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# Two New Amidato-Bridged Dimolybdenum(II) Compounds: Tetrakis[*N*-(2,6-dimethylphenyl)formamido]dimolybdenum Bis(tetrahydrofuranate) and Tetrakis(*N*-phenylpivalamido)dimolybdenum

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Two new amidato-bridged dimolybdenum compounds, $Mo_2[(2\text{-xylyl})NC(H)O]_4(ax\text{-THF})_2$ (**1**) and $Mo_2[PhNC(CMe_3)O]_4$ (**2**), have been prepared and their structures determined. The structure of compound **1** was solved in the monoclinic space group $C2/c$ with unit cell parameters $a = 11.892$ (2) Å, $b = 25.274$ (3) Å, $c = 14.668$ (1) Å, $\beta = 96.16$ (2)°, $V = 4383$ (2) Å$^3$, and $Z = 4$. Each molecule resides on a crystallographic $C_2$ axis that is collinear with the Mo–Mo bond. The two THF molecules are axially coordinated. The Mo–O(THF) distance, 2.577 (5) Å, is the shortest that has been observed to date, and this may be related to the relatively long Mo–Mo distance, 2.113 (1) Å. The structure of **2** was solved in the triclinic space group $P\bar{1}$ with unit cell parameters $a = 11.254$ (3) Å, $b = 11.751$ (2) Å, $c = 9.531$ (4) Å, $\alpha = 103.36$ (2)°, $\beta = 113.00$ (3)°, $\gamma = 70.35$ (4)°, $V = 1085$ (1) Å$^3$, and $Z = 1$. Each molecule resides on a center of inversion. Thus, the ligand arrangements in the two molecules are different, with the core arrangements being trans for **1** and cis for **2**. The Mo–Mo bond length in this compound, 2.070 (1) Å, is markedly shorter than that in **1**, while the other bond lengths within the cores of the two molecules are essentially the same.

## Introduction

We have recently isolated and examined the structures of several dichromium compounds of the type $Cr_2[RNC(R')O]_4L_2$, where R = $C_6H_5$, 2-xylyl, or $p\text{-}Me_2NC_6H_4$, R′ = $CH_3$ or $NHC_6H_5$, and L = $CH_2Cl_2$, THF, or $C_5H_5N$.[1-3] This work has shown that in the absence of axial ligands these compounds have extremely short Cr–Cr bonds, while in the presence of axial ligands we find substantially longer Cr–Cr bonds. Ligands of the type RNC(R′)O appear, therefore, to favor the formation of compounds having not only intrinsically short metal–metal bonds but also a marked sensitivity toward axial coordination. For further information concerning the influence of RNC(R)O ligands on multiply bonded bimetallic compounds, our investigations have been extended to include the analogous dimolybdenum compounds. Only one dimolybdenum analogue, $Mo_2[PhNC(CH_3)O]_4\cdot 2THF$,[1] had previously been studied. We have now succeeded in preparing two additional compounds, $Mo_2[(2\text{-xylyl})NC(H)O]_4\cdot 2THF$ (**1**) and $Mo_2\{PhNC[C(CH_3)_3]O\}_4$ (**2**), and now present a detailed description of their structures.

## Experimental Section

2′,6′-Dimethylformanilide was prepared by reacting 2,6-xylidine with formic acid. Trimethylacetanilide was prepared by reacting aniline with pivalic acid. The compounds were recrystallized from ethanol/water to form colorless needles. All reactions were carried out under an atmosphere of dry argon.

**Preparation of $Mo_2[(2\text{-xylyl})NC(H)O]_4\cdot 2THF$ (1).** A solution of 0.30 g (2 mM) of 2′,6′-dimethylformanilide in 35 mL of THF was treated with 1 equiv of *n*-BuLi to form the anion $[(2\text{-xylyl})NC(H)O]^-$. To this was added 0.22 g (0.5 mM) of tetrakis(acetato)dimolybdenum, and the mixture was stirred for 15 h. Subsequent filtration yielded a yellow solution which was subjected to slow evaporation by a continuous flow of argon, whereupon very pale yellow crystals formed, which were suitable for X-ray crystallographic analysis.

**Preparation of $Mo_2\{C_6H_5NC[C(CH_3)_3]O\}_4$ (2).** A solution of 0.34 g (2 mM) of *N*-phenyl-2,2-dimethylpropanamide in 25 mL of THF was treated with 1 equiv of *n*-BuLi to form the anion $[PhNC[C(CH_3)_3]O]^-$. To this was added 0.22 g (0.5 mM) of molybdenum acetate, and the mixture was stirred for 15 h. Subsequent filtration yielded a yellow solution. Crystals (~2 mg) were obtained by slow diffusion of a layer of hexane into the THF solution.

