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# The Crystal and Molecular Structure of Tetrakis-(*N*,*N*-diethyldithiocarbamato)tin(IV)

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The crystal structure of tetrakis-(*N*,*N*-diethyldithiocarbamato)tin(IV) has been determined from three-dimensional X-ray diffraction data. Unit-cell dimensions are $a = 15{\cdot}64 \pm 0{\cdot}02$, $b = 15{\cdot}75 \pm 0{\cdot}02$, $c = 13{\cdot}91 \pm 0{\cdot}02$ Å, and $\beta = 112{\cdot}5 \pm 0{\cdot}2°$. The density by flotation is 1·50 g.cm$^{-3}$. Four molecules in the unit cell give a calculated density of 1·492 g.cm$^{-3}$. By visual estimation of film data, the intensities of 1341 independent reflections were obtained. The structure was solved by three-dimensional Patterson and Fourier methods and refined by full-matrix least squares to a conventional $R$ value of 10·2%. Within the limitations of the data, the space group is $I2/a$. The arrangement of sulfur atoms about the tin atom is distorted octahedral with two bidentate and two monodentate ligands. The latter occupy *cis* positions. Sulfur–sulfur distances and sulfur–tin–sulfur angles suggest some weak interactions between sulfur atoms in different ligands. The Sn–S distances average 2·546 (7) Å for bidentate ligands. One of the sulfur atoms of the monodentate ligand is 2·504 (7) Å from the tin.

## Introduction

Recent X-ray studies of tin(IV) and organotin(IV) compounds have revealed coordination numbers for the tin of six, seven, and eight. For example, dimethyltin bis-(8-hydroxyquinolinate) was found (Schlemper, 1967) to have tin in a six-coordinate distorted octahedral geometry with *cis* methyl groups. In chlorotris-(tropolonato)tin(IV) (Park, Collins & Hoard, 1970), the tin is in a nearly perfect pentagonal bipyramidal environment. In bis-(phthalocyaninato)tin(IV) (Bennett, Broberg & Baenziger, 1967), the tin coordination is approximately square antiprismatic. In $Sn(NO_3)_4$ (Garner, Sutton & Wallwork, 1967) the tin coordination number can be considered to be eight with a dodecahedral geometry.

Our current interest is in a series of *N*,*N*-diethyldithiocarbamate (dtc) complexes of tin(IV). These complexes were the subject of Mössbauer and infrared studies by Kazimir, Cefola & Erickson (1967). The solid infrared spectrum of Sn(dtc)$_4$ was compared with that of U(dtc)$_4$, known to be eight-coordinate (Brown, Holah & Rickard, 1970), and the presence of extra bands interpreted as indicative of more than one type of dtc environment in the tin complex. One possibility suggested was Sn(dtc)$_3^+$dtc$^-$, and the workers were able to prepare Sn(dtc)$_3^+$B(C$_6$H$_5$)$_4^-$ from a CH$_3$CN solution of Sn(dtc)$_4$ by addition of B(C$_6$H$_5$)$_4^-$. They indicate that their findings would also be in keeping with the presence of mono- and bidentate dtc ligands in a neutral complex in the solid state. The Mössbauer spectra of Sn(dtc)$_4$ and Sn(dtc)$_3^+$B(C$_6$H$_5$)$_4^-$ were identical as was expected if both contain six-coordinate tin. A considerable difference in isomer shift was expected for an eight-coordinate complex.

Our X-ray study of Sn(dtc)$_4$ was undertaken to clearly establish the nature of the coordination of the dithiocarbamate ligands as well as to extend our studies of higher coordination geometries of tin(IV).

## Experimental

### *Crystal preparation*

Crystals of tetrakis-(*N*,*N*-diethyldithiocarbamato)-tin(IV) were prepared by the following method. Solutions of 0·75 g of SnCl$_4$.5H$_2$O in 20 ml of absolute ethanol and 3·8 g of sodium *N*,*N*-diethyldithiocarbamate trihydrate in 50 ml of absolute ethanol were prepared and filtered. The tin tetrachloride solution was then added dropwise with stirring to the solution containing the ligand, which was present in an 8:1 molar excess. The bright red-orange crystals which precipitated were filtered, air dried, and recrystallized from dichloromethane. Single crystals suitable for X-ray diffraction were recovered.

### *X-ray data*

Tetrakis-(*N*,*N*-diethyldithiocarbamato)tin(IV) crystallizes in the monoclinic crystal system with four molecules in a unit cell of dimensions: $a = 15{\cdot}64 \pm 0{\cdot}02$, $b = 15{\cdot}75 \pm 0{\cdot}02$, $c = 13{\cdot}91 \pm 0{\cdot}02$ Å, and $\beta = 112{\cdot}5 \pm 0{\cdot}2°$. A crude flotation measurement of the density in aqueous KI solution gave a value of $1{\cdot}50 \pm 0{\cdot}01$ g.cm$^{-3}$. A calculated density of $1{\cdot}492 \pm 0{\cdot}005$ g.cm$^{-3}$ was obtained assuming four molecules per unit cell. The systematic extinctions were for $hkl$, $h+k+l$ odd, and for $h0l$, $h$ odd, indicating that the space group is either $Ia$ or $I2/a$.

A crystal approximately 0·4 × 0·4 × 0·4 mm mounted along the crystallographic $c$ axis was chosen for intensity measurements. Using a zirconium filter and brass interleaving sheets, multiple film Mo $K\alpha$ Weissenberg photographs were taken of the $hk0$–$hk12$ zones. Multiple exposures were taken of the $h0l$, $h1l$, $h2l$, $0kl$, $1kl$, and $2kl$ zones by the precession method. The relative intensities were estimated by visual comparison

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with a series of timed exposures of a selected reflection. There were 1341 independent reflections of measurable intensity. The usual Lorentz and polarization corrections were made. Absorption corrections were not made ($\mu=6{\cdot}4$ cm$^{-1}$). The maximum effect of absorption (*International Tables for X-ray Crystallography*, 1958) for a given Weissenberg layer was estimated to be less than 10%. The data were placed on a common scale using a modification of the method of Rollett & Sparks (1960).

### *Determination of the structure*

The calculations described above and below were made on the IBM 7040 computer of the Computer Research Center of the University of Missouri. The programs used in this work were A. Zalkin's *FORDAP* program, W. R. Busing and H. A. Levy's *ORFLS* least-squares and *ORFFE* error function programs, and data handling programs of W. C. Hamilton and J. A. Ibers.

A three-dimensional Patterson synthesis was prepared. The positions of the tin atom and of three sulfur atoms were located, assuming space group $I2/a$.

In structure factor calculations, SCF scattering factors (*International Tables for X-ray Crystallography*, 1962) for neutral carbon, nitrogen, and sulfur and Thomas–Fermi–Dirac values for neutral tin including $f'$ and $f''$ dispersion factors were used. The effects of anomalous dispersion were included in $F_c$ (Ibers & Hamilton, 1964)

A three-dimensional Fourier synthesis with the phases from the calculated structure factors based on the tin and three sulfur atoms and the magnitudes from

