

to the octahedral environment of the Sr^{2+} and is too far from other atoms to form hydrogen bonds. Table 3 gives the distances and angles between the O(2) and O(4) atoms of water molecules and the atoms to which hydrogen-bonding is presumed (Chidambaram, Sequeira & Sikka, 1964; Holzbecher, Knop & Falk, 1971).

We thank Dr Varetti for helpful discussions and Dr Aymonino for suggesting this work and for critical reading of the manuscript. Most of the calculations were carried out on an IBM 360 computer with the NRC system of programs of Ahmed, Pippy & Huber, to whom we are grateful.

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Acta Cryst. (1977). **B33**, 1728–1732

The Crystal and Molecular Structure of Bis(tetraphenylarsonium) Nitroprusside

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(Received 5 October 1976; accepted 13 November 1976)

$[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5\text{NO}]$ is monoclinic, space group $P2_1/c$, with $a = 9.09$ (1), $b = 21.43$ (2), $c = 24.51$ (1) Å, $\beta = 104.3$ (3)°, $Z = 4$. 1607 visual data were used. The final R is 0.120. The nitroprusside anion has a somewhat distorted octahedral configuration with $\text{Fe}-\text{N} = 1.61$ (5) and $\text{Fe}-\text{C} = 1.92$ (2) Å (mean). The two independent cations differ in the orientation of the phenyl groups. The packing of the structure is such that the ions are all relatively distant from each other, the shortest $\text{Fe}-\text{As}$ distance being 6.53 Å.

Introduction

The structure determination of $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5\text{NO}]$ was undertaken as part of a study of some nitroprusside compounds (Lanfranconi, Alvarez & Castellano, 1973; Varetti & Aymonino, 1973; Castellano, Piro & Rivero, 1977; Alvarez, Aymonino, Baran, Gentil, Lanfranconi & Varetti, 1976).

Experimental

From a crystal mounted along a 1607 reflexions above background were visually estimated from equi-inclination Weissenberg photographs of the 0–6 k l layers. The intensities were corrected for Lorentz and polarization effects but not for absorption or extinction. The As and Fe atoms were located from a Patterson map. A Fourier synthesis phased on these atoms showed all the non-hydrogen atoms of the asymmetric unit. A block-diagonal isotropic least-squares refine-

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† Supported by a Fellowship from the CONICET.

Table 1. Final positional parameters ($\times 10^4$), with estimated standard deviations in parentheses, and isotropic thermal parameters of all non-hydrogen atoms

