Inorg. Chem. **2001,** *40,* 420−426

Articles

Dinuclear and Heteropolynuclear Complexes Containing Mo_2^{4+} Units

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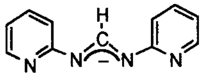
Received September 1, 2000

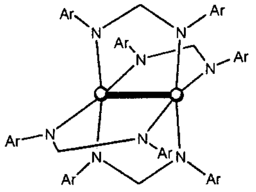
The quadruply bonded compound $Mo_2(DpyF)_4$ (**1**), where $DpyF^-$ is the anion of *N*,*N′*-di(2-pyridyl)formamidine, has been prepared by ligand substitution reactions of $Mo_2(OOCCF_3)_4$ and either the neutral ligand, HDpyF, at ambient temperature or its lithium salt, LiDpyF, under refluxing conditions. An X-ray structural analysis shows that **1** has a paddlewheel structure with a $Mo\overset{4}{—}Mo$ distance of 2.1108(6) Å. Reaction of **1** with $CoCl_2$ in methanol produces the paramagnetic compound $[Mo_2Co(DpyF)_4][CoCl_4]\cdot 2MeOH$ (**2**). The Co(II) atom in the cation $[Mo_2Co(DpyF)_4]^{2+}$ resides on a low-spin hexacoordinate environment ($S = {}^1/_2$) with a Co···Mo separation of 2.979(6) Å, suggesting there is no direct bonding interaction between the Co and Mo atoms. The Mo−Mo distance of 2.1096(5) Å is similar to that in **1**. Reaction of **1** and CuCl in methanol yields $[Mo_2Cu_4(DpyF)_4Cl_2][CuCl_2]_2\cdot 2MeOH\cdot Et_2O$ (**3**). In the cation there are two copper atoms on each side of the Mo_2 core. Each is coordinated to two pyridyl nitrogen atoms of the cis $DpyF^-$ ligands and loosely bridged to the other by a chloride ion. As a result, the Cu(I) atoms are not aligned with the Mo_2 unit. The Cu to Mo separations are in the range 3.003(1)−3.015(1) Å, and the Mo−Mo distance of 2.127(1) Å is comparable to those in **1** and **2**.

Introduction

There is an emerging interest in the use of multidentate ligands to incorporate metal atoms into homonuclear linear chains. It has been reported recently that homonuclear compounds with three[1] and four metal centers[2] can be prepared with di(2-pyridyl)formamidinate (DpyF, **I**), which has up to four N atoms available for coordination.



DpyF (**I**)



$M_2(DArF)_4$ (**II**)

The DpyF ligand is related to the aryl-substituted bidentate ligands DArF (where DArF = *N*,*N′*-diarylformamidinate),[3] which have been used to bridge dimetal units producing paddlewheel structures of type **II**.[4] As an extension of the formamidinate chemistry, we report here the synthesis of $Mo_2(DpyF)_4$ (**1**) in which the quadruply bonded Mo_2^{4+} unit is supported by four DpyF ligands. The dangling N atoms on the pyridyl rings allows the possibility of incorporating other metal ions and thus forming heteronuclear clusters. In fact, two heteropolynuclear compounds have been obtained from the reactions of **1** with $CoCl_2$ and CuCl in solution, and they are reported here. Up to now, only a few heteronuclear compounds that consist of M···Mo−Mo (M = Ru, Pd, and Pt)[5] and M···Mo−Mo···M arrays (M = Pd and Pt)[5,6] have been prepared through the use of tridentate ligands that can bridge the Mo_2 unit as well M atoms.

Experimental Section

Materials. All manipulations were performed under an atmosphere of argon using standard Schlenk techniques. Solvents were purified by conventional methods and were freshly distilled under nitrogen prior to use. HDpyF was prepared by high-temperature (175 °C) condensation

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10.1021/ic001002n CCC: $20.00

Table 1. Crystal Data and Structure Refinement for $Mo_2(DPyF)_4$ (**1**), $[Mo_2Co(DPyF)_4][CoCl_4]{\cdot}2MeOH$ (**2**), and $[Mo_2Cu_4(DPyF)_4Cl_2][CuCl_2]_2{\cdot}2MeOH\ Et_2O$ (**3**)

empirical formula	$C_{44}H_{36}Mo_2N_{16}$ (**1**)	$C_{46}H_{44}Cl_4Co_2Mo_2N_{16}O_2$ (**2**)	$C_{50}H_{54}Cl_6Cu_6Mo_2N_{16}O_3$ (**3**)
fw	980.77	1304.51	1712.91
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	*Pbca*	$C222_1$	$P2_12_12$
a, Å	12.1384(4)	15.792(2)	14.588(2)
b, Å	18.494(1)	17.561(4)	19.945(3)
c, Å	18.543(1)	20.451(3)	10.3753(9)
V, $Å^3$	4162.7(3)	5672(2)	3018.8(7)
Z	4	4	2
temp, K	295(2)	213(2)	213(2)
D_{calc}, g cm^{-3}	1.565	1.528	1.884
μ (Mo Kα), mm^{-1}	0.657	1.246	2.793
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.040, 0.099	0.075, 0.174	0.043, 0.122
R1,[a] wR2[b] (all data)	0.046, 0.111	0.078, 0.182	0.045, 0.128

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{0.5}$.

of 2-aminopyridine with triethyl orthoformate,[7] and $Mo_2(OOCCF_3)_4$ was prepared according to a published procedure.[8] Anhydrous $CoCl_2$ and $CrCl_2$ were purchased from Aldrich and used without further purification.

