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1,3-Diphenyltriazine Complexes of Dichromium(II), Dimolybdenum(II), and Chromium(III)

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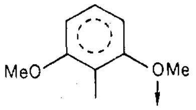
The reactions of 1,3-diphenyltriazine with the $M_2(CH_3)_8^{4-}$ anions, M = Cr or Mo, have been employed to obtain triazino-bridged Cr–Cr and Mo–Mo quadruple bonds. The reaction with $Cr_2(CH_3)_8^{4-}$ gives only a small quantity of $Cr_2(PhN_3Ph)_4$, I, the major product being $Cr(PhN_3Ph)_3$, II. The compound $Mo_2(PhN_3Ph)_4$, III, has also been prepared. All three molecules have been studied by X-ray crystallography. I crystallizes in space group $P\bar{1}$ with a = 10.302 (3) Å, b = 16.045 (6) Å, c = 13.600 (6) Å, α = 100.18 (3)°, β = 95.88 (3)°, γ = 102.93 (3)°, V = 2133 (3) Å^3, and Z = 2. The structure is qualitatively as expected, but the Cr–Cr distance is one of the shortest known, viz., 1.858 (1) Å. II crystallizes in the space group $C2/c$ with a = 20.619 (6) Å, b = 16.216 (3) Å, c = 13.534 (4) Å, β = 120.17 (2)°, V = 3912 (4) Å^3, and Z = 4. The chromium(III) is coordinated by three chelating PhN_3Ph^- ligands to give distorted octahedral geometry. III crystallizes as a toluene solvate in space group $P\bar{1}$ with a = 9.981 (2) Å, b = 24.814 (5) Å, c = 9.657 (2) Å, α = 93.79 (2)°, β = 93.81 (1)°, γ = 83.55 (2)°, V = 2367 (1) Å^3, and Z = 2. The $Mo_2(PhN_3Ph)_4$ molecule has the expected structure, and the Mo–Mo bond length, 2.083 (2) Å, is not unusual.

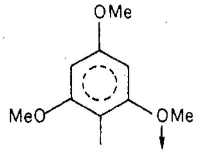
Introduction

The discovery that in certain dichromium(II) compounds of the type Cr_2L_4 there are exceptionally short Cr–Cr distances (below 1.90 Å) was made only a short time ago. The first such compound,[1] with $L^{(1)}$, having a Cr–Cr distance of 1.847 (1) Å has been followed by others with the ligands $L^{(2)}$–$L^{(7)}$, with

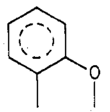
$L^{(1)}$ 1.847 (1) Å[1]



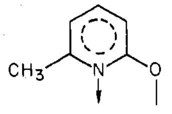
$L^{(2)}$ 1.849 (1) Å[2]



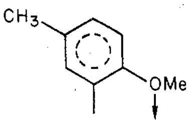
$L^{(3)}$ 1.830 (4) Å[3]



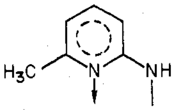
$L^{(4)}$ 1.889 (1) Å[4]



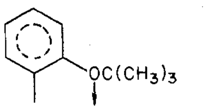
$L^{(5)}$ 1.828 (2) Å[5]



$L^{(6)}$ 1.870 (3) Å[6]



$L^{(7)}$ 1.862 (1) Å[7]



the distances indicated. In the case of $L^{(7)}$, the compound contains only two $L^{(7)}$ ligands: $Cr_2(O_2CCH_3)_2L_2^{(7)}$. The Cr–Cr bond lengths in these compounds are in sharp contrast to the much longer ones found in $Cr_2(O_2CR)_4$ compounds[8,9] which range from 2.214 (1) Å when R = O to 2.541 (1) Å when R = CF_3.

Table I. Crystallographic Parameters for the Three Compounds

parameter	$Cr_2(C_6H_5NNNC_6H_5)_4$, I	$Cr(C_6H_5NNNC_6H_5)_3\cdot C_7H_8$, II	$Mo_2(C_6H_5NNNC_6H_5)_4\cdot {}^1/_2C_7H_8$, III
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a, Å	10.302 (3)	20.619 (6)	9.981 (2)
b, Å	16.045 (6)	16.216 (3)	24.814 (5)
c, Å	13.600 (6)	13.534 (4)	9.657 (2)
α, deg	100.18 (3)	(90)	93.79 (2)
β, deg	95.88 (3)	120.17 (2)	93.81 (1)
γ, deg	102.93 (3)	(90)	83.55 (2)
V, Å^3	2133 (3)	3912 (4)	2367 (1)
d_x, g/cm^3	1.38	1.24	1.37
Z	2	4	2
formula wt	888.93	732.837	1022.88
cryst size, mm	0.35 × 0.30 × 0.20	0.2 × 0.2 × 0.45	0.2 × 0.25 × 0.35
μ, cm^{-1}	5.85	6.38	5.70
range of 2θ, deg	0–45	0–45	0–40
no. unique data	4552	2790	3889
no. data $I > 3(\sigma)$	3284	971	1834
no. variables	319	143	279
R_1	0.072	0.108	0.075
R_2	0.096	0.113	0.085
esd	1.866	1.735	1.526
largest peak, e/Å^3	0.99	0.88	0.69

In an effort to establish by experiment what features of the ligands are important in promoting the shortest Cr–Cr bonds, we have considered a number of factors and attempted to prepare and structurally characterize dichromium(II) compounds that would incorporate selected changes in these factors. One factor we have considered is the presence of an aromatic ring, since each of the compounds just mentioned contains one. Another factor is the accessibility of the Cr_2 unit to coordination by axial ligands. In all the carboxylato compounds and the carbonato compound axial ligands are present whereas in all of the compounds with supershort Cr–Cr bonds (<1.90 Å) they are absent and are probably excluded either by steric factors or by high charge on the Cr_2L_4 unit as in the case where we have $L^{(3)}$.

We report here the Cr_2L_4 compound in which L = $C_6H_5NNNC_6H_5^-$ (abbreviated PhN_3Ph). The preparation of this compound in crystalline form afforded some difficulty but was finally accomplished by the action of PhN(H)NNPh on the $Cr_2(CH_3)_8^{4-}$ ion. Surprisingly, the major isolated product of the reaction was the Cr(III) compound $Cr(PhN_3Ph)_3$ of which we determined the structure as a means of unequivocal identification. We have also prepared and characterized the corresponding molybdenum compound, $Mo_2(PhN_3Ph)_4$, since the ligands that give the very short Cr–Cr bonds have usually