Table 1. *Observed and calculated structure factors for tetrakis-*(*N,N-diethyldithiocarbamato*)*tin*(IV)

| K | L | FO | FC |
|---|---|---|---|
| H= 0 | | | |
| 0 | 4 | 1375 | 1494 |
| 0 | 6 | 494 | 511 |
| 0 | 8 | 910 | 1040 |
| 0 | 10 | 381 | 398 |
| 0 | 14 | 397 | 347 |
| 0 | 16 | 380 | 432 |
| 1 | 3 | 2196 | 2352 |
| 1 | 5 | 626 | 531 |
| 1 | 7 | 1863 | 2066 |
| 1 | 9 | 618 | 624 |
| 1 | 15 | 382 | 436 |
| 2 | 2 | 622 | 343 |
| 2 | 4 | 1852 | 1976 |
| 2 | 6 | 547 | 443 |
| 2 | 8 | 762 | 846 |
| 2 | 10 | 417 | 434 |
| 2 | 12 | 352 | 237 |
| 2 | 14 | 536 | 357 |
| 3 | 1 | 1150 | 974 |
| 3 | 3 | 1810 | 1866 |
| 3 | 5 | 1155 | 1033 |
| 3 | 7 | 1038 | 1056 |
| 3 | 9 | 356 | 207 |
| 3 | 11 | 596 | 619 |
| 4 | 0 | 952 | 838 |
| 4 | 2 | 959 | 932 |
| 4 | 4 | 1965 | 2085 |
| 4 | 6 | 504 | 332 |
| 4 | 10 | 525 | 506 |
| 4 | 12 | 547 | 448 |
| 5 | 1 | 717 | 659 |
| 5 | 3 | 1008 | 832 |
| 5 | 7 | 581 | 589 |
| 5 | 11 | 606 | 575 |
| 6 | 2 | 1470 | 1358 |
| 6 | 6 | 583 | 419 |
| 6 | 8 | 351 | 241 |
| 7 | 1 | 1070 | 1065 |
| 7 | 3 | 299 | 266 |
| 7 | 5 | 669 | 616 |
| 7 | 9 | 458 | 312 |
| 8 | 0 | 1007 | 1084 |
| 8 | 2 | 1407 | 1368 |
| 8 | 4 | 377 | 266 |
| 8 | 6 | 463 | 442 |
| 8 | 8 | 672 | 559 |
| 8 | 10 | 382 | 339 |
| 9 | 1 | 1546 | 1643 |
| 9 | 3 | 707 | 722 |
| 9 | 5 | 381 | 372 |
| 9 | 7 | 581 | 592 |
| 9 | 9 | 728 | 754 |
| 10 | 0 | 1163 | 1220 |
| 10 | 2 | 902 | 887 |
| 10 | 4 | 334 | 337 |
| 10 | 6 | 961 | 1007 |
| 10 | 8 | 725 | 640 |
| 10 | 10 | 388 | 369 |
| 11 | 1 | 555 | 537 |
| 11 | 3 | 596 | 586 |
| 11 | 5 | 804 | 855 |
| 11 | 7 | 587 | 567 |
| 11 | 9 | 529 | 489 |
| 11 | 13 | 375 | 363 |
| 12 | 0 | 487 | 315 |
| 12 | 2 | 348 | 275 |
| 12 | 4 | 824 | 804 |
| 12 | 6 | 788 | 715 |
| 12 | 8 | 386 | 328 |
| 12 | 10 | 392 | 412 |
| 12 | 12 | 469 | 472 |
| 13 | 3 | 751 | 761 |
| 13 | 5 | 702 | 680 |
| 13 | 9 | 393 | 331 |
| 13 | 11 | 387 | 419 |
| 13 | 13 | 348 | 355 |
| 14 | 2 | 375 | 233 |
| 14 | 4 | 520 | 555 |
| 14 | 6 | 389 | 302 |
| H= 1 | | | |
| 1 | 2 | 1505 | 1513 |
| 1 | 4 | 260 | 159 |
| 2 | 3 | 419 | 359 |
| 2 | 5 | 700 | 564 |
| 2 | 11 | 341 | 278 |
| 2 | 13 | 367 | 365 |
| 3 | 0 | 501 | 517 |
| 3 | 2 | 2677 | 2399 |
| 3 | 4 | 1394 | 1337 |
| 3 | 6 | 388 | 493 |
| 3 | 10 | 416 | 326 |
| 3 | 12 | 513 | 387 |
| 4 | 1 | 377 | 201 |
| 4 | 3 | 1373 | 1240 |
| 4 | 5 | 1163 | 1184 |
| 4 | 11 | 654 | 623 |
| 4 | 13 | 566 | 536 |
| 5 | 0 | 472 | 390 |
| 5 | 2 | 1125 | 1211 |
| 5 | 4 | 1322 | 1235 |
| 5 | 6 | 881 | 841 |
| 5 | 10 | 675 | 595 |
| 5 | 12 | 757 | 674 |
| 6 | 1 | 1424 | 1342 |
| 6 | 3 | 1454 | 1290 |
| 6 | 5 | 1452 | 1331 |
| 6 | 7 | 387 | 440 |
| 6 | 9 | 444 | 462 |
| 6 | 11 | 687 | 650 |
| 6 | 13 | 463 | 431 |
| 7 | 0 | 872 | 854 |
| 7 | 2 | 1777 | 1688 |
| 7 | 4 | 1095 | 978 |
| 7 | 6 | 1037 | 888 |
| 7 | 8 | 898 | 890 |
| 7 | 10 | 719 | 645 |
| 8 | 1 | 1696 | 1702 |
| 8 | 3 | 705 | 581 |
| 8 | 5 | 831 | 763 |
| 8 | 7 | 1163 | 988 |
| 8 | 9 | 762 | 780 |
| 9 | 0 | 714 | 693 |
| 9 | 2 | 739 | 748 |
| 9 | 4 | 512 | 357 |
| 9 | 6 | 928 | 916 |
| 9 | 8 | 938 | 896 |
| 9 | 10 | 447 | 285 |
| 10 | 1 | 591 | 596 |
| 10 | 5 | 600 | 389 |
| 10 | 7 | 645 | 699 |
| 10 | 9 | 566 | 309 |
| 11 | 6 | 414 | 284 |
| 12 | 1 | 382 | 303 |
| 13 | 0 | 398 | 356 |
| 13 | 2 | 445 | 305 |
| 13 | 4 | 417 | 350 |
| 13 | 6 | 435 | 247 |
| 14 | 1 | 416 | 299 |
| 14 | 3 | 425 | 420 |
| 14 | 5 | 586 | 491 |
| 15 | 2 | 434 | 373 |
| 15 | 4 | 443 | 451 |
| 16 | 1 | 446 | 451 |
| 16 | 5 | 459 | 362 |
| 16 | 7 | 465 | 401 |
| 17 | 6 | 468 | 298 |
| 17 | 8 | 465 | 421 |
| 1 | -4 | 402 | 212 |
| 1 | -6 | 476 | 407 |
| 1 | -8 | 497 | 436 |
| 2 | -3 | 422 | 326 |
| 2 | -5 | 1157 | 1199 |
| 2 | -7 | 887 | 914 |
| 2 | -9 | 304 | 208 |
| 3 | -2 | 2507 | 3072 |
| 3 | -4 | 1997 | 2166 |
| 3 | -6 | 1066 | 1082 |
| 3 | -8 | 557 | 482 |
| 3 | -12 | 460 | 418 |
| 4 | -5 | 3082 | 3264 |
| 4 | -1 | 1698 | 1565 |
| 4 | -3 | 3159 | 3147 |
| 4 | -7 | 661 | 720 |
| 4 | -11 | 658 | 775 |
| 5 | -2 | 2605 | 2491 |
| 5 | -4 | 3399 | 3465 |
| 5 | -6 | 1614 | 1614 |
| 5 | -8 | 548 | 461 |
| 5 | -10 | 694 | 696 |
| 5 | -12 | 770 | 693 |
| 6 | -1 | 1039 | 819 |
| 6 | -3 | 1755 | 1659 |
| 6 | -5 | 1630 | 1607 |
| 6 | -7 | 795 | 757 |
| 6 | -9 | 738 | 641 |
| 6 | -11 | 750 | 843 |
| 7 | -2 | 1255 | 1120 |
| 7 | -6 | 746 | 600 |
| 7 | -8 | 1223 | 1131 |
| 7 | -10 | 679 | 579 |
| 8 | -1 | 1614 | 1550 |
| 8 | -3 | 821 | 664 |
| 8 | -5 | 374 | 161 |
| 8 | -7 | 873 | 856 |
| 8 | -9 | 767 | 665 |
| 8 | -11 | 447 | 399 |
| 9 | -2 | 428 | 322 |
| 9 | -4 | 498 | 356 |
| 9 | -6 | 429 | 178 |
| 9 | -8 | 958 | 901 |
| 9 | -10 | 440 | 374 |
| 10 | -1 | 673 | 541 |
| 10 | -3 | 467 | 349 |
| 12 | -1 | 380 | 314 |
| 12 | -5 | 575 | 406 |
| 13 | -2 | 401 | 380 |
| 14 | -3 | 421 | 343 |
| H= 2 | | | |
| 0 | 2 | 1606 | 1669 |
| 0 | 4 | 604 | 617 |
| 0 | 6 | 1459 | 1585 |
| 0 | 8 | 1228 | 1317 |
| 0 | 10 | 683 | 646 |
| 0 | 12 | 324 | 216 |
| 0 | 14 | 492 | 447 |
| 0 | 16 | 489 | 442 |
| 1 | 1 | 653 | 517 |
| 1 | 3 | 246 | 171 |
| 1 | 5 | 523 | 376 |
| 1 | 7 | 1288 | 1303 |
| 1 | 9 | 1140 | 1192 |
| 1 | 11 | 314 | 250 |
| 1 | 13 | 501 | 462 |
| 2 | 0 | 3367 | 2657 |
| 2 | 2 | 1190 | 1232 |
| 2 | 4 | 307 | 236 |
| 2 | 6 | 1192 | 1234 |
| 2 | 8 | 440 | 364 |
| 2 | 10 | 730 | 764 |
| 2 | 12 | 378 | 387 |
| 2 | 14 | 395 | 293 |
| 3 | 1 | 911 | 940 |
| 3 | 3 | 1605 | 1599 |
| 3 | 5 | 574 | 633 |
| 3 | 7 | 358 | 329 |
| 3 | 9 | 614 | 607 |
| 3 | 11 | 486 | 497 |
| 3 | 13 | 517 | 419 |
| 4 | 0 | 743 | 598 |
| 4 | 2 | 1940 | 1921 |