Physical Measurements. Infrared spectra were recorded in the range 4000−400 cm^{-1} on a Perkin-Elmer 16-PC spectrometer using KBr pellets. ^1H NMR spectra were recorded on a Varian Unity-plus 300 spectrometer at 300 MHz. Electronic absorption and near-IR spectra were measured on a Cary 17 spectrophotometer. Magnetic susceptibility measurements in the solid state were performed with the use of a Quantum Design superconducting quantum interference device (SQUID) magnetometer MPMS-5 (housed in the Department of Physics and Astronomy at Michigan State University). Data for compound **2**, in the range 5−300 K at 1000 G, were obtained on a finely divided polycrystalline sample (28.7 mg). The magnetic susceptibility values were corrected for the sample holder and for the experimental diamagnetic contribution of -4.0×10^{-4} emu mol^{-1}. This value is in good agreement with the value of -6.1×10^{-4} emu mol^{-1} calculated from Pascal's constants.[9] Elemental analyses were performed by Canadian Microanalytical Services; the results were satisfactory.

Preparation of $Mo_2(DpyF)_4$ (1). Method a. A solution of LiDpyF was prepared by adding 8.0 mL of 1.0 M methyllithium to a solution of HDpyF (1.52 g, 8.0 mmol) in THF (40 mL) at −78 °C. When the LiDpyF solution reached ambient temperature, it was transferred to a flask containing a solution of $Mo_2(OOCCF_3)_4$ (1.29 g, 2.00 mmol in 20 mL of THF). A red solution formed immediately. It was stirred until some yellow solid began to precipitate. The mixture was then heated to reflux temperature for 1 h; more yellow solid formed. After the mixture was cooled to room temperature, the solid was filtered out, washed with methanol (3 × 10 mL) and hexanes (2 × 10 mL), and dried under vacuum to give a yellow powder. Yield: 0.68 g (35%). +FAB-MS: $m/z = 981$ $[M + 1]^+$. ^1H NMR (CD_2Cl_2, δ): 10.09 (s, 4H, NC(*H*)N), 7.84 (d, 8H, pyridyl), 7.25 (t, 8H, pyridyl), 6.80 (d, 8H, pyridyl), 6.65 (t, 8H, pyridyl). There are also singlets of lower intensity at 10.28, 10.21, 10.16, 10.05, and 10.03 ppm for methine protons NC(*H*)N and overlapping multiplets of the pyridyl groups; see text for more details. IR (cm^{-1}): 3080 (w), 3043 (m), 3008 (w), 2974 (w), 1591 (m), 1572 (m), 1533 (s), 1463 (s), 1430 (s), 1310 (s), 1285 (m), 1264 (m), 1247 (m), 1230 (m), 1154 (w), 1100 (w), 956 (w), 864 (w), 791 (m), 734 (w), 682 (w), 627 (w), 560 (w), 522 (w), 432 (w), 410 (w). UV/vis, nm (ϵ, M^{-1} cm^{-1}): 432 (sh, 5820), 516 (sh, 1970). Anal. Calcd for $C_{44}H_{36}N_{16}Mo_2$: C, 53.88; H, 3.70; N, 22.84. Found C, 53.75; H, 3.93; N, 22.43.

Method b. A solution of HDpyF (0.76 g, 4.0 mmol) in THF (15 mL) was carefully layered slowly on top of a solution of $Mo_2(OOCCF_3)_4$ (0.65 g, 1.0 mmol) in CH_2Cl_2 (15 mL). Small, yellow crystals of **1** suitable for X-ray diffraction studies were obtained in 2 days.

Preparation of $[Mo_2Co(DpyF)_4][CoCl_4]{\cdot}2MeOH$ (2). Methanol (25 mL) was added to a mixture of $Mo_2(DpyF)_4$ (0.49 g, 0.50 mmol) and $CoCl_2$ (0.14 g, 1.1 mmol) in a round-bottom flask while stirring; a brown suspension formed. After the mixture was stirred overnight, a greenish brown solution was obtained. The solution was filtered and layered with diethyl ether (20 mL). Dark-green crystals were obtained in 10 days. Yield: 0.26 g (40%). +FAB MS: $m/z = 1040$ $[M + 1]^+$. IR (cm^{-1}): 2963 (w), 1590 (s, br), 1562 (w), 1543 (s, br), 1467 (s), 1436 (s), 1335 (s, br), 1295 (s), 1261 (s), 1228 (m), 1160 (m) 1099 (m, br), 1023 (m), 951 (w), 778 (s, br), 739 (w), 635 (vw), 532 (vw), 433 (w). UV/vis/near-IR, nm (ϵ , M^{-1} cm^{-1}): 434 (sh, 4913), 562 (4064), 1588 (2312), 1702 (2659). Anal. Calcd for $C_{46}H_{44}Cl_4Co_2Mo_2N_{16}O_2$: C, 42.35; H, 3.40; N, 17.18. Found C, 42.06; H, 3.13; N, 17.11.

Preparation of $[Mo_2(DpyF)_4Cu_4Cl_2][CuCl_2]_2{\cdot}2MeOH{\cdot}Et_2O$ (3). A suspension of $Mo_2(DpyF)_4$ (0.25 g, 0.25 mmol) and CuCl (0.15 g, 1.5 mmol) in methanol (25 mL) was stirred overnight to give an orange solution and some yellow solid, presumably unreacted starting material. After filtration, the filtrate was layered with diethyl ether. Orange crystals grew in 2 weeks. Yield: 0.12 g (28%). ^1H NMR (CD_3OD, δ): 9.01 (s, 4H, NC(H)N), 8.32 (dd, 8H, $^3J_{HH} = 5.7$, $^4J_{HH} = 1.5$, pyridyl), 7.63 (dt, 8H, $^3J_{HH} = 8.4$, $^4J_{HH} = 1.8$, pyridyl), 7.28 (d, 8H, $^3J_{HH} = 8.4$, pyridyl), 6.88 (dt, 8H, $^3J_{HH} = 6.9$, $^4J_{HH} = 1.2$) (all *J* values are in hertz). IR (cm^{-1}): 1601 (s), 1579 (m), 1539 (s), 1476 (s), 1432 (s), 1336 (s), 1302 (s), 1269 (m), 1247 (m), 1166 (w), 1107 (w), 1025 (w), 945 (w), 857 (w), 778 (m), 747 (w), 687 (w), 668 (w). UV/vis, nm (ϵ , M^{-1} cm^{-1}): 422 (sh, 2658), 510 (sh, 330). Anal. Calcd for $C_{44}H_{36}Cl_6Cu_6Mo_2N_{16}$ (the interstitial solvent molecules in **3** were removed under vacuum at 50 °C): C, 33.56; H, 2.30; N, 14.23. Found C, 34.07; H, 2.45; N, 13.94.