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Table II

(A) Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr_2(C_6H_5NNNC_6H_5)_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr(1)	0.2294 (1)	0.30796 (8)	0.2127 (1)	2.22 (5)	2.99 (5)	2.22 (5)	0.71 (4)	0.45 (4)	0.78 (5)
Cr(2)	0.1486 (1)	0.21369 (8)	0.2659 (1)	2.25 (5)	2.84 (5)	2.38 (5)	0.65 (4)	0.55 (5)	0.76 (5)
N(1)	0.3538 (7)	0.1633 (4)	0.1556 (5)	2.9 (3)	2.9 (3)	2.6 (3)	1.0 (2)	0.3 (3)	0.9 (2)
N(3)	−0.0035 (7)	0.2046 (4)	0.0729 (5)	3.0 (3)	3.2 (3)	3.1 (3)	1.2 (2)	0.6 (3)	0.5 (3)
N(5)	0.0179 (7)	0.3504 (4)	0.3272 (5)	2.6 (3)	3.6 (3)	3.3 (3)	1.2 (2)	0.8 (3)	0.7 (3)
N(7)	0.3828 (7)	0.3222 (4)	0.4079 (5)	2.8 (3)	3.8 (3)	2.4 (3)	0.8 (3)	0.5 (3)	0.9 (3)
N(11)	0.3445 (6)	0.2380 (4)	0.1338 (5)	2.7 (3)	3.0 (3)	2.4 (3)	1.0 (2)	0.8 (2)	1.1 (2)
N(21)	0.2743 (6)	0.1388 (4)	0.2195 (5)	2.5 (3)	2.8 (3)	2.5 (3)	0.5 (2)	0.8 (2)	0.9 (2)
N(31)	0.0859 (6)	0.2787 (4)	0.0908 (5)	2.5 (3)	2.0 (3)	3.0 (3)	0.4 (2)	0.4 (2)	0.6 (2)
N(41)	0.0135 (6)	0.1569 (4)	0.1386 (5)	2.5 (3)	2.7 (3)	2.5 (3)	0.4 (2)	0.4 (2)	0.9 (2)
N(51)	0.1236 (7)	0.3876 (4)	0.2938 (5)	2.8 (3)	3.1 (3)	2.5 (3)	0.7 (2)	0.5 (2)	0.8 (2)
N(61)	0.0017 (7)	0.2671 (4)	0.3177 (5)	2.5 (3)	3.2 (3)	3.1 (3)	0.5 (2)	0.7 (3)	0.8 (3)
N(71)	0.3884 (7)	0.3530 (4)	0.3257 (5)	2.7 (3)	3.0 (3)	2.3 (3)	0.6 (2)	0.4 (2)	0.9 (2)
N(81)	0.2711 (7)	0.2621 (4)	0.4029 (5)	2.6 (3)	2.9 (3)	2.7 (3)	0.2 (2)	0.6 (2)	1.0 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.4366 (8)	0.2643 (5)	0.0667 (6)	2.3 (2)	C(51)	0.1533 (8)	0.4816 (5)	0.3222 (6)	2.8 (2)
C(12)	0.3962 (9)	0.3016 (6)	−0.0108 (7)	3.4 (2)	C(52)	0.2693 (9)	0.5307 (6)	0.2954 (7)	3.4 (2)
C(13)	0.4872 (10)	0.3272 (6)	−0.0789 (8)	4.5 (2)	C(53)	0.3064 (9)	0.6209 (6)	0.3280 (7)	3.9 (2)
C(14)	0.6172 (10)	0.3154 (6)	−0.0632 (8)	4.7 (2)	C(54)	0.2286 (10)	0.6615 (6)	0.3877 (8)	4.5 (2)
C(15)	0.6592 (10)	0.2784 (6)	0.0151 (7)	4.4 (2)	C(55)	0.1126 (10)	0.6135 (6)	0.4141 (8)	4.6 (2)
C(16)	0.5671 (9)	0.2541 (6)	0.0822 (7)	3.8 (2)	C(56)	0.0739 (9)	0.5220 (6)	0.3820 (7)	3.5 (2)
C(21)	0.2748 (8)	0.0551 (5)	0.2384 (6)	2.8 (2)	C(61)	−0.1249 (8)	0.2210 (5)	0.3390 (6)	2.8 (2)
C(22)	0.3147 (10)	−0.0044 (6)	0.1709 (7)	4.4 (2)	C(62)	−0.1328 (9)	0.1387 (6)	0.3563 (7)	3.6 (2)
C(23)	0.3117 (13)	−0.0877 (8)	0.1923 (10)	6.9 (3)	C(63)	−0.2562 (10)	0.0885 (7)	0.3737 (8)	4.6 (2)
C(24)	0.2701 (11)	−0.1072 (7)	0.2811 (9)	5.7 (3)	C(64)	−0.3667 (10)	0.1237 (6)	0.3734 (8)	4.6 (2)
C(25)	0.2278 (11)	−0.0481 (7)	0.3479 (8)	5.1 (2)	C(65)	−0.3577 (10)	0.2065 (6)	0.3548 (8)	4.7 (2)
C(26)	0.2297 (9)	0.0354 (6)	0.3248 (7)	3.9 (2)	C(66)	−0.2339 (9)	0.2581 (6)	0.3380 (7)	3.5 (2)
C(31)	0.0703 (8)	0.3285 (5)	0.0139 (6)	2.8 (2)	C(71)	0.5089 (8)	0.4189 (5)	0.3289 (6)	2.8 (2)
C(32)	0.1370 (10)	0.4140 (6)	0.0352 (7)	4.2 (2)	C(72)	0.5969 (8)	0.4573 (5)	0.4173 (6)	3.0 (2)
C(33)	0.1327 (11)	0.4665 (7)	−0.0367 (8)	5.1 (2)	C(73)	0.7089 (10)	0.5259 (6)	0.4155 (7)	4.2 (2)
C(34)	0.0574 (10)	0.4274 (7)	−0.1326 (8)	4.7 (2)	C(74)	0.7324 (10)	0.5544 (6)	0.3250 (7)	4.3 (2)
C(35)	−0.0079 (11)	0.3422 (7)	−0.1527 (8)	5.2 (2)	C(75)	0.6428 (9)	0.5146 (6)	0.2384 (7)	3.7 (2)
C(36)	−0.0017 (10)	0.2880 (6)	−0.0812 (7)	4.1 (2)	C(76)	0.5311 (9)	0.4466 (5)	0.2380 (7)	3.2 (2)
C(41)	−0.0940 (8)	0.0785 (5)	0.1216 (6)	2.7 (2)	C(81)	0.2663 (8)	0.2310 (5)	0.4941 (6)	3.1 (2)
C(42)	−0.0640 (9)	0.0009 (6)	0.1203 (7)	3.6 (2)	C(82)	0.3803 (10)	0.2137 (7)	0.5419 (8)	4.6 (2)
C(43)	−0.1720 (10)	−0.0746 (6)	0.1070 (7)	4.4 (2)	C(83)	0.3720 (12)	0.1800 (8)	0.6319 (9)	6.6 (3)
C(44)	−0.3020 (10)	−0.0671 (6)	0.0996 (7)	4.4 (2)	C(84)	0.2519 (12)	0.1637 (8)	0.6694 (9)	6.5 (3)
C(45)	−0.3301 (10)	0.0120 (7)	0.1013 (8)	4.7 (2)	C(85)	0.1412 (11)	0.1838 (7)	0.6212 (9)	5.7 (3)
C(46)	−0.2276 (10)	0.0872 (6)	0.1118 (7)	4.0 (2)	C(86)	0.1463 (9)	0.2166 (6)	0.5309 (7)	3.9 (2)

(B) Positional and Thermal Parameters and Their Estimated Standard Deviations for $Cr(C_6H_5NNNC_6H_5)_3$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	0.5000 (0)	0.2481 (3)	0.7500 (0)	3.8 (1)	2.9 (1)	3.6 (1)	0	1.87 (8)	0
N(11)	0.5625 (5)	0.2292 (7)	0.6767 (8)	3.4 (5)	3.5 (7)	2.6 (5)	−0.0 (5)	1.0 (3)	−0.1 (5)
N(1)	0.5184 (5)	0.1719 (8)	0.6032 (9)	2.2 (4)	4.3 (6)	4.8 (5)	−0.1 (5)	1.6 (3)	0.3 (6)
N(21)	0.4625 (6)	0.1641 (7)	0.6237 (8)	3.8 (5)	1.9 (5)	3.1 (5)	−0.2 (5)	1.2 (3)	−0.3 (5)
N(31)	0.4608 (5)	0.3546 (7)	0.6649 (9)	2.2 (5)	2.9 (6)	3.3 (5)	−1.2 (5)	0.4 (4)	−0.9 (5)
N(3)	0.5000 (0)	0.4024 (10)	0.7500 (0)	5.0 (8)	2.6 (8)	4.8 (8)	0	2.3 (5)	0

