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A Novel New Metallocycle: Cyclohexa-1,4-(tetracarbonylchromium)-2,3,5,6-(dimethylarsenic)

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The unusual metallocyclic compound, cyclohexa-1,4-(tetracarbonylchromium)-2,3,5,6-(dimethylarsenic), $(OC)_4\overline{Cr{-}AsMe_2AsMe_2Cr(CO)_4AsMe_2AsMe_2}$, *has been prepared inadvertently from the reaction of cacodylic acid,* $Me_2As(O)OH$ *with chromium carbonyl. Large, well-formed yellow crystals were grown from* CH_2Cl_2, *and the structure was determined as a means of definitive identification. The crystals are monoclinic and were assigned to the non-standard space group I2/m, with unit cell parameters:* $a = 9.920(2)$ Å, $b = 10.976(2)$ Å, $c = 12.233(2)$ Å, $\beta = 107.56(1)°$, $V = 1269.8(4)$ Å^3, $Z = 2$. *The structure was solved and refined using 727 nonredundant reflections for which* $F_o^2 > 3\sigma(F_o^2)$, *to final residuals of* $R_1 = 0.029$ *and* $R_2 = 0.047$. *The molecule is a six-membered ring made up of* $Cr(CO)_4$ *groups in the 1 and 4 positions with* $(CH_3)_2As$ *groups in the remaining positions. The ring has a chair configuration and has crystallographic 2/m symmetry. The two-fold axis passes through the midpoints of the As–As bonds and the chromium atoms lie in the mirror plane. Some important dimensions are: Cr–As, 2.480(1) Å; As–As, 2.442(1) Å; As–C(av), 1.971(6) Å; Cr–C (trans to As), 1.87(1) Å; Cr–C (cis to As), 1.90(1) Å and 1.87(1) Å; <AsAsCr, 120.97(3)°; <AsCrAs, 92.15(5)°. Proton nmr spectra from room temperature to –70° C indicate that the chair conformation inverts with a free energy of activation around 10 kcal mol*$^{-1}$.

Introduction

A number of recent reports have indicated the importance of the dimeric ion Mo_2^{4+} in the chemistry of reduced molybdenum complexes.[1] The corresponding chromium(II) dimer is considerably less well-known. We have been engaged in synthesizing such complexes and in studying their structural and spectroscopic properties, and were interested in the possibility of producing cacodylate (dimethylarsinate) analogs of the acetates of these metals, utilizing the reaction of cacodylic acid with the metal carbonyls, in analogy to the usual method of preparing dimolybdenum(II) carboxylates.[2]

Neither reaction proceeded as planned. Chemical evidence suggests that the molybdenum product contains a higher oxidation state than Mo(II); the ir spectrum points tentatively to an oxo-bridged dimer of Mo(V). Two products have been obtained from the chromium reaction, an intractable green solid and, in low yield, a soluble yellow solid, which we have identified crystallographically as the (tetramethyldiarsine) tetracarbonylchromium(0) dimer. We are reporting its structure because the molecule has some interesting and unusual structural features and because no molecule of this kind has been previously described.

Experimental

Preparation

Chromium hexacarbonyl (1.0 g, 4.5 mmol) and cacodylic acid (1.3 g, 9.4 mmol) were heated together in freshly distilled diglyme (50 ml) for 24 hours at 130° C under nitrogen. The liquid phase began to turn yellow almost as soon as heating was begun, and an extremely malodorous compound, ALMOST CERTAINLY A VOLATILE ARSENICAL (CAUTION!), was evolved. The reaction mixture was cooled, and the green solid was filtered off under nitrogen. The yellow product was recovered by evaporation of the solvent.

No attempt has been made to optimize the yield of this complex; the proportions given above are those chosen for the synthesis of the dimeric chromium(II) complex. The use of undistilled diglyme or of diglyme distilled from calcium hydride does not appear to affect the course of reaction.

The compound is moderately soluble in dichloromethane and acetone, sparingly soluble in ether and chloroform, and insoluble in hydrocarbon solvents. It is stable to air and moisture, both in the solid state and in solution. The compound decomposes without melting at *ca.* 225° C. Mass spectral data suggested the presence of the $As(CH_3)_2$ fragment in the product but not the AsO_2 group. The ir spectrum indicated the presence of carbonyl ligands on chromium; bands were observed at 2005(m), 1912(s) and 1880(sh) cm^{-1}. Elemental analyses were not reproducible and did not prove helpful in identifying the compound. Invariably, low percentages were obtained. A typical result was: C, 21.4; H, 2.8; Cr, 9.1; As, 26.6, which corresponds to an atom ratio H:C:As:Cr of 16:10:2:1. The theoretical percentages for the correct composition are: C, 25.67; H, 3.24; Cr, 13.91; As, 40.17.

