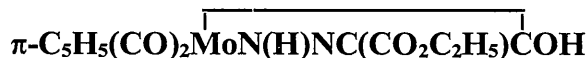


## The Structure of a Nitrogeno-molybdenum Carbene Chelate:



BY J. R. KNOX\* AND C. K. PROUT

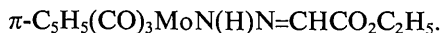
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$\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{MoN(H)NC(CO}_2\text{C}_2\text{H}_5)\text{COH}$  crystallizes in space group  $C2/c$  with  $a=21.36$ ,  $b=8.26$ ,  $c=16.11$  Å,  $\beta=97.8^\circ$  and with  $Z=8$ . The structure was determined from photographic X-ray data and refined by the least-squares method to  $R=0.085$  for 1969 reflexions. Ethyl diazoacetate reacts with  $\text{Na}[\pi\text{-C}_5\text{H}_5(\text{CO})_3\text{Mo}]$  to give a planar five-atom ring containing a protonated carbonyl group. This group is joined to molybdenum by a carbene bond  $\text{Mo}=\text{C} < (2.09 \pm 0.01 \text{ \AA})$ . All the remaining bonds in the chelate ring are also shorter than single-bond distances: Mo-N, N-N, N-C and C-C are 2.11, 1.30, 1.36 and 1.39 Å respectively.

### Introduction

Nitrogen-fixing bacteria require molybdenum for the reduction of  $\text{N}_2$  to  $\text{NH}_3$ , and nitrogeno-aryl molybdenum compounds have been used in model studies (Parshall, 1967). As there is evidence for enzyme bound  $\text{HN}=\text{NH}$  and  $\text{H}_2\text{N}-\text{NH}_2$  intermediates (Hardy & Knight, 1967), Green & Sanders (1967) studied the reactions of a molybdenum compound with the hydrazone formulation



The nitrogen system is found to be part of an unexpected carbene ring.

### Experimental

Yellow crystals of the compound were supplied by M. L. H. Green of Oxford University. The crystal data are:  $\text{MoC}_{12}\text{O}_5\text{N}_2\text{H}_{12}$ ,  $M=360.1$ ,  $F(000)=1440$ , monoclinic,  $a=21 \pm 36 \pm 0.01$ ,  $b=8.26 \pm 0.01$ ,  $c=16.11 \pm 0.01$  Å and  $\beta=97.8 \pm 0.3^\circ$ .  $D_m=1.696 \text{ g.cm}^{-3}$  by flotation,  $Z=8$ ,  $D_c=1.699 \text{ g.cm}^{-3}$ .  $\text{Cu K}\alpha$ ,  $\lambda=1.5418$  Å,  $\mu=81.4 \text{ cm}^{-1}$ . Systematic extinctions:  $h+k=2n+1$  for  $hkl$ ,  $l=2n+1$  for  $h0l$ . Space group  $Cc(C_2^2, \text{No. 9})$  or  $C2/c(C_{2h}^6, \text{No. 15})$ .

Cell dimensions were calibrated with aluminum powder lines superposed on Weissenberg films. From a crystal measuring  $0.09 \times 0.57 \times 0.18$  mm sealed in a glass capillary, equi-inclination Weissenberg photography with  $\text{Cu K}\alpha$  radiation of the  $h0l$  to  $h6l$  layers produced 1892 observable reflexions. Another crystal approximately 0.12 mm cube gave 313  $hk0$  and  $hk2$  reflexions. The visually estimated data were corrected for Lorentz and polarization effects but not for absorption. The 185 reflexions common to both axial sets were

used to obtain layer scale factors by the method of Hamilton, Rollett & Sparks (1965) with weights proportional to  $|F_o|^2$ . The merging  $R$  index  $\Sigma |F_1^2 - F_2^2| / \Sigma (F_1^2 + F_2^2)$  was 0.08 and 1971 observable independent reflexions were obtained.