	x	y	z	B_{iso}
As(1)	1240 (6)	3771 (2)	466 (2)	3.042
As(2)	8204 (5)	824 (2)	1304 (2)	2.746
Fe(1)	3525 (8)	2781 (3)	3533 (3)	3.325
C(1)	4587 (53)	2264 (23)	4151 (21)	4.715
C(2)	3605 (46)	2100 (19)	3056 (18)	2.865
C(3)	5593 (61)	2972 (25)	3459 (24)	6.294
C(4)	3668 (47)	3491 (19)	4046 (19)	3.020
C(5)	2835 (55)	3327 (23)	2925 (22)	4.889
N(1)	5175 (45)	1953 (19)	4498 (18)	5.366
N(2)	3637 (44)	1641 (19)	2802 (18)	5.239
N(3)	6696 (48)	3080 (20)	3374 (19)	6.166
N(4)	3613 (39)	3838 (17)	4375 (15)	3.709
N(5)	2414 (40)	3621 (16)	2506 (16)	3.941
N(6)	1804 (51)	2667 (21)	3579 (20)	6.956
O(1)	586 (41)	2631 (17)	3641 (17)	7.294
C(101)	-593 (44)	3838 (19)	724 (18)	2.448
C(102)	-1423 (44)	3320 (19)	684 (18)	2.358
C(103)	-2800 (55)	3363 (24)	846 (22)	4.992
C(104)	-3288 (62)	3892 (26)	1060 (25)	6.293
C(105)	-2254 (50)	4386 (20)	1116 (20)	3.745
C(106)	-886 (53)	4365 (22)	955 (22)	4.472
C(111)	2563 (42)	4477 (17)	762 (17)	1.649
C(112)	3070 (50)	4902 (21)	437 (20)	3.660
C(113)	4015 (51)	5406 (21)	733 (21)	4.047
C(114)	4349 (50)	5439 (21)	1271 (20)	3.784
C(115)	3594 (60)	4976 (25)	1651 (24)	5.913
C(116)	3000 (53)	4477 (21)	1349 (21)	4.236
C(121)	2173 (38)	3019 (16)	677 (15)	0.619
C(122)	2626 (52)	2605 (22)	336 (21)	4.494
C(123)	3258 (48)	2004 (20)	527 (19)	3.462
C(124)	3577 (44)	1933 (18)	1149 (18)	2.419
C(125)	3030 (59)	2261 (25)	1438 (24)	5.765
C(126)	2465 (47)	2829 (20)	1273 (19)	3.284
C(131)	693 (47)	3828 (20)	-326 (19)	3.313
C(132)	1884 (51)	3867 (22)	-652 (21)	4.175
C(133)	1475 (61)	3866 (26)	-1216 (25)	6.445
C(134)	-20 (61)	3783 (27)	-1483 (24)	6.324
C(135)	-1128 (54)	3721 (24)	-1236 (22)	4.994
C(136)	-806 (48)	3728 (21)	-624 (19)	3.547
C(201)	8091 (45)	1548 (19)	1756 (18)	2.687
C(202)	9211 (55)	1990 (23)	1758 (22)	3.887
C(203)	9201 (46)	2552 (19)	2081 (19)	2.893
C(204)	8106 (52)	2610 (22)	2371 (21)	4.242
C(205)	7079 (61)	2131 (25)	2381 (24)	6.200
C(206)	7069 (52)	1607 (22)	2098 (21)	4.329
C(211)	9770 (43)	252 (18)	1685 (17)	2.077
C(212)	9643 (51)	-329 (22)	1609 (21)	4.209
C(213)	10732 (54)	-707 (23)	1861 (21)	4.865
C(214)	11949 (54)	-580 (23)	2302 (22)	4.689
C(215)	12047 (55)	98 (23)	2343 (22)	4.875
C(216)	10996 (51)	502 (21)	2114 (21)	3.811
C(221)	6314 (42)	343 (18)	1218 (17)	1.913
C(222)	5249 (45)	491 (18)	662 (18)	2.376
C(223)	3865 (46)	136 (19)	586 (18)	2.739
C(224)	3641 (44)	-255 (18)	993 (18)	2.308
C(225)	4632 (45)	-333 (19)	1469 (18)	2.611
C(226)	5970 (51)	18 (22)	1584 (21)	4.011
C(231)	8594 (41)	1084 (17)	587 (16)	1.556
C(232)	9775 (47)	867 (21)	417 (19)	3.388
C(233)	10103 (58)	1041 (23)	-74 (23)	5.419
C(234)	9286 (52)	1508 (22)	-338 (21)	4.325
C(235)	8082 (43)	1758 (18)	-193 (17)	1.989
C(236)	7762 (43)	1539 (18)	290 (18)	2.052

Table 1 (cont.)

	x	y	z
H(102)	-1026	2923	533
H(103)	-3516	2997	814
H(104)	-4345	3910	1158
H(105)	-2497	4780	1301
H(106)	-138	4714	997
H(112)	2726	4859	0
H(113)	4499	5755	540
H(114)	4966	5837	1400
H(115)	4329	5031	2077
H(116)	2638	4113	1556
H(122)	2484	2766	-71
H(123)	3421	1668	245
H(124)	4288	1637	1410
H(125)	3059	2097	1843
H(126)	2237	3099	1588
H(132)	3026	3907	-493
H(133)	2317	3930	-1432
H(134)	-408	3733	-1916
H(135)	-2170	3663	-1509
H(136)	-1651	3664	-403
H(202)	10011	1913	1537
H(203)	9971	2908	2113
H(204)	8091	3023	2574
H(205)	6249	2173	2597
H(206)	6343	1261	2157
H(212)	8668	-484	1322
H(213)	10679	-1156	1734
H(214)	12758	-722	2592
H(215)	13064	243	2588
H(216)	11120	964	2249
H(222)	5457	799	368
H(223)	2974	159	237
H(224)	2675	-523	943
H(225)	4405	-642	1749
H(226)	6763	18	1968
H(232)	10459	546	665
H(233)	10935	833	-227
H(234)	9519	1694	-693
H(235)	7448	2096	-433
H(236)	6853	1722	409

ment was performed to convergence. The 40 H atoms of the phenyl groups were then placed in their most probable positions. Further isotropic least-squares cycles, with the weighting scheme $w = 1$ if $F_o < 220$; $w = 1/F_o$ if $F_o \geq 220$, converged at $R = 0.12$. Unobserved reflexions were omitted from the refinement. Anisotropic refinement was not considered appropriate

