HAMILTON, W. C. & IBERS, J. A. (1968). *Hydrogen Bonding in Solids: Methods of Molecular Structure Determination.* Amsterdam: Benjamin.
International Tables for X-ray Crystallography (1962). Vol. III, pp. 202–206. Birmingham: Kynoch Press.
KARLE, J. & KARLE, I. L. (1963). *Acta Cryst.* **16**, 969–975.
KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849–859.
LEVY, H. A. & PETERSON, S. W. (1957). *J. Chem. Phys.* **26**, 220–221.
OSKARSSON, Å. (1973). *Acta Cryst.* B**29**, 1747–1751.
OSKARSSON, Å. (1974). *Acta Cryst.* B**30**, 780–783.
PADMANABHAN, V. M., SRIKANTHA, S. & ALI, S. M. (1965). *Acta Cryst.* **18**, 567–568.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1974). B**30**, 1188

Hexaaquocobalt(II) Bis(hydrogen-2,2′-dithiobisbenzoate)-hexahydrate–Tetrakismethanol and its Isostructural Nickel(II) Homologue

BY T. OTTERSEN,* L. G. WARNER AND K. SEFF

Chemistry Department, University of Hawaii, Honolulu, Hawaii 96822, *U.S.A.*

(*Received* 9 *July* 1973; *accepted* 16 *October* 1973)

$CoS_4O_{24}C_{32}H_{58}$, or $Co(H_2O)_6(HOOC–C_6H_4–SS–C_6H_4–COO)_2(H_2O)_6(CH_3OH)_4$, triclinic, $P\bar{1}$, $a=7·549$ (1), $b=12·988$ (2), $c=13·073$ (2) Å, $\alpha=107·06$ (1)°, $\beta=97·19$ (1)°, $\gamma=94·30$ (1)°, $V=1207·2$ Å^3 at 19°C, $D_x=1·400$ g cm^{-3}, $D_{obs}=1·41$ (2) g cm^{-3}. The structure consists of one hexaaquocobalt(II) cation at the origin and two $C_{14}H_9S_2O_4^-$ anions, all linked together in a hydrogen-bonding scheme involving six additional waters and four methanol molecules, two of which are disordered. $NiS_4O_{24}C_{32}H_{58}$ is isostructural: $a=7·545$ (1), $b=12·946$ (5), $c=13·050$ (2) Å, $\alpha=106·96$ (2), $\beta=97·08$ (1), $\gamma=94·12$ (3)° and $V=1202·1$ Å^3.

Introduction

Transition metal ions such as mercury(II) (Challenger, 1959), palladium(II) (Kawanishi, Yokoyama & Tanaka, 1972; Boschi, Crociani, Toniolo & Belluco, 1970) and copper(I) (Ottersen, Warner & Seff, 1973) function as electrophiles in the cleavage of the sulfur–sulfur bond in organic disulfides. Also, transition metal ion–organic disulfide interactions can behave 'non-innocently' in the functioning of metalloenzymes (Hemmerich, 1966). Thus, the study of transition metal ion–organic disulfide complexes is of some importance.

When aqueous methanol solutions of Co(II) or Ni(II) salts and 2,2′-dithiobisbenzoic acid are mixed in the presence of the hindered base 2,6-dimethylpyridine, and the solutions slowly concentrated, pink crystals of the Co(II) title compound or green crystals of the Ni(II) homologue are produced. The compositions of the crystals, and their stability relative to loss of solvent and the accompanying crystal degradation and color change, depend upon the water:methanol ratio of the mother liquor. When this ratio is approximately 3:1, the crystals are the most stable. (Solvent exchange or loss in flotation liquids prevented an accurate density measurement.) The structure determination was carried out to study the disulfide, *i.e.* the CSSC dihedral angle and the S–S bond length, and to investigate possible interactions between the metal ion and the disulfide anion. Although spectral evidence indicated no direct interactions, it was hoped that a structural investigation might help in explaining the spectral changes which indicated alterations in the Co(II) coordination environment upon loss of solvent.