### Solution and refinement of the structure

A Patterson synthesis gave Mo-Mo vectors consistent with space group  $C2/c$ . The position of molybdenum near  $y=0$  produced false mirror symmetry in the electron density map. A model could be recognized for

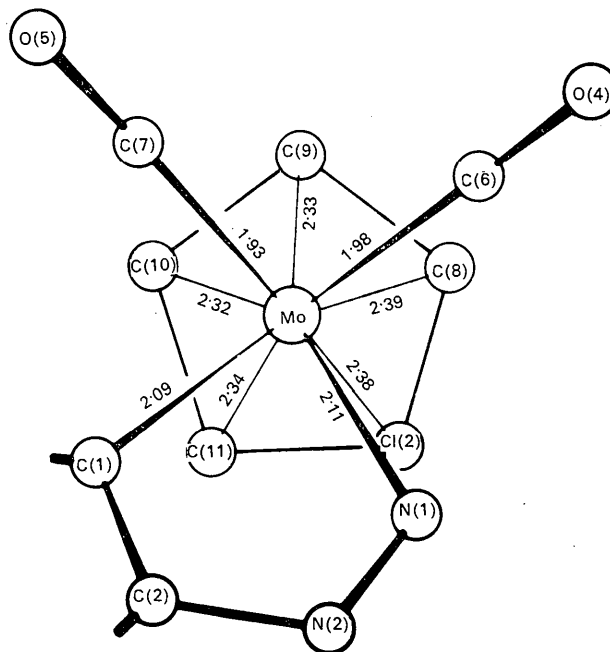


Fig. 1. Molybdenum coordination viewed down the normal to the cyclopentadienyl plane.

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Table 1. Observed structure amplitudes and calculated structure factors ( $\times 2.5$ )  
Each  $hk$  column contains  $I$ ,  $F_o$  and  $F_c$ . The last two reflexions were not used in refinement.

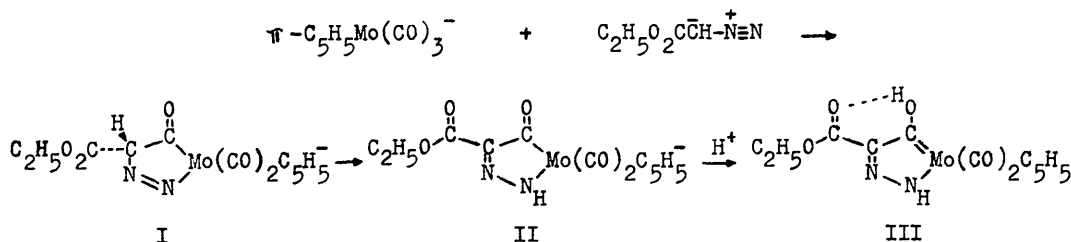
$h$	$k$	$I$	$F_o$	$F_c$
0	0	1000	1000	1000
0	1	100	100	100
0	2	100	100	100
0	3	100	100	100
0	4	100	100	100
0	5	100	100	100
0	6	100	100	100
0	7	100	100	100
0	8	100	100	100
0	9	100	100	100
0	10	100	100	100
0	11	100	100	100
0	12	100	100	100
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0	14	100	100	100
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1	96	100	100	100
1	97	100	100	100
1	98	100	100	100
1	99	100	100	100
1	100	100	100	100



effect ( $-0.5 e$ ). With isotropic temperature factors the refinement proceeded smoothly through six cycles, giving final parameter shifts less than 0.05 of the estimated standard deviations. Layer scale factors were not refined. The  $R$  index was 0.121. Anisotropic temperature factors were assigned to molybdenum and the refinement was continued for three cycles until all shifts were less than  $0.37\sigma$ , at which point  $R=0.085$  for 1969 observed reflexions. A final difference map did not show any unusual features. Observed structure amplitudes and calculated structure factors are given in Table 1. Positional and thermal parameters with standard deviations are in Table 2. Table 3 is a listing of important distances and angles. The application of an absorption correction to these data should not change the positional parameters or stereochemical details of this molecule (Srivastava & Lingafelter, 1966).

