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The Structure of the Nitrogeno Molybdenum Chelate: $(\pi\text{-}C_5H_5(CO)_2MoN.N(CH_3).C(CO_2C_2H_5)COH)PF_6$

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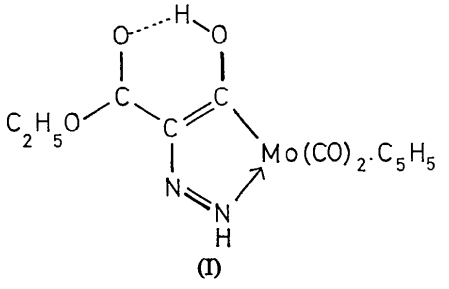
$(\pi\text{-}C_5H_5(CO)_2MoN.N(CH_3).C(CO_2C_2H_5)COH)PF_6$ crystallizes in space group $P\bar{1}$ with $a=12{\cdot}02$, $b=7{\cdot}53$, $c=10{\cdot}83$ Å; $\alpha=95{\cdot}9$, $\beta=92{\cdot}8$, $\gamma=70{\cdot}1°$ and two formula units in the unit cell. The structure was determined from photographic X-ray data, and refined by the least-squares method to $R=0{\cdot}138$ 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 $(\pi C_5H_5Mo(CO)_3)^-$ with diazoacetic ester yields a yellow crystalline complex which Knox & Prout (1969) claimed to be the nitrogeno molybdenum carbene chelate (I).



(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

$MoC_{13}O_5N_2H_{14}.PF_6$, M.W. 519·14, $F(000)=514$.
Triclinic $a=12{\cdot}02\pm0{\cdot}01$, $b=7{\cdot}53\pm0{\cdot}01$, $c=10{\cdot}83\pm0{\cdot}01$ Å;
$\alpha=95{\cdot}5°\pm0{\cdot}3$, $\beta=92{\cdot}8°\pm0{\cdot}3$, $\gamma=70{\cdot}1°\pm0{\cdot}3$.
$D_m=1{\cdot}877$ g.cm^{-3}, $D_c=1{\cdot}878$ g.cm^{-3}, Cu $K\alpha$, $\lambda=1{\cdot}54178$ Å, $\mu=41{\cdot}53$ cm^{-3}.
No systematic extinction. $Z=2$. Space group $P1(C_1^1$, No. 1) or $P\bar{1}(C_i^1$, 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 $P\bar{1}$. Subsequent Fourier syntheses clearly showed the positions of all the light atoms.

The structure was refined by the method of least-squares 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 $R=15{\cdot}6\%$, and with anisotropic temperature factors, after a further three cycles, at $R=13{\cdot}8\%$. 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**.

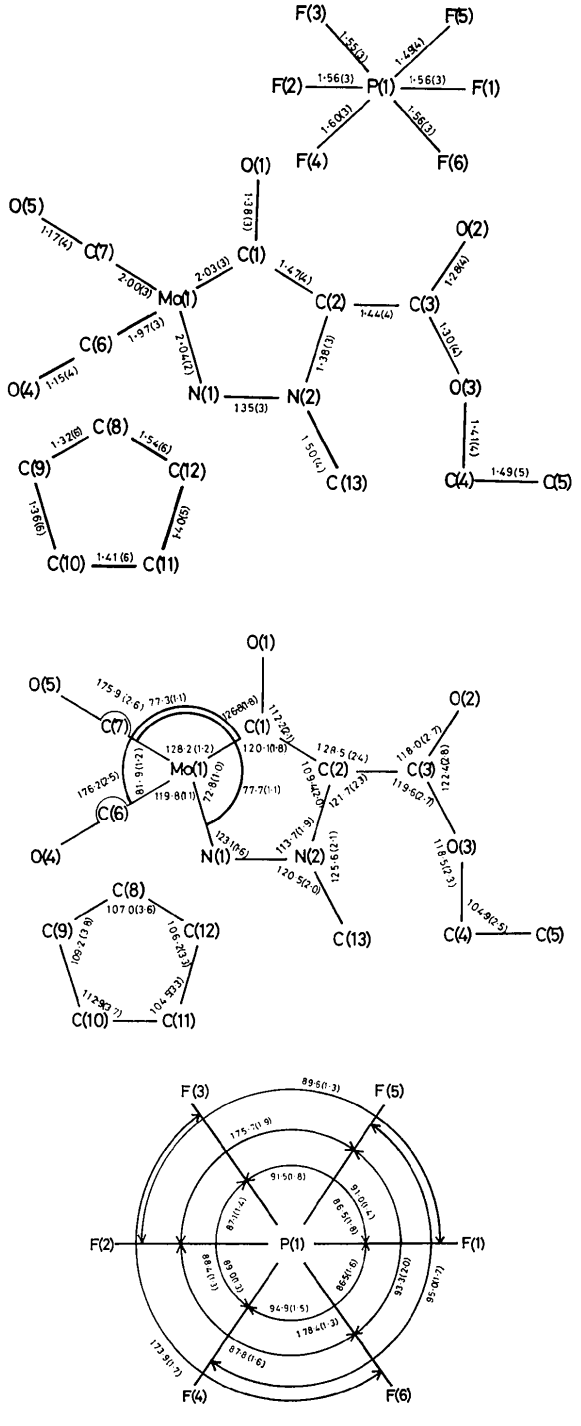
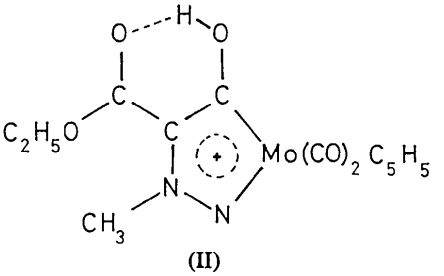


