Acta Cryst. (1972). B28, 32

# The Structure of the Nitrogeno Molybdenum Chelate: $(\pi-C_5H_5(CO)_2M_0N.N(CH_3).C(CO_2C_2H_5)COH)PF_6$

BY C.K. PROUT, T.S. CAMERON AND A.R. GENT

Chemical Crystallography Laboratory, South Parks Road, Oxford, England

(Received 29 December 1970)

 $(\pi$ -C<sub>5</sub>H<sub>5</sub>(CO)<sub>2</sub>MoN.N(CH<sub>3</sub>).C(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)COH)PF<sub>6</sub> crystallizes in space group  $P\overline{1}$  with  $a=12\cdot02$ ,  $b=7\cdot53$ ,  $c=10\cdot83$  Å;  $\alpha=95\cdot9$ ,  $\beta=92\cdot8$ ,  $\gamma=70\cdot1^{\circ}$  and two formula units in the unit cell. The structure was determined from photographic X-ray data, and refined by the least-squares method to  $R=0\cdot138$  for 2090 independent reflexions. In the cation a planar five-atom ring is joined to molybdenum by a carbene bond Mo=C, 2·03 Å. The remaining bonds in the chelate ring are also shorter than single-bond distances. The molecular structure can only be written as a non-classical ion analogous to that derived from a sydnone.

#### Introduction

Green & Sanders (1967) reported that the treatment of the sodium salt of the anion  $(\pi C_5 H_5 Mo(CO)_3)^-$  with diazoacetic ester yields a yellow crystalline complex which Knox & Prout (1969) claimed to be the nitrogeno molybdenum carbene chelate (I).



This chelate protonates reversibly in aqueous acids and reacts reversibly with bases to form anionic species. Treatment of a tetrahydrofuran solution of the anion with methyl iodide gives the neutral methylated complex. The methylated complex also protonates reversibly and the hexafluophosphate salt of the cation forms a red crystalline solid. The crystal structure of this red complex has been determined, to confirm that it is also a carbene chelate, and to locate the positions of the methyl group.

### **Experimental**

The crystals were prepared by the method of Green & Sanders (1967).

Crystal data

MoC<sub>13</sub>O<sub>5</sub>N<sub>2</sub>H<sub>14</sub>.PF<sub>6</sub>, M.W. 519·14, F(000) = 514. Triclinic  $a = 12 \cdot 02 \pm 0.01$ ,  $b = 7 \cdot 53 \pm 0.01$ ,  $c = 10 \cdot 83 \pm 0.01$  Å;  $\alpha = 95 \cdot 5^{\circ} \pm 0.3$ ,  $\beta = 92 \cdot 8^{\circ} \pm 0.3$ ,  $\gamma = 70 \cdot 1^{\circ} \pm 0.3$ .  $D_m = 1.877$  g.cm<sup>-3</sup>,  $D_c = 1.878$  g.cm<sup>-3</sup>, Cu K $\alpha$ ,  $\lambda = 1.54178$  Å,  $\mu = 41 \cdot 53$  cm<sup>-3</sup>. No systematic extinction. Z=2. Space group  $P1(C_1^1, No. 1)$  or  $P\overline{1}(C_1^1, No. 2)$ .

For all X-ray photography the crystals were sealed in glass capillaries. The unit-cell dimensions were determined from calibrated zero layer Weissenberg films. The intensities of 2090 independent reflexions were measured from equi-inclination Weissenberg photographs about the c axis (hk0-hk8).

The visually estimated data were corrected for Lorentz and polarization effects, but not for absorption. The data were placed on a common scale by the ratio of their exposure times. The films were such that data of high quality were not expected.

## Solution and refinement of the structure

From an unsharpened Patterson synthesis, tentative positions were assigned to molybdenum and phosphorus atoms in the space group  $P\overline{1}$ . Subsequent Fourier syntheses clearly showed the positions of all the light atoms.

The structure was refined by the method of leastsquares with a block-diagonal approximation to the normal matrix which neglected the cross terms between the space and temperature parameters, and between the temperature parameters of the anion and the cation.

The refinement with isotropic temperature factors converged, after four cycles, at R = 15.6%, and with anisotropic temperature factors, after a further three cycles, at R = 13.8%. The weighting scheme used was  $w = \{1 + [(50|F_o| - 3000)/2000]^2\}^{-1}$ . Table 1 lists the observed structure amplitudes and structure factors calculated from the atomic parameters in Table 2. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), and the curve for neutral molybdenum was corrected for the real part of the anomalous dispersion effect. Fig. 1 shows the interatomic distances and interbond angles and Fig. 2 the projection of the structure down c.



