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Structure Determinations of Halotetrakis(*tert*-butyl isocyanide)((*N*,*N'*-di-*tert*-butyldiamino)acetylene)molybdenum(II) Complexes[1,2]

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The reductive coupling of adjacent isocyanide ligands in the heptacoordinate $[Mo(t\text{-}BuNC)_6X]^+$ complexes produces $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)X]^+$ cations that contain the novel (*N*,*N'*-dialkyldiamino)acetylene molecule coordinated to molybdenum(II). The structures of three compounds containing these cations, with X = Br or I, have been determined in single-crystal X-ray diffraction studies. The isomorphous compounds $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)I]Y$, Y = I (**1**) and PF_6 (**2**), crystallize in the orthorhombic system, space group *Pbca*, with $Z = 8$. The unit cell dimensions for **1** are $a = 21.995$ (3) Å, $b = 19.849$ (3) Å, and $c = 18.536$ (3) Å and for **2** are $a = 22.215$ (3) Å, $b = 20.160$ (3) Å, and $c = 18.884$ (3) Å. The third compound, $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)Br]_2ZnBr_4$ (**3**), crystallizes in orthorhombic space group $P2_12_12_1$, $a = 43.621$ (11) Å, $b = 16.912$ (5) Å, and $c = 11.603$ (3) Å with $Z = 4$, and has two crystallographically independent cations. The geometries of all four halotetrakis(*tert*-butyl isocyanide)((*N*,*N'*-di-*tert*-butyldiamino)acetylene)molybdenum(II) cations are very similar and resemble those of the starting, capped trigonal-prismatic $[Mo(t\text{-}BuNC)_6X]^+$ complexes. In **1** and **2** the average Mo–I bond length is 2.894 (1) Å, while the Mo–CNR distances range from 2.115 (8) to 2.126 (8) Å. The average Mo–C bond length to the coupled ligand is 2.034 (4) Å. The mean coupled ligand C–C distance is 1.353 (10) Å, and the average C–N distance is 1.327 (9) Å. Hydrogen (N–H) atoms of the coordinated (*N*,*N'*-di-*tert*-butyldiamino)acetylene ligands in **1** and **2** were located and refined. These atoms are hydrogen bonded to the respective anion in the crystal lattice. The geometry of the two cations in **3** closely approximates that of **1** and **2**, except for the Mo–Br bonds, 2.684 (3) and 2.681 (3) Å, which are shorter as expected. The geometries of the tetrabromozincate(II), hexafluorophosphate, and *tert*-butyl groups are normal. In all these compounds the coupled ligand may be formally considered as a four-electron-donating (dialkyldiamino)acetylene.

Introduction

Seven-coordinate molybdenum(II) and tungsten(II) alkyl isocyanide (L) complexes of general formulas ML_7^{2+}, ML_6X^+ (X = Cl, Br, I, CN), and ML_5X_2 have been the subject of considerable study.[3-10] Previously we reported the reductive coupling of adjacent ligands in iodohexakis(*tert*-butyl isocyanide)molybdenum(II) iodide to form $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)I]I$ (**1**) (eq 1).[11] This compound contains

$$[Mo(CNR)_6I]^+ \xrightarrow{Zn/THF/H^+} [Mo(CNR)_4(RHNCCNHR)I]^+ \quad (1)$$

a new ligand that may be regarded formally as (*N*,*N'*-di-*tert*-butyldiamino)acetylene. Continuing studies of this reaction[12] led to isolation of a hexafluorophosphate salt, **2**, and of the bromo analogue, $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)Br]^+$, obtained as the tetrabromozincate(II) salt (**3**). The structure determination of all three of these compounds by single-crystal X-ray diffraction methods was an important part of their characterization. The precise nature of compound **3**, for example, was uncertain until the X-ray study revealed that divalent zinc, the oxidation product of reaction 1, was incorporated into the product as $ZnBr_4^{2-}$. Here we present the results of these three X-ray investigations and compare the geometries of four crystallographically independent molybdenum(II) cations containing the novel coupled ligand.

Experimental Procedure and Results

Collection and Reduction of X-ray Data. Iodotetrakis(*tert*-butyl isocyanide)((*N*,*N'*-di-*tert*-butyldiamino)acetylene)molybdenum(II) Iodide and Hexafluorophosphate Salts. The iodide salt was prepared as described previously[11] and recrystallized from acetone/diethyl ether solutions as rose red, elongated thick plates, mostly occurring as conglomerates. Crystals of a similar shape and hue were obtained for the hexafluorophosphate salt[12] by recrystallization from tetrahydrofuran/diethyl ether solutions. Preliminary X-ray photographs taken by the precession and Weissenberg methods indicated that the two salts are isomorphous, crystallizing in the orthorhombic system, space group *Pbca*—D_{2h}^{15},[13a] as uniquely determined by the systematic absences.

Single crystals were examined on a Picker four-circle diffractometer under control of the FACS-I-DOS system. The mounting direction was in each case misset from an axis by a few degrees. Preliminary ω scans were made to ensure satisfactory mosaicity. During data collection, diffracted beams were attenuated with Al foil when the counting rate exceeded ~10 000 counts/s. Further details of data collection and reduction are given in Table I.

Bromotetrakis(*tert*-butyl isocyanide)((*N*,*N'*-di-*tert*-butyldiamino)acetylene)molybdenum(II) tetrabromozincate(II) was obtained[12b] as deep red crystals by slow diffusion of diethyl ether vapor into a concentrated tetrahydrofuran solution of the complex. Preliminary X-ray photographs and intensity measurements were obtained as reported for the iodo complexes. The space group was uniquely shown by the extinctions to be $P2_12_12_1$—D_2^4. Because of the long *a* axis, Cu $K\bar{\alpha}$ radiation was chosen for data collection to avoid overlapping of reflections that would have occurred had Mo $K\bar{\alpha}$ radiation been used. Table I summarizes the data collection and reduction steps.

Determination and Refinement of the Structures. The Iodotetrakis(*tert*-butyl isocyanide)((*N*,*N'*-di-*tert*-butyldiamino)acetylene)molybdenum(II) Cation, Iodide Salt. The structure was

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[1] Part 9 of a continuing series on higher coordinate cyanide and isocyanide complexes. For part 8, see ref 2.

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Table I. Experimental Details of the X-ray Diffraction Studies on the Salts $[MoL_4L'X]Y$, Where L = *t*-BuNC and L' = *t*-BuHNCCNH-*t*-Bu

