  98        8 126 131        8 151 157        -5  91  91        5 243 245        7 140 142       -7 214 215
   2 793 797        0  7  L         6 315 315        1 313 301       -3 113 120        9 105 100        9 144 134       -4 106 106        2 263 163        8 163 163       -6 219 223
   3 558 565                        7 210 213        2 574 565       -2 242 242                         10 149 147       -3  65  66        3 360 361        9 171 160       -5 317 320
   4 647 660       -6 109 119        8 144 144        3 727 725       -1 235 237         3  5  L         11 122 122       -2  47  48        2 398 394                         0     672
   5 528 537       -5  72  78        9 114 110        4 636 638        0 163 168                         12  66  68       -1 131 129        1 328 332       11  44  41         1 392 398
   6 345 357       -4 124 124       10 141 138        5 452 447        1  92 100       -9 120 111                         0 183 181        0 229 239                         2 229 230
   7 290 299       -3 149 148       11 102 107        6 392 397        2 131 134       -8 168 167         4  2  L         1 131 130        1 186 183         6  3  L         3 211 211
   8 253 265       -2 139 149                         7 350 350        3 162 162       -7 171 174                         2  85  74        2 226 227                         4 334 333
   9 184 185       -1 102 107         1  5  L         8 354 361        4  99 100       -6  91  86       -11  93  90        3  67  85        3 264 260       -10  63  62        5 253 255
  10 147 152        0  67  69                         9 275 276                        -5 159 157       -9 200 200        4 135 132        4 175 175        9  76  72        5  98  92
  11 109 106        1  89 103      -10  72  52       10 146 150         2  8  L        -4 339 340       -8 153 151        5 111 110        5 130 131        8  68  71        2 124 123
  12  73  74        2 140 150       -9 117 118       11 114 115                        -3 425 429       -7 103 105                         6 146 146        7 187 186        7  53  43
                    3 155 153       -8 199 202       12  87  81       -2 120 114       -2 382 386       -6 286 289         4  8  L         7 159 172       -6 304 304        8 169 171
   0  2  L          4 130 133       -7 190 189                       -1 103 109       -1 430 434       -5 533 540                         8 133 127       -5 355 353        9 181 183
                    5  75  82       -6 210 207         2  2  L        0  74  80        0 430 434       -4 457 464        0  63  59        9  84  84       -4 263 260       10 104  98
 -12  91  87        6 123 119       -5 331 336                        1  68  68        1 520 525       -3 210 204                                         -3 281 278
 -11 138 137                       -4 410 415      -12  73  78        2 112 114        2 489 491       -2 194 191         5  6  L                         -2 511 509         8  1  L
 -10 107 109        0  8  L        -3 461 462      -11 100  93                          3 269 271       -1 618 603                        -11 453 456      -1 453 456
  -9  43  47                       -2 440 448      -10 144 135         3  1  L          4 236 240        0 837 806       -12  86  81        0 318 316        0 188 105      -10 104 104
  -8 174 183       -3  52  53       -1 353 358       -9 164 170                          5 308 308        1 520 504      -11  73  65        1 139 137        9 140  92       -9 122 127
  -7 407 417       -2  49  63        0 507 503       -8 144 148      -12  83  74         6 211 209        2 195 186       -9  89  89        2 154 151                        -8 148 151
  -6 437 447       -1  57  65        1 468 464       -7 257 266      -11  84  81         7 131 132        3 363 355       -8 132 130       -4 167 187         7  3  L         5 130 127
  -5 212 223        0  40  25        2 236 237       -6 365 357       -9 122 121         8 168 167        4 581 579       -7 195 198        3 107 111                        6 209 214
  -4 229 227        1  57  60        3 203 210       -5 440 441       -8 221 223         9  73  78        5 416 419       -6 148 145       -2 168 171       -10  79  83       5 316 321
  -3 600 596        2  56  60        4 246 251       -4 438 434       -7 258 262                          6 206 209       -5 276 280       -1 185 186       -9 141 139       4 345 344
  -2 851 860        3  48  53        5 265 267        3 460 458       -6 149 154         3  6  L          7 161 153       -4 121 124        0 153 153       -8 164 162       3 366 368
  -1 588 585                        6 193 196       -2 673 666       -5 240 238                          8 212 215       -3 423 415        1 157 162       -7 112 121       2 358 361
   0 137 128        1  1  L          7  91  91       -1 745 726       -4 194 194       -8  66  64        9 188 189       -2 205 206        2 189 189       -6 129 125       1 413 415
   1 585 581                        8  76  76        0 609 598       -3 200 201       -7  93  94       10 107 101       -1  92  83        3 178 183       -5 230 232       0 561 566
   2 855 858      -10 140 142        9 142 146        1 442 431       -2  93  98       -6 156 165       11  52  44        0 104 104        4 165 161       -4 245 248       1 510 510
   3 612 606       -9 172 177       10 129 126        2 694 688       -1 240 239       -5 137 141                         1 504 497        5 130 134       -3 188 185       2 340 340
   4 235 231       -8  48  39                         3 633 628       0 695 689       -4 114 121         4  3  L          2 573 574       6 154 152       -2 184 283       3 227 235
   5 214 217       -7 135 136         1  6  L         4 409 402        1 100 100       -3 146 151                         3 177 180       -9  71  59       -1 320 324       307 314
   6 435 446      -10 103 103                         5 240 247       2 124 125       -2 186 188      -11  39  40                         6 158 154       0 325 324       6 207 218
   7 407 418       -5 207 208       -8 122 120        6 267 272       3 266 260       -1 181 187      -10  67  62        5  7  L                          1 320 321       7 153 155
   8 176 186       -4  93  99       -7 214 212        7 292 298       4 427 224        0 186 190       -9 150 147                        -5 151 151       2 246 251       8 147 143
   9  56  48        3 411 410       -6 238 236        8 229 232       5  80  82        1 230 234       -8 192 184       -11 137 128       -4 143 154       3 204 209       9 116 114
  11 134 126       -2 707 709       -5 199 202        9 130 131       6 190 194        2 288 291       -7 236 231       -10 101  96       -3 126 124       4 214 219       10  89  89
  12  88  88       -1 648 640       -4 204 213       10  82  82       7 227 231        3 281 281       -6 182 189       -9 205 199       -2 145 145       5 236 239
