Crystal Structure of Tris(diethyldithiocarbamato)iridium(III)

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The crystal structure of the title compound has been determined by the heavy-atom method from *X*-ray diffractometer data, and refined by full-matrix least-squares to *R* 0.064 for 3 292 observed reflections. Crystals are monoclinic, space group *C*2/*c*, and isostructural with the cobalt(III) analogue: $a = 14.071(5)$, $b = 10.477(3)$, $c = 16.980(5)$ Å, $\beta = 108.61(2)°$, $Z = 4$. Mean Ir–S is 2.36_7 Å.

CONTINUING our determination of molecular geometries and structural types among the tris(diethyldithiocarbamate)metal(III) derivatives, $[M(S_2C{\cdot}NEt_2)_3]$, we now report the crystal structure of the iridium(III) derivative, which is isostructural with its cobalt(III) analogue.[1,2] It was prepared by the usual method [3] and recrystallized initially from chloroform as a solvate; recrystallization from acetone yielded unsolvated crystals. A crystal 0.12 × 0.18 × 0.14 mm (*b*, *c* as face diagonals) was used for the crystallographic work.

EXPERIMENTAL

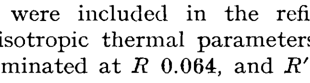
Unit-cell calibration was carried out by a least-squares fit of the angular parameters of 15 reflections with 2θ *ca.* 20° centred in the counter aperture of a Syntex $P\bar{1}$ four-circle diffractometer. A unique data set was collected by a conventional 2θ—θ scan within the range $2\theta < 60°$, to yield 3 479 independent reflections, of which 3 292 with $I > \sigma(I)$ were considered observed and used in the structure solution and refinement, after correction for absorption.

Crystal Data.—$C_{15}H_{30}Ir_3N_3S_6$, $M = 637.0$, Monoclinic, $a = 14.071(5)$, $b = 10.477(4)$, $c = 16.980(5)$ Å, $\beta = 108.61(2)°$, $U = 2\,372(1)$ Å^3, $D_m = 1.78(1)$, $Z = 4$, $D_c = 1.783$ g cm^{-3}, $F(000) = 1\,256$. Mo-K_α radiation (monochromatic), $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_\alpha) = 64.8$ cm^{-1}. Neutral-atom scattering factors,[4,5] those for Ir, S being corrected for anomalous dispersion ($\Delta f'$, $\Delta f''$).[6] Space group *C*2/*c* (C^6_{2h}, No. 15).

A Patterson function confirmed that the Ir compound was isostructural with the cobalt(III) derivative, and the parameters of the latter were used in the initial refinement by full-matrix least squares, with anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. Hydrogen atoms were all located in a difference map but not all methyl hydrogens would refine successfully and eventually all were included in the refinement as invariants with isotropic thermal parameters $U = 0.10$ Å^2. Refinement terminated at *R* 0.064, and R' $[= (\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2)^{\frac{1}{2}}]$ 0.071, a weighting scheme of the form $w = [\sigma^2(F_o) + 3 \times 10^{-4}(F_o)^2]^{-1}$ being found appropriate. No parameter shift in the final cycle was $>0.2\sigma$. A few low-angle reflections showed apparent extinction effects and were deleted from the final refinement cycles.

Computation was carried out on a CDC 6200 machine with the '*X*-Ray '72 program system.[7] Structure factors are deposited as Supplementary Publication No. SUP 21549 (14 pp., 1 microfiche).†

Labelling of atoms within the ligands is as shown [because



of its orientation about a two-fold axis, only the top half is relevant for ligand (1), comprising S(1), N(1), C(1)—(3)];

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† For details, see Notice to Authors, No. 7, in *J.C.S Dalton*, 1975, Index issue.

[1] S. Merlino, *Acta. Cryst.*, 1968, **B24**, 1441.

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[3] C. G. Sceney and R. J. Magee, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 595.

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[5] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[6] D. T. Cromer, *Acta Cryst.*, 1965, **18**, 7.