	$[MoL_4L'I]I$	$[MoL_4L'I]PF_6$	$[MoL_4L'Br]_2ZnBr_4$
(A) Crystal Data at 23 (3) °C			
space group	*Pbca*	*Pbca*	$P2_12_12_1$
cell dimens *a*, Å	21.995 (3)[a]	22.215 (3)[b]	43.621 (11)[c]
b, Å	19.849 (3)	20.160 (3)	16.912 (5)
c, Å	18.536 (3)	18.884 (3)	11.603 (3)
cell vol, Å^3	8092 (3)	8457 (3)	8560 (4)
no. of formula units in the unit cell, *Z*	8	8	4
fw	850.6	868.6	1738.3
obsd density, g/mL	1.395 (2)[d]	1.352 (2)[d]	1.352 (1)[e]
calcd density, g/mL	1.396	1.364	1.349
(B) Measurement of X-ray Intensities			
radiation	Mo Kα (graphite monochromator)	Mo Kα (graphite monochromator)	Cu Kα (nickel filter)
cryst			
principal faces	(±1,0,0), (0,±1,0), (0,0,±1)	(0,±1,0), (±1,0,0), (0,0,−1), (±1,1,3)	(±1,0,0), (0,±1,0), (0,0,±1)
dimens, mm^3	0.27 × 0.43 × 0.15	0.25 × 0.45 × 0.33	0.03 × 0.09 × 0.38
peak width at half-height on ω scans, deg	0.08–0.11	0.06–0.09	0.06–0.09
takeoff angles, deg	1.5	1.3	1.8
cryst–detector dist, cm	32	30	33
scan range in 2θ for θ–2θ data collection ($K\alpha_1$-$K\alpha_2$ dispersion is added to this), deg	1.4	1.2	1.2
std reflctns	(083), (0,0,10), (220)	(083), (0,0,10), (10,0,0)	$(11\bar{3})$, (031), $(\overline{41}3)$
no. of data between std reflctns	97	97	47
2θ range, deg	0–48, 48–55, 0–40	0–30, 30–45, 45–55	0–90, 90–100, 100–128
octant	*hkl*, *hkl*, $\bar{h}kl$	*hkl*, *hkl*, *hkl*	$hk\bar{l}$, $hk\bar{l}$, $hk\bar{l}$
scan rate, deg/min	1.0, 1.0, 2.0	2.0, 2.0, 1.0	1.0, 0.5, 0.5
bkgd counting times each end of scan, s	20, 20, 10	10, 10, 20	20, 20, 40
aperture size, in front of detector, width × height, mm^2	6 × 6, 5 × 6, 6 × 6	6 × 6, 4 × 6, 4 × 6	4 × 4, 4 × 4, 4 × 4
(C) Data Reduction[f]			
correction for decomposition, based on std reflctns	1.00–1.04	1.01–1.05	0.91–1.09[g]
estimated std dev value of ε[h]	0.04	0.04	0.05
linear abs coeff μ, in cm^{-1}	18.5	11.1	63.5
range of transmission factors	0.62–0.76	0.70–0.78	0.47–0.84
averaging equivalent reflctns mean percent deviation from $\langle F^2\rangle$	1.7 (*h* = 0–4), 4.8 (*h* = 15–28)		
no. of independent reflctns	9335	9765	7855
no. of obsd reflctns	4038	4046	4225
criteria for obsd reflctns	$F^2 > 3\sigma(F^2)$	$F^2 > 3\sigma(F^2)$	$F^2 > 2\sigma(F^2)$
(D) Least-Squares Refinement			
heavy atoms only, *R* and R_w[i]	0.30, 0.39	0.30, 0.41	0.23, 0.33
all atoms, isotropic, *R* and R_w	0.11, 0.15	0.12, 0.15	
heavy atoms anisotropic, light atoms isotropic, *R* and R_w	0.059, 0.079	0.082, 0.118	0.083, 0.087
(E) Final Model			
R, R_w	0.043, 0.054	0.048, 0.063	0.072, 0.072
no. of atoms refined	41	56	81
fixed methyl H atoms	yes	yes	no
no. of variables	360	438	730
error in observn of unit weight[j]	1.5	1.8	1.5
highest peak on final difference Fourier, e/Å^3 (% of C atom peak)	0.7 (30)	0.4 (20)	0.8 (30)
max (Δ/σ) final cycle	0.1	0.1	0.7

[a] From a least-squares fit to the setting angles of 25 reflections having $30° \leq 2\theta \leq 50°$. [b] From a least-squares fit of 30 reflections as in footnote *a*. The unit cell initially chosen for the PF_6^- salt had the axes in the order *b, c, a* with respect to the unit cell for the I^- salt. The unit cell, the Miller indices, and the atomic coordinates were transformed so as to match the I^- salt at the end of the structure determination. [c] From a least-squares fit to the setting angles of 25 reflections in the 2θ range 44–87°. [d] By suspension in aqueous KI solutions. [e] By suspension in CCl_4/hexane mixtures. [f] Programs for an IBM 360/91 computer used in this work include: UMAT, the local version of the Brookhaven diffractometer setting, cell constant, and orientation refinement program; PROCESS, for background and attenuator correction, with tape checking and statistics, by Corfield; ORABS, for absorption correction by numerical integration on a Gaussian grid, by Wehe, Busing, and Levy; AVSORT, for averaging equivalent reflections and sorting, by Gill; XDATA, the Brookhaven Wilson plot and scaling program; FORDAP, the Zalkin Fourier program; CUGLS, a local version of the Busing–Martin–Levy program ORFLS, modified by Ibers and Doedens for rigid-body refinement; ORFFE, the Busing–Martin–Levy molecular geometry and error function program; ORTEP II, the Johnson thermal ellipsoid plotting program; various other local programs. [g] Anisotropic decay of standards was corrected for (see: Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* 1974, *13*, 1427, footnote 12). [h] Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* 1967, *6*, 197. [i] $R = \Sigma|\Delta|/\Sigma|F_o|$ and $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$, where $\Delta = |F_o| - |F_c|$. [j] $[\Sigma w\Delta^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observed data used and N_v is the number of variable parameters.

Table II. Final Positional and Thermal Parameters for $[(t\text{-BuNC})_4(t\text{-HNCCNH-}t\text{-Bu})\text{I}]\text{I}^{a,b}$

