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Metal Complexes of Polycyclic Tertiary Amines. V.* Structure of 1,3,5,7-Tetraazaadamantanepentacarbonylmolybdenum(0), $(CH_2)_6N_4 \cdot Mo(CO)_5$

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X-ray analysis of the octahedral coordination compound $(CH_2)_6N_4 \cdot Mo(CO)_5$ *has established that the axial and equatorial carbonyl groups have distinctly different dimensions, and the overall molecular geometry indicates significant steric repulsion between the organic ligand and the equatorial carbonyl groups. Moving away from the quaternary nitrogen atom, the three non-equivalent sets of C–N bonds vary in the order long, short and normal, relative to the standard bond length in the unsubstituted* $(CH_2)_6N_4$ *cage system. A survey of the crystallograpic data for representative* $(CH_2)_6N_4$ *adducts utilizing only one nitrogen lone pair leads to the conclusion that cage distortion decreases in the order methylation > borine adduct formation ≅ N-oxide formation ≅ protonation > metal coordination.*

The crystals are orthorhombic, space group Pbca, *with* a = *12.800(2),* b = *13.377(2),* c = *17.524(3) Å, and Z = 8. The structure has been refined to* R = *0.039 for 2491 observed MoKα data.*

Introduction

Crystallographic [2–5] and theoretical [6] studies have shown that quaternization of one nitrogen atom of the 1,3,5,7-tetraazaadamantane [$(CH_2)_6N_4$, commonly known as hexamethylenetetramine, hexamine, or urotropine] system, such as in protonation [2], N-oxide formation [3], or methylation [4, 5], profoundly affects its idealized $\bar{4}3m$ (T_d) molecular geometry. Moving away from the quaternary nitrogen atom (which bears a formal positive charge), the three non-equivalent sets of C–N bonds vary in the order long, short and normal, relative to the standard bond distance of 1.476(2) Å in the unsubstituted cage molecule [7]. Verification of this pattern of bond-length variation for the case of coordinate bonding, as in anhydrous or hydrated metal complexes, proved difficult due to the $(CH_2)_6N_4$ ligand's pronounced tendency to generate polymeric structures through metal coordination and hydrogen bonding involving two or more nitrogen lone pairs [1, 8]. Accordingly, the present study was conducted to determine the extent to which $(CH_2)_6N_4$ cage geometry might be affected by coordination to a single zero-valent metal centre. The investigation is of additional interest since, to our knowledge, few organometallic compounds containing the $(CH_2)_6N_4$ moiety are known [9, 10] and none has been subjected to X-ray analysis.

Experimental

The title compound was prepared according to the literature method [9] and recrystallized from petroleum ether. A roughly spherical crystal of mean diameter 0.25 mm was mounted on a Nicolet R3m diffractometer system. The procedures used for data collection and reduction were standard in our laboratory and have been described previously [11]. Pertinent crystallographic parameters are summarized in Table I.

Structure Solution

The Mo atom was located from a sharpened Patterson function, and a subsequent different map (computed at $R = 0.32$) revealed the positions of the remaining twenty non-hydrogen atoms in the asymmetric unit. After several cycles of blocked-cascade [12] anisotropic least-squares refinement, all methylene H atoms were geometrically generated (idealized H–C–H bond angle, C–H bond length fixed at 0.96 Å), assigned the same isotropic temperature factor

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*Part IV: $(CH_2)_6N_4 \cdot 4AgCl$ [1].

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TABLE I. Data Collection and Processing Parameters.

Molecular formula	$(CH_2)_6N_4 \cdot Mo(CO)_5$
Molecular weight	376.18
Cell constants	a = 12.800(2) Å
	b = 13.377(2)
	c = 17.524(3)
	V = 3000.6(7) $Å^3$
Density (Calcd.)	1.666 g cm^{-3} for $Z = 8$
Density (Exptl.)	1.67 g cm^{-3} (flotation in CCl_4/CH_2BrCH_2Br)
Space Group	*Pbca* (No. 61)
Absorption coefficient	8.77 cm^{-1}
Mean μr	0.11
Transmission factors	0.714–0.743
Scan type and speed	ω–2θ; 2.55–8.37 deg min^{-1}
Scan range	1° below $K\alpha_1$ to 1° above $K\alpha_2$
Background counting	stationary counts for one-half of scan time at each end of scan
Collection range	h, k, l; $2\theta_{max} = 55°$
Unique data measured	3465
Observed data with $\|F\| > 3\sigma(\|F\|), n$	2491
Number of variables, p	190
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.039
Weighting scheme	$w = [\sigma^2(F) + 0.0008\|F\|^2]^{-1}$
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.046
$S = [\Sigma w(\|F_o\| - \|F_c\|)^2/(n - p)]^{1/2}$	1.023

