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[*N*-(2-Pyridyl)acetamido-*N*,*N*′]dimolybdenum: The (New) Shortest Known Molybdenum–Molybdenum Quadruple Bond

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The reaction of $Mo_2(O_2CCH_3)_4$ with the anion of *N*-(2-pyridyl)acetamide gives $Mo_2[(C_5NH_4)NC(O)CH_3]_4$, a moderately air-sensitive, red, crystalline compound. An X-ray crystallographic study of this substance has shown that it has the ligands coordinated through the two nitrogen atoms. The Mo–Mo distance is 2.037 (3) Å, which makes it the shortest Mo–Mo distance known, the previously shortest one, which occurs in $Mo_2[2,6\text{-}(MeO)_2C_6H_3]_4$, having been 2.064 (1) Å. The compound crystallizes in the tetragonal system with $a = 9.050$ (1) Å, $c = 17.438$ (3) Å, and $Z = 2$. From systematic absences the possible space groups were $I4$, $I\bar{4}$, and $I4/m$, of which only the last two were consistent with the Patterson function. The structure could not be refined in $I\bar{4}$ but using a disordered model it behaved satisfactorily in $I4/m$. Each ligand is treated as having two equally populated orientations; the actual symmetry of an individual molecule thus remains unknown but is probably D_{2d}.

Introduction

Although the strength of the quadruple bond between a pair of molybdenum atoms does not vary as extravagantly as does that between chromium atoms,[1,2] there is, nonetheless, considerable variation. Thus far, the lengths of $Mo\overset{4}{-}Mo$ bonds, as observed in some 46 structures,[3] have ranged from 2.064 (1) Å in $Mo_2[2,6\text{-}(MeO)_2C_6H_3]_4$ to 2.183 (2) Å in $Mo_2(allyl)_4$. The possible causes of this moderate variability in bond length are several, of which the following have been explicitly considered: (1) axial interaction (this has been shown[4,5] to have a real effect, but a small one); (2) twist angle (this also has been found to cause a measurable change in bond length, but, again, not a large one);[6] (3) simple inductive effect (the results for $Mo_2(O_2CR)_4$ compounds, in which the electronegativity of R has been varied over the range from CF_3 through Ph, H, CH_3, to $C(CH_3)_3$, have shown that bond length is essentially unaffected by changes in this parameter[5]).

It must be admitted that despite the results of these systematic studies, we are left with the existence of many variations that have no obvious explanation. This is not to say that it is particularly surprising that a change in the set of ligands from, e.g., four SO_4^{2-} ions to four 2-oxypyridinato ions might change the Mo–Mo bond length by as much ca. 0.05 Å but simply that this change could not have been predicted and cannot now be explicitly rationalized. Our understanding of the subject is still not sufficiently refined to account for such things, let alone predict them and it is, therefore, still necessary and important to conduct experimental studies to see whether further variations may occur as still other ligands are used.

In this paper we report a new dimolybdenum compound in which there is a shorter Mo–Mo quadruple bond than any previously seen. It is shorter by a nontrivial amount, 0.027 Å, despite the fact that the ligand involved would not appear to be markedly different from others previously used.

Experimental Section

A literature method[7] for the preparation of *N*-(2-pyridyl)acetamide, by condensation of 2-aminopyridine with acetic anhydride, was used. The product was recrystallized from ethanol and its identity confirmed by ^1H NMR spectroscopy.

Preparation of the Dimolybdenum Complex. The monoanion of *N*-(2-pyridinyl)acetamide was prepared by reacting the ligand (0.27 g, 2 mmol) with 1.3 mL of 1.6 M hexane solution of *n*-butyllithium in 25 mL of THF. Since even a slight excess of *n*-BuLi results in a yellow color, the anion can be made quantitatively by a "titration". Dimolybdenum tetraacetate (0.22 g, 0.5 mmol) was added and a red color developed immediately. After 1 day a red precipitate had formed which was partly dissolved by addition of more solvent (10 mL). The mixture was filtered, and the red solution was slowly evaporated in a stream of argon, whereupon red crystals deposited on the glass wall. They were only moderately sensitive to air and proved to be suitable for X-ray crystallography.