atom	x	y	z	β_{11} or B^c	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I1	0.53612 (3)	0.28306 (3)	−0.04567 (3)	2.561 (16)	3.75 (2)	3.29 (2)	−0.386 (17)	0.354 (15)	0.793 (19)
I2	0.28735 (3)	0.03581 (4)	0.25117 (5)	3.38 (2)	5.47 (3)	6.12 (3)	−0.96 (2)	−0.04 (2)	2.30 (3)
Mo	0.45637 (3)	0.21485 (3)	0.05485 (3)	1.469 (12)	1.974 (19)	2.230 (19)	0.147 (16)	−0.214 (15)	0.087 (19)
N1	0.4325 (4)	0.1187 (4)	0.1981 (4)	2.19 (18)	3.8 (3)	2.8 (2)	0.25 (19)	−0.07 (18)	0.6 (2)
N2	0.3216 (3)	0.1681 (4)	0.1182 (4)	1.96 (17)	2.8 (3)	3.3 (3)	−0.10 (16)	−0.13 (17)	0.7 (2)
N3	0.5544 (3)	0.2923 (3)	0.1583 (3)	2.24 (16)	2.7 (2)	3.0 (2)	−0.27 (16)	−0.44 (16)	−0.4 (2)
N4	0.3935 (3)	0.3630 (4)	0.0541 (4)	2.30 (17)	2.7 (2)	4.5 (3)	0.30 (17)	−0.1 (2)	0.3 (2)
N5	0.5597 (3)	0.1014 (4)	0.0248 (4)	2.15 (17)	2.9 (2)	3.4 (3)	0.44 (17)	0.02 (17)	−0.2 (2)
N6	0.3929 (3)	0.1821 (4)	−0.1006 (4)	2.37 (17)	3.1 (2)	2.7 (2)	−0.24 (17)	−0.49 (17)	0.01 (20)
C1	0.4291 (3)	0.1573 (4)	0.1402 (4)	1.85 (17)	2.1 (2)	2.4 (3)	0.11 (17)	0.13 (18)	0.1 (2)
C11	0.4862 (4)	0.0875 (5)	0.2349 (4)	3.1 (2)	3.6 (3)	2.5 (3)	0.3 (2)	−0.5 (2)	0.6 (3)
C12	0.5409 (4)	0.1356 (5)	0.2329 (5)	3.0 (3)	4.2 (4)	5.0 (4)	−0.1 (3)	−1.4 (3)	1.4 (3)
C13	0.5006 (6)	0.0210 (5)	0.1991 (6)	5.3 (4)	2.4 (4)	6.1 (5)	0.7 (3)	−0.6 (4)	−0.1 (4)
C14	0.4670 (5)	0.0765 (6)	0.3124 (5)	3.9 (3)	7.2 (5)	3.3 (3)	−0.0 (4)	−0.9 (3)	2.0 (4)
C2	0.3797 (3)	0.1792 (4)	0.1042 (4)	1.84 (18)	1.7 (2)	2.6 (3)	0.20 (17)	0.08 (18)	0.04 (19)
C21	0.2668 (4)	0.1888 (5)	0.0809 (5)	1.9 (2)	3.6 (3)	4.2 (4)	−0.1 (2)	−0.3 (2)	0.3 (3)
C22	0.2489 (7)	0.1301 (7)	0.0338 (9)	6.8 (6)	5.6 (6)	13.8 (11)	−0.7 (5)	−6.5 (7)	0.9 (6)
C23	0.2734 (4)	0.2472 (7)	0.0324 (8)	2.2 (2)	7.5 (6)	10.8 (8)	−0.2 (3)	−1.3 (4)	4.5 (6)
C24	0.2184 (6)	0.1981 (11)	0.1322 (8)	4.1 (4)	21.6 (15)	6.4 (6)	6.6 (7)	1.1 (4)	2.4 (8)
C3	0.5184 (3)	0.2630 (4)	0.1261 (4)	1.87 (17)	2.3 (3)	2.4 (3)	0.22 (17)	0.10 (18)	0.1 (2)
C31	0.6061 (4)	0.3289 (6)	0.1852 (5)	2.6 (3)	4.7 (4)	4.3 (4)	−1.5 (3)	−0.5 (3)	−0.6 (3)
C32	0.6613 (6)	0.2860 (9)	0.1678 (10)	2.6 (3)	13.6 (11)	15.8 (12)	0.2 (5)	−0.8 (5)	−6.4 (10)
C33	0.6001 (6)	0.3388 (8)	0.2638 (6)	6.2 (5)	10.5 (8)	3.7 (5)	−4.5 (5)	−0.4 (4)	−2.0 (5)
C34	0.6133 (8)	0.3879 (8)	0.1383 (8)	10.6 (8)	7.5 (7)	8.9 (8)	−6.6 (7)	−4.8 (7)	3.7 (6)
C4	0.4136 (3)	0.3107 (4)	0.0543 (5)	1.89 (18)	2.4 (3)	3.4 (3)	0.24 (18)	−0.2 (2)	0.2 (3)
C41	0.3742 (5)	0.4348 (5)	0.0478 (6)	4.2 (3)	2.1 (3)	5.8 (5)	1.0 (3)	−0.9 (4)	0.5 (3)
C42	0.4309 (8)	0.4782 (6)	0.0318 (12)	7.1 (6)	2.8 (5)	21.8 (18)	−1.6 (4)	−3.7 (9)	1.4 (7)
C43	0.3344 (8)	0.4398 (7)	−0.0184 (10)	7.6 (7)	6.5 (6)	11.9 (10)	2.2 (5)	−4.2 (7)	1.6 (7)
C44	0.3471 (11)	0.4560 (7)	0.1158 (9)	20.7 (15)	6.3 (7)	8.1 (8)	8.5 (8)	8.3 (9)	2.6 (6)
C5	0.5214 (4)	0.1384 (4)	0.0359 (4)	2.14 (19)	2.4 (3)	2.8 (3)	0.15 (19)	−0.12 (19)	−0.2 (2)
C51	0.6135 (4)	0.0604 (5)	0.0094 (5)	2.2 (2)	3.8 (4)	4.2 (4)	1.0 (2)	0.6 (3)	−0.3 (3)
C52	0.5965 (6)	−0.0130 (7)	0.0035 (11)	4.9 (5)	2.7 (4)	17.2 (12)	1.0 (4)	2.1 (6)	−0.4 (6)
C53	0.6573 (6)	0.0707 (10)	0.0679 (8)	2.9 (3)	19.0 (13)	7.6 (7)	3.7 (6)	−1.6 (4)	−4.9 (8)
C54	0.6387 (6)	0.0894 (9)	−0.0593 (7)	5.0 (5)	13.6 (10)	6.9 (7)	3.8 (6)	3.0 (5)	2.9 (7)
C6	0.4139 (3)	0.1901 (4)	−0.0442 (4)	1.92 (18)	2.5 (3)	3.0 (3)	0.10 (17)	0.05 (20)	0.6 (2)
C61	0.3699 (4)	0.1849 (5)	−0.1735 (5)	2.8 (3)	4.1 (4)	3.0 (3)	−0.3 (3)	−0.7 (2)	−0.1 (3)
C62	0.3255 (5)	0.1278 (6)	−0.1849 (6)	4.5 (4)	7.1 (6)	4.1 (4)	−2.2 (4)	−0.9 (3)	−0.6 (4)
C63	0.3365 (6)	0.2525 (7)	−0.1806 (6)	5.7 (5)	7.5 (6)	4.8 (5)	0.7 (5)	−1.7 (4)	1.9 (5)
C64	0.4227 (5)	0.1824 (7)	−0.2238 (5)	4.0 (3)	10.3 (7)	3.1 (4)	−1.3 (4)	1.2 (3)	0.3 (4)
H1	0.396 (4)	0.125 (5)	0.215 (5)	8 (3)					
H2	0.318 (3)	0.140 (3)	0.155 (3)	1.6 (14)					

[a] Numbers in parentheses are errors in the last significant digit(s). [b] The anisotropic temperature factors are times 10^3. The anisotropic temperature factors are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] B values in Å^2.

solved by conventional Patterson, Fourier, and least-squares refinement techniques. Following refinement with anisotropic thermal parameters for all nonhydrogen atoms, difference electron density maps calculated in the planes of the methyl carbon atoms for each of the six *tert*-butyl groups indicated a possible alternative set of positions for the methyl carbon atoms attached to C31 and C41. Attempts to allow for the peaks in these difference maps with a reasonable disordered model were not successful, however. The agreement between calculated and observed structure factors for the low-order planes remained poor; the thermal parameters for the disordered methyl carbon atoms were large; and complete convergence in the least squares was not achieved. The model with disordered methyl carbon atoms was therefore rejected, and continued refinements were based on a single orientation for each of the *tert*-butyl groups.

The model was improved considerably by including hydrogen atom contributions. A difference electron density section calculated in a plane containing Mo, N1, and N2 showed peaks interpreted as hydrogen atoms bonded to N1 and N2. This section of the electron density is reproduced in Figure 1a. The coordinates and isotropic temperature factors for these two hydrogen atoms, H1 and H2, were refined. Difference electron density sections were also calculated in planes through the expected hydrogen atom positions for all of the methyl groups. With assumption of local C_{3v} symmetry for the methyl groups, these sections were used to give hydrogen atom positions for all methyl groups attached to C11, C21, C51, and C61. Fixed contributions from these 36 hydrogen atoms were included in the structure factor calculations, with isotropic temperature factors fixed at 1.0 Å^2 more than the B value equivalent to the anisotropic thermal parameters of the adjacent carbon atoms. Refinement of the model with allowance for these 38 hydrogen atoms led to satisfactory convergence. Final residuals are given in Table I, which also shows progress in refinement of all three compounds described in this paper. The average value of the quantity $w\Delta^2$ was 14.5 for the 200 planes with lowest θ, much larger than the average value of 1.3 for the 2000 planes with highest θ. This discrepancy probably reflects uncertainty in the best model for the *tert*-butyl groups, rather than errors in the data. Final refined positional and thermal parameters for the iodide salt are given in Table II. A listing of important interatomic distances and angles appears in Tables V and VI. Tables S1–S3 listing the positional and thermal parameters for the fixed hydrogen atoms, root-mean-square amplitudes of thermal motion for anisotropically refined atoms, and the final list of observed and calculated structure factor amplitudes are available as supplementary material. The molecular geometry and atom labeling scheme are shown in Figure 2. The unit cell packing is displayed in Figure 3.

The Hexafluorophosphate Salt. The structure was determined by Patterson methods in the same way as for the iodide salt, prior to the recognition that the two compounds are isomorphous. The electron density maps based on phases from the Mo and I atoms alone were complicated because of the pseudo center of inversion that appears at ($^1/_4$, 0, 0) in the unit cell originally chosen (Table I). Parameters for all carbon and nitrogen atoms were found, however, after a series of least-squares refinement and difference Fourier calculations. Even at this stage it was apparent that the electron density maps in the regions near some of the methyl carbon atoms could not be interpreted solely on the basis of a single preferred orientation of the *tert*-butyl groups. In the final model chosen, two alternative sets of positions for the methyl carbon atoms associated with atoms C2, C3, and C4 were refined. In the case of the C4 *tert*-butyl group, the electron density in the neighborhood of the methyl carbon atoms was very

