(1965) have made a similar observation for γ-sulphanilamide in which they have found an S–N bond of 1·67 Å. Sabine & Cox (1967) have found the S–N bond in $S_4N_4H_4$ to be 1·65 Å and a trigonal nitrogen configuration.

In potassium sulphamate the S–N bond is not significantly longer but the configuration is sp^3. The sulphamate ion configuration is the same as that of the sulphamic acid molecule except for the absence of one of the hydrogen atoms from the nitrogen atom.

Hydrogen bonding

The intermolecular O···H distance of 2·15 Å is significantly less than the van der Waals contact distance of 2·8 Å and constitutes a weak hydrogen bond joining the suphamate molecules in infinite chains parallel to the *c* axis. The N–H bonds are staggered from the S–O bonds with respect to rotation about the S–N bond with a dihedral angle of 60·8° between the SNO(1) and SNH planes.

The potassium ion environment

The potassium ions are located between the chains of sulphamate molecules. Each potassium ion is surrounded by six oxygen atoms, two at each of the distances 2·729 (O(1)], 2·729 [O(2)] and 2·961 Å [O(2)]. The average S–O distance of 1·455 Å is close to the value 1·439 Å for sulphamic acid found by Sass.

Thermal vibrations

A detailed analysis of the thermal vibration parameters was not made; however, inspection of Table 4 shows that the maximum vibration is along **a**, which is normal to the direction of hydrogen bonding.

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The Crystal and Molecular Structure of a Dimethyl Sulfoxide Complex of Iron(III) Chloride

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A three-dimensional X-ray structure determination of the dimethyl sulfoxide (DMSO) compound of empirical formula $FeCl_3(DMSO)_2$ has shown it to be composed of *trans*-$[FeCl_2(DMSO)_4]^+$ and $FeCl_4^-$ ions. It crystallizes in the space group $I4_1/a$ of the tetragonal system with unit-cell dimensions $a = 11{\cdot}60 \pm 0{\cdot}01$, $c = 20{\cdot}33 \pm 0{\cdot}01$ Å. There are four of the true (ionic) formula units in each cell, with all iron atoms occupying positions of $\bar{4}$ symmetry. The DMSO molecules are coordinated through their oxygen atoms. The S–O distance ($1{\cdot}541 \pm 0{\cdot}006$ Å) is slightly but significantly greater than that in DMSO itself.

Introduction

The pronounced ability of dimethyl sulfoxide (hereafter abbreviated DMSO) to function as a donor or Lewis base toward a wide variety of acceptors or Lewis acids was clearly demonstrated by the isolation of a large number of complexes several years ago (Cotton & Francis, 1960). Subsequent studies showed that other sulfoxides possess similar bonding capacities (Francis & Cotton, 1961; Francis, 1964) but not to the same degree as DMSO.

On the basis of infrared spectra (Cotton, Francis & Horrocks, 1960) it was postulated that in the majority of DMSO complexes, the DMSO is attached to the acceptor or Lewis acid through the oxygen atom. In one such compound, *viz.* $BF_3.DMSO$, this has been substantiated by an X-ray study (McGandy, 1961). It was also postulated, in the same infrared study, that in DMSO complexes of Pd(II) and Pt(II) attachment is through the sulfur atom, and this too has been substantiated in one case, *viz.* $PdCl_2(DMSO)_2$ (Bennett, Cotton & Weaver, 1966; Bennett, Cotton, Weaver, Williams & Watson, 1967).

One of the more interesting compounds believed to contain O-bonded DMSO is $FeCl_3(DMSO)_2$, a yellow solid which can be sublimed in vacuum at about 190°C. The volatility of the substance together with the presence of five instead of four or six ligands per metal ion raised questions as to its structure. The structure of the crystalline solid has been determined in detail by the investigation described here.

Experimental

The compound was prepared by treatment of anhydrous ferric chloride with DMSO as previously described (Cotton & Francis, 1960). Crystals suitable for X-ray investigation were obtained by slow evaporation of an ethanol solution of the compound.

Collection and reduction of data

Crystals were examined by Weissenberg and precession methods and found to belong to the tetragonal system with Laue symmetry $4/m$. From the extinction conditions observed, namely for hkl, $h+k+l \neq 2n$; for $hk0$, $h(k) \neq 2n$; for $00l$, $l \neq 4n$, the space group $I4_1/a$ is thus uniquely determined. The unit-cell dimensions found from Buerger precession photographs are $a = 11{\cdot}60 \pm 0{\cdot}01$, $c = 20{\cdot}33 \pm 0{\cdot}01$ Å. (λ Cu $K\alpha = 1{\cdot}5418$ Å). A density of $1{\cdot}56 \pm 0{\cdot}05$ g.cm^{-3} measured by flotation in a carbon tetrachloride and bromobenzene mixture is to be compared with a calculated density of $1{\cdot}55$ g.cm^{-3} for eight $FeCl_3(DMSO)_2$ formula units in a unit cell.