| 4 | 4 | 712 | 651 |
| 4 | 6 | 982 | 906 |
| 4 | 8 | 433 | 211 |
| 4 | 10 | 306 | 299 |
| 4 | 12 | 432 | 373 |
| 5 | 1 | 232 | 297 |
| 5 | 3 | 1347 | 1345 |
| 5 | 5 | 719 | 686 |
| 5 | 7 | 355 | 132 |
| 6 | 0 | 466 | 409 |
| 6 | 2 | 853 | 888 |
| 6 | 6 | 385 | 289 |
| 6 | 8 | 649 | 567 |
| 6 | 10 | 309 | 174 |
| 6 | 12 | 327 | 265 |
| 7 | 1 | 398 | 329 |
| 7 | 3 | 621 | 562 |
| 7 | 7 | 415 | 179 |
| 7 | 11 | 555 | 418 |
| 8 | 0 | 923 | 957 |
| 8 | 2 | 527 | 373 |
| 8 | 4 | 401 | 374 |
| 8 | 8 | 707 | 516 |
| 8 | 10 | 418 | 253 |
| 8 | 14 | 333 | 213 |
| 9 | 1 | 1116 | 1133 |
| 9 | 3 | 414 | 318 |
| 9 | 5 | 321 | 249 |
| 9 | 7 | 639 | 612 |
| 9 | 9 | 464 | 354 |
| 10 | 0 | 1390 | 1528 |
| 10 | 2 | 558 | 540 |
| 10 | 4 | 729 | 695 |
| 10 | 6 | 499 | 428 |
| 10 | 8 | 871 | 776 |
| 10 | 10 | 320 | 234 |
| 11 | 1 | 1104 | 1247 |
| 11 | 3 | 1043 | 1126 |
| 11 | 5 | 645 | 635 |
| 11 | 7 | 662 | 728 |
| 12 | 0 | 698 | 768 |
| 12 | 2 | 615 | 615 |
| 12 | 4 | 1143 | 1250 |
| 12 | 6 | 537 | 475 |
| 13 | 3 | 937 | 1078 |
| 13 | 5 | 853 | 877 |
| 14 | 2 | 644 | 343 |
| 14 | 4 | 750 | 796 |
| 15 | 3 | 428 | 390 |
| 0 | -4 | 1378 | 964 |
| 0 | -6 | 1808 | 1914 |
| 0 | -8 | 2104 | 2437 |
| 0 | -10 | 951 | 1069 |
| 0 | -12 | 310 | 358 |
| 0 | -16 | 565 | 523 |
| 1 | -3 | 644 | 620 |
| 1 | -5 | 2007 | 2019 |
| 1 | -7 | 1769 | 1985 |
| 1 | -9 | 1707 | 2174 |
| 1 | -13 | 431 | 391 |
| 1 | -15 | 334 | 349 |
| 2 | -2 | 2178 | 2012 |
| 2 | -4 | 1343 | 1470 |
| 2 | -6 | 1029 | 1122 |
| 2 | -8 | 1173 | 1288 |
| 2 | -10 | 624 | 731 |
| 2 | -12 | 721 | 713 |
| 2 | -16 | 336 | 284 |
| 3 | -1 | 3034 | 3130 |
| 3 | -3 | 1628 | 1544 |
| 3 | -5 | 1884 | 1999 |
| 3 | -7 | 236 | 116 |
| 3 | -9 | 652 | 655 |
| 3 | -11 | 477 | 467 |
| 3 | -13 | 433 | 431 |
| 4 | -2 | 682 | 670 |
| 4 | -4 | 1526 | 1510 |
| 4 | -6 | 464 | 270 |
| 4 | -10 | 408 | 257 |
| 4 | -12 | 667 | 550 |
| 5 | -3 | 326 | 330 |
| 5 | -5 | 819 | 813 |
| 5 | -7 | 740 | 670 |
| 5 | -13 | 323 | 278 |
| 6 | -2 | 513 | 538 |
| 6 | -4 | 924 | 774 |
| 6 | -10 | 605 | 499 |
| 6 | -12 | 316 | 194 |
| 7 | -1 | 326 | 149 |
| 7 | -3 | 1521 | 1572 |
| 7 | -5 | 363 | 246 |
| 7 | -7 | 1132 | 970 |
| 7 | -9 | 647 | 575 |
| 7 | -11 | 605 | 429 |
| 8 | -2 | 787 | 736 |
| 8 | -4 | 688 | 666 |
| 8 | -6 | 1157 | 1131 |
| 8 | -8 | 794 | 819 |
| 8 | -10 | 815 | 722 |
| 9 | -1 | 610 | 550 |
| 9 | -3 | 611 | 608 |
| 9 | -5 | 246 | 128 |
| 9 | -7 | 1445 | 1311 |
| 9 | -9 | 772 | 646 |
| 9 | -11 | 384 | 372 |
| 9 | -13 | 329 | 233 |
| 10 | -2 | 353 | 302 |
| 10 | -4 | 514 | 393 |
| 10 | -6 | 701 | 700 |
| 10 | -8 | 672 | 636 |
| 10 | -10 | 590 | 527 |
| 10 | -14 | 471 | 438 |
| 11 | -1 | 569 | 598 |
| 11 | -3 | 787 | 841 |
| 11 | -7 | 493 | 458 |
| 11 | -11 | 453 | 399 |
| 11 | -13 | 468 | 479 |
| 11 | -15 | 330 | 286 |
| 12 | -2 | 566 | 557 |
| 12 | -4 | 840 | 895 |
| 12 | -6 | 522 | 487 |
| 12 | -10 | 317 | 313 |
| 12 | -12 | 329 | 433 |
| 12 | -14 | 331 | 321 |
| 13 | -3 | 824 | 794 |
| 13 | -5 | 405 | 437 |
| 13 | -11 | 327 | 350 |
| 13 | -13 | 332 | 329 |
| 14 | -4 | 662 | 685 |
| 15 | -3 | 298 | 336 |
| H= 3 | | | |
| 1 | 0 | 594 | 566 |
| 1 | 2 | 1381 | 1242 |
| 1 | 6 | 564 | 561 |
| 1 | 8 | 719 | 698 |
| 1 | 10 | 384 | 213 |
| 2 | 3 | 390 | 354 |
| 2 | 5 | 756 | 825 |
| 2 | 7 | 684 | 642 |
| 2 | 9 | 803 | 789 |
| 2 | 11 | 350 | 289 |
| 2 | 15 | 475 | 93 |
| 3 | 0 | 1013 | 772 |
| 3 | 2 | 658 | 607 |
| 3 | 4 | 1231 | 1097 |
| 3 | 6 | 927 | 986 |
| 3 | 8 | 701 | 699 |
| 3 | 10 | 842 | 760 |
| 3 | 12 | 636 | 582 |
| 4 | 1 | 503 | 499 |
| 4 | 3 | 1323 | 1159 |
| 4 | 5 | 1465 | 1437 |
| 4 | 9 | 504 | 517 |
| 4 | 11 | 858 | 875 |
| 5 | 0 | 512 | 474 |
| 5 | 2 | 1273 | 1289 |
| 5 | 4 | 1986 | 1944 |
| 5 | 6 | 742 | 615 |
| 5 | 10 | 820 | 661 |
| 5 | 12 | 953 | 736 |
| 6 | 1 | 1012 | 1118 |
| 6 | 3 | 1127 | 970 |
| 6 | 5 | 1373 | 1325 |
| 6 | 9 | 521 | 526 |
| 6 | 11 | 575 | 498 |
| 7 | 0 | 1144 | 1099 |
| 7 | 2 | 1025 | 1063 |
| 7 | 6 | 670 | 658 |
| 7 | 8 | 752 | 616 |
| 8 | 1 | 1896 | 1939 |
| 8 | 5 | 756 | 601 |
| 8 | 7 | 552 | 608 |
| 9 | 0 | 1506 | 1568 |
| 9 | 2 | 919 | 956 |
| 9 | 8 | 577 | 553 |
| 11 | 2 | 655 | 10 |
| 12 | 3 | 419 | 275 |
| 13 | 2 | 627 | 234 |
| 15 | 0 | 483 | 540 |
| 17 | 0 | 524 | 634 |
| 1 | -2 | 459 | 314 |
| 1 | -4 | 638 | 550 |
| 1 | -6 | 846 | 927 |
| 1 | -8 | 869 | 862 |
| 1 | -14 | 416 | 327 |
| 2 | -5 | 1682 | 1841 |
| 2 | -7 | 1310 | 1586 |
| 2 | -9 | 623 | 642 |
| 2 | -11 | 560 | 489 |
| 3 | -2 | 1098 | 825 |
| 3 | -4 | 943 | 977 |
| 3 | -6 | 1190 | 1287 |
| 3 | -8 | 821 | 898 |
| 3 | -10 | 694 | 749 |
| 3 | -12 | 934 | 1012 |
| 3 | -14 | 484 | 514 |
| 4 | -1 | 646 | 496 |
| 4 | -3 | 1553 | 1350 |
| 4 | -5 | 1772 | 1731 |
| 4 | -7 | 665 | 621 |
| 4 | -9 | 583 | 664 |
| 4 | -11 | 925 | 1286 |
| 5 | -2 | 1893 | 1916 |
| 5 | -4 | 1956 | 1805 |
| 5 | -6 | 583 | 646 |
| 5 | -8 | 688 | 565 |
| 5 | -10 | 904 | 744 |
| 5 | -12 | 996 | 1063 |
| 6 | -1 | 758 | 702 |
| 6 | -3 | 1752 | 1747 |
| 6 | -5 | 1693 | 1621 |
| 6 | -7 | 579 | 475 |
| 6 | -9 | 773 | 742 |
| 6 | -11 | 732 | 799 |
| 7 | -2 | 1622 | 1729 |
| 7 | -4 | 991 | 963 |
| 7 | -6 | 1239 | 1125 |
| 7 | -8 | 980 | 908 |
| 8 | -1 | 1579 | 1532 |
| 8 | -5 | 553 | 474 |
| 8 | -7 | 896 | 894 |
| 8 | -9 | 692 | 569 |
| 9 | -2 | 1267 | 1151 |
| 9 | -8 | 833 | 760 |
| 10 | -1 | 662 | 677 |
| 10 | -5 | 443 | 326 |
| 11 | -2 | 534 | 639 |
| 12 | -3 | 404 | 190 |
| 14 | -1 | 454 | 554 |
| 14 | -3 | 444 | 399 |
| 15 | -2 | 649 | 691 |
| 15 | -4 | 638 | 542 |
| 16 | -1 | 494 | 674 |
| 16 | -3 | 484 | 567 |