(0.08 $Å^2$), and allowed to ride on their respective parent C atoms. The discrepancy indices R and R_w and 'goodness-of-fit' parameter S converged to the values shown in Table I. The final difference map was virtually flat, with residual extrema lying between 0.34 and −0.61 $eÅ^{-3}$.

All computations were performed on a Data General Corporation Nova 3/12 minicomputer with the SHELXTL program package [13]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [14].

The final positional and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table II; atom labelling is shown in Fig. 1. Hydrogen coordinates are given in Table III, and bond distances and angles in Table IV. Tables of anisotropic temperature factors and structure factors are available on request from the last author.

Discussion

The structure of the $(CH_2)_6N_4 \cdot Mo(CO)_5$ complex (Fig. 1) can be described as an axially-distorted octahedron with an apical nitrogen lone pair of the organic ligand coordinated to the metal atom, in agreement with the previous assignment based on ν(CO) spectral data [15]. The Mo–N(1) bond of 2.337(3) Å, apparently the first such example involving a tertiary amine, is slightly longer than Mo–N-

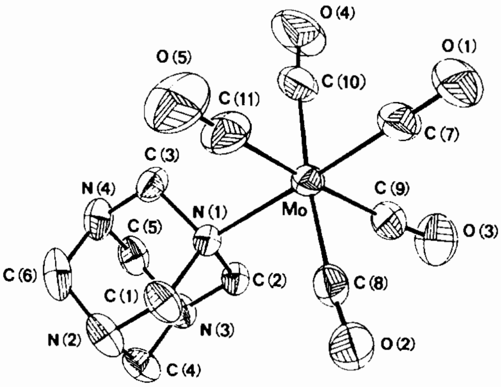

Fig. 1. A perspective view of the $(CH_2)_6N_4 \cdot Mo(CO)_5$ complex. The atoms are drawn as 40% probability ellipsoids, and the labelling scheme corresponds to that of Table II. Hydrogen atoms have been omitted for clarity.

TABLE II. Atomic Coordinates (× 10^5 for Mo; × 10^4 for other atoms) and Equivalent Isotropic Temperature Factors[a] (Å^2 × 10^4 for Mo; × 10^3 for other atoms).

Atom	x	y	z	U_{eq}
MO	42560(2)	21896(2)	21560(2)	423(1)
N(1)	3472(2)	1394(2)	1115(2)	36(1)
N(2)	2220(3)	1616(3)	97(2)	66(1)
N(3)	2419(2)	−81(3)	697(2)	50(1)
N(4)	3715(3)	581(3)	−146(2)	59(1)
C(1)	2714(3)	2098(3)	749(2)	55(1)
C(2)	2922(3)	417(3)	1340(2)	42(1)
C(3)	4200(3)	1076(3)	499(2)	52(1)
C(4)	1715(3)	659(3)	359(3)	64(2)
C(5)	3181(3)	−344(3)	122(2)	58(1)
C(6)	2983(4)	1308(4)	−461(2)	74(2)
C(7)	4947(3)	2881(4)	3003(3)	68(2)
O(1)	5357(3)	3272(3)	3508(2)	104(2)
C(8)	3026(3)	3073(3)	2407(2)	52(1)
O(2)	2362(3)	3551(3)	2609(2)	79(1)
C(9)	3768(3)	1167(4)	2958(2)	58(1)
O(3)	3518(3)	678(3)	3464(2)	101(2)
C(10)	5518(3)	1312(5)	2015(3)	80(2)
O(4)	6237(3)	854(5)	1998(3)	137(2)
C(11)	4776(3)	3339(4)	1445(3)	74(2)
O(5)	5056(3)	4016(3)	1078(3)	124(2)

[a] Calculated as one-third of the trace of the orthogonalized U_{ij} matrix.