The mass spectrum (300 °C, 10^{-6} torr) had a peak at m/e 736.033 414 while the value calculated for the principal isotopic species of $Mo_2[(C_5NH_4)NC(O)CH_3]_4$ is 736.035 260.

X-ray Crystallography. A crystal of approximate dimensions 0.25 × 0.10 × 0.20 mm was covered with epoxy cement and mounted on the end of a thin glass fiber. Rotation and oscillation photographs along with data collected in a preliminary data set (range $18° \leq 2\theta \leq 25°$) showed that the crystal had tetragonal symmetry with systematic absences $h + k + l = 2n$, indicating the possible space groups $I4$, $I\bar{4}$, or $I4/m$. The widths at half-height (ω scans) of several strong reflections were found to be <0.30°. Cell constants, obtained by carefully centering 15 reflections in the range $18° \leq 2\theta \leq 25°$, were found to be $a = 9.050$ (1) Å and $c = 17.438$ (3) Å giving a calculated volume of 1428.2 (6) $Å^3$ which is consistent with two molecules per unit cell.

The automatic centering and autoindexing procedures followed have been previously described.[8] The linear absorption coefficient for Mo Kα radiation is 18.31 cm^{-1} and absorption corrections were therefore considered unnecessary.

Intensities were measured at 22 ± 4 °C on a Syntex $P\bar{1}$ autodiffractometer by using the θ–2θ scan technique. A total of 477 independent data were measured with Mo Kα (λ 0.71073 Å) radiation in the 2θ range from 1 to 45°. A variable scan speed of 4–24° min^{-1} was used with a scan range of $K\alpha_1 - 0.8°$ to $K\alpha_2 + 0.8°$ and a scan to background time ratio of 2. The intensities of three standard reflections were monitored throughout data collection and showed no significant decrease in intensity during the period of data collection.

Solution and Refinement.[9] The position of the crystallographically unique Mo atom was determined from a three-dimensional Patterson function which indicated that the space group is either $I\bar{4}$ or $I4/m$. Results of an NZ-test favored the space group $I\bar{4}$ but attempts to solve the structure in this space group failed. Attempts to solve the structure

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mo(1)	0.0000 (0)	0.0000 (0)	0.05839 (8)	4.84 (7)	4	4.16 (5)	0	0	0
O(1)	0.182 (2)	0.081 (2)	0.1848 (8)	16 (1)	11.1 (9)	6.1 (6)	1.6 (9)	−2.6 (8)	−0.6 (8)
N(1)	0.2203 (7)	0.0963 (7)	0.0646 (4)	5.7 (3)	5.1 (3)	6.5 (3)	0.0 (3)	−1.8 (3)	−0.7 (3)
C(1)	0.294 (1)	0.126 (1)	0.0000 (0)	6.5 (6)	3.6 (5)	9.1 (8)	0.9 (5)	0	0
C(2)	0.445 (2)	0.186 (2)	0.0000 (0)	5.1 (7)	9.0 (9)	23 (2)	−1.2 (7)	0	0
C(3)	0.499 (3)	0.213 (3)	0.0835 (17)	5.9 (9)	12 (2)	20 (2)	−4 (1)	2 (1)	0 (2)
C(4)	0.415 (1)	0.186 (2)	0.1501 (8)	10.3 (7)	16 (1)	17.0 (9)	−3.9 (7)	−6.2 (6)	−3.3 (8)
C(5)	0.273 (1)	0.121 (1)	0.1356 (6)	8.6 (6)	10.1 (7)	8.0 (6)	−1.2 (6)	−2.3 (5)	−0.4 (5)