Table I. Crystallographic Parameters

| parameter | 1 | 2 |
|---|---|---|
| space group | $C2/c$ | $P\bar{1}$ |
| $a$, Å | 11.892 (2) | 11.254 (3) |
| $b$, Å | 25.274 (3) | 11.751 (2) |
| $c$, Å | 14.668 (1) | 9.531 (4) |
| $\alpha$, deg | 90.0 | 103.36 (2) |
| $\beta$, deg | 96.16 (2) | 113.00 (3) |
| $\gamma$, deg | 90.0 | 70.35 (4) |
| $V$, Å$^3$ | 4383 (2) | 1085 (1) |
| $Z$ | 4 | 1 |
| fw | 928.84 | 896.84 |
| cryst size, mm | 0.20 × 0.25 × 0.32 | 0.10 × 0.30 × 0.30 |
| $\mu$, cm$^{-1}$ | 6.151 | 6.146 |
| 2$\theta$ range, deg | 0–45 | 0–45 |
| no. of data | 2923 | 3818 |
| $F_o^2 > 3\sigma(F_o^2)$ | 2184 | 2701 |
| no. of variables | 235 | 244 |
| $R_1$ | 0.052 | 0.063 |
| $R_2$ | 0.073 | 0.074 |
| esd | 1.982 | 1.677 |
| $d_X$, g/cm$^3$ (calcd) | 1.407 | 1.372 |

**X-ray Crystallography.** Suitable crystals of each compound were embedded in epoxy cement within a thin glass capillary and mounted on an Enraf-Nonius CAD-4F automatic diffractometer. Procedures for both data collection and solution and refinement of the structure have been discussed previously.[4] Pertinent crystallographic parameters are summarized in Table I.

## Results and Discussion

The structure of **1** was solved in the monoclinic space group $C2/c$. The atomic parameters are listed in Table II, and bond lengths and bond angles are given in Tables III and IV, respectively. Each molecule lies on a crystallographic $C_2$ axis that is collinear with the Mo–Mo bond. Associated with each molecule are two THF molecules which occupy the axial positions and conform to the crystallographic $C_2$ axis by adopting the twist conformation. The (2-xylyl)NC(H)O ligands are so bonded that the O and N atoms of each ligand are trans to their own kind, to be consistent with the $C_2$ symmetry axis. Each molybdenum atom is, of course, bonded to two oxygen and two nitrogen atoms, and the ligands that are trans to one another have their phenyl groups facing each other. The 2-xylyl groups of each ligand are rotated ap-

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(2) Cotton, F. A.; Ilsley, W. H.; Kaim, W. *J. Am. Chem. Soc.* **1980**, *102*, 3464.
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**Table II.** Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2[(2\text{-xylyl})NC(H)O]\cdot 2THF$ (1)[a]