Table III. Final Positional and Thermal Parameters for $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)I]PF_6$[a, b]

atom	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
I	0.54095 (3)	0.28465 (4)	−0.04559 (3)	2.67 (2)	4.44 (3)	3.67 (3)	−0.53 (2)	0.29 (2)	0.87 (2)
Mo	0.46156 (3)	0.21704 (4)	0.05208 (3)	1.41 (1)	2.28 (2)	2.32 (2)	0.04 (2)	−0.24 (2)	0.18 (2)
P	0.2710 (2)	0.0304 (2)	0.2560 (2)	3.56 (9)	5.5 (2)	6.9 (2)	−1.17 (9)	−0.4 (1)	2.5 (2)
F1	0.2660 (4)	−0.0446 (4)	0.2399 (6)	8.3 (4)	6.0 (4)	11.7 (6)	0.1 (3)	2.1 (4)	1.6 (4)
F2	0.2741 (6)	0.0421 (5)	0.1745 (5)	14.2 (6)	7.7 (4)	8.1 (5)	−0.2 (4)	1.5 (5)	3.1 (4)
F3	0.2731 (6)	0.0154 (6)	0.3321 (5)	12.2 (6)	12.4 (6)	5.5 (3)	2.0 (5)	−0.9 (4)	1.9 (4)
F4	0.2843 (5)	0.1035 (4)	0.2627 (6)	13.8 (6)	4.2 (3)	12.8 (6)	−2.1 (3)	−4.4 (5)	−1.5 (4)
F5	0.2061 (3)	0.0381 (5)	0.2537 (7)	3.6 (2)	12.3 (6)	16.9 (8)	1.9 (3)	−0.1 (4)	−0.1 (6)
F6	0.3395 (4)	0.0185 (6)	0.2523 (9)	4.1 (3)	12.3 (6)	24.5 (11)	−2.3 (3)	−0.3 (5)	3.6 (7)
N1	0.4373 (3)	0.1214 (4)	0.1913 (4)	1.8 (2)	3.5 (3)	3.5 (3)	−0.1 (2)	−0.1 (2)	1.2 (2)
N2	0.3271 (3)	0.1745 (4)	0.1119 (4)	1.4 (2)	4.0 (3)	3.6 (3)	−0.3 (2)	−0.3 (2)	1.3 (2)
N3	0.5596 (3)	0.2883 (4)	0.1554 (4)	2.1 (1)	3.3 (2)	2.9 (2)	−0.3 (2)	−0.4 (2)	0.0 (2)
N4	0.4007 (3)	0.3649 (4)	0.0529 (4)	2.6 (2)	2.6 (2)	3.6 (3)	0.3 (2)	−0.1 (2)	0.0 (2)
N5	0.5609 (3)	0.1019 (4)	0.0185 (4)	2.1 (2)	2.8 (2)	4.0 (3)	0.2 (2)	0.0 (2)	0.0 (2)
N6	0.4005 (3)	0.1856 (4)	−0.0998 (4)	2.1 (2)	3.2 (2)	2.5 (2)	−0.2 (2)	−0.2 (2)	−0.1 (2)
C1	0.4340 (3)	0.1609 (4)	0.1345 (4)	1.7 (2)	2.3 (2)	2.5 (2)	0.2 (2)	−0.2 (2)	0.1 (2)
C11	0.4900 (4)	0.0907 (5)	0.2278 (5)	2.6 (2)	3.2 (3)	3.7 (3)	0.3 (2)	−0.7 (2)	1.4 (3)
C12	0.5447 (4)	0.1356 (6)	0.2256 (6)	3.1 (3)	5.2 (4)	5.2 (4)	0.3 (3)	−1.5 (3)	1.9 (3)
C13	0.5016 (6)	0.0251 (6)	0.1944 (7)	5.3 (4)	5.0 (5)	6.0 (6)	2.0 (4)	−1.3 (4)	−0.1 (4)
C14	0.4707 (5)	0.0813 (6)	0.3055 (6)	4.6 (4)	6.5 (5)	4.0 (4)	0.2 (4)	−0.6 (3)	2.2 (4)
C2	0.3851 (3)	0.1832 (4)	0.0987 (4)	1.7 (2)	2.5 (2)	2.6 (2)	−0.2 (2)	0.0 (2)	−0.1 (2)
C21	0.2729 (4)	0.1972 (5)	0.0742 (5)	1.5 (2)	4.8 (4)	4.4 (4)	0.0 (2)	−0.2 (3)	1.4 (3)
C22	0.2604 (7)	0.1355 (9)	0.0233 (9)	6.9 (5)					
C23	0.2827 (8)	0.2574 (9)	0.0336 (9)	5.8 (4)					
C24	0.2211 (8)	0.2046 (9)	0.1277 (9)	6.4 (4)					
C25	0.2499 (17)	0.260 (2)	0.129 (2)	11.7 (13)					
C26	0.2863 (11)	0.2331 (12)	0.0023 (13)	4.2 (6)					
C27	0.2205 (15)	0.1608 (17)	0.0972 (18)	7.7 (9)					
C3	0.5241 (3)	0.2611 (4)	0.1228 (4)	1.8 (2)	2.6 (2)	2.4 (2)	0.2 (2)	0.0 (2)	0.0 (2)
C31	0.6122 (5)	0.3233 (6)	0.1831 (6)	2.9 (3)	5.0 (5)	3.5 (4)	−1.9 (3)	−0.5 (3)	−0.6 (3)
C32	0.6646 (10)	0.2655 (12)	0.1794 (12)	9.2 (8)					
C33	0.6022 (8)	0.3407 (10)	0.2569 (11)	6.6 (5)					
C34	0.6241 (10)	0.3806 (11)	0.1321 (11)	8.0 (6)					
C35	0.5767 (17)	0.3996 (19)	0.197 (2)	12.6 (13)					
C36	0.6308 (14)	0.2905 (17)	0.2549 (19)	10.4 (10)					
C37	0.6562 (14)	0.3304 (16)	0.1346 (17)	9.0 (9)					
C4	0.4200 (3)	0.3118 (4)	0.0534 (4)	1.8 (2)	2.9 (3)	2.8 (3)	0.0 (2)	−0.2 (2)	0.0 (2)
C41	0.3817 (5)	0.4339 (5)	0.0457 (6)	3.8 (3)	2.7 (3)	5.0 (5)	1.0 (3)	0.0 (3)	0.3 (3)
C42	0.4444 (14)	0.4717 (13)	0.025 (2)	5.3 (10)	2.9 (8)	8.1 (15)	−1.3 (7)	1.2 (11)	0.0 (10)
C43	0.339 (2)	0.4365 (17)	−0.016 (3)	6.3 (14)	4.1 (11)	11 (3)	1.7 (11)	−4.2 (17)	2.6 (14)
C44	0.367 (3)	0.4585 (17)	0.118 (2)	13 (3)	3.2 (11)	7.5 (17)	4.0 (15)	5.2 (20)	0.3 (10)
C45	0.398 (3)	0.453 (2)	−0.026 (2)	15 (3)	5.0 (17)	5.3 (14)	4.2 (19)	2 (2)	3.5 (13)
C46	0.416 (2)	0.4743 (16)	0.098 (2)	6.5 (13)	4.1 (10)	8.5 (20)	0.0 (10)	−3.8 (13)	−3.4 (13)
C47	0.3138 (10)	0.4345 (12)	0.066 (4)	1.9 (5)	2.6 (8)	19 (3)	0.6 (5)	0.9 (12)	−1.3 (15)
C5	0.5243 (3)	0.1401 (4)	0.0310 (4)	1.9 (2)	2.8 (3)	2.6 (3)	−0.2 (2)	−0.2 (2)	0.3 (2)
C51	0.6130 (5)	0.0635 (5)	−0.0010 (6)	2.3 (2)	3.8 (4)	5.0 (5)	0.6 (3)	0.7 (3)	0.1 (4)
C52	0.5966 (7)	−0.0091 (8)	−0.0025 (12)	5.3 (5)	4.7 (5)	19.2 (14)	0.3 (5)	5.1 (7)	−3.0 (8)
C53	0.6600 (6)	0.0760 (11)	0.0539 (9)	3.3 (4)	20.0 (14)	9.3 (9)	4.0 (6)	−2.8 (5)	−3.9 (9)
C54	0.6322 (7)	0.0848 (9)	−0.0721 (8)	6.3 (6)	11.9 (10)	7.4 (7)	4.2 (6)	4.2 (5)	2.3 (7)
C6	0.4198 (3)	0.1943 (4)	−0.0460 (4)	1.7 (2)	2.6 (2)	2.8 (3)	0.0 (2)	0.0 (2)	0.3 (2)
C61	0.3795 (5)	0.1856 (6)	−0.1728 (5)	2.8 (3)	4.6 (4)	2.8 (3)	−0.5 (3)	−0.8 (2)	0.1 (3)
C62	0.3361 (7)	0.1288 (8)	−0.1819 (7)	8.6 (6)	9.4 (8)	5.3 (5)	−5.6 (6)	−2.4 (5)	−0.1 (5)
C63	0.3439 (8)	0.2491 (9)	−0.1810 (7)	9.9 (8)	10.3 (9)	5.3 (6)	2.5 (8)	−3.0 (6)	1.2 (6)
C64	0.4330 (6)	0.1836 (9)	−0.2208 (6)	4.9 (4)	16.2 (11)	3.2 (4)	−2.0 (6)	0.2 (4)	−1.1 (6)
H1	0.403 (3)	0.102 (3)	0.201 (4)	3.5 (18)					
H2	0.322 (3)	0.149 (4)	0.140 (4)	3.1 (20)					

[a] See footnote *a*, Table II. [b] See footnote *b*, Table II.

difficult to interpret, and positions and anisotropic temperature factors for six partial carbon atoms were refined with occupancy factors fixed at 0.50. In the case of the C2 and C3 *tert*-butyl groups, positions and isotropic temperature factors were refined for six partial carbon atoms. Occupancy factors for the two sets of methyl carbon atoms on each of these *tert*-butyl groups were refined, with the constraint that the total occupancy associated with each *tert*-butyl group was 1.0. The occupancy factors finally found for the sets C22–C24 and C32–C34 were 0.63 (2) and 0.57 (2), respectively.