[7] '*X*-Ray' program system, Technical Report TR 192, of the Computer Science Centre, University of Maryland, U.S.A., June, 1972.

TABLE 1

Atomic fractional cell parameters (for Ir, ×10^5; S, ×10^4; others, ×10^3) and thermal parameters (×10^3 Å^2) with least-squares estimated standard deviations in parentheses

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	50 000	25 333(3)	25 000	31.1(2)	23.3(2)	36.1(2)	0(–)	8.9(2)	0(–)
Ligand (1)									
S(1)	3 987(2)	0 720(2)	2 468(1)	36(1)	35(1)	51(1)	−6(1)	7(1)	4(1)
C(1)	500	−021(1)	250	52(7)	23(5)	37(6)	0(–)	0(1)	0(–)
N	500	−148(1)	250	75(9)	18(5)	80(8)	0(–)	22(7)	0(–)
C(2)	409(1)	−221(1)	248(1)	120(11)	30(5)	61(6)	−20(6)	9(7)	3(4)
C(3)	412(1)	−260(1)	336(1)	183(20)	86(11)	88(11)	−41(10)	54(12)	13(8)
Ligand (2)									
S(1)	3 709(2)	4 086(2)	2 216(1)	46(1)	40(1)	38(1)	11(1)	13(1)	−1(1)
S(2)	4 402(2)	2 799(2)	1 040(1)	39(1)	33(1)	38(1)	4(1)	13(1)	−2(1)
C(1)	358(1)	391(7)	118(4)	33(4)	28(4)	37(4)	−4(3)	9(3)	−3(3)
N	293(1)	456(1)	057(0)	37(4)	46(4)	45(4)	12(3)	8(3)	−1(3)
C(2)	293(1)	443(1)	−029(1)	51(5)	50(5)	43(4)	6(4)	6(4)	10(4)
C(3)	343(1)	550(1)	−056(1)	94(10)	85(9)	75(8)	−26(8)	44(7)	−3(7)
C(4)	230(1)	558(1)	075(1)	52(6)	51(6)	59(5)	19(5)	9(5)	−5(5)
C(5)	123(1)	560(2)	016(1)	51(7)	116(12)	129(12)	31(8)	11(8)	−24(10)

C(3) and C(5) are disposed on either side of the ligand plane. The ligand number [(1) or (2)] precedes the atom number. Results are shown in Tables 1—3 and Figure 1.

DISCUSSION

Determination of the structure of [Ir($S_2C{\cdot}NEt_2)_3$] shows the cell to be comprised of discrete molecules located on a two-fold symmetry axis passing through the metal atom and the axis of one ligand, and to be isostructural with the cobalt(III) derivative; ligand geometries are as expected, the S_2CNC_2 sections defining reasonably good planes (Table 3), particularly for ligand (1). Ligand (2) is slightly but trivially distorted and, unlike ligand (1), exhibits a significant but small metal atom deviation. The mean Ir–S distance (2.36_7 Å) lies in the range reported for non-bridging sulphur–iridium distances found in [$Ir_2(C_7H_7S_2)_3(CO)_2(PPh_3)_2$], the only other iridium–sulphur complex studied structurally.[8]