| H= 4 | | | |
| 0 | 0 | 1948 | 2007 |
| 0 | 2 | 737 | 759 |
| 0 | 4 | 818 | 869 |
| 0 | 6 | 1265 | 1341 |
| 0 | 8 | 2010 | 2172 |
| 0 | 10 | 554 | 649 |
| 1 | 1 | 2520 | 2764 |
| 1 | 3 | 358 | 301 |
| 1 | 5 | 957 | 1043 |
| 1 | 7 | 1473 | 1542 |
| 1 | 9 | 1080 | 1070 |
| 1 | 11 | 406 | 372 |
| 2 | 0 | 1378 | 1366 |
| 2 | 2 | 1124 | 1104 |
| 2 | 4 | 1469 | 1553 |
| 2 | 6 | 1168 | 1124 |
| 2 | 8 | 1086 | 1037 |
| 2 | 12 | 369 | 413 |
| 3 | 1 | 1069 | 1005 |
| 3 | 3 | 787 | 828 |
| 3 | 5 | 1098 | 1190 |
| 3 | 11 | 458 | 393 |
| 4 | 2 | 328 | 308 |
| 4 | 4 | 1013 | 1072 |
| 5 | 1 | 486 | 278 |
| 5 | 7 | 515 | 396 |
| 6 | 6 | 674 | 605 |
| 7 | 1 | 385 | 307 |
| 7 | 3 | 911 | 845 |
| 7 | 5 | 614 | 631 |
| 7 | 7 | 788 | 572 |
| 8 | 0 | 1062 | 1021 |
| 8 | 2 | 615 | 731 |
| 8 | 6 | 956 | 967 |
| 8 | 8 | 576 | 517 |
| 9 | 1 | 953 | 835 |
| 9 | 3 | 650 | 613 |
| 9 | 7 | 1034 | 857 |
| 10 | 0 | 964 | 1038 |
| 10 | 2 | 640 | 732 |
| 10 | 8 | 621 | 492 |
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| 11 | 3 | 767 | 782 |
| 12 | 2 | 634 | 644 |
| 12 | 4 | 486 | 459 |
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| 7 | -5 | 370 | 296 |
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| 8 | -2 | 516 | 614 |
| 8 | -6 | 623 | 462 |
| 8 | -8 | 667 | 469 |
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| 9 | -5 | 596 | 576 |
| 9 | -7 | 724 | 495 |
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| 10 | -4 | 594 | 594 |
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| 3 | 4 | 1541 | 1450 |
| 3 | 6 | 657 | 599 |
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| 6 | 3 | 1336 | 1293 |
| 6 | 5 | 1074 | 1057 |
| 6 | 7 | 561 | 550 |
| 6 | 11 | 632 | 427 |
| 7 | 0 | 1624 | 1579 |
| 7 | 2 | 633 | 670 |
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| 9 | 0 | 954 | 998 |
| 9 | 9 | 621 | 557 |
| 11 | 2 | 530 | 455 |
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| 1 | -12 | 398 | 318 |
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| 0 | 8 | 710 | 518 |
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| 1 | 7 | 778 | 776 |
| 2 | 0 | 991 | 1010 |
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| 2 | 4 | 459 | 501 |
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| 2 | 8 | 469 | 445 |
| 2 | 10 | 357 | 302 |
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| 3 | 5 | 769 | 805 |
| 3 | 7 | 739 | 683 |
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| 4 | 4 | 797 | 820 |
| 4 | 6 | 857 | 841 |
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| 6 | 0 | 555 | 549 |
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| 9 | 1 | 1130 | 1279 |
| 10 | 0 | 660 | 778 |
| 10 | 2 | 951 | 991 |
| 11 | 1 | 578 | 606 |
| 11 | 5 | 545 | 560 |
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| 12 | 4 | 512 | 501 |
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| 1 | 6 | 358 | 208 |
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| 2 | 3 | 934 | 949 |
| 3 | 0 | 1298 | 1135 |
| 3 | 2 | 857 | 837 |
| 3 | 4 | 620 | 580 |
| 3 | 10 | 470 | 343 |
| 4 | 1 | 346 | 363 |
| 4 | 3 | 887 | 926 |
| 5 | 0 | 506 | 521 |
| 5 | 2 | 593 | 444 |
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| 6 | 5 | 764 | 817 |
| 7 | 0 | 1117 | 1100 |
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| 7 | 4 | 914 | 1030 |
| 7 | 6 | 567 | 563 |
| 8 | 1 | 957 | 887 |
| 8 | 3 | 638 | 615 |
| 9 | 0 | 845 | 972 |
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| 7 | -12 | 557 | 527 |
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| 0 | 4 | 700 | 597 |
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| 0 | 8 | 746 | 821 |
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| 1 | 7 | 387 | 396 |
| 1 | 9 | 820 | 689 |
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| 2 | 2 | 775 | 718 |
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| 2 | 8 | 349 | 286 |
| 3 | 1 | 487 | 362 |
| 3 | 3 | 353 | 290 |
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| 4 | 4 | 437 | 327 |
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| 5 | 1 | 483 | 477 |
| 5 | 3 | 388 | 438 |
| 5 | 5 | 496 | 503 |
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| 6 | 2 | 880 | 972 |
| 7 | 1 | 512 | 474 |
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| 8 | 2 | 332 | 325 |
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| 10 | 2 | 726 | 846 |
| 11 | 1 | 868 | 958 |
| 11 | 3 | 652 | 717 |
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| 12 | 2 | 656 | 676 |
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| 11 | -5 | 509 | 493 |
| 11 | -7 | 610 | 647 |
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| 14 | -4 | 533 | 449 |
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| 2 | 11 | 389 | 223 |
| 3 | 0 | 434 | 361 |
| 3 | 2 | 565 | 523 |
| 3 | 4 | 686 | 656 |
| 3 | 8 | 460 | 381 |
| 3 | 10 | 493 | 401 |
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| 4 | 3 | 781 | 874 |
| 4 | 5 | 724 | 708 |
| 5 | 0 | 382 | 340 |
| 5 | 2 | 454 | 451 |
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| 6 | 3 | 589 | 630 |
| 6 | 5 | 531 | 478 |
| 7 | 0 | 813 | 873 |
| 7 | 2 | 337 | 408 |
| 8 | 1 | 1009 | 1047 |
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| 1 | -8 | 520 | 386 |
| 1 | -12 | 463 | 417 |
| 1 | -14 | 598 | 519 |
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| 2 | -3 | 338 | 259 |
| 2 | -5 | 989 | 992 |
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| 2 | -9 | 673 | 495 |
| 2 | -11 | 355 | 377 |