After inspection of observed and calculated structure factors, an attempt was made to improve the model by adding hydrogen atom contributions and also by refining an extinction parameter. The positions of hydrogen atoms H1 and H2, bonded to N1 and N2, are clearly indicated on a difference Fourier section calculated in a plane containing Mo, N1, and N2, as shown in Figure 1b. Coordinates and isotropic temperature factors for these atoms were refined. Fixed atom contributions for 45 hydrogen atoms associated with the *tert*-butyl groups were assigned in the same way as in the iodide salt. For the disordered methyl carbon atoms, hydrogen atom positions were assigned only for C22–C24 and C32–C34. An isotropic extinction parameter was refined after the manner of Larson,[14] with final value $g = 2.7\ (9) \times 10^3$. Satisfactory convergence was now achieved in the least-squares refinements, details for which appear in Table I. Final refined positional and thermal parameters for the hexafluorophosphate salt are given in Table III. The geometry is reported in Tables V–VII, Tables S4–S6 respectively list the fixed hydrogen atom parameters, root-mean-square thermal amplitudes, and final observed and calculated structure factor amplitudes. The cation geometry and

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(14) Larson, A. C. In "Crystallographic Computing"; Ahmed, F. R., Ed.; Munksgaard: Copenhagen, 1970; p 291.

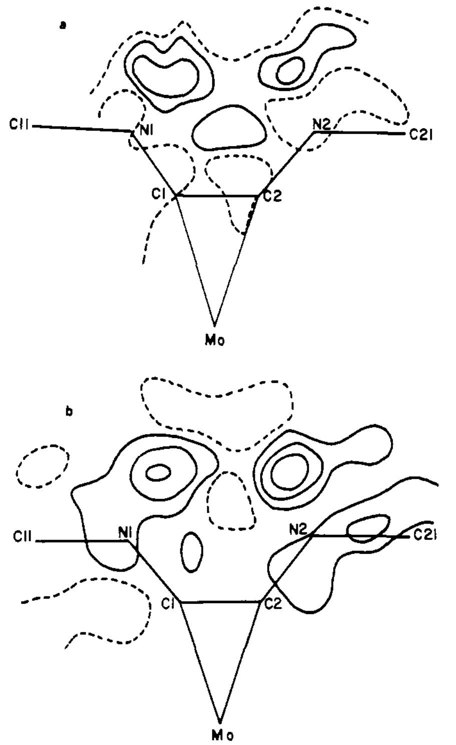

Figure 1. Difference electron density map in the plane of the coupled ligand, showing hydrogen atom positions (a) for [Mo(t-BuNC)$_4$(t-BuHNCCNH-t-Bu)I]I (contour lines at 0.1 e Å^{-3}) and (b) for [Mo(t-BuNC)$_4$(t-BuHNCCNH-t-Bu)I]PF$_6$ (contour lines at 0.1 e Å^{-3}). In both cases, the dashed line represents 0 e Å^{-3}.

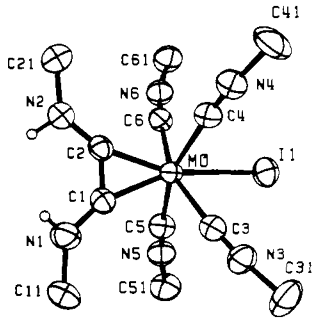

Figure 2. Structure of the [Mo(t-BuNC)$_4$(t-BuHNCCNH-t-Bu)I]$^+$ cation, showing the atom labeling scheme and the 50% probability thermal ellipsoids. For clarity, the methyl carbon atoms have been omitted. The methyl carbon atoms on C11 are numbered C12–C14, etc.

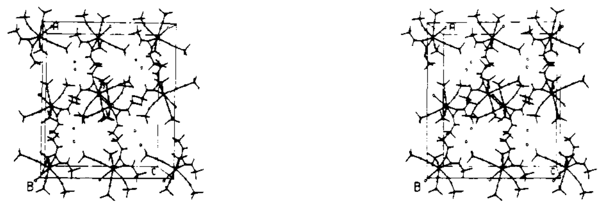

Figure 3. Stereoscopic view of the crystal packing in [Mo(t-BuNC)$_4$(t-BuHNCCNH-t-Bu)I]I, with 20% probability ellipsoids. The imino hydrogen atoms are shown.

Table IV. Final Positional Parameters for [Mo(t-BuNC)$_4$(t-BuHNCCNH-t-Bu)Br]$_2$ZnBr$_4$[a]