                    0 207 201       -3 182 190       11 110  97       8 132 155        4 245 253       -5 208 209       -8 374 363       -1 159 157       6 237 242        8  2  L
   0  3  L          1  85  84       -2 193 197       12  83  76       9  79  72        5 208 208       -4 245 253       -7 148 154        0 153 153       7 174 180
                    2 267 261       -1 208 208                       10  44  46        6 209 206       -3 346 346       -6 292 294        1 174 176       8 122 124      -10  75  76
 -11  78  71        3 267 261        0 201 205         2  3  L       11 112 101        7 174 174       -2 197 188       -5 185 188        2  88  83        9 108 102       -9 122 113
 -10  70  77        4 510 511        1 188 193                       12  64  62        8 127 125       -1 434 426       -4 366 363        3  88  85       10  74  72       -8 182 183
  -9 120 124        5 419 418        2 145 151       -8 165 163                                         0 459 449       -3 185 188        4  50  49                        -1 197 205
  -8 133 140        6 172 176        3 141 144       -7 162 165         3  2  L         3  7  L         1 313 304       -2 245 246        5  65  63         7  4  L        -6 156 163
  -7 179 184        7  91  91        4 169 170       -6  36  37                                         2 245 246       -1 434 426        6  62  62                        -5 167 177
  -6 316 325        8 133 133        5 172 177       -5 255 254      -11  65  59       -6 158 151        3 358 349       -3 577 578        7  76  74       -9  82  75       -4 236 237
  -4 241 248        9 152 147        6 133 131       -4 455 451      -10 116 106       -5 153 145        4 387 384       -2 564 560        9  66  63       -8  81  79       -3 382 382
  -3 440 443       10  93  90        7 110 112       -3 542 541       -9  96  95        -4  98  99        5 324 324       -1 396 303                        -7 169 165       -2 371 370
  -2 467 468                        8 156 154       -2 611 603       -8  93  83        -3 136 132        6 164 165        0 619 605         6  0  L         -6 215 215       -1 186 194
  -1 408 407        1  2  L                         -1 876 871       -7 293 290       -2 225 226        7 137 138        1 571 556                         -5 186 190        0 225 222
   0 310 310                          1  7  L        0 594 589       -6 345 346        1 279 278        8 108 112        2 532 522      -11 137 128       -4 160 171        1 362 362
   1 423 422      -11  52  53                         1 667 662       -5 442 440       -6 607 602        9 126 122        3 338 336      -10 101  96       -3 277 284       2 440 435
   2 477 478      -10  52  53       -6 140 139        2 442 440       -4 607 602       -3 387 386       10 103 105        4 192 186       -9 205 199       -2 376 384       3 280 282
   3 432 432       -9 122 122       -5 121 124        3 234 229       -3 387 388       -2 648 633       11  42  44        5 236 240        -8 374 363       -1 341 338       4 196 194
   5 365 367       -8 153 156       -4 136 135        4 197 194       -2 648 633        1 619 605                         6 205 203       -7 119 123        0 252 251       5 180 187
   6 327 330       -7  69  68       -3 207 204        5 231 233       -1 619 005        0 381 369        4  4  L          7 103 103       -6  85  87        1 279 286       6 218 223
   7 180 182       -6 167 166       -2 253 256        6 130 129        0 381 369        1 314 297                         8  60  57       -5 625 625        2 361 363       7 173 173
   8 131 134       -5 360 348       -1 267 260        7  66  69        1 314 297        2 385 377      -10  44  32        9 169 171       -4 529 523        3 314 319       8 100  95
   9 120 128       -4 263 258        0 150 147        8 131 129        2 385 377        3 325 313       -9  70  58                         -3 615 625        4 231 232       9  71  62
  10  83  81       -3 283 279        1 136 137        9  51  56        3 325 313        4 115 114       -8 151 148                         -2 594 601        5 116 121      10  92  76
  11  73  69       -2 646 631        2 206 203       10  96  94        4 115 114                        -7  73  73         6  6  L         -1 650 661        6 134 140
                   -1 677 665        3 232 229                         5  68  66         2  4  L       -6  56  60                          0 494 502        7  62  66        8  3  L
   0  4  L          0 914 903        4 167 169        2  4  L         6 242 243                         -5 112 109                         2 686 664        8  60  62
                    1 537 530        5  59  59                        7 228 227       -9  75  66       -4  66  65        -6  63  59        3 646 647                       -10  59  90
 -11  49  56        2 792 778        6  62  50       -9  75  66        8 145 144       -8 167 170       -3  93  90       -6 105  98        4 457 453         6  6  L        -9  78  82
 -10 112 117        3 718 702                        -7 167 170        9  47  43       -7  60 111       -2  91  87       -5  57  55        5 318 319                       -8  88  87
  -9 125 129        4 587 578        1  8  L         -6 109 111       10  43  54        6  10  49       -1 208 203       -4 167 166        6 345 350       -9  62  59       -7 141 147
  -8 106 109        3 314 315                        -5  87  92       11  79  78        4  0  L         0 147 141       -3  81  87        7 345 348       -6 105  98       -6 126 141
  -7  83  91        6 184 185       -3  59  56       -4 221 219       12  75  75                        1 231 236       -2 208 205       10 126 112       -5 153 154       -5 248 252
  -6 156 156        7 188 188       -2  85  86                                        -12  83  80        2 190 189      -11 137 128       11 111 102       -4 196 204       -4 196 204
  -5 188 199        8  97  94       -1  75  72         3  3  L       -11  90  82        3 168 167                                         -4 167 166                       -3 257 255
  -4 164 170        9 105 104        0 131 129                       -10 175 175       -9  99  97        4 160 163         6  1  L                           7  5  L        -2 239 231
  -3 197 205       10  52  54        1 137 129      -11 112 106        1 255 250        -8 166 169       5 156 155                                                         -1 390 392
  -2 139 143                         2 103 101      -10 175 175        2 156 159       -7 485 491        6 212 211      -11 106 105       -10 122 123       -8 102 103       0 225 225
  -1 199 200        1  3  L          3  88  71        2 156 159                         7 196 193        1 520 511       0 506 499                          -7 153 154       1 244 250
                                                                                                                                                                          2 281 274
```

Table 4 (cont.)