| 2 | -13 | 961 | 970 |
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| 3 | -4 | 573 | 576 |
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| 9 | -2 | 667 | 633 |
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| 2 | 6 | 552 | 576 |
| 2 | 8 | 621 | 487 |
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| 4 | 4 | 484 | 453 |
| 5 | 1 | 480 | 418 |
| 6 | 0 | 446 | 364 |
| 8 | 2 | 510 | 470 |
| 9 | 1 | 648 | 614 |
| 10 | 2 | 659 | 702 |
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| 6 | -4 | 601 | 438 |
| 6 | -6 | 849 | 615 |
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| 6 | 1 | 445 | 544 |
| 6 | 3 | 645 | 725 |
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| 7 | 2 | 520 | 538 |
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| 1 | -4 | 392 | 227 |
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| 2 | -7 | 691 | 659 |
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| 9 | -6 | 811 | 772 |
| 9 | -8 | 847 | 572 |
| 9 | -10 | 652 | 528 |
| H=12 | | | |
| 0 | 2 | 983 | 957 |
| 0 | 4 | 345 | 329 |
| 0 | 6 | 407 | 300 |
| 1 | 1 | 620 | 607 |
| 1 | 3 | 703 | 606 |
| 2 | 0 | 732 | 783 |
| 2 | 2 | 519 | 551 |
| 2 | 4 | 351 | 327 |
| 2 | 6 | 525 | 378 |
| 3 | 3 | 435 | 333 |
| 3 | 5 | 461 | 410 |
| 6 | 0 | 451 | 515 |
| 9 | 1 | 404 | 549 |
| 0 | -2 | 643 | 688 |
| 0 | -4 | 1317 | 1313 |
| 0 | -6 | 701 | 603 |
| 0 | -8 | 1229 | 1093 |
| 0 | -12 | 687 | 562 |
| 0 | -16 | 380 | 469 |
| 0 | -18 | 323 | 415 |
| 1 | -1 | 1345 | 1417 |
| 1 | -3 | 663 | 716 |
| 1 | -5 | 1306 | 1294 |
| 1 | -7 | 838 | 768 |
| 1 | -9 | 682 | 635 |
| 1 | -11 | 542 | 572 |
| 2 | -2 | 1228 | 1189 |
| 2 | -4 | 1110 | 1068 |
| 2 | -8 | 921 | 1049 |
| 0 | 0 | 1266 | 1245 |
| 2 | -12 | 763 | 666 |
| 3 | -1 | 1159 | 1250 |
| 3 | -3 | 732 | 633 |
| 3 | -5 | 699 | 606 |
| 3 | -9 | 750 | 669 |
| 3 | -11 | 685 | 664 |
| 4 | -2 | 336 | 333 |
| 4 | -4 | 449 | 505 |
| 4 | -8 | 930 | 659 |
| 5 | -3 | 588 | 559 |
| 5 | -5 | 487 | 447 |
| 6 | -2 | 1079 | 1053 |
| 6 | -8 | 566 | 495 |
| 7 | -1 | 557 | 704 |
| 7 | -3 | 847 | 946 |
| 7 | -9 | 541 | 333 |
| 8 | -2 | 632 | 725 |
| 8 | -8 | 602 | 326 |
| 8 | -10 | 652 | 522 |
| 9 | -7 | 641 | 703 |
| 10 | -4 | 520 | 479 |
| 10 | -6 | 868 | 869 |
| 11 | -5 | 574 | 573 |
| 11 | -7 | 684 | 662 |
| H=13 | | | |
| 1 | 2 | 399 | 364 |
| 2 | 1 | 543 | 591 |
| 3 | 0 | 574 | 491 |
| 3 | 2 | 499 | 522 |
| 1 | -4 | 842 | 625 |
| 1 | -6 | 1066 | 995 |
| 2 | -3 | 532 | 499 |
| 2 | -5 | 1402 | 1362 |
| 2 | -7 | 1188 | 1046 |
| 3 | -2 | 596 | 559 |
| 3 | -4 | 825 | 776 |
| 3 | -6 | 1273 | 1255 |
| 3 | -8 | 563 | 588 |
| 4 | -1 | 713 | 712 |
| 4 | -3 | 938 | 882 |
| 4 | -5 | 712 | 855 |
| 4 | -7 | 834 | 828 |
| 4 | -9 | 811 | 685 |
| 5 | -2 | 734 | 873 |
| 5 | -4 | 832 | 758 |
| 5 | -6 | 793 | 765 |
| 5 | -8 | 580 | 672 |
| 5 | -10 | 1078 | 829 |
| 6 | -3 | 769 | 807 |
| 6 | -5 | 739 | 639 |
| 6 | -7 | 615 | 644 |
| 6 | -9 | 650 | 801 |
| 7 | -2 | 526 | 531 |
| 7 | -6 | 830 | 799 |
| 7 | -10 | 658 | 487 |
| H=14 | | | |
| 0 | 2 | 490 | 354 |
| 1 | 1 | 574 | 443 |
| 2 | 6 | 390 | 224 |
| 0 | -2 | 711 | 776 |
| 0 | -4 | 781 | 755 |
| 0 | -6 | 1236 | 1165 |
| 0 | -8 | 754 | 690 |
| 0 | -10 | 900 | 887 |
| 0 | -12 | 605 | 638 |
| 0 | -14 | 551 | 470 |
| 1 | -1 | 559 | 468 |
| 1 | -3 | 865 | 853 |
| 1 | -5 | 1011 | 1029 |
| 1 | -7 | 661 | 725 |
| 1 | -9 | 896 | 948 |
| 1 | -11 | 499 | 583 |
| 1 | -13 | 603 | 628 |
| 2 | -2 | 738 | 808 |
| 2 | -4 | 486 | 391 |
| 2 | -6 | 845 | 770 |
| 2 | -8 | 814 | 748 |
| 2 | -10 | 1002 | 1071 |
| 2 | -12 | 631 | 519 |
| 3 | -1 | 442 | 468 |
| 3 | -3 | 443 | 505 |
| 3 | -9 | 929 | 927 |
| 3 | -11 | 538 | 506 |
| 4 | -2 | 523 | 482 |
| 6 | -8 | 622 | 566 |
| 6 | -10 | 948 | 560 |
| 7 | -9 | 646 | 667 |
| 7 | -11 | 895 | 597 |
| 8 | -8 | 653 | 574 |
| 8 | -10 | 707 | 479 |
| 9 | -11 | 671 | 447 |
| 11 | -5 | 614 | 398 |
| H=15 | | | |
| 1 | 2 | 423 | 306 |
| 2 | 1 | 367 | 346 |
| 2 | 3 | 379 | 299 |
| 2 | -5 | 356 | 472 |
| 3 | -6 | 880 | 797 |
| 3 | -8 | 621 | 569 |
| 2 | -13 | 673 | 631 |
| 2 | -7 | 596 | 578 |
| 3 | -10 | 493 | 510 |
| 3 | -12 | 507 | 582 |
| 3 | -14 | 518 | 580 |
| 4 | -5 | 555 | 456 |
| 4 | -7 | 922 | 826 |
| 4 | -9 | 900 | 721 |
| 5 | -2 | 392 | 498 |
| 5 | -6 | 617 | 564 |
| 5 | -8 | 904 | 771 |
| 5 | -10 | 473 | 735 |
| 6 | -3 | 484 | 572 |
| 6 | -5 | 571 | 341 |
| 6 | -7 | 673 | 587 |
| 6 | -9 | 660 | 639 |
| 7 | -6 | 639 | 477 |
| H=16 | | | |
| 0 | 0 | 571 | 451 |
| 0 | 2 | 405 | 440 |
| 0 | 4 | 556 | 484 |
| 1 | 1 | 427 | 402 |
| 1 | 3 | 614 | 495 |
| 2 | 0 | 526 | 411 |
| 0 | -4 | 558 | 448 |
| 0 | -8 | 602 | 513 |
| 0 | -10 | 628 | 669 |
| 0 | -12 | 870 | 833 |
| 0 | -14 | 532 | 655 |
| 1 | -3 | 413 | 368 |
| 1 | -7 | 415 | 399 |
| 1 | -11 | 830 | 866 |
| 1 | -13 | 425 | 565 |
| 1 | -15 | 416 | 475 |
| 2 | -4 | 544 | 477 |
| 2 | -8 | 534 | 428 |
| 2 | -10 | 624 | 629 |
| 2 | -12 | 383 | 399 |
| 2 | -14 | 390 | 430 |
| 3 | -1 | 476 | 466 |
| 3 | -3 | 471 | 515 |
| H=17 | | | |
| 1 | 2 | 433 | 301 |
| 5 | -2 | 426 | 513 |
| H=18 | | | |
| 0 | 0 | 393 | 255 |
| 0 | 2 | 519 | 402 |
| 0 | -2 | 502 | 496 |
| 0 | -4 | 563 | 651 |
| 0 | -6 | 685 | 620 |
| 0 | -12 | 373 | 482 |
| 1 | -1 | 430 | 417 |
| 1 | -3 | 427 | 460 |
| 1 | -5 | 756 | 688 |
| 1 | -9 | 424 | 344 |
| 1 | -11 | 423 | 345 |
| 2 | -2 | 673 | 615 |
| 2 | -8 | 364 | 427 |
| H=19 | | | |
| 2 | -5 | 546 | 559 |
| 2 | -7 | 545 | 411 |
| H=20 | | | |
| 0 | -4 | 518 | 483 |
| 0 | -6 | 641 | 541 |
| 0 | -10 | 637 | 561 |
| 2 | -10 | 544 | 497 |