Intensity data were collected at room temperature on a manually operated General Electric XRD-5 diffractometer using Zr filtered Mo $K\alpha$ radiation. A single yellow crystal in the approximate shape of an octahedron was mounted with [110] parallel to the φ axis. An examination of the mosaic spread of the crystal showed that a scan of 2·66° in 2θ would be most satisfactory. The data set was collected using a modified version of Furnas's moving-crystal moving-counter method (Cotton & Elder, 1964) at a scan rate of 4° per minute. All independent reflections (635) accessible within the range $\theta_{\text{Mo}} \leq 20{\cdot}1°$ were collected and corrected for the usual Lorentz–polarization factors. The crystal on which intensities were measured had dimensions of $0{\cdot}1 \times 0{\cdot}1 \times 0{\cdot}15$ mm and a maximum μR of 0·3; therefore no absorption corrections were made.

Solution and refinement of structure*

A three-dimensional Patterson map readily showed that the eight iron atoms are located at two sets of $\bar{4}$ special positions. The two independent chlorine atoms and the sulfur atom were also located from the Patterson function by image seeking about the Fe–Fe vectors. A Fourier synthesis phased on the above five atoms revealed the location of the remaining two carbon atoms and the oxygen atom. The structure was found to consist of *trans*-$FeCl_2(OSMe_2)_4^+$ and tetrahedral $FeCl_4^-$ groups.

The coordinates and isotropic temperature factors were varied for all atoms (except hydrogen) for two cycles of least-squares refinement at which point the residual R_F (defined as $\Sigma ||F_{\text{obs}}| - |F_{\text{calc}}||/\Sigma |F_{\text{obs}}|$) stood at 0·225. Three additional cycles of refinement in which all parameters were varied including the single scale factor led to a residual of 0·135. It was noted at this point that the iron atom in the octahedral unit had an isotropic B of 2·5 whereas that of the iron atom in the tetrahedral unit was 5·2. Likewise, the octahedral chlorine atom had a B of 3·6 *versus* a B of 10·0 for the tetrahedral chlorine atom. Also, the Fe–Cl_{tet} vectors on the Patterson map were more diffuse and roughly one-half the value of the Fe–Cl_{oct} vectors. This evidence suggested a rather large thermal motion of the $FeCl_4^-$ unit. The anisotropy of this thermal motion about the tetrahedral iron and chlorine atoms was readily confirmed from a difference Fourier map.

Four cycles of full-matrix least-squares refinement using anisotropic temperature factors, defined as

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)],$$

for all atoms (except hydrogen) were now carried out. The residual, R_F, was thus reduced to 0·067. Throughout these and all previous cycles of refinement unit weights were used. A systematic analysis of the variation of $(F_{\text{obs}} - F_{\text{calc}})^2$ with F_{obs} indicated only slight curvature. Nevertheless, an empirical weighting scheme based on the slight deviations from the horizontal in this plot was tested. It led to entirely insignificant

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* The following programs for the IBM 7094 computer were used and are gratefully acknowledged:

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changes in the parameters and their standard deviations. The final cycle of refinement showed a maximum shift of one-half the standard deviation with an average shift of one-fifth of the standard deviation. A final difference Fourier map* showed no electron density higher than one-third e. Å^{-3}. Scattering factors used were those for the neutral atoms tabulated by Ibers (1962).

The final positional coordinates and anisotropic thermal parameters are listed in Table 1. The observed and calculated structure factors are given in Table 2.

Description of structure

Molecular dimensions

Important bond lengths and angles are listed in Table 3. Each of the structural units, *trans*-[$FeCl_2(DMSO)_4$]$^+$ and $FeCl_4^-$, is shown in projection down the *a* axis in Fig. 1.

The $FeCl_4^-$ ion is very nearly tetrahedral as evidenced by the two independent angles of 108·2 and 112·2°. The Fe–Cl distance of 2·162 Å is in good agreement with that of 2·19 Å found in [$(C_6H_5)_4As$][$FeCl_4$] (Zaslow & Rundle, 1957). In the [$(C_6H_5)_4As$][$FeCl_4$] structure the iron atom also lies on a $\bar{4}$ position and the two independent angles were 107 and 114·5° respectively.

The cationic unit, *trans*-[$FeCl_2(DMSO)_4$]$^+$, is a tetragonally distorted octahedron with Fe–O distances of 2·01 Å and Fe–Cl distances of 2·37 Å. The Fe–O distance can be compared with those in $Fe(OH_2)(EDTA)^-$

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* It has been suggested by Dr R. E. Marsh that we mention the fact that an electron density section in the plane where hydrogen atoms are expected shows three peaks containing about one-third electron at acceptable positions for the hydrogen atoms. For our purposes, the inclusion of these peaks, which are of borderline significance, in refinement did not seem warranted.

Table 1. *Positional* and thermal parameters† with their estimated standard deviations* (σ)

	x	y	z	$\beta_{11}(\sigma)$	$\beta_{22}(\sigma)$	$\beta_{33}(\sigma)$	$\beta_{12}(\sigma)$	$\beta_{13}(\sigma)$	$\beta_{23}(\sigma)$
Fe_{oct}	0·0	0·25	0·625	51 (2)	51	13 (1)	0·0	0·0	0·0
Fe_{tet}	0·0	0·25	0·125	111 (3)	111	24 (1)	0·0	0·0	0·0
Cl_{oct}	0·0	0·25	0·5086 (2)	89 (4)	81 (4)	13 (1)	−19 (3)	0·0	0·0
Cl_{tet}	0·1432 (5)	0·3085 (4)	0·0647 (3)	300 (8)	126 (5)	74 (2)	−14 (5)	95 (4)	7 (3)
S	0·0737 (2)	−0·0015 (2)	0·5851 (1)	61 (3)	61 (3)	17 (1)	3 (1)	0·0 (1)	−6 (1)
O	0·0976 (5)	0·1073 (5)	0·6264 (3)	72 (6)	67 (6)	16 (2)	6 (5)	−5 (3)	−8 (3)
C(1)	0·1038 (11)	−0·1180 (9)	0·6413 (5)	159 (15)	66 (10)	21 (4)	0·0 (10)	−5 (6)	11 (5)
C(2)	0·1981 (9)	−0·0129 (10)	0·5330 (6)	78 (11)	112 (11)	32 (4)	−3 (9)	−30 (5)	12 (5)

* Origin at $\bar{1}$.
† $\beta_{ij} \times 10^4$.