X-ray Structure Determinations. Geometric and intensity data for compounds **1**−**3** were collected on a Nonius FAST area detector system, utilizing the program MADNES.[10] The structures were solved by direct methods and refined routinely using the SHELXTL programs.[11] Non-hydrogen atoms are refined anisotropically, and hydrogen atoms were included in calculated positions. Although the Mo_2Co core in **2** does not have C_2 symmetry, the cation lies on a crystallographic 2-fold axis perpendicular to the Mo−Mo−Co vector. Thus, both Mo and Co atoms are disordered and have occupancies of 50%. Disorder was also observed for the $CoCl_4^{2-}$ counteranion and the interstitial methanol molecules. The Co atom and one of the chlorine atoms were found to be disordered in two positions about a crystallographic 2-fold axis. All ordered non-hydrogen atoms were refined anisotropically. Pertinent information regarding data collection and refinement for **1**−**3** are given in Table 1.

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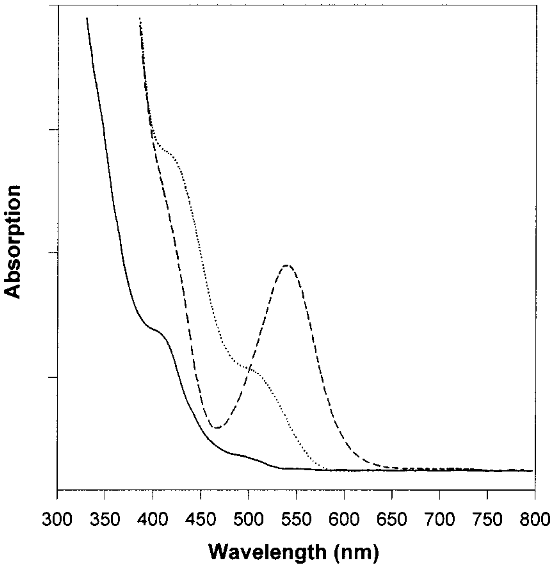


Figure 1. Electronic spectra of (a) **1** (dotted line ···), (b) **2** (dashed line - - -), and (c) **3** (solid line −) at room temperature in methanol.

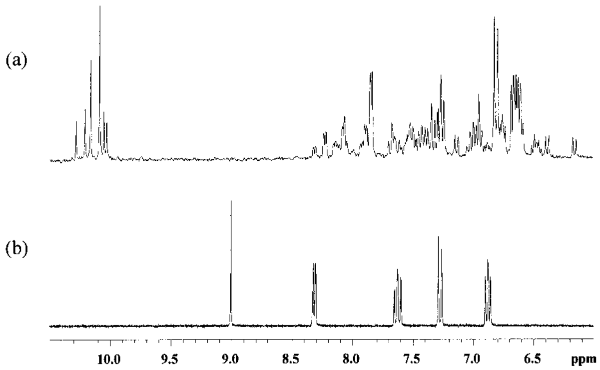
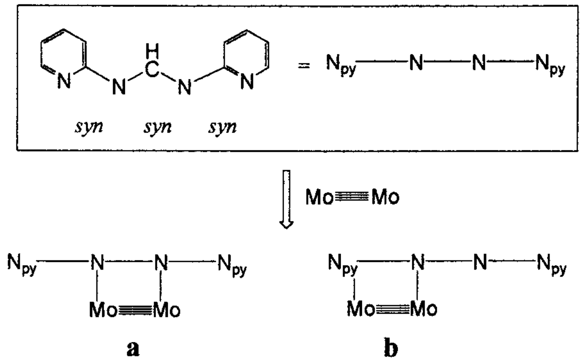


Figure 2. ^{1}H NMR spectra of (a) crystals of **1** in CD$_2$Cl$_2$ and (b) crystals of **3** in CD$_3$OD.

Chart 1



Results and Discussion

Mo$_2$(DpyF)$_4$ (1). Reaction of excess LiDpyF with the quadruply bonded compound Mo$_2$(OOCCF$_3$)$_4$ [12] in refluxing THF,

$$\mathrm{Mo_2(OOCCF_3)_4 + 4LiDpyF \rightarrow Mo_2(DpyF)_4 + 4LiOOCCF_3} \quad (1)$$

yields a yellow solid and a red supernatant liquid.

After filtration, the yellow solid was washed several times with methanol and hexanes to remove lithium trifluoroacetate and unreacted ligand. The +FAB mass spectrum of **1** shows a parent ion peak at 981 *m*/*z*, consistent with the composition of Mo$_2$(DpyF)$_4$. The formamidine NC(H)N stretching vibrations in **1** were observed at 1591 and 1572 cm^{-1} in the IR spectrum, which is also consistent with the formation of bridges by the DpyF ligands. These values are similar to those of the di(*p*-tolyl)formamidinate compound, Mo$_2$(DTolF)$_4$ (1602, 1576 cm^{-1}).[13] As shown in Figure 1a, the electronic spectrum of **1** exhibits two shoulders at 432 and 516 nm in the visible region; the lower energy band can be assigned to a $\delta \rightarrow \delta^*$ excitation of the Mo−Mo quadruple bond.[14] The shoulder at 432 nm may originate from a ligand to metal $\pi \rightarrow \delta^*$ charge transfer (LMCT) transition.

The procedure discussed above can produce gram quantities of the yellow product. However, evidence from proton NMR spectroscopy clearly indicates that in solution this is not a homogeneous material. The spectrum in CD$_2$Cl$_2$ shows a major signal at 10.09 ppm for the methine proton but also five other singlets of significantly lower intensity (ca. 15−30% of the intensity of the major component) in the 10.28−10.03 ppm region. Likewise, there are overlapping multiplets corresponding to the pyridyl groups between 8.4 and 6.1 ppm; again, some of these signals clearly correspond to what appear to be minor components. These observations contrast with the elemental analysis and mass spectrum, which agree well with the composition of **1**. We believe this is consistent with the presence in solution of a mixture of isomers of composition Mo$_2$(DpyF)$_4$.