the observed structure factors was then prepared. From this synthesis it was possible to obtain approximate positions for the other sulfur atom and the nitrogen and carbon atoms in keeping with the expected ligand geometry. Full-matrix least-squares refinement of the atom positions and isotropic temperature factors was carried out assuming the space group *I*2/*a*. This refinement with all 17 atoms converged with $R^*=\sum|F_o^2-k^2F_c^2|/\sum F_o^2=0{\cdot}225$ and $r=(\sum w(F_o^2-k^2F_c^2)^2/\sum wF_o^4)^{1/2}=0{\cdot}353$ where $w=1/\sigma^2$. In the final refinement the weighting scheme (Lalancette, Cefola, Hamilton & La Placa, 1967) was chosen to make $|F_o^2-F_c^2|/\sigma$ nearly independent of $F_o^2$. This resulted in

$$\sigma=-0{\cdot}0513\ (kF_o)^4+1{\cdot}20(kF_o)^2$$

for

$$(kF_o)^2\le 15{\cdot}0;\ \sigma=-0{\cdot}00496(kF_o)^4+0{\cdot}54(kF_o)^2$$

**for**

$$15{\cdot}0\le(\mathrm{K}F_o)^2 50{\cdot}0;\ \sigma=-0{\cdot}00029(kF_o)^4+0{\cdot}295(kF_o)^2$$

for

$$50{\cdot}0<(kF_o)^2\le 420{\cdot}0;$$

and

$$\sigma=0{\cdot}000494(kF_o)^4-0{\cdot}05(kF_o)^2$$

for

$$(kF_o)^2>420{\cdot}0$$

where

$$k=0{\cdot}103.$$

With the tin and four sulfur atoms anisotropic, refinement converged with $R^*=0{\cdot}167$ and $r=0{\cdot}250$. In all least-squares refinement the numerator of $r$ was minimized. The conventional agreement factor $R=\sum|F_o-F_c|/\sum F_o$ was 0·102. The standard deviation of an observation of unit weight was 0·85. In the final cycle of refinement, the shifts in all parameters were less than 20% of the corresponding standard deviations. A difference Fourier synthesis using the final model showed no peaks greater than 1 e.Å$^{-3}$ except within 1 Å of the tin position. Owing to this and the goodness of fit with the assumed twofold molecular symmetry, no attempt was made to refine the structure in *Ia*. Such an attempt would not be fruitful because of the limitations in the quality of the data. It must be concluded that the space group symmetry is *I*2/*a* or that the deviation from that symmetry is minor.

The observed and calculated structure factors (× 10) are in Table 1. The final positional parameters and temperature factors are in Table 2.