| atom | *x* | *y* | *z* | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo(1) | 0.00177 (7) | 0.02772 (6) | 0.11191 (7) | 2.76 (2) | 2.66 (2) | 1.90 (2) | −0.74 (2) | 1.32 (1) | 0.07 (2) |
| O(1) | 0.1799 (5) | −0.1040 (4) | 0.2038 (5) | 3.4 (2) | 3.0 (2) | 2.4 (2) | −0.6 (2) | 1.3 (1) | 0.1 (2) |
| O(2) | 0.1135 (5) | 0.1499 (4) | 0.1562 (5) | 4.0 (2) | 3.4 (2) | 2.2 (2) | −1.5 (1) | 1.7 (1) | −0.3 (1) |
| N(1) | 0.1754 (6) | −0.1755 (5) | −0.0364 (6) | 3.6 (2) | 2.8 (2) | 2.5 (2) | −0.9 (2) | 1.8 (2) | −0.1 (2) |
| N(2) | 0.1115 (6) | 0.0967 (5) | −0.0845 (6) | 3.4 (2) | 3.0 (2) | 2.3 (2) | −1.1 (2) | 1.3 (2) | 0.0 (2) |
| C(1) | 0.2357 (7) | −0.1829 (6) | 0.1140 (8) | 3.1 (3) | 2.7 (3) | 3.1 (3) | −0.9 (2) | 1.4 (2) | 0.3 (2) |
| C(2) | 0.3671 (8) | −0.2729 (7) | 0.1948 (9) | 3.4 (3) | 4.1 (3) | 3.8 (3) | −0.1 (3) | 1.1 (3) | 1.1 (3) |
| C(3) | 0.4701 (12) | −0.3124 (15) | 0.1116 (14) | 5.0 (5) | 18 (1) | 8.6 (6) | 3.8 (7) | 4.3 (4) | 5.8 (6) |
| C(4) | 0.4286 (14) | −0.2137 (11) | 0.3585 (14) | 6.8 (7) | 7.6 (7) | 5.5 (6) | 0.7 (6) | −2.3 (6) | −1.2 (5) |
| C(5) | 0.3328 (13) | −0.3839 (9) | 0.2116 (16) | 8.7 (7) | 6.2 (4) | 12.8 (8) | −2.0 (4) | −0.0 (6) | 5.8 (4) |
| C(6) | 0.2050 (8) | −0.2701 (7) | −0.1541 (8) | 3.4 (3) | 3.1 (3) | 2.5 (3) | 0.2 (3) | 1.5 (2) | 0.1 (2) |
| C(7) | 0.1525 (9) | −0.3695 (7) | −0.1846 (10) | 5.4 (4) | 2.7 (3) | 4.4 (4) | −0.7 (3) | 1.1 (3) | −0.0 (3) |
| C(8) | 0.1698 (11) | −0.4593 (9) | −0.3064 (12) | 7.6 (6) | 4.6 (5) | 5.7 (5) | −0.7 (4) | 2.5 (4) | −0.5 (4) |
| C(9) | 0.2376 (13) | −0.4494 (10) | −0.3933 (11) | 9.4 (7) | 5.4 (5) | 3.3 (4) | 1.1 (5) | 1.8 (4) | −1.0 (4) |
| C(10) | 0.2911 (11) | −0.3490 (10) | −0.3620 (11) | 8.3 (5) | 7.6 (6) | 4.6 (4) | 1.8 (5) | 4.0 (3) | 1.5 (4) |
| C(11) | 0.2734 (9) | −0.2582 (9) | −0.2410 (9) | 6.2 (4) | 5.7 (4) | 4.2 (3) | −0.3 (3) | 3.8 (2) | 0.4 (3) |
| C(12) | 0.1480 (7) | 0.1632 (6) | 0.0476 (8) | 2.8 (3) | 2.9 (3) | 2.8 (3) | −1.1 (2) | 1.0 (2) | 0.4 (2) |
| C(13) | 0.2286 (8) | 0.2565 (7) | 0.0934 (9) | 5.9 (3) | 4.9 (3) | 3.1 (3) | −3.4 (2) | 1.7 (2) | −0.1 (2) |
| C(14) | 0.3785 (11) | 0.1846 (12) | 0.1407 (16) | 4.2 (4) | 10.0 (7) | 11.4 (9) | −3.4 (4) | 1.8 (5) | −0.6 (6) |
| C(15) | 0.2064 (10) | 0.3410 (9) | 0.2355 (11) | 12.2 (5) | 7.9 (4) | 5.7 (4) | −7.6 (3) | 5.7 (3) | −4.0 (3) |
| C(16) | 0.1917 (13) | 0.3319 (9) | −0.0386 (12) | 16.9 (7) | 7.9 (4) | 5.3 (5) | −8.2 (4) | 1.9 (4) | 1.4 (3) |
| C(17) | 0.1428 (7) | 0.1014 (6) | −0.2157 (8) | 3.9 (3) | 3.1 (3) | 3.1 (3) | −1.3 (2) | 1.9 (2) | 0.6 (2) |
| C(18) | 0.0408 (9) | 0.1593 (8) | −0.3381 (9) | 5.0 (4) | 6.6 (4) | 2.9 (3) | −2.2 (3) | 1.1 (2) | 1.5 (3) |
| C(19) | 0.0706 (10) | 0.1627 (9) | −0.4670 (10) | 6.2 (5) | 7.4 (5) | 3.6 (4) | −2.0 (4) | 0.5 (3) | 2.3 (3) |
| C(20) | 0.1991 (10) | 0.1034 (9) | −0.4744 (10) | 7.3 (4) | 7.8 (5) | 3.2 (3) | −3.7 (3) | 2.3 (3) | −0.1 (3) |
| C(21) | 0.2971 (9) | 0.0442 (9) | −0.3545 (10) | 6.7 (4) | 6.7 (4) | 4.5 (3) | −2.9 (3) | 3.8 (2) | −0.5 (3) |
| C(22) | 0.2703 (8) | 0.0405 (7) | −0.2232 (9) | 4.3 (3) | 4.2 (3) | 4.5 (3) | −1.1 (3) | 2.8 (2) | 0.1 (3) |

[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.** Bond Distances (Å) for $Mo_2[(2\text{-xylyl})NC(H)O]_4(ax\text{-THF})_2$ (1)