A computer-controlled Syntex $P\bar{1}$ automated diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($K\alpha_1$, $\lambda=0·70926$ Å; $K\alpha_2$, $\lambda=0·71354$ Å) and a pulse-height analyzer was used to study the Co(II) complex further. A crystal approximately $0·4\times0·3\times0·1$ mm in size was used. Diffraction intensities were collected by the θ–2θ scanning mode with scan speed variable from 1° to 24° min^{-1}, depending on the peak intensity of the reflection. Three check reflections remeasured after every 100 during data collection showed no systematic variations, so no decay correction was applied. Standard deviations of the individual reflections were taken as the square root of the total counts with a 2% addition for instrumental instability. Of the 3176 symmetry independent reflections measured, all those for which $2\theta<45°$, 2512 had intensities greater

* Present address: Department of Pharmacy, University of Oslo, Oslo 3, Norway.

than three times their standard deviations; only these were used in structure solution and refinement.

A three-dimensional Patterson function indicated that the structure was centric, and allowed the Co(II) and the two sulfur positions to be located. Successive cycles of Fourier refinement, coupled with least-squares, served to reveal the entire structure, which was in good agreement with elemental analysis. Atomic scattering factors of Doyle & Turner (1968) were used. Fourier functions were generated with a modified version of *ALFF* (Hubbard, Quicksall & Jacobson, 1971). Two methanol molecules, whose oxygen atoms are located at special positions, are disordered and have created disorder among their neighbors. This disorder gives some unacceptable non-bonding distances, some as short as 1·7 Å, among the solvent molecules. The sol-

Table 1. *Positional and thermal parameters (all* $\times 10^4$*) with estimated standard deviations*