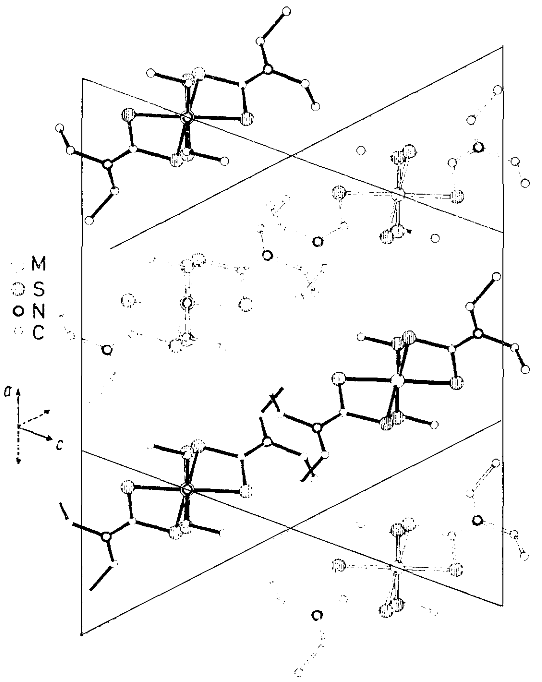

FIGURE 1 Unit-cell contents projected down *b*; the dotted lines give the axes of the related $P2_1/c$ cell in Figure 2

TABLE 2

Interatomic distances (Å) and angles (°), with least-squares estimated standard deviations in parentheses

(Superscript I denotes atoms related by the intramolecular two-fold rotation)

(*a*) The IrS_6 core			
S(11)–Ir–S(21)	97.45(8)	S(21)–Ir–S(21^{I})	93.31(8)
S(11)–Ir–S(22)	93.46(7)	S(21)–Ir–S(22^{I})	97.20(7)
S(11)–Ir–S(21^{I})	166.65(7)	S(22)–Ir–S(22^{I})	166.47(7)
S(11)–Ir–S(22^{I})	97.40(8)		
(*b*) Ligand (1)			
Ir–S(1)	2.365(2)	S(1)–Ir–S(1^{I})	73.13(8)
S(1)–C(1)	1.715(7)	Ir–S(1)–C(1)	88.2(3)
C(1)–N	1.33(1)	S(1)–C(1)–N	124.7(3)
N–C(2)	1.48(2)	C(1)–N–C(2)	121.1(6)
C(2)–C(3)	1.53(2)	N–C(2)–C(3)	111(1)
S(1) · · · S(1^{I})	2.818(4)	C(2)–N–C(2^{I})	117.7(9)
		S(1)–C(1)–S(1^{I})	110.5(6)
(*c*) Ligand (2)			
Ir–S(1)	2.370(2)	S(1)–Ir–S(2)	73.32(8)
Ir–S(2)	2.367(2)	Ir–S(1)–C(1)	87.8(3)
S(1)–C(1)	1.720(8)	Ir–S(2)–C(1)	88.0(3)
S(2)–C(1)	1.714(8)	S(1)–C(1)–N	124.7(7)
C(1)–N	1.326(9)	S(2)–C(1)–N	124.3(7)
N–C(2)	1.46(1)	C(1)–N–C(2)	121.0(8)
N–C(4)	1.48(1)	C(1)–N–C(4)	120.8(7)
C(2)–C(3)	1.47(2)	C(2)–N–C(4)	117.4(7)
C(4)–C(5)	1.51(2)	N–C(2)–C(3)	113.3(8)
S(1) · · · S(2)	2.828(4)	N–C(4)–C(5)	114.3(9)
		S(1)–C(1)–S(2)	110.9(4)

From previous studies of derivatives of the type [M($S_2C{\cdot}NEt_2)_3$], it appears that, in those complexes in which no electronic distortion mechanism is inherent, the MS_6 core geometry is a good approximation to D_3 and that the structural type is subtly dependent on the metal–sulphur distance r. Thus, in derivatives with $\langle r \rangle < ca.$ 2.35 Å (Co,[1,2] low-temperature Fe,[9] 2.25_8, 2.30_6 Å), the cell symmetry is $C2/c$; as r increases >2.35 Å (room-temperature Fe,[9] Cr,[10] Ru,[11,12] 2.35_7,

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[8] G. P. Khare and R. Eisenberg, *Inorg. Chem.*, 1972, **11**, 1385.

[9] J. G. Liepoldt and P. Coppens, *Inorg. Chem.*, 1973, **12**, 2269.

2.39_6, 2.37_6 Å) the structure becomes distorted by a tilt of the axial ligand slightly away from *b* so that the cell symmetry is degraded to $P2_1/c$ (Figure 2). (In these cases, one terminal methyl group becomes disordered also.)