TABLE III. Hydrogen Coordinates (× 10^4 and Assigned Isotropic Temperature Factors[a] (Å^2 × 10^3).

Atom	x	y	z	U
H(1*a*)	3049	2721	585	80
H(1*b*)	2214	2274	1120	80
H(2*a*)	2426	596	1714	80
H(2*b*)	3392	−64	1558	80
H(3*a*)	4679	598	710	80
H(3*b*)	4537	1693	324	80
H(4*a*)	1379	331	−62	80
H(4*b*)	1234	845	742	80
H(5*a*)	3657	−815	345	80
H(5*b*)	2857	−680	−301	80
H(6*a*)	3324	1919	−643	80
H(6*b*)	2649	972	−879	80

[a] Form of isotropic temperature factor: $\exp(-8\pi^2 U \sin^2\theta/\lambda^2)$.

(secondary amine) bonds in the range 2.219(4)–2.321(3) Å [16].

All metal-carbonyl systems deviate from exact linearity as a consequence of crystal packing, with Mo–C–O angles ranging from 172.5(4) to 178.8(4)° (Table IV). As a good σ but poor π acceptor, the $(CH_2)_6N_4$ ligand is expected to strengthen the bond-

TABLE IV. Bond Distances (Å) and Angles (deg).

$(CH_2)_6N_4$ ligand

N(1)–C(1)	1.500(5)	N(2)–C(4)	1.472(6)
N(1)–C(2)	1.503(4)	N(2)–C(6)	1.468(6)
N(1)–C(3)	1.510(5)	N(3)–C(4)	1.462(5)
N(2)–C(1)	1.457(5)	N(3)–C(5)	1.473(5)
N(3)–C(2)	1.458(5)	N(4)–C(5)	1.461(5)
N(4)–C(3)	1.450(5)	N(4)–C(6)	1.459(6)
C(1)–N(1)–C(2)	106.3(3)	C(1)–N(2)–C(4)	108.5(3)
C(1)–N(1)–C(3)	107.0(3)	C(1)–N(2)–C(6)	108.7(3)
C(2)–N(1)–C(3)	106.2(3)	C(4)–N(2)–C(6)	107.7(3)
C(2)–N(3)–C(4)	109.1(3)	C(3)–N(4)–C(5)	108.8(3)
C(2)–N(3)–C(5)	108.0(3)	C(3)–N(4)–C(6)	108.5(3)
C(4)–N(3)–C(5)	108.4(3)	C(5)–N(4)–C(6)	108.1(3)
N(1)–C(1)–N(2)	112.8(3)	N(2)–C(4)–N(3)	111.7(3)
N(1)–C(2)–N(3)	112.8(3)	N(3)–C(5)–N(4)	111.9(3)
N(1)–C(3)–N(4)	112.8(3)	N(2)–C(6)–N(4)	112.7(3)

$Mo(CO)_5$ group

Mo–C(7)	1.960(5)	C(7)–O(1)	1.155(6)

(continued overleaf)

TABLE IV. *(continued)*

Mo–C(8)	2.044(4)	C(8)–O(2)	1.135(6)
Mo–C(9)	2.029(4)	C(9)–O(3)	1.136(6)
Mo–C(10)	2.043(5)	C(10–O(4)	1.126(7)
Mo–C(11)	2.050(5)	C(11)–O(5)	1.142(7)
Mo–C(7)–O(1)	178.8(4)	Mo–C(10)–O(4)	174.1(4)
Mo–C(8)–O(2)	174.2(3)	Mo–C(11)–O(5)	176.4(5)
Mo–C(9)–O(3)	172.5(4)		
C(7)–Mo–C(8)	88.1(2)	C(8)–Mo–C(9)	87.1(2)
C(7)–Mo–C(9)	85.3(2)	C(9)–Mo–C(10)	89.7(2)
C(7)–Mo–C(10)	87.2(2)	C(10)–Mo–C(11)	92.3(2)
C(7)–Mo–C(11)	88.6(2)	C(8)–Mo–C(11)	90.4(2)
Metal-ligand bonding			
Mo–N(1)	2.337(3)		
Mo–N(1)–C(1)	112.0(2)	N(1)–Mo–C(8)	92.7(1)
Mo–N(1)–C(2)	112.2(2)	N(1)–Mo–C(9)	96.6(1)
Mo–N(1)–C(3)	112.7(2)	N(1)–Mo–C(10)	92.1(2)
N(1)–Mo–C(7)	177.9(1)	N(1)–Mo–C(11)	89.5(2)