As depicted in Chart 1, there are two possible coordination modes for a DpyF ligand with an Mo$_2^{4+}$ unit, with **a** representing the coordination of two formamidinate N atoms and **b** the coordination of one formamidinate N atom and one pyridyl N atom to the Mo$_2^{4+}$ unit. The assembly of four DpyF ligands in the paddlewheel structural motif could generate six coordination isomers, namely, Mo$_2$**a**$_4$, Mo$_2$**a**$_3$**b**, *cis*-Mo$_2$**a**$_2$**b**$_2$, *trans*-Mo$_2$**a**$_2$**b**$_2$, Mo$_2$**ab**$_3$, and Mo$_2$**b**$_4$.

The existence of isomers, together with the low solubility of the product, has made it difficult to grow single crystals of these isomers suitable for X-ray diffraction studies. So far, the best way we have found to grow crystals is by layering of a THF solution of neutral HDpyF onto a CH$_2$Cl$_2$ solution containing Mo$_2$(OOCCF$_3$)$_4$ at room temperature. In this way we obtained yellow crystals of **1** belonging to the space group *Pbca* and having a molecule residing on a crystallographic inversion center. With the possibility of other isomers in mind, we examined many crystals by X-ray crystallography. Every one of them produced the same crystallographic unit cell. We then looked at the ^{1}H NMR spectrum of a solution obtained by dissolving large crystals (Figure 2a). Again, a complicated spectrum similar to that obtained from the powder material was observed. This is consistent with there being a distribution of isomers in solution.

In Figure 3 we show the molecular structure of the isomer found in the crystals that corresponds to the structure Mo$_2$**a**$_4$ in Chart 1. Each of the four DpyF ligands bridges the dimolybdenum unit, utilizing the two nitrogen atoms of the central amidinate group to give a paddlewheel structure. Selected bond distances and angles are listed in Table 2. The Mo−Mo distance is 2.1096(5) Å and the Mo−N distances are in the range 2.160(3)−2.186(3) Å. The Mo$_2$N$_8$ core has an essentially eclipsed

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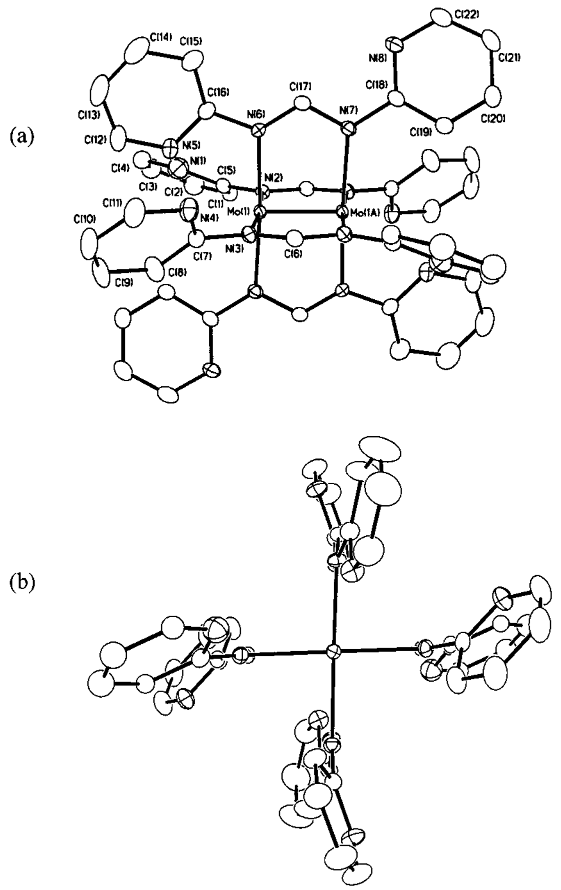

Figure 3. (a) Perspective view of $Mo_2(DpyF)_4$ (**1**). Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. (b) View of **1** down the Mo_2 axis.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $Mo_2(DpyF)_4$ (**1**)[a]

Mo(1)−Mo(1A)	2.1096(5)	Mo(1)−N(2)	2.185(3)
Mo(1)−N(3)	2.160(3)	Mo(1)−N(6)	2.151(3)
Mo(1)−N(7A)	2.186(3)		

Mo(1A)−Mo(1)−N(2)	92.75(7)	Mo(1A)−Mo(1)−N(3A)	92.34(8)
Mo(1A)−Mo(1)−N(6)	89.72(8)	Mo(1A)−Mo(1)−N(7A)	94.38(7)
N(2)−Mo(1)−N(3A)	174.9(1)	N(2)−Mo(1)−N(6)	94.1(1)
N(2)−Mo(1)−N(7A)	86.9(1)	N(3A)−Mo(1)−N(6)	86.3(1)
N(3A)−Mo(1)−N(7A)	92.4(1)	N(6)−Mo(1)−N(7A)	175.7(1)

[a] Symmetry transformations used to generate equivalent atoms: (A) $-x + 1, -y + 1, -z$.

coordination geometry with an average N−Mo−Mo−N torsional angle of less than 1°. When rotational orientations of the pyridyl groups are neglected, the molecule in the solid state has idealized D_{4h} point group symmetry.

