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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Tetrakis(2-amino-4-methylbenzothiazolato)dimolybdenum Tetrahydrofuranate, Tris(2-amino-4-methylbenzothiazolato)(acetato)dimolybdenum Bis(tetrahydrofuranate), and Tetrakis(2-amino-4-chlorobenzothiazolato)dimolybdenum Bis(tetrahydrofuranate). Quadruply Bonded Compounds with Bridging Ligands Derived from a Five-Membered Ring System

F. ALBERT COTTON* and WILLIAM H. ILSLEY

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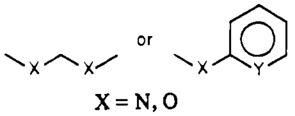
The structures of $Mo_2(ambt)_3(CH_3CO_2)\cdot 2THF$ (**1**), $Mo_2(ambt)_4\cdot THF$ (**2**) (ambt = the anion of 2-amino-4-methylbenzothiazole, obtained by removal of one amine hydrogen atom), and $Mo_2(acbt)_4\cdot 2THF$ (**3**) (acbt = the anion of 2-amino-4-chlorobenzothiazole, obtained by removal of one amine hydrogen atom) are reported. These are the first examples of compounds in which the ligand bridge system is derived from a five-membered heterocyclic ring system. Compound **1** crystallizes in the monoclinic space group $P2_1/n$ with unit cell parameters $a = 10.934$ (3) Å, $b = 25.005$ (7) Å, $c = 13.648$ (2) Å, $\beta = 92.74$ (2)°, $V = 3727$ (3) Å^3, and $Z = 4$. Each molecule resides on a general position, and the THF molecules occupy the voids between the molecules. The Mo–Mo bond length is 2.093 (3) Å, and the rotational conformation is essentially eclipsed. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters $a = 13.201$ (2) Å, $b = 10.967$ (2) Å, $c = 14.075$ (2) Å, $\beta = 115.33$ (3)°, $V = 1842$ (1) Å^3, and $Z = 2$. Each molecule as well as each of the THF molecules resides on a center of inversion of the unit cell, the latter being, therefore, disordered. The ligands are arranged so as to give idealized C_{2h} symmetry, but there are inequalities in the N–Mo–N angles in response to methyl–methyl repulsions. The Mo–Mo bond length is 2.103 (1) Å. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 10.422$ (2) Å, $b = 12.041$ (2) Å, $c = 10.129$ (1) Å, $\alpha = 97.63$ (1)°, $\beta = 118.47$ (1)°, $\gamma = 66.88$ (1)°, $V = 1025.3$ (4) Å^3, and $Z = 1$. Each molecule resides on a center of inversion of the unit cell, and the THF molecules occupy the voids between the molecules. As in **2**, the ligands are arranged so as to give idealized C_{2h} symmetry, but this is again reduced to only inversion symmetry by angle changes in response to repulsions between the chlorine atoms. The Mo–Mo bond length is 2.117 (1) Å. Each compound shows two distinctly different Mo–N distances of ~2.14 and 2.21 Å, which can be accounted for by steric repulsions between the methyl groups of the ambt or chlorine atoms of the acbt ligands. Distances in compound **1** also suggest that there may be a trans effect in this molecule since the Mo–O distances of ~2.15 Å are significantly larger than those previously observed, i.e., 2.10–2.11 Å.

Introduction

Since the characterization of the quadruple bond, in $[Re_2Cl_8]^{2-}$, in 1964, a wide range of quadruply bound bimetallic compounds has been prepared and characterized crystallographically.[1] The most extensively studied have been the dimolybdenum species since they are in general the easiest to prepare and handle. Among the vast number of such compounds that have been studied,[2] the majority have been derived from the ligand types



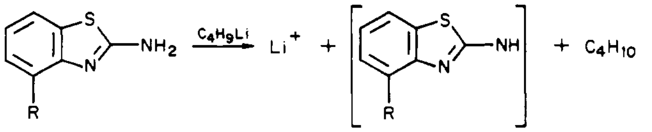
X = N, O
Y = C, N, O

where the bridge is part of an alkyl system or derived from a six-membered ring system. There have been no examples in which the bridge system is derived from a five-membered ring system. Although a number of attempts have been made in this laboratory to prepare such complexes, the products have heretofore invariably been insoluble, though crystalline, materials. We have now succeeded in obtaining soluble compounds, with ligands derived from 2-amino-4-methylbenzothiazole, Hambt, and 2-amino-4-chlorobenzothiazole, Hacbt. These molecules can be deprotonated to anions, by using butyllithium, as shown in eq 1.

We have prepared and characterized three compounds, $Mo_2(ambt)_3(CH_3CO_2)\cdot 2THF$ (**1**), $Mo_2(ambt)_4\cdot THF$ (**2**), and $Mo_2(acbt)_4\cdot 2THF$ (**3**), and we present here a detailed discussion of their structures.

Table I. Crystallographic Parameters

parameter	1	2	3
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a, Å	10.934 (3)	13.201 (2)	10.422 (2)
b, Å	25.005 (7)	10.967 (2)	12.041 (2)
c, Å	13.648 (2)	14.075 (2)	10.129 (1)
α, deg	90.0	90.0	97.63 (1)
β, deg	92.74 (2)	115.33 (3)	118.47 (1)
γ, deg	90.0	90.0	66.88 (1)
Z	4	2	1
fw	884.81	916.88	1070.66
cryst size, mm	0.20 × 0.20 × 0.20	0.20 × 0.30 × 0.25	0.10 × 0.30 × 0.25
μ, cm^{-1}	8.695	9.307	11.008
2θ range, deg	0–45	0–45	0–45
no. data	3329	1794	2652
$F_o^2 > 3\sigma(F_o^2)$	1768	1554	2262
no. of variables	262	140	229
R_1	0.091	0.062	0.048
R_2	0.119	0.085	0.066
ESD	2.230	1.710	2.103
d_x(calcd), g/cm^3	1.577	1.653	1.734



Hambt, R = CH_3
Hacbt, R = Cl

ambt$^-$, R = CH_3
acbt$^-$, R = Cl

(1)

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(1) Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225.
(2) Bino, A.; Cotton, F. A. Proceedings of the 3rd International Conference on the Chemistry and Uses of Molybdenum, Ann Arbor, Mich., August, 1979.