Fig. 1. Distances and angles in the aniou and cation.

#### Discussion

The crystals are formed from isolated anions and cations in general positions in the unit cell (Fig. 2). There are no interionic hydrogen bonds. The structure of the cation is that of the heterocyclic metal chelate (II),



analogous to the chelate (I), but methylated at the nitrogen atom, N(2), which is not bonded to the molybdenum atom. The electronic structure of the cation must therefore be written as that of a non-classical ion derived from the sydnone (III).



The electronic structure of sydnones has been discussed by Baker & Ollis (1957).



Fig. 2. The crystal structure projected down c.

יני, האוויוניוניוי, האווינייוי, האווינייה, האווינייה, האוויניה, אווינייה, האווינייה, האוויני, אוויני, אוויני, א אַ אַ אַנוּטַרעטון אַ אַראָעטען אַ אַראָעטעער אַ אַראָעטעע, אין אַ אַראָעטעע, אין אַ אָראָעטעע, אין אַ אָראָעטע אַ גַּעַאַאַאַעטעען אַנאַאַאַעטעען אַראַעטעעע גענעעעעעעעעעעעעעעעעעעעעעעעעעעעעעעע	مىسىمەدلىك مىمىسىمىدادلىلىكى مىمىسمايلىلىك. قۇرجىڭچىچى قادىمقىزىدۇرۇغۇرغىيى يەۋەردۇرۇغۇرۇپ يەخەرمەرنىلىلىكى يەكەردۇخەرۋەردىكى ئەرتىك يۇزۇچۇرەخ جەڭرەردۇغۇرغۇرغۇرغۇ يۇغۇرۇۋۇغۇ يۇغۇرۇغۇغ ياغىرىكى ئۆزىيارلەرلۇۋۇرۇيورۇغ كەرئىغۇ
ער איינאנאנט אַאַנאַנאַנער אַראָראָריין אַראָראָראָראָראָראָראָראָראָראָראָראָראָר	asteritiekse sooren einenis sooren einen ooren einen ooren einen einen einen ooren einen ooren sooren sooren s Steritiester bekäreisteris, seteisesteren, alsenösis, sooren aren astren sooren sooren sooren sooren sooren so Steritiesteritiester istaatsisteriis sieteisteristeriis, sooren sooren sooren sooren sooren sooren sooren soore
anmunoittitta, ammunoittittitti. 201822424824243333, Edget285.co1928482, S25243242825, 232432424582, 5225254, 52243, 522525, 3234, 828 20182242622342825 2634285261525825, S25243252525, 232432526, 23243, 2525526, 3234, 828	ete secretettette soonde oordete secretettet. Bes Secretesses unstattes secretes kareteres kareteres secretet. Éersesteresses secretere berekeres secretere serie secretettette secreteres secreteres secreteres
utidities and the second of the second s Justices second secon Second second	Lauge and the second state of the
utuk unvertetete einete vertie is vie vertete vertete ververtetetete. Adde soodsatstage statstates is soods of all and use states soodstades saas biss soodstatstage states is soods of soods and soodstates soodstates saas	
ütite enserentitite. erenerativitie zurativitie ereneratioite ereneratiete annaativite veraat Band ussattestattes saaksissesseri zäheksisses erenessesser. Eläitevaste Bast ussestidestides äheksisses elaetiss elaetissitet istelliste	، مەنىلىلەلىمىسىمىي شائىلىلىلىسىيى مىلەلىلىلىلىسىيى بىلىدىلىلىدىسىيى غانملىلىلىدىسىيى مەنىلىلىلىسىمىمى . 2. ئۆكۈچۈچۈچى يەرۋاردۇندۇرغۇرغۇر يەرۋەرتەرۋەردۇر دەركەرلاردى تەركۈلەردىلىدى يەرۋاردۇر يەرۋاردۇر . 2. ئۇلاردۇر يۇزۇردۇرلاردۇردۇغ يەۋەرۋاردۇغ يەرۋەرۋەردۇغ يەرۋاردۇر ئەرۋاردۇر ئەرۋاردۇر يەرۋاردۇر يەرۋاردۇر يەرۋە
ىمىلى بىل بىمارىلىلى بىرمانلىلىلانى مەسىرمانلىلىلە مىمىسىرمانلىلىلە مەسىرمانلىلىلە مەسىرمانلىلەلە مەسىرمانل 1945, كىلا ئۆلەتلاكىنى ئۆلۈلەترىكىلەر رەبۇنىۋاتلارتىنى يەرمىنىلىلىلىكىلىكىلىكىلىكىلىكىلىكىلىكىلىكىل	ىلىلى مىسىمانىلى مىمانىن مىم بىلىلى مىمانىن مىسىمانىنى مىسىمانىنىلى مەمىسىمانىنىلى مەمىسىمانىنىلى 14. <del>1247-14</del> 12-1 1342-1313 132412 بىلغەتلەرلەر 14842-1423 بەلمانلەتتە 1742-1423 14 1424-14242-1434 142 142142 1421442 14214421 142144421 142144421 1421444421 1421444421 1421444421 1421444421
	ى مىسىمىنىنى مىسىمىنىنىنىنى مىسىمىنىنىنى مىسىمىنىنىنى مىسىمىنىنىنى مىسىمىنىنىنىنى مىسىمىنى . 1. ئۆتۈكۈنۈنى ئۆلۈتۈنىغانلۇقىنىزىلى بۆتكانتىنىنى بالايەلىقىنى بەتخانلايە يەتخانلەيە 1454-ئەلغانغانغانغانغانغانغان ئۆتۈكۈنى ئۆتۈكۈنى ئۆتۈكۈنى ئۆتۈكۈنى ئەزىلالايە ئۆلۈك ئۆتۈك
اللالالماسمار الماليان الماليانيان الماليانيان الماليانيان الماليانيان الماليانيان الماليانيان الماليانيان الم المحققة: وجمودموهجيني الالفاقية: المالية: المالية: المالية: المالية: المالية: المالية: المالية: المالية: المالي المحفقة: المحفة: المحفة	مانانانات
	<sup>Lille</sup> ««««««««««««««««««««»»»»»»»»»»»»»»»»»