Table 2. *Calculated and observed structure factors*

All values on a scale 25 × absolute

H	K	FOBS	FCAL
****L = 0******			
0	2	5979	-6405
2	2	4720	-4005
4	2	7355	-7766
6	2	6266	-6435
8	2	3991	-4021
10	2	1052	-1016
0	4	3737	3919
2	4	2514	2664
4	4	5214	5287
6	4	3497	3568
8	4	822	768
10	4	2016	1927
0	6	501	-404
2	6	4042	-3916
4	6	2895	-2825
6	6	3484	-3557
0	8	2944	2996
2	8	5136	5190
4	8	1469	1285
6	8	1531	1516
0	10	662	-611
2	10	1321	-1241
4	10	1786	-1898
****L = 1******			
0	1	3031	2804
0	1	3031	2804
4	1	2321	2249
6	1	351	-389
8	1	1416	1341
10	1	291	-73
1	2	3777	-3243
3	2	3272	3320
5	2	1043	958
7	2	1981	2088
9	2	174	189
0	3	1721	-1808
2	3	2353	-2166
4	3	844	-630
6	3	563	317
8	3	204	-168
10	3	641	-674
1	4	2498	-2571
3	4	2876	-2866
5	4	245	-259
7	4	361	-290
9	4	531	382
0	5	196	113
2	5	2534	2702
4	5	1488	1494
6	5	1854	1742
8	5	280	8
1	6	559	601
3	6	1223	1353
5	6	112	144
7	6	1769	1764
9	6	1250	1245
0	7	433	463
2	7	1479	-1606
4	7	1434	1295
6	7	1139	-1260
8	7	331	-149
1	8	3170	-3281
3	8	117	-172
5	8	125	38
7	8	234	278
0	9	700	555
2	9	1673	1545
4	9	464	476
6	9	865	801
1	10	291	259
3	10	133	-213
0	11	1006	-1043
****L = 2******			
1	1	6947	-7488
3	1	7528	-7797
5	1	4824	-4824
7	1	2716	-2763
9	1	757	658
11	1	761	-766
0	2	566	449
2	2	1895	1896
4	2	1446	1399
6	2	332	-266
8	2	478	-440
10	2	132	-90
1	3	1602	-1787
3	3	2666	2667
5	3	2739	2963
7	3	3294	3390
9	3	936	866
0	4	2825	2844
0	4	2825	2844
4	4	266	306
6	4	151	-163
8	4	761	-766
10	4	136	-44
1	5	520	-529
3	5	3899	-3876
5	5	2211	-2244
7	5	2142	-2320
9	5	375	-342
0	6	1366	1277
2	6	1328	1305
4	6	1517	-1573
6	6	391	-331
8	6	1010	-920
1	7	2154	2055
3	7	1905	1779
5	7	780	723
7	7	635	654
0	8	654	659
2	8	356	-463
4	8	666	716
6	8	652	-517
1	9	2899	-2871
3	9	2131	-2203
5	9	2108	-2191
0	10	625	702
2	10	323	-174
4	10	236	-216
1	11	1281	1210
****L = 3******			
0	1	1410	-1373
2	1	4452	4242
4	1	1332	1564
6	1	280	-277
8	1	729	-875
10	1	992	-956
1	2	4431	4187
3	2	2211	1827
5	2	1848	1815
7	2	362	-403
9	2	1327	1316
0	3	2156	2464
2	3	1112	1163
4	3	412	448
6	3	1162	1184
8	3	337	-355
10	3	830	-810
1	4	3391	-3242
3	4	1937	1821
5	4	519	-499
7	4	757	822
9	4	1422	-1339
0	5	2150	-2081
2	5	1644	1507
4	5	288	108
6	5	277	424
8	5	438	-401
1	6	1130	1218
3	6	295	-287
5	6	506	501
7	6	413	-246
9	6	195	-11
0	7	984	-980
2	7	899	938
4	7	1684	1610
4	7	1684	1610
8	7	577	-599
1	8	702	706
3	8	560	-596
5	8	126	-47
7	8	828	-763
0	9	536	464
2	9	942	957
4	9	450	411
6	9	674	567
1	10	754	-613
3	10	750	840
0	11	311	-318
****L = 4******			
0	0	7995	-7999
1	1	1748	-1448
3	1	3862	3667
5	1	1620	-1439
7	1	406	153
9	1	124	73
0	2	2416	1973
2	2	1559	-1386
4	2	3207	3124
6	2	1968	1752
8	2	1042	1020
10	2	133	230
1	3	413	218
3	3	3843	-3942
5	3	139	370
7	3	1147	-1164
9	3	723	829
0	4	1026	776
2	4	1327	-1526
4	4	2240	-2266
6	4	799	-732
8	4	478	499
10	4	663	-538
1	5	1294	-1269
3	5	831	-802
5	5	2719	-2624
7	5	483	530
9	5	190	288
0	6	490	-366
2	6	1901	1870
4	6	549	606
6	6	1092	1176
8	6	373	288
1	7	1597	-1517
3	7	696	-583
5	7	342	-349
7	7	131	12
0	8	1348	-1413
2	8	2111	-2181