Since the classical data just summarized did not allow us to identify the compound, recourse was had to x-ray crystallography. Large, well-formed crystals were obtained by slow recrystallization at 0° C from dichloromethane. The crystal chosen was 0.51 × 0.10 × 0.08 mm, bounded by the faces 100, 011, 01$\bar{1}$, $\bar{1}$00, 0$\bar{1}\bar{1}$, and 0$\bar{1}$1. It was mounted on a glass fiber with the long axis of the crystal approximately aligned with Φ and examined on the diffractometer. The crystal belonged to the monoclinic system, with a = 9.920(2)Å, b = 10.976(2) Å, c = 12.233(2) Å and β = 107.56(1)°, with V = 1269.8(4) Å^3, as determined by careful centering of fifteen intense reflections in the range 29.0° < 2Θ < 32.0°. The systematic absences (hkl for h + k + l odd) indicated a body-centered cell, with possible space groups I2, Im, I2/m. Transforming this cell to the standard C-centered cell gives a = 9.920 Å, b = 10.976 Å, c = 13.240 Å, and β = 118.14°. The more nearly orthogonal body-centered cell was retained in further work. The density was determined to be 1.98(3) g/cm^3 by flotation in a mixture of carbon tetrachloride and bromoform; for Z = 2, the calculated density is 1.96 g/cm^3. The molecule is required to possess 2, m, or 2/m (C_2, C_s, or C_{2h}) symmetry, depending on the space group.

Data were collected at 20 ± 1° C on a Syntex P$\bar{1}$ autodiffractometer using Mo Kα radiation as described previously,[3] in the range 0° < 2Θ < 45.0°. The $\Theta/2\Theta$ scan technique with a variable scan rate (4.0–24.0°/min) and a scan range of $2\Theta(K\alpha_1)$ −0.7° to $2\Theta(K\alpha_2)$ +0.9° was used. A total of 935 unique data were collected of which 727 were judged to be observed ($F_o^2 > 3\sigma(F_o^2)$). The parameter p used in calculating σ was set equal to 0.07. Four standard reflections were remeasured after every 96 reflections; they did not change appreciably in intensity. The linear absorption coefficient is 64.0 cm^{-1}; a numerical absorption correction was applied to the data. Transmission factors ranged from 0.524 to 0.606, with the average 0.585. No extinction correction was necessary.

Solution of the Structure[4]

The arsenic and chromium atoms were readily located from the three-dimensional Patterson function, which suggested that the heavy atoms were related by 2/m symmetry. Two cycles of least-squares refinement on these positions in space group I2/m resulted in R_1 of 0.199 and R_2 of 0.270.[5] A difference Fourier revealed all carbon and oxygen atoms; isotropic refinement on these atoms reduced R_1 to 0.053 and R_2 to 0.077. After applying the absorption correction, three cycles of full-matrix anisotropic refinement of all atoms were carried out, producing R_1 of 0.029 and R_2 of 0.047. In the last cycle, no parameter shifted by more than one fifth of a standard deviation, and the error in an observation of unit weight was 1.15. A difference Fourier was computed at this stage; the maximum peak density was 1.1 e/Å^3, compared with 6.3 e/Å^3 for a carbon atom previously. Methyl hydrogen atoms could be located cleanly for one methyl group but not the other. Refinement was terminated at this point.

Scattering factors for neutral As, Cr, C, and O were obtained from Cromer.[6] Anomalous dispersion effects for As and Cr were included in F_c;[7] the values of $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[8]

The fractional coordinates and thermal parameters for the unique atoms are given in Table I. Tables II and III present data on bond distances and bond angles. Table IV lists the final values of $|F_o|$ and $|F_c|$. The molecule is depicted in Figure 1, which also illustrates the numbering scheme.