Fig. 1. Distances and angles in the anion and cation.

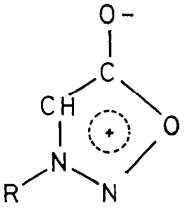
Discussion

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),



(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).



(III)

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

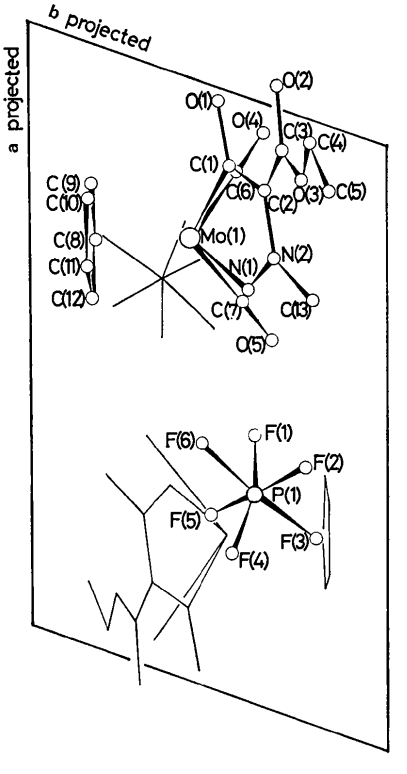


Fig. 2. The crystal structure projected down **c**.

Table 1. *Observed structure amplitudes and calculated structure factors* ($\times 50$)

Each *hk* column contains *l*, F_o and F_c.