atom	x	y	z
Mo1	0.46549 (4)	−0.08349 (9)	0.6258 (1)
Br1	0.40888 (5)	−0.09228 (14)	0.7157 (2)
Mo2	0.22784 (4)	0.23608 (11)	0.6719 (2)
Br2	0.25756 (6)	0.09771 (15)	0.6862 (3)
Zn	0.38556 (6)	0.42231 (17)	0.1891 (2)
Br3	0.33186 (6)	0.44258 (14)	0.1412 (3)
Br4	0.41500 (6)	0.52812 (16)	0.1004 (3)
Br5	0.40471 (8)	0.30419 (18)	0.0978 (3)
Br6	0.39166 (7)	0.41858 (20)	0.3935 (2)
1N1	0.5412 (4)	−0.0690 (9)	0.6468 (14)
1N2	0.5141 (3)	−0.0766 (10)	0.4099 (13)
1N3	0.4632 (4)	0.0586 (9)	0.8171 (16)
1N4	0.4319 (4)	0.0560 (10)	0.4749 (18)
1N5	0.4732 (4)	−0.2181 (10)	0.8263 (15)
1N6	0.4355 (4)	−0.2331 (12)	0.4793 (17)
2N1	0.1803 (4)	0.3673 (11)	0.5465 (16)
2N2	0.2065 (4)	0.4102 (13)	0.7836 (17)
2N3	0.2690 (4)	0.2426 (13)	0.4384 (17)
2N4	0.2951 (5)	0.2789 (13)	0.7774 (19)
2N5	0.1812 (6)	0.1096 (12)	0.5535 (20)
2N6	0.1974 (6)	0.1608 (16)	0.9183 (22)
1C1	0.5115 (4)	−0.0738 (12)	0.617 (2)
1C2	0.5004 (5)	−0.0782 (13)	0.509 (2)
1C3	0.4666 (5)	0.0066 (11)	0.752 (2)
1C4	0.4457 (5)	0.0043 (10)	0.521 (2)
1C5	0.4728 (5)	−0.1715 (11)	0.755 (2)
1C6	0.4478 (5)	−0.1785 (14)	0.527 (2)
2C1	0.1998 (5)	0.3242 (12)	0.616 (2)
2C2	0.2123 (5)	0.3448 (14)	0.717 (2)
2C3	0.2533 (5)	0.2450 (14)	0.515 (2)
2C4	0.2699 (5)	0.2703 (13)	0.748 (2)
2C5	0.1970 (6)	0.1572 (15)	0.591 (2)
2C6	0.2083 (5)	0.1893 (16)	0.836 (3)
1C11	0.5557 (5)	−0.0751 (14)	0.767 (2)
1C12	0.5616 (6)	−0.1558 (13)	0.790 (2)
1C13	0.5877 (4)	−0.0292 (12)	0.761 (2)
1C14	0.5353 (5)	−0.0373 (12)	0.859 (2)
1C21	0.5019 (5)	−0.0926 (25)	0.290 (2)
1C22	0.4685 (5)	−0.0846 (13)	0.275 (2)
1C23	0.5242 (6)	−0.0708 (23)	0.199 (2)
1C24	0.5019 (8)	−0.2004 (16)	0.287 (3)
1C31	0.4525 (7)	0.1131 (12)	0.908 (2)
1C32	0.4536 (8)	0.0691 (18)	1.021 (2)
1C33	0.4760 (5)	0.1839 (14)	0.912 (2)
1C34	0.4200 (5)	0.1422 (16)	0.864 (3)
1C41	0.4147 (6)	0.1181 (14)	0.415 (2)
1C42	0.3972 (9)	0.1548 (23)	0.506 (3)
1C43	0.3958 (7)	0.0834 (15)	0.318 (2)
1C44	0.4372 (8)	0.1744 (19)	0.358 (4)
1C51	0.4650 (6)	−0.2785 (13)	0.910 (2)
1C52	0.4478 (8)	−0.2400 (18)	1.007 (3)
1C53	0.4437 (8)	−0.3306 (16)	0.848 (3)
1C54	0.4958 (6)	−0.3243 (19)	0.943 (3)
1C61	0.4198 (8)	−0.2963 (18)	0.425 (3)
1C62	0.4029 (9)	−0.2718 (20)	0.324 (3)
1C63	0.3980 (10)	−0.3302 (22)	0.521 (3)
1C64	0.4454 (10)	−0.3636 (19)	0.400 (5)
2C11	0.1668 (6)	0.3401 (16)	0.435 (2)
2C12	0.1553 (6)	0.4143 (14)	0.373 (2)
2C13	0.1383 (6)	0.2844 (18)	0.472 (3)
2C14	0.1912 (6)	0.2928 (17)	0.364 (2)
2C21	0.2201 (8)	0.4257 (17)	0.901 (3)
2C22	0.2507 (11)	0.4703 (17)	0.868 (3)
2C23	0.2313 (9)	0.3615 (19)	0.974 (2)
2C24	0.2002 (8)	0.4897 (22)	0.950 (3)
2C31	0.2891 (8)	0.2342 (17)	0.341 (2)
2C32	0.2759 (8)	0.2784 (22)	0.241 (3)
2C33	0.2898 (13)	0.1479 (26)	0.313 (3)
2C34	0.3227 (7)	0.2746 (23)	0.376 (4)
2C41	0.3264 (7)	0.2814 (23)	0.807 (3)
2C42	0.3381 (7)	0.3600 (21)	0.834 (4)
2C43	0.3431 (6)	0.2338 (28)	0.735 (4)
2C44	0.3269 (9)	0.2418 (28)	0.936 (5)
2C51	0.1662 (11)	0.0385 (23)	0.508 (4)
2C52	0.1650 (11)	0.0345 (21)	0.384 (3)
2C53	0.1341 (11)	0.0530 (26)	0.536 (6)
2C54	0.1777 (13)	−0.0248 (17)	0.590 (5)
2C61	0.1881 (12)	0.1145 (24)	1.010 (3)
2C62	0.1715 (13)	0.163 (3)	1.092 (3)
2C63	0.1776 (18)	0.038 (3)	0.977 (5)
2C64	0.2178 (14)	0.102 (4)	1.068 (5)

[a] Numbers in parentheses are errors in the last significant digit(s).

Table V. Selected Interatomic Distances (Å) in the $[MoL_4L'X]^+$ Cation, Where L = *t*-BuNC and L′ = *t*-BuHNCCNH-*t*-Bu

	$[MoL_4L'I]^+$		$[MoL_4L'Br]^+$	
	as I^- salt	as PF_6^- salt	cation 1	cation 2
Mo-X	2.895 (1)	2.893 (1)	2.684 (3)	2.681 (3)
Mo-C1	2.042 (8)	2.019 (8)	2.02 (2)	2.04 (2)
Mo-C2	2.045 (8)	2.032 (8)	2.04 (2)	2.03 (2)
Mo-C3	2.126 (8)	2.122 (8)	2.11 (2)	2.14 (2)
Mo-C4	2.122 (8)	2.122 (9)	2.10 (2)	2.12 (2)
Mo-C5	2.115 (8)	2.123 (9)	2.14 (2)	2.11 (3)
Mo-C6	2.118 (8)	2.121 (8)	2.12 (2)	2.23 (3)
C1-C2	1.348 (10)	1.358 (10)	1.35 (2)	1.34 (3)
C1-N1	1.320 (9)	1.338 (9)	1.34 (2)	1.38 (2)
C2-N2	1.323 (9)	1.324 (9)	1.30 (2)	1.37 (3)
N1-H1	0.86 (9)	0.87 (6)		
N2-H2	0.88 (6)	0.75 (7)		
H1-H2	2.08 (10)	2.34 (9)		
N1-C11	1.50 (1)	1.49 (1)	1.53 (2)	1.50 (3)
N2-C21	1.45 (1)	1.47 (1)	1.52 (3)	1.51 (3)
C3-N3	1.150 (9)	1.142 (9)	1.17 (2)	1.12 (2)
C4-N4	1.130 (9)	1.153 (9)	1.19 (2)	1.16 (2)
C5-N5	1.136 (9)	1.145 (10)	1.14 (2)	1.15 (3)
C6-N6	1.153 (9)	1.117 (9)	1.20 (2)	1.17 (3)
N3-C31	1.44 (1)	1.46 (1)	1.48 (2)	1.43 (3)
N4-C41	1.49 (1)	1.46 (1)	1.47 (3)	1.41 (2)
N5-C51	1.47 (1)	1.44 (1)	1.45 (3)	1.47 (3)
N6-C61	1.44 (1)	1.46 (1)	1.42 (3)	1.38 (3)
mean C-C(methyl)	1.498 (13)[a]	1.504 (15)[b]	1.54 (3)	1.51 (4)
range	1.44-1.54	1.47-1.54	1.42-1.82	1.37-1.67

[a] Standard deviations quoted are the average of the standard deviations of the individual bond lengths. [b] For ordered methyl carbon atoms only. Corresponding figures for all methyl carbon atoms including disordered atoms are 1.528 (24) Å for the mean C-C distance, with a range of 1.35-1.75 Å.

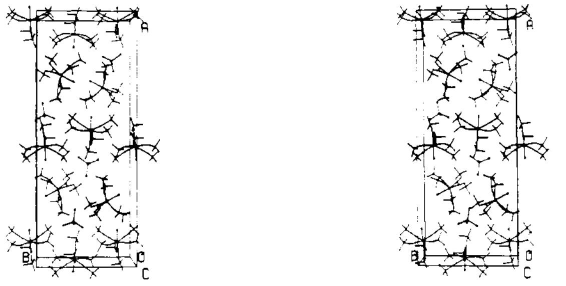

Figure 4. Stereoscopic view of the crystal packing in $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)Br]_2ZnBr_4$.

atom labeling scheme are virtually identical with that of the iodide salt (Figure 2).

Bromotetrakis(*tert*-butyl isocyanide)((*N*,*N*′-di-*tert*-butyldiamino)acetylene)molybdenum(II) Tetrabromozincate(II). A Patterson map revealed the positions of the nine heavy atoms (2 Mo, 6 Br, Zn) which were used to assign phases. The structure solution proceeded normally. Following refinement with anisotropic temperature factors assigned for the heavy atoms and individual isotropic temperature factors for the 72 carbon and nitrogen atoms, a check on the handedness of the structure was made by refining the identical model with coordinates of all atoms changed to $\bar{x}, \bar{y}, \bar{z}$. The conventional R factor rose from 0.083 to 0.088, and the weighted R factor rose from 0.087 to 0.093. This change is very significant and confirms the handedness of the crystal structure here presented.

Difference electron density maps were calculated in the planes of the methyl carbon atoms in the same manner as for the iodo salts. No clear indication of disordering of the methyl groups was observed.