Table 2. Intramolecular angles ($^\circ$) in the nitroprusside ion with estimated standard deviations in parentheses

C(1)-Fe-C(2)	87 (2)	C(3)-Fe-N(6)	176 (2)
C(1)-Fe-C(3)	84 (2)	C(4)-Fe-C(5)	89 (2)
C(1)-Fe-C(4)	90 (2)	C(4)-Fe-N(6)	89 (2)
C(1)-Fe-C(5)	170 (2)	C(5)-Fe-N(6)	91 (2)
C(1)-Fe-N(6)	99 (2)	Fe-C(1)-N(1)	178 (5)
C(2)-Fe-C(3)	85 (2)	Fe-C(2)-N(2)	173 (4)
C(2)-Fe-C(4)	174 (2)	Fe-C(3)-N(3)	175 (5)
C(2)-Fe-C(5)	93 (2)	Fe-C(4)-N(4)	169 (4)
C(2)-Fe-N(6)	96 (2)	Fe-C(5)-N(5)	173 (4)
C(3)-Fe-C(4)	89 (2)	Fe-N(6)-O(1)	174 (4)
C(3)-Fe-C(5)	86 (2)		

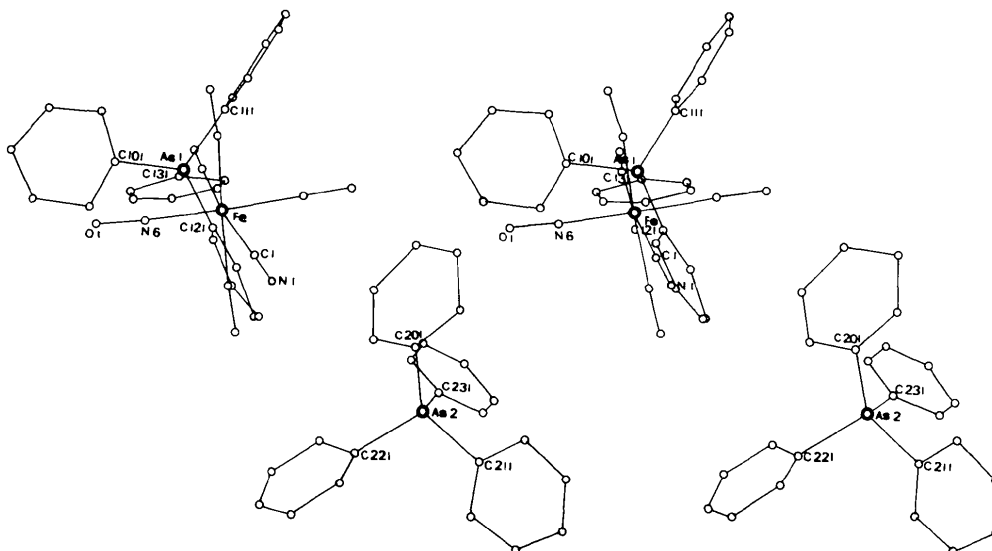


Fig. 1. Stereoscopic projection of $[\text{As}(\text{C}_6\text{H}_5)_4]_2[\text{Fe}(\text{CN})_5\text{NO}]$ as viewed down c .

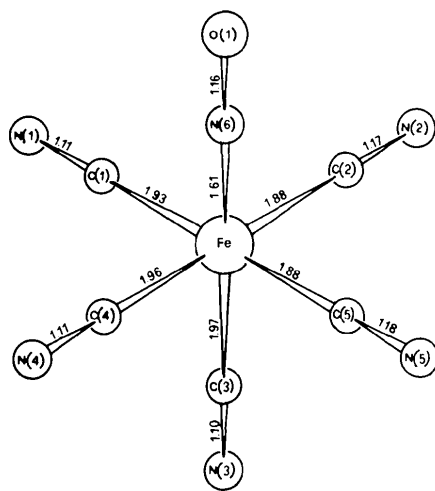


Fig. 2. Perspective drawing of the nitroprusside ion, showing bond distances and atom numbering. Standard deviations are 0.04 to 0.07 Å.

because of the low ratio of observed reflexions to the number of parameters (2.8). The final difference map contained only random background. The final parameters are given in Table 1.* A stereoscopic view of the asymmetric unit along c is shown in Fig. 1. Bond distances and atom numbering of the nitroprusside anion and the two cations are shown in Figs. 2 and 3,

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32314 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

respectively. Fig. 3 also shows the angles in the phenyl groups. The angles in the nitroprusside anion are given in Table 2.

