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THE CRYSTAL AND MOLECULAR STRUCTURE OF CYCLOPENTADIENYLIRON DICARBONYL ISOTHIOCYANATE

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Summary

The crystal structure of $(\eta^5\text{-}C_5H_5)Fe(CO)_2NCS$ has been determined by single crystal X-ray methods. The title compound has a monoclinic unit cell with *a* 6.400(6), *b* 7.907(4), *c* 9.115(8) Å and γ 91.48(8)° containing two formula units. The space group is $P_{2_1/m}$ and the calculated density is 1.69 g cm^{-3}. The structure was refined by least-squares methods to a conventional *R* index of 0.10 using multiple-film equi-inclination Weissenberg data. The FeNCS fragment is essentially linear and the FeNCS and FeCO linkages are approximately orthogonal. The shortest non-bonded Fe···S interaction is 4.52(1) Å.

Introduction

Transition metal complexes of the thiocyanate ligand have been studied for many years, as they provide an extensive series of examples of the linkage isomerism phenomenon. Solid state structures have been determined by diffraction methods for a large number of "classical" complexes, i.e. those in which the metal is in the +2 or +3 oxidation state and other ligands bound to the metal are ammonia, cyanide and the like [1]. A striking feature of the data reported is the near-linearity of the M—N—C—S linkages (M—N—C angles 165—180°) versus severe bending in the case of the M—S—CN mode of attachment (M—S—C angles 89.5°—115°) [1]. To our knowledge there have been no previous reports of structure determinations of metal carbonyl complexes containing the —NCS or —SCN ligands. With this in mind and in view of differences in photoreactivity [2,3] and Mössbauer effect parameters [4] for the linkage isomers $(\eta^5\text{-}C_5H_5)Fe(CO)_2NCS$ and $(\eta^5\text{-}C_5H_5)Fe(CO)_2SCN$ which were tentatively ascribed to differing bond angles, we have undertaken the crystal structure determination of the former complex. This paper describes the results of

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our study, along with further comments on correlation of the observed structure with chemical and spectroscopic properties of the subject complex and its linkage isomer.

Experimental

$(\eta^5\text{-}C_5H_5)Fe(CO)_2NCS$ was prepared along with its linkage isomer $(\eta^5\text{-}C_5H_5)Fe(CO)_2SCN$ by the method of Sloan and Wojcicki [5]. The isomers were separated by column chromatography (Florasil, CH_2Cl_2 eluant) and the subject complex crystallized from 1/3 methylene chloride/hexane at 0° C. $(\eta^5\text{-}C_5H_5)Fe(CO)_2NCS$ exhibits C—O stretches ($CHCl_3$ solution) at 2070 and 2025 cm^{-1} and $\nu(C\equiv N)$ at 2120 cm^{-1}, indicating that bonding to these ligands is normal [2].

The crystals chosen for data collection were approximately 0.1 × 0.3 × 1.0 mm. Multiple-film equi-inclination Weissenberg data were collected from two crystals for layers $h0l$-$h4l$ and $hk0$-$hk5$ with Ni-filtered CuK_α radiation (λ = 1.54178 Å). Intensities were estimated visually using a calibrated intensity strip and were corrected for Lorentz and polarization effects.

The unit cell was found to be monoclinic with a 6.400(6), b 7.907(4), c 9.115(8) Å, and γ 91.48(8)°. The lattice constants were determined from a powder pattern, calibrated by mixing NaCl with the sample, and indexed with the aid of the single crystal data. Standard deviations in the lattice constants were estimated by a least-squares analysis.

The Laue symmetry in $2/m$. Systematic absences of $00l$ reflections for l odd indicate the space group to be either P_2, or $P_{2_1/m}$. The space group $P_{2_1/m}$ was confirmed by solution of the structure. The density calculated for $Z = 2$ is 1.69 g cm^{-3}.

The structure was determined by heavy-atom techniques. A three-dimensional Patterson map showed the Fe and S atoms lying on a mirror plane in space group $P_{2_1/m}$. Structure factors were calculated and the signs of these were used to calculate a three-dimensional electron density map from which all non-hydrogen atoms were located.

The structure was refined by full-matrix least-squares to a final value of $R = (\Sigma|F_O - Fc|/\Sigma|Fo|)$, of 0.10. The minimized function was $\Sigma w(Fo - Fc)^2$ with weights assigned according to:

$$w = A/Fo \text{ for } Io \geqslant \sqrt{A}\, I_{\min}$$

$$w = I_0^2/I_{\min}^2 Fo \text{ for } I_0 \leqslant \sqrt{A}\, I_{\min}$$

where $I_{\min} = 1$ and A was chosen as 16. The largest atomic shift observed in the last least-squares cycle was 0.65 σ.