The e.s.d.'s are in the units of the least significant digit given for the corresponding parameter. The anisotropic temperature factor is of the form $\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	0	0	0	109 (3)	39 (1)	39 (1)	18 (2)	27 (2)	30 (1)
O(2)	9719 (10)	1558 (5)	−56 (5)	357 (17)	56 (4)	68 (4)	110 (13)	126 (14)	66 (7)
O(3)	7276 (7)	9722 (5)	84 (5)	132 (10)	81 (4)	71 (4)	3 (10)	23 (10)	− 7 (7)
O(4)	469 (7)	644 (4)	1703 (4)	173 (10)	53 (4)	44 (3)	29 (9)	27 (9)	34 (5)
S(5)	8709 (2)	4368 (2)	2212 (1)	132 (3)	54 (1)	50 (1)	3 (3)	50 (3)	24 (2)
S(6)	8940 (3)	5923 (2)	2133 (1)	236 (5)	66 (2)	42 (1)	−54 (4)	−15 (4)	55 (2)
O(7)	5639 (9)	1235 (5)	1467 (6)	182 (12)	55 (5)	109 (6)	2 (12)	−17 (13)	−22 (8)
O(8)	8262 (7)	2264 (4)	1885 (4)	129 (11)	48 (4)	64 (4)	31 (9)	21 (10)	− 5 (6)
O(9)	100 (18)	7828 (6)	1809 (6)	846 (43)	68 (5)	63 (6)	−183 (23)	−85 (22)	88 (10)
O(10)	153 (33)	9350 (9)	2922 (10)	1803 (111)	115 (9)	141 (10)	649 (55)	714 (59)	203 (17)
C(11)	6562 (9)	4167 (6)	2623 (6)	119 (13)	59 (6)	40 (4)	40 (13)	13 (12)	37 (8)
C(12)	5717 (9)	3113 (6)	2393 (13)	113 (13)	46 (5)	39 (4)	3 (12)	8 (12)	29 (8)
C(13)	4033 (11)	2959 (7)	2688 (7)	146 (15)	65 (6)	68 (6)	16 (15)	28 (15)	56 (10)
C(14)	3230 (12)	3842 (8)	3253 (9)	155 (17)	93 (8)	108 (9)	74 (19)	127 (19)	77 (14)
C(15)	4102 (13)	4874 (8)	3489 (9)	175 (18)	85 (8)	99 (8)	87 (19)	78 (19)	28 (13)
C(16)	5727 (11)	5034 (6)	3162 (7)	158 (16)	52 (5)	73 (6)	59 (14)	71 (16)	29 (9)
C(17)	6593 (10)	2127 (6)	1857 (6)	146 (16)	42 (5)	47 (5)	16 (14)	−11 (13)	4 (8)
C(18)	9863 (9)	6789 (6)	3456 (6)	126 (13)	61 (6)	43 (5)	13 (13)	20 (12)	52 (8)
C(19)	287 (10)	7899 (6)	3619 (6)	148 (14)	49 (5)	58 (5)	36 (13)	60 (13)	56 (9)
C(20)	890 (12)	8573 (7)	4666 (7)	206 (17)	57 (6)	63 (6)	3 (15)	62 (16)	34 (10)
C(21)	1107 (12)	8176 (7)	5553 (7)	213 (18)	76 (7)	55 (6)	−19 (17)	45 (16)	32 (10)
C(22)	719 (10)	7080 (7)	5373 (6)	153 (14)	74 (6)	48 (5)	− 2 (15)	17 (13)	54 (9)
C(23)	89 (10)	6394 (6)	4351 (6)	162 (14)	55 (5)	46 (5)	15 (13)	16 (13)	53 (8)
C(24)	174 (12)	8380 (7)	2703 (8)	223 (18)	61 (6)	75 (8)	50 (16)	109 (17)	83 (12)
O(25)	$\frac{1}{2}$	$\frac{1}{2}$	0	308 (32)	201 (17)	51 (7)	148 (36)	−12 (28)	49 (17)
O(26)	$\frac{1}{2}$	0	$\frac{1}{2}$	258 (30)	85 (12)	383 (37)	91 (28)	36 (49)	126 (29)
O(27)	2476 (22)	4164 (12)	565 (11)	554 (42)	173 (13)	128 (10)	−22 (36)	14 (35)	87 (19)
O(28)	5874 (32)	9593 (19)	2655 (19)	688 (65)	227 (21)	236 (22)	64 (56)	113 (59)	139 (34)
O(29)	6304 (27)	8327 (17)	1204 (19)	546 (49)	229 (20)	277 (25)	−64 (48)	124 (53)	204 (37)
O(30)	3565 (23)	6629 (19)	973 (11)	541 (39)	415 (29)	126 (11)	690 (59)	91 (33)	12 (28)
C(31)*	3729 (25)	5264 (18)	496 (14)	148 (34)	112 (17)	37 (10)	63 (39)	17 (35)	50 (21)
C(32)*	5442 (20)	9130 (13)	4846 (16)	297 (30)	92 (12)	200 (18)	36 (30)	99 (36)	123 (22)
C(33)	3822 (31)	3895 (19)	65 (15)	257 (45)	112 (19)	50 (12)	27 (46)	60 (39)	59 (25)

* The occupancy parameter for these atoms, which are bonded to oxygen atoms at inversion centers, is 0·5.

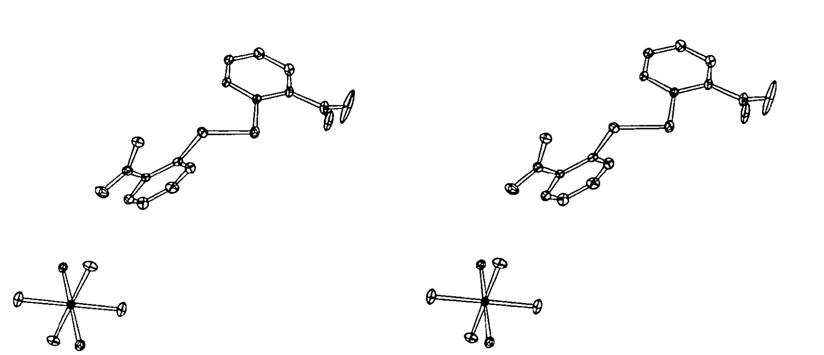

Fig. 1. A stereo view, prepared with *ORTEP* (Johnson, 1965), of part of the crystal structure. The hydrated Co(II) cation and one anion are shown. Ellipsoids of 15% probability are used.

vent region is continuous (see Fig. 3) and some loss of solvent might have occurred during data collection, although no indications of this were found in the variations of the check reflection intensities. Nevertheless, the inclusion of all ten solvent molecules in ordered positions, except for two methyl carbons (those whose oxygen atoms are placed at inversion centers) which were each refined as two half-carbon atoms, and with anisotropic temperature factors, lowered the error indices by approximately 0·08. A more careful treatment of the disorder has not been undertaken.