### Discussion

A heterocyclic metal chelate (I) results when  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3^-$  reacts with ethyl diazoacetate,  $\text{C}_2\text{H}_5\text{O}_2\text{CCH-N}\equiv\text{N}$ . This electrophilic attack by a diazo ester on a conjugated double bond is often used for organic ring syntheses. In this case, a hydrogen shift produces structure II, and a proton then adds to the carbonyl oxygen with the formation in III of an intraligand hydrogen bond.



Of the metal-ligand bonds (Fig. 1) the Mo-C(1) distance of 2.09 Å is considerably shorter than the 2.38 Å

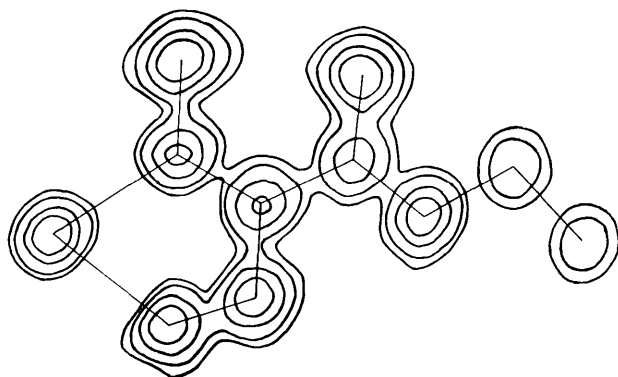


Fig. 2. Electron density through chelate. Atom numbering as in Fig. 3. Contour intervals ( $e.\text{Å}^{-3}$ ) are 10, 20, 40, 60 for Mo, and 1, 2, 4, 6 for C, N, O.

$\sigma$ -bonds in  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{C}_2\text{H}_5$  (Bennett & Mason, 1963) and  $[\text{C}_{10}\text{H}_8\text{Mo}(\text{CO})_3\text{CH}_3]_2$  (Bird & Churchill, 1968), or the 2.36 Å bond in



(Ariyaratne, Bjerrum, Green, Ishaq & Prout, 1969). It is 0.17 Å shorter than the acetyl bond in  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{P}(\text{C}_6\text{H}_5)_3]\text{COCH}_3$  (Churchill & Fennessey, 1968), which is thought to involve  $p\pi-d\pi$  back donation. The chelate bond must then be represented as a carbene  $\text{Mo}=\text{C}<$  with a bond order of about 1.5 (Cotton & Wing, 1965). Baikie, Fischer & Mills (1967) observed a 2.09 Å Cr-C carbene bond in  $(\text{CO})_5\text{CrC}(\text{CH}_3)\text{N}(\text{H})\text{CH}_3$ . As the Cr and Mo radii differ by approximately 0.14 Å (Cotton & Richardson, 1966) the higher bond order of the molybdenum-carbene is apparent. The Mo-N( $sp^2$ ) bond at 2.11 Å, after a 0.03 Å correction for hybridization, is below the Mo-N( $sp^3$ ) single-bond distance of 2.23 Å in  $\text{Na}_2\text{Mo}_2\text{O}_4(\text{cysteine})_2 \cdot 5\text{H}_2\text{O}$  (Knox & Prout, 1968), 2.21 Å in Mo(dien)  $(\text{CO})_3$  (Cotton & Wing, 1965); it is nearer the Mo-N( $sp$ ) 2.09 Å bond in  $\text{K}_3\text{Mo}(\text{NCS})_6 \cdot \text{H}_2\text{O} \cdot \text{CH}_3\text{CO}_2\text{H}$  (Knox, & Eriks, 1968), which may contain some  $\pi$ -bond character.