4	8	213	50
6	8	226	86
1	9	634	705
3	9	1739	-1600
5	9	190	295
0	10	132	-4
2	10	189	193
4	10	138	147
****L = 5******			
0	1	2416	-2604
2	1	5201	5262
4	1	1370	1403
6	1	1892	1953
6	1	1892	1953
10	1	377	415
1	2	2209	2174
3	2	1369	1181
5	2	2390	-2332
7	2	371	-470
9	2	219	6
0	3	517	378
2	3	1296	-1275
4	3	442	521
6	3	107	181
8	3	1088	-1056
10	3	797	-768
1	4	962	-1065
3	4	1478	-1459
5	4	820	-718
7	4	1125	-978
9	4	349	-137
0	5	3013	2855
2	5	1980	1940
4	5	1156	1157
6	5	852	-819
8	5	463	515
1	6	552	378
3	6	1716	1869
5	6	259	266
7	6	179	-130
0	7	2325	-2305
2	7	837	808
4	7	657	-630
6	7	492	524
8	7	691	-817
1	8	1068	1038
3	8	471	550
5	8	1200	-1335
7	8	478	-570
0	9	719	779
2	9	336	-342
4	9	323	354
1	10	1238	1131
3	10	193	225
****L = 6******			
1	1	1776	1877
3	1	2774	2758
5	1	2867	2754
7	1	832	809
9	1	977	926
0	2	1601	-1579
2	2	840	-996
4	2	1701	-1555
6	2	1625	1637
8	2	297	-191
10	2	638	563
1	3	2116	-2237
3	3	3318	-3316
5	3	1986	-1858
7	3	1215	-1141
9	3	226	-71
0	4	3015	-2811
2	4	684	-666
4	4	1032	-1009
6	4	1410	1506
8	4	902	819
1	5	2114	2199
3	5	2350	2416
5	5	1641	1622
7	5	1058	984
9	5	1254	1226
0	6	1259	-1062
2	6	2884	-2921
4	6	1997	1979
6	6	325	94
8	6	1332	1199
1	7	2700	-2639
3	7	1448	-1476
5	7	411	-352
7	7	916	-912
0	8	1086	-1114
2	8	171	236
4	8	489	-549
6	8	1637	1532
1	9	1422	1359
3	9	1036	1120
5	9	670	632
0	10	686	-599
2	10	235	-235
****L = 7******			
0	1	2637	-2255
2	1	4478	-4415
4	1	548	-481
6	1	1548	-1517
8	1	384	290
10	1	236	-192
1	2	1274	1237
3	2	807	780
5	2	410	511
7	2	433	501
9	2	770	-818
0	3	1829	-1579
2	3	181	-209
4	3	331	-271
6	3	1360	1398
8	3	601	549
1	4	4298	4310
3	4	1426	-1348
5	4	2048	-2034
7	4	2010	-2110
9	4	135	-46
0	5	573	-517
2	5	1181	1174
4	5	1936	-1956
6	5	207	85
8	5	527	-530
1	6	929	804
3	6	859	866
5	6	119	-89
7	6	676	-647
0	7	1836	1767
2	7	231	-407
4	7	596	552
6	7	567	-559
1	8	243	-373
3	8	651	-670
5	8	722	-679
0	9	616	-693
2	9	368	-478
4	9	1273	-1249
1	10	1117	1210
****L = 8******			
0	0	3799	3577
1	1	330	-123
3	1	900	781
5	1	1869	1772
7	1	606	-669
9	1	293	-329
0	2	5017	-4911
2	2	5627	-5698
4	2	3648	-3388
6	2	2087	-1981
8	2	1147	-1061
1	3	1239	-1165
3	3	2820	2825
5	3	1148	-1128
7	3	1038	996
9	3	919	-932
0	4	2514	2586
2	4	4508	4543
4	4	4664	4699
6	4	2953	2843
8	4	1762	1742
1	5	910	788
3	5	1652	784
5	5	1702	1579
7	5	766	-743
0	6	4195	-4096
2	6	3247	-3390
4	6	2568	-2719
6	6	1149	-1071
8	6	1996	-1920
1	7	452	404
3	7	661	604
5	7	1393	1426
7	7	137	-33
0	8	2771	2856
2	8	1907	1938
4	8	1396	1433
6	8	1219	1287
1	9	227	-128
3	9	1130	1112
0	10	2226	-2111
****L = 9******			
0	1	3296	3247
2	1	1152	976
4	1	537	428
6	1	1153	1082
8	1	655	664
1	2	1788	1685
3	2	616	-630
5	2	3240	3245
7	2	640	533
9	2	839	897
0	3	636	-635
2	3	1459	-1330
4	3	3847	-3788
6	3	1939	-1963
8	3	258	79
1	4	1322	-1300
3	4	1342	1327
5	4	2664	-2655
7	4	126	-39
9	4	1040	-994
0	5	184	165
2	5	776	-784
4	5	488	-562
6	5	536	546
8	5	922	919
1	6	972	987
3	6	731	775
5	6	972	1002
7	6	520	414
0	7	930	-1015
2	7	1916	-1844
4	7	1804	-1752
6	7	520	-310
1	8	520	-630
3	8	1838	-1827
5	8	470	-323