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Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(ambt)_3(CH_3CO_2)\cdot 2THF$ (**1**)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.5322 (3)	0.3707 (1)	0.6884 (2)	5.1 (1)	4.2 (1)	4.8 (1)	−0.5 (1)	−0.2 (1)	0.6 (1)
Mo(2)	0.4563 (2)	0.4464 (1)	0.6609 (2)	3.9 (1)	4.4 (1)	4.5 (1)	−0.4 (1)	0.3 (1)	0.4 (1)
S(1)	0.6699 (9)	0.4732 (4)	0.9579 (6)	8.4 (6)	9.5 (6)	3.8 (4)	−2.0 (5)	−0.7 (4)	−0.6 (4)
S(2)	0.8369 (8)	0.4620 (3)	0.5211 (7)	5.1 (5)	5.8 (5)	9.0 (5)	−0.5 (4)	1.9 (4)	−0.5 (4)
S(3)	0.1455 (9)	0.3614 (4)	0.8237 (7)	7.6 (6)	10.1 (6)	7.0 (5)	−3.6 (5)	2.0 (4)	0.3 (5)
O(1)	0.458 (2)	0.3398 (7)	0.551 (1)	8 (1)	4.6 (9)	3.5 (8)	0.7 (9)	−0.4 (9)	0.7 (8)
O(2)	0.374 (2)	0.4192 (8)	0.524 (1)	6 (1)	5 (1)	7 (1)	1.2 (9)	1.4 (9)	0.3 (9)
N(1)	0.613 (2)	0.3931 (9)	0.826 (1)	11 (2)	6 (1)	2.7 (9)	3 (1)	−2 (1)	2.3 (9)
N(2)	0.535 (2)	0.4791 (9)	0.796 (2)	5 (1)	5 (1)	5 (1)	1 (1)	3 (1)	−0 (1)
N(3)	0.706 (2)	0.3924 (8)	0.614 (1)	2 (1)	5 (1)	6 (1)	1 (1)	−0.3 (9)	0 (1)
N(4)	0.607 (2)	0.4765 (9)	0.579 (1)	2 (1)	6 (1)	4 (1)	−0 (1)	−0.7 (9)	0 (1)
N(5)	0.359 (2)	0.3464 (9)	0.759 (1)	6 (1)	7 (1)	4 (1)	−3 (1)	−0 (1)	−1 (1)
N(6)	0.289 (2)	0.4321 (9)	0.729 (2)	3 (1)	7 (1)	7 (1)	−2 (1)	0 (1)	2 (1)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(3)	0.275 (3)	0.188 (1)	0.434 (2)	12.4 (9)	C(17)	0.860 (3)	0.318 (1)	0.634 (2)	5.7 (7)
O(4)	0.586 (3)	−0.003 (1)	0.290 (2)	15.4 (11)	C(18)	0.769 (3)	0.280 (1)	0.675 (2)	7.5 (9)
C(1)	0.394 (3)	0.371 (1)	0.501 (2)	5.3 (7)	C(19)	0.276 (3)	0.385 (1)	0.761 (2)	6.1 (8)
C(2)	0.338 (3)	0.351 (1)	0.399 (2)	5.5 (7)	C(20)	0.327 (3)	0.297 (1)	0.809 (2)	6.8 (8)
C(3)	0.600 (2)	0.443 (1)	0.849 (2)	4.6 (6)	C(21)	0.211 (3)	0.300 (1)	0.843 (2)	6.9 (8)
C(4)	0.543 (3)	0.531 (1)	0.832 (2)	5.2 (7)	C(22)	0.152 (4)	0.254 (2)	0.890 (3)	9.5 (11)
C(5)	0.610 (3)	0.534 (1)	0.923 (2)	6.6 (8)	C(23)	0.231 (3)	0.209 (1)	0.898 (2)	8.0 (9)
C(6)	0.626 (3)	0.586 (1)	0.969 (2)	8.1 (9)	C(24)	0.341 (3)	0.201 (1)	0.868 (2)	8.3 (10)
C(7)	0.573 (3)	0.628 (1)	0.930 (3)	8.3 (10)	C(25)	0.397 (3)	0.249 (1)	0.826 (2)	7.0 (8)
C(8)	0.504 (3)	0.628 (1)	0.845 (3)	8.5 (10)	C(26)	0.523 (3)	0.245 (1)	0.788 (3)	8.5 (10)
C(9)	0.482 (3)	0.575 (1)	0.791 (2)	5.9 (7)	C(27)	0.382 (5)	0.159 (2)	0.468 (4)	14.7 (17)
C(10)	0.407 (3)	0.574 (1)	0.702 (2)	7.8 (9)	C(28)	0.349 (5)	0.162 (2)	0.579 (4)	16.8 (19)
C(11)	0.704 (2)	0.441 (1)	0.575 (2)	3.8 (6)	C(29)	0.280 (6)	0.211 (2)	0.600 (4)	17.6 (21)
C(12)	0.822 (2)	0.370 (1)	0.603 (2)	4.4 (6)	C(30)	0.221 (5)	0.210 (2)	0.513 (4)	15.1 (17)
C(13)	0.906 (2)	0.400 (1)	0.554 (2)	4.3 (6)	C(31)	0.553 (6)	−0.052 (3)	0.230 (5)	19.5 (23)
C(14)	1.031 (3)	0.387 (1)	0.540 (2)	6.6 (8)	C(32)	0.472 (10)	−0.052 (5)	0.348 (8)	34.9 (48)
C(15)	1.058 (3)	0.336 (1)	0.573 (2)	7.1 (8)	C(33)	0.386 (5)	−0.040 (2)	0.264 (4)	15.0 (17)
C(16)	0.979 (3)	0.302 (1)	0.619 (2)	7.5 (9)	C(34)	0.460 (7)	0.021 (3)	0.291 (5)	22.8 (28)

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

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(ambt)_4\cdot THF$ (2)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.48609 (7)	0.05850 (8)	0.05242 (6)	3.39 (3)	3.35 (3)	2.74 (2)	−0.49 (4)	1.74 (2)	−0.87 (3)
S(1)	0.8309 (2)	−0.1251 (3)	0.2616 (2)	4.2 (1)	6.2 (2)	4.3 (1)	−0.2 (1)	0.7 (1)	0.2 (1)
S(2)	0.7242 (2)	0.2834 (3)	−0.0499 (2)	5.2 (1)	3.6 (1)	4.69 (9)	−0.9 (1)	3.00 (7)	−0.40 (9)
N(1)	0.6389 (6)	0.0062 (8)	0.1826 (6)	3.6 (3)	4.1 (4)	3.1 (3)	−0.4 (3)	1.1 (2)	−0.1 (3)
N(2)	0.6675 (6)	−0.1345 (8)	0.0724 (5)	3.1 (3)	3.9 (4)	3.3 (3)	−0.3 (3)	1.6 (2)	−0.5 (3)
N(3)	0.5813 (6)	0.2028 (7)	0.0295 (5)	4.0 (3)	3.9 (4)	3.4 (3)	−0.4 (3)	2.4 (2)	−0.3 (3)
N(4)	0.6064 (6)	0.0812 (7)	−0.0969 (5)	3.5 (3)	3.6 (4)	3.1 (2)	−0.9 (3)	2.0 (2)	−1.1 (3)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
O(1)	0.028 (1)	0.617 (2)	0.447 (1)	7.2 (4)	C(10)	0.6588 (7)	0.0900 (9)	−0.1659 (7)	3.3 (2)
C(1)	0.7009 (7)	−0.0761 (9)	0.1656 (7)	3.4 (2)	C(11)	0.7279 (7)	0.1917 (9)	−0.1489 (7)	3.3 (2)
C(2)	0.7437 (8)	−0.2247 (9)	0.0783 (7)	3.5 (2)	C(12)	0.7942 (8)	0.2118 (10)	−0.2031 (8)	4.2 (2)
C(3)	0.8392 (8)	−0.2306 (10)	0.1732 (8)	4.2 (2)	C(13)	0.7828 (8)	0.1280 (10)	−0.2805 (7)	4.0 (2)
C(4)	0.9288 (10)	−0.3169 (13)	0.1925 (9)	5.8 (3)	C(14)	0.7111 (8)	0.0313 (10)	−0.3032 (8)	4.1 (2)
C(5)	0.9127 (10)	−0.3925 (13)	0.1111 (9)	5.9 (3)	C(15)	0.6463 (8)	0.0113 (10)	−0.2490 (8)	4.3 (2)
C(6)	0.8186 (9)	−0.3969 (12)	0.0188 (9)	5.3 (3)	C(16)	0.5657 (13)	−0.0941 (17)	−0.2815 (12)	8.9 (4)
C(7)	0.7315 (9)	−0.3110 (11)	0.0004 (9)	5.1 (3)	C(17)	0.0543 (11)	0.4976 (15)	0.4510 (11)	7.4 (4)
C(8)	0.6210 (14)	−0.3295 (18)	−0.0950 (13)	9.9 (5)	C(18)	−0.0595 (12)	0.5879 (16)	0.4689 (12)	8.4 (4)
C(9)	0.6262 (8)	0.1806 (10)	−0.0372 (7)	3.6 (2)					

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

Experimental Section

Materials. 2-Amino-4-methylbenzothiazole, Hambt, 2-amino-4-chlorobenzothiazole, Hacbt, and *n*-butyllithium were purchased from Aldrich Chemical Co., Inc. All other compounds and solvents were of reagent grade or better from commercial sources. All solvents were dried over Na/K alloy and deoxygenated prior to use. Reactions were performed under argon by using standard Schlenk techniques.