L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC	L	FO	FC
3	253	262	-2	114	111	9	3	L	-3	152	156				-5	199	192				-1	126	130	-2	245	254	6	95	91	2	139	141	-5	156	153
4	153	157	-1	101	95				-2	189	191	-9	105	90	-4	283	276	-4	60	49	0	165	164	-1	230	243	7	46	53	3	70	74	-4	206	204
5	118	117	0	78	83	-4	47	46	-1	166	163	-8	66	62	-3	226	224	-8	73	65	1	219	223	0		112				4	41	27	-3	207	208
6	162	160	1	73	76	-6	138	134	0	157	155	-7	67	65	-2	166	159	-6	114	120	2	210	208	1	79	82	12	3	L	5	42	37	-2	114	116
7	164	163	2	90	93	-7	133	130	1	168	168	-6	138	137	-1	59	55	-5	150	153	3	174	167	2	146	149							-1	98	100
8	115	114				-8	59	49	2	109	107	-5	157	159	0	110	112	-4	54	57	4	145	146	3	140	147	-6	50	62	13	2	L	0		214
			9	1	L	-5	74	71	3	143	136	-4	168	166	1	183	184	-3	49	46	5	146	137	4	82	81	-5	103	102				1	230	246
8	4	L				-4	203	209	4	147	145	-3	224	227	2	68	65	-2	78	84	6	151	144	5	106	105	-4	138	135	-6	151	140	2	185	192
			-10	92	83	-3	288	296	5	143	140	-2	253	253	5	79	77	-1	148	151	7	132	123	6	159	163	-3	101	101	-5	112	111	3	151	150
-4	123	122	-9	80	73	-2	237	240	6	142	137	-1	341	341	6	68	75	0	109	115				7	126	127	-2	84	84	-4	160	157	4	128	125
-3	99	104	-8	88	86	-1	206	212	7	111	107	0	340	340	7	70	62	1	109	111	11	4	L	8	101	91	-1	144	146	-3	196	193	5	127	126
-2	59	74	-7	88	87	0	310	316				1	334	336	8	51	50	2	123	119							0	163	166	-2	179	176			
-1	143	145	-6	78	73	1	353	354	9	6	L	2	427	424				3	145	146	-6	93	85	12	1	L	1	165	162	-1	112	109	14	1	L
0	61	62	-5	194	198	2	333	334				3	375	373	10	4	L	4	139	141	-5	178	172				2	119	123	0	55	63			
1	71	65	-4	42	48	3	231	232	-5	102	96	4	296	295				5	63	68	-4	202	202	-8	84	83	3	82	84	1	78	73	-5	76	79
2	179	187	-3	100	106	4	204	202	-4	137	131				-7	50	35	6	105	102	-3	181	181	-7	126	117	4	102	103	2	130	129	-4	159	161
3	229	234	-2	111	118	5	196	195	-3	122	120	5	225	226	-6	61	60	7	92	88	-2	140	142	-6	162	162	5	142	146	3	111	113	-3	201	204
4	213	213	-1	417	425	6	159	160	-2	127	123	6	204	199	-5	94	91	8	81	76	-1	177	179	-5	210	218	6	121	116	4	55	50	-2	174	176
5	125	124	0	331	337	7	125	121	-1	117	116	7	177	180	-4	79	84				0	268	265	-4	184	194				6	68	62	-1	163	169
6	95	96	1	156	153	8	68	63	0	137	133	8	138	134	-3	108	110	11	2	L	1	213	211	-3	198	203	12	4	L				0	193	197
7	121	114	2	117	124	9	57	48	1	153	150	9	95	88	-2	188	189				2	144	145	-2	262	268				13	3	L	1	221	224
8	80	69	3	230	230				2	143	140				-1	187	187	-8	113	108	3	124	118	-1	252	253	-4	45	29				2	223	227
9	44	40	4	243	247	9	4	L	3	134	133	10	2	L	0	172	171	-7	173	166	4	128	132	0	230	243	-3	73	72	-5	114	116	3	162	161
			5	114	118				4	164	158				1	85	89	-6	179	174	5	135	128	1	197	201	-2	58	62	-4	87	81	4	130	132
8	5	L	6	58	55	-8	137	135				-9	94	92	2	68	68	-5	111	111	6	106	103	2	191	199	-1	66	66	-3	127	130	5	116	114
			8	72	73	-7	171	169	10	0	L	-8	169	165	3	69	66	-4	102	105				3	185	192	0	145	142	-2	214	215			
-7	47	40				-6	186	182				-7	165	164	4	67	68	-3	64	60	11	5	L	4	141	144	1	157	161	-1	206	209	14	2	L
-4	39	60	9	2	L	-5	131	130	-9	187	172	-6	122	113	5	66	59	-2	116	120				5	108	107	2	118	116	0	156	155			
-2	68	70				-4	171	177	-8	144	142	-5	128	122	6	61	58	-1	134	134	-5	184	182	6	135	130	3	83	83	1	128	127	-5	118	114
-1	90	90	-9	102	98	-3	243	249	-7	151	147	-4	238	240				0	73	73	-4	232	225	7	123	126	4	101	102	2	150	147	-4	86	82