Large-block diagonal least-squares refinement (alternately refining different groups by full-matrix methods) using anisotropic temperature factors converged* at $R_1=0{\cdot}104$ and R_2 (weighted)$=0{\cdot}103$. The least-squares program utilized (*UCLALS*4) was that of Gantzel, Sparks & Trueblood [ACA Library (old) no. 317], modified. The assigned weights were the reciprocal squares of σ, the standard deviation of each observation. The final difference Fourier function showed two peaks of 0·6 and 0·4 e Å^{-3} in the vicinity of the solvent molecules; these are probably due to the inadequate treatment of the disorder. Otherwise, the highest and lowest points were 0·2 and $-0{\cdot}1$ e Å^{-3}, approximately the same as the e.s.d. of the electron density, 0·2 e Å^{-3}. The final parameters are given in Table 1.

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30249 (16 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances and angles*

Estimated standard deviations are in the units of the least significant digit given for the corresponding parameter.

Co(1)–O(2)	2·079 (7) Å	O(2)—Co(1)–O(3)	90·6 (5)°
Co(1)–O(3)	2·082 (7)	O(2)—Co(1)–O(4)	92·4 (5)
Co(1)–O(4)	2·109 (7)	O(3)—Co(1)–O(4)	92·0 (5)
S(5) —S(6)	2·047 (3)	S(6) —S(5) —C(11)	105·4 (2)
S(5) —C(11)	1·795 (7)	S(5) —C(11)–C(12)	119·3 (5)
C(11)–C(12)	1·397 (10)	S(5) —C(11)–C(16)	121·4 (6)
C(12)–C(13)	1·391 (10)	C(11)–C(12)–C(13)	119·3 (7)
C(13)–C(14)	1·395 (13)	C(12)–C(13)–C(14)	120·5 (8)
C(14)–C(15)	1·379 (14)	C(13)–C(14)–C(15)	119·3 (8)
C(15)–C(16)	1·369 (13)	C(14)–C(15)–C(16)	120·4 (9)
C(16)–C(11)	1·383 (11)	C(15)–C(16)–C(11)	121·1 (8)
C(12)–C(17)	1·511 (10)	C(16)–C(11)–C(12)	119·3 (7)
C(17)–O(7)	1·248 (10)	C(11)–C(12)–C(17)	122·1 (6)
C(17)–O(8)	1·254 (9)	C(13)–C(12)–C(17)	118·6 (6)
S(6) —C(18)	1·784 (7)	C(12)–C(17)–O(7)	118·5 (7)
C(18)–C(19)	1·399 (10)	C(12)–C(17)–O(8)	116·6 (6)
C(19)–C(20)	1·389 (11)	O(7)—C(17)–O(8)	124·7 (7)
C(20)–C(21)	1·397 (12)	S(5) —S(6) —C(18)	107·2 (2)
C(21)–C(22)	1·374 (12)	S(6) —C(18)–C(19)	119·3 (6)
C(22)–C(23)	1·373 (11)	S(6) —C(18)–C(23)	121·5 (6)
C(23)–C(18)	1·407 (10)	C(18)–C(19)–C(20)	118·5 (7)
C(19)–C(24)	1·501 (12)	C(19)–C(20)–C(21)	122·1 (8)
C(24)–O(9)	1·170 (12)	C(20)–C(21)–C(22)	118·5 (8)
C(24)–O(10)	1·209 (14)	C(21)–C(22)–C(23)	120·9 (7)
O(25)–C(31)	1·24 (2)	C(22)–C(23)–C(18)	120·9 (7)
O(26)–C(32)	1·17 (2)	C(23)–C(18)–C(19)	119·1 (6)
O(27)–C(33)	1·30 (3)	C(18)–C(19)–C(24)	122·6 (7)
		C(20)–C(19)–C(24)	118·2 (7)
		C(19)–C(24)–O(9)	120·6 (9)
		C(19)–C(24)–O(10)	117·7 (14)
		O(9)—C(24)–O(10)	121·6 (15)