TABLE 3

Equations of least-squares planes in the form $pX + qY + rZ = s$ (where $X = ax + cz\cos\beta$, $Y = by$, $Z = cz\sin\beta$), through the S_2CNC_2 portion of the ligands. σ(Å) is the estimated standard deviation of the defining atoms; atom deviations (Å) are given in square brackets. χ^2 is given for 5° of freedom

	10^4p	10^4q	10^4r	s	σ	χ^2
Ligand (1)	−0314	0 000	9 995	3.843	0.007	2.50
[S(1) −0.007, C(1) 0.000, N(1) 0.000, C(2) 0.008, Ir 0.000]						
Ligand (2)	7 060	7 001	1 067	6.196	0.036	115.0
[S(1) 0.020, S(2) 0.012, C(1) −0.024, N −0.062, C(2) 0.032, C(3) 1.368, C(4) 0.023, C(5) −0.892, Ir 0.103]						

A gap exists in the data for the range 2.39—2.42 Å, but at $\langle r\rangle > 2.43$ Å (Ga, In,[13] 2.43_6, 2.59_7 Å) a further lattice type is generated, closely related in its cell dimensions, but with symmetry $A2/a$ and related by a twist of the molecules by some 60° about the two-fold axis.

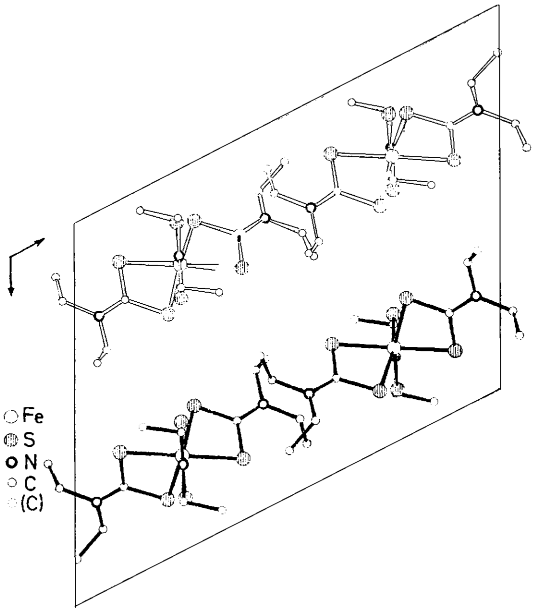

FIGURE 2 Unit-cell contents of the complex $[Fe(S_2C{\cdot}NEt_2)_3]$, projected down *b* (from the data of ref. 15). (C) denotes disordered terminal carbon

(In addition, it appears that, possibly influenced by the choice of solvent, it is possible for some symmetrical members to crystallize in a cell of the As,[14,15] Mn [16] type; see data for *e.g.* the Rh complex.[15])

Thus far, the story appears fairly self consistent; a plot of the angle of twist about the three-fold axis, as a function of ligand–metal distance, against bite (Figure 3) yields a good straight line closely fitting Kepert's ligand repulsion model [17] for $n = 6$ (Table 4, Figure 4).

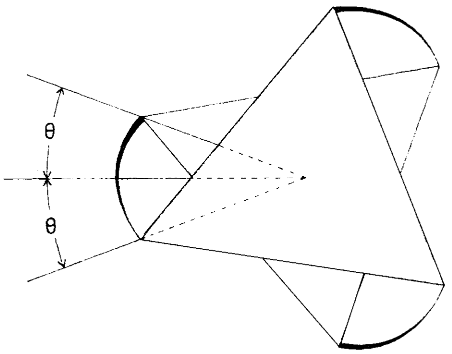

FIGURE 3 Idealized geometry of the MS_6 core projected down the three-fold axis

When the iridium derivative is considered, it appears to be anomalous. For $\langle r\rangle = 2.36_7$ Å, the complex clearly should crystallize as $P2_1/c$ in the foregoing series.