0	50	39	-8	135	132	-2	292	294	-6	278	276	-3	334	332	10	5	L	1	80	78	-3	176	168	8	82	76	5	94	88	3	155	152	-3	86	86
1	37	23	-7	111	112	-1	228	235	-5	309	300	-2	262	263				2	131	131	-2	153	146							4	112	116	-2	134	140
2	59	51	-6	188	189	0	165	171	-4	218	212	-1	187	188	-6	69	67	3	105	112	-1	168	160	12	2	L	12	5	L	5	70	74	-1	161	165
3	81	85	-5	289	292	1	209	204	-3	280	274	0	206	205	-5	75	71	4	107	103	0	182	177										0	115	117
			-4	253	257	2	272	274	-2	422	427	1	248	247	-2	44	51	5	97	95	1	183	181	-7	105	106	-3	57	55	13	4	L	1	84	82
8	6	L	-3	271	277	3	218	224	-1	393	400	2	278	278	-1	51	41	6	101	95	2	150	143	-6	132	131							2	105	105
			-2	414	419	4	182	180	0		302	3	196	197	0	44	39	7	124	117	3	110	103	-5	149	149	13	1	L	-3	88	91	3	117	115
-6	81	83	-1	342	344	5	170	174	1	317	324	4	145	144	1	75	67	8	121	110	4	93	85	-4	126	132				-2	119	116	4	113	113
-5	43	39	0	338	340	6	164	159	2	311	317	5	163	157	2	52	42							-3	136	143	-7	77	62	-1	160	159	5	81	77
-4	45	49	1	171	170	7	128	118	3	355	356	6	62	59				11	3	L	12	0	L	-2	169	167	-6	57	51	0	161	160			
-2	73	80	2	80	85	8	95	87	4	368	373				10	6	L							-1	224	227	-5	60	59	1	122	116	14	3	L
-1	109	113	3	212	210				5	236	233	9	73	68				-7	101	84	-8	168	157	0	232	236	-4	109	108	2	100	97			
2	88	81	4	209	210	9	5	L	6	139	134				-1	51	44	-6	140	97	-7	262	250	1	174	180	-3	183	185	3	114	115	-3	33	31
3	82	82	5	154	154				7	153	146	10	3	L	0	76	65	-5	85	78	-6	281	274	2	111	121	-2	160	162				-2	72	70
4	73	69				-7	175	173	8	184	169				1	50	45	-4	160	161	-5	230	229	3	127	132	-1	114	119	14	0	L	-1	61	65
						-6	251	249	9	133	129	-8	147	141				-3	188	190	-4	222	230	4	182	163	0	81	86				0	57	64
8	7	L				-5	193	189				-7	168	161	11	1	L	-2	130	133	-3	213	215	5	147	143	1	164	170	-6	65	60	3	81	85
						-4	157	157	10	1	L	-6	134	127																								

Fig. 2. Configuration of atoms in cadmium ethylxanthate within the sectional layer, $0 \leq z < 1\cdot0$, viewed along the c axis. Thick circles and lines denote atoms and bonds within the layer $0\cdot5 \leq z < 1\cdot0$.
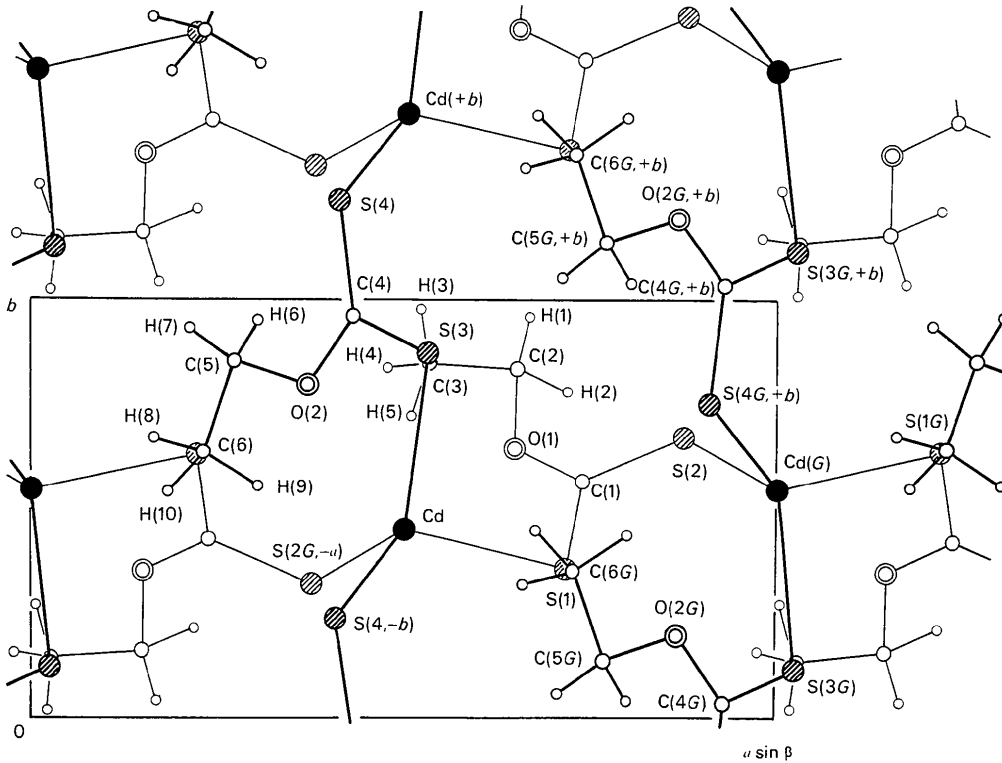
The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The correction factors of the anomalous dispersion were assumed as follows: $\Delta f' = -0\cdot85$, $\Delta f'' = 1\cdot50$ for the Cd atom and $\Delta f' = 0\cdot10$, $\Delta f'' = 0\cdot20$ for the S atoms. The angular dependence of these quantities were neglected.

The final atomic coordinates for non-hydrogen atoms are given in Table 1, the anisotropic thermal parameters for non-hydrogen atoms in Table 2, and the atomic coordinates and isotropic thermal parameters for hydrogen atoms in Table 3. The observed and calculated structure factors are compared in Table 4.

Absolute structure

The crystal of CdEX is polar in the *a*-axis direction. A typical example of the external shape of the crystal is shown in Fig. 1. With the space group *Pa*, the reflexions *hkl* and *h̄k̄l̄* are not equivalent as the result of the breakdown of Friedel's law. Since the inequality in intensity for *hkl* and *h̄k̄l̄* reflexions is reversed for the reversed structure, this reversed structure model was checked and also refined by block-diagonal least-squares methods. The final *R* value became 0·024.