TABLE I. Positional and Thermal Parameters for Non-hydrogen Atoms in $[Cr(CO)_4(As_2(CH_3)_4)]_2$.[a,b]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As	0.0857(1)	0.1628(1)	−0.0537(1)	57.9(9)	43.8(8)	51.7(7)	−1.3(6)	19.8(5)	3.6(4)
Cr	0.0841(1)	0	−0.1947(1)	55.9(18)	64.8(16)	43.2(12)	0	18.9(11)	0
O(1)	0.4060(7)	0	−0.1235(7)	56(9)	156(11)	112(8)	0	26(6)	0
O(2)	0.2323(8)	0	−0.3119(7)	83(10)	114(9)	105(8)	0	0(6)	0
O(3)	0.0989(6)	0.1895(6)	−0.3671(5)	159(8)	148(8)	87(5)	12(7)	54(5)	65(6)
C(1)	0.2852(10)	0	−0.1442(7)	67(13)	75(10)	48(7)	0	17(7)	0
C(2)	0.1123(10)	0	−0.2602(8)	79(14)	61(10)	51(8)	0	17(8)	0
C(3)	0.0917(7)	0.1208(8)	−0.3005(6)	63(8)	100(9)	59(6)	2(6)	25(5)	12(6)
C(4)	0.0591(9)	0.3288(6)	−0.1178(7)	164(12)	43(7)	97(8)	7(7)	62(8)	32(6)
C(5)	0.2603(7)	0.1844(7)	0.0750(6)	61(8)	83(8)	73(6)	−21(6)	2(5)	−9(6)

[a] The numbers in parentheses in this and other tables are the estimated deviations in the least significant digits. [b] The anisotropic thermal parameters are of the form $\exp[-10^{-4}(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

TABLE II. Bond Distances (Å).

As–As	2.442(1)
As–Cr	2.480(1)
As–C(4)	1.970(7)
As–C(5)	1.972(6)
Cr–C(1)	1.902(10)
Cr–C(2)	1.869(10)
Cr–C(3)	1.870(8)
C(1)–O(1)	1.148(11)
C(2)–O(2)	1.168(10)
C(3)–O(3)	1.128(8)

TABLE III. Bond Angles(°).[a]

As–As–Cr	120.97(3)
As–As–C(4)	100.5(2)
As–As–C(5)	99.1(2)
Cr–As–C(4)	114.6(3)
Cr–As–C(5)	117.5(2)
C(4)–As–C(5)	100.8(3)
As–Cr–As'	92.15(5)
As–Cr–C(1)	89.3(2)
As–Cr–C(2)	94.9(2)
As–Cr–C(3)	177.3(2)
As–Cr–C(3)'	88.7(2)
C(1)–Cr–C(2)	173.9(4)
C(1)–Cr–C(3)	88.1(3)
C(2)–Cr–C(3)	87.6(3)
C(3)–Cr–C(3)'	90.3(5)
Cr–C(1)–O(1)	174.1(9)
Cr–C(2)–O(2)	173.0(9)
Cr–C(3)–O(3)	176.6(7)

[a] Primed superscripts indate the atom to be related to the unprimed atom by reflection in the xOz plane.

Nmr Spectra

These were recorded at various temperatures using a Varian HA–100 spectrometer equipped with a variable-temperature probe. Dichloromethane served as an internal standard. Temperatures were measured using a copper–constantan thermocouple placed in the nitrogen stream immediately below the sample and attached to a Leeds and Northrup Model 713 digital thermometer.

Results and Discussion

The structure of the (tetramethyldiarsine)tetracarbonylchromium(0) dimer consists of a six-membered ring of arsenic and chromium atoms, with methyl substituents on arsenic and carbonyl groups on chromium. The ring exhibits an exemplary chair conformation, with a fold angle of 42°. The chromium atoms lie 1.15 Å out of the plane defined by the four arsenic atoms. The molecule possesses rigorous 2/m (C_{2h}) symmetry, with the chromium atoms and four of the carbonyl groups in the mirror plane and the arsenic–arsenic bonds bisected by the C_2 axis. The distances around the ring appear normal. The bond angles at chromium are negligibly distorted from 90°; the right angle in the ring at that point introduces some distortion at the arsenic atoms. The largest bond angle at arsenic is 121°, as compared with the tetrahedral angle of cyclohexane (109.5°). The angles (97°) in gray arsenic,[9] which contains a six-membered ring (also a chair) of arsenic atoms and $(C_6H_5As)_6$[9] (91°) are much smaller, but angles in the range 90–100° are a characteristic feature of the 3-connected arsenic atom. In the present compound we are dealing with 4-con-