The scattering factors were taken from the International Tables for X-ray Crystallography [6]. No corrections were applied for anomalous dispersion, extinction or absorption. The hydrogen atoms were included in the structure factor calculations but no attempt was made to refine their positions. A three-dimensional difference electron density map calculated after the last refinement showed no peaks larger than 1.2 e.

The final atomic parameters and the temperature factors for each atom are

TABLE 1

FINAL ATOMIC PARAMETERS

Atom	*x*	*y*	*z*	*B*
Fe	0.5665(11)	0.6708(7)	0.250	2.7(3)
N	0.426(6)	0.458(4)	0.250	4.0(9)
C(1)	0.318(6)	0.347(5)	0.250	3.9(13)
S	0.195(2)	0.149(1)	0.250	4.4(4)
C(2)	0.407(5)	0.752(3)	0.104(3)	5.5(6)
O	0.318(3)	0.807(2)	0.015(2)	4.1(9)
C(3)	0.839(7)	0.529(5)	0.250	4.8(14)
C(4)	0.834(5)	0.630(3)	0.119(3)	4.6(11)
C(5)	0.823(4)	0.796(4)	0.173(3)	5.8(11)

given in Table 1. The numbers in parentheses are the standard deviations in the least significant figure as estimated from the least-squares analysis. The observed and calculated structure factors are given in Table 5.

Discussion

Pentahapto(cyclopentadienyl)irondicarbonyl isothiocyanate consists of discrete molecules of the familiar "piano stool" geometry adopted by complexes containing one sandwich bonded aromatic ligand [7]. In more conventional terms, the coordination geometry of iron can be described as distorted octahedral, the cyclopentadienyl ligand occupying three coordination positions [8]. The same basic structural features are exhibited by the isoelectronic chromium complex, $(\eta^5\text{-}C_5H_5)Cr(NO)_2NCO$ [9].

A projection of the contents of one unit cell down the [100] axis is illustrated in Fig. 1. The molecule possesses a mirror plane and the two molecules in the unit cell are related by a two-fold screw-axis. Interatomic distances within the molecule are given in Table 2 and interatomic angles are given in Table 3. The shortest intermolecular distance, 2.55 Å, occurs between hydrogen atoms while a C(1)...H distance of 2.57 Å is also observed. Table 4 lists all intermolecular distances less than 3.1 Å, the atoms between which they occur and the coordinates of the atoms from which the distances were calculated.

The cyclopentadienyl group is planar with an average displacement from the least squares plane of 0.013 Å. Ring carbon—carbon distances are equal within the accuracy of the data, averaging 1.42 Å. These separations are consistent with data for a wide variety of similar complexes [8,10,11]. The average and individual values for iron—ring carbon distances are also as expected from related structures, indicating that bonding between the metal and the $\eta^5\text{-}C_5H_5$ ligand is normal. Likewise, the iron—carbonyl carbon and carbon—oxygen distances are consistent with accepted values, [8,10,11] and the near linearity (176°) of the Fe—C—O moiety is as expected.

The FeNCS fragment is essentially linear, consistent with expectations based on previously reported structures [1]. This suggests that the electronic structure of the isothiocyanate group is dominated by resonance form I rather than II and that there is relatively little iron—nitrogen π bonding. The latter conclu-