Table 2. *Positional parameter and temperature factors**

Positional parameters (× 10$^3$) and temperature parameters (× 10)

| | $x$ | $y$ | $z$ | $B$ |
|---|---|---|---|---|
| Sn | 0 | 205·1 (2) | $\frac{1}{4}$† | 33 (1) |
| S(1) | 18·0 (4) | 98·6 (4) | 120·7 (5) | 44 (2) |
| S(2) | 330·0 (4) | 327·9 (4) | 200·2 (4) | 42 (2) |
| S(3) | 482·5 (4) | 174·1 (4) | 127·0 (5) | 47 (2) |
| S(4) | 311·8 (5) | 255·6 (6) | −26·5 (5) | 64 (2) |
| N(1) | 460 (1) | 218 (1) | −65 (2) | 59 (5) |
| N(2) | 195 (1) | 71 (1) | 159 (1) | 37 (3) |
| C(1) | 419 (2) | 219 (2) | 3 (2) | 48 (5) |
| C(2) | 135 (1) | 110 (1) | 118 (2) | 39 (4) |
| C(3) | 62 (2) | 299 (2) | −44 (2) | 74 (7) |
| C(4) | 406 (2) | 238 (2) | −178 (3) | 78 (8) |
| C(5) | 170 (2) | 13 (2) | 68 (2) | 44 (5) |
| C(6) | 297 (2) | 77 (2) | 223 (2) | 51 (5) |
| C(7) | 77 (3) | 395 (2) | −63 (3) | 89 (9) |
| C(8) | 400 (2) | 333 (2) | −202 (3) | 78 (8) |
| C(9) | 175 (3) | 58 (3) | −25 (3) | 92 (9) |
| C(10) | 329 (2) | −2 (2) | 289 (2) | 70 (7) |

Anisotropic temperature parameters (× 10$^4$)‡

| | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|
| Sn | 32 (1) | 40 (1) | 48 (1) | 0 | 24 (1) | 0 |
| S(1) | 38 (3) | 53 (4) | 72 (4) | −4 (3) | 20 (3) | −16 (3) |
| S(2) | 37 (3) | 51 (3) | 66 (4) | 0 (2) | 22 (3) | −17 (3) |
| S(3) | 63 (4) | 45 (3) | 67 (4) | 5 (3) | 33 (3) | − 2 (3) |
| S(4) | 61 (4) | 84 (5) | 87 (5) | −3 (4) | 35 (4) | −14 (4) |

Root-mean-square components of thermal displacement along the principal ellipsoid axes (× 10$^3$)

| | Axis 1 | Axis 2 | Axis 3 |
|---|---|---|---|
| Sn | 152 (3) | 207 (3) | 224 (3) |
| S(1) | 196 (7) | 218 (9) | 284 (9) |
| S(2) | 185 (8) | 209 (8) | 280 (8) |
| S(3) | 208 (8) | 241 (8) | 264 (8) |
| S(4) | 236 (8) | 264 (9) | 332 (9) |

* In this Table and other parts of the paper values in parentheses are standard deviations from the least-squares refinement.

† This value is not multiplied by 10$^4$.

‡ Anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)]$.

## Discussion

### *Nature of the structure*

The molecular structure is shown in Figs. 1 and 2 with the atom numbering system given in Fig. 2. The tin atom is six coordinate with distorted octahedral geometry. Two of the dithiocarbamate ligands are chelated while the other two are monodentate and occupy *cis* positions in the octahedron. The only other known structure (Domenicano, Vaciago, Zambonelli, Loader & Venanzi, 1966) containing both bidentate and monodentate dithiocarbamate ligands is that of Ru(NO) (dtc)$_3$ in which the monodentate ligand is *cis* to the NO in a distorted octahedron. The largest deviations from octahedral geometry are due to the steric requirements of the four membered chelate rings. The twofold symmetry axis bisects the S(1)–Sn–S(1) and S(3)–Sn–S(3) angles. The structure consists of discrete monomeric molecules with no unusually short intermolecular contacts. The intermolecular distances less than 4·0 Å are included in Table 3.

Table 3. *Intermolecular distances*

| | | | |
|---|---|---|---|
| S(1)–C(5) | 3·57 Å | S(4)–C(3) | 3·89 Å |
| S(3)–C(6) | 3·62 | S(3)–C(10) | 3·89 |
| S(1)–C(9) | 3·73 | C(7)–C(10) | 3·90 |
| S(4)–C(9) | 3·78 | C(8)–C(9) | 3·92 |
| C(5)–C(8) | 3·79 | S(3)–C(6) | 3·95 |
| C(4)–C(10) | 3·87 | C(7)–C(10) | 3·96 |

The sulfur–sulfur intramolecular contacts are interesting in that those between ligands are all 3·62 Å or longer except S(3)–S(3) (3·26 Å) and S(2)–S(4) (3·26 Å). A normal van der Waals contact would be 3·70 Å (Pauling, 1960). Since it is difficult to rationalize these shorts contacts on the basic of steric requirements, there may be a weak bonding interaction between these sulfur atoms. This interaction is also manifested in the S(3)–Sn–S(3) angle of 81·1°.

The root-mean-square components of thermal motion along the principal ellipsoid axes are given in Table 2. The orientation of the ellipsoids can be seen in Fig. 1. The maximum vibrations of S(1), S(2), and S(3) are essentially perpendicular to the Sn–S bond directions and that of the tin is directed roughly toward a triangular face of the octahedron. The thermal motion of corresponding atoms is more pronounced in the monodentate ligand than in the bidentate ligand.

### *Interatomic distances and angles*

The interatomic distances and angles within the molecule are given in Fig. 2. The Sn–S distances of the chelated ligand Sn–S(1) of 2·557 (7) Å and Sn–S(2) of 2·534 (7) Å are significantly longer than those of the monodentate ligand where the Sn–S(3) distance is 2·504 (7) Å. The longer distances to the chelated sulfur atoms may be due to the geometric strain of the four membered chelate ring. This is not, however, in keeping with the structure of Ru(NO)dtc$_3$, the only other known structure containing both bidentate and monodentate dithiocarbamate ligands. In that compound the Ru–S distances average 2·402 Å for the bidentate ligands, and the Ru–S distance for the monodentate ligand of 2·398 Å is nearly the same. The difference in Sn–S(1) and Sn–S(2) distances is of marginal significance. All of the Sn–S distances are somewhat longer than the sum of the single bond covalent radii (Pauling, 1960) (2·44 Å) and also longer than that observed (Sheldrick & Sheldrick, 1970) for (CH$_3$)$_3$SnS(S)CN(CH$_3$)$_2$ 2·47 (1) Å. In that complex the dithiocarbamate ligand is essentially monodentate to give basically a four-coordinate tin atom.

The S–Sn–S bond angles deviate markedly from 90° octahedral angles, ranging from 70·6° in the chelate ring to 99·7° for the S(2)–Sn–S(3) angle between ligands. The most surprising deviation is the S(3)–Sn–S(3) angle of 81·1 (3)° between monodentate ligands (see earlier discussion).

The geometries of the chelated and the monodentate ligands are considerably different, the most pronounced difference being in the C–S distances. The C–S distances of 1·71 (2) and 1·75 (2) Å for the chelated ligand

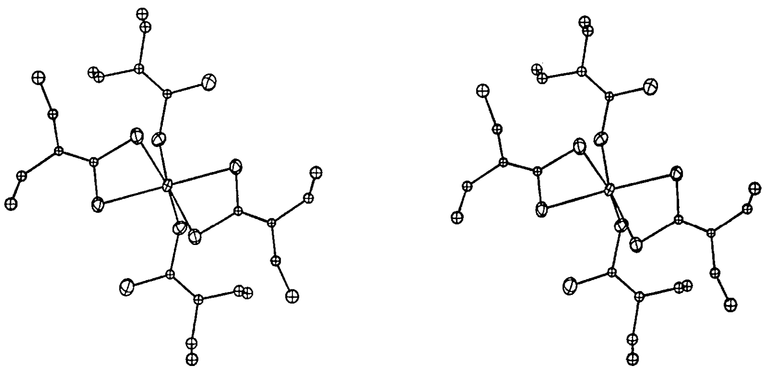

Fig. 1. Stereoscopic pair showing the geometry of the molecule and the thermal motion. The ellipsoids of the tin and sulfur are plotted at the 20% probability level whereas those of the light isotropic atoms are plotted at a lower probability level to minimize overlap.

are probably not significantly different. However, the C–S distances of 1·67(2) and 1·77(2) Å for the monodentate ligand are significantly different. All of these distances are intermediate between the sum of the single bond radii (Pauling, 1960) (1·81 Å) and the sum of the double bond radii (1·61 Å). There is delocalized multiple bonding in the $NCS_2$ portion of the ligand. In the chelated ligand, the delocalization is symmetrical resulting in equivalent C–S distances with significant multiple bonding. In the monodentate ligand the multiple bonding is more localized in the C(1)–S(4) bond. This bond, involving the sulfur not coordinated to the tin, is near to a double bond while the C(1)–S(3) bond is essentially a single bond. The C(1)–N(1) and C(2)–N(2) distances of 1·34 (3) and 1·31 (3) Å respectively are also indicative of the delocalized $\pi$ bonding since the sum of the single bond radii (Pauling, 1960) is 1·47 Å and sum of the double bond radii is 1·29 Å. The other C–N distances and the C–C distances are in keeping with those expected for single bonds. The bond angles in the ligand are not unusual and are in keeping with near $sp^2$ hybridization of the nitrogens and C(1) and C(2). There is the usual contraction from 120° of the angles opposite the C(1)–N(1) and C(2)–N(2) bonds indicative of the high multiple bond character in these bonds.