Discussion

Part of the structure is shown in Fig. 1. The Co(II) ion is at an inversion center, taken to be the origin, and is octahedrally coordinated by six water molecules. The average Co(II)–oxygen distance is 2·09 Å (see Table 2). This value compares favorably with the Co(II)–oxygen distance (2·11 Å) in the water octahedron of cobalt sulfate hexahydrate (Zalkin, Ruben & Templeton, 1962).

The dibasic anion, one per asymmetric unit, is neutralized at only the O(7), C(17), O(8) end (see Fig. 2). At the other (acid) end of the anion, the bond lengths (Fig. 2) and thermal parameters (Fig. 1) indicate the effects of disorder. The angle between the planes of the two phenyl rings of a single anion, as defined in Table 3, is 75·0°.

Of interest, and worthy of comparison, is the geom-

Table 3. *Deviations from least-squares planes* (Å × 10^3)

Boldface deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table 1 lies between that plane and the origin. The direction cosines (× 10^4), q, are with respect to orthogonal axes. The r.m.s. deviation (Å × 10^3) of the boldface atoms from the plane is δ. D is the distance (in Å) from the plane to the origin.

	Plane 1		Plane 2
C(11)	**−2**	C(18)	**4**
C(12)	**−11**	C(19)	**4**
C(13)	**15**	C(20)	**−10**
C(14)	**4**	C(21)	**7**
C(15)	**−17**	C(22)	**4**
C(16)	**11**	C(23)	**−8**
S(5)	−10	S(6)	106
C(17)	90	C(24)	−77
O(7)	−187	O(9)	−409
O(8)	495	O(10)	226
$q_{b\times(a\times b)}$	3215		−9743
q_b	−3663		1782
$q_{a\times b}$	8731		1377
D	2·78 Å		−4·76 Å
δ	11		7

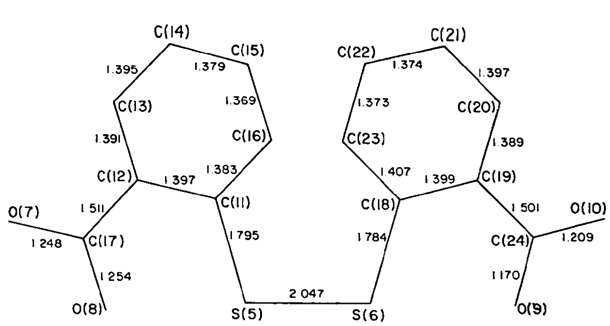

Fig. 2. The disulfide anion, schematically drawn, indicating the numbering system and the bond lengths.

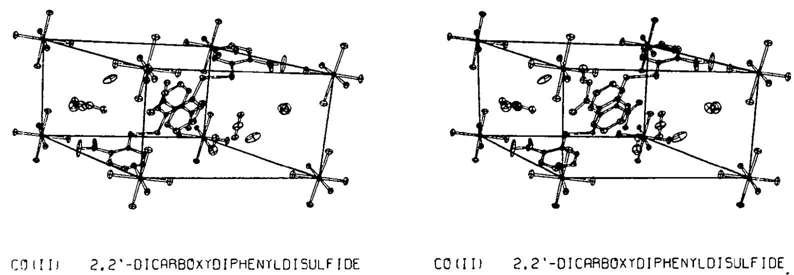

Fig. 3. A stereo view of the packing within the unit cell using ellipsoids of 15% probability. Three-atom 'molecules' are methanol oxygen atoms with two disordered half-carbon atoms. Two-atom molecules are methanol, and a water molecule is represented by only its oxygen atom. The view is nearly along **c**, with **b** horizontal and **a** vertical in the plane of the page.

etry of the disulfide linkage. The C(11)–S(5)–S(6)–C(18) dihedral angle is 86·7° and the S(5)–S(6) bond is 2·047 (3) Å. These values can be compared to those of 90·5° and 2·060 (3) Å found in an analogous compound, 2,2'-diaminodiphenyl disulfide (Lee & Bryant, 1970), (to illustrate the similarity, the present anion may be named hydrogen-2,2'-dicarboxylate diphenyl disulfide), as well as to many other organic disulfides (Hordvik, 1966; Lee, 1972). A stereo view of the packing is shown in Fig. 3.