Refinement continued with assignment of anisotropic temperature factors to all atoms. Parameters for the light atoms were refined in alternate cycles, while the scale factor and heavy-atom parameters were refined on every cycle. No attempt was made to allow for contributions from hydrogen atoms. While the number of variables used in these final cycles was very large, there was a significant improvement in the agreement factors. The Hamilton "R factor ratio" was 1.19, much larger than the maximum ratio of 1.06 expected at the 99.5% confidence level for purely random thermal parameters for the carbon atoms. Details on the final cycle of least-squares refinement are given in Table I. A weighting analysis showed average values of $w\Delta^2$ varying by no more than a factor of about 3 over various ranges in $|F|$ and in $(\sin\theta)/\lambda$. Final refined positional and thermal parameters for the tetrabromozincate salt are given in Tables IV and S7, respectively, and the geometry is reported in Tables V, VI, and VIII. Table S8 lists the root-mean-square thermal amplitudes and Table S9 the final observed and calculated structure factor amplitudes. The geometries of the two cations are virtually identical with that of the iodide salt (Figure 2). The atom labeling scheme is the same as for the iodo salts, with a prefix numerical added to differentiate the cations. A packing diagram is provided in Figure 4.

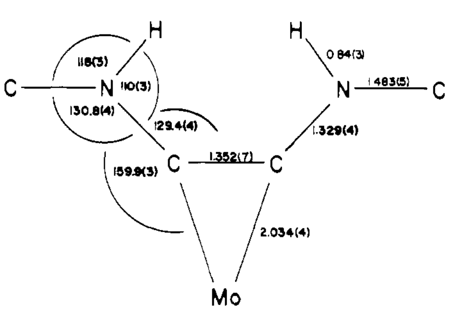

Figure 5. Some weighted average dimensions of the coupled ligand *t*-BuHNCCNH-*t*-Bu. Numbers in parentheses are standard deviations, defined as $[\sum_i(\sigma_i^{-2})]^{-1/2}$, where σ_i is the estimated standard deviation in the *i*th bond length.

Description and Discussion of the Structures

The crystals of all of the three salts reported in this paper are made up of $[MoL_4L'X]^+$ cations and of the respective counterions I^-, PF_6^-, and $ZnBr_4^{2-}$. The first two salts are isomorphous, with the PF_6^- and I^- anions occupying the same lattice sites. In each of the cations, there is a coupled ligand, *t*-BuHNCCNH-*t*-Bu ≡ L′, which is trans to the halogen atom (Figure 2). The coordination geometries of the four crystallographically independent cations in these three salts are very similar. The geometries are compared with those of the parent complexes $[MoL_6I]^+$[4] and $[MoL_6Br]^+$[5b] in Table IX. Formation of the coupled ligand leads to a slight increase in the metal-halogen distance, Mo-I increasing from 2.862 Å in $[MoL_6I]^+$ to 2.894 Å in $[MoL_4L'I]^+$ and Mo-Br increasing from 2.673 Å in $[MoL_6Br]^+$ to 2.683 Å in $[MoL_4L'Br]^+$. The Mo-C distances adjacent to the halogen atom appear to increase by about 0.01 Å, and the Mo-C distances trans to the halogen atom appear to decrease by about 0.01 Å on the formation of the coupled ligand. The geometry of the $[MoL_4L'X]^+$ cations can be described as that of the capped trigonal prism, in the same way as for the parent $[MoL_6X]^+$ ions. The prism edge opposite the capped face is reduced to 1.35 Å because of the formation of the coupled ligand, and the edges joining the capped face to the carbon atoms of the coupled ligand are increased from 2.53 to 2.87 Å. Alternatively, the geometry can be viewed as octahedral, with the coupled ligand occupying one coordination site, rather than two. In either case, the idealized symmetry of the $[MoC_6X]$ inner coordination sphere would be C_{2v}, with the mirror planes intersecting in the Mo-I or Mo-Br bond. The geometry actually found for the parent complexes approximates this symmetry, but the coupled ligand complexes show significant deviations, as can be seen from the C···C distances bordering the capped face given in Table IX. The distortions for the two iodo salts are quite similar with the two "vertical" (r) edges, C3-C4 and C5-C6, differing by 0.15 Å. These edges are crystallographically identical in the parent $[MoL_6I]^+$ cation. The "horizontal" (t) edges differ only slightly in the iodo complexes, whereas there are significant distortions involving

Table VI. Selected Bond Angles (Deg) in the $[MoL_4L'X]^+$ Cation, Where L = *t*-BuNC and L′ = *t*-BuHNCCNH-*t*-Bu

			$[MoL_4L'Br]_2ZnBr_4$	
atoms	$[MoL_4L'I]I$	$[MoL_4L'I]PF_6$	molecule 1	molecule 2
X-Mo-C3	78.4 (2)	78.8 (2)	78.0 (6)	82.1 (7)
X-Mo-C4	81.1 (2)	81.3 (2)	83.5 (5)	78.1 (6)
X-Mo-C5	79.6 (2)	79.9 (2)	79.9 (6)	77.5 (6)
X-Mo-C6	79.5 (2)	79.2 (2)	80.3 (6)	79.8 (6)
C1-Mo-C2	38.5 (3)	39.2 (3)	38.8 (7)	38.6 (7)
C1-Mo-C3	87.6 (3)	87.0 (3)	87.3 (9)	89.3 (9)
C1-Mo-C5	85.8 (3)	86.2 (3)	86.8 (8)	86.4 (8)
C2-Mo-C4	86.9 (3)	86.2 (3)	83.7 (8)	86.3 (9)
C2-Mo-C6	86.8 (3)	86.6 (3)	86.9 (8)	88.5 (9)
C3-Mo-C4	83.4 (3)	84.3 (3)	84.3 (8)	83.4 (9)
C3-Mo-C5	89.5 (3)	89.7 (3)	90.7 (7)	89.8 (9)
C4-Mo-C6	90.5 (3)	90.8 (3)	94.2 (7)	94.2 (9)
C5-Mo-C6	89.3 (3)	88.0 (3)	84.6 (8)	84.9 (10)
Mo-C1-N1	159.6 (6)	159.2 (6)	162 (2)	161 (2)
Mo-C2-N2	160.5 (6)	160.1 (7)	159 (2)	160 (2)
Mo-C3-N3	172.9 (7)	173.4 (7)	171 (2)	171 (2)
Mo-C4-N4	176.8 (7)	175.8 (7)	171 (2)	168 (2)
Mo-C5-N5	174.4 (7)	175.3 (8)	172 (2)	174 (2)
Mo-C6-N6	173.6 (7)	175.0 (8)	174 (2)	176 (2)
C1-C2-N2	128.9 (8)	129.9 (8)	131 (2)	129 (2)
C2-C1-N1	129.5 (8)	129.8 (7)	126 (2)	129 (2)
C1-N1-C11	130.9 (8)	131.3 (7)	129 (2)	126 (2)
C2-N2-C21	131.5 (8)	131.5 (8)	131 (2)	125 (2)
C1-N1-H1	99 (7)	113 (5)		
C2-N2-H2	110 (4)	112 (6)		
C11-N1-H1	129 (7)	113 (5)		
C21-N2-H2	118 (4)	116 (6)		
C3-N3-C31	168.4 (8)	167.9 (9)	166 (2)	176 (3)
C4-N4-C41	172.2 (9)	173.0 (9)	178 (2)	174 (3)
C5-N5-C51	173.5 (9)	170.2 (9)	165 (2)	169 (3)
C6-N6-C61	169.4 (9)	170.0 (9)	178 (3)	169 (3)
mean N-C-C(methyl)				
groups 1 and 2	109.5 (8)[a]	108.5 (8)[b]	109 (2)	108 (2)
groups 3-6	107.8 (8)	107.8 (9)	107 (2)	108 (2)
mean C(methyl)-C-C(methyl)				
groups 1 and 2	109.4 (8)	110.4 (9)	109 (2)	110 (3)
groups 3-6	111.0 (9)	111.1 (13)	111 (3)	111 (4)

[a] Standard deviations quoted are the averages of the standard deviations of the individual bond angles. [b] For ordered methyl carbon atoms only.