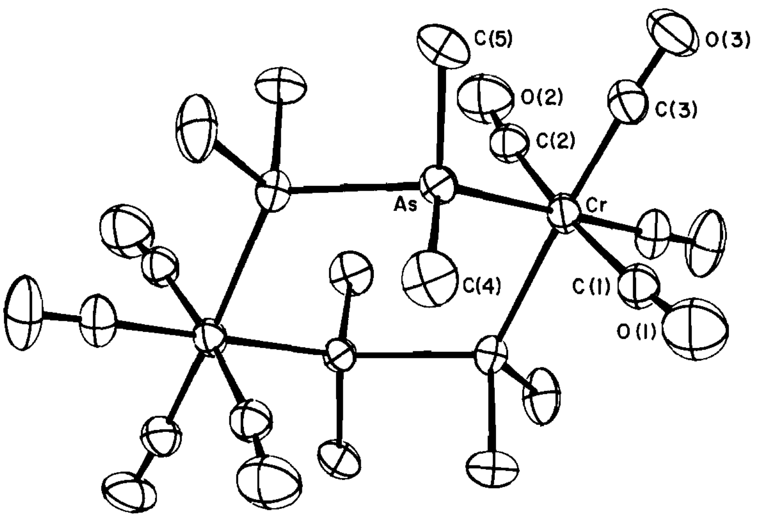


Figure 1. An ORTEP drawing of the molecular structure, showing the atom numbering scheme. Each atom is represented by its thermal vibration ellipsoid, scaled to enclose 50% of its electron density.

TABLE IV. Values of $10F_o$ and $10F_c$ in Electrons.

H= 0

K	L	FOBS	FCALC
0	2	744	661
0	4	390	301
0	6	444	436
0	8	1390	1373
0	10	534	575
0	12	587	583
1	1	1519	1523
1	3	323	298
1	5	119	134
1	7	648	696
1	9	603	623
1	11	199	198
2	0	234	159
2	2	2019	1942
2	4	221	201
2	6	628	659
2	8	129	103
2	10	690	669
2	12	151	91
3	1	1324	1317
3	3	2296	2276
3	5	405	429
3	7	1014	1043
3	9	1125	1152
3	11	645	679
4	0	281	235
4	2	1556	1525
4	4	200	189
4	6	687	697
4	8	334	359
4	10	541	530
5	1	931	893
5	3	122	53
5	5	392	387
5	7	679	695
5	9	384	391
6	0	2871	2920
6	2	732	764
6	6	381	431
6	8	962	925
6	10	494	475
7	5	150	130
7	7	410	419
7	9	509	518
8	2	763	796
8	6	296	331
9	1	833	833
9	3	804	785
9	7	505	509
10	0	197	231
10	2	745	743
10	6	358	362
11	1	293	258

H= 1

K	L	FOBS	FCALC
0	-9	1048	1063
0	-7	1808	1947
0	-5	116	94
0	-1	969	[illegible]
0	1	2994	2970
0	3	1775	1847
0	5	538	541
0	7	511	525
0	9	833	820
0	11	345	332
1	-12	224	210
1	-8	1069	1106
1	-6	700	687
1	-4	844	785
1	-2	970	957
1	0	1990	2053
1	2	592	676
1	4	483	484
1	6	469	496
1	8	714	714
1	10	179	191
1	12	294	311
2	-11	246	253
2	-9	603	601
2	-7	212	243
2	-5	998	1047
2	-3	720	699
2	-1	823	765
2	1	730	735
2	3	967	1087
2	5	206	223
2	11	488	495
3	-10	909	884
3	-8	944	972
3	-6	1149	1196
3	-4	1305	1344
3	-2	2513	2448
3	0	1341	1453
3	2	1175	1214
3	4	1246	1278
3	6	121	73
3	8	208	195
3	10	921	913
4	-11	295	317
4	-9	561	540
4	-7	236	247
4	-5	1392	1405
4	-3	496	525
4	-1	835	779
4	1	1029	944
4	3	1155	1166
4	9	361	370
4	11	533	553
5	-8	523	558
5	-6	504	546
5	-4	591	553
5	-2	330	329
5	0	971	1013
5	2	500	440
5	6	445	468
5	8	407	407
5	10	154	161
6	-11	264	262
6	-9	785	763
6	-7	1260	1270
6	-5	171	197
6	-3	304	302
6	-1	912	916
6	1	1794	1827
6	3	962	996
6	5	634	613
6	7	344	384
6	9	607	605
7	-8	835	822
7	-6	634	606
7	-4	283	244
7	-2	354	380
7	0	1066	1087
7	2	820	807
7	4	499	491
7	6	200	218
7	8	475	507
8	-9	351	339
8	-5	379	358
8	-3	292	194
8	-1	377	371
8	1	197	189
8	3	451	459
9	-8	562	567
9	-6	736	719
9	-4	445	441
9	-2	975	853
9	4	677	680
9	4	677	680
10	-7	234	260
10	-5	634	649
10	-1	537	495
10	1	507	524
10	3	650	658
11	-4	226	220
11	0	313	295