Preparation of $Mo_2(ambt)_3(CH_3CO_2)\cdot 2THF$. The monoanion of 2-amino-4-methylbenzothiazole, Hambt, was prepared by reacting the ligand (0.328 g, 2.0 mmol) with 1.3 mL of 1.6 M hexane solution of *n*-butyllithium in 25 mL of THF. Dimolybdenum tetraacetate (0.214 g, 0.5 mmol) was added and the reaction mixture stirred for approximately 1 h. The mixture was filtered to give a red solution. Yellow crystals (ca. 2 mg) were obtained by slow diffusion of a layer of hexane into the THF solution.

Preparation of $Mo_2(ambt)_4\cdot THF$. This compound was obtained in a manner analogous to that described above except that the reaction was allowed to proceed for 36 h before filtration and layering. About 3 mg of product was isolated.

Preparation of $Mo(acbt)_4\cdot 2THF$. The monoanion of 2-amino-4-chlorobenzothiazole, Hacbt, was prepared by reacting the ligand (0.368 g, 2.0 mmol) with 1.3 mL of a 1.6 M hexane solution of *n*-butyllithium in 25 mL of THF. Dimolybdenum tetraacetate (0.214 g, 0.5 mmol)

Table IV. Positional and Thermal Parameters and Their Estimated Standard Deviations of $Mo_2(acbt)_4 \cdot 2THF$ (3)[a]

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.59356 (5)	0.91418 (4)	0.03402 (5)	1.96 (1)	2.63 (2)	2.21 (2)	−0.56 (1)	0.80 (1)	0.11 (1)
Cl(1)	1.0010 (2)	0.7551 (2)	0.2509 (2)	3.38 (5)	4.26 (7)	3.79 (6)	−0.38 (5)	1.62 (4)	0.05 (6)
Cl(2)	0.2443 (2)	1.3764 (2)	−0.1186 (3)	4.57 (5)	4.24 (8)	15.3 (1)	−0.30 (5)	5.77 (5)	1.93 (8)
S(1)	0.6771 (2)	1.0870 (2)	0.4913 (2)	3.44 (5)	4.31 (7)	2.51 (5)	−0.87 (5)	1.15 (4)	−0.34 (5)
S(2)	0.7926 (2)	1.1433 (2)	−0.1031 (2)	3.36 (4)	4.46 (7)	4.15 (5)	−1.22 (4)	2.10 (3)	0.53 (5)
N(1)	0.4876 (5)	1.1432 (4)	0.1896 (5)	2.6 (2)	3.2 (2)	2.8 (2)	−0.9 (1)	0.7 (1)	0.0 (2)
N(2)	0.7057 (5)	0.9605 (4)	0.2676 (5)	2.2 (1)	3.1 (2)	2.3 (2)	−0.6 (1)	0.7 (1)	0.1 (1)
N(3)	0.7396 (5)	0.9708 (5)	−0.0118 (5)	2.8 (1)	3.4 (2)	3.0 (2)	−0.6 (1)	1.4 (1)	0.4 (2)
N(4)	0.5434 (5)	1.1623 (4)	−0.0811 (5)	2.4 (1)	1.8 (2)	3.2 (2)	−0.3 (1)	1.0 (1)	0.8 (1)
C(1)	0.6127 (6)	1.0659 (5)	0.2972 (6)	2.9 (2)	3.9 (2)	2.6 (2)	−1.6 (2)	1.2 (1)	−0.5 (2)
C(2)	0.8452 (6)	0.9070 (5)	0.3980 (6)	2.5 (2)	3.0 (2)	2.8 (2)	−1.2 (1)	0.7 (1)	0.2 (2)
C(3)	0.8519 (7)	0.9622 (6)	0.5321 (6)	3.7 (2)	3.9 (2)	2.7 (2)	−1.5 (2)	1.3 (1)	0.0 (2)
C(4)	0.9824 (7)	0.9232 (6)	0.6707 (7)	3.7 (2)	4.0 (3)	2.7 (2)	−1.3 (2)	0.3 (2)	0.4 (2)
C(5)	1.1163 (7)	0.8264 (6)	0.6787 (7)	3.8 (2)	3.5 (3)	3.6 (3)	−1.1 (2)	0.6 (2)	0.6 (2)
C(6)	1.1173 (7)	0.7716 (6)	0.5508 (7)	3.8 (2)	3.9 (2)	3.3 (2)	−1.7 (2)	0.8 (2)	0.6 (2)
C(7)	0.9822 (6)	0.8147 (5)	0.4101 (6)	2.8 (2)	3.0 (2)	2.7 (2)	−1.1 (2)	0.8 (1)	0.0 (2)
C(8)	0.6882 (6)	1.0816 (5)	−0.0591 (6)	2.9 (2)	2.2 (2)	2.4 (2)	−0.4 (1)	1.1 (1)	0.2 (2)
C(9)	0.5210 (6)	1.2769 (6)	−0.1229 (6)	3.3 (2)	3.9 (2)	3.1 (2)	−1.5 (2)	1.3 (1)	−0.1 (2)
C(10)	0.6430 (7)	1.2836 (6)	−0.1420 (7)	3.5 (2)	4.4 (3)	3.3 (2)	−1.5 (2)	1.2 (2)	0.5 (2)
C(11)	0.6365 (7)	1.3939 (6)	−0.1815 (8)	4.6 (2)	4.5 (3)	5.2 (3)	−1.4 (2)	2.1 (2)	1.3 (2)
C(12)	0.5047 (8)	1.4968 (7)	−0.2041 (9)	5.5 (2)	5.2 (3)	7.8 (4)	−2.7 (2)	3.0 (2)	0.9 (3)
C(13)	0.3810 (8)	1.4938 (7)	−0.1848 (9)	5.2 (3)	3.9 (3)	8.2 (4)	−1.4 (2)	3.0 (2)	1.3 (3)
C(14)	0.3935 (7)	1.3821 (7)	−0.1454 (8)	3.3 (2)	4.7 (3)	7.0 (3)	−1.1 (2)	2.6 (2)	0.9 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
C(102)	0.143 (1)	0.366 (1)	0.178 (1)	9.5 (3)	C104	0.199 (2)	0.345 (2)	0.435 (2)	17.6 (7)
C(103)	0.116 (2)	0.305 (2)	0.281 (2)	17.5 (7)	C105	0.322 (1)	0.386 (1)	0.429 (1)	10.8 (4)
					O(101)	0.2919 (7)	0.3702 (6)	0.2779 (7)	8.2 (2)