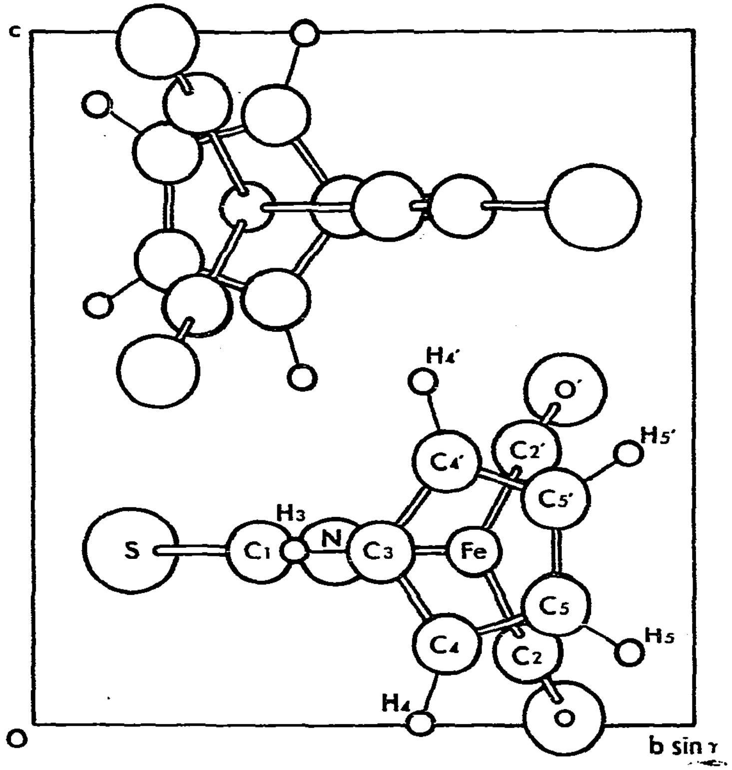


Fig. 1. The contents of one unit cell viewed in projection down the [100] axis. The labelling of the atoms in the molecule is indicated.

TABLE 2

INTERATOMIC DISTANCES (Å)

Fe—N	1.89(3)
Fe—C(1)	2.98(4)
Fe—S	4.71(1)
N—C(1)	1.10(5)
N—S	2.82(3)
C(1)—S	1.73(4)
Fe—C(2)	1.80(3)
Fe—O	2.90(2)
C(2)—O	1.09(4)
Fe—C(3)	2.10(5)
Fe—C(4)	2.12(3)
Fe—C(5)	2.02(3)
C(3)—C(4)	1.44(4)
C(4)—C(5)	1.41(4)
C(5)—C(5')	1.40(5)
C(3)—C(5)	2.29(5)
C(4)—C(4')	2.39(6)
C(4)—C(5')	2.31(4)

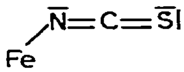
TABLE 3

INTERATOMIC ANGLES (°)

Fe—N—C(1)	169(4)
Fe—N—S	177(2)
N—C(1)—S	168(4)
Fe—C(2)—O	176(3)
N—Fe—C(2)	93(1)
C(2)—Fe—C(2′)	95(2)
C(3)—C(4)—C(5)	103(3)
C(4)—C(5)—C(5′)	111(2)
C(4)—C(3)—C(4′)	112(4)

sion was reached previously on the basis of the Mössbauer effect parameters of

(I)



(II)

the subject complex [4]. The observed C—N distance of 1.10 Å is equal (within one standard deviation to the accepted value for formal carbon—nitrogen triple bonds [9.]

As previously noted [2,3], the subject complex and its linkage isomer (η^5-C_5H_5)Fe(CO)$_2$SCN are interconverted photochemically in solution by an intramolecular mechanism involving prior CO dissociation. The isomerization does not proceed thermally in solution [2,3,5] but the (η^5-C_5H_5)Fe(CO)$_2$SCN → (η^5-C_5H_5)Fe(CO)$_2$NCS interconversion is rapid upon melting the former [5]. Sloan and Wojcicki have suggested that the solid state isomerization could proceed via Fe—NCS—Fe bridged intermediates, pointing out that such a process is not likely to occur in solution [5]. The shortest observed Fe···S non-bonded distance is 4.52(1) Å, between molecules separated by a translation along the *b* direction of one unit cell. This distance is large enough so as to leave undecided the question of the existence of a bridged intermediate.

TABLE 4

INTERMOLECULAR DISTANCES

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	Distance (Å)
H(4)	0.84	0.59	0.00	H(4)	1.16	0.41	0.00	2.55(2)
C(1)	0.32	0.35	0.25	H(4)	0.16	0.41	0.00	2.57(2)
C(1)	0.32	0.35	0.25	H(4)	0.16	0.41	0.50	2.57(2)
O	0.32	0.81	0.01	H(5)	0.18	1.10	−0.11	2.72(2)
N	0.43	0.46	0.25	H(4)	0.16	0.41	0.00	2.88(2)
N	0.43	0.46	0.25	H(4)	0.16	0.41	0.50	2.88(2)
C(1)	0.32	0.35	0.25	H(3)	−0.15	0.40	0.25	2.98(4)
C(4)	0.83	0.63	0.12	H(4)	1.16	0.41	0.00	2.98(3)
S	0.19	0.15	0.25	H(3)	−0.15	0.40	0.25	3.02(1)
O	0.32	0.81	0.01	H(3)	0.15	0.60	−0.25	3.08(2)
H(4)	0.84	0.59	0.00	H(3)	1.15	0.60	−0.25	3.08(2)