0	9	399	436
2	9	921	954
4	9	139	31
****L = 10******			
1	1	3793	-3585
3	1	1891	-1851
5	1	1654	-1641
7	1	1682	-1731
9	1	1994	-1910
0	2	1525	1531
2	2	1271	-1245
4	2	466	-563
6	2	849	-681
8	2	225	24
1	3	5097	5091
3	3	3540	3580
5	3	4398	4376
7	3	453	539
9	3	1176	1141
0	4	480	450
2	4	643	629
4	4	568	519
6	4	1389	-1201
8	4	191	84
1	5	3086	-3085
3	5	924	-907
5	5	2037	-1927
7	5	1743	-1692
0	6	283	175
2	6	1200	1209
4	6	390	-359
6	6	263	125
1	7	2491	2404
3	7	2386	2358
5	7	1318	1315
0	8	1082	1170
2	8	225	255
4	8	572	277
1	9	1343	-1273
3	9	1117	-1106
****L = 11******			
0	1	99	327
2	1	382	302
4	1	2581	-2603
6	1	1299	1308
8	1	372	-227
1	2	968	-982
3	2	764	-722
5	2	503	-488
7	2	801	781
0	3	747	718
2	3	428	456
4	3	872	-960
6	3	603	-565
8	3	587	546
1	4	1647	-1777
3	4	865	-836
5	4	1704	1698
7	4	131	111
0	5	482	401
2	5	1349	-1275
4	5	1170	1257
6	5	551	-462
1	6	1270	-1277
3	6	708	-689
5	6	1096	1076
0	7	761	-699
2	7	126	95
4	7	1479	-1504
1	8	322	70
3	8	135	202
0	9	195	279
****L = 12******			
0	0	388	-387
1	1	524	-465
3	1	775	-631
5	1	687	-672
7	1	340	408
0	2	1754	1626
2	2	3297	3295
4	2	345	-117
6	2	555	523
8	2	679	-652
1	3	490	-574
3	3	113	21
5	3	243	264
7	3	132	17
0	4	586	584
2	4	501	543
4	4	2038	-2121
6	4	1688	-1691
1	5	456	-352
3	5	171	-31
5	5	463	436
7	5	138	-143
0	6	2127	2185
2	6	124	230
4	6	951	873
6	6	823	-797
1	7	872	851
3	7	132	-100
5	7	478	-477
0	8	901	-943
2	8	136	156
****L = 13******			
0	1	1868	1672
2	1	272	27
4	1	1174	1145
6	1	252	146
8	1	993	1072
1	2	157	-193
3	2	1470	1440
5	2	123	26
7	2	1580	1552
0	3	1870	-1838
2	3	163	73
4	3	121	230
6	3	225	57
1	4	975	-1051
3	4	1137	-1160
5	4	1182	1065
7	4	477	-414
0	5	271	-497
2	5	1637	1715
4	5	725	689
6	5	1300	1329
1	6	219	-180
3	6	130	-52
5	6	527	570
0	7	415	412
2	7	133	159
4	7	477	423
1	8	965	-840
****L = 14******			
1	1	2116	2011
3	1	567	-660
5	1	628	567
7	1	331	377
0	2	304	360
2	2	563	668
4	2	389	356
6	2	983	-1061
1	3	1841	-1883
3	3	871	-943
5	3	2880	-2873
7	3	266	-239
0	4	593	520
2	4	122	4
4	4	544	469
6	4	236	-6
1	5	217	176
3	5	965	-927
5	5	765	762
0	6	224	19
2	6	509	368
4	6	527	-554
1	7	1160	-1150
3	7	1207	-1184
****L = 15******			
0	1	118	-414
2	1	876	-880
4	1	1111	1149
6	1	134	-5
1	2	1123	1155
3	2	554	-507
5	2	130	907
0	3	122	64
2	3	832	743
4	3	1729	1756
6	3	137	185
1	4	398	-421
3	4	289	311
5	4	899	-811
0	5	465	364
2	5	392	240
4	5	135	-111
1	6	1072	1127
3	6	194	221
0	7	366	333
****L = 16******			
0	0	2102	2048
1	1	772	-773
3	1	661	-558
5	1	668	-685
0	2	2988	-3021
2	2	2593	-2602
4	2	1979	-2018
6	2	1791	-1768
1	3	719	785
3	3	865	-918
5	3	335	316
0	4	908	707
2	4	669	685
4	4	2112	2265
1	5	353	-383
3	5	305	-246
0	6	2126	-2510
2	6	1196	-1294
****L = 17******			
0	1	271	42
2	1	1918	1952
4	1	424	450
1	2	1511	1488
3	2	1367	1312
5	2	277	413
0	3	694	-663
2	3	637	-553
4	3	413	-522
1	4	402	376
3	4	1162	-1185
0	5	1274	1381
2	5	461	569
****L = 18******			
1	1	2452	-2640
3	1	1471	-1458
0	2	1429	-1388
2	2	135	-155
1	3	1509	1513
3	3	1746	1836
0	4	718	-796
****L = 19******			
0	1	1228	1272
2	1	571	-565
1	2	340	-352