TABLE V. Distortion of the $(CH_2)_6N_4$ Cage System through Quaternization of one Nitrogen Atom.[a]

Type	Compound	C_α–N_q	C_α–N	C–N	C_α–N_q–$C_{\alpha'}$	Ref.
	$(CH_2)_6N_4$	1.476(2)	1.476(2)	1.476(2)	107.2(1)	7
Methylation	$[(CH_2)_6N_4CH_3]Br{\cdot}H_2O$	1.535(15)	1.430(5)	1.469(9)	107.8(5)	5
Borine adduct formation	$(CH_2)_6N_4{\cdot}BH_3$[b]	1.527(5)	1.475(6)	1.475(6)	107.4(3)	18
N-oxide formation	$(CH_2)_6N_4O$	1.514(2)	1.445(7)	1.474(4)	107.4(2)	3
Protonation	$[(CH_2)_6N_4H]Br$	1.512(8)	1.458(7)	1.465(5)	109.7(3)	2
Coordination	$[(CH_2)_6N_4]_4OCu_4Cl_6$	1.514(6)	1.453(10)	1.468(12)	107.0(9)[c]	19
Coordination	$(CH_2)_6N_4{\cdot}Mo(CO)_5$	1.504(5)	1.455(4)	1.466(6)	106.5(4)	This work

[a] The quaternary nitrogen atom is indicated by subscript q, and a carbon atom bonded to it by subscript α. [b] The measured C_α–N bond in this compound is abnormally long and does not fit the general pattern of C–N bond length variation. [c] Value not given in the original paper but calculated from the reported atomic coordinates.

ing between the axial carbonyl group and the metal centre. This '*trans* influence' results in significantly shorter M–C [1.960(5) Å] and longer C–O [1.155(6) Å] bond lengths for the axial carbonyl group as compared to the corresponding averages, 2.042(5) and 1.135(6) Å respectively, for the four equatorial carbonyl groups. Two distinctly different types of metal-carbonyl interactions have also been observed in the structurally similar phosphatriaza-adamantane complex, $P(CH_2)_6N_3{\cdot}Mo(CO)_5$ [17], which crystallizes in the same space group as $(CH_2)_6N_4{\cdot}Mo(CO)_5$ but differs from it with regard to unit cell dimensions and hence molecular packing. One notable difference between these two structures is that the $P(CH_2)_6N_3$ complex exhibits a smaller distortion from regular octahedral coordination geometry, since steric repulsion between the cage ligand and the equatorial carbonyls is lessened by virtue of the longer Mo–P bond [2.479(5) Å] and smaller C–P–C bond angles [average value 97.6(9)°]. The more substantial steric influence of the $(CH_2)_6N_4$ ligand accounts for the fact that three of the four independent

N(1)–Mo–C bond angles significantly exceed a right angle (Table IV).

The measured dimensions of the organic ligand (Table IV) clearly reflect the expected pattern of C–N bond length variation generated by metal coordination. The extent of distortion of the $(CH_2)_6N_4$ cage system by various means of quaternizing one of its four bridge-head nitrogen atoms is compared in Table V. It may be concluded from the tabulated data that cage distortion decreases in the order methylation > borine adduct formation ≅ N-oxide formation ≅ protonation > coordination and that, in the last instance, variation of the formal oxidation state of the metal atom produces virtually no effect. The abnormally large and small values for the C_α–N_q–$C_{\alpha'}$ angle, as observed in protonation and metal coordination respectively, are explicable in terms of the steric requirements of the individual acceptor groups.

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