H= 2

K	L	FOBS	FCALC
0	-10	160	130
0	-8	737	786
0	-6	2148	2157
0	-4	1394	1347
0	-2	825	661
0	0	1478	1454
0	2	1475	1394
0	4	1467	1372
0	6	1433	1465
0	8	202	193
0	10	479	476
1	-13	154	156
1	-7	1410	1447
1	-5	233	277
1	-3	403	419
1	-1	529	430
1	1	1230	1264
1	3	372	354
1	5	1095	1012
1	7	416	424
1	9	562	559
2	-12	265	251
2	-10	349	366
2	-8	311	308
2	-6	137	110
2	-4	1631	1641
2	0	344	371
2	2	504	496
2	4	1157	1175
2	8	295	284
2	10	266	287
3	-9	1062	1065
3	-7	642	663
3	-5	1608	1621
3	-3	646	660
3	-1	491	437
3	1	841	894
3	3	2492	2533
3	5	993	1005
3	7	260	261
3	11	780	763
4	-12	384	375
4	-10	290	286
4	-8	665	646
4	-6	196	203
4	-4	1526	1535
4	0	592	541
4	2	831	774
4	8	224	230
4	10	296	279
5	-7	925	924
5	-3	455	452
5	-1	164	222
5	1	552	586
5	3	276	272
5	5	697	708
5	7	212	209
5	9	259	253
6	-8	606	619
6	-6	1539	1554
6	-4	666	684
6	-2	605	614
6	0	867	869
6	2	1335	1360
6	4	781	838
6	6	987	983
6	8	167	140
7	-7	945	969
7	-5	523	521
7	-3	370	384
7	1	871	888
7	3	409	410
7	5	734	725
7	7	253	246
7	9	457	444
8	-4	599	610
8	-2	134	128
8	2	258	265
8	4	441	423
8	8	215	215
9	-7	434	443
9	-5	947	930
9	-3	438	448
9	-1	268	250
9	1	382	395
9	3	1139	1143
9	5	673	675
10	-6	392	373
10	-4	663	673
10	0	292	260
10	2	593	596
10	4	639	619
11	1	170	167

H= 3

K	L	FOBS	FCALC
0	-13	726	719
0	-9	482	439
0	-7	1204	1226
0	-5	1418	1368
0	-3	2606	2507
0	-1	2333	2246
0	1	2773	2584
0	3	1464	1352
0	5	1086	1076
0	7	1104	1125
0	9	262	260
1	-10	214	236
1	-6	1094	1139
1	-4	901	853
1	-2	712	718
1	0	174	186
1	2	895	873
1	4	511	505
1	6	903	927
1	10	200	167
2	-13	252	237
2	-11	525	517
2	-9	567	576
2	-7	148	116
2	-5	937	961
2	-3	1367	1335
2	1	125	158
2	3	1208	1175
2	5	656	674
2	9	432	414
3	-12	819	833
3	-10	411	419
3	-8	782	790
3	-6	1304	1301
3	-4	2106	2167
3	-2	467	478
3	0	224	224
3	2	330	305
3	4	2127	2180
3	6	893	892
3	8	502	486
3	10	172	199
4	-11	457	452
4	-9	299	283
4	-7	173	148
4	-5	1134	1116
4	-3	979	968
4	1	170	160
4	3	976	964
4	5	857	856
4	9	278	283
5	-10	247	247
5	-6	1065	1070
5	-4	277	260
5	-2	519	538
5	2	604	610
5	4	214	206
5	6	826	822
6	-7	840	810
6	-5	1123	1142
6	-3	1420	1462
6	-1	1030	1046
6	1	1095	1139
6	3	962	1004
6	5	889	869
6	7	755	751
6	9	155	125
7	-8	158	150
7	-6	722	717
7	-4	501	519
7	-2	721	701
7	2	667	654
7	4	308	314
7	6	684	679
7	8	165	162
8	-9	389	375
8	-5	421	414
8	-3	581	622
8	3	540	570
8	5	301	271
9	-8	425	430
9	-6	678	668
9	-4	999	974
9	-2	497	490
9	2	337	342
9	4	979	964
9	6	531	526
10	-5	632	616
10	-3	561	550
10	3	529	534
11	-2	178	159