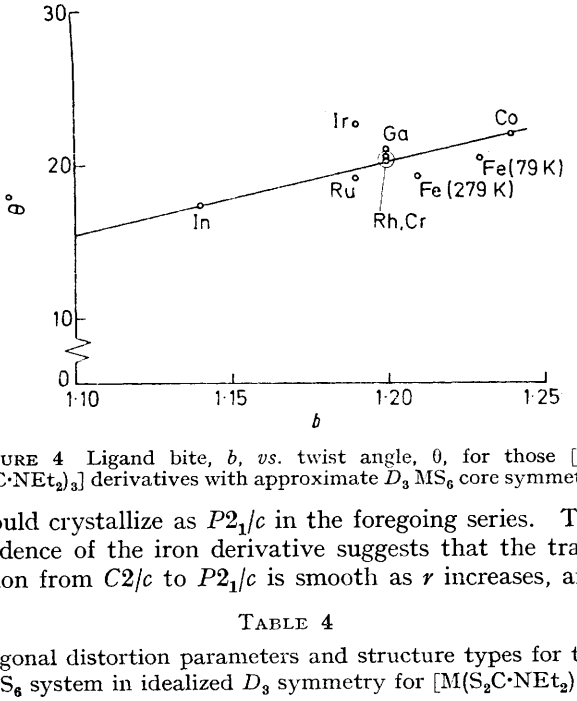

FIGURE 4 Ligand bite, *b*, *vs.* twist angle, θ, for those $[M(S_2C{\cdot}NEt_2)_3]$ derivatives with approximate D_3 MS_6 core symmetry

The evidence of the iron derivative suggests that the transition from $C2/c$ to $P2_1/c$ is smooth as *r* increases, and

TABLE 4

Trigonal distortion parameters and structure types for the MS_6 system in idealized D_3 symmetry for $[M(S_2C{\cdot}NEt_2)_3]$

Metal	$\langle r\rangle$	Space group	b	θ
Co [a]	2.25_8	$C2/c$	1.24	21.9
Fe(79 K) [b]	2.30_6	$C2/c$	1.23	20.2
Fe(297 K)	2.35_7	$P2_1/c$	1.21	18.8
Ru [c]	2.37_6	$P2_1/c$	1.19	19.0
Cr [d]	2.39_6	$P2_1/c$	1.20	20.2
Ga [e]	2.43_6	$A2/a$	1.20	20.7
In [e]	2.59_1	$A2/a$	1.14	17.2
Ir [f]	2.36_8	$C2/c$	1.19	22.2
Rh [g]	2.36_5	$P2_1/c$*	1.20	20.1

* This $P2_1/c$ case is different from those above (see text).

[a] Refs. 1 and 2. [b] Ref. 9. [c] Refs. 11 and 12. [d] Ref. 10. [e] Ref. 13. [f] This work. [g] Ref. 15.

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[11] L. Pignolet, *Inorg. Chem.*, 1974, **13**, 2051.

[12] A. Domenicano, A. Vaciago, L. Zambonelli, P. Loader, and A. M. Venanzi, *Chem. Comm.*, 1966, 476.

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[14] M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, *Chem. Comm.*, 1968, 302.

[15] C. L. Raston and A. H. White, *J.C.S. Dalton*, 1975, 2425.

[16] P. C. Healy and A. H. White, *J.C.S. Dalton*, 1972, 1883.

[17] D. L. Kepert, *Inorg. Chem.*, 1972, **11**, 1561.

should accommodate changes in packing forces, *etc.*, by a simple adaptation of cell size. In relation to Figure 4, the position of the iridium derivative is clearly slightly but significantly anomalous, being distorted rather more than expected towards the octahedral extreme; moreover, there does not appear to be a uniform Co, Rh, Ir trend which might assist in explaining the anomaly. The possibility of a misassigned space group (*i.e.* as $C2/c$ rather than $P2_1/c$) in the present case has been thoroughly checked (by long-exposure Weissenberg photographs) in the light of the foregoing and dismissed, so that the cause of the anomaly remains obscure.

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