Although the difference in the *R* values is small for both structures, a detailed examination of the individual reflexions and standard deviations of parameters clearly excludes the possibility of obtaining a better structure by the reversal of the atomic coordinates. Therefore, the parameters given in Table 1 correspond to the correct absolute structure with reference to the external shape of the crystal shown in Fig. 1.

Discussion

The structure in general

The structure as seen along the *c* axis is shown in Fig. 2. Each cadmium atom is surrounded by four sulphur atoms arranged almost tetrahedrally around it. Each sulphur atom belongs to a different xanthic group, which, in turn, bridges two adjacent cadmium atoms in such a way that $-S(1)C(1)S(2)-$ bridges them in the *a*-axis direction, while $-S(3)C(4)S(4)-$ bridges them in the *b*-axis direction completing a two-dimensional network consisting of the cadmium atoms and xanthic groups. The ethyl groups protrude on both sides of the network. This situation is clearly seen in Fig. 3, which shows the structure as seen along the *b* axis. The con-

Table 5. *Atomic distances and bond angles for the non-hydrogen atoms with standard deviations*

Bond distances		Bond angles	
Cd—S(1)	2·590 (0·003) Å	S(1)———Cd–S(2G, – a)	107·98 (0·07)°
Cd—S(2G, – a)	2·554 (0·002)	S(1)———Cd–S(3)	94·47 (0·05)
Cd—S(3)	2·552 (0·002)	S(1)———Cd–S(4, – b)	116·10 (0·06)
Cd—S(4, – b)	2·544 (0·002)	S(2G,–a)-Cd–S(3)	121·29 (0·05)
C(1)–S(1)	1·690 (0·004)	S(2G,–a)-Cd–S(4, – b)	103·05 (0·06)
C(1)–S(2)	1·685 (0·005)	S(3)———Cd–S(4, – b)	114·42 (0·05)
C(4)–S(3)	1·685 (0·005)	Cd———S(1)–C(1)	97·8 (0·2)
C(4)–S(4)	1·691 (0·004)	Cd(G)—S(2)–C(1)	100·8 (0·2)
C(1)–O(1)	1·331 (0·005)	Cd———S(3)–C(4)	107·5 (0·2)
C(4)–O(2)	1·323 (0·005)	Cd(+ b)–S(4)–C(4)	103·6 (0·2)
O(1)–C(2)	1·457 (0·007)	S(1)———C(1)–S(2)	124·9 (0·3)
C(2)–C(3)	1·498 (0·009)	S(1)———C(1)–O(1)	114·5 (0·3)
O(2)–C(5)	1·459 (0·006)	S(2)———C(1)–O(1)	120·6 (0·3)
C(5)–C(6)	1·499 (0·008)	S(3)———C(4)–S(4)	123·4 (0·3)
		S(3)———C(4)–O(2)	116·8 (0·3)
		S(4)———C(4)–O(2)	119·8 (0·3)
		C(1)———O(1)–C(2)	120·9 (0·4)
		O(1)———C(2)–C(3)	106·3 (0·5)
		C(4)———O(2)–C(5)	120·6 (0·4)
		O(2)———C(5)–C(6)	107·2 (0·4)

Table 5 *(cont.)*

Van der Waals contact distances

CH₃–CH₃:	
C(3, + c)–C(6)	3·97 (0·01) Å
C(3, + c)–C(6G)	3·95 (0·01)
C(3, + c)–C(6G, + b)	4·08 (0·01)

CH₃–CH₂:	
C(3, + c)–C(5)	3·61 (0·01)
C(3, + c)–C(5G, + b)	3·91 (0·01)
C(6G)–C(2, + c)	3·71 (0·01)
C(6G, + b)–C(2, + c)	3·93 (0·01)

CH₂–CH₂:	
C(2, + c)–C(5G, + b)	3·64 (0·01)

figuration of atoms within the network is quite similar to that of Cdn-BX and ZnEX. The difference arises in the packing mode of these networks by van der Waals contact. With Cdn-BX and ZnEX the methyl ends of the alkyl groups of the network are brought into van der Waals contact with those of the neighbouring network through twofold screw axes or symmetry centres, whereas in CdEX the methyl and methylene groups of the ethyl groups of the network are brought into van der Waals contact with those of the network translated along the *c* axis. Van der Waals contacts are shown by broken lines in Fig. 3.

Atomic distances and bond angles are listed in

Table 6. *Bond distances and angles for the hydrogen atoms with standard deviations*

Bond distances

C(2)–H(1)	0·96 (0·07) Å
C(2)–H(2)	1·00 (0·07)
C(3)–H(3)	0·94 (0·12)
C(3)–H(4)	0·86 (0·07)
C(3)–H(5)	1·00 (0·11)
C(5)–H(6)	0·96 (0·08)
C(5)–H(7)	1·02 (0·07)
C(6)–H(8)	0·96 (0·08)
C(6)–H(9)	1·14 (0·11)
C(6)–H(10)	1·08 (0·12)

O···H van der Waals
contact distances

O(1)–H(4)	2·45 (0·07) Å
O(1)–H(5)	2·70 (0·11)
O(2)–H(9)	2·62 (0·10)
O(2)–H(10)	2·73 (0·12)

Bond angles

O(1)–C(2)–H(1)	107 (4)°
O(1)–C(2)–H(2)	97 (4)
H(1)–C(2)–H(2)	112 (6)
H(1)–C(2)–C(3)	115 (4)
H(2)–C(2)–C(3)	117 (4)
C(2)–C(3)–H(3)	113 (7)
C(2)–C(3)–H(4)	111 (5)
C(2)–C(3)–H(5)	118 (7)
H(3)–C(3)–H(4)	110 (9)
H(3)–C(3)–H(5)	107 (10)
H(4)–C(3)–H(5)	97 (8)
O(2)–C(5)–H(6)	108 (5)
O(2)–C(5)–H(7)	109 (4)
H(6)–C(5)–H(7)	112 (6)
H(6)–C(5)–C(6)	111 (5)
H(7)–C(5)–C(6)	109 (4)
C(5)–C(6)–H(8)	107 (5)
C(5)–C(6)–H(9)	108 (5)
C(5)–C(6)–H(10)	112 (7)
H(8)–C(6)–H(9)	109 (7)
H(8)–C(6)–H(10)	102 (8)
H(9)–C(6)–H(10)	118 (8)

Tables 5 and 6 with standard deviations in parentheses.