| | | | |
|---|---|---|---|
| Mo(1)–Mo(2) | 2.113 (1) | C(3)–C(4) | 1.402 (9) |
| –O(1) | 2.095 (3) | –C(9) | 1.52 (1) |
| –O(3) | 2.590 (7) | C(4)–C(5) | 1.43 (1) |
| –N(2) | 2.185 (4) | C(5)–C(6) | 1.38 (1) |
| Mo(2)–O(2) | 2.096 (3) | C(6)–C(7) | 1.403 (8) |
| –O(4) | 2.564 (5) | C(7)–C(8) | 1.484 (9) |
| –N(1) | 2.188 (4) | C(11)–C(12) | 1.399 (8) |
| O(1)–C(1) | 1.300 (6) | –C(16) | 1.378 (8) |
| O(2)–C(10) | 1.299 (6) | C(12)–C(13) | 1.392 (9) |
| O(3)–C(19) | 1.483 (11) | –C(18) | 1.548 (9) |
| O(4)–C(21) | 1.436 (8) | C(13)–C(14) | 1.36 (1) |
| N(1)–C(1) | 1.303 (6) | C(14)–C(15) | 1.40 (1) |
| –C(2) | 1.413 (6) | C(15)–C(16) | 1.410 (9) |
| N(2)–C(10) | 1.309 (6) | C(16)–C(17) | 1.535 (9) |
| –C(11) | 1.437 (6) | C(19)–C(20) | 1.54 (2) |
| C(2)–C(3) | 1.413 (8) | C(20)–C(20)′ | 1.41 (3) |
| –C(7) | 1.403 (8) | C(21)–C(22) | 1.45 (1) |
| | | C(22)–C(22)′ | 1.47 (2) |

**Table IV.** Bond Angles (Deg) for $Mo_2[(2\text{-xylyl})NC(H)O]_4(ax\text{-THF})_2$ (1)

| | | | |
|---|---|---|---|
| Mo(2)–Mo(1)–O(1) | 93.56 (9) | N(1)–C(2)–C(3) | 119.7 (5) |
| –N(2) | 90.4 (1) | –C(7) | 120.1 (5) |
| O(1)–Mo(1)–O(1)′ | 172.9 (2) | C(3)–C(2)–C(7) | 120.1 (5) |
| –N(2) | 89.2 (1) | C(2)–C(3)–C(4) | 120.1 (6) |
| –N(2)′ | 90.7 (1) | –C(9) | 121.6 (5) |
| N(2)–Mo(1)–N(2)′ | 179.2 (2) | C(4)–C(3)–C(9) | 118.2 (6) |
| Mo(1)–Mo(2)–O(2) | 93.74 (9) | C(3)–C(4)–C(5) | 118.4 (7) |
| –N(1) | 90.5 (1) | C(4)–C(5)–C(6) | 121.4 (6) |
| O(2)–Mo(2)–O(2)′ | 172.5 (2) | C(5)–C(6)–C(7) | 120.1 (7) |
| –N(1) | 90.2 (2) | C(2)–C(7)–C(6) | 119.7 (6) |
| –N(1)′ | 89.8 (2) | –C(8) | 119.9 (5) |
| N(1)–Mo(2)–N(1)′ | 179.0 (2) | C(6)–C(7)–C(8) | 120.3 (6) |
| Mo(1)–O(1)–C(1) | 118.4 (3) | O(1)–C(10)–N(2) | 120.8 (5) |
| Mo(2)–O(2)–C(10) | 118.4 (3) | N(2)–C(11)–C(12) | 120.1 (5) |
| C(19)–O(3)–C(19) | 112 (1) | –C(16) | 119.3 (5) |
| C(21)–O(4)–C(21) | 110.3 (7) | C(12)–C(11)–C(16) | 120.6 (5) |
| Mo(2)–N(1)–C(1) | 116.5 (3) | C(11)–C(12)–C(13) | 118.7 (6) |
| –C(2) | 126.2 (3) | –C(18) | 120.6 (5) |
| C(1)–N(1)–C(2) | 117.3 (4) | C(13)–C(12)–C(18) | 120.6 (6) |
| Mo(1)–N(2)–C(10) | 116.7 (3) | C(12)–C(13)–C(14) | 121.4 (7) |
| –C(11) | 127.7 (3) | C(13)–C(14)–C(15) | 120.4 (7) |
| C(10)–N(2)–C(11) | 115.5 (4) | C(14)–C(15)–C(16) | 119.0 (7) |
| O(1)–C(1)–N(1) | 121.0 (5) | C(11)–C(16)–C(15) | 119.9 (6) |
| C(15)–C(16)–C(17) | 117.8 (7) | –C(17) | 122.2 (6) |
| O(3)–C(19)–C(20) | 103.7 (9) | O(4)–C(21)–C(22) | 106.9 (6) |
| C(19)–C(20)–C(20)′ | 109.8 (7) | C(21)–C(22)–C(22)′ | 107.7 (5) |

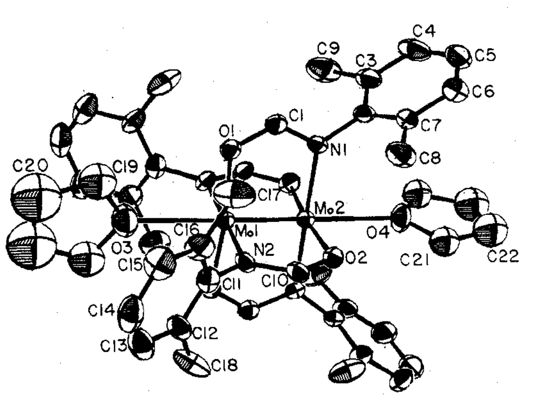

**Figure 1.** Structure of the formula unit $Mo_2[(2,6\text{-}Me_2C_6H_3)NC(H)O]_4(THF)_2$ (**1**) showing the atomic labeling scheme. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of the electron density.

