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Crystal structure of bis[(tetracarbonyl)(μ-arsenodiphenyl)manganese(I)], $Mn_2(CO)_8(AsPh_2)_2$

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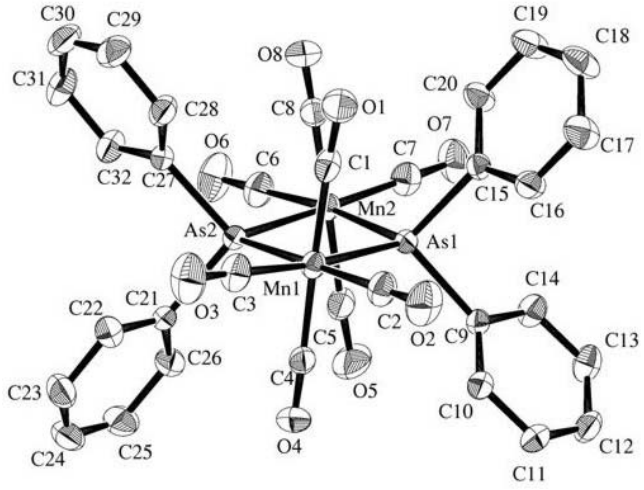

Abstract

$C_{32}H_{20}As_2Mn_2O_8$, monoclinic, $P2_1/n$ (no. 14), a = 12.1457(8) Å, b = 16.549(1) Å, c = 15.910(1) Å, β = 101.995(1)°, V = 3128.1 Å^3, Z = 4, $R_{gt}(F)$ = 0.027, $wR_{ref}(F)$ = 0.028, T = 273 K.

Source of material

$[Ph_2AsMn(CO)_4]_2$ had been prepared from Ph_3As and $Mn_2(CO)_{10}$ in the 1960's [1,2] and several other ways since then. However, the lack of a reported crystal structure reflects the difficulty of crystallizing suitable crystals. The crystal used for this analysis was prepared by adding a 2.2 molar excess of Ph_3As to a toluene solution containing pentacarbonylmanganese(I) bromide and refluxed for 24 h. Suitable yellow plate-like crystals for X-ray diffraction were obtained by slow evaporative recrystallization of the reaction mixture.

Experimental details

All the hydrogen atoms were added at calculated positions d(C—H) = 1.080 Å, but not refined.

Discussion

In the 1980's, a peak of interest was reached for the respective dimeric and trimeric metal carbonyl complexes, $[M_2(CO)_x(\mu\text{-}Y_y)_z]$ and $[M_3(CO)_x(\mu\text{-}Y_y)_z]$, (where, M = Co, Mn, Re, Tc, V; Y = As, Me, P; x = 2, 3; y = 1, 2; z = 1, 2) [3,4]. The focus was on their synthesis, properties, ESR and IR spectral studies for the structural predictions and metal-metal interactions. Among the above complexes, the molecular structure of the dimer, $[Mn_2(CO)_8(\mu\text{-}AsPh_2)_2]$, reported here is fully consistent with the spectral and magnetic properties, except that in the solid state the predicted symmetry, D_{2h}, is reduced. Our interest in this complex is due to its bioactivity and its potential use in medicine [5,6].

The dimer results from the two $AsPh_2$ ligands being in μ-bridging coordination modes to the two $Mn(CO)_4$ units. The Mn_2As_2 central core is a planar diamond with the average bond length and angles, d(Mn—As), ∠As–Mn–As and ∠Mn–As–Mn, equal to 2.4752(5) Å, 77.93(2)° and 101.98(2)°, respectively. The four phenyl groups are located above and below this plane. As the spectral results predicted, there is no metal-metal bonding involved. The d(Mn1···Mn2) is equal to 3.8455(8) Å and is clearly outside the bonding range. The molecule has a two-fold axis of symmetry that extendes out perpendicularly to the Mn_2As_2 plane. The vertical carbonyl groups of the $Mn(CO)_4$ units are slighty staggered, and the carbonyls coordinate to the manganese atoms with the average bonding distances d(Mn—C1,4,5,8) and d(Mn—C2,3,6,7) equal to 1.842(5) Å and 1.826(5) Å, respectively. The shorter latter distance is understood in terms of the *trans* influence of the arsenic atoms on the metal-carbonyls' back bonding of the carbonyls co-planar with the Mn_2As_2 core [7]. The corresponding C=O bond averages are much closer due to the multiple bond nature of the carbonyls, namely 1.132(3) Å and 1.138(3) Å.

Table 1. Data collection and handling.