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(11)	0.6234 (6)	0.2577 (10)	0.6653 (9)	3.0 (3)	C(32)	0.4290 (8)	0.4747 (10)	0.5397 (12)	4.7 (4)
C(12)	0.6250 (7)	0.2427 (11)	0.5646 (10)	4.4 (3)	C(33)	0.3870 (9)	0.5063 (11)	0.4289 (13)	5.8 (5)
C(13)	0.6877 (8)	0.2753 (10)	0.5604 (12)	5.2 (4)	C(34)	0.3331 (9)	0.4614 (11)	0.3379 (13)	5.8 (5)
C(14)	0.7419 (8)	0.3206 (10)	0.6520 (12)	5.3 (4)	C(35)	0.3188 (8)	0.3769 (11)	0.3550 (13)	5.7 (5)
C(15)	0.7406 (8)	0.3347 (10)	0.7505 (12)	4.2 (4)	C(36)	0.3650 (8)	0.3411 (10)	0.4669 (12)	4.6 (4)
C(16)	0.6785 (7)	0.3026 (9)	0.7584 (11)	3.8 (4)	C(1)	0.5431 (16)	0.1110 (21)	0.2331 (24)	5.2 (9)
C(21)	0.4125 (7)	0.0996 (8)	0.5682 (10)	3.0 (3)	C(2)	0.5307 (16)	0.1808 (23)	0.2396 (26)	6.9 (11)
C(22)	0.4184 (7)	0.0470 (9)	0.4888 (11)	3.5 (4)	C(3)	0.5256 (15)	0.3390 (22)	0.2273 (24)	5.9 (9)
C(23)	0.3638 (8)	−0.0194 (10)	0.4383 (12)	4.4 (4)	C(4)	0.5000 (0)	0.0941 (33)	0.2500 (0)	6.7 (14)
C(24)	0.3079 (9)	−0.0272 (11)	0.4665 (13)	5.4 (4)	C(5)	0.4460 (16)	0.2008 (21)	0.2845 (26)	5.5 (9)
C(25)	0.2985 (9)	0.0280 (11)	0.5369 (13)	6.0 (5)	C(6)	0.5000 (0)	0.2747 (36)	0.2500 (0)	8.5 (17)
C(26)	0.3540 (8)	0.0937 (10)	0.5937 (12)	5.0 (4)	C(7)	0.4550 (14)	0.2574 (24)	0.2720 (22)	5.6 (8)
C(31)	0.4148 (7)	0.3902 (9)	0.5526 (11)	3.9 (4)					

(C) Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(C_6H_5NNNC_6H_5)_4$[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.3866 (2)	0.30428 (8)	0.1819 (2)	3.6 (1)	3.19 (9)	4.7 (1)	−1.63 (8)	0.04 (9)	0.76 (9)
Mo(2)	0.3290 (2)	0.23173 (8)	0.2430 (2)	3.06 (9)	3.25 (9)	4.5 (1)	−1.54 (8)	−0.19 (9)	1.15 (9)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
N(11)	0.200 (2)	0.3487 (7)	0.244 (2)	4.8 (5)	C(44)	0.506 (3)	0.1187 (10)	0.735 (3)	5.7 (6)
N(1)	0.112 (2)	0.3242 (7)	0.310 (2)	4.6 (5)	C(45)	0.459 (3)	0.1070 (10)	0.599 (3)	6.3 (7)
N(21)	0.150 (2)	0.2743 (7)	0.324 (2)	3.4 (4)	C(46)	0.430 (3)	0.1489 (11)	0.504 (3)	6.3 (7)
N(31)	0.482 (2)	0.3193 (6)	0.303 (2)	3.4 (4)	C(51)	0.686 (2)	0.2880 (8)	0.057 (2)	3.3 (5)

Table II (*Continued*)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
N(3)	0.494 (2)	0.2839 (7)	0.480 (2)	4.0 (4)	C(52)	0.691 (2)	0.3428 (9)	0.102 (2)	4.2 (6)
N(41)	0.440 (2)	0.2399 (7)	0.441 (2)	4.1 (4)	C(53)	0.800 (2)	0.3698 (10)	0.053 (3)	5.3 (6)
N(51)	0.574 (2)	0.2639 (6)	0.113 (2)	3.3 (4)	C(54)	0.886 (3)	0.3416 (10)	−0.033 (3)	5.9 (7)
N(5)	0.599 (2)	0.2106 (7)	0.116 (2)	3.9 (4)	C(55)	0.880 (3)	0.2857 (11)	−0.074 (3)	6.3 (7)
N(61)	0.501 (2)	0.1876 (7)	0.166 (2)	4.3 (4)	C(56)	0.768 (2)	0.2594 (9)	−0.028 (2)	4.5 (6)
N(71)	0.297 (2)	0.2914 (7)	−0.024 (2)	4.4 (5)	C(61)	0.542 (2)	0.1315 (9)	0.165 (2)	4.9 (6)
N(7)	0.229 (2)	0.2489 (8)	−0.057 (2)	5.4 (5)	C(62)	0.440 (2)	0.0958 (9)	0.158 (2)	4.1 (5)
N(81)	0.224 (2)	0.2172 (7)	0.045 (2)	4.5 (5)	C(63)	0.470 (2)	0.0417 (10)	0.162 (3)	5.3 (6)
C(11)	0.154 (2)	0.4057 (8)	0.227 (2)	2.8 (5)	C(64)	0.602 (2)	0.0163 (10)	0.179 (3)	5.8 (7)
C(12)	0.050 (2)	0.4305 (9)	0.305 (2)	4.2 (5)	C(65)	0.704 (3)	0.0509 (11)	0.191 (3)	6.7 (7)
C(13)	0.012 (2)	0.4882 (10)	0.284 (3)	5.7 (7)	C(66)	0.675 (3)	0.1103 (11)	0.187 (3)	6.8 (7)
C(14)	0.071 (2)	0.5127 (10)	0.182 (3)	5.6 (6)	C(71)	0.290 (2)	0.3253 (8)	−0.138 (2)	3.4 (5)
C(15)	0.177 (3)	0.4866 (11)	0.108 (3)	7.1 (8)	C(72)	0.186 (2)	0.3274 (9)	−0.241 (2)	4.4 (6)
C(16)	0.218 (3)	0.4293 (10)	0.127 (3)	6.1 (7)	C(73)	0.189 (2)	0.3616 (10)	−0.347 (3)	5.4 (6)
C(21)	0.052 (2)	0.2486 (9)	0.390 (2)	4.4 (6)	C(74)	0.297 (2)	0.3954 (9)	−0.350 (2)	4.9 (6)
C(22)	−0.085 (3)	0.2592 (10)	0.336 (3)	6.1 (7)	C(75)	0.395 (3)	0.3919 (10)	−0.248 (3)	5.9 (7)
C(23)	−0.178 (3)	0.2298 (10)	0.404 (3)	5.9 (7)	C(76)	0.401 (2)	0.3562 (10)	−0.143 (3)	4.9 (6)
C(24)	−0.142 (3)	0.2009 (10)	0.519 (3)	6.2 (7)	C(81)	0.160 (2)	0.1699 (9)	0.001 (2)	3.8 (5)
C(25)	−0.011 (3)	0.1928 (11)	0.570 (3)	7.3 (8)	C(82)	0.175 (2)	0.1456 (9)	−0.128 (2)	4.8 (6)
C(26)	0.091 (2)	0.2189 (10)	0.505 (3)	5.5 (6)	C(83)	0.115 (3)	0.0950 (10)	−0.164 (3)	6.0 (7)
C(31)	0.563 (2)	0.3649 (8)	0.426 (2)	3.2 (5)	C(84)	0.035 (3)	0.0767 (10)	−0.063 (3)	6.4 (7)
C(32)	0.672 (2)	0.3566 (10)	0.520 (3)	5.5 (6)	C(85)	0.025 (3)	0.0997 (10)	0.071 (3)	6.0 (7)
C(33)	0.745 (3)	0.4046 (10)	0.554 (3)	6.3 (7)	C(86)	0.087 (2)	0.1507 (10)	0.107 (3)	5.1 (6)
C(34)	0.704 (3)	0.4497 (10)	0.486 (3)	6.2 (7)	C(1)	0.168 (5)	0.0131 (22)	0.419 (6)	6.7 (14)
C(35)	0.592 (3)	0.4599 (10)	0.401 (3)	5.8 (7)	C(2)	0.053 (5)	0.0401 (21)	0.435 (5)	6.4 (14)
C(36)	0.515 (2)	0.4124 (8)	0.365 (2)	3.7 (5)	C(3)	0.044 (5)	−0.0524 (19)	0.517 (5)	5.3 (12)
C(41)	0.460 (2)	0.2007 (9)	0.543 (2)	3.9 (5)	C(4)	−0.054 (5)	0.0148 (22)	0.517 (6)	7.3 (16)
C(42)	0.504 (3)	0.2139 (10)	0.680 (3)	6.0 (7)	C(5)	0.166 (7)	−0.0374 (28)	0.436 (7)	10.1 (20)
C(43)	0.530 (3)	0.1706 (12)	0.773 (3)	7.6 (8)					