# THE STRUCTURE OF $(\pi$ -C<sub>5</sub>H<sub>5</sub>(CO)<sub>2</sub>MoN.N(CH<sub>3</sub>).C(CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>)COH)PF<sub>6</sub>

Table 1. Observed structure amplitudes and calculated structure factors ( $\times$  50)Each hk column contains l,  $F_o$  and  $F_o$ .

34

Table 1 (cont.)

างอาปนาน" ความหน้า ความหน้า ความหน้า ความหน้า ความหน้าได้ได้ได้ ความหน้าอย่างไม่ได้ อนารีสาทธิ์น วิเวริเวริเวริเวริเวริเริริเริริเริริเร	ى مىمىسىغانىلەل مىمىسىمانى مىسىمانى سىمۇر سىلىل -دۇ. سەمايلەلە سىسىدىك - ئىمىغلاغانىغان بىلىغىتىغان يېنىغىدىم. يېزىلى ئەچ يەنىغى يەسەيدىدى ئۆكىيىدى 4 ئىلغانغان ئۆلەر ئالغان يىشلام. بەر يەلغۇ ئەتتە ئالغا ئىلىغان ئىلغەلدە	ามาเมน การสมเหน การสมเม ภาพระเมม ภาพระเมน การสมเม เมน สหรับว่า อีนีกระกับสุขภัณฑ์สุดี ระกับได้สัตร์ รรณีเชียร์ ประกับว่า อีนีกระกับระกับสิ่งได้ ระกับได้สัตร์ ระกับสารี	ل مالىدىدىلىلى مىساداتلەل مىسادىلىلە. سىلىل -نا، مەرلىل مەلىلىلى رەرداتىۋتۈتە. يەزئىتىلەن ئايەيىيىيىنى ياغومىي بىتى ھىكەن يەلىلىلى ئەلىيىنىدۆتۈنى ياغۇرنۇنچۇن يالىلائىتىدۇنى ئېغومۇنى يىغ بىلايەت ئەنتىئى			مانان من	لملد، مالى بالمال مالى مالغان مال 1914 مالغان ماليا ماليا مالغان مالغان 1914 مالغان ماليا مالغان ما	المالية المالية من ماليا. مالي ماليال الماليات المالية المالية المالية. 1944: محمد الله الاطلاح تحدة الالالالة المالية المالية اللالالة اللالالة اللالة 1944: المالية المالية المالية الالالالة المالية المالية المالية المالية المالية المالية المالية المالية المالية	ಯು <sup>ಕ</sup> ರ್ಕಾಕ್ ಗಾರ್ ಕ್ರಿಂಗ್ ಇಂ <sup>ರ</sup> ಿಗ್ ಇಂಗ್ ಕ್ರಾ ಇಂ <sup>ರ</sup> ಇಂ <sup>ರ</sup> ್ ಕ್ರಾಂಗ್ ಕ್ರಾಂಗ್ ಇಂ
៶៰៴៸៸៰៰៓៶៲៶៸៓ <sub>៲</sub> ៳៶៸៶៴៹៰៹៓	**** *********************************	ร้างสงคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็น เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็นสายคราม เป็	4.4.5	್ತ -ಂಬಿಸಿ <sub>ರ</sub> ಇಲಂಬಿಸಿಸಿ <sub>ರ</sub> ಇ ಸೈ ಜೀವಣ್ಣ ಸತ್ಯತ್ಯುತ್ತೆ ಕನ ಸೈ ಬಿತ್ತಕ್ಕು ಜಿತ್ತೇಕ್ಕೊಂತ್ರಿ ಪ್ರೇ	2		້າ 		