Crystal:	yellow plate, size 0.20 × 0.15 × 0.10 mm
Wavelength:	Mo K_α radiation (0.7107 Å)
μ:	29.57 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18526, 5510
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 4135
$N(param)_{refined}$:	397
Programs:	SHELXTL [8], ORTEP [9]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(1)	4*e*	–0.1789	0.2189	0.1186	0.060
H(2)	4*e*	–0.3418	0.1420	0.1464	0.070
H(3)	4*e*	–0.3231	0.0625	0.2792	0.068
H(4)	4*e*	–0.1450	0.0607	0.3836	0.072
H(5)	4*e*	0.0184	0.1372	0.3560	0.064
H(6)	4*e*	–0.1107	0.3449	0.2847	0.066
H(7)	4*e*	–0.1092	0.4327	0.4103	0.085
H(8)	4*e*	0.0668	0.4560	0.5151	0.085

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(9)	4*e*	0.2409	0.3921	0.4965	0.078
H(10)	4*e*	0.2388	0.3007	0.3734	0.065
H(11)	4*e*	0.1869	0.2884	–0.1024	0.067
H(12)	4*e*	0.1511	0.2124	–0.2391	0.081
H(13)	4*e*	0.1326	0.0653	–0.2389	0.084
H(14)	4*e*	0.1558	–0.0075	–0.1035	0.082
H(15)	4*e*	0.1900	0.0666	0.0344	0.065
H(16)	4*e*	0.2751	0.4238	0.0853	0.066
H(17)	4*e*	0.4536	0.4939	0.0810	0.084
H(18)	4*e*	0.6166	0.4174	0.0589	0.080
H(19)	4*e*	0.6045	0.2716	0.0394	0.081
H(20)	4*e*	0.4282	0.1989	0.0457	0.065