The bond order of the carbene bond is higher than that of the Mo-N bond. A *trans* effect lessens the bond orders of the Mo-C(6) and Mo-C(8) bonds and allows a strengthening of the bond to C(11). In terms of the ratio  $t=(l_1-l_2)/(\sigma_1^2+\sigma_2^2)^{1/2}$  (Lipson & Cochran, 1966),

the difference between the chemically equivalent carbonyl bonds Mo-C(6) and Mo-C(7) is 2.69, between Mo-C(8) and Mo-C(10), 2.74, and between Mo-C(11) and Mo-C(12), 1.68. Though the latter difference is only possibly significant, all differences can be explained if the two chelate bonds are of unequal bond order.

The C-C distance in the cyclopentadienyl ring only partially reflects the asymmetry in the metal-to-ring  $\pi$ -bonding. Just as the shortest bond C(8)-C(12) is associated with the longest Mo-C distances, the longest bond C(10)-C(11) is associated with two of the shorter Mo-C distances. But although this observation explains the possibly significant difference of 0.08 Å ( $t=2.13$ ) in these two C-C bonds, it fails to correlate the C(9)-C(10) distance with the Mo-C distances. In most  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{X}$  systems the orientation of the ring is such that X is above a ring carbon atom and the CO groups are above midpoints of C-C bonds (Churchill & Fennessey, 1968; Chaiwasie & Fenn, 1968).

The ring in Fig. 1 has this orientation if X is N(1) and if the carbene bond is simply considered as a substituted carbonyl bond. Churchill & Fennessey (1968) pointed out that the longest Mo-C(ring) distance is usually to the carbon below X. While we observe a long Mo-C(12) distance, there is an equally long distance to C(8) resulting from the opposite carbene bond. However, the relative ring orientation is preserved.

The two Mo-C-O angles are within  $1.5\sigma$  of  $180^\circ$ . The CO bonds are equal and average  $1.175 \text{ \AA}$ . The bond length difference in the CO bonds was expected to be not more than  $0.02 \text{ \AA}$  even though the two Mo-Co bonds differ in bond order by  $0.3$  (Cotton & Wing, 1965).

Fig. 2 shows the electron density in plane 3 (Table 4). The ester group is almost coplanar with the metal-chelate ring (plane 1) and its dimensions are similar to those of ethyl carbamate  $C_2H_5O_2CNH_2$  (Bracher & Small, 1967); the largest difference  $0.036 \text{ \AA}$ , appears in the ethyl bond at the end of the chain. The two C-O bonds in the ester have the expected values of  $1.23$  and  $1.32 \text{ \AA}$ , as does the C(2)-C(3)  $sp^2-sp^2$  bond,  $1.47 \text{ \AA}$  (Sutton, 1965). The N-N bond,  $1.30 \text{ \AA}$ , is seen to have appreciable multiple bond character when compared with distances in conjugated heterocyclics; pyrazole,  $1.36 \text{ \AA}$  (Ehrlich, 1960); diphenyl- $\Delta^2$ -pyrazoline,  $1.34 \text{ \AA}$  (Duffin, 1968); 1,3-dimethyl-5-imidotetrazole cation,  $1.31 \text{ \AA}$  (Bryden, 1955). The ring N-C and C-C distances,  $1.36$  and  $1.39 \text{ \AA}$ , are also equal to conjugated

bond distances (Sutton, 1965). All ring distances and the close planarity of the five chelate atoms suggest there may be electron delocalization around the ring, and several resonance structures in addition to III can be drawn. However, any resonance must be dominated by those canonical forms containing the  $Mo=C<$  carbene bond.