Table VII. Geometry of the PF_6^- Anion in $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)I]PF_6$

	Distances, Å		
P-F1	1.55 (1)	P-F4	1.51 (1)
P-F2	1.56 (1)	P-F5	1.45 (1)
P-F3	1.47 (1)	P-F6	1.54 (1)
	Angles, Deg		
F1-P-F2	87.6 (6)	F3-P-F5	94.8 (7)
F1-P-F3	89.6 (6)	F3-P-F6	88.9 (7)
F1-P-F5	91.6 (5)	F4-P-F5	95.3 (6)
F1-P-F6	84.8 (6)	F4-P-F6	87.8 (6)
F2-P-F4	85.8 (5)	F1-P-F4	170.4 (7)
F2-P-F5	89.9 (7)	F2-P-F3	174.6 (7)
F2-P-F6	86.3 (7)	F5-P-F6	174.8 (9)
F3-P-F4	96.5 (7)		

Table VIII. Geometry of the $ZnBr_4^{2-}$ Anion in $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)Br]_2ZnBr_4$

	Distances, Å		
Zn-Br3	2.432 (4)	Zn-Br5	2.411 (4)
Zn-Br4	2.431 (4)	Zn-Br6	2.387 (4)
	Angles, Deg		
Br3-Zn-Br4	108.0 (1)	Br4-Zn-Br5	104.0 (2)
Br3-Zn-Br5	110.5 (2)	Br4-Zn-Br6	112.4 (2)
Br3-Zn-Br6	109.8 (2)	Br5-Zn-Br6	112.1 (2)

both horizontal and vertical edges in the bromo complexes $[MoL_4L'Br]^+$.

The geometry of the coupled ligand *t*-BuHNCCNH-*t*-Bu is depicted in Figure 5, where the weighted averages of distances and angles for the four independent cations are shown. We may consider the coupled ligand formally as an (*N*,*N*′-di-*tert*-butyldiamino)acetylene molecule, stabilized by coordination to the molybdenum atom. The increase of the C–C distance from 1.20 Å in acetylene to 1.35 Å in the complex parallels the changes in ethynyl geometry normally found on π bonding of acetylenes to metal atoms, as does the reduction in the N—C≡C angle from 180 to 130°, as the acetylene substituents are pushed back from the metal atom.[15] It should be noted, however, that the near planarity of the amino groups (Figure 5) suggests contributions from other resonance forms (see ref 11 for discussion). Studies of alkyne ligands bound to Mo and W have shown that the formal number of electrons donated to the metal center can vary from 2 to 4 in order to satisfy the electronic requirements of the metal.[16] From the ^{13}C chemical shift data[11,16] it is apparent that the coupled ligand is formally a four-electron donor and that the molybdenum atom in the $[MoL_4L'X]^+$ cations achieves a closed-shell configuration.

The *tert*-butyl isocyanide ligands and the PF_6^- and $ZnBr_4^{2-}$ anions have the expected geometries. The NCCN atoms of the (dialkyldiamino)acetylene ligand are rigidly coplanar, and the molybdenum and coordinated halogen atoms also lie in this plane. In the case of the iodo complexes, none of these six atoms deviates by more than 0.01 Å from the mean plane. The *tert*-butyl carbon atoms, C11 and C21, are distorted out of this plane, by amounts varying from 0.03 to 0.14 Å. The

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[15] Mason, R. *Nature (London)* **1968**, *217*, 543.

[16] Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

Table IX. Comparison of Coordination Geometries in $[MoL_6X]^+$ and $[MoL_4L'X]^+$ Cations, Where L = *t*-BuNC, L′ = *t*-BuHNCCNH-*t*-Bu, and X = Br or I

atoms	edge	$[MoL_4L'I]^{+a}$	$[MoL_6I]^{+b}$	$[MoL_4L'Br]^{+c}$	$[MoL_6Br]^{+d}$
		Distances (Å) and Angles (Deg)			
Mo–X		2.89_4	2.86_2	2.68_3	2.67_3
Mo–C (trans to X)		2.03_5	2.04_5	2.03_3	2.04_9
Mo–C (cis to X)		2.12_1	2.11_5	2.13_5	2.11_6
X–Mo–C (capped face)		79.7	81.5	79.9	81.9
X–Mo–C (unique edge)		160.6	145.1	160.7	145.4
		Nonbonded Contacts (Å) along Polyhedral Edges[e]			
C3···C4	*r*	2.84	2.87	2.83	2.83
C5···C6	*r*	2.96	(2.87)	2.90	(2.83)
C3···C5	*t*	2.99	3.01	3.02	3.09
C4···C6	*t*	3.02	3.07	3.14	3.09
C1···C3	*p*	2.87	2.51	2.85	2.52
C1···C5	*p*	2.83	(2.51)	2.91	(2.52)
C2···C4	*p*	2.85	2.54	2.90	2.54
C2···C6	*p*	2.85	(2.54)	2.81	(2.54)
C1···C2	*c*	1.35	2.36	1.34	2.33
mean *r*		2.90	2.87	2.87	2.83
mean *t*		3.00	3.04	3.08	3.09
mean *p*		2.87	2.53	2.87	2.53

[a] Mean values for the two $[MoL_4L'I]^+$ cations reported in this paper. [b] Reference 4. [c] Mean values for the $[MoL_4L'Br]^+$ cations reported in this paper. [d] Reference 5b. [e] Polyhedron edges are labeled (see ref 6) as

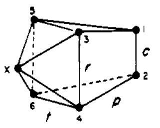

Table X. Proposed N-H···Y Hydrogen Bonds between Cations $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}BuX]^+$ and Anions Y

X	Y	N···Y, Å		H···Y, Å	N-H···Y, deg
I	I	N1···I2	3.72	3.05	136
		N2···I2	3.68	2.81	167
I	PF_6	N1···F6	3.22	2.40	155
		N2···F2	3.15	2.49	148
Br	$ZnBr_4$	2N1···Br3	3.44		
		2N2···Br3	3.43		

protons bonded to the nitrogen atoms are perforce distorted out of the mean plane, so as to diminish the H···H overcrowding that would result if they were coplanar with the NCCN fragment. For the $[MoL_4L'I]I$ compound, H1 is distorted downward from the plane by 0.3 Å, in an opposite sense to the *tert*-butyl groups, while H2 is distorted upward by a smaller amount, 0.05 Å. These two protons appear to be hydrogen bonded to the iodide ion. Relevant distances and angles are given in Table X. In the $[MoL_4L'I]PF_6$ salt, the protons H1 and H2 are displaced 0.1 and 0.2 Å out of the molecular plane of the coupled ligand. These distortions are both in the same direction and appear to result from hydrogen bonding to the PF_6^- ion. Fluorine atoms F2 and F6 of this group are also on the same side of the coupled ligand plane. The protons in $[MoL_4L'Br]_2ZnBr_4$ were not located, but hydrogen bonding to $ZnBr_4^{2-}$ for at least one of the cations is indicated (see Table X).

The isomorphism observed for the two $[MoL_4L'I]^+$ salts is similar to that observed[5b,17] in the $[MoL_6X]Y$ salts, where X = Y = Cl, Br, or I and X = CN and Y = PF_6. Contacts between methyl carbon atoms of different cations are all greater than 3.6 Å in the I^- salt, except for a short C42···C42 contact across the inversion center at ($^1/_2$, $^1/_2$, 0). Contacts between methyl carbon atoms in the PF_6^- salt are shorter, but all are greater than 3.3 Å, except for the C42···C42 contact which is 2.9 Å. Fluorine···carbon contacts range upward from 3.1 Å. The packing in the $ZnBr_4^{2-}$ salt appears to be rather more open, with one contact between methyl carbon atoms being 3.6 Å and the rest all longer than 3.7 Å. All contacts involving the Br atoms of the anion are longer than 3.8 Å, other than those to the hydrogen-bonded nitrogen atoms of the coupled ligand.

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Supplementary Material Available: Tables S1–S3 listing fixed methyl hydrogen atom parameters, root-mean-square thermal amplitudes, and observed and calculated structure factor amplitudes for $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)I]I$, Tables S4–S6 listing the same respective information for the hexafluorophosphate salt, and Tables S7–S9 listing, respectively, the final thermal parameters, root-mean-square thermal amplitudes, and observed and calculated structure factor amplitudes for $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)Br]_2ZnBr_4$ (83 pages). Ordering information is given on any current masthead page.

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(17) Szalda, D. J.; Dewan, J. C.; Hanau, L. H.; Giandomenico, C. M.; Lippard, S. J., to be submitted for publication.