This work was supported by the National Institutes of Health (grant no. GM-18813-01). We are also indebted to the National Science Foundation for their assistance (grant no. GP-13213) in the purchase of the diffractometer, and to the University of Hawaii Computing Center.

References

BOSCHI, T., CROCIANI, B., TONIOLO, L. & BELLUCO, U. (1970). *Inorg. Chem.* **9**, 532–537.
CHALLENGER, F. (1959). *Aspects of the Organic Chemistry of Sulphur*. London: Butterworths.
DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.
HEMMERICH, P. (1966). *The Biochemistry of Copper*, edited by PEISACH, AISEN & BLUMBERG, pp. 15–34. New York: Academic Press.
HORDVIK, A. (1966). *Acta Chem. Scand.* **20**, 1885–1891.
HUBBARD, C. R., QUICKSALL, C. O. & JACOBSON, R. A. (1971). *ALFF*, Ames Laboratory Fast Fourier, Iowa State Univ., U.S.A.
KAWANISHI, S., YOKOYAMA, A. & TANAKA, H. (1972). *Chem. Pharm. Bull.* **20**, 262–268.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
LEE, J. D. (1972). *Naturwissenschaften*, **59**, 36–37.
LEE, J. D. & BRYANT, M. W. R. (1970). *Acta Cryst.* B**26**, 1729–1735.
OTTERSEN, T., WARNER, L. G. & SEFF, K. (1973). *Chem. Commun.* 876–877.
ZALKIN, A., RUBEN, H. & TEMPLETON, D. H. (1962). *Acta Cryst.* **15**, 1219–1223.

Acta Cryst. (1974). B**30**, 1191

The 2:1 Crystal Complex of 5,5-Diethylbarbituric Acid (Barbital) and Caffeine

BY B. M. CRAVEN AND G. L. GARTLAND*

Department of Crystallography, University of Pittsburgh, Pittsburgh, Pennsylvania 15260, *U.S.A.*

(*Received* 5 *September* 1973; *accepted* 19 *October* 1973)

Triclinic, $P\bar{1}$; $a=14{\cdot}627$ (4), $b=14{\cdot}160$ (4), $c=6{\cdot}902$ (2) Å, $\alpha=92{\cdot}25$ (4), $\beta=92{\cdot}80$ (4), $\gamma=100{\cdot}75$ (4)°; $Z=2$ for $2C_8H_{12}N_2O_3.C_8H_{10}N_4O_2$; $D_{meas}=1{\cdot}344$ g cm^{-3}, $D_x=1{\cdot}334$ g cm^{-3}; m.p. 142°C; μ(Cu $K\alpha$)= 8·67 cm^{-1}. The crystal structure was determined by direct methods from 4665 intensity data which were measured with a computer-controlled four-circle diffractometer and nickel-filtered Cu $K\alpha$ radiation. Refinement by a block-diagonal least-squares procedure gave a final R index of 0·053. Bond lengths and angles are similar to those observed in related crystal structures.

Introduction

The crystals were prepared as described by Higuchi & Lach (1954). Integrated intensity data were collected from a crystal elongated along **c** and exhibiting the forms {100}, {010}, and {001}. The crystal was mounted with the c^* reciprocal axis along the diffractometer φ axis. 4665 independent reflections in the range $\sin\theta/\lambda \le 0{\cdot}59$ Å^{-1} were scanned in the θ–2θ mode at a rate of 2° min^{-1}. A variable 2θ scan width was used, based on a minimum of 1·5°. Stationary

* Present address: The University of Alabama Medical Center, Birmingham, Alabama 35233, U.S.A.