Discussion

The ligands around the Fe atom form a somewhat distorted octahedron. The Fe-N distance is 1.62 (5) Å, shorter than Fe-C (mean 1.91 Å) in agreement with other determinations on nitroprusside salts (Manoharan & Hamilton, 1963; Lanfranconi, Alvarez & Castellano, 1973; Castellano, Piro & Rivero, 1977). This supports the interpretation of Ballhausen & Gray (1963) and also molecular orbital calculations (Manoharan & Gray, 1965) which suggest that the strong Fe-NO bond dominates the electronic structure of the levels involved in the optical transition and those of the near-UV region of the anion absorption spectrum.

Both cations have a tetrahedral configuration corresponding to the expected sp^3 hybridization of the As atoms. The two cations are not geometrically identical, differing in the relative orientation of the phenyl groups, probably because of their different environments and the relative freedom of the phenyl groups to rotate.

Bond distances and angles of the eight phenyl groups are somewhat spread from the values expected for undistorted rings. This is probably because of the low ratio between the number of observed intensities and the number of parameters, which precluded allowance for anisotropic vibrations, and also because considerable flapping may be expected to occur.

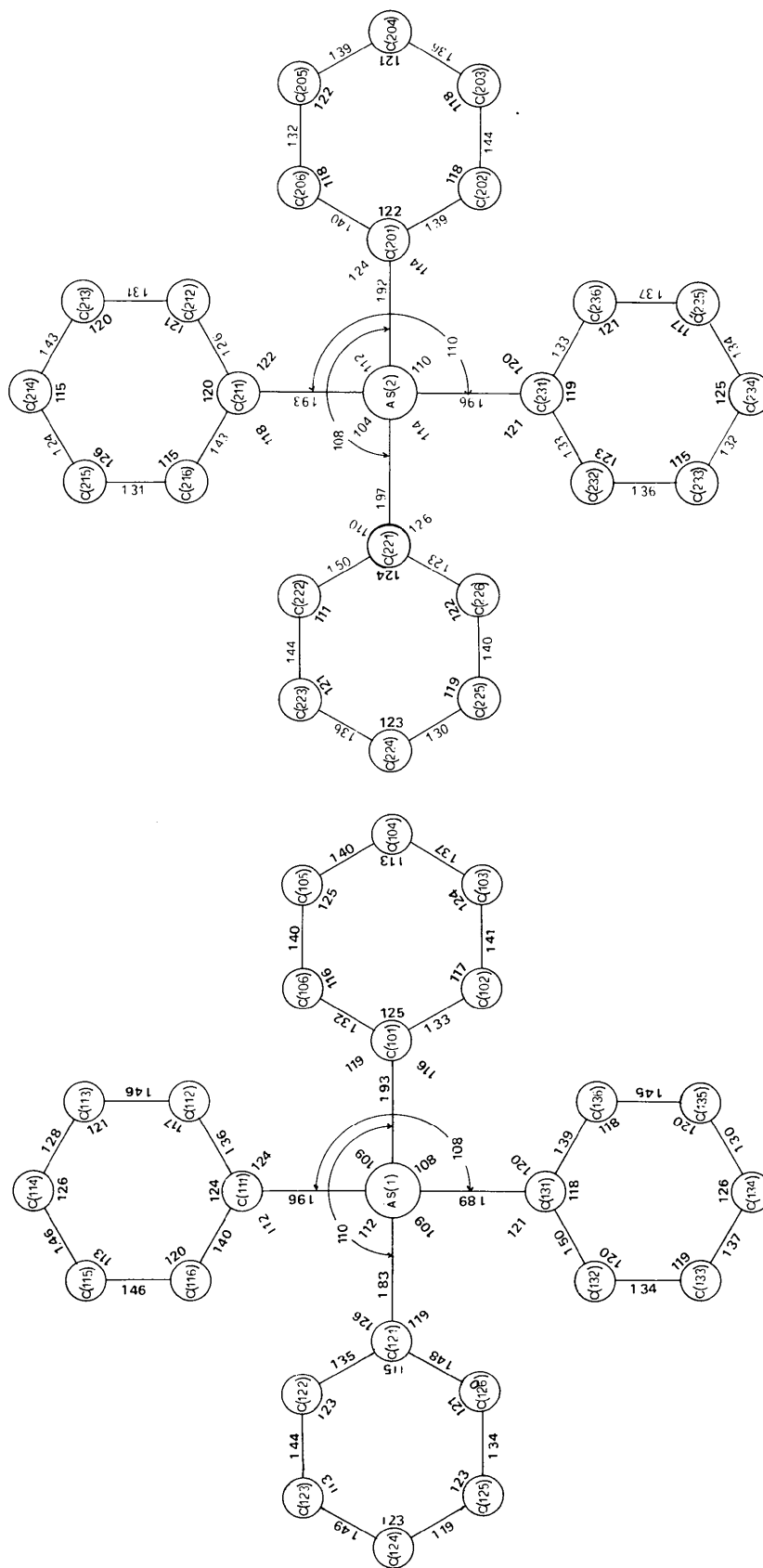


Fig. 3. Schematic drawing of the two independent tetraphenylarsonium cations, showing bond distances, angles and atom numbering. Standard deviations are 0.03 to 0.08 Å and 2–5°.

The packing of the structure is such that the centres of the ions are all relatively far apart. The shortest Fe—As distance of 6.53 Å is longer than the corresponding distance in alkaline and alkaline-earth nitroprussides. The crystal field acting on the anion is therefore weak and, though the nitroprusside ion is a somewhat distorted octahedron located in a site of C_1 symmetry, a single peak in the CN stretching region is observed (Gentil & Aymonino, 1977).

The nitrosyl groups are neither oriented in a given specific direction nor are they close to each other, as in $\text{Sr}[\text{Fe}(\text{CN})_5\text{NO}]\cdot 4\text{H}_2\text{O}$ (Castellano, Piro & Rivero, 1977). This explains the much narrower NO stretching band as compared with the Sr salt (Gentil & Aymonino, 1977).

The authors thank Dr L. A. Gentil and Dr P. J. Aymonino, who kindly supplied the crystals. Most of the calculations were carried out on an IBM 360 com-