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

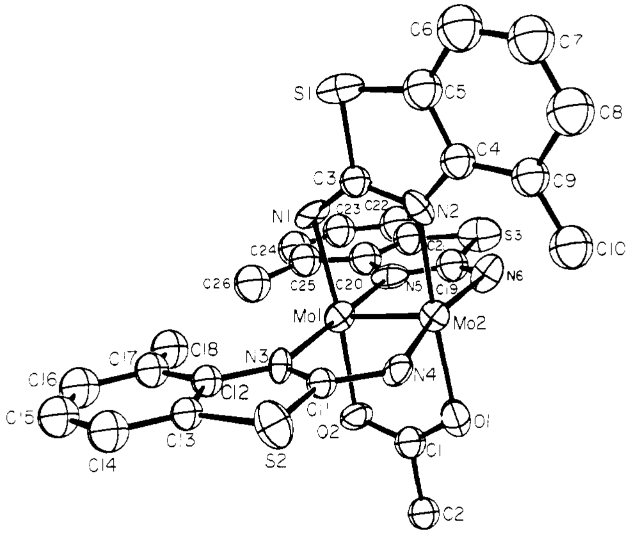

Figure 1. ORTEP drawing of the $Mo_2(ambt)_3(CH_3CO_2)$ molecule (1). Ellipsoids of thermal motion, scaled to enclose 30% of the electron density, represent each atom.

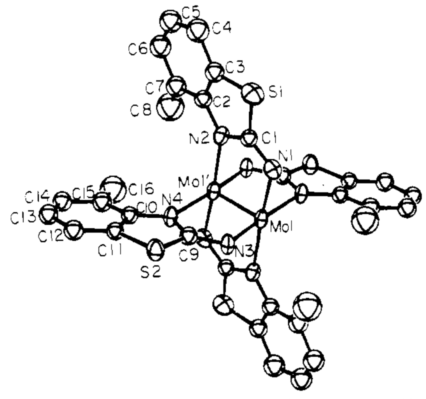

Figure 2. ORTEP drawing of the $Mo_2(ambt)_4$ molecule (2). Ellipsoids of thermal motion, scaled to enclose 30% of the electron density, represent each atom.

Table V. Bond Distances for $Mo_2(ambt)_3(O_2CCH_3)\cdot 2THF$ (1)

atoms	dist, Å	atoms	dist, Å
Mo(1)–Mo(2)	2.093 (3)	C(31)–C(32)	1.88 (8)
–O(1)	2.16 (1)	C(32)–C(33)	1.48 (8)
–N(1)	2.11 (2)	C(33)–C(34)	1.77 (7)
–N(3)	2.26 (2)	N(4)–C(11)	1.39 (2)
–N(5)	2.25 (2)	N(5)–C(19)	1.33 (3)
Mo(2)–O(2)	2.15 (1)	–C(20)	1.45 (3)
–N(2)	2.16 (2)	N(6)–C(19)	1.28 (3)
–N(4)	2.17 (2)	C(1)–C(2)	1.58 (3)
–N(6)	2.12 (2)	C(4)–C(5)	1.41 (3)
S(1)–C(3)	1.81 (2)	–C(9)	1.38 (3)
–C(5)	1.71 (2)	C(5)–C(6)	1.44 (3)
S(2)–C(11)	1.74 (2)	C(6)–C(7)	1.30 (3)
–C(13)	1.77 (2)	C(7)–C(8)	1.36 (3)
S(3)–C(19)	1.79 (3)	C(8)–C(9)	1.53 (3)
–C(21)	1.71 (2)	C(9)–C(10)	1.44 (3)
O(1)–C(1)	1.23 (2)	C(12)–C(13)	1.39 (2)
O(2)–C(1)	1.25 (2)	–C(17)	1.42 (3)
O(3)–C(27)	1.44 (4)	C(13)–C(14)	1.43 (3)
–C(30)	1.36 (4)	C(14)–C(15)	1.38 (3)
O(4)–C(31)	1.52 (5)	C(15)–C(16)	1.38 (3)
–C(34)	1.50 (6)	C(16)–C(17)	1.40 (3)
N(1)–C(3)	1.30 (2)	C(17)–C(18)	1.51 (3)
N(2)–C(3)	1.34 (2)	C(20)–C(21)	1.37 (3)
–C(4)	1.39 (2)	–C(25)	1.44 (3)
N(3)–C(11)	1.33 (2)	C(21)–C(22)	1.47 (3)
–C(12)	1.40 (2)	C(22)–C(23)	1.44 (3)
C(27)–C(28)	1.58 (5)	C(23)–C(24)	1.30 (3)
C(28)–C(29)	1.48 (5)	C(24)–C(25)	1.48 (3)
C(29)–C(20)	1.34 (5)	C(25)–C(26)	1.49 (3)

was added and the reaction mixture stirred for approximately 16 h. The reaction mixture was then filtered, and orange crystals (ca. 3–4 mg) were obtained by slow diffusion of a layer of hexane into the THF solution.

X-ray Crystallography. Crystals suitable for X-ray analysis were embedded in epoxy cement within a glass capillary and mounted on either a Syntex P$\bar{1}$ or Enraf-Nonius CAD-4F automatic diffractometer. The procedures used for data collection as well as methods used in the solution and refinement of the structure were standard and have been described previously for both Syntex[3a] and CAD-4[3b] data.

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(3) (a) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chem.* **1979**, *18*, 3569. (b) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

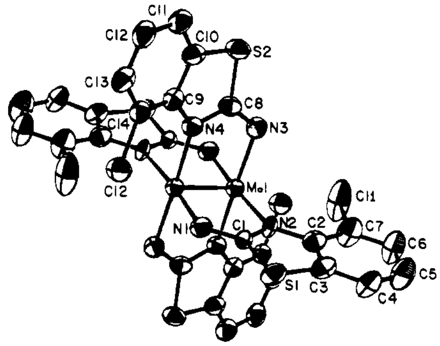


Figure 3. ORTEP drawing of the $Mo_2(acbt)_4$ molecule (**2**). Ellipsoids of thermal motion, scaled to enclose 30% of the electron density, represent each atom.

Table VI. Bond Angles for $Mo_2(ambt)_3(O_2CCH_3)\cdot 2THF$ (1)