Table 3. *Intramolecular distances and angles with their estimated standard deviations*

Bond distances		e.s.d.
Fe_{oct}–O	2·006 Å	0·006 Å
Fe_{oct}–Cl_{oct}	2·366	0·003
Fe_{tet}–Cl_{tet}	2·162	0·005
S–O	1·541	0·006
S–C(1)	1·804	0·011
S–C(2)	1·795	0·022
Angles		
Cl–Fe_{oct}–O	90·8°	0·2°
Cl_{tet}–Fe_{tet}–$Cl_{tet}(y-\frac{1}{4}, \frac{1}{4}-x, \frac{1}{4}-z)$	108·1	0·3
Cl_{tet}–Fe_{tet}–$Cl_{tet}(-x, \frac{1}{2}-y, z)$	112·2	0·3
C(1)–S–C(2)	99·4	0·5
C(1)–S–O	103·5	0·5
C(2)–S–O	103·7	0·4
Fe_{oct}–O–S	124·5	0·4

(EDTA = ethylenediaminetetraacetate) which range from 1·97 to 2·11 Å. (Lind, Hamor, Hamor & Hoard, 1964). The four oxygen atoms are coplanar within the limits of experimental error and the coordination sphere of the cation has D_{4h} symmetry. The S–C bond lengths are the same as those in free DMSO (Viswamitra & Kannan, 1966; Thomas, Shoemaker & Eriks, 1966) and $PdCl_2(DMSO)_2$. However, the S–O bond length is 1·54 Å as compared with a shorter value in free DMSO. This difference will be discussed later.

Molecular packing

Intermolecular distances up to 8·0 Å were calculated. All contacts less than 4·1 Å are included in Table 4 as well as the shortest interionic Fe–Fe and Cl–Cl distance. The intermolecular structure is ionic and is composed of *trans*-$[FeCl_2(DMSO)_4]^+$ octahedral cations and tetrahedral $[FeCl_4]^-$ anions arranged in a NaTl-type array (Wells, 1962). Each octahedral cationic unit is surrounded by a cubic array of eight nearest neighbors so that the Fe atoms are 7·71 Å apart. This set of eight neighbors consists of four octahedral cationic units and four tetrahedral anionic units forming two interpenetrating tetrahedra. This is illustrated schematically in Fig. 2(*a*).

Table 4. *Intermolecular distances*

Atom of reference molecule	Atom in neighboring molecule	Distance
S	$Cl_{oct}(\bar{x}, \bar{y}, 1-z)$	3·56 Å
	S $(\bar{x}, \bar{y}, 1-z)$	3·86
	C(2) $(\bar{x}, \bar{y}, 1-z)$	3·97
Cl_{oct}	C(1) $(\bar{x}, \bar{y}, 1-z)$	3·62
	C(2) $(\bar{x}, \bar{y}, 1-z)$	3·68
Cl_{tet}	C(1) $(x, -\frac{1}{2}\ \frac{1}{2}+y, z-\frac{1}{2})$	3·99
	C(1) $(\frac{1}{4}+y, \frac{1}{4}-x, z-\frac{3}{4})$	4·00
	C(1) $(-\frac{1}{4}-y, \frac{1}{4}+x, z-\frac{3}{4})$	4·02
	C(2) $(x-\frac{1}{2}, \frac{1}{2}+y, z-\frac{1}{2})$	3·94
	C(2) $(\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$	3·60
O	C(2) $(\frac{1}{4}+y, \frac{1}{4}-x, \frac{1}{4}+z)$	3·63
Cl	C(1) $(\bar{x}, -\frac{1}{2}-y, z)$	3·89
Cl	C(2) $(\frac{1}{4}+y, \frac{1}{4}-x, \frac{1}{4}+z)$	3·82
Cl_{oct}	$Cl_{tet}(\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}-z)$	6·81
Fe_{oct}	$Fe_{tet}(\frac{1}{2}, \frac{1}{4}, \frac{3}{8})$	7·71
	$Fe_{oct}(\frac{1}{2}, \frac{1}{4}, \frac{7}{8})$	7·71
Fe_{tet}	$Fe_{tet}(\frac{1}{2}, \frac{1}{4}, \frac{3}{8})$	7·71

In addition there are two tetrahedral anionic units, one above and one below along the *c* axis. These two are next nearest neighbors and lie at a distance of *c*/2 or 10·16 Å. Likewise each tetrahedral iron atom unit is surrounded by eight nearest neighbors and their disposition is entirely similar as can be seen in Fig. 2(*b*).