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

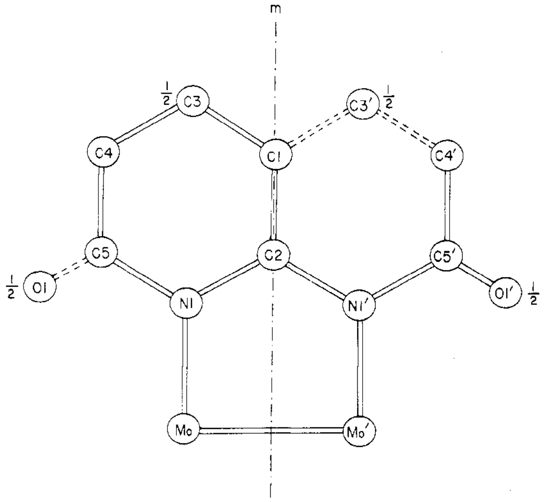

Figure 1. A schematic representation of the disordered ligand. The trace of the mirror plane (m) is shown by the –•–• line. Primes indicate atoms (or half atoms) related to others by reflection.

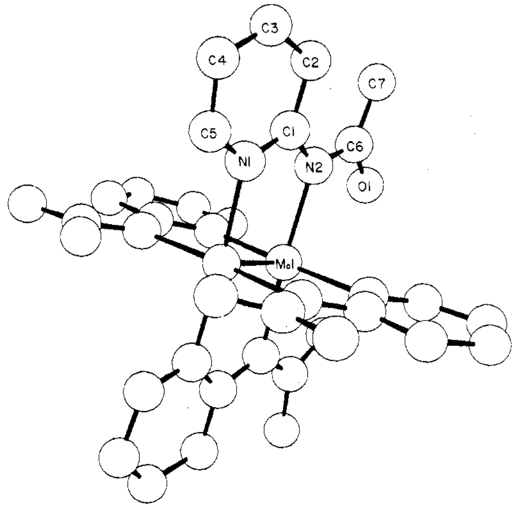

Figure 2. An overall view of the molecule showing it in the presumed D_{2d} configuration.

Table II. Bond Angles and Distances

	Bond Distances, Å		
Mo–Mo'	2.037 (3)	C(1)–C(2)	1.472 (21)
Mo–N(1)	2.178 (6)	C(2)–C(3)	1.554 (36)
O(1)–C(5)	1.244 (18)	C(3)–C(4)	1.409 (29)
N(1)–C(1)	1.335 (8)	C(4)–C(5)	1.429 (16)
N(1)–C(5)	1.346 (11)	Mo–O(1)	2.849 (15)
	Bond Angles, Deg		
Mo–Mo'–N(1)	92.8 (2)	N(1)–C(1)–C(2)	122.5 (6)
N(1)–Mo–N(1)''	174.3 (4)	C(1)–C(2)–C(3)	110.4 (1.1)
N(1)–Mo–N(1)'''	89.86 (2)	C(2)–C(3)–C(4)	125.2 (2.0)
Mo–N(1)–C(1)	119.6 (8)	C(3)–C(4)–C(5)	114.0 (1.8)
Mo–N(1)–C(5)	116.1 (7)	O(1)–C(5)–N(1)	110.4 (1.3)
C(1)–N(1)–C(5)	124.3 (8)	O(1)–C(5)–C(4)	126.2 (1.5)
N(1)–C(1)–N(1)	115.0 (1.3)	N(1)–C(5)–C(4)	123.4 (1.2)

in the acentric space group $I\bar{4}$ may be summarized as follows. Both configurations of the ligand were tried as well as the two possible enantiomorphs without success. It was possible to get the discrepancy factors down to 0.065 and 0.081 for R_1 and R_2, respectively, with a goodness of fit parameter of 1.67; however, the bond distances and bond angles made no chemical sense. The C–C distances in the benzene ring ranged from 1.198 to 1.795 Å and the C–C–C angles ranged from 98 to 129.9°. The C–N distances were 1.05 and 1.40 Å, respectively, while the C–O and C–C bonds in the acetyl group were 1.32 and 1.40 Å, respectively. Substantially the same results were obtained regardless of the ligand configuration or enantiomer tried. It may be noted that the Mo atom position and, hence, the Mo–Mo distance, did not vary significantly in either $I\bar{4}$ or $I4/m$ regardless of how the positions of other atoms shifted.