atoms	angle, deg	atoms	angle, deg
Mo(2)-Mo(1)-O(1)	92.2 (4)	N(5)-C(19)-N(6)	125 (2)
-N(1)	93.8 (5)	N(5)-C(20)-C(21)	112 (2)
-N(3)	92.1 (4)	-C(25)	130 (2)
-N(5)	89.3 (5)	C(21)-C(20)-C(25)	119 (2)
O(1)-Mo(1)-N(1)	174.0 (6)	Mo(1)-N(1)-C(3)	115 (1)
-N(3)	89.0 (5)	Mo(2)-N(2)-C(3)	112 (1)
-N(5)	89.3 (5)	-C(4)	132 (1)
N(1)-Mo(1)-N(3)	90.6 (6)	C(3)-N(2)-C(4)	115 (2)
-N(5)	90.9 (6)	Mo(1)-N(3)-C(11)	114 (1)
N(3)-Mo(1)-N(5)	177.9 (6)	-C(12)	137 (1)
Mo(1)-Mo(2)-O(2)	90.9 (4)	C(11)-N(3)-C(12)	108 (1)
-N(2)	92.9 (5)	Mo(2)-N(4)-C(11)	114 (1)
-N(4)	95.8 (4)	Mo(1)-N(5)-C(19)	114 (2)
-N(6)	96.4 (5)	-C(20)	131 (2)
O(2)-Mo(2)-N(2)	176.1 (6)	C(19)-N(5)-C(20)	115 (2)
-N(4)	87.5 (5)	Mo(2)-N(6)-C(19)	115 (2)
-N(6)	89.7 (6)	O(1)-C(1)-O(2)	125 (2)
N(2)-Mo(2)-N(4)	91.8 (6)	-C(2)	118 (2)
-N(6)	90.2 (6)	O(2)-C(1)-C(2)	117 (2)
N(4)-Mo(2)-N(6)	167.5 (6)	S(1)-C(3)-N(1)	124 (2)
C(3)-S(1)-C(5)	90 (1)	-N(2)	110 (2)
C(11)-S(2)-C(13)	89 (1)	N(1)-C(3)-N(2)	126 (2)
C(19)-S(3)-C(21)	92 (1)	N(2)-C(4)-C(5)	112 (2)
Mo(1)-O(1)-C(1)	115 (1)	-C(9)	124 (2)
Mo(2)-O(2)-C(1)	116 (1)	C(5)-C(4)-C(9)	123 (2)
C(13)-O(4)-C(34)	98 (4)	S(1)-C(5)-C(4)	112 (2)
C(7)-C(8)-C(9)	119 (2)	-C(6)	130 (2)
C(4)-C(9)-C(8)	115 (2)	C(4)-C(5)-C(6)	118 (2)
-C(10)	126 (2)	C(5)-C(6)-C(7)	121 (2)
C(8)-C(9)-C(10)	119 (2)	C(6)-C(7)-C(8)	124 (3)
S(2)-C(11)-N(3)	117 (2)	S(3)-C(21)-C(20)	112 (2)
-N(4)	119 (2)	-C(22)	125 (2)
N(3)-C(11)-N(4)	125 (2)	C(20)-C(21)-C(22)	123 (2)
N(3)-C(12)-C(13)	117 (2)	C(21)-C(22)-C(23)	112 (3)
-C(17)	126 (2)	C(22)-C(23)-C(24)	131 (3)
C(13)-C(12)-C(17)	117 (2)	C(23)-C(24)-C(25)	115 (3)
S(2)-C(13)-C(12)	108 (2)	C(20)-C(25)-C(24)	120 (2)
-C(14)	125 (2)	-C(26)	120 (2)
C(12)-C(13)-C(14)	126 (2)	C(24)-C(25)-C(26)	119 (2)
C(13)-C(14)-C(15)	112 (2)	O(3)-C(27)-C(28)	93 (3)
C(14)-C(15)-C(16)	126 (2)	C(27)-C(28)-C(29)	112 (4)
C(15)-C(16)-C(17)	119 (2)	C(28)-C(29)-C(30)	92 (4)
C(12)-C(17)-C(16)	119 (2)	C(29)-C(30)-O(3)	120 (4)
-C(18)	121 (2)	O(4)-C(31)-C(32)	69 (4)
C(16)-C(17)-C(18)	120 (2)	C(31)-C(32)-C(33)	69 (4)
S(3)-C(19)-N(5)	110 (2)	C(32)-C(33)-C(34)	75 (4)
-N(6)	125 (2)	C(33)-C(34)-O(4)	94 (4)

Pertinent crystallographic parameters for the three compounds are summarized in Table I.

Results

Atomic positional and thermal parameters for $Mo_2(ambt)_3(CH_3CO_2)\cdot 2THF$ (**1**), $Mo_2(ambt)_4\cdot THF$ (**2**), and $Mo_2(acbt)_4\cdot 2THF$ (**3**) are listed in Tables II–IV, respectively. Figures 1–3 show the molecular structures and atomic labeling schemes for the three compounds. Bond distances and angles are presented in Tables V and VI for **1**, in Tables VII and VIII for **2**, and in Tables IX and X for **3**.

Table VII. Bond Distances for $Mo_2(ambt)_4\cdot THF$ (2)

atoms	dist, A	atoms	dist, A
Mo(1)-Mo(1)′	2.103 (1)	C(3)-C(4)	1.45 (1)
-N(1)	2.143 (7)	C(4)-C(5)	1.36 (1)
-N(2)′	2.201 (7)	C(5)-C(6)	1.36 (1)
-N(3)	2.130 (7)	C(6)-C(7)	1.42 (1)
-N(4)′	2.211 (7)	C(7)-C(8)	1.52 (2)
S(1)-C(1)	1.754 (9)	C(10)-C(11)	1.40 (1)
-C(3)	1.74 (1)	-C(15)	1.41 (1)
S(2)-C(9)	1.783 (9)	C(11)-C(12)	1.40 (1)
-C(11)	1.736 (8)	C(12)-C(13)	1.38 (1)
N(1)-C(1)	1.31 (1)	C(13)-C(14)	1.36 (1)
N(2)-C(1)	1.35 (1)	C(14)-C(15)	1.39 (1)
-C(2)	1.39 (1)	C(15)-C(16)	1.50 (2)
N(3)-C(9)	1.33 (1)	C(17)-C(18)	1.45 (2)
N(4)-C(9)	1.33 (1)	-O(1)	1.36 (2)
-C(10)	1.42 (1)	C(18)-O(1)	1.36 (2)
C(2)-C(3)	1.39 (1)		
-C(7)	1.40 (1)		

Table VIII. Bond Angles for $Mo_2(ambt)_4\cdot THF$ (2)

atoms	angle, deg	atoms	angle, deg
Mo(1)′-Mo(1)-N(1)	93.0 (2)	S(1)-C(3)-C(2)	110.4 (7)
-N(2)′	92.8 (2)	-C(4)	126.8 (8)
-N(3)	93.2 (2)	C(2)-C(3)-C(4)	122.8 (9)
-N(4)′	93.4 (2)	C(3)-C(4)-C(5)	115 (1)
N(1)-Mo(1)-N(2)′	173.0 (2)	C(4)-C(5)-C(6)	125 (1)
-N(3)	85.8 (3)	C(5)-C(6)-C(7)	119 (1)
-N(4)′	90.2 (3)	C(2)-C(7)-C(8)	122 (1)
N(2)′-Mo(1)-N(3)	90.0 (3)	-C(6)	119.4 (9)
N(2)′-Mo(1)-N(4)′	93.2 (3)	C(6)-C(7)-C(8)	118 (1)
N(3)-Mo(1)-N(4)′	172.5 (2)	S(2)-C(9)-N(3)	121.2 (7)
C(1)-S(1)-C(3)	89.6 (4)	-N(4)	114.1 (6)
C(9)-S(2)-C(11)	89.1 (4)	N(3)-C(9)-N(4)	124.7 (8)
Mo(1)-N(1)-C(1)	117.6 (6)	C(11)-C(10)-N(4)	114.3 (7)
Mo(1)′-N(2)-C(1)	113.6 (6)	-C(15)	127.7 (8)
-C(2)	135.6 (6)	C(15)-C(10)-N(4)	118.0 (8)
C(1)-N(2)-C(2)	110.7 (7)	S(2)-C(11)-C(10)	111.1 (6)
Mo(1)-N(3)-C(9)	116.2 (6)	-C(12)	125.7 (7)
Mo(1)′-N(4)-C(9)	111.8 (5)	C(10)-C(11)-C(12)	123.1 (8)
-C(10)	137.1 (5)	C(11)-C(12)-C(13)	116.2 (8)
C(9)-N(4)-C(10)	110.9 (7)	C(12)-C(13)-C(14)	122.2 (9)
S(1)-C(1)-N(1)	123.6 (7)	C(13)-C(14)-C(15)	121.5 (9)
-N(2)	114.0 (7)	C(10)-C(15)-C(14)	118.7 (9)
N(1)-C(1)-N(2)	122.3 (8)	-C(16)	122.8 (9)
N(2)-C(2)-C(3)	115.2 (8)	C(14)-C(15)-C(16)	118 (1)
-C(7)	126.6 (8)	O(1)-C(18)-C(17)	125 (2)
C(3)-C(2)-C(7)	118.2 (9)	C(17)-O(1)-C(18)	89 (1)