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

also given the shortest (ca. 2.06–2.07 Å) Mo–Mo bonds. The triazinato ligand differs from those above already known to give very short Cr–Cr bonds in not having a ligating atom incorporated into an aromatic ring but resembles most of them in providing a steric barrier to the approach of axial ligands.

Experimental Section

Preparations. All reactions were conducted in an argon atmosphere. Crystals were examined under a layer of heavy, degassed mineral oil and mounted in glass capillaries with epoxy cement.

The starting materials, 1,3-diphenyltriazene,[10] lithium octamethyldichromium(II),[11] and lithium octamethyldimolybdenum(II),[12] were prepared by methods available in the literature.

$Cr_2(C_6H_5NNNC_6H_5)_4$, I, and $Cr(C_6H_5NNNC_6H_5)_3(solvent)_{1/2}$, II. In a typical experiment, a solution of 0.17 g (0.31 mmol) of $[Li(THF)]_4[Cr_2(CH_3)_8]$ in 20 mL of THF was treated with 0.60 g (3.0 mmol) of 1,3-diphenyltriazene in 10 mL of THF. Mixing of the two pale yellow solutions was accompanied by effervescence and a change in color to deep red. Half (15 mL) of the resulting solution was placed in a Schlenk tube and covered with an equal volume of heptane. Slow diffusion of heptane into the solution precipitated a mixture of yellow needles, presumed to be pure 1,3-diphenyltriazene, and red blocky crystals shown, vide infra, to contain the oxidation product $Cr(C_6H_5NNNC_6H_5)_3$.

The remainder of the original reaction mixture was stripped of THF and dried to a dark mass. The residue was extracted with 20 mL of toluene, and the toluene solution was filtered into a Schlenk tube and covered with 15 mL of heptane. The precipitate in this case contained, again, yellow needles of the free ligand and red blocks of the Cr(III) product but additionally contained some orange blocks of $Cr_2(C_6H_5NNNC_6H_5)_4$.

$Mo_2(C_6H_5NNNC_6H_5)_4{\cdot}xC_6H_5CH_3$, III. A solution of 1.10 g (1.75 mmol) of $[Li(THF)]_4[Mo_2(CH_3)_8]$ in 90 mL of THF was treated with a solution of 2.80 g (14.2 mmol) of $C_6H_5N(H)NNC_6H_5$ in 35 mL of THF. Rapid effervescence due to evolution of methane was accompanied by a change in color from the deep red of the octamethyldimolybdenum(II) complex to an intense brown-red. The solvent was stripped and the residue dried under vacuum. The solid was treated with 40 mL of dry toluene. The resulting solution was filtered into a 50-mL flask. Upon standing, this solution deposited a precipitate of pale orange-brown solvated crystals of $Mo_2(C_6H_5NNNC_6H_5)_4$.

X-ray Data Collection. Data for all three compounds were collected at 21 ± 2 °C on a Syntex $P\bar{1}$ automated diffractometer using Mo Kα radiation with a graphite crystal monochromator in the incident beam. The automatic centering and indexing procedures used have been described previously.[13] Data for the chromium dimer were collected with a modified version of the standard Syntex θ–2θ data collection program. In this new procedure, devised by Dr. P. E. Fanwick of our laboratories, only if the counts during a fast prescan exceed a predetermined limit are data collected for a reflection. Therefore, weak peaks were not collected, and no output was made to the tape file for further processing. The cell constants and other crystallographic parameters for all three compounds are collected in Table I.

Solution of the Structures. During data collection for the $Cr_2(C_6H_5NNNC_6H_5)_4$, I, compound, it was recognized that this structure was isotypic with the Cu, Ni, and Pd analogues, whose structures had been published previously.[14] Refinement was commenced using the atomic parameters of the nickel analogue. The refinement was carried to convergence by use of anisotropic thermal parameters for the Cr and N atoms and isotropic thermal parameters for the C atoms. The highest peak in the final difference Fourier map had an intensity of 0.99 e/Å^3. The structure of $Cr(C_6H_5NNNC_6H_5)_3$, II, was solved by direct methods. The MULTAN program yielded two solutions with high figures of merit, with each solution corresponding to a single chromium atom chelated by three diphenyltriazenato ligands. One of these solutions placed the chromium atom upon an inversion center, requiring that the ligands be disordered. This was tested and abandoned in favor of the second solution with the chromium atom lying on a twofold axis, at the position ($^1/_2$, $^1/_4$, $^3/_4$). The chromium-containing molecule was completed by successive difference Fourier maps and refinement cycles. A difference Fourier map based upon the entire $Cr(C_6H_5NNNC_6H_5)_3$ molecule revealed a number of peaks around the point ($^1/_2$, $^1/_4$, $^1/_4$). These are doubtless due to a disordered solvent molecule of crystallization, but numerous attempts to build up a chemically reasonable molecule in this area failed, and the problem was abandoned as unworthy of further effort.

The solution of the structure of $Mo_2(C_6H_5NNNC_6H_5)_4$, III, was initiated by determination of the Mo positions from a Patterson function and completed by successive difference Fourier maps and full-matrix least-squares refinements. As with II, a difference Fourier map based upon the metal-containing molecule revealed a cluster of weak peaks that we attribute to a disordered solvent molecule. This appears to be a toluene molecule lying upon the inversion center at