proximately perpendicular to the $OMo_2N$ planes as evidenced by the average dihedral angle of 91.2°. All these features can be seen in Figure 1. The Mo–Mo distance is 2.113 (1) Å and is significantly longer than the Mo–Mo bond length, 2.086 (2) Å, found in the related compound $Mo_2[PhNC(CH_3)O]_4\cdot 2THF$.[1] The much longer distance in **1** is presumably due to the presence of the axial THF molecules, with a mean Mo–O distance of 2.577 (5) Å.

The average Mo–O and Mo–N bond lengths are 2.095 (3) and 2.186 (4) Å, respectively, and are essentially identical with those observed in $Mo_2[PhNC(CH_3)O]_4\cdot 2THF$.[1] The remaining distances and angles show no unusual features and will therefore not be discussed.

The presence of axially coordinated THF molecules in this compound is interesting for two reasons. The first is that dimolybdenum compounds have not, in general, shown much

**Table V.** Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2\{PhNC[C(CH_3)_3]O\}_4$ (**2**)[a]

| atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Mo(1) | 0.0000 (0) | 0.16834 (3) | 0.2500 (0) | 2.96 (3) | 2.92 (3) | 4.01 (4) | 0 | 0.39 (3) | 0 |
| Mo(2) | 0.0000 (0) | 0.25197 (3) | 0.2500 (0) | 2.72 (3) | 2.88 (3) | 4.35 (4) | 0 | 0.65 (3) | 0 |
| O(1) | 0.0998 (4) | 0.1632 (2) | 0.1410 (3) | 3.8 (2) | 3.5 (2) | 4.9 (2) | −0.0 (2) | 0.9 (2) | −0.5 (2) |
| O(2) | −0.1424 (4) | 0.2574 (2) | 0.1531 (3) | 3.5 (2) | 3.9 (2) | 5.0 (2) | 0.1 (2) | 0.3 (2) | 0.9 (2) |
| O(3) | 0.0000 (0) | 0.0659 (3) | 0.2500 (0) | 11.5 (6) | 5.3 (4) | 9.3 (5) | 0 | 2.7 (5) | 0 |
| O(4) | 0.0000 (0) | 0.3534 (3) | 0.2500 (0) | 6.6 (4) | 3.3 (3) | 9.7 (5) | 0 | −0.5 (4) | 0 |
| N(1) | 0.1103 (4) | 0.2527 (2) | 0.1398 (4) | 2.9 (2) | 3.5 (2) | 4.4 (3) | −0.5 (2) | 1.0 (2) | −0.0 (2) |
| N(2) | −0.1512 (4) | 0.1678 (2) | 0.1512 (4) | 3.2 (2) | 3.5 (2) | 4.7 (3) | −1.0 (2) | 0.0 (2) | 0.6 (2) |
| C(1) | 0.1374 (6) | 0.2068 (3) | 0.1083 (5) | 3.4 (3) | 4.2 (3) | 5.1 (3) | −0.1 (3) | 0.4 (3) | −0.0 (3) |
| C(2) | 0.1589 (5) | 0.2979 (3) | 0.1032 (5) | 3.8 (3) | 4.0 (3) | 4.9 (3) | −0.2 (2) | 2.1 (2) | −0.6 (3) |
| C(3) | 0.2673 (6) | 0.3151 (3) | 0.1404 (6) | 4.7 (3) | 5.5 (4) | 6.5 (4) | −1.2 (3) | 2.2 (3) | −0.9 (3) |
| C(4) | 0.3139 (7) | 0.3614 (4) | 0.1077 (6) | 7.0 (4) | 6.8 (4) | 9.8 (5) | −3.4 (3) | 4.4 (3) | −2.8 (4) |
| C(5) | 0.2501 (8) | 0.3898 (3) | 0.0357 (7) | 10.0 (5) | 4.6 (4) | 12.4 (6) | −0.5 (4) | 7.0 (4) | 0.2 (4) |
| C(6) | 0.1458 (7) | 0.3723 (4) | −0.0019 (6) | 6.8 (4) | 5.7 (4) | 8.9 (5) | 0.2 (4) | 3.2 (4) | 0.9 (4) |
| C(7) | 0.0996 (6) | 0.3258 (3) | 0.0305 (5) | 5.1 (3) | 5.0 (3) | 6.4 (4) | 0.9 (3) | 2.7 (3) | 1.9 (3) |
| C(8) | −0.0092 (7) | 0.3048 (4) | −0.0141 (6) | 4.3 (4) | 9.8 (5) | 7.8 (5) | −0.5 (4) | −0.2 (4) | 3.8 (4) |
| C(9) | 0.3377 (8) | 0.2837 (4) | 0.2148 (8) | 4.4 (4) | 11.9 (7) | 9.0 (6) | −1.9 (4) | −0.0 (4) | 0.8 (5) |
| C(10) | −0.1908 (6) | 0.2139 (3) | 0.1225 (5) | 3.3 (3) | 4.1 (3) | 5.5 (3) | −1.0 (2) | 0.5 (3) | 0.5 (3) |
| C(11) | −0.2103 (6) | 0.1225 (3) | 0.1105 (5) | 4.3 (3) | 3.9 (3) | 5.0 (3) | −0.0 (3) | −1.2 (3) | −0.1 (3) |
| C(12) | −0.2926 (6) | 0.0972 (3) | 0.1561 (5) | 4.0 (3) | 5.1 (4) | 6.6 (4) | −1.4 (3) | −0.7 (3) | 1.0 (3) |
| C(13) | −0.3477 (7) | 0.0533 (4) | 0.1151 (7) | 6.2 (4) | 5.7 (4) | 9.3 (6) | −1.8 (4) | −2.0 (4) | 1.6 (4) |
| C(14) | −0.3230 (8) | 0.0349 (3) | 0.0323 (8) | 8.2 (5) | 4.3 (4) | 11.4 (7) | −0.0 (4) | −2.7 (5) | −0.9 (4) |
| C(15) | −0.2400 (7) | 0.0595 (4) | −0.0133 (7) | 6.5 (5) | 6.5 (5) | 9.4 (6) | −1.1 (4) | −2.0 (4) | −2.2 (4) |
| C(16) | −0.1847 (6) | 0.1045 (3) | 0.0265 (6) | 4.5 (4) | 6.3 (4) | 6.5 (4) | −0.3 (3) | −0.6 (3) | −0.9 (4) |
| C(17) | −0.1020 (8) | 0.1338 (4) | −0.0293 (6) | 6.4 (5) | 11.7 (7) | 6.9 (5) | −2.3 (5) | 1.0 (4) | −3.1 (5) |
| C(18) | −0.3282 (7) | 0.1201 (4) | 0.2466 (6) | 7.1 (4) | 10.8 (6) | 7.0 (5) | −4.8 (4) | 1.3 (4) | 0.6 (4) |
| C(19) | 0.0496 (10) | 0.0332 (6) | 0.1804 (9) | 11.5 (4) | | | | | |
| C(20) | 0.0327 (17) | −0.0239 (8) | 0.2126 (14) | 20.6 (8) | | | | | |
| C(21) | −0.0850 (8) | 0.3859 (4) | 0.2006 (6) | 8.0 (3) | | | | | |
| C(22) | 0.0502 (10) | 0.4406 (5) | 0.2837 (9) | 11.3 (4) | | | | | |