The strucure of **1** was solved in the monoclinic space group $P2_1/n$. Each molecule occupies a general position within the unit cell, and as a result the molecule has no crystallographically imposed symmetry. The molecule is, therfore, not restricted to the totally eclipsed configuration but is free to adopt a staggered configuration. There does appear to be a slight tendency for this to occur, since there is an average 1.85° twist of the ligands about the metal-metal bond. (See Table XI). However, the magnitude of the twist is about at the level of the uncertainties and has no chemical significance. Each molecule has three ambt ligands and one acetate ligand. The two ambt ligands that are opposite to each other are related by a virtual mirror plane containing the other thiazole ligand (which has the opposite orientation) and the acetate ligand. The virtual symmetry of the molecule is thus derived solely from one mirror plane. The two THF molecules per molecule of complex occupy the voids between the molecules, and there are no axially coordinated ligands. As is typical of THF molecules occupying such positions, they are poorly defined under refinement and have extremely high temperature factors. Whether this is a result of partial occupancy, high thermal

Table IX. Bond Distances for $Mo_2(acbt)_4·THF$ (3)

atoms	dist, Å	atoms	dist, Å
Mo(1)–Mo(1)′	2.117 (1)	C(3)–C(4)	1.376 (7)
–N(1)′	2.131 (4)	C(4)–C(5)	1.397 (7)
–N(2)	2.191 (3)	C(5)–C(6)	1.376 (7)
–N(3)	2.137 (4)	C(6)–C(7)	1.412 (7)
–N(4)′	2.216 (3)	C(9)–C(10)	1.408 (7)
Cl(1)–C(7)	1.742 (5)	–C(14)	1.374 (7)
Cl(2)–C(14)	1.728 (5)	C(10)–C(11)	1.405 (7)
S(1)–C(1)	1.768 (4)	C(11)–C(12)	1.383 (8)
–C(3)	1.745 (5)	C(12)–C(13)	1.408 (8)
S(2)–C(8)	1.766 (5)	C(13)–C(14)	1.394 (8)
–C(10)	1.721 (5)	O(101)–C(102)	1.41 (1)
N(1)–C(1)	1.309 (6)	–C(105)	1.41 (1)
N(2)–C(1)	1.360 (6)	C(102)–C(103)	1.53 (2)
–C(2)	1.390 (6)	C(103)–C(104)	1.50 (2)
N(3)–C(8)	1.289 (6)	C(104)–C(105)	1.58 (2)
N(4)–C(8)	1.362 (6)	Cl(1)–Cl(2)	3.192 (2)
–C(9)	1.395 (6)	Mo(1)–Cl(1)	3.516 (2)
C(2)–C(3)	1.414 (6)	–Cl(2)	3.257 (2)
–C(7)	1.383 (6)		

Table X. Bond Angles for $Mo_2(acbt)_4·2THF$ (3)

atoms	angle, deg	atoms	angle, deg
Mo(1)′–Mo(1)–N(1)′	92.5 (1)	C(102)–O(101)–C(105)	115.6 (7)
–N(2)	93.09 (9)	O(101)–C(102)–C(103)	101.0 (9)
–N(3)	93.4 (1)	C(102)–C(103)–C(104)	105 (1)
–N(4)′	91.74 (9)	C(103)–C(104)–C(105)	105 (1)
N(1)′–Mo(1)–N(2)	173.1 (1)	C(104)–C(105)–O(101)	101.8 (9)
–N(3)	86.6 (1)	N(2)–C(2)–C(3)	115.4 (4)
–N(4)′	91.5 (1)	–C(7)	127.9 (4)
N(2)–Mo(1)–N(3)	89.2 (1)	C(3)–C(2)–C(7)	116.4 (4)
–N(4)′	92.2 (1)	S(1)–C(3)–C(2)	109.8 (3)
N(3)–Mo(1)–N(4)′	174.6 (1)	–C(4)	127.0 (4)
C(1)–S(1)–C(3)	89.6 (2)	C(2)–C(3)–C(4)	123.1 (5)
C(8)–S(2)–C(10)	90.3 (2)	C(3)–C(4)–C(5)	118.5 (5)
Mo(1)′–N(1)–C(1)	117.9 (3)	C(4)–C(5)–C(6)	120.6 (5)
Mo(1)–N(2)–C(1)	112.9 (3)	C(5)–C(6)–C(7)	119.6 (5)
–C(2)	136.7 (3)	Cl(1)–C(7)–C(2)	121.3 (3)
C(1)–N(3)–C(2)	110.3 (4)	–C(6)	116.9 (4)
Mo(1)–N(3)–C(8)	118.8 (3)	C(2)–C(7)–C(6)	121.6 (4)
Mo(1)–N(4)–C(8)	114.6 (3)	S(2)–C(8)–N(3)	124.8 (4)
–C(9)	135.4 (3)	–N(4)	113.8 (3)
C(8)–N(4)–C(9)	109.9 (4)	N(3)–C(8)–N(4)	121.4 (4)
S(1)–C(1)–N(1)	124.2 (4)	N(4)–C(9)–C(10)	115.8 (4)
–N(2)	113.8 (3)	–C(14)	126.4 (4)
N(1)–C(1)–N(2)	122.0 (4)	C(10)–C(9)–C(14)	117.8 (5)
C(12)–C(13)–C(14)	117.6 (6)	S(2)–C(10)–C(9)	110.1 (4)
Cl(2)–C(14)–C(9)	118.6 (4)	–C(11)	128.3 (4)
–C(13)	118.4 (4)	C(9)–C(10)–C(11)	121.6 (5)
C(9)–C(14)–C(13)	123.0 (5)	C(10)–C(11)–C(12)	118.1 (5)
		C(11)–C(12)–C(13)	121.9 (5)

motion, disorder, or some combination of these could not be determined.

The structure of **2** was solved in the monoclinic space group $P2_1/c$. The molecules reside on the inversion centers at $^1/_2$, 0, 0 and $^1/_2$, 0, $^1/_2$, with the inversion center at the midpoint of each Mo–Mo bond. This requires the ligand arrangement shown in Figure 2, where ligands oriented in the same direction are cis to each other. The maximum point symmetry permitted with this ligand arrangment is C_{2h}, and the molecule has virtually this symmetry. There are, however, deviations from equality of all N–Mo–N angles about each Mo atom, which are evidently caused by repulsion between the methyl groups. Thus, the N(2)′–Mo(1)–N(4)′ angle, 93.2 (3)°, is greater and the N(1)–Mo(1)–N(3) angle, 85.8 (3)°, less than the mean angle of 89.8 (3)°. The THF molecules are required to be disordered since they reside on crystallographic inversion centers. As is usually the case, they do not refine well.

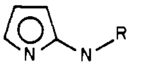
The structure of **3** was solved in the triclinic space group $P\bar{1}$. Each molecule resides on a center of inversion in the unit cell with the center of inversion at the midpoint of the Mo–Mo bond. The ligand arrangement is identical with that in **2** where the ligands that are oriented in the same direction are cis to each other. Here, also, there are distortions of the N–Mo–N angles, very similar to those for **2**, from the maximum C_{2h} virtual symmetry as a result of repulsions between the chlorine atoms. Thus, the N(2)–Mo(1)–N(4)′ angle, 92.2 (1)°, is greater and the N(1)′–Mo(1)–N(3) angle, 86.6 (1)°, less than the mean angle of 89.4 (1)°, all of which are quite similar to the angles in **2**. The THF molecules again occupy the voids between the molecules, but in this case they are reasonably well-defined.