Table III. Bond Distances and Angles in the $M_2(C_6H_5NNNC_6H_5)_4$ dimers

	M = Cr	M = Mo		M = Cr	M = Mo
(a) Distances (Å)					
M(1)-M(2)	1.858 (1)	2.083 (2)	C(34)-C(35)	1.35 (1)	1.36 (3)
-N(11)	2.061 (5)	2.15 (2)	C(35)-C(36)	1.42 (1)	1.49 (3)
-N(31)	2.016 (5)	2.13 (2)	C(36)-C(31)	1.391 (9)	1.38 (2)
-N(51)	2.100 (5)	2.15 (2)	C(41)-C(42)	1.346 (9)	1.40 (3)
-N(71)	2.032 (5)	2.15 (2)	C(42)-C(43)	1.42 (1)	1.43 (3)
M(2)-N(21)	2.027 (5)	2.14 (2)	C(43)-C(44)	1.37 (1)	1.36 (3)
-N(41)	2.036 (5)	2.16 (2)	C(44)-C(45)	1.36 (1)	1.39 (3)
-N(61)	2.027 (5)	2.08 (2)	C(45)-C(46)	1.39 (1)	1.42 (3)
-N(81)	2.058 (5)	2.15 (2)	C(46)-C(41)	1.409 (9)	1.38 (3)
N(11)-C(11)	1.431 (7)	1.46 (2)	C(51)-C(52)	1.397 (9)	1.40 (2)
-N(1)	1.306 (7)	1.34 (2)	C(52)-C(53)	1.389 (9)	1.46 (3)
N(21)-N(1)	1.305 (7)	1.27 (2)	C(53)-C(54)	1.38 (1)	1.34 (3)
-C(21)	1.412 (8)	1.43 (2)	C(54)-C(55)	1.39 (1)	1.43 (3)
N(31)-C(31)	1.441 (8)	1.48 (2)	C(55)-C(56)	1.41 (1)	1.46 (3)
-N(3)	1.297 (7)	1.32 (2)	C(56)-C(51)	1.392 (9)	1.32 (2)
N(41)-N(3)	1.299 (7)	1.30 (2)	C(61)-C(62)	1.369 (9)	1.42 (3)
-C(41)	1.444 (8)	1.41 (2)	C(62)-C(63)	1.41 (1)	1.35 (2)
N(51)-C(51)	1.443 (8)	1.47 (2)	C(63)-C(64)	1.38 (1)	1.40 (2)
-N(5)	1.286 (7)	1.32 (2)	C(64)-C(65)	1.38 (1)	1.40 (3)
N(61)-N(5)	1.291 (7)	1.32 (2)	C(65)-C(66)	1.42 (1)	1.47 (3)
-C(61)	1.433 (8)	1.41 (2)	C(66)-C(61)	1.384 (9)	1.38 (3)
N(71)-C(71)	1.430 (8)	1.42 (2)	C(71)-C(72)	1.383 (9)	1.39 (2)
-N(7)	1.301 (7)	1.33 (2)	C(72)-C(73)	1.411 (9)	1.37 (3)
N(81)-N(7)	1.312 (7)	1.31 (2)	C(73)-C(74)	1.41 (1)	1.44 (3)
-C(81)	1.418 (8)	1.43 (2)	C(74)-C(75)	1.38 (1)	1.34 (2)
C(11)-C(12)	1.374 (9)	1.38 (2)	C(75)-C(76)	1.396 (9)	1.38 (3)
C(12)-C(13)	1.43 (1)	1.46 (2)	C(76)-C(71)	1.410 (8)	1.42 (2)
C(13)-C(14)	1.39 (1)	1.39 (3)	C(81)-C(82)	1.39 (1)	1.36 (2)
C(14)-C(15)	1.38 (1)	1.39 (3)	C(82)-C(83)	1.43 (1)	1.46 (3)
C(15)-C(16)	1.42 (1)	1.46 (3)	C(83)-C(84)	1.37 (1)	1.42 (3)
C(16)-C(11)	1.389 (9)	1.39 (3)	C(84)-C(85)	1.38 (1)	1.38 (3)
C(21)-C(22)	1.367 (9)	1.44 (3)	C(85)-C(86)	1.42 (1)	1.48 (3)
C(22)-C(23)	1.41 (1)	1.46 (3)	C(86)-C(81)	1.368 (9)	1.42 (3)
C(23)-C(24)	1.38 (1)	1.36 (3)	C(1)-C(2)		1.27 (6)
C(24)-C(25)	1.37 (1)	1.36 (3)	C(2)-C(3′)		1.11 (5)
C(25)-C(26)	1.42 (1)	1.46 (3)	C(3′)-C(4)		1.03 (6)
C(26)-C(21)	1.369 (9)	1.38 (3)	C(4)-C(3)		1.83 (8)
C(31)-C(32)	1.354 (9)	1.38 (2)	C(3)-C(5)		1.58 (8)
C(32)-C(33)	1.40 (1)	1.47 (3)	C(5)-C(1)		1.23 (7)
C(33)-C(34)	1.41 (1)	1.34 (3)			
(b) Bond Angles (deg)					
M(2)-M(1)-N(11)	92.9 (1)	91.7 (5)	N(71)-C(71)-C(72)	122.3 (6)	124 (2)
-N(31)	94.0 (1)	90.4 (4)	-C(76)	116.7 (6)	115 (2)
-N(51)	90.8 (1)	91.5 (4)	N(81)-C(81)-C(82)	120.0 (6)	121 (2)
-N(71)	95.0 (2)	92.0 (5)	-C(86)	118.0 (6)	113 (2)
N(11)-M(1)-N(31)	91.0 (2)	91.2 (6)	C(11)-C(12)-C(13)	119.9 (6)	116 (2)
-N(51)	175.8 (2)	176.7 (6)	C(12)-C(13)-C(14)	118.7 (7)	119 (2)
-N(71)	88.1 (2)	89.9 (6)	C(13)-C(14)-C(15)	121.8 (7)	123 (2)
N(31)-M(1)-N(51)	90.8 (2)	89.6 (6)	C(14)-C(15)-C(16)	118.4 (7)	119 (2)
-N(71)	171.0 (2)	177.3 (7)	C(15)-C(16)-C(11)	120.4 (6)	117 (2)
N(51)-M(1)-N(71)	89.5 (2)	89.1 (6)	C(16)-C(11)-C(12)	120.7 (6)	126 (2)
M(1)-N(11)-N(1)	118.6 (4)	120 (1)	C(21)-C(22)-C(23)	118.8 (7)	113 (2)
-C(11)	129.3 (4)	128 (1)	C(22)-C(23)-C(24)	119.8 (9)	123 (2)
N(1)-N(11)-C(11)	111.2 (5)	112 (2)	C(23)-C(24)-C(25)	121.3 (9)	122 (2)
M(1)-N(31)-N(3)	119.1 (4)	123 (1)	C(24)-C(25)-C(26)	118.3 (8)	119 (2)
-C(31)	128.4 (4)	126 (1)	C(25)-C(26)-C(21)	119.9 (7)	118 (2)
N(3)-N(31)-C(31)	112.4 (5)	110 (2)	C(26)-C(21)-C(25)	121.8 (7)	124 (2)
M(1)-N(51)-N(5)	118.3 (4)	120 (1)	C(31)-C(32)-C(33)	121.4 (7)	114 (2)
-C(51)	129.5 (4)	128 (1)	C(32)-C(33)-C(34)	117.9 (7)	118 (2)
N(5)-N(51)-C(51)	112.1 (5)	112 (1)	C(33)-C(34)-C(35)	119.9 (8)	128 (2)
M(1)-N(71)-N(7)	118.7 (4)	121 (1)	C(34)-C(35)-C(36)	122.6 (8)	115 (2)
-C(71)	127.8 (4)	129 (1)	C(35)-C(36)-C(31)	116.4 (7)	117 (2)
N(7)-N(71)-C(71)	113.5 (5)	110 (2)	C(36)-C(31)-C(32)	121.7 (7)	127 (2)
N(11)-N(1)-N(21)	112.7 (5)	112 (2)	C(41)-C(42)-C(43)	118.1 (7)	118 (2)
N(31)-N(3)-N(41)	113.1 (5)	113 (2)	C(42)-C(43)-C(44)	120.2 (7)	123 (2)
M(1)-M(2)-N(2)	95.1 (1)	90.4 (5)	C(43)-C(44)-C(45)	120.7 (8)	118 (2)
-N(41)	93.8 (1)	91.9 (5)	C(44)-C(45)-C(46)	120.9 (7)	121 (2)
-N(61)	95.6 (2)	91.7 (5)	C(45)-C(46)-C(41)	117.5 (7)	120 (2)
-N(81)	92.4 (2)	91.5 (5)	C(46)-C(41)-C(42)	122.5 (6)	120 (2)
N(21)-M(2)-N(41)	90.8 (2)	91.7 (6)	C(51)-C(52)-C(53)	120.0 (6)	117 (2)
-N(61)	169.0 (2)	177.9 (7)	C(52)-C(53)-C(54)	119.6 (7)	119 (2)
-N(81)	90.6 (2)	91.0 (6)	C(53)-C(54)-C(55)	120.9 (7)	123 (2)
N(41)-M(2)-N(61)	86.2 (2)	88.3 (6)	C(54)-C(55)-C(56)	120.2 (7)	118 (2)
-N(81)	173.5 (2)	175.7 (6)	C(55)-C(56)-C(51)	118.5 (7)	117 (2)
N(61)-M(2)-N(81)	91.3 (2)	88.9 (6)	C(56)-C(51)-C(52)	120.7 (6)	126 (2)