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

**Table VI.** Bond Distances for $Mo_2[C_6H_5NC(CMe_3)O]_4$ (**2**)

| | | | |
|---|---|---|---|
| Mo–Mo′ | 2.070 (1) | C(6)–C(7) | 1.403 (9) |
| -O(1) | 2.086 (4) | -C(11) | 1.387 (9) |
| -O(2) | 2.083 (4) | C(7)–C(8) | 1.40 (1) |
| -N(1)′ | 2.153 (5) | C(8)–C(9) | 1.37 (1) |
| -N(2)′ | 2.156 (5) | C(9)–C(10) | 1.42 (1) |
| O(1)–C(1) | 1.284 (7) | C(10)–C(11) | 1.40 (1) |
| O(2)–C(12) | 1.295 (7) | C(12)–C(13) | 1.535 (9) |
| N(1)–C(1) | 1.335 (8) | C(13)–C(14) | 1.54 (1) |
| -C(6) | 1.439 (7) | -C(15) | 1.54 (1) |
| N(2)–C(12) | 1.312 (7) | -C(16) | 1.55 (1) |
| -C(17) | 1.441 (7) | C(17)–C(18) | 1.392 (9) |
| C(1)–C(2) | 1.528 (9) | -C(22) | 1.393 (9) |
| C(2)–C(3) | 1.54 (1) | C(18)–C(19) | 1.41 (1) |
| -C(4) | 1.54 (1) | C(19)–C(20) | 1.40 (1) |
| -C(5) | 1.54 (1) | C(20)–C(21) | 1.37 (1) |
| | | C(21)–C(22) | 1.410 (9) |