Configuration of sulphur atoms about the cadmium atom

As shown in Fig. 4(a) four sulphur atoms are coordinated to a cadmium atom in a distorted tetrahedral configuration. Of the four cadmium–sulphur bonds, three, Cd(G)–S(4G, +b): 2·544 (0·002), Cd(G)–S(3G): 2·552 (0·002) and Cd(G)–S(2): 2·554 (0·002) Å, are almost equal in length, while the other one, Cd(G)–S(1G): 2·590 (0·003) Å, is by far the longest. These bond lengths are all longer than the sum of the tetrahedral covalent radii of cadmium and sulphur atoms, 2·52 Å (Pauling, 1960). The S–Cd–S bond angles of the distorted tetrahedral configuration range from 94·47 (0·05)° to 121·29 (0·05)°. The configuration is similar to that of Cdn-BX shown in Fig. 4(b) for comparison. However, when Cd–S bond lengths are compared for CdEX and Cdn-BX along each corresponding bond direction, they are all shorter for the former. The difference between the Cd(G)–S(3G) and Cd–S(21) bond lengths, −0·008 (0·009) Å, is insigni-
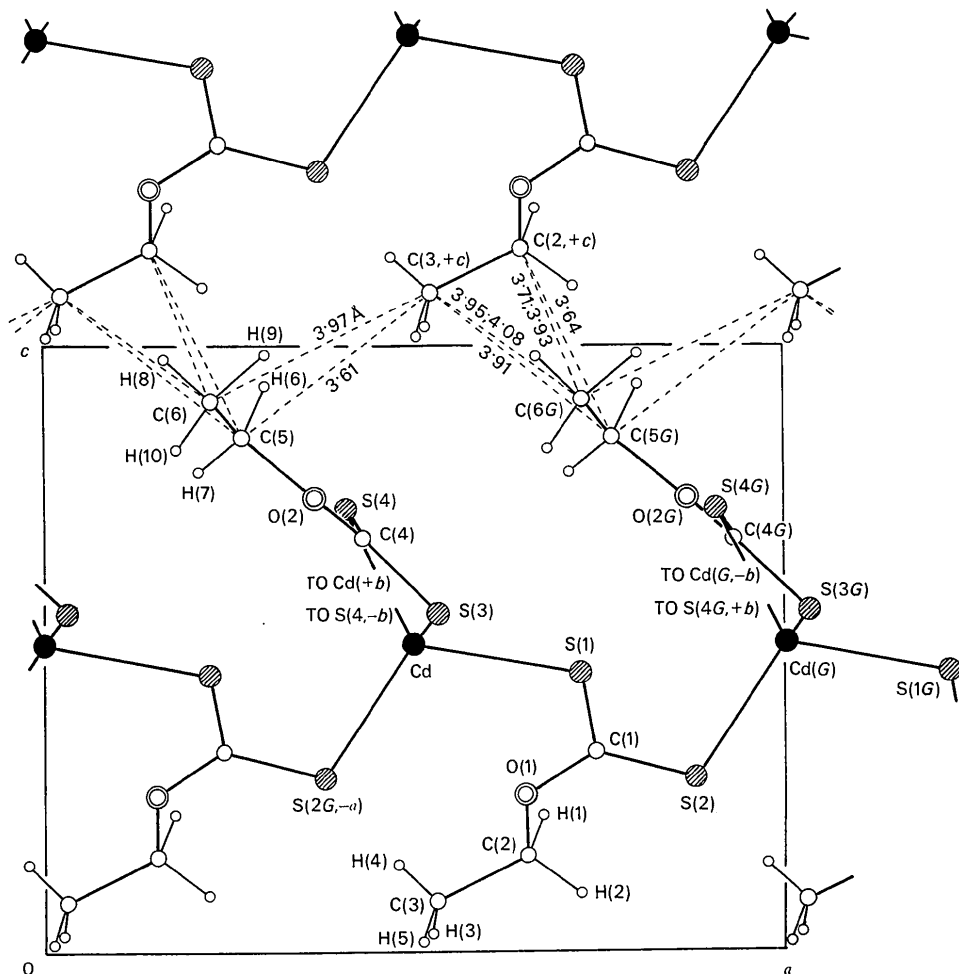
Fig. 3. Structure of cadmium ethylxanthate viewed along the *b* axis. Broken lines denote van der Waals contact.

ficant, while the differences of the Cd–S bond lengths along the other three bond directions, -0.029 (0.008), -0.036 (0.009) and -0.058 (0.011) Å, are all significant. The covalent bond character of the coordinate bond is, therefore, concluded to be stronger for CdEX than for Cdn–BX. As compared with ZnEX in which four Zn–S bond lengths are equal to the sum of the tetrahedral covalent radii of zinc and sulphur atoms, 2·35 Å, within the error limit, the covalent character of the metal atom–sulphur atom bond is thought to be stronger for the Zn–S bonds in ZnEX than the Cd–S bonds in CdEX. Distortion of the tetrahedral configuration is much less for ZnEX than for CdEX; the maximum deviation of the S–metal–S bond angles from the tetrahedral angle of 109·5° being 6·9° for ZnEX and 15·0° for CdEX. This also supports the conclusion

of a stronger covalent character for the Zn–S bond than for the Cd–S bond with these crystals.