Table III (*Continued*)

	M = Cr	M = Mo		M = Cr	M = Mo
M(2)-N(21)-N(1)	118.7 (4)	125 (1)	C(61)-C(62)-C(63)	119.5 (7)	122 (2)
-C(21)	126.9 (4)	123 (1)	C(62)-C(63)-C(64)	119.2 (7)	124 (2)
N(1)-N(21)-C(21)	113.8 (5)	111 (2)	C(63)-C(64)-C(65)	120.6 (8)	116 (2)
N(2)-N(41)-N(3)	117.7 (4)	121 (1)	C(64)-C(65)-C(66)	120.8 (7)	122 (2)
-C(41)	128.3 (4)	126 (1)	C(65)-C(66)-C(61)	117.1 (6)	118 (2)
N(3)-N(41)-C(41)	111.7 (5)	113 (2)	C(66)-C(61)-C(62)	122.6 (6)	119 (2)
M(2)-N(61)-N(5)	118.0 (4)	123 (1)	C(71)-C(72)-C(73)	118.9 (6)	119 (2)
-C(61)	126.6 (4)	130 (1)	C(72)-C(73)-C(74)	120.9 (7)	121 (2)
N(5)-N(61)-C(61)	115.3 (5)	107 (2)	C(73)-C(74)-C(75)	118.7 (7)	118 (2)
N(2)-N(81)-N(7)	118.7 (4)	121 (2)	C(74)-C(75)-C(76)	121.6 (7)	123 (2)
-C(81)	129.4 (4)	126 (1)	C(75)-C(76)-C(71)	119.0 (6)	117 (2)
N(7)-N(81)-C(81)	111.0 (5)	112 (2)	C(76)-C(71)-C(72)	120.9 (6)	121 (2)
N(51)-N(5)-N(61)	113.3 (5)	113 (2)	C(81)-C(82)-C(83)	119.1 (8)	119 (2)
N(71)-N(7)-N(81)	112.2 (5)	114 (2)	C(82)-C(83)-C(84)	120.0 (9)	117 (2)
N(11)-C(11)-C(12)	119.6 (6)	119 (2)	C(83)-C(84)-C(85)	119.3 (9)	125 (2)
-C(16)	119.7 (6)	115 (2)	C(84)-C(85)-C(86)	121.8 (8)	118 (2)
N(21)-C(21)-C(22)	120.8 (6)	116 (2)	C(85)-C(86)-C(81)	117.9 (7)	116 (2)
-C(26)	117.4 (6)	120 (2)	C(86)-C(81)-C(82)	121.9 (7)	125 (2)
N(31)-C(31)-C(32)	117.5 (6)	120 (2)	C(1)-C(2)-C(3)′		157 (7)
-C(36)	120.6 (6)	113 (2)	C(2)-C(3)′-C(1)		96 (6)
N(41)-C(41)-C(42)	119.5 (6)	122 (2)	C(3)′-C(4)-C(3)		135 (5)
-C(46)	118.0 (6)	118 (2)	C(4)-C(3)-C(5)		97 (5)
N(51)-C(51)-C(52)	118.5 (6)	113 (2)	C(3)-C(5)-C(1)		116 (6)
-C(56)	120.5 (6)	121 (2)	C(5)-C(1)-C(2)		112 (6)
N(61)-C(61)-C(62)	116.8 (6)	118 (2)			
-C(66)	120.5 (6)	123 (2)			

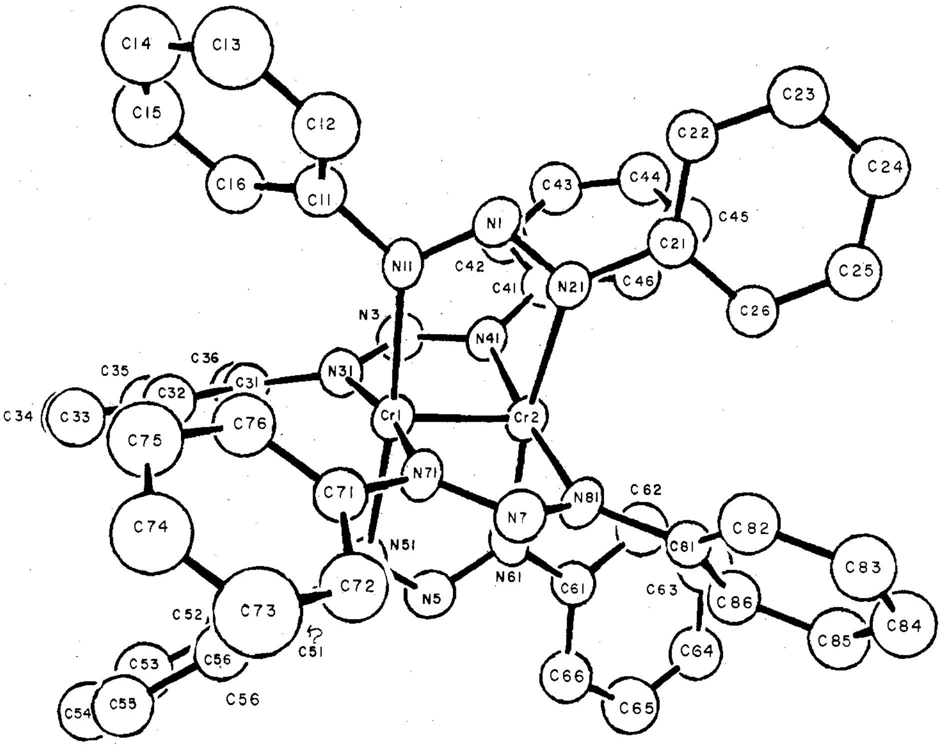

Figure 1. ORTEP drawing of the molecule in compound I, $Cr_2(C_6H_5NNNC_6H_5)_4$. Note that C(51) is obscured from view by C(73).

(0, 0, $^1/_2$), but again the atoms in the unit were poorly defined in all models of the disorder that we tested.

Results and Discussion

Of the three crystalline compounds examined here, only in the case of compound I, $Cr_2(C_6H_5NNNC_6H_5)_4$, may the structure be said to be completely solved with the positions of all nonhydrogen atoms unequivocally determined. However, of the three compounds, it is the structure of I that is of greatest interest. For the others, especially II, the chief objective was simply to identify the metal complex, and this has been accomplished unambiguously, despite problems with disordered solvent molecules.

The positional and thermal parameters for compounds I, II, and III are presented in Table IIA–C, respectively, while the bond distances and angles for the two dinuclear molecules are compared in Table III. The bond distances and angles for the Cr monomer are presented in Table IV. Figure 1 illustrates the numbering scheme in the Cr dimer. The same numbering scheme was used for the Mo structure. Figure 2 illustrates the numbering scheme in the Cr monomer and the location of the twofold axis.