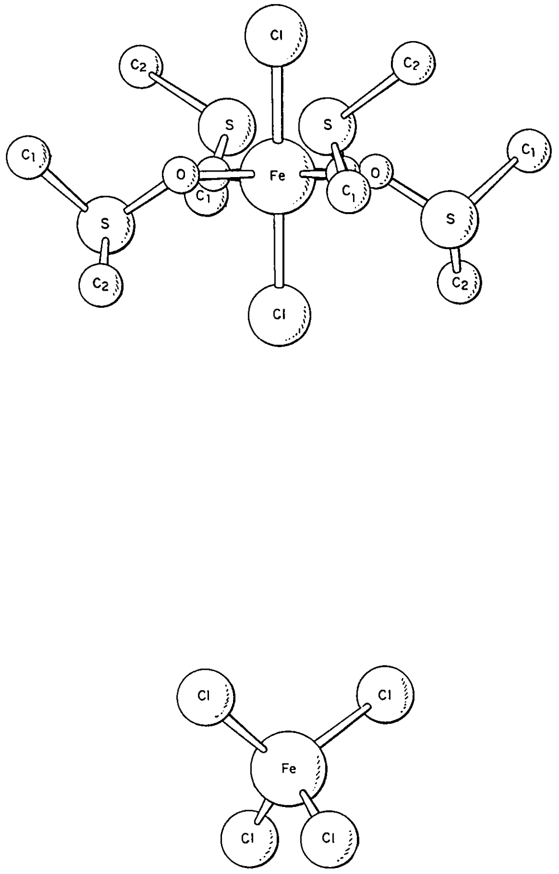


Fig. 1. The molecular structure of *trans*-$[FeCl_2(DMSO)_4]$ $[FeCl_4]$, projected down the crystallographic *a* axis.

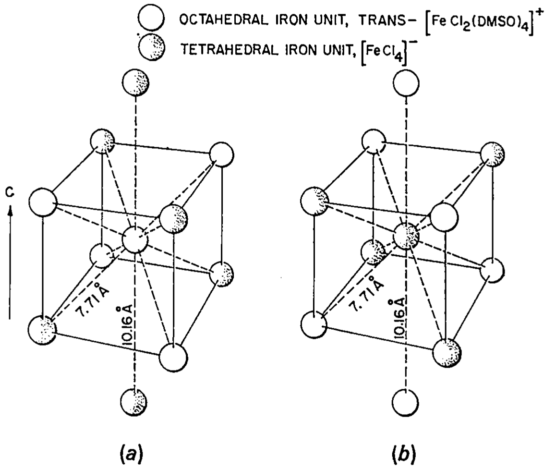


Fig. 2. NaTl-type packing of the iron atoms in *trans*-$[FeCl_2(DMSO)_4][FeCl_4]$.

The Cl_{oct} to Cl_{tet} distance of 6·81 Å along the *c* axis is attributable to the fact that the tetrahedral and octahedral units are prevented from stacking closer together along the *c* axis by interactions between adjacent octahedral units (interactions numbered 1, 4, 5 and 13 in Table 4), and by Cl_{tet}–C contacts. The arrangement of the molecules projected down the *a* axis is shown in Fig. 3.

Anisotropic motion

Root mean square amplitudes of the atomic vibrational ellipsoid axes are given in Table 5. The direction cosines of the principal axes with respect to the orthogonal crystal axis system are also given. In the *trans*-$[FeCl_2(DMSO)_4]^+$ unit the iron atom traces an oblate vibrational ellipsoid with the minor axis in the **c** direction. The one independent oxygen atom vibrates so that its major axis is in the square plane formed by the four oxygen atoms and perpendicular to the Fe–O bond. Likewise the sulfur atom has its major axis roughly in the same plane and perpendicular to the S–O bond. The chlorine atom in this group has its minor axis along the Fe–Cl bond, *i.e.* along the **c** direction and its major axis in the *ab* plane.

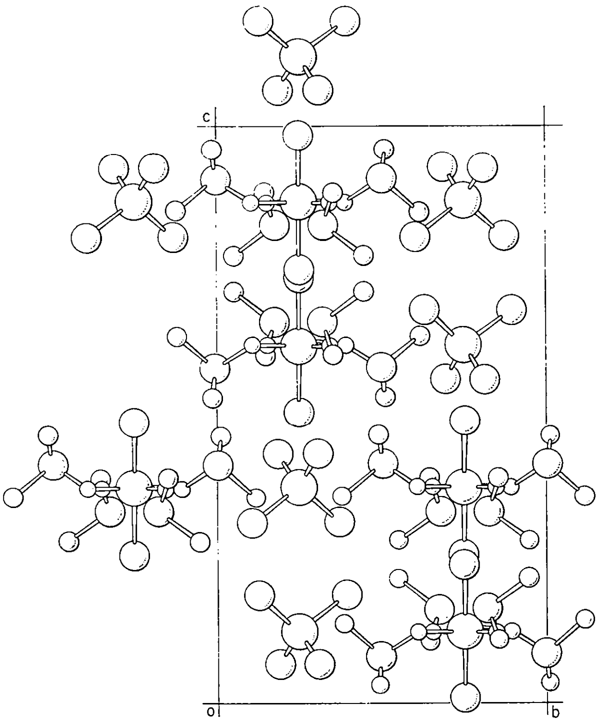


Fig. 3. Crystal packing in *trans*-$[FeCl_2(DMSO)_4][FeCl_4]$ projected down the *a* axis.