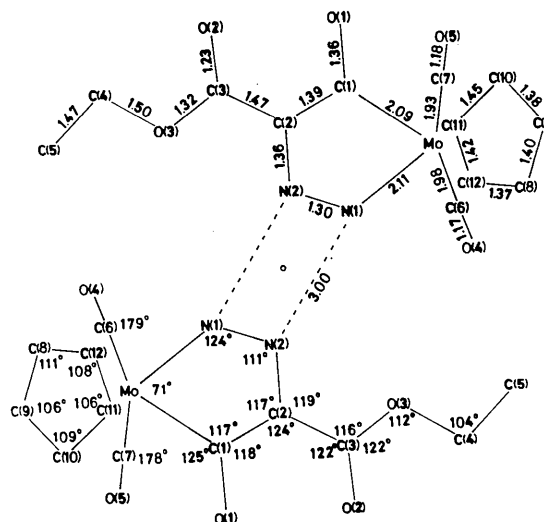


Fig. 3. Distances and angles in molecules related by inversion centre.

Table 3. Distances ( $\text{\AA}$ ,  $\sigma \times 10^3$ ) and angles ( $\text{deg}$ ,  $\sigma \times 10$ ) with standard deviations in parentheses

Mo-C(1)	2.092 (12)	C(1)-Mo-N(1)	71.4 (4)
Mo-N(1)	2.109 (11)	C(1)-Mo-C(7)	73.5 (6)
Mo-C(6)	1.983 (15)	N(1)-Mo-C(6)	77.6 (5)
Mo-C(7)	1.926 (15)	C(6)-Mo-C(7)	82.0 (6)
Mo-C(8)	2.386 (17)	C(1)-Mo-C(6)	123.1 (5)
Mo-C(9)	2.329 (18)	N(1)-Mo-C(7)	118.9 (5)
Mo-C(10)	2.316 (19)	Mo-C(6)-O(4)	178.6 (13)
Mo-C(11)	2.338 (20)	Mo-C(7)-O(5)	178.1 (13)
Mo-C(12)	2.382 (19)		
N(1)-N(2)	1.304 (15)	Mo-N(1)-N(2)	123.6 (8)
C(1)-C(2)	1.387 (17)	N(1)-N(2)-C(2)	110.7 (10)
N(2)-C(2)	1.356 (16)	Mo-C(1)-C(2)	117.0 (9)
C(1)-O(1)	1.359 (16)	Mo-C(1)-O(1)	125.0 (9)
C(2)-C(3)	1.466 (18)	C(2)-C(1)-O(1)	117.8 (11)
C(3)-O(2)	1.228 (17)	C(1)-C(2)-N(2)	117.3 (11)
C(3)-O(3)	1.317 (17)	C(1)-C(2)-C(3)	123.9 (11)
O(3)-C(4)	1.495 (20)	N(2)-C(2)-C(3)	118.8 (11)
C(4)-C(5)	1.473 (27)	C(2)-C(3)-O(2)	122.2 (12)
C(6)-O(4)	1.169 (19)	O(2)-C(3)-O(3)	122.1 (12)
C(7)-O(5)	1.180 (19)	C(2)-C(3)-O(3)	115.7 (12)
C(8)-C(9)	1.405 (25)	C(3)-O(3)-C(4)	112.3 (11)
C(8)-C(12)	1.369 (24)	O(3)-C(4)-C(5)	103.6 (14)
C(9)-C(10)	1.385 (26)		
C(10)-C(11)	1.446 (27)	C(12)-C(8)-C(9)	111.1 (15)
C(11)-C(12)	1.419 (26)	C(8)-C(9)-C(10)	106.0 (16)
		C(9)-C(10)-C(11)	109.3 (17)
N(1)⋯N(2')	2.995 (15)	C(10)-C(11)-C(12)	105.6 (16)
O(1)⋯O(2)	2.609 (14)	C(11)-C(12)-C(8)	107.8 (15)
O(1)⋯O(2')	3.098 (14)		
O(2)⋯O(2')	2.945 (14)		

Transformations:

$$\begin{array}{l} \text{"} \\ \text{' } \end{array} \begin{array}{l} -x, \quad y, \quad \frac{1}{2}-z \\ -x, \quad -y, \quad 1-z \end{array}$$

Table 4. *Least-squares planes*  
Distances (Å) of atoms from plane.  
Parentheses denote atoms not in calculation.