**Table VII.** Bond Angles (Deg for $Mo_2\{C_6H_5NC[C(CH_3)_3]O\}_4$ (**2**)

| | | | |
|---|---|---|---|
| Mo(1)′-Mo(1)–O(1) | 94.0 (1) | C(3)–C(2)–C(4) | 109.5 (8) |
| -O(2) | 94.7 (1) | -C(5) | 110.6 (8) |
| -N(1)′ | 90.4 (1) | C(4)–C(2)–C(5) | 106.8 (8) |
| -N(2)′ | 89.6 (1) | N(1)–C(6)–C(7) | 117.1 (6) |
| O(1)–Mo(1)–O(2) | 88.9 (2) | -C(11) | 121.0 (6) |
| -N(1)′ | 174.4 (2) | C(7)–C(6)–C(11) | 121.8 (6) |
| -N(2)′ | 90.0 (2) | C(6)–C(7)–C(8) | 119.1 (8) |
| O(2)–Mo(1)–N(1)′ | 87.4 (2) | C(7)–C(8)–C(9) | 120.0 (9) |
| -N(2)′ | 175.6 (2) | C(8)–C(9)–C(10) | 120.9 (8) |
| N(1)′-Mo(1)–N(2)′ | 93.4 (2) | C(9)–C(10)–C(11) | 119.5 (9) |
| Mo(1)–O(1)–C(1) | 119.8 (4) | C(6)–C(11)–C(10) | 118.7 (8) |
| Mo(1)–O(2)–C(12) | 118.9 (4) | O(2)–C(12)–N(2) | 117.4 (5) |
| Mo(1)′-N(1)–C(1) | 118.3 (4) | -C(13) | 114.1 (5) |
| -C(6) | 116.1 (4) | N(2)–C(12)–C(13) | 128.5 (6) |
| C(1)–N(1)–C(12) | 124.6 (5) | C(12)–C(13)–C(14) | 106.9 (6) |
| Mo(1)′-N(2)–C(12) | 119.4 (4) | -C(15) | 109.4 (6) |
| -C(17) | 116.9 (4) | -C(16) | 112.4 (6) |
| C(12)–N(2)–C(17) | 123.7 (5) | C(14)–C(13)–C(15) | 107.3 (7) |
| O(1)–C(1)–N(1) | 117.3 (6) | -C(16) | 110.4 (8) |
| -C(2) | 114.9 (6) | C(15)–C(13)–C(16) | 110.3 (7) |
| N(1)–C(1)–C(2) | 127.8 (6) | N(2)–C(17)–C(18) | 118.7 (6) |
| C(1)–C(2)–C(3) | 113.8 (6) | -C(22) | 120.0 (6) |
| -C(4) | 108.3 (6) | C(18)–C(17)–C(22) | 121.2 (6) |
| -C(5) | 107.7 (6) | C(17)–C(18)–C(19) | 118.8 (7) |
| C(18)–C(19)–C(20) | 120.2 (8) | C(20)–C(21)–C(22) | 120.9 (8) |
| C(19)–C(20)–C(21) | 120.1 (7) | C(17)–C(22)–C(21) | 118.7 (7) |

tendency to accept axial ligands. In the dithio-bridged $Mo_2^{4+}$ compounds $Mo_2(S_2CR)_4(THF)_2$ (R = Ph, $CH_3$)[5] and $Mo_2(S_2COEt)_4(THF)_2$,[6] the Mo–O(THF) distances are quite long, viz., ca. 2.70 Å. In the trifluoroacetate compounds $Mo_2(O_2CCF_3)_4(NC_5H_5)_2$[7] and $Mo_2(O_2CCF_3)_4(Et_2O)_2$,[8] the Mo–N(pyridine) and Mo–O(THF) distances are shorter, 2.548 (8) and 2.575 (4) Å, respectively. The latter is very similar to those found here, which average 2.57 ± 0.02 Å.

The second reason for interest in the presence of axially coordinated THF molecules in **1** is that in the case of $Mo_2[PhNC(CH_3)O]_4 \cdot 2THF$,[1] despite the similarity of the ligands and the overall formula, the two THF molecules were *not* coordinated to the molybdenum atoms but were placed on sites between the $Mo_2[PhNC(CH_3)O]_4$ molecules. The explanation for this difference lies at least in part in the effect of the 2- and 6-methyl groups on the phenyl rings, causing them to adopt rotational orientations that afford the least possible steric hindrance to ligands approaching the axial positions.

Compound **2** forms triclinic crystals, with one molecule per unit cell in space group $P\bar{1}$, thus imposing inversion symmetry upon the molecule. The atomic parameters are listed in Table V, and the bond lengths and angles are given in Tables VI and VII, respectively. The structure of the molecule is shown in Figure 2. The crystallographic inversion symmetry necessitates a different ligand arrangement from that in **1**. In this