The anisotropic motion of the $[FeCl_4]^-$ anion is particularly interesting. The high thermal parameters for this ion are in agreement with the long Cl_{oct}–Cl_{tet} contact distance of 6·81 Å which is indicative of the anion lying in a rather large 'hole' in the lattice. The major axis for the chlorine atom lies roughly in the *ac* plane at 45° from **a**. When all four chlorine atoms are considered this thermal motion resembles the *E*-type fundamental bending mode for the $FeCl_4^-$ anion. The median axis for the Cl atom corresponds to a librational motion around the *c* axis. This librational motion was also evident on the difference Fourier map. The tetrahedral iron atom traces an oblate vibrational ellipsoid with the minor axis in the *c* direction.

Discussion

The effect of coordination of DMSO through its oxygen atom may be observed by comparing the structural parameters for the DMSO in $[FeCl_2(DMSO)_4]^+$ with those of DMSO. For this comparison we shall employ the results of Thomas, Shoemaker & Eriks, since they pertain to a temperature close to that of the present study and appear to have been subjected to more thorough refinement.

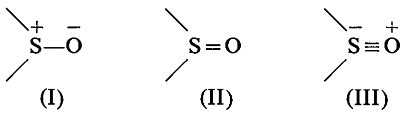
On the view that the electronic structure of the S–O bond may be represented as a suitably weighted hybrid of the canonical forms (I), (II) and (III), it is to be expected that coordination *via* oxygen should decrease the bond order by enhancing the contribution of (I).

Table 5. *Principal axes of the atomic vibration ellipsoids*

Directions cosines are relative to the orthogonal crystal axes.

		$(\bar{u}_{max}^2)^{\frac{1}{2}}$			$(\bar{u}_{med}^2)^{\frac{1}{2}}$			$(\bar{u}_{min}^2)^{\frac{1}{2}}$	
Fe_{oct}		0·186			0·186			0·163	
	0·0,	1·0,	0·0	1·0,	0·0,	0·0	0·0,	0·0,	1·0
Cl_{oct}		0·266			0·212			0·163	
	0·776,	−0·631,	0·0	0·631,	0·776,	0·0	0·0,	0·0,	1·0
O		0·238			0·209			0·164	
	0·668,	0·623,	−0·408	0·731,	−0·649,	0·206	0·137,	0·437,	0·889
S		0·216			0·202			0·177	
	0·334,	0·803,	−0·492	0·933,	−0·210,	0·291	−0·129,	0·558,	0·820
C(1)		0·330			0·239			0·174	
	−0·994,	0·026,	0·105	0·089,	0·733,	0·674	0·059,	−0·681,	0·730
C(2)		0·321			0·268			0·151	
	−0·543,	0·431,	−0·721	0·378,	0·892,	0·247	0·750,	−0·137,	−0·647
Fe_{tet}		0·275			0·275			0·226	
	0·0	1·0,	0·0	1·0,	0·0,	0·0	0·0,	0·0,	1·0
Cl_{tet}		0·543			0·303			0·239	
	0·780,	−0·010,	0·625	−0·255,	0·908,	0·334	0·571,	−0·419,	0·706

Thus the bond length should increase.



(I) (II) (III)

This is found to be the case, though the effect is quite small. Thus, the S–O bond length uncorrected for thermal motion reported by Thomas, Shoemaker & Eriks is 1·513 (5) Å, while in *trans*-$[FeCl_2(DMSO)_4]^+$ we find 1·541 (6). In $BF_3(DMSO)$ McGandy reported a distance of 1·52 (1) Å, which differs insignificantly from that in DMSO itself and thus left unresolved the question of whether there is any increase in length upon coordination *via* oxygen. Our results show that there is indeed a small effect of this nature.

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The Crystal Structure of the Intermetallic Compound Cu_4Cd_3*

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A determination of the crystal structure of the intermetallic compound Cu_4Cd_3 has been carried out with the use of packing maps [Samson, *Acta Cryst.* (1964), **17**, 491]. The structure has been refined by three-dimensional, least-squares techniques employing intensity data of 2537 reflections. The crystals are cubic, space group $F\bar{4}3m$ (T_d^2), with $a_0 = 25{\cdot}871 \pm 0{\cdot}002$ Å. There are 1124 atoms in the unit cell, distributed among 29 crystallographically different positions. The unit cube contains 568 icosahedra, 288 pentagonal prisms, 144 polyhedra of ligancy 15 (μ-phase polyhedra), and 124 Friauf polyhedra. Evidence has been found for a small degree of substitutional disorder.

The structure comprises two different substructures that interpenetrate, and each one is of considerable complexity. Each substructure represents a diamond-like arrangement, in one case of Friauf polyhedra, in the other case of icosahedra.

Introduction

The existence of the intermetallic compound Cu_4Cd_3 was established by Jenkins & Hanson (1924); the compound does not form on solidification of the melt but appears only after prolonged annealing at 450 to 500 °C through a reaction of a metastable eutectic mixture of the two phases, Cu_2Cd and Cu_5Cd_8, that always seem to be precipitated first.

Laves & Möller (1938) concluded from observation of powder patterns that Cu_4Cd_3 is isomorphous with β-Mg_2Al_3, which later was found by Perlitz (1944, 1946) to be cubic, space group $Fd3m$ (O_h^7), with approximately 1166 atoms per unit cube of edge $a_0 = 28{\cdot}22$ Å. A compound with structure apparently similar to those of Cu_4Cd_3 and β-Mg_2Al_3 is $NaCd_2$, which has a cubic unit cell of edge $a = 30{\cdot}56$ Å, space group $Fd3m$.

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