The most notable point with regard to the $Cr(C_6H_5NNNC_6H_5)_3$ molecule in II is that it is obtained at all under the conditions employed. One would not ordinarily think of a triazene molecule as an oxidant, and yet the Cr(III) product seems to be the major one obtained by the method used here. The ready formation of II is even more surprising since the

Table IV. Bond Distances (Å) and Angles (deg) for the $Cr(C_6H_5NNNC_6H_5)_3$ Molecule

	Distances		
Cr-N(11)	2.00 (1)	C(16)-C(11)	1.40 (1)
-N(21)	2.01 (1)	C(21)-C(22)	1.43 (2)
-N(31)	2.01 (1)	C(22)-C(23)	1.46 (2)
N(11)-N(1)	1.33 (1)	C(23)-C(24)	1.39 (2)
-C(11)	1.42	C(24)-C(25)	1.39 (2)
N(21)-N(1)	1.32 (1)	C(25)-C(26)	1.47 (2)
-C(21)	1.39 (1)	C(26)-C(21)	1.41 (2)
N(31)-N(3)	1.28 (1)	C(31)-C(32)	1.430 (2)
-C(31)	1.45 (1)	C(32)-C(33)	1.40 (2)
C(11)-C(12)	1.40 (1)	C(33)-C(34)	1.38 (2)
C(12)-C(13)	1.42 (1)	C(34)-C(35)	1.44 (2)
C(13)-C(14)	1.39 (2)	C(35)-C(36)	1.45 (2)
C(14)-C(15)	1.37 (2)	C(36)-C(31)	1.35 (2)
C(15)-C(16)	1.44 (2)		
	Angles		
N(11)-Cr-N(11)′	162.4 (6)	C(12)-C(11)-C(16)	124 (1)
-N(21)	62.9 (4)	C(11)-C(12)-C(13)	116 (1)
-N(21)′	104.4 (4)	C(12)-C(13)-C(14)	120 (1)
-N(31)	91.3 (4)	C(13)-C(14)-C(15)	124 (1)
-N(31)′	104.0 (5)	C(14)-C(15)-C(16)	118 (1)
N(21)-Cr-N(21)′	94.8 (5)	C(15)-C(16)-C(11)	118 (1)
-N(31)	102.9 (4)	N(21)-C(21)-C(22)	122 (1)
-N(31)′	160.4 (4)	N(21)-C(21)-C(26)	114 (1)
N(31)-Cr-N(31)′	61.2 (6)	C(22)-C(21)-C(26)	123 (1)
Cr-N(11)-N(1)	96.3 (8)	C(21)-C(22)-C(23)	117 (1)
-C(11)	146.0 (9)	C(22)-C(23)-C(24)	119 (1)
N(1)-N(11)-C(11)	117 (1)	C(23)-C(24)-C(25)	123 (1)
Cr-N(21)-N(1)	96.4 (8)	C(24)-C(25)-C(26)	119 (1)
-C(21)	146.1 (9)	C(25)-C(26)-C(21)	117 (1)
N(1)-N(21)-C(21)	116 (1)	N(31)-C(31)-C(32)	116 (1)
N(11)-N(1)-N(21)	104 (1)	-C(36)	119 (1)
Cr-N(31)-N(3)	96.6 (9)	C(32)-C(31)-C(36)	125 (1)
-C(31)	143.9 (9)	C(31)-C(32)-C(33)	115 (1)
N(3)-N(31)-C(31)	119 (1)	C(32)-C(33)-C(34)	123 (1)
N(31)-N(3)-N(31)′	106 (1)	C(33)-C(34)-C(35)	120 (1)
N(11)-C(11)-C(12)	120 (1)	C(34)-C(35)-C(36)	118 (1)
-C(16)	116 (1)	C(35)-C(36)-C(31)	118 (1)

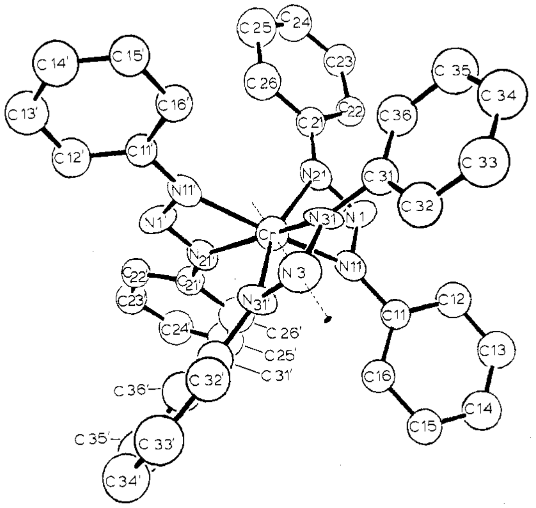

Figure 2. ORTEP drawing of the $Cr(C_6H_5NNNC_6H_5)_3$ molecule, II.

$Cr(PhN_3Ph)_3$ molecule appears to have severe angle strain within the four-membered CrN_3 rings, whereas the minor product, I, has no such strain. The internal geometries of the CNNNC chains in I and II are essentially identical. In view of our failure to identify the solvent of crystallization, we considered the possibility that the "vacant" spaces in the cell might contain cations of the type [Li(solvent)$^+$], in which case the chromium would be in the oxidation state (II). This was rejected on the basis of two observations. First, the coordination geometry around the chromium atom, though distorted, is essentially octahedral, and this would not be expected for chromium(II). Also, the void in the cell appears to be too small to accommodate more than one solvent molecule plus a lithium ion, and lithium might be expected to have more than one associated donor. The crystallographic data on II are therefore adequate to define the chromium-containing molecule, but not the complete cell contents. Accordingly, we report in Table IV only those distances and angles which define the coordination geometry of the chromium atom.

Table V. Torsional Angles (deg) in $M_2(C_6H_5NNNC_6H_5)_4$

planes defining angle		M =	M =
atoms in plane 1	atoms in plane 2	Cr	Mo
N(11), M(1), M(2)	M(1), M(2), N(21)	10.4	5.0
N(31), M(1), M(2)	M(1), M(2), N(41)	10.5	10.4
N(51), M(1), M(2)	M(1), M(2), N(61)	14.9	13.1
N(71), M(1), M(2)	M(1), M(2), N(81)	15.3	13.4
mean angle		12.8	10.5

The $M_2(PhN_3Ph)_4$ molecules, M = Cr or Mo, have the geometric structures expected except, perhaps, in one respect. They show torsional rotations away from the perfectly eclipsed configuration that are greater than those seen in $M_2(O_2CR)_4$ molecules. The four smallest independent NMMN torsion angles are listed for each molecule in Table V. Those in the chromium compound average 12.8° and those in the molybdenum compound average 10.5°. These small rotations will have only a very slight effect on the strength of the δ bond, since the δ overlap varies as $\cos^2 2\phi$, where ϕ is the angle, and no effect on σ or π overlaps. It is probable that these rotations are caused by repulsive interaction between the phenyl groups, either intra- or intermolecular, or both. In $Mo_2(N_2CPh_3)_4$, which is somewhat similar, there is no net deviation from the eclipsed configuration; however, this molecule resides on a crystallographic C_2 axis, whereas the $M_2(PhN_3Ph)_4$ molecules have no crystallographically imposed symmetry.

The molecule $Mo_2(C_6H_5NNNC_6H_5)_4$ has no surprising structural features. The Mo–Mo distance, 2.083 (2) Å, may be slightly shorter than those found in $Mo_2(O_2CR)_4$ compounds, viz., 2.093 (1) Å in the acetate[15] and 2.090 (4) Å in the trifluoroacetate.[16] It may also be slightly shorter than that, 2.090 (1) Å, in the amidino compound $Mo_2(N_2CPh_3)_4$.[17] We do not see any chemical significance to these small differences which are, in any case, barely if at all outside the experimental uncertainties if the $>3\sigma$ criterion is used.