The structure was successfully solved in the space group $I4/m$ by using a disordered model in which each ligand is allowed to point randomly up or down along the z axis. Figure 1 shows schematically the nature of this disorder for one ligand and defines the numbering of the atoms. In effect this means that ring carbon atoms C(1) and C(2) were placed in the mirror plane at x, y, 0 and assigned full weights. The N atom and C(4) and C(5) were also given full weight, each of them representing half of the appropriate ring atoms and half of the appropriate $NC(O)CH_3$ nitrogen and carbon atoms. The oxygen atom and C(3) were each given half weight. This model is physically somewhat imperfect as indicated by the rather large components of the vibrational tensor for C(2), C(3), C(4), O and, to a lesser extent, C(5). However, it fits rather well for C(1) and N, to judge by their "almost normal" thermal parameters.

By use of this model, full-matrix anisotropic least-squares refinement of the nonhydrogen atoms yielded final discrepancy indices of

$$R_1 = (\sum||F_o| - |F_c||)/\sum|F_o| = 0.049$$

$$R_2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.061$$

and a goodness of fit parameter of 1.30. The function $\sum w(|F_o| - |F_c|)^2$ was minimized with the weighting factor, w, equal to $4F_o^2/\sigma(F_o^2)^2$. All structure factor calculations and least-squares refinements were executed by using 396 reflections having $I \geq 3\sigma(I)$. A table of the observed and calculated structure factors is available as supplementary material.

Results and Discussion

The atomic positional parameters are listed in Table I. Figure 1 shows schematically the way in which each ligand is disordered and how the atoms are numbered. Figure 2 shows a complete molecule having D_{2d} symmetry; be it noted again that while this seems likely to be the arrangement, we cannot be certain of it because of the nature of the disorder. The interatomic distances and angles are listed in Table II.

This investigation was not undertaken with the idea of obtaining an unusual Mo–Mo bond. Instead, the purpose was to see which way the ligand would coordinate since it is simultaneously a 2-amidopyridine, which could (and does), like 2-amino-6-methylpyridine,[10] use two nitrogen atoms, and an N-(2-pyridyl)acetamide, which, like N-phenylacetamide (acetanilide), could use the N and O atoms of the amido unit.[11] In effect, the preference shown by the Mo_2^{4+} unit is for the pyridine nitrogen atom over the amido oxygen atom since the amido nitrogen atom is common to both possible arrangements. This is not necessarily predictable although the obvious rationalization is that the more basic donor set is preferred.

The structure found invites comparison with that of tetrakis(2-amino-6-methylpyridine)dimolybdenum, $Mo_2(map)_4$, which we recently reported.[10] Before doing this it is important to emphasize that most of the interatomic distances and angles determined here cannot be taken as reliable in the usual way, say to $\pm 3\sigma$, because of the effects of the disorder. All that can be said of most of the distances is that the values obtained are reasonable under the circumstances and do nothing to vitiate the assumed model of the disorder.

The only distances that could be expected to have meaningful accuracy are the Mo–Mo′ distance, which should, in fact, be as reliable as the esd of 0.003 Å implies, and, with some qualification, the Mo–N distance. The Mo–N distance, 2.178 (6) Å, is an average of the two chemically different kinds. In $Mo_2(map)_4$ the two kinds had values of 2.18 (1) Å (for pyridine) and 2.14 (1) Å. All things considered, the present value is then a very reasonable one. It was also found in the $Mo_2(map)_4$ structure that the two kinds of Mo′–Mo–N angles, to ring nitrogen and exo nitrogen atoms, had equal average values, viz., 92.9 ± 0.4 and 93.1 ± 0.2°. In the present structure the available value for such angles is 92.8°. It is probable that the close similarity of the intrinsic Mo–N distances and Mo′–Mo–N angles for the two sorts of nitrogen atoms helps make possible the disordered packing of the molecules and also leads to the "almost normal" thermal parameters for the nitrogen atoms despite the disordered structure.