The Mo−Mo distance of 2.1096(5) Å is only slightly longer (0.025 Å) than that of the quadruply bonded $Mo_2(DTolF)_4$, which was reported to be 2.085(4) Å.[14] So far, reported Mo−Mo distances in the family of Mo_2(formamidinate)$_4$ compounds have been in the narrow range of 2.085−2.097 Å.[14,15] Two factors may contribute to the slight lengthening of the $\mathrm{Mo}\overset{4}{-}\mathrm{Mo}$ quadruple bond in **1**. One is the decreased donor strength (weaker basicity) of the DpyF ligand compared to that of the more basic DTolF ligand. It has been reported that a change of basicity of the ligands alone will lead to small changes (~0.02 Å) in the Mo−Mo distances.[16] Another factor is the axial ligation of the dangling pyridyl N atoms to the Mo_2 unit. Effective axial coordination of ligands can lead to significant elongations of quadruple bonds (~0.4 Å for Cr_2^{4+} and ~0.03 Å for Mo_2^{4+}).[17] Qualitatively the effect of axial coordination depends on the direction angle (the Mo−N−C−N_{py} torsional angle). When close to zero, there is an efficient overlap between the metal-centered π^* orbital and the axial nitrogen lone pair orbitals. For the eight pyridyl N atoms in **1**, only N(5) and N(1) lie at distances within 3.2 Å to the Mo atoms. The corresponding torsion angles, 7.15(4)° for Mo(1)−N(6)−C(16)−N(5) and 32.46(4)° for Mo(1)−N(2)−C(5)−N(1), deviate from the 0° angle required for maximum axial coordination. Thus, it is likely that both weak axial coordination and the lower basicity of the ligand lead to a slight increase of Mo−Mo distance in **1**, but the influence of both factors is quite small in this case.

We believe that the explanation for the complex ^{1}H NMR spectrum of **1** is as follows. While all six of the possible coordination isomers enumerated above exist in solution, only the $Mo_2\mathbf{a}_4$ isomer crystallizes out, whether for thermodynamic or kinetic reasons. When the crystals are redissolved, the distribution of isomers is readily reestablished in solution. The observed spectrum of this mixture of isomers is too complex to permit an assignment, but the fact that there are exactly six lines in the region where methine protons are known to occur for a ligand of type **a** is in perfect agreement with the number of coordination isomers when we take three additional points into consideration.

(1) For the $Mo_2\mathbf{a}_3\mathbf{b}$ isomer there will be one **a** trans to **b** and two **a** ligands cis to the **b** ligand so that this one isomer will give two methine signals in a 1:2 ratio.

(2) The $Mo_2\mathbf{a}_2\mathbf{b}_2$ isomer could exist with the two **b** ligands cis or trans to each other, and for each of these the **b** ligands could each point in the same direction or in opposite directions. We think it likely that the trans isomer with the **b** ligands pointing in opposite directions will be more stable in solution, although this cannot be considered certain.

(3) There could be three forms of the $Mo_2\mathbf{a}\mathbf{b}_3$ isomer, depending on the relative orientations of the **b** ligands. However, it is unlikely that those in which all three, or even two that are cis to each other, point the same way will be stable. Therefore, only one is likely to be present. It is also possible that the chemical shift of the methine proton in the **a** ligand is insensitive to the directions of the **b** ligands.

With these points in mind, we would expect the collection of isomers present in solution to give a total of six methine lines in the ^{1}H NMR spectrum. This is exactly what is seen.

To add more credibility to our explanation, we note that we have found that the chromium compound $Cr_2(DpyF)_4$ actually crystallizes with all molecules in one form of the $Cr_2\mathbf{a}\mathbf{b}_3$ isomer, namely, **III**.[18]

$[Mo_2Co(DpyF)_4][CoCl_4]\cdot 2MeOH$ (2). Although the dinuclear compound **1** itself is only slightly soluble in methanol, it reacts smoothly, in this solvent, with anhydrous $CoCl_2$ at room temperature to produce a dark-green solution from which the paramagnetic compound $[Mo_2Co(DpyF)_4]$ $[CoCl_4]\cdot 2MeOH$ (**2**) is obtained:

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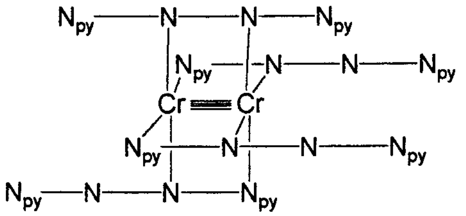
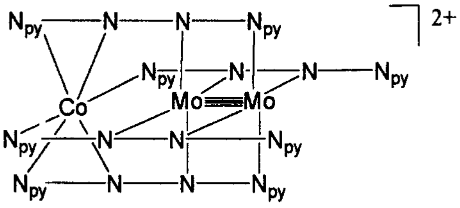


III

$$\mathrm{Mo_2(DpyF)_4 + 2CoCl_2 + 2MeOH \rightarrow [Mo_2Co(DpyF)_4][CoCl_4]{\cdot}2MeOH} \quad (2)$$

The structure of the cation $[Mo_2Co(DpyF)_4]^{2+}$ in **2** is shown in Figure 4a, and selected bond distances and angles are listed in Table 3. It contains a linear Mo_2Co^{6+} unit. The $[Mo_2Co(DpyF)_4]^{2+}$ ion resides on a special position that imposes crystallographic C_2 symmetry; the C_2 axis is close to the disordered Mo(1) atom. Because of the symmetry requirement, Co(1) and Mo(2) are also disordered and each has a 50% occupancy. The Mo_2Co core has a short Mo(1)−Mo(2) distance of 2.115(5) Å and a long Mo(1)···Co(1) separation of 2.979(6) Å. The dimolybdenum unit is coordinated by two different sets of $DpyF^-$ ligands with a trans $Mo_2\mathbf{a}_2\mathbf{b}_2$ configuration, shown schematically in **IV**. One set of the trans $DpyF^-$ ligands bridges the Mo_2 core, using the formamidinate nitrogen atoms to bind to the molybdenum atoms; another set uses one formamidinate nitrogen atom and one pyridyl nitrogen atom of each $DpyF^-$ ligand to bind to the Mo atoms. The Mo−Mo distance is essentially the same as that in **1**. The six-coordinate Co(1) atom in the cation occupies an axial position and possesses an irregular coordination geometry, as shown in Figure 4b. The Co−N distances are in the range 2.20(1)−2.24(1) Å, which are comparable with those of other six-coordinate cobalt(II) complexes,[19] but the N−Co−N angles vary widely, as shown in the lower part of Table 3.