puter with the NRC system of programs of Ahmed, Pippy & Huber, to whom we are grateful.

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Acta Cryst. (1977). **B33**, 1732–1737

Crystal and Molecular Structures of Trinuclear Rhodium(III) Complexes: *trans*- μ_3 -Oxo-tris[bis(acetato)aquarhodium(III)] Perchlorate Dihydrate and Monohydrate

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(Received 12 October 1976; accepted 13 November 1976)

The structures of *trans*- μ_3 -oxo-tris[bis(acetato)aquarhodium(III)] perchlorate dihydrate (*A*) and monohydrate (*B*) have been determined by single-crystal X-ray diffraction. *A* is monoclinic, space group $P2_1/c$, with $a = 11.737$ (2), $b = 14.962$ (4), $c = 15.200$ (4) Å, $\beta = 92.11$ (3)°, $Z = 4$. *B* is monoclinic, space group $P2_1$, with $a = 8.105$ (3), $b = 13.959$ (5), $c = 11.515$ (4) Å, $\beta = 93.95$ (3)°, $Z = 2$. The structures were solved by the heavy-atom technique and refined by full-matrix least squares to $R = 0.049$ for 2435 counter reflexions (*A*), and 0.055 for 1489 reflexions (*B*), for which $F > 3.92\sigma(F)$. The trinuclear complex cation contains three Rh atoms at the vertices of an equilateral triangle with a bridging O atom in the centre. The average Rh—Rh length is 3.33 Å.

Introduction

The Rh—carboxylic acid compound which has been most thoroughly examined is the dinuclear complex, $\text{Rh}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$. X-ray studies (Poray-Koshits & Antschishkina, 1962; Cotton, De Boer, La Prade, Pipal & Ucko, 1971) have shown that it contains an $\text{H}_2\text{O}-\text{Rh}-\text{Rh}-\text{H}_2\text{O}$ group with a multiple metal—metal bond (2.385 Å). Uemura, Spencer & Wilkinson (1973) obtained an Rh^{III} complex of formula $[\text{Rh}_3\text{O}(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{ClO}_4\cdot 2\text{H}_2\text{O}$ by ozonization

of the binuclear complex in acetic acid. On the basis of electronic, IR and NMR spectra and from the results of electrochemical reduction, these authors have shown that the complex contains an $M_3\text{O}$ group, found earlier for Cr (Figgis & Robertson, 1965; Chang & Jeffrey, 1970), Mn (Hessel & Romers, 1969), Fe (Figgis & Robertson, 1965; Anzenhofer & De Boer, 1969) and Ru (Cotton & Norman, 1972) compounds.

Baranovski, Mazo & Dikareva (1971) prepared the same compound by reacting Rh^{III} chloride monohydrate with Ag acetate. From the powder photo-