	1	2	3	4
Mo	0.0014		(0.0291)	(2.022)
N(1)	-0.0025		0.0111	
N(2)	0.0023		0.0058	
O(1)	(-0.0801)	-0.0313	-0.0667	
O(2)	(0.0753)	0.0287	0.0672	
O(3)	(-0.0183)		-0.0345	
C(1)	-0.0008	0.0379	0.0126	
C(2)	-0.0004	-0.0110	0.0029	
C(3)	(0.0282)	-0.0244	0.0207	
C(4)	(0.0281)		0.0012	
C(5)	(0.0151)		-0.0203	
C(8)				-0.0178
C(9)				0.0215
C(10)				-0.0171
C(11)				0.0063
C(12)				0.0070

Equations of planes:  $lX+mY+nZ=p$  with  $X=xa+zc \cos \beta$ ,  
 $Y=yb$  and  $Z=zc \sin \beta$ .

Plane	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
1	0.4856	0.4144	0.7698	5.523
2	0.5173	0.4010	0.7560	5.417
3	0.4924	0.4101	0.7677	5.498
4	-0.1672	0.5795	0.7976	2.296

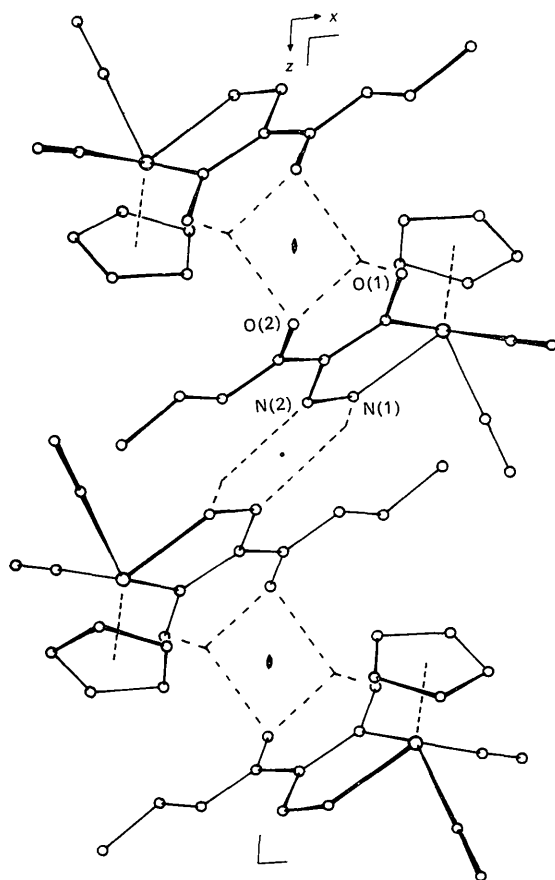
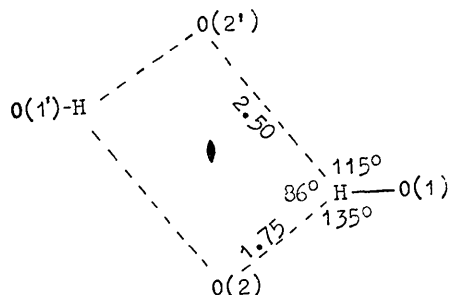


Fig. 4. Projection down *y*.

The plane of the diazoester carbene ligand (plane 3) is parallel to, and only 0.19 Å from, the corresponding plane in the adjacent molecule across the space group inversion centre (Fig. 3). This intermolecular alignment is a result of two parallel N-H...N hydrogen bonds of 3.00 Å, comparable to the 2.92–3.11 Å bonds between coplanar rings in guanine–cytosine complexes (O'Brien, 1967). The existence of the hydrogen on the nitrogen next to molybdenum is indicated by mass spectroscopy (Green & Sanders, 1967). The calculated N-H...H angle is 123°.