IV

Upon reaction of **1** with $CoCl_2$ in solution, rearrangement of the ligands is necessary to change the coordination geometry from $Mo_2\mathbf{a}_4$ in **1** to $Mo_2\mathbf{a}_2\mathbf{b}_2$ in **2**. This again supports the idea of facile isomerization of **1** discussed above. A similar rearrangement has been observed for the dinuclear chromium compound $Cr_2(dpa)_4$ (where dpa is the anion of di(2-pyridyl)amine), which reacts with $CrCl_2$, giving a trinuclear chain $Cr_3(dpa)_4Cl_2$.[20] The Co(II) ion in $[Mo_2Co(DpyF)_4]^{2+}$ is six-coordinate. The tendency for the cation in **2** to adopt the trans $Mo_2Co\mathbf{a}_2\mathbf{b}_2$ configuration, **IV**, may be due to the formation of a thermodynamically favorable six-coordination site for the Co(II) ion instead of having it bound to the Mo_2^{4+} core to form a delocalized trinuclear chain.

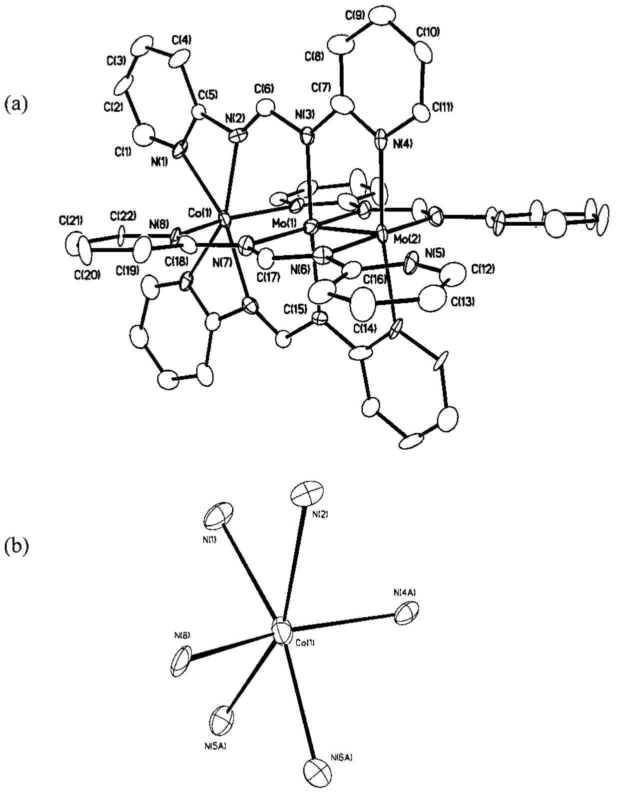


Figure 4. (a) Perspective view of the dication $[Mo_2Co(DpyF)_4]^{2+}$ in **2**. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. (b) Coordination sphere of the cobalt(II) atom in the dication.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2Co(DpyF)_4][CoCl_4]{\cdot}2MeOH$ (**2**)[a]

Mo(1)−Mo(2)	2.115(5)	Co(1)−Mo(1)	2.979(6)
Co(1)−N(1)	2.24(1)	Co(1)−N(2)	2.20(1)
Co(1)−N(8)	2.23(1)	Mo(1)−N(3)	2.13(1)
Mo(2)−N(4)	2.17(1)	Mo(2)−N(6)	2.088(9)
Mo(1)−N(7)	2.181(9)		
Mo(2)−Mo(1)−Co(1)	178.8(2)	N(1)−Co(1)−N(2)	59.7(3)
N(1)−Co(1)−N(4A)	97.1(4)	N(1)−Co(1)−N(5A)	97.0(4)
N(1)−Co(1)−N(6A)	156.4(4)	N(1)−Co(1)−N(8)	99.3(4)
N(2)−Co(1)−N(4A)	86.1(4)	N(2)−Co(1)−N(5A)	156.5(4)
N(2)−Co(1)−N(6A)	143.9(4)	N(2)−Co(1)−N(8)	86.1(3)
N(4A)−Co(1)−N(5A)	101.5(3)	N(4A)−Co(1)−N(6A)	86.3(3)
N(4A)−Co(1)−N(8)	154.9(4)	N(5A)−Co(1)−N(6A)	59.5(3)
N(5A)−Co(1)−N(8)	95.1(4)	N(6A)−Co(1)−N(8)	86.1(5)
N(3)−Mo(1)−N(3A)	89.6(5)	N(3)−Mo(1)−N(7)	91.4(3)
N(3)−Mo(1)−N(7A)	178.2(4)	N(3A)−Mo(1)−N(7A)	89.2(3)
N(7)−Mo(1)−N(7A)	89.6(5)	N(2A)−Mo(2)−N(4)	90.3(3)
N(2A)−Mo(2)−N(6)	178.2(4)	N(2A)−Mo(2)−N(8A)	88.8(3)
N(4)−Mo(2)−N(6)	91.4(3)	N(6)−Mo(2)−N(8A)	89.6(4)

[a] Symmetry transformations used to generate equivalent atoms: (A) $x, -y, -z + 1$.

The spectrum of compound **2** in methanol solution is shown in Figure 1. The main feature is a band centered at 545 nm, with a molar absorbance at the peak of 4 × 10^3. This band must be due almost entirely to the cation but not primarily to the Mo_2^{4+} moiety therein. The latter will have a $\delta \rightarrow \delta^*$ transition in this region but with an extinction coefficient of only about 200. The cobalt atom in the $CoCl_4^{2-}$ ion, which is present in the solid state, becomes a six-coordinate Co(II) ion in solution, possibly $Co(CH_3OH)_6^{2+}$. It has an absorption band at about 522 nm but with ϵ equal to only about 20.[21,22] Whether the observed band in the methanol solution of **2** can be assigned to a transition that is essentially localized on the six-coordinate cobalt(II) is uncertain. We note that it might also be due to a charge-transfer transition of the unpaired electron on the cobalt atom to the δ^* or π^* orbitals of the Mo_2^{4+} moiety.