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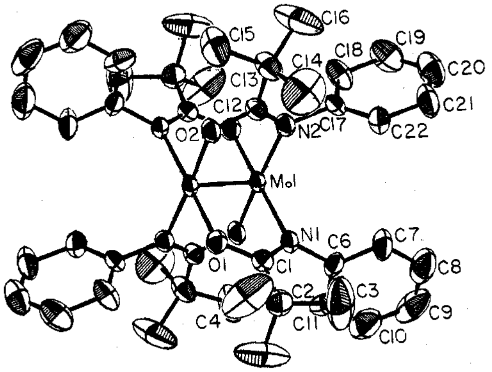
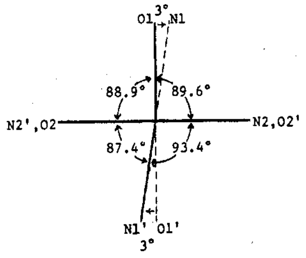


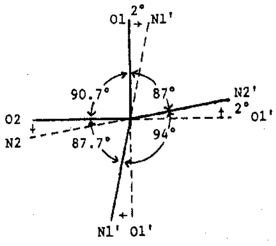
**Figure 2.** Structure of the $Mo_2[PhNC(CMe_3)O]_4$ (**2**) molecule showing the atomic labeling scheme. Each unlabeled atom is related to a labeled one by the inversion center at the midpoint of the Mo–Mo bond. Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of the electron density.

case, as in a number of others previously studied, notably $Mo_2[PhNC(CH_3)O]_4$,[1] the ligands that point in the same direction are cis to each other, and the virtual symmetry is $C_{2h}$.

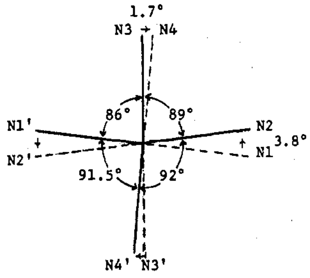
In this ligand arrangement the phenyl groups of adjacent ligands are necessarily close to each other, and there are significant repulsive interactions between these groups. This results in movements of the ligands to minimize these repulsions. Thus, there is a displacement by about 3° of the *N(1)*-phenyl group away from the *N(2)*-phenyl group, as shown in I. The position of the *N(2)*-phenyl group remains unchanged. Although not discussed in the report, a similar displacement also occurs in $Mo_2[PhNC(CH_3)O]_4{\cdot}2THF$[1] as shown in II. However, in this case the positions of both *N*-phenyl groups are displaced ca. 2° in order to relieve steric repulsive interactions; the positions of the oxygen atoms appear to remain unaltered. Similar displacements are also observed in $Mo_2(acbt)_4{\cdot}2THF$[9] (III) and $Mo_2(ambt)_4{\cdot}THF$[9] (IV). In $Mo_2(acbt)_4{\cdot}THF$ the interactions are relieved predominantly by a ~3.8° displacement of two of the ligands away from the adjacent chlorine atoms, although there is also a small, 1.7°, displacement of the remaining two ligands. In $Mo_2(ambt)_4{\cdot}THF$ all of the ligands are displaced away from the adjacent methyl groups.



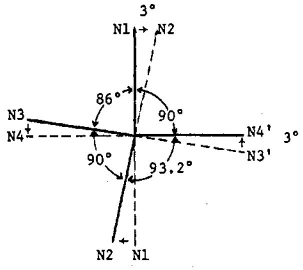
I



II



III



IV

The phenyl rings in **2** have dihedral angles, relative to the O(1)–C(1)–N(1) and O(2)–C(12)–N(2) planes, of 83.5 and 103.6°, respectively. The Mo–Mo bond length, 2.070 (1) Å, is among the shorter Mo–Mo bond distances known. Comparable bond lengths are found in $Mo_2(map)_4{\cdot}2THF$,[10] 2.070 (1) Å, and $Mo_2(dmhp)_4$,[11] 2.072 (1) Å. There are only three Mo–Mo distances that are shorter, and they are found in the compounds $Mo_2(mhp)_4$,[12] 2.065 (1) Å, $Mo_2(dmp)_4$,[13] 2.064 (1) Å, and $Mo_2(C_6H_4NNC(CH_3)O)_4$,[14] 2.037 (3) Å. The Mo–Mo bond length in **2** is somewhat shorter than that found in $Mo_2[PhNC(CH_3)O]_4{\cdot}2THF$,[1] 2.086 (1) Å. In line, therefore, with what has been observed in the case of dichromium compounds,[2] the more basic the ligand, the shorter will be the metal–metal bond. The shorter Mo–O, 2.084 (4) Å, and Mo–N, 2.154 (5) Å, bond lengths in **2** as compared with the corresponding bond lengths in $Mo_2[PhNC(CH_3)O]_4$ (i.e., 2.10 (1) and 2.16 (2) Å, respectively) are also indicative of the better donor ability of the PhNC(H)O ligand. The remaining bond lengths and angles show no unusual features and will, therefore, not be discussed.

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**Registry No.** **1**, 75112-19-5; **2**, 75112-20-8; tetrakis(acetato)dimolybdenum, 14221-06-8.

**Supplementary Material Available:** Tables of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

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