Since methylation takes place at N(2) it appears necessary to modify the formula of the nitrogeno molybdenum carbene chelate (I) that was suggested by Knox & Prout (1969) to the similar chelate (IV) that is protonated at N(2). The chelate (IV),



is also analagous to a sydnone with the molybdenum atom replacing the oxygen in the heterocyclic ring. The electronic structure of this chelate is that of an nonclassical meso-ion. The reformation of chelate (I) to the meso-ion (IV) presents no difficulties in the interpretation of its crystal structure as N(1) and N(2) in that structure are joined by a hydrogen bond (Knox & Prout, 1969, Fig. 4) in which the hydrogen atom could not be seen.

In the present structure, the bond lengths and interbond angles have standard deviations which are sufficiently large to preclude any detailed comparative discussion of the structural features of the methylated cation and neutral metal chelate. However the distances and interbond angles in the two are sufficiently similar for there to be no doubt that they are closely related. In particular the short molybdenum–carbon bond within the chelate ring that was a notable feature of the neutral molecule is found again in the cation (Fig. 1).

The relation of the chelate ring to the cyclopentadienyl plane (Fig. 3) is slightly different from that found in the neutral chelate, and the side chain of the ethyl diazoacetate residue is not coplanar with the metal chelate system (Table 3). The metal chelate ring itself is planar within experimental error.

The indications of the hexafluorophosphate group are very diffuse in the  $F_{obs}$  maps, which suggests either that this group is disordered or that it possesses considerable thermal vibration. The high thermal parameters and large estimated standard deviations in the group reflect this uncertainty in the positional parameters.



Fig. 3. Molybdenum coordination viewed down the normal to the cyclopentadienyl plane.

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) and thermal parameters with standard deviations in parentheses The temperature has the form:

 $\exp\left[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{23}klb^*c^*+2U_{31}lhc^*a^*+2U_{12}hka^*b^*)\right].$ 