It is pertinent to point out that axial ligation to the Mo_2^{4+}

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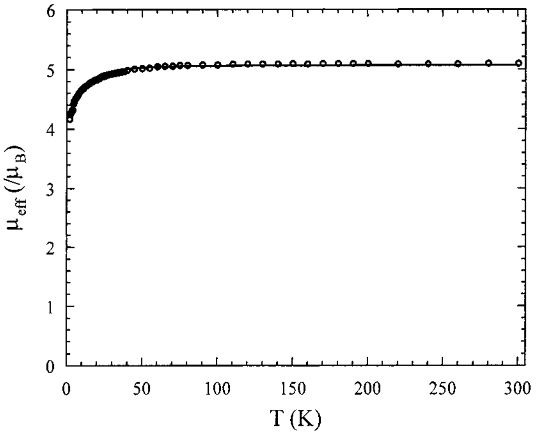

Figure 5. Temperature dependence of the effective moment in Bohr magneton measured at 1000 G for compound **2**. The solid line represents the best fit of the data (○, experimental data; −, fitted results).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Mo_2Cu_4(DpyF)_4Cl_2][CuCl_2]_2\cdot 2MeOH\ Et_2O$ (**3**)[a]

Mo(1)−Mo(1A)	2.1269(11)	Mo(1)−Cu(2)	3.0152(11)
Mo(1)−Cu(3)	3.0031(12)	Cu(2)−Cu(3)	2.789(2)
Mo(1)−N(1)	2.190(6)	Mo(1)−N(3)	2.194(6)
Mo(1)−N(5)	2.174(5)	Mo(1)−N(7)	2.181(5)
Cu(1)−Cl(3)	2.096(3)	Cu(1)−Cl(4)	2.070(3)
Cu(2)−Cl(3)	2.618(2)	Cu(2)−N(4)	1.940(6)
Cu(2)−N(8)	1.933(6)	Cu(3)−N(2)	1.929(6)
Cu(3)−N(6)	1.917(6)	Cu(3)−Cl(3)	2.433(2)

Mo(1A)−Mo(1)−Cu(3)	152.34(4)	Mo(1A)−Mo(1)−Cu(2)	152.43(4)
N(1)−Mo(1)−N(3)	176.1(2)	N(5)−Mo(1)−N(1)	97.2(2)
N(7)−Mo(1)−N(1)	83.0(2)	N(5)−Mo(1)−N(3)	83.6(2)
N(7)−Mo(1)−N(3)	95.9(2)	N(5)−Mo(1)−N(7)	175.7(2)
N(8)−Cu(2)−N(4)	161.6(3)	N(2)−Cu(3)−N(6)	153.7(2)
N(4)−Cu(2)−Cl(3)	99.3(2)	N(8)−Cu(2)−Cl(3)	98.2(2)
N(2)−Cu(3)−Cl(3)	102.3(2)	N(6)−Cu(3)−Cl(3)	101.7(2)
Cu(3)−Cl(3)−Cu(2)	66.93(6)		

[a] Symmetry transformations used to generate equivalent atoms: (A) $-x + 1, -y + 1, z$.

unit by metal ions has been observed for heteronuclear compounds containing late-transition metal atoms. Our group has reported[23] recently a Cu(I) compound $[Mo_2Cu_2(DPhIP)_4(CH_3CN)][CuCl_2]_2$, where DPhIP represents 2,6-di(phenylimino)piperidine, in which the Cu(I) ion is not bound directly to the Mo_2 core. Direct axial interaction of metal ions with a Mo_2^{4+} core has been observed for the heteronuclear compounds $[Mo_2PtX_2(pyphos)_2(O_2CR)_2]_2$ and $Mo_2Pd_2(pyphos)_4$, where pyphos is a tridentate ligand 6-(diphenylphosphino)-2-pyridonate.[5c]

Magnetic susceptibility measurements in the solid state were performed on a polycrystalline sample. As the plot in Figure 5 indicates, μ_{eff} is constant at 5.1 μ_B between 60 and 300 K. This effective moment reflects the presence of two types of uncoupled Co(II) entities, namely, the tetrahedral Co(II) ion in $[Co^{II}Cl_4]^{2-}$ and the Co(II) ion in $[Mo_2Co(DpyF)_4]^{2+}$. The magnetic contribution of $[Co^{II}Cl_4]^{2-}$ is known from experimental measurements to be 4.7−4.8 μ_B.[24] The subtraction of this contribution leads to 1.75−2.00 μ_B as an estimate of the effective moment at room temperature for the Co(II) ion in the cation. This result is in agreement with an $S = {}^1/_2$ Co(II) in a six-coordinate geometry. Below 50 K, the slight decrease of the effective moment can be modeled by the zero-field splitting contribution of the anion with a zero-field splitting parameter D of 18.6 K. This value is slightly higher than the ones found in Cs_2CoCl_4 ($D = 13.5$ K) and $(NEt_4)_2CoCl_4$ ($D = 9.4$ K) but is still in the range expected for an $S = {}^3/_2$ Co(II) ion with a tetrahedral coordination symmetry.