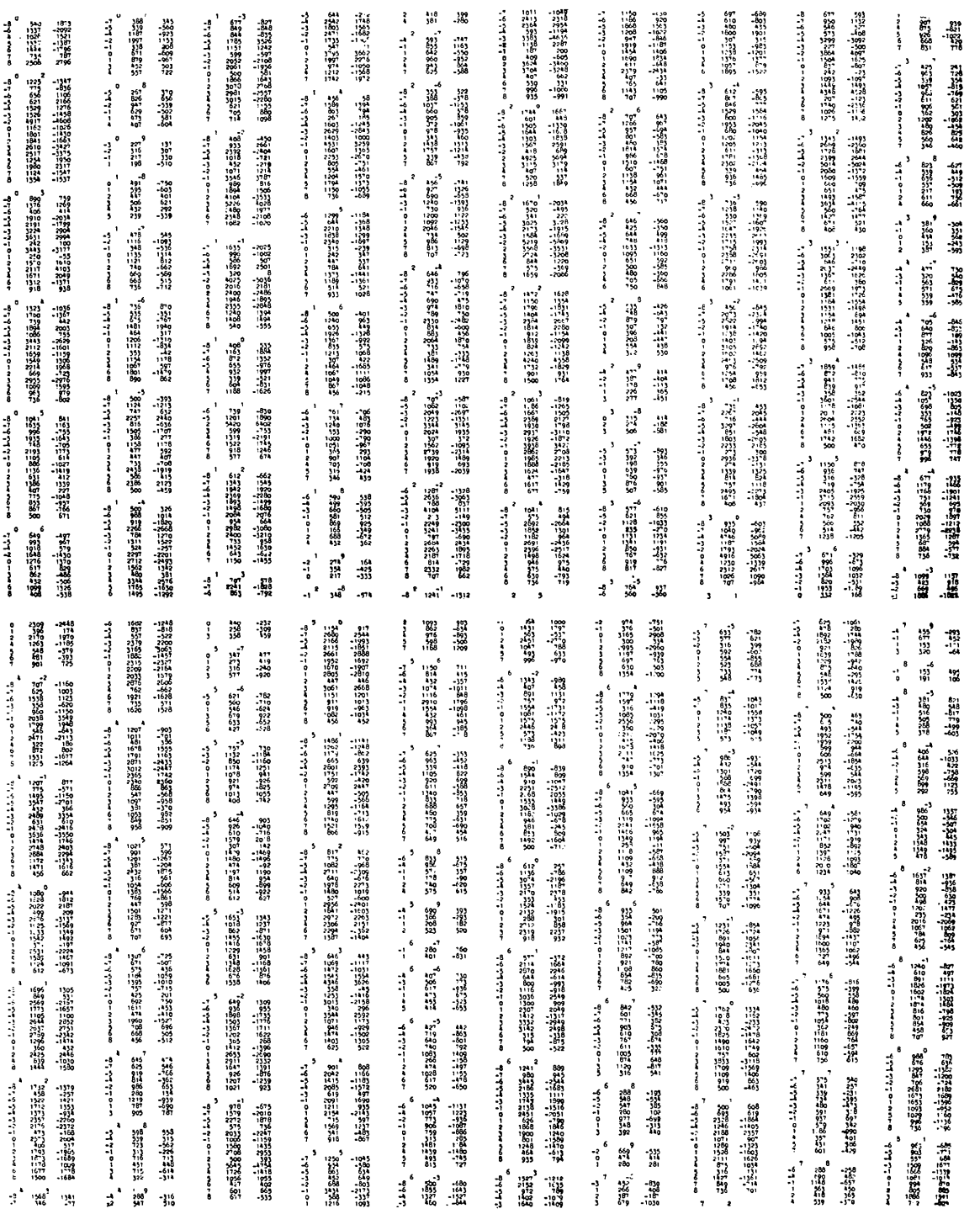
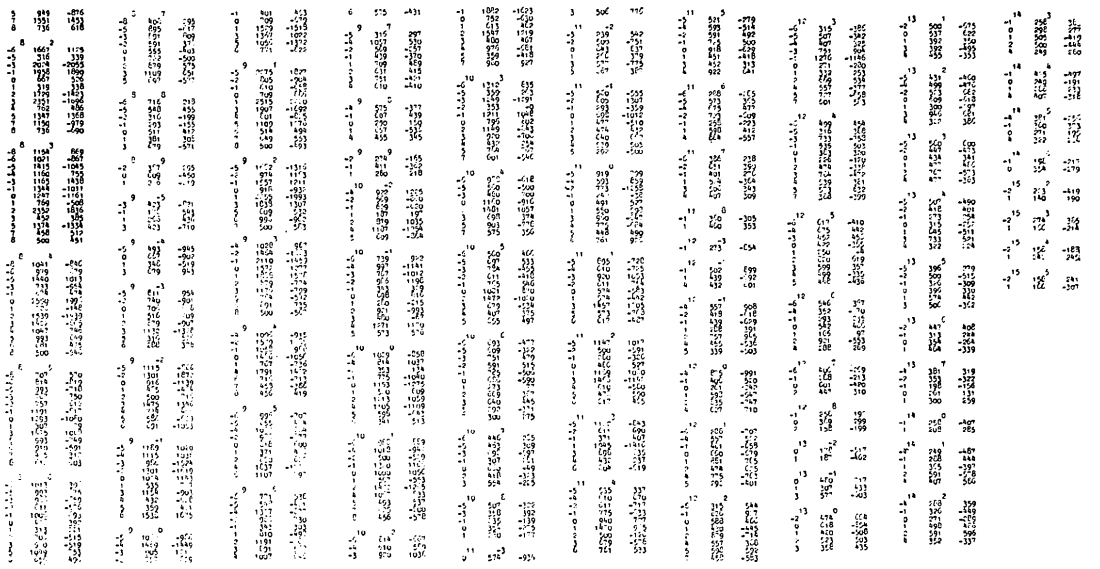
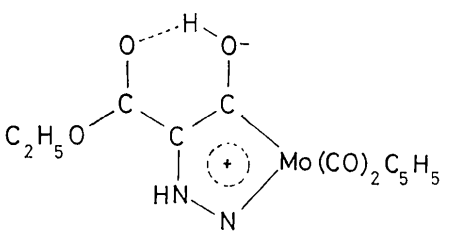


Table 1 (*cont.*)



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),



(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 non-classical 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.

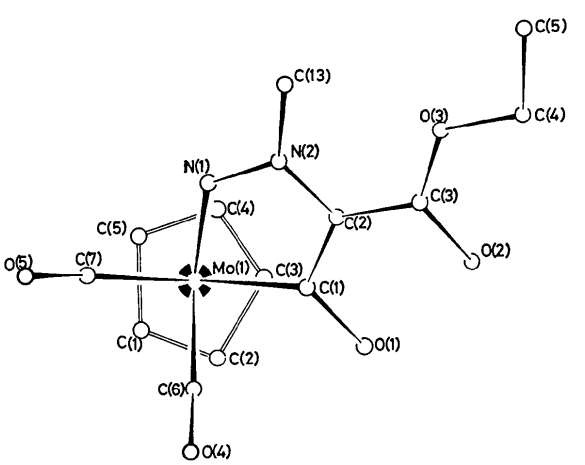


Fig. 3. Molybdenum coordination viewed down the normal to the cyclopentadienyl plane.

Table 2. *Fractional atomic coordinates* ($\times 10^4$) *and thermal parameters with standard deviations in parentheses*

The temperature has the form:

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

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
Mo	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)
C(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)	610 (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)
C(13)	3037 (24)	8588 (41)	5106 (31)	648 (17)	818 (19)	879 (25)	528 (34)	−645 (33)	−832 (30)
P(1)	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.

	I	II	III	IV	V
Mo	−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	

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