The remarkable feature of this molecule is that it establishes a new record for the shortness of Mo–Mo bonds, 2.037 (3) Å. This is a nontrivial change, viz., 0.027 Å, from the previous record, viz., 2.064 (1) Å, found in tetrakis(2,6-dimethoxyphenyl)dimolybdenum. It may also be compared with the distance in $Mo_2(map)_4$, namely, 2.070 (1) Å. It seems likely that the difference between the present molecule and $Mo_2(map)_4$ is essentially an electronic one, resulting from the replacement of H by CH_3CO on the exo nitrogen atoms, but certainly we cannot offer any explanation of why this causes the Mo–Mo bond to become shorter.

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Registry No. $Mo_2[(C_5NH_4)NC(O)CH_3]_4$, 71097-02-4.

Supplementary Material Available: A table of final calculated and observed structure factors (2 pages). Ordering information is given on any current masthead page.

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Reformulation from X-ray Crystallography of a Dinuclear Thiocyanate Complex of Rhenium. The First Observation of Solely N-Bonded, Bridging Thiocyanate

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We report the correct identification and the crystal structure of $(n\text{-}Bu_4N)_3Re_2(NCS)_{10}$, a compound previously reported with a formula also including two CO groups, $(n\text{-}Bu_4N)_3Re_2(NCS)_8(CO)_2$. The IR bands which afforded the only positive reason for supposing the CO groups to be present are now recognized to arise from CN stretching in N-bridging NCS ligands, a structural element sometimes mentioned but never previously documented. The $[Re_2(NCS)_{10}]^{3-}$ anion consists of two octahedra sharing an edge formed by the nitrogen atoms of bridging NCS ions. The virtual D_{2h} symmetry of the inner Re_2N_{10} set of atoms implies that the unpaired electron in this formally mixed-valence (+3, +4) complex is delocalized equally over both metal atoms. The Re–Re distance of 2.613 (1) Å indicates the existence of a metal–metal bond. The crystals may be assigned to space group $I2/a$ with $a = 24.016$ (8) Å, $b = 14.340$ (2) Å, $c = 24.798$ (5) Å, $\beta = 110.5°$, $V = 7999$ (3) $Å^3$, and $Z = 4$. The structure has been refined to discrepancy indices of $R_1 = 0.043$ and $R_2 = 0.060$ by using 3663 reflections with $I > 3\sigma(I)$ collected on a spherical crystal.

Introduction

In 1966, in the course of some of the earliest investigations[2] of the chemical reactivity of quadruple bonds, there was found among the products of the reaction of sodium thiocyanate with $(n\text{-}Bu_4N)_4Re_2Cl_8$ a substance for which the formula $(n\text{-}Bu_4N)_3Re_2(NCS)_{10}(CO)_2$ was suggested. This suggestion rested primarily on two pieces of evidence. First, strong bands in the infrared spectrum at ca. 1920 and ca. 1885 cm^{-1} were taken to indicate the presence of two CO groups (presumed to have been derived from the reaction solvent, acetone). This postulate was considered necessary since there was no known form of coordinated thiocyanate ion giving rise to strong infrared bands in that frequency range. Second, the proposed formula agreed with analytical data. Magnetic and conductance measurements were also consistent with this formula, of which the pertinent features are an odd number of electrons and a 3:1 cation to anion ratio, respectively.

The formula $(n\text{-}Bu_4N)_3Re_2(NCS)_{10}(CO)_2$ has, however, always seemed somewhat overendowed with ligands and, on that ground, questionable. Proof of its correctness through

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