H= 4

K	L	FOBS	FCALC
0	-12	728	725
0	-10	623	630
0	-8	254	226
0	-6	1259	1276
0	-4	1393	1317
0	-2	1411	1398
0	0	1604	1559
0	2	679	711
0	4	664	677
0	6	1172	1185
0	8	676	656
1	-13	512	522
1	-9	632	667
1	-7	498	525
1	-5	831	810
1	-3	230	229
1	-1	1488	1493
1	1	363	338
1	3	213	229
1	5	246	231
1	7	872	876
2	-12	400	405
2	-10	363	388
2	-8	153	191
2	-6	160	158
2	-4	1039	1038
2	-2	629	610
2	0	120	134
2	2	302	309
2	4	879	932
2	8	265	251
2	10	243	243
3	-11	967	982
3	-7	153	166
3	-5	1053	1090
3	-3	2378	2396
3	-1	436	451
3	1	335	351
3	3	273	300
3	5	1233	1247
3	7	517	520
3	9	637	613
4	-12	520	514
4	-10	325	338
4	-4	1272	1307
4	-2	792	770
4	0	338	330
4	2	272	264
4	4	908	931
4	6	265	248
4	8	439	433
5	-9	281	293
5	-7	251	225
5	-5	653	676
5	-1	751	746
5	1	197	198
5	3	243	246
5	7	606	598
6	-10	482	477
6	-8	183	179
6	-6	839	829
6	-4	854	887
6	-2	1321	1323
6	0	890	886
6	2	498	496
6	4	383	383
6	6	964	957
6	8	479	486
7	-9	531	523
7	-7	289	295
7	-5	604	603
7	-3	348	349
7	-1	995	1040
7	3	264	261
7	5	342	344
7	7	646	648
8	-8	221	188
8	-4	410	395
8	-2	294	315
8	2	173	185
8	4	413	403
9	-5	674	680
9	-3	1067	1046
9	-1	352	358
9	1	429	419
9	3	308	298
9	5	710	689
10	-4	651	631
10	-2	569	587
10	0	179	211

H= 5

K	L	FOBS	FCALC
0	-11	372	391
0	-9	1096	1089
0	-7	748	760
0	-5	782	754
0	-3	1167	1165
0	-1	1971	2000
0	1	926	855
0	3	186	161
0	5	191	173
0	7	992	1004
0	9	644	658
1	-12	330	354
1	-10	314	321
1	-8	696	716
1	-6	413	418
1	-4	294	295
1	-2	498	483
1	0	1415	1428
1	2	284	281
1	4	294	298
1	6	419	415
1	8	581	577
2	-11	495	494
2	-9	175	172
2	-7	219	204
2	-5	325	342
2	-3	1218	1258
2	-1	331	320
2	1	531	526
2	3	483	484
2	5	592	556
2	7	198	219
2	9	323	315
3	-12	686	698
3	-10	930	968
3	-8	282	296
3	-6	244	245
3	-4	813	823
3	-2	1271	1295
3	0	1254	1258
3	2	1283	1336
3	4	599	613
3	6	702	692
3	8	619	623
4	-11	622	626
4	-9	400	405
4	-5	315	317
4	-3	1273	1274
4	-1	585	578
4	1	584	558
4	3	354	373
4	5	720	704
4	7	215	207
5	-10	297	297
5	-8	352	330
5	-6	361	365
5	-2	332	349
5	0	832	853
5	4	232	229
5	6	297	293
6	-9	784	783
6	-7	536	532
6	-5	669	630
6	-3	667	695
6	-1	1498	1510
6	1	758	746
6	7	757	748
7	-10	312	300
7	-8	551	557
7	-6	172	172
7	-4	395	389
7	-2	578	560
7	0	908	909
7	6	380	386
8	-7	154	128
8	-3	540	535
8	1	242	263
8	3	198	192
8	5	187	188
9	-4	520	520
9	-2	856	870
9	0	482	497
9	2	708	693
10	-3	632	638
10	-1	394	407
10	1	415	379