Xanthic radicals

The bond lengths and angles of the two asymmetric xanthic radicals are shown in Fig. 5. The four C–S bond lengths, 1·690 (0·004), 1·685 (0·005), 1·685 (0·005) and 1·691 (0·004) Å are equal to each other. The deviation of each bond length from the mean value, 1·688 Å, is insignificant. As compared with the case of diethyldixanthogen crystal (Watanabe, 1971), in which C–S single bond and C=S double bond lengths are 1·729 (0·013) and 1·620 (0·009) Å respectively, the C–S bonds in CdEX are interpreted to have a nature intermediate between single and double bond character. CdEX is different from Cdn-BX or ZnEX in this respect. With Cdn-BX the lengths of the two C–S bonds differ markedly from each other in each of the two asymmetric xanthic groups. The average value of the longer C–S bonds is 1·75 ± 0·03 Å and of the shorter ones 1·63 ± 0·03 Å. These values agree well with the C–S and C=S bond lengths found in diethyldixanthogen. In ZnEX the four C–S bond lengths are 1·61, 1·69, 1·70 and 1·70 Å, all ± 0·03 Å. One bond distance, 1·61 Å, corresponds to the C=S bond, and the remaining three to distances intermediate between C–S and C=S bonds.

The C(1)–O(1) and C(4)–O(2) bond lengths, 1·331 (0·005) Å and 1·323 (0·005) Å respectively, are equal. They are shorter than the C–O single bond distance of 1·43 Å and longer than the C=O double bond distance of 1·29 Å (Pauling, 1960). O(1)–C(2) and O(2)–C(5) bond lengths, 1·457 (0·007) Å and 1·459 (0·006) Å, are also equal to each other. They are a little longer than but are almost in conformity with the C–O single bond distance. Thus, when bond nature intermediate between a single bond and a double bond is represented with the symbol $=---=$, the following bond type is concluded for the xanthic group in CdEX.

$$\begin{array}{c} S \\ {\scriptstyle\diagdown} \\ {\scriptstyle\diagup} C - - - O \\ S \end{array}$$
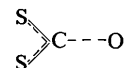
This type of bonding has been found with potassium ethyl xanthate (KEX) and interpreted by a resonance among the three possible electronic structures of the xanthic group (Mazzi & Tadini, 1963).

The SSCO groups are both planar. The deviation of the C(1) atom from the plane defined by S(1), S(2) and O(1) and that of the C(4) atom from the plane defined by S(3), S(4) and O(2) are 0·017 Å and -0.012 Å respectively, as shown in Fig. 5. They are not significant.

Bond lengths between carbon atoms in the ethyl groups, C(2)–C(3): 1·498 (0·009) Å and C(5)–C(6): 1·499 (0·008) Å, are almost in conformity with the C–C single bond distance of 1·53–1·54 Å. The bond angles, O(1)–C(2)–C(3): 106·3 (0·5)° and O(2)–C(5)–C(6): 107·2 (0·4)°, are also almost in conformity with the
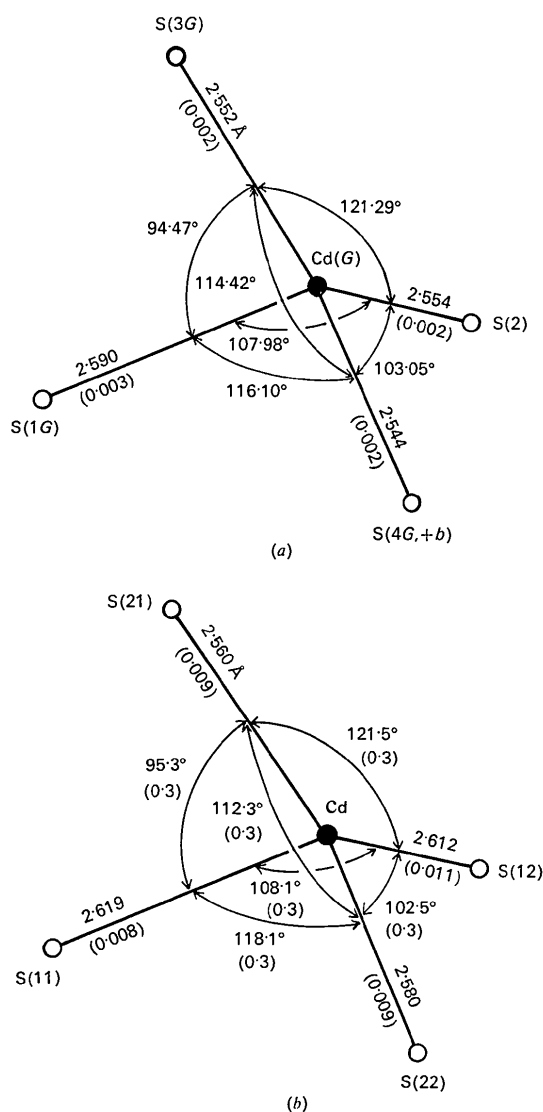
Fig. 4. Configuration of four sulphur atoms about a cadmium atom in (a) cadmium ethylxanthate and (b) cadmium n-butylxanthate (Rietveld & Maslen, 1965) crystals.

tetrahedral angle 109·5°. The carbon atoms of each ethyl group are not coplanar with the plane of SSCO-atoms. Their deviations from each plane are shown in Fig. 5 and can be explained in terms of the small rotations of the ethyl groups about the O–C bonds as in the case of ZnEX.

Van der Waals contact of the ethyl groups

Van der Waals contact distances are shown in Fig. 3 and with standard deviations in Table 5. The distances between two methyl groups range from 3·95 to 4·08 Å, between methyl and methylene groups from 3·61 to 3·93 Å and between two methylene groups 3·64 Å. These distances are best explained by assigning the methyl and methylene groups the van der Waals radii 2·0 Å and 1·8 Å respectively.

Hydrogen atoms

The atomic coordinates and isotropic thermal parameters of the hydrogen atoms were determined by a difference Fourier synthesis and least-squares refinements. The results are listed in Table 3. The bond lengths and bond angles in which the hydrogen atoms are involved

Fig.5. Configuration of the two asymmetric ethylxanthate ligands in cadmium ethylxanthate.