	x/a	у/b	z/c	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{31}$	$U_{12}$
Мо	2659 (2)	4804 (3)	1878 (2)	406 (1)	367 (1)	425 (1)	176 (2)	-45 (2)	-208(1)
N(1)	3201 (19)	6513 (29)	3165 (21)	640 (13)	619 (13)	488 (17)	515 (22)	149 (23)	-367(21)
N(2)	2575 (17)	7389 (24)	4180 (19)	563 (11)	440 (10)	393 (14)	355 (18)	-125(20)	-429 (17)
O(1)	250 (14)	5678 (23)	3086 (18)	489 (9)	533 (9)	884 (15)	359 (19)	- 327 (19)	- 394 (16)
O(2)	-272 (15)	7632 (28)	5228 (20)	439 (10)	944 (14)	848 (16)	631 (23)	-114(20)	- 365 (19)
O(3)	1162 (14)	8443 (24)	6300 (16)	536 (10)	705 (11)	376 (13)	116 (17)	146 (18)	-426 (17)
O(4)	470 (17)	6576 (28)	166 (20)	641 (12)	810 (13)	907 (17)	649 (23)	-478(23)	-491(20)
O(5)	3838 (18)	6814 (30)	166 (20)	750 (14)	1074 (16)	709 (17)	1068 (26)	-184(23)	-485(23)
C(1)	1309 (22)	6026 (30)	3083 (25)	744 (16)	442 (12)	532 (19)	557 (23)	549 (27)	-762 (23)
C(2)	1485 (20)	7157 (29)	4214 (22)	528 (13)	459 (12)	340 (17)	487 (22)	-191 (24)	-404(20)
C(3)	752 (25)	7789 (35)	5295 (30)	676 (17)	489 (14)	836 (26)	627 (29)	-264(33)	-378(25)
C(4)	501 (24)	8804 (38)	7389 (30)	546 (16)	683 (17)	752 (25)	-370(31)	308 (32)	-368(27)
C(5)	1222 (27)	9467 (37)	8358 (27)	983 (21)	598 (15)	374 (20)	- 192 (26)	115 (31)	-459 (29)
C(6)	1303 (24)	5924 (36)	765 (27)	658 (17)	596 (15)	515 (21)	349 (27)	32 (29)	-352(26)
<b>C</b> (7)	3435 (24)	6076 (42)	833 (26)	652 (17)	963 (20)	287 (20)	63 (29)	168 (28)	- 605 (30)
C(8)	3262 (35)	1968 (36)	674 (32)	1406 (30)	362 (14)	755 (27)	-3 (29)	677 (44)	-213(33)
C(9)	2352 (32)	1943 (37)	1294 (38)	1146 (26)	440 (15)	1159 (33)	61 <b>0</b> (35)	-934 (47)	-644(32)
C(10)	2621 (29)	1997 (35)	2529 (42)	835 (21)	278 (12)	1773 (40)	570 (36)	- 188 (47)	-178(26)
C(11)	3774 (23)	2053 (32)	2791 (33)	563 (16)	330 (12)	1264 (29)	584 (29)	-407 (34)	-38(22)
C(12)	4251 (26)	1965 (35)	1628 (38)	680 (18)	411 (14)	1344 (35)	725 (35)	874 (41)	357 (25)
<b>C</b> (13)	3037 (24)	8588 (41)	5106 (31)	648 (17)	818 (19)	879 (25)	528 (34)	- 645 (33)	-832(30)
<b>P(1)</b>	6528 (6)	6744 (9)	3097 (7)	564 (4)	523 (4)	623 (6)	290 (7)	-152 (7)	- 373 (6)
F(1)	5408 (16)	7265 (27)	2238 (22)	800 (12)	972 (13)	1418 (19)	666 (25)	-910 (24)	-638 (21)
F(2)	5826 (20)	8255 (34)	4114 (21)	1062 (16)	1475 (16)	851 (17)	- 398 (28)	252 (26)	-24 (28)
F(3)	6910 (21)	8330 (31)	2621 (24)	1389 (18)	1197 (16)	1600 (22)	1667 (30)	- 806 (31)	-1632(28)
F(4)	7665 (18)	6261 (30)	4003 (21)	977 (14)	1352 (17)	1067 (17)	1267 (27)	- 770 (25)	-1049 (25)
F(5)	7134 (28)	5372 (51)	2053 (30)	1684 (27)	2432 (34)	1187 (26)	- 1767 (49)	- 740 (41)	1018 (48)
F(6)	6017 (23)	5319 (30)	3612 (31)	1537 (21)	1301 (18)	2906 (36)	2777 (43)	-614 (44)	-1754 (33)

### Table 3. Least-squares planes

#### Distances (Å) of atoms from plane. Parentheses denote atoms not in the calculation for the plane.

	Ι	II	III	IV	v
Мо	-0.0460	(-0.6553)		(-0.4105)	
N(1)	0.0474	(-0.0968)		-0.0579	
N(2)	-0.0191	(-0.0968)		0.1109	
O(1)	(-0.0147)	(	0.0269	-0.0256	
O(2)	(-0.1925)	-0.0033	0.0460	0.2592	
O(3)	(-0.5882)	-0.0033		0.0061	
C(1)	0.0555		0.0102	0.0075	
C(2)	-0.0379	-0.0029	0.0341	0.1407	
C(3)	(-0.2722)	0.0095	0.0635	0.1477	
C(4)	(-0.9918)	(-0.1778)		-0.1698	
C(5)	(-0.3176)	(-0.1879)		-0.3418	
C(8)	. ,				0.0172
C(9)					0.0082
C(10)					0.0054
C(11)					-0.0160
C(12)					0.0196
C(13)	(0.0217)	(-0.4332)		0.3334	
•	, ,	· /			

We thank Dr M. L. H. Green for helpful chemical discussions and the S.R.C. for a research fellowship for TSC.

## References

BAKER, W. & OLLIS, W. D. (1957). Quart. Rev. 11, 15.

GREEN, M. L. H. & SANDERS, J. R. (1967). Chem. Commun. p. 956.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

KNOX, J. R. & PROUT, C. K. (1969). Acta Cryst. B25, 1952.