Sharing the C(1)–C(2) bond with the metal-chelate ring is a six-membered ring closed by a 2.61 Å intraligand hydrogen bond between O(1) and O(2), the hydrogen atom being assumed to be on the longer bond to O(1). This ring is coplanar (within 2°) with the five-atom ring, but is more distorted from planarity because the O(1)–H donates not only to O(2) but also to O(2') of a neighbouring molecule, and O(1) is pulled out of plane towards O(2'). The weak bifurcated hydrogen bonding is shown viewed down the twofold axis:



The angle between the plane of O(1)O(2)O(2') and O(1')O(2)O(2') is 113°. In the crystal (Fig. 4) this oxygen network and the stronger N-H...N hydrogen bonds link molecules in zigzag chains along *z*. The minimum and maximum root mean square thermal displacement of molybdenum are 0.179 and 0.235 Å with the major vibration axis 37° to the chelate plane normal. However, in the absence of an absorption correction, thermal parameters may be in error.

This investigation lends support to King & Bisnette's (1966) postulation of carbonyl insertion in a methyl

pyridine compound  $\pi\text{-C}_5\text{H}_5(\text{CO})_2\text{MoNC}_6\text{H}_4\text{CH}_2\text{C}=\text{O}$  similar to I. Although in their formulation there is an  $sp^3$  carbon atom in the ring, an enol structure would also be possible, resulting in a planar stabilized chelate system not unlike that found here.

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## The Crystal Structure of Ammonium Thorium(IV) Octafluoride, $(\text{NH}_4)_4\text{ThF}_8^*$

BY R. R. RYAN, R. A. PENNEMAN, AND A. ROSENZWEIG

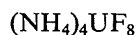
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Crystals of  $(\text{NH}_4)_4\text{ThF}_8$  are triclinic, space group  $P\bar{1}$ , with  $a=8.477$  (10),  $b=8.364$  (8),  $c=7.308$  (7) Å,  $\alpha=88^\circ 23'$  (3'),  $\beta=96^\circ 5'$  (3'),  $\gamma=106^\circ 20'$  (3'),  $Z=2$ ,  $D_x=3.06$ ,  $D_m=3.08$  g.cm<sup>-3</sup>. Each thorium atom has nine fluorine neighbors at an average distance of 2.38 Å; the polyhedron is a distorted trigonal prism with the three equatorial fluorine ions approximately normal to the face centers. The polyhedra are joined into infinite chains paralleling the  $b$  axis by sharing two edges in each polyhedron. The remaining fluoride ion is not involved in the coordination sphere of thorium; the closest thorium atom to this fluoride ion is at a distance of 4.98 Å. This fluoride ion is coordinated to five ammonium ions which are in approximately a square pyramidal configuration.

### Introduction

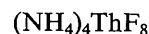
The tetravalent actinide fluorides of Pa, U, Np, Pu, and Am form with ammonium fluoride an isostructural series of complex compounds having the formula  $(\text{NH}_4)_4\text{MF}_8$ . The corresponding cerium(IV) compound has also been found to be isostructural (Penneman & Rosenzweig, 1969). Of these, the structure of



has been determined in detail (Rosenzweig & Cromer, 1968). It is monoclinic, space group  $C2/c$ , and contains

isolated  $[\text{UF}_8]^{4-}$  polyhedra in the form of distorted square antiprisms.

Recently a compound of thorium tetrafluoride and ammonium fluoride was prepared which has X-ray powder diffraction and optical properties distinctly different from those of the  $(\text{NH}_4)_4\text{UF}_8$  prototype, even though chemical analysis established the formula as  $(\text{NH}_4)_4\text{ThF}_8$ . Crystals of  $(\text{NH}_4)_4\text{UF}_8$  clearly show monoclinic symmetry; however, those of  $(\text{NH}_4)_4\text{ThF}_8$  have habits and optical properties which suggest triclinic symmetry. Consideration of intensities and cell constants estimated from precession photographs showed that the thorium-thorium distance is much shorter in



\* This work performed under the auspices of the U.S. Atomic Energy Commission.