TABLE 5

ABSOLUTE VALUES OF CALCULATED AND OBSERVED STRUCTURE FACTORS

h	k	l	F_0	F_C	h	k	l	F_0	F_C	h	k	l	F_0	F_C
1	0	0	98	99	—5	1	2	<21	18	—3	2	0	61	63
2	0	0	34	41	—4	1	2	26	35	—2	2	0	91	95
3	0	0	58	63	—3	1	2	19	23	—1	2	0	17	14
4	0	0	31	29	—2	1	2	99	94	0	2	0	142	132
5	0	0	38	42	—1	1	2	202	202	1	2	0	97	108
1	0	1	14	16	0	1	2	74	68	2	2	0	68	78
2	0	1	17	13	1	1	2	57	65	3	2	0	52	57
3	0	1	52	53	2	1	2	16	26	4	2	0	<—20	4
4	0	1	40	42	3	1	2	48	45	—5	2	1	<—22	10
5	0	1	25	19	4	1	2	49	53	—4	2	1	19	23
0	0	2	154	156	5	1	2	<21	15	—3	2	1	76	81
1	0	2	43	46	—5	1	3	<23	9	—2	2	1	42	39
2	0	2	32	31	—4	1	3	24	24	—1	2	1	29	28
3	0	2	67	73	—3	1	3	<21	6	0	2	1	101	94
4	0	2	<19	4	—2	1	3	76	69	1	2	1	22	24
5	0	2	37	39	—1	1	3	23	24	2	2	1	<—14	9
1	0	3	12	9	0	1	3	45	31	3	2	1	20	18
2	0	3	73	78	1	1	3	64	63	4	2	1	22	26
3	0	3	70	69	2	1	3	52	56	—5	2	2	41	41
4	0	3	21	23	3	1	3	<17	14	—4	2	2	17	18
5	0	3	34	29	4	1	3	25	31	—3	2	2	30	35
0	0	4	132	120	5	1	3	<23	10	—2	2	2	40	48
1	0	4	68	66	—4	1	4	33	45	—1	2	2	38	31
2	0	4	<16	7	—3	1	4	47	45	0	2	2	10	7
3	0	4	<21	7	—2	1	4	83	77	1	2	2	24	21
4	0	4	<26	3	—1	1	4	67	69	2	2	2	78	81
1	0	5	29	29	0	1	4	29	24	3	2	2	80	87
2	0	5	40	40	1	1	4	17	14	4	2	2	17	26
3	0	5	45	47	2	1	4	<17	4	5	2	2	19	15
4	0	5	<31	18	3	1	4	42	45	—5	2	3	<—20	2
0	0	6	75	72	4	1	4	45	54	—4	2	3	25	26
0	0	8	63	61	—4	1	5	<29	23	—3	2	3	65	71
—4	1	0	57	68	—3	1	5	<25	18	—2	2	3	80	76
—3	1	0	41	42	—2	1	5	51	45	—1	2	3	61	56
—2	1	0	19	10	—1	1	5	31	29	0	2	3	73	66
—1	1	0	140	136	0	1	5	<13	11	1	2	3	25	22
0	1	0	78	70	1	1	5	78	75	2	2	3	41	41
1	1	0	36	41	2	1	5	40	42	3	2	3	16	20