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
As(1)	4*e*	0.06117(3)	0.24805(2)	0.22039(2)	0.0301(2)	0.0401(2)	0.0321(2)	–0.0007(2)	0.0070(1)	–0.0018(2)
As(2)	4*e*	0.20665(3)	0.24622(2)	0.08081(2)	0.0340(2)	0.0364(2)	0.0361(2)	–0.0038(2)	0.0107(2)	–0.0025(2)
Mn(1)	4*e*	0.03730(5)	0.32770(4)	0.08664(4)	0.0353(3)	0.0447(3)	0.0397(3)	0.0029(3)	0.0093(3)	0.0056(3)
Mn(2)	4*e*	0.23652(5)	0.17255(4)	0.21947(4)	0.0348(3)	0.0414(3)	0.0401(3)	0.0031(3)	0.0100(3)	0.0023(3)
O(1)	4*e*	0.1642(3)	0.4527(2)	0.2020(2)	0.097(3)	0.055(2)	0.090(3)	–0.024(2)	0.038(2)	–0.025(2)
O(2)	4*e*	–0.1729(3)	0.4067(3)	0.1092(3)	0.054(2)	0.107(3)	0.109(3)	0.033(2)	0.027(2)	0.011(3)
O(3)	4*e*	0.0436(4)	0.4206(3)	–0.0715(3)	0.114(3)	0.106(3)	0.079(3)	0.020(3)	0.035(2)	0.052(3)
O(4)	4*e*	–0.0789(3)	0.1902(3)	–0.0145(2)	0.057(2)	0.120(3)	0.068(2)	–0.032(2)	0.009(2)	–0.037(2)
O(5)	4*e*	0.0874(4)	0.0336(2)	0.1565(3)	0.098(3)	0.068(3)	0.124(4)	–0.039(2)	0.046(3)	–0.028(2)
O(6)	4*e*	0.4397(3)	0.0878(2)	0.1893(3)	0.069(2)	0.090(3)	0.124(3)	0.035(2)	0.051(2)	0.016(3)
O(7)	4*e*	0.2552(3)	0.1097(3)	0.3960(2)	0.094(3)	0.106(3)	0.051(2)	0.016(2)	0.017(2)	0.029(2)
O(8)	4*e*	0.3822(3)	0.3144(3)	0.2799(2)	0.071(2)	0.102(3)	0.072(2)	–0.040(2)	0.011(2)	–0.024(2)
C(1)	4*e*	0.1187(4)	0.4048(3)	0.1574(3)	0.054(3)	0.043(2)	0.064(3)	0.001(2)	0.029(2)	0.005(2)
C(2)	4*e*	–0.0929(4)	0.3760(3)	0.1006(3)	0.049(3)	0.068(3)	0.058(3)	0.007(2)	0.015(2)	0.011(2)
C(3)	4*e*	0.0425(4)	0.3847(3)	–0.0108(3)	0.061(3)	0.064(3)	0.066(3)	0.012(2)	0.021(3)	0.017(3)
C(4)	4*e*	–0.0355(3)	0.2429(3)	0.0249(3)	0.033(2)	0.083(3)	0.038(2)	–0.004(2)	0.005(2)	0.001(2)
C(5)	4*e*	0.1430(4)	0.0872(3)	0.1777(3)	0.055(3)	0.052(3)	0.061(3)	–0.005(2)	0.025(2)	–0.002(2)
C(6)	4*e*	0.3609(4)	0.1195(3)	0.2005(3)	0.052(3)	0.059(3)	0.063(3)	0.007(2)	0.019(2)	0.010(2)
C(7)	4*e*	0.2479(4)	0.1337(3)	0.3282(3)	0.048(3)	0.059(3)	0.057(3)	0.010(2)	0.011(2)	0.008(2)
C(8)	4*e*	0.3252(3)	0.2610(3)	0.2574(3)	0.039(2)	0.074(3)	0.040(2)	0.000(2)	0.007(2)	–0.002(2)
C(9)	4*e*	–0.0700(3)	0.1831(2)	0.2343(2)	0.036(2)	0.039(2)	0.038(2)	–0.002(2)	0.013(2)	–0.004(2)
C(10)	4*e*	–0.1705(3)	0.1841(3)	0.1770(3)	0.044(2)	0.065(3)	0.043(2)	–0.009(2)	0.012(2)	0.000(2)
C(11)	4*e*	–0.2628(4)	0.1408(3)	0.1925(3)	0.041(2)	0.078(3)	0.059(3)	–0.016(2)	0.012(2)	–0.005(3)
C(12)	4*e*	–0.2521(4)	0.0965(3)	0.2668(3)	0.051(3)	0.054(3)	0.072(3)	–0.013(2)	0.030(2)	–0.004(2)
C(13)	4*e*	–0.1525(4)	0.0952(3)	0.3252(3)	0.061(3)	0.061(3)	0.066(3)	0.002(2)	0.026(2)	0.018(2)
C(14)	4*e*	–0.0606(4)	0.1383(3)	0.3096(3)	0.045(2)	0.061(3)	0.054(3)	0.003(2)	0.010(2)	0.015(2)
C(15)	4*e*	0.0655(3)	0.3171(2)	0.3215(2)	0.040(2)	0.039(2)	0.038(2)	0.000(2)	0.013(2)	–0.003(2)
C(16)	4*e*	–0.0335(4)	0.3545(3)	0.3313(3)	0.037(2)	0.069(3)	0.057(3)	0.004(2)	0.007(2)	–0.017(2)
C(17)	4*e*	–0.0323(4)	0.4041(3)	0.4016(3)	0.058(3)	0.077(4)	0.076(4)	0.019(3)	0.013(3)	–0.028(3)
C(18)	4*e*	0.0664(5)	0.4170(3)	0.4605(3)	0.076(4)	0.072(3)	0.060(3)	0.018(3)	0.002(3)	–0.031(3)
C(19)	4*e*	0.1634(4)	0.3811(3)	0.4505(3)	0.056(3)	0.075(3)	0.057(3)	0.013(3)	–0.006(2)	–0.025(3)
C(20)	4*e*	0.1621(4)	0.3302(3)	0.3807(3)	0.043(2)	0.068(3)	0.048(2)	0.012(2)	0.003(2)	–0.016(2)
C(21)	4*e*	0.1882(3)	0.1820(3)	–0.0253(2)	0.033(2)	0.050(2)	0.041(2)	–0.008(2)	0.012(2)	–0.008(2)
C(22)	4*e*	0.1788(4)	0.2234(3)	–0.1021(3)	0.062(3)	0.062(3)	0.048(3)	–0.005(2)	0.017(2)	–0.005(2)
C(23)	4*e*	0.1591(4)	0.1804(4)	–0.1789(3)	0.064(3)	0.098(4)	0.041(3)	0.002(3)	0.011(2)	–0.006(3)
C(24)	4*e*	0.1493(4)	0.0980(4)	–0.1790(3)	0.063(3)	0.090(4)	0.056(3)	–0.005(3)	0.009(2)	–0.031(3)
C(25)	4*e*	0.1613(5)	0.0576(3)	–0.1033(4)	0.074(4)	0.058(3)	0.076(4)	–0.010(3)	0.017(3)	–0.027(3)
C(26)	4*e*	0.1808(4)	0.0992(3)	–0.0254(3)	0.062(3)	0.049(3)	0.053(3)	–0.008(2)	0.016(2)	–0.011(2)
C(27)	4*e*	0.3411(3)	0.3069(2)	0.0682(2)	0.039(2)	0.047(2)	0.035(2)	–0.008(2)	0.012(2)	–0.002(2)
C(28)	4*e*	0.3478(4)	0.3897(3)	0.0765(3)	0.054(3)	0.050(3)	0.069(3)	–0.011(2)	0.029(2)	–0.007(2)
C(29)	4*e*	0.4478(5)	0.4291(3)	0.0733(4)	0.071(4)	0.058(3)	0.089(4)	–0.023(3)	0.028(3)	–0.010(3)
C(30)	4*e*	0.5389(4)	0.3865(3)	0.0608(3)	0.048(3)	0.078(4)	0.077(4)	–0.022(3)	0.015(3)	0.010(3)
C(31)	4*e*	0.5324(4)	0.3048(3)	0.0504(3)	0.044(3)	0.082(4)	0.081(4)	0.004(3)	0.026(2)	0.015(3)
C(32)	4*e*	0.4331(4)	0.2638(3)	0.0540(3)	0.047(2)	0.056(3)	0.068(3)	–0.002(2)	0.024(2)	0.002(2)

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