The $Cr_2(C_6H_5NNNC_6H_5)_4$ molecule is, however, of unusual structural interest. It contains another supershort Cr–Cr bond, 1.858 (1) Å. It thus serves to demonstrate conclusively that it is not essential that any of the ligating atoms be incorporated into an aromatic ring in order to achieve such a Cr–Cr bond. It is also interesting that the Mo–Mo bond is not in the 2.06–2.07 Å range even though the Cr–Cr bond is in the supershort range, whereas for all the ligands $L^{(1)}$ to $L^{(6)}$ such a correlation has been observed.

The triazinato ligand differs from the carboxylato ligand in two obvious ways, even though there is a broad similarity in the qualitative equivalences of N with RC and RN with O. First, the Ph groups on the terminal nitrogen atoms sterically exclude axial coordination of any sort to the Cr_2 unit. In every known crystal structure of tetrakis(carboxylato)dichromium compounds axial coordination occurs, and there appears to be no way to exclude it. Second, the RN_3R^- ions are much stronger bases than the RCO_2^- ions. Whether one or both of these differences can be held responsible for the vastly different effects of RN_3R^- and RCO_2^- on the Cr–Cr bond length is now the pertinent question.

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Registry No. I, 69351-81-1; II, 69351-82-2; III, 69351-84-4; $[Li(THF)]_4[Cr_2(CH_3)_8]$, 69351-85-5; $[Li(THF)]_4[Mo_2(CH_3)_8]$, 53307-60-1.

Supplementary Material Available: Tables of observed and calculated structure factors for all three compounds (27 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Cotton, F. A.; Koch, S.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7372.
(2) Cotton, F. A.; Millar, M. *Inorg. Chim. Acta* **1977**, *25*, L105.
(3) Cotton, F. A.; Koch, S. *Inorg. Chem.* **1978**, *17*, 2021.
(4) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.
(5) Cotton, F. A.; Koch, S. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2084.
(6) Cotton, F. A.; Niswander, R. H.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3541.
(7) Cotton, F. A.; Millar, M. *Inorg. Chem.* **1978**, *17*, 2014.
(8) Cotton, F. A.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 2004.
(9) Cotton, F. A.; Extine, M. W.; Rice, G. W. *Inorg. Chem.* **1978**, *17*, 176.
(10) Hartman, W. W.; Dickey, J. B. *Org. Synth.* **1943**, *2*, 163.
(11) Kurras, E.; Otto, J. *J. Organomet. Chem.* **1965**, *4*, 114.
(12) Cotton, F. A.; Troup, J. M.; Webb, T. R.; Williamson, D. H.; Wilkinson, G. *J. Am. Chem. Soc.* **1974**, *96*, 3825.
(13) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.
(14) Corbett, M.; Hoskins, B. F.; McLeod, N. J.; O'Day, B. P. *Aust. J. Chem.* **1975**, *28*, 2377.
(15) Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr. Sect. B* **1974**, *30*, 2768.
(16) Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161.
(17) Cotton, F. A.; Inglis, T.; Kilner, M.; Webb, T. R. *Inorg. Chem.* **1975**, *14*, 2023.

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A Quadruply Bonded Dimolybdenum Compound with Bridging Pyrimidinethiol Ligands

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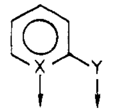
The reaction of dimolybdenum tetraacetate with the sodium salt of 4,6-dimethyl-2-mercaptopyrimidine (Hdmmp) affords $Mo_2(dmmp)_4$. Recrystallization from dichloromethane solution by slow addition of hexane gave mainly acicular crystals of $Mo_2(dmmp)_4 \cdot 2CH_2Cl_2$, but also some rectangular crystals of $Mo_2(dmmp)_4 \cdot CH_2Cl_2$. The structure of one of the latter crystals was determined. The space group was $P2_1/n$, and the unit cell had the following dimensions: $a = 10.927$ (2) Å, $b = 10.660$ (2) Å, $c = 28.149$ (5) Å, $\beta = 101.36$ (2)°, $V = 3214$ (1) Å^3. With $Z = 4$, the formula unit is the asymmetric unit. The structure is of the expected general type. It has a ligand arrangement with two trans S atoms and two trans N atoms on each molybdenum. The Mo–Mo bond length, 2.083 (2) Å, is slightly longer than those in the four other molecules containing quadruply bonded Mo_2^{4+} and ligands of the same general class. Other bond lengths and angles have values that are not surprising in comparison with those in comparable molecules.

Introduction

Over the past year and a half, we have discovered a series of new compounds containing $M\overset{4}{-}M'$ bonds with M and M′ being Cr, Mo, or W and including the mixed $Cr\overset{4}{-}Mo$ and $Mo\overset{4}{-}W$ species.[1-8] The ligands in these compounds are all of the type represented schematically in **1**, where the donor atoms X and Y may be C, N, or O, in various combinations. The common feature of all these ligands is the presence of an aromatic or heteroaromatic ring. We shall discuss the detailed nature of these ligands more fully later.



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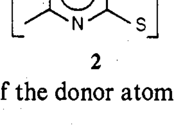
These compounds have been especially interesting for the following reasons. (1) The Cr_2 species all have supershort (<1.91 Å) metal-metal bonds. (2) Stable $W\overset{4}{-}W$ compounds became accessible for the first time with such ligands. (3) This type of ligand allows considerable variability in the identity of the donor atoms and the steric properties of the ligand.

We have now succeeded in preparing and structurally characterizing a $M\overset{4}{-}Mo$ compound containing a ligand, **2**, of type **1** in which one of the donor atoms is sulfur. The greater size and polarizability of the S atom, as compared to N and O atoms, aroused our interest in the detailed structural properties of the $M\overset{4}{-}M$ complexes, and we describe here, in full, the nature of the compound formed by this ligand, which is the anion 4,6-dimethyl-2-mercaptidopyrimidine, dmmp, with $Mo\overset{4}{-}Mo$, viz., $Mo_2(dmmp)_4$.



2

Experimental Section

Preparation. All operations were conducted in an atmosphere of nitrogen. 4,6-Dimethyl-2-mercaptopyrimidine (Hdmmp) was purchased from Aldrich Chemical Co. and used as received. The Hdmmp, 1.40 g (10 mmol), was dissolved in 100 mL of absolute ethanol and 0.54 g (10 mmol) of $NaOCH_3$ added. To this mixture was added 1.11 g (2.5 mmol) of $Mo_2(O_2CCH_3)_4$. The heterogeneous reaction mixture immediately turned red; it was stirred at room temperature for 6 h.

The product was separated by filtration, washed with 25 mL of ethanol, and dried under vacuum. It was then dissolved in 50 mL of dichloromethane, to produce a saturated solution, which was filtered through a medium glass frit into a tubular flask. A layer of hexane was gently introduced over the CH_2Cl_2 solution, and over a period of three days, as the two solvents mixed by diffusion, small acicular crystals were formed. They were collected on a filter and dried by brief pumping at room temperature. Anal. Calcd for $C_{26}H_{32}N_8S_4Cl_4Mo_2$: C, 34.06; H, 3.06; N, 12.22. Found: C, 34.2; H, 3.25; N, 12.0.

When the crystalline product was examined under a microscope it was found that in addition to the predominant acicular crystals there were also a few rectangular ones. One of the latter was selected for X-ray analysis, and it was found from the structure that the rectangular crystals differ in their solvent content from the acicular ones, having the composition $Mo_2(dmmp)_4 \cdot CH_2Cl_2$.

X-ray Crystallography.[9] Preliminary examination and systematic absences showed the space group to be $P2_1/n$ with unit cell dimensions $a = 10.927$ (2) Å, $b = 10.660$ (2) Å, $c = 28.149$ (5) Å, and $\beta = 101.36$ (2)°, $Z = 4$. With a unit cell volume of 3214 (1) Å, the asymmetric

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