H= 6

K	L	FOBS	FCALC
0	-12	543	534
0	-10	479	478
0	-8	1425	1416
0	-6	607	588
0	-2	836	845
0	0	2653	2672
0	2	405	428
0	4	181	222
0	6	208	184
0	8	748	735
1	-11	255	225
1	-9	537	547
1	-7	771	771
1	-5	274	279
1	-1	739	768
1	1	943	951
1	3	164	166
1	7	297	290
2	-10	627	618
2	-6	676	662
2	-2	1122	1143
2	0	150	155
2	2	810	803
2	6	247	267
3	-11	739	725
3	-9	1205	1185
3	-7	652	664
3	-5	573	555
3	-3	1169	1224
3	-1	908	926
3	1	1035	1081
3	3	1096	1090
3	5	248	262
3	7	473	479
4	-10	548	526
4	-8	382	379
4	-6	584	579
4	-2	900	920
4	0	262	288
4	2	804	773
4	4	175	156
4	6	269	284
5	-9	416	416
5	-7	645	647
5	-5	460	466
5	-1	528	560
5	1	634	650
6	-10	430	417
6	-8	1002	986
6	-6	484	499
6	-2	601	651
6	0	1585	1627
6	2	510	497
6	4	187	154
6	6	196	161
7	-9	435	427
7	-7	522	509
7	-1	658	635
7	1	670	663
7	3	170	141
8	-6	334	344
8	-2	598	608
8	2	410	405
9	-5	261	251
9	-3	522	513
9	-1	618	616
9	1	604	609

H= 7

K	L	FOBS	FCALC
0	-11	366	343
0	-9	659	670
0	-7	1484	1470
0	-5	308	307
0	-1	433	440
0	1	1350	1318
0	3	766	754
0	5	418	422
1	-12	216	203
1	-8	872	869
1	-6	447	450
1	-4	174	177
1	-2	371	363
1	0	818	812
1	2	413	417
1	4	315	298
1	6	291	264
2	-11	193	156
2	-9	598	585
2	-5	721	711
2	-3	202	190
2	-1	435	429
2	1	337	334
2	3	490	470
3	-10	802	782
3	-8	768	755
3	-6	910	889
3	-4	794	808
3	-2	954	927
3	0	646	652
3	2	842	845
3	4	750	735
4	-11	245	209
4	-9	495	489
4	-7	214	218
4	-5	909	932
4	-3	193	197
4	1	461	478
4	3	573	576
5	-8	468	471
5	-6	398	385
5	-4	285	282
5	-2	183	196
5	0	464	458
5	2	276	280
6	-9	521	506
6	-7	1077	1067
6	-5	299	289
6	-3	177	187
6	-1	488	499
6	1	924	917
6	3	540	543
7	-8	669	656
7	-6	428	432
7	-2	223	219
7	0	611	598
7	2	443	459
8	-5	312	294
8	-1	274	254

H= 8

K	L	FOBS	FCALC
0	-10	220	223
0	-8	619	632
0	-6	1299	1337
0	-4	743	761
0	-2	392	401
0	0	465	457
0	2	744	735
0	4	588	620
1	-7	831	835
1	-5	313	326
1	-3	339	333
1	1	589	575
1	5	466	471
2	-10	208	227
2	-8	218	232
2	-6	242	230
2	-4	746	757
2	2	252	268
3	-9	704	694
3	-7	461	468
3	-5	1014	1021
3	-3	614	643
3	1	463	485
3	3	1081	1083
4	-10	238	219
4	-8	412	396
4	-6	250	236
4	-4	828	857
4	2	337	341
4	4	638	646
5	-7	489	498
5	-3	304	305
5	1	295	306
6	-8	466	470
6	-6	1021	1022
6	-4	492	507
6	-2	368	374
6	0	368	369
6	2	643	642
7	-5	381	380
7	-3	260	270

H= 9

K	L	FOBS	FCALC
0	-9	372	374
0	-7	682	694
0	-5	858	874
0	-3	1062	1017
0	-1	736	735
0	1	763	765
0	3	374	367
1	-6	537	541
1	-4	400	384
1	-2	481	467
1	2	466	462
2	-9	210	225
2	-5	560	569
2	-3	537	523
2	1	218	195
2	3	424	431
3	-8	443	430
3	-6	628	623
3	-4	1072	1094
3	-2	427	421
3	0	164	137
3	2	187	179
4	-7	235	178
4	-5	548	554
4	-3	479	488
4	1	172	145
5	-6	487	496
5	-4	169	118
5	-2	386	389
6	-5	724	711
6	-3	699	712
5	-1	483	477

H= 10

K	L	FOBS	FCALC
0	-8	239	223
0	-6	578	571
0	-4	572	546
0	-2	681	641
0	0	663	658
1	-7	211	241
1	-5	315	309
1	-1	666	663
2	-4	514	508
2	-2	288	309
3	-5	425	447
3	-3	1040	1029
3	-1	240	230
4	-4	611	609

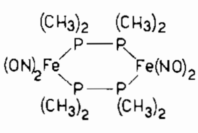
nected arsenic atoms where the idealized angle would be 109.5°. It is therefore to this reference value that the Cr–As–As and C–As–C angles should be compared Whatever else might be said concerning the large Cr–As–As angle it does not appear to cause any marked instability in the compound.