The bond lengths observed for the chelated ligands in $Sn(dtc)_4$ are comparable with those observed for the dodecahedral $Th(dtc)_4$ complex (Brown, Holah & Rickard, 1970), the octahedral $Co(dtc)_3$ complex (Merlino, 1968; Brennan & Bernal, 1969), the square planar $Ni(dtc)_2$ complex (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1968), and the tetrahedral $Zn(S_2CNMe_2)$ complex (Klug, 1966). The virtual lack of dependence of the chelated ligand geometry on the nature of the metal atom or on the geometry of the complex has been noted earlier (Merlino, 1968). The distances in the monodentate ligand compare favorably with the ligand distances in $As(dtc)_3$ (Colapietro, Domenicano, Scaramuzza & Vaciago, 1968) where the ligands are essentially monodentate. In that complex the C–S distances for the essentially nonbonded sulfurs are again approaching those expected for a double bond. Similar behavior is observed (Sheldrick & Sheldrick, 1970) for the C–S distances in the essentially monodentate $S_2CN(CH_3)_2$ ligand in $(CH_3)_3SnS_2CN(CH_3)_2$.

The chelated ligands in $Sn(dtc)_4$ are planar except for the terminal methyl groups. A weighted least-squares plane through the six atom $S_2CNC_2$ grouping is described by the equation: $3{\cdot}96x+12{\cdot}48y-8{\cdot}48z-0{\cdot}28=0$. All six atoms are within $1\frac{1}{2}$ standard deviations from the plane, the largest deviation being for C(6) which is 0·033 ± 0·022 Å from the plane. The tin atom is 0·16 Å out of this plane. The monodentate ligands deviate considerably from planar with the weighted least squares plane through the six atom $S_2CNC_2$ grouping being described by the equation: $4{\cdot}22x+14{\cdot}27y+2{\cdot}74z-5{\cdot}74=0$. The $S_2CN$ portion is planar with the maximum deviation from the above plane being 0·017 ± 0·025 Å for C(1). C(3) and C(4) are on opposite sides of the plane and off the plane by 0·25 ± 0·04 Å. The deviation from octahedral tin coordination is observed in attempts to put planes through groups of sulfur atoms and the tin atom. For example S(1) deviates 0·19 ± 0·01 Å from the plane through S(1), S(2), S(3), and Sn which is described by the equation: $4{\cdot}94x+10{\cdot}97y-0{\cdot}97z+0{\cdot}22=0$. There is then no good plane described by four sulfur atoms and the tin atom.

## Summary

As far as we are aware, tetrakis-(*N*,*N*-diethyldithiocarbamato)tin(IV) is the first established example of a complex, containing only dithiocarbamate ligands, when some of these ligands are chelating and some are monodentate. This leads to a six-coordinate tin atom in a distorted octahedron. There is good evidence (Bonati, Minghetti & Cenini, 1968) that the complex in polar organic solvents may be different than in the solid state in that the electrical conductivity of the solutions indicates a 1:1 electrolyte formulated as $Sn(dtc)_3^+(dtc)^-$. Further evidence for $Sn(dtc)_3^+$ was provided (Kazimir, 1969) by the isolation of $Sn(dtc)_3^+$ $B(C_6H_5)_4^-$ from solution. It is possible that an equilibrium exists between neutral $Sn(dtc)_4$ molecules and $Sn(dtc)_3^+(dtc)^-$ in these solutions.

The short intramolecular nonbonding sulfur contacts (~3·2 Å) between the coordinated sulfurs of the monodentate ligands and between the noncoordinated sulfur and a sulfur of the bidentate ligand are reminiscent of those observed (Eisenberg & Gray, 1967) (~3·1 Å) in transition metal dithiolates. Similar non-

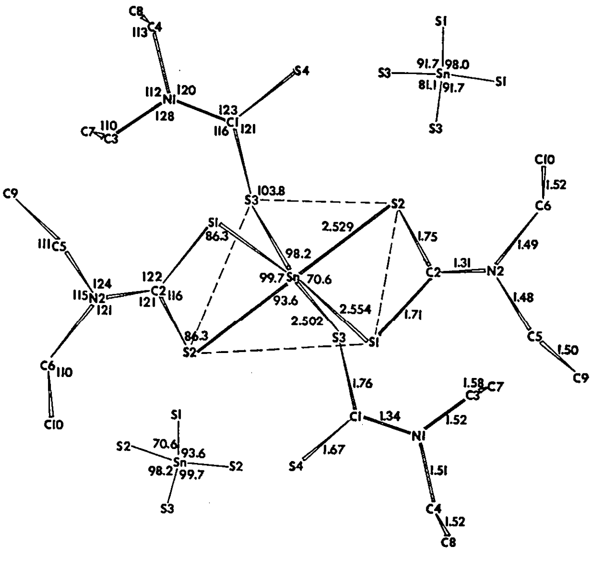

Fig. 2. Bond distances (Å) and angles (°). The standard deviations are Sn–S (± 0·007 Å), C–S (± 0·02 Å), C–N (± 0·03–0·04 Å), C–C (± 0·04–0·05 Å), S–Sn–S (± 0·2–0·3°), Sn–S–C (± 0·8°), and other angles (± 1–2°). There is a twofold axis nearly perpendicular to the Figure.

bonding distances are observed in polysulfide ions and in the sulfur rings of elemental sulfur. There is apparently a weak interaction between these nonbonded sulfurs.

A recent X-ray study (Colapietro, Vaciago, Bradley, Hursthouse & Rendall, 1970) has shown that Ti(dtc)$_4$, V(dtc)$_4$, and Zr(dtc)$_4$ all have eight coordinate dodecahedral structures in contrast to the six coordinate Sn(dtc)$_4$.

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# The Crystal and Molecular Structure of the 1:1 Hydrogen Bond Complex Between α-D-Glucose and Urea

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The crystal structure of the 1:1 α-D-glucose-urea complex has been determined by the application of the tangent formula. The space group is $P2_12_12_1$ with four molecules in a unit cell of dimensions $a=6{\cdot}913$, $b=9{\cdot}152$ and $c=16{\cdot}509$ (all $\sigma=0{\cdot}003$) Å. The α-D-glucose and urea molecules are associated by a three-dimensional system of hydrogen bonds which involves all oxygen and nitrogen atoms. The molecular parameters found for urea and glucose in the complex are the same as those for the pure compounds, except for the conformation of the primary alcohol group of glucose.

## Introduction

The possibility for donor–acceptor action enables the carbohydrates to form a variety of complexes. In general, these compounds fall into two categories; those involving metals such as alkali and alkaline earth salts (Rendleman, 1966) and those involving simple organic bases such as pyridine (Strain, 1934, 1937), urea (Quehl, 1938) and various amides (Rendleman, Baker & Hodge, 1967). There have been a number of crystal structure investigations of complexes which fall into the first category, *e.g.* sucrose.NaBr.2H$_2$O (Beevers & Cochran, 1947) and di-fructose.SrCl$_2$.3H$_2$O (Eiland & Pepinsky, 1950). Glucose–urea and glucitol–pyridine (Kim, Jeffrey & Rosenstein, 1970) are the only ex-

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