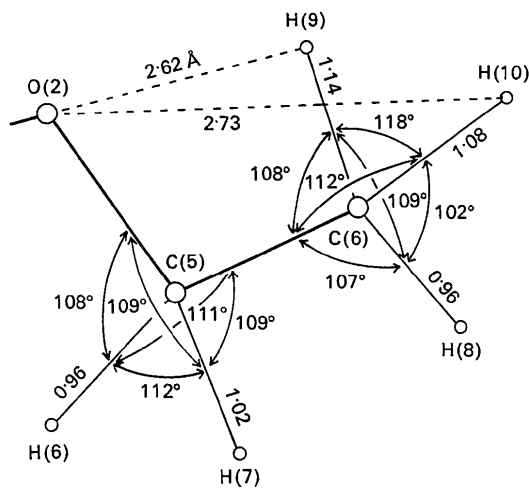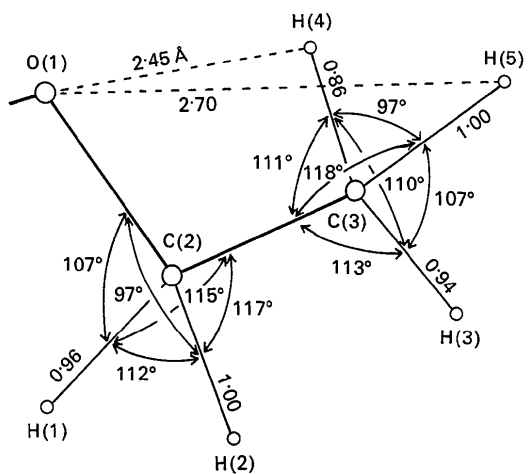
Fig.6. Configuration of the hydrogen atoms in the ethyl groups of cadmium ethylxanthate.

and the oxygen–hydrogen van der Waals contact distances are listed in Table 6 and shown in Fig. 6. C–H bond lengths and O–C–H, C–C–H and H–C–H bond angles are in conformity with the C–H bond length of $1·09 \pm 0·01$ Å (Pauling, 1960) and the tetrahedral angle of $109·5°$ when the error limit of $\pm 2\sigma$ is considered, except for C(3)–H(4): $0·86$ $(0·07)$ Å and O(1)–C(2)–H(2): 97 $(4)°$. For the former the lengthening of the bond distance and for the latter the widening of the bond angle both by about 3σ are necessary so that H(4) and H(2) atoms will occupy expected reasonable positions. The distances between oxygen and hydrogen atoms, O(1)–H(4): $2·45$ $(0·07)$, O(1)–H(5): $2·70$ $(0·11)$, O(2)–H(9): $2·62$ $(0·10)$ and O(2)–H(10): $2·73$ $(0·12)$ Å, are in conformity with the sum of the van der Waals radii of oxygen and hydrogen atoms, $2·6$ Å.

The numerical calculations were performed on the FACOM 270-30 computer of this Institute with the universal crystallographic computation program system *UNICS* (Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967).

References

BONAMICO, M., MAZZONE, G., VACIAGO, A. & ZAMBONELLI, L. (1965). *Acta Cryst.* **19**, 898.
BOND, W. L. (1960). *Acta Cryst.* **13**, 814.
DOMENICANO, A., TORELLI, L., VACIAGO, A. & ZAMBONELLI, L. (1968). *J. Chem. Soc.* (*A*), p. 1351.
HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609.
IKEDA, T. & HAGIHARA, H. (1966). *Acta Cryst.* **21**, 919.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
LAWTON, S. L. & KOKOTAILO, G. T. (1969). *Inorg. Chem.* **8**, 2410.
MAZZI, F. & TADINI, C. (1963). *Z. Kristallogr.* **118**, 378.
PAULING, L. (1960). *The Nature of the Chemical Bond.* 3rd ed. Ithaca: Cornell Univ. Press.
RIETVELD, H. M. & MASLEN, E. N. (1965). *Acta Cryst.* **18**, 429.
SAKURAI, T., ITO, T. & IIMURA, Y. (1970). *Rep. Inst. Phys. Chem. Res.* **46**, 82.
SAKURAI, T., ITO, T., IWASAKI, H., WATANABE, Y. & FUKUHARA, M. (1967). *Rep. Inst. Phys. Chem. Res.* **43**, 62.
WATANABE, Y. (1971). *Acta Cryst.* **B27**, 644.

The Crystal Structure of Potassium *O,O*-Dibenzylphosphorodithioate KS₂P(O-CH₂-C₆H₅)₂

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The crystal structure of potassium *O,O*-dibenzylphosphorodithioate [KS₂P(O–CH₂–C₆H₅)₂] has been determined with diffractometer data. The space group is triclinic, $P\bar{1}$, and the unit cell contains two formula units. The unit-cell dimensions at $23°C$ are $a = 11·468$ (6), $b = 11·735$ (6), $c = 6·542$ (4) Å, $\alpha = 99·48$ (4), $\beta = 98·50$ (3), $\gamma = 69·09$ $(2)°$. The intensities were measured by the 2θ-scan method with Mo $K\alpha$ radiation. The structure was solved using symbolic addition procedures and refined by block-diagonal least-squares methods to an R value of $0·043$. The K⁺ ion is coordinated to four sulfur atoms at an average distance of $3·319$ Å and to three oxygen atoms at an average distance of $2·971$ Å. The P–O distances are both $1·619$ (3) Å and the average P–S distance is $1·957$ Å. The conformation of the ester groups with respect to the phosphorodithioate group is synclinal, and antiperiplanar.

Introduction

The phosphorodithioate anion is an analog of the phosphate ion in which two oxygen atoms have been replaced by sulfur. Both simple and extended Hückel calculations on the π-bonding system in phosphate diesters that uses the $3d$ orbitals on phosphorus suggest that the conformation stabilized most by π bonding is one in which the ester groups are rotated $90°$ about the P–O bond out of the plane of the phosphorus and esterified oxygen atoms (Collin, 1966, 1969).

The same stable conformation would be predicted for the analogous *O,O*-diester phosphorodithioate ion in which the π bonding should be similar to that in the phosphate diester.

The crystal structure of potassium *O,O*-dimethylphosphorodithioate, KPS₂(O–CH₃)₂, has been solved by Coppens, MacGillavry, Hovenkamp & Douwes (1962), and the conformation does agree closely with that expected from the Hückel calculations (Collin, 1966). However, the large thermal motion of the carbon and oxygen atoms, together with an anomalously