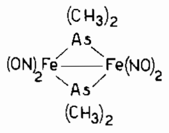
There is no significant difference between the axial Cr–C bond lengths, with a mean value of $1.88_5 \pm$

0.020 Å and the equatorial ones, which are crystallographically equal at 1.870(8) Å.

The equatorial (C(4)) and axial (C(5)) methyl groups are not symmetry-related; however, flipping the ring to the other, equivalent chair conformation will interchange these groups. At temperatures sufficiently high that the inversion is rapid, the pmr spectrum should consist of a singlet. Such a spectrum is observed at room temperature (τ8.33 in CD_2Cl_2). This signal broadens as the solution is cooled below –50° C. However, increasing solvent viscosity prevented observations of the true coalescence point and the low-temperature limiting spectrum. Recourse to other solvents failed because of the low solubility of the compound. We estimate that the coalescence temperature lies in the neighborhood of –90° C. This, in turn would lead to an estimate of about 10 kcal mol^{-1} as the activation energy for interconverting the two chair conformations.

While a considerable number of purely inorganic ring compounds are known,[10] there does not appear to be more than one known compound which is at all similar to the one described here. That compound is X obtained by reaction of Me_4P_2 with $Fe(CO)_2(NO)_2$.[11]


X


Y

Interestingly, the analogous reaction with Me_4As_2 led to As–As bond scission and the formation of Y. It is interesting that Hayter and Williams[11] observed that "molecular models show that Me_4P_2 can form complexes" like X "with little if any strain when the metal is tetrahedral. Attempts to make models of analogous compounds involving an octahedral metal, however, were unsuccessful owing to strain in forming the ring." They went on to suggest that this might account, in part, for Hayter's earlier observation[12] that complexes he isolated with the empirical formula $[M(CO)_4(Me_4As_2)]_n$ (M = Cr, Mo) appeared to be polymers with n = 13–20, rather than cyclic dimers (see below).

The present work, of course, refutes the conclusion drawn from model building by Hayter and Williams, by showing that the cyclic dimer is a quite stable and conformationally satisfactory structure.

After our compound had been identified, a literature search was made to see if any similar ones, or perhaps even the same compound, had previously been reported. It was found that in 1964 Hayter[12] had reported $[Cr(CO)_4As_2Me_4]_n$, which he prepared in 5% yield as a byproduct (the major one being $Cr_2(CO)_{10}As_2(CH_3)_4$) of the reaction of $As_2(CH_3)_4$ with $Cr(CO)_6$ in refluxing ethylcyclohexane. As already mentioned, he formulated this as a polymer with n having an average value of 13 on the basis of an osometric molecular weight determination in CH_2Br_2. The color, decomposition point and infrared spectrum of our compound all appear to be identical to the corresponding properties reported by Hayter. We are inclined to believe that the two compounds are the same and that perhaps some error was made in the molecular weight measurement. It is also possible though unlikely that the cyclic molecules may have undergone ring opening and oligomerization during the molecular weight measurement.

References

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4 The following computer programs written for the IBM360 were used: TRACER, a lattice transformation and cell reduction program by Lawton; DATARED, a data reduction program by Frenz; FOURIER, a Fourier summation program (based on Zalkin's FORDAP) by Dellaca and Robinson and modified by Hodgson; NUCLS, a full-matrix least-squares program (minimizing $\Sigma w(|F_o|-|F_c|)^2$ by Ibers and Doedens, similar to Busing and Levy's ORFLS; SADIAN, a distances and angles program by Baur, rewritten by Frenz and Brice; AGNOST, an absorption correction program by Cahen based on Coppens' DATAP and Tompa analytical subroutines of Cullen's program; PERFACT, a program for analysis of structure factors by Frenz; ORFFE, a function and error program by Busing, Martin, and Levy as modified by Brown, Johnson, and Theissen; ORTEP, a plotting program by Johnson; and LIST, a program for listing the data by Snyder.

5 We define $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma wF_o^2]^{1/2}$

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