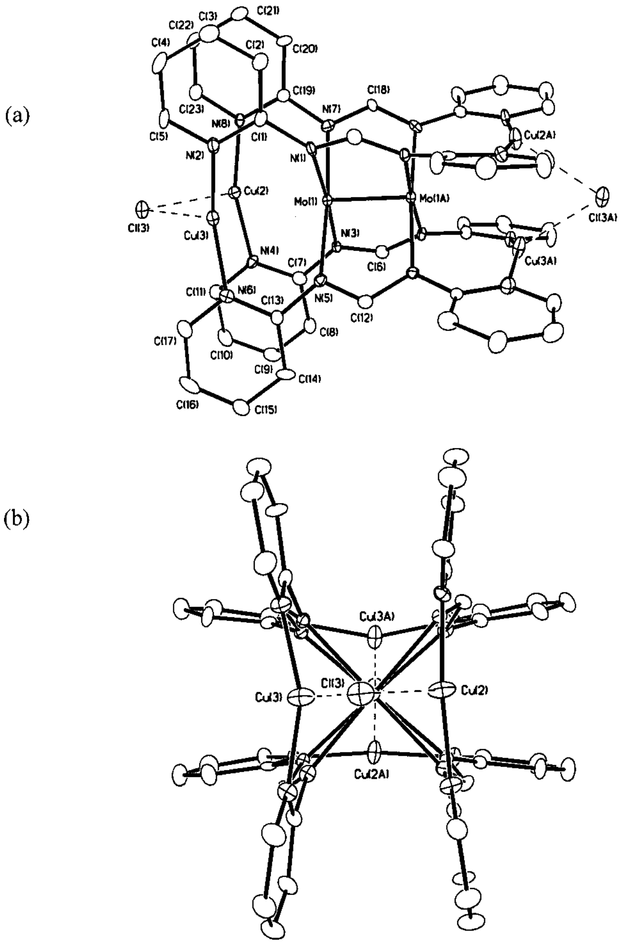

Figure 6. (a) Perspective view of the cation $[Mo_2Cu_4(DpyF)_4Cl_2]^{2+}$ in **3**. Atoms are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity. (b) View of the cation in **3** down the Mo_2 axis.

$[Mo_2Cu_4(DpyF)_4Cl_2][CuCl_2]_2\cdot 2MeOH\cdot Et_2O$ (3). Compound **1** reacted with 6 equiv of CuCl in methanol to give a red solution. After it was layered with diethyl ether, red crystals of **3** were obtained: The crystal structure of **3** consists of a

$$Mo_2(DpyF)_4 + 6CuCl + 2\ MeOH + Et_2O \rightarrow [Mo_2Cu_4(DpyF)_4Cl_2][CuCl_2]_2\cdot 2MeOH\cdot Et_2O \quad (3)$$

hexanuclear cation $[Mo_2Cu_4(DpyF)_4Cl_2]^{2+}$, shown in Figure 6, and two $[CuCl_2]^-$ counteranions. Selected bond distances and angles are listed in Table 4. It crystallizes in the orthorhombic space group $P2_12_12$. The cation resides on a special position and possesses crystallographic C_2 symmetry with a 2-fold axis passing through atoms C(18), C(12) and the midpoint of the Mo−Mo bond. The central molybdenum atoms are bridged by formamidine nitrogen atoms in a paddlewheel $Mo_2\mathbf{a}_4$ geometry, similar to that observed for **1**. In addition, the pyridyl N atoms of the ligands are also bound to four Cu(I) ions, as shown schematically in **V**. Each Cu atom is bound to a pair of $DpyF^-$ ligands in cis positions and to a bridging chloride ion, giving a

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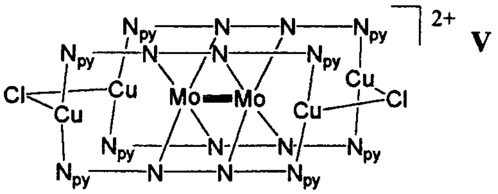

V

T-shaped coordination geometry. The Cu···Cu separation of 2.789(2) Å indicates there is no direct metal-to-metal bonding between the Cu atoms. The copper atoms are far from the axial positions (defined by the Mo_2 vector) with Mo···Cu distances of 3.005(1) and 3.015(1) Å. The Mo−Mo distance of 2.127(1) Å in the cation is similar to those in **1** and **2**. The two-coordinate Cu(I) atom in the anion, $[CuCl_2]^-$, has Cu−Cl distances of 2.070(3) and 2.096(3) Å; the Cl−Cu−Cl angle of 176.7(1)° is common in two-coordinate Cu(I)-containing complexes.[25]

The coordination of the d^{10} Cu(I) ions to the pyridyl N atoms in **3** has effectively "frozen" the arrangement of the pyridyl rings around the Mo_2 core. Thus, a well-resolved solution ^1H NMR spectrum can be obtained, as shown in Figure 2b. The presence of only one signal at 9.01 ppm for the methine protons of the formamidine groups, NC(*H*)N, in the ^1H NMR spectrum is also consistent with the symmetrical $Mo_2\mathbf{a}_4$ coordination of the formamidinate ligands observed in the crystal structure. An electronic spectrum similar to that of **1** but having lower absorption intensities was observed for **3**, as shown in Figure 1c. The $\delta \rightarrow \delta^*$ transition is observed at 510 nm, while a LMCT transition is at 422 nm.

Conclusions

Reaction of the dinuclear compound **1** with $CoCl_2$ in methanol gives a trinuclear compound **2**. By addition of a Co(II) atom at one axial position of the Mo_2 core, it is found that the Mo−Mo quadruple bond remains intact. The Co atom in the cation resides in a six-coordinate environment, while another Co atom is present as the well-known tetrahedral $CoCl_4^{2-}$ ion. The stable six-coordinate Co ion in the cation acts to make **2** a thermodynamic sink, and there is no further incorporation of metal ions to form any compound of higher nuclearity.

In contrast to Co(II), the Cu(I) ion favors lower coordination. Reaction of the dinuclear compound **1** with CuCl produces compound **3**. There are two Cu(I) atoms on each side of the Mo_2 core to form a hexanuclear species. Each of the Cu(I) atoms is coordinated to two pyridyl nitrogen atoms of cis $DpyF^-$ ligands and loosely bridged by a chloride ion. As a result, the Cu(I) atoms are not in a linear arrangement with the Mo_2 core.

Electronic spectra for **1** and **3** show $\delta \rightarrow \delta^*$ transitions in the narrow range of 510−516 nm for the Mo−Mo quadruple bond (Figure 1). These values are ∼2700 cm^{-1} lower in energy than those of the $Mo_2(DArF)_4$ compounds. The small red shifts of $\delta \rightarrow \delta^*$ transitions in these DpyF containing compounds correlate with the slightly longer Mo−Mo distances (∼0.015 Å) but may also result from the differences in the electronic properties of the pyridyl and aryl groups.

Acknowledgment. We are grateful to the National Science Foundation for financial support.

Supporting Information Available: X-ray crystallographic data for compounds **1**−**3**, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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