Table XI. Selected Torsional Angles for $Mo_2(ambt)_3(CH_3CO_2)·2THF$

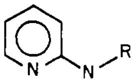
atoms	angle, deg
N(3)–Mo(1)–Mo(2)–N(4)	2.8
N(1)–Mo(1)–Mo(2)–N(2)	1.5
N(5)–Mo(1)–Mo(2)–N(6)	1.8
O(2)–Mo(1)–Mo(2)–O(1)	1.3
	av 1.9

Discussion

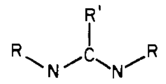
As noted in the Introduction, this work was undertaken to see if ligands in which the bridging N–C–N system is derived from a five-membered ring, a, rather than from a six-membered ring, b, or an open chain, c, would be able to give stable compounds and, if so, to see what effect the necessarily larger N–C–N angle might have on the other structure parameters.



a



b



c

For an idealized ligand of type a, that is, with a regular pentagonal ring, the N–C–N angle would be 126°, whereas for an idealized ligand of type b the corresponding angle would be only 120°. Naturally, in real cases we do not expect precisely these angles, but there should be a tendency for a ligand of type a to have an N–C–N angle 5–10° larger than that in a ligand of type b.

Our first important result is that ligands of type a are capable of forming the same type of complex as those of type b. The preparations can be accomplished by the displacement of acetato ligands from the convenient starting material $Mo_2(O_2CCH_3)_4$, using the monoanions of the new ligands. It is to be noted, however, that the displacement of *all* acetato ligands from $Mo_2(O_2CCH_3)_4$ occurs only upon prolonged reaction as shown by the formation of **1** after only a 1 h reaction time and **2** after allowing a much longer (ca. 36 h) time. In the preparation of **3** a long (ca. 16 h) reaction time was allowed.

The larger N–C–N angle expected for ligands of type a might be expected to allow less overlap with metal atom orbitals and might also result in somewhat different M′–M–N bond angles as compared to those already known for ligands of type b and c. Table XII presents a comparison of the bridge angles and the M′–M–N angles in several pertinent compounds. For compounds **1**–**3** the bridge angle averages 123.7°, and this is indeed significantly greater than the average value of 116.4° for the compounds containing type b ligands and 116.7° for the amidinato-bridged (type c) compound. The M′–M–N angles, however, are essentially the same for all three ligand types.

The lack of any trend in the M′–M–N angles, despite real changes in the N–C–N angles from type a ligands on the one hand to type b and c on the other, is not a paradox, however.

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Table XII. Comparison of Structural Parameters for Compounds with a N–C–N Bridge

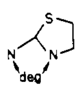
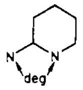
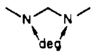
compd				Mo–Mo, Å	Mo–Mo′–N, deg	ref
$Mo_2(ambt)_4$·THF	122.3 (8) 124.7 (8)			2.103 (1)	93.1 (N-hetero) 93.1 (N-amino) 93.1 (av)	this work
$Mo_2(ambt)_3(CH_3CO_2)$·2THF	126 (2) 125 (2) 125 (2)			2.093 (3)	91.4 (N-hetero) 95.3 (N-amino) 93.9 (av)	this work
$Mo_2[(C_6H_4N)NC(CH_3)O]_4$		115.0 (13)		2.037 (3)	92.8	4
$Mo_2[PhC(NPh)_2]_4$			118 (1) 114 (1) 118 (1)	2.090 (1)	92.4	5
$Mo_2(map)_4$·2THF		116.7 (9) 116.2 (8) 117.5 (9) 116.6 (9)		2.070 (1)	92.9 (N-hetero) 93.1 (N-amino) 93.0 (av)	6
$Mo_2(acbt)_4$·2THF	122.0 (4) 121.4 (4)			2.117 (1)	92.4 (N-hetero) 93.0 (N-amino) 92.7 (av)	this work

Table XIII. Average Mo–O Bond Lengths in Selected Carboxylato Compounds

compd	M–O, Å	ref
$Mo_2(OBut)_4(O_2COBut)_2$	2.126	7
$Mo_2(O_2CH)_4$	2.11	8
$Mo_2(O_2CCH_3)_4$	2.12	9
$Mo(O_2CCF_3)_4$	2.06	10
$Mo_2(O_2CCH_3NH_3]_4{}^{4+}$	2.13	11
$Mo_2(O_2CC_6H_5)_4$·2diglyme	2.11	12

It must be noted that in compounds **1**–**3**, as well as in $Mo_2(map)_4$·2THF, steric repulsions between methyl groups (or Cl atoms, in **3**) cause lengthening of one of the Mo–N bonds and slight twisting of the ligand, and these distortions have the effect of reducing the M′–M–N angle. Another factor that negates any simple relationship between M′–M–N angles and N–C–N angles is the inconstancy of the Mo–Mo bond lengths, which, as may be seen in Table XII, increase in the order $Mo_2(map)_4$, 2.070 (1) Å < $Mo_2[PhC(NPh)_2]_4$, 2.090 (1) Å < $Mo_2(ambt)_4$, 2.103 (1) Å < $Mo_2(acbt)_4$, 2.117 (1) Å.

The nonbonded repulsions in these compounds have noticeable effects on the metal–ligand bonds. Table V shows that in **1**, for example, there are two distinctly different Mo–N(hetero) bond distances, one at 2.16 Å and two at ~2.25 Å. The shortest Mo–N(hetero) bond distance, 2.16 Å, is associated with the ambt ligand that is trans to the acetato ligand and the longest, ~2.25 Å, Mo-N(hetero) distance with the ambt ligands that are trans to each other. This increase of ~0.10 Å is a result of repulsions between the methyl groups of the ambt ligands. Where there is little or no repulsion, as for the ambt ligand trans to the acetate ligand, a normal Mo–N bond distance is observed. Repulsive interactions between the methyl groups of the trans ambt ligands may be relieved either by a rotation of the ambt ligands, about a line passing through the bridge carbon atoms and bisecting the Mo–Mo bond, so that the methyl groups are rotated away from each other, or by increasing of the Mo–N bond lengths, or both. In compound **1**, increasing the Mo–N bond length is the prime mode of reduction. However, as previously pointed out, there is also a small rotation of ~0.9° of the ambt ligands about the bridge carbon atoms. A similar situation occurs in compounds **2** and **3**, but with one significant difference. In **2** and **3** the repulsive interactions are between methyl groups or chlorine atoms on ligands that are cis to each other. These repulsive interactions are relieved both by rotations of the ambt and acbt ligands, which makes the N–Mo–N angles unequal, and by increases in the Mo–N(hetero) bond lengths. However, the nature of the distortions in the N–Mo–N angles is somewhat different for the two compounds. In **2** the angular distortions result from an equivalent rotation of all of the ambt ligands about a line passing through the bridge carbon atoms and bisecting the Mo–Mo bond. The rotations are such that the methyl groups, of the ambt ligands that are cis to one another, are rotated away from each other and the amine nitrogens are rotated toward each other. The N(2)′–Mo(1)–N(4)′ angle, 93.2 (3)°, is, therefore, greater and the N(1)–Mo(1)–N(3) angle, 85.8 (3)°, less than the ~90° angles expected between cis Mo–N bonds. However, in compound **3** the angular distortions appear to arise from rotations involving only two of the acbt ligands (i.e., those involving the N(1)–C(1)–N(2) and N(1)′–C(1)′–N(2)′ bridges). Although all of the acbt ligands are displaced, those involving the N(3)–C(8)–N(4) and N(3)′–C(8)′–N(4)′ bridges are rotated only 0.85°, about a line passing through the bridge carbon atoms and bisecting the Mo–Mo bond, away from the adjacent chlorine atom. This gives rise to an N(3)–Mo_2–N(4) dihedral angle of only 1.7°. The positions of the N(3), N(4), N(3)′, and N(4)′ atoms remain essentially unchanged. On the other hand, the actb ligands involving the N(1)–C(1)–N(2) and N(1)′–C(1)′–N(2)′ bridges are rotated 1.45° away from the adjacent chlorine atom about a line passing through C(1) and bisecting the Mo–Mo bond, giving rise to an N(1)–Mo_2–N(2) dihedral angle of 3.9°. The angular distortions are, therefore, predominantly due to rotations about C(1) and C(1)′. Although the distortions in **3** are different than in **2**, the results are essentially identical. The N(2)–Mo(1)–N(4)′ angle, 92.2 (1)°, is again greater, and the N(1)′–Mo(1)′–N(3) angle, 86.6 (1)°, is less than the average angle expected. These angles correspond directly to the N(2)–Mo(1)–N(4)′ and N(1)–Mo(1)–N(3) angles in compound **2**. The cis arrangement of the ambt and acbt ligands appears to be well suited to allowing rotation to relieve steric repulsions, and as a result, a somewhat smaller increase in the Mo–N(hetero) bond distance is necessitated than in compound **1** (i.e., from ~2.16 to 2.205 (7) (average) and 2.203 (3) Å (average in **2** and **3**, respectively, to 2.22 (2) Å (average) in **1**).