2	1	0	105	105	3	1	5	<26	3	4	2	3	<−19	19
3	1	0	<22	9	4	1	5	<30	19	5	2	3	29	40
4	1	0	86	93	−2	1	6	42	41	−3	2	4	54	49
−5	1	1	<25	20	−1	1	6	70	63	−2	2	4	81	72
−4	1	1	52	53	0	1	6	45	32	−1	2	4	13	10
−3	1	1	18	12	1	1	6	<23	8	0	2	4	27	21
−2	1	1	86	82	2	1	6	<24	9	1	2	4	30	30
−1	1	1	20	20	−2	1	7	33	41	2	2	4	62	68
0	1	1	108	103	−1	1	7	31	16	3	2	4	27	36
1	1	1	107	120	0	1	7	<25	16	−4	2	5	<−26	16
2	1	1	31	33	1	1	7	56	50	−3	2	5	64	58
3	1	1	35	34	2	1	7	30	27	−2	2	5	55	46
4	1	1	<21	20	−4	2	0	25	20	−1	2	5	14	12
0	2	5	60	48	−4	3	5	38	38	−2	4	5	<−23	1
1	2	5	33	32	−3	3	5	<25	26	−1	4	5	45	41
2	2	5	19	17	−2	3	5	27	26	0	4	5	53	43
3	2	5	<23	0	1	3	5	28	27	1	4	5	<−22	16
4	2	5	<26	13	0	3	5	<19	15	2	4	5	33	40
−2	2	6	<25	11	1	3	5	40	41	3	4	4	27	37
−1	2	6	<22	19	2	3	5	22	24	−2	4	6	23	11
0	2	6	22	12	3	3	5	<25	27	−1	4	6	<−23	5
1	2	6	22	24	4	3	5	29	37	0	4	6	25	22
2	2	6	45	45	−1	3	6	34	27	1	4	6	<−23	1
0	2	7	59	49	0	3	6	45	33	2	4	6	<−24	21
−4	3	0	<28	14	1	3	6	53	49	0	4	7	46	37
−3	3	0	<18	9	−1	3	7	<27	10	−2	5	0	19	16
−2	3	0	54	54	0	3	7	<27	7	−1	5	0	23	16
−1	3	0	<16	8	1	3	7	27	33	0	5	0	<−18	1
0	3	0	16	6	−3	4	0	60	56	1	5	0	63	68
1	3	0	102	113	−2	4	0	51	54	2	5	0	38	47
2	3	0	92	86	−1	4	0	<9	6	−3	5	1	<−20	22
3	3	0	<19	11	0	4	0	37	36	−2	5	1	65	65
4	3	0	<29	4	1	4	0	15	20	−1	5	1	50	41
−5	3	1	46	39	2	4	0	78	78	0	5	1	<−17	11
−4	3	1	61	61	3	4	0	<19	11	1	5	1	31	35
−3	3	1	49	43	−5	4	1	28	32	2	5	1	<−19	15
−2	3	1	30	33	−4	4	1	<21	11	3	5	1	<−20	18
−1	3	1	19	20	−3	4	1	18	17	−1	5	2	<−15	0
0	3	1	48	45	−2	4	1	<15	2	0	5	2	42	43
1	3	1	63	71	−1	4	1	58	62	1	5	2	57	62
2	3	1	42	39	0	4	1	60	56	−2	5	3	54	53
3	3	1	45	46	1	4	1	41	45	−1	5	3	53	59
4	3	1	44	54	2	4	1	71	68	0	5	3	17	15

TABLE 5 (continued)

h	k	l	F_0	F_C	h	k	l	F_0	F_C	h	k	l	F_0	F_C
−4	3	2	<18	11	3	4	1	49	52	1	5	3	40	39
−3	3	2	41	32	−3	4	2	43	44	2	5	3	25	34
−2	3	2	56	52	−2	4	2	24	30	−3	5	4	<−22	11
−1	3	2	92	90	−1	4	2	<14	0	−2	5	4	<−21	6
0	3	2	48	44	0	4	2	51	42	−1	5	4	<−20	1
1	3	2	72	76	1	4	2	31	40	0	5	4	20	23
2	3	2	32	33	2	4	2	38	34	1	5	4	26	27
3	3	2	36	34	3	4	2	27	31	2	5	4	<−21	23
4	3	2	<15	2	−5	4	3	27	31	3	5	4	<−22	22
−5	3	3	35	32	−4	4	3	<19	3	−2	5	5	41	38
−4	3	3	44	47	−4	4	3	<20	2	−1	5	5	57	48
−3	3	3	31	25	−2	4	3	<16	0	0	5	5	<−24	9
−2	2	3	41	40	−1	4	3	78	79	1	5	5	<−24	16
−1	3	3	33	33	0	4	3	66	61	2	5	5	25	21
0	3	3	<13	13	1	4	3	15	15	−1	6	0	29	34
1	3	3	16	15	2	4	3	43	48	0	6	0	52	54
2	3	3	24	25	3	4	3	28	31	1	6	0	<−21	13
3	3	3	46	51	4	4	3	<19	5	−3	6	1	45	47
4	3	3	51	52	5	4	3	<19	2	−2	6	2	<−20	20
5	3	3	<20	26	−3	4	4	25	27	−1	6	1	<−20	2
−3	3	4	<20	6	−2	4	4	52	46	0	6	1	19	16
−2	3	4	65	55	−1	3	4	38	39	1	6	1	<−20	11
−1	3	4	41	42	0	4	4	40	31	2	6	1	46	38
0	3	4	<15	2	1	4	4	<18	6	0	6	2	53	48
1	3	4	61	59	2	4	4	28	35	0	6	3	<−18	3
2	3	4	44	47	3	4	4	23	22	0	6	4	48	49
3	3	4	<21	16	−3	4	5	<24	3					

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