We address one final comment to the Mo–O distances in **1**. Table XIII presents a summary of the average Mo–O

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distances in selected acetato-bridged dimolybdenum compounds. From the table it is clear that a typical Mo–O distance is 2.10–2.11 Å. In **1**, however, the Mo–O distance is 2.155 Å (average). Although, it is impossible to generalize from only one structure, it appears possible that this increase in the Mo–O bond distance is a result of a trans labilization of the acetate ligand by the ambt ligand. Since this is the first trisubstituted mixed-ligand complex of the quadruply bonded system, there is no precedent for an observed trans effect in these bimetallic complexes. Attempts are now being made to prepare further mixed-ligand complexes.

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Registry No. **1**, 75534-39-3; **2**, 75534-41-7; **3**, 75534-43-9; dimolybdenum tetraacetate, 14221-06-8.

Supplementary Material Available: Tables of observed and calculated structure factors for the three structures (25 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

π Acidity of Tris(2-cyanoethyl)phosphine. X-ray Structural Studies of $M(CO)_5P(CH_2CH_2CN)_3$ (M = Cr, Mo) and $Mo(CO)_5P(C_6H_5)_3$

F. ALBERT COTTON,* DONALD J. DARENSBOURG, and WILLIAM H. ILSLEY

Received July 1, 1980

The X-ray crystal structures and IR spectra of the compounds $M(CO)_5P(CH_2CH_2CN)_3$, M = Cr (**1**) and Mo (**2**), and $Mo(CO)_5P(C_6H_5)_3$ (**3**) are reported. Compounds **1** and **2** are isomorphous and crystallize in the monoclinic space group $P2_1/n$ with unit cell parameters a = 16.913 (5) Å, 17.140 (2) Å, b = 6.538 (3) Å, 6.639 (1) Å, c = 17.402 (4) Å, 17.574 (2) Å, β = 117.91 (2)°, 118.09 (1)°, v = 1700 (2) Å^3, 1764.3 (9) Å^3, and Z = 4, 4, where the two figures for each parameter refer to the Cr and Mo compounds, respectively. Each molecule occupies a general position within the unit cell. The M–P distances are 2.364 (1) and 2.506 (1) Å for the Cr and Mo compounds, and the average M–CO$_{ax}$ and M–CO$_{eq}$ distances are 1.876 (4) and 1.891 (4) Å and 2.008 (4) and 2.044 (5) Å, respectively. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 9.653 (5) Å, b = 12.301 (5) Å, c = 9.503 (8) Å, α = 90.88 (5)°, β = 95.73 (5)°, γ = 74.89 (4)°, V = 1084 (2) Å^3, and Z = 2. Again, each molecule occupies a general position within the cell. The Mo–P distance is 2.560 (1) Å and the average Mo–CO$_{ax}$ and Mo–CO$_{eq}$ distances are 1.995 (3) and 2.046 (4) Å, respectively. On the basis of these structural data as well as ν(CO) infrared data, tris(2-cyanoethyl)phosphine can be described as a good π-acceptor ligand.

Introduction

Spectroscopic data (ν(CO) and ^{13}C NMR)[1,2] for low-valent metal carbonyl complexes containing trivalent phosphorus ligands strongly imply that the 2-cyanoethyl substituent on phosphorus is very electron withdrawing relative to the ethyl group. This is a somewhat surprising result since the CN substituent is separated from the phosphorus atom by two saturated carbon atoms. Concomitantly, the tris(2-cyanoethyl)phosphine is a much poorer base than is triethylphosphine, having a ΔHNP value of 679 relative to 111 for the latter phosphine.[3]

In general trivalent phosphorus ligands bearing good electron-withdrawing groups exhibit strong metal–phosphorus binding in low-valent organo–transition-metal derivatives.[4] In order to examine the bonding properties of this rather unique ligand, we have carried out X-ray structural investigations of the $M(CO)_5P(CH_2CH_2CN)_3$ species, where M = Cr and Mo. In addition the X-ray structure of $Mo(CO)_5P(C_6H_5)_3$ was determined for comparative purposes.

Experimental Section

Preparations. A procedure similar to that described by Connor et al.[5] was employed in the synthesis of the $M(CO)_5P(CH_2CH_2CN)_3$ (M = Cr, Mo) complexes. A methylene chloride solution of 0.54 g (1.2 mmol) of $[(C_2H_5)_4N][Mo(CO)_5Br]$, 0.25 g (1.3 mmol) of P-

Table I. Crystallographic Parameters

parameter	compd 1	compd 2	compd 3
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	16.913 (5)	17.140 (2)	9.653 (5)
b, Å	6.538 (3)	6.639 (1)	12.301 (5)
c, Å	17.402 (4)	17.574 (2)	9.503 (8)
α, deg	90.0	90.0	90.88 (5)
β, deg	117.91 (2)	118.09 (1)	95.73 (5)
γ, deg	90.0	90.0	74.89 (4)
V, Å^3	1700 (2)	1764.3 (9)	1084 (2)
Z	4	4	2
d_x, g/cm^3 (calcd)	1.505	1.616	1.527
fw	385.24	429.18	498.29
cryst size, mm	0.20 × 0.30 × 0.30	0.20 × 0.25 × 0.30	0.20 × 0.30 × 0.30
μ, cm^{-1}	8.250	8.518	7.027
2θ range, deg	0–45	0–45	0–50
no. of data	1532	2617	3199
$F_o^2 > 3\sigma(F_o^2)$	1433	1793	3081
no. of variables	269	269	331
R_1	0.027	0.026	0.024
R_2	0.038	0.034	0.035
esd	0.974	1.052	0.808
diffractometer	Syntex P$\bar{1}$	CAD-4F	Syntex P$\bar{1}$

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