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Reactions of Phosphines with Tetrakis(trifluoroacetato)dimolybdenum(II)

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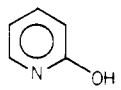
Reactions of $Mo_2(O_2CCF_3)_4$ with several phosphines have been examined, and X-ray crystal structures of the products have been determined. $Mo_2(O_2CCF_3)_4(PPh_3)_2$ (**1**) made by the method of Girolami, Mainz, and Andersen (GMA) was found to have the axial diadduct structure assigned to it by GMA, but for technical crystallographic reasons the structure was not fully refined. Crystallographic data for **1** are as follows: space group, $P\bar{1}$; a = 9.083 (2), b = 19.897 (6), c = 18.838 (3) Å; α = 134.62 (3), β = 98.34 (2), γ = 94.12 (2)°; V = 2323 (3) Å^3; Z = 2. $Mo_2(O_2CCF_3)_4(PPhEt_2)_2$ (**2**) was prepared by reaction in ether and shown by X-ray work to contain nonaxial phosphines which have displaced one oxygen atom of each of two CF_3CO_2 ligands from the molybdenum atoms, to give an $Mo_2(\widehat{OO})_2P_2O_2$ core with C_{2h} symmetry. The Mo–Mo bond length is 2.100 (1) Å. The crystallographic data for **2** are as follows: space group, $P\bar{1}$; a = 8.785 (1), b = 11.184(2), c = 11.283 (5) Å; α = 120.89 (2), β = 103.11 (2), γ = 91.50 (1)°; V = 912 (1) Å^3; Z = 1. When the reaction of $Mo_2(O_2CCF_3)_4$ with PPh_2Me was carried out in ether, the only crystalline product isolated was $Mo_2(O_2CCF_3)_4(Et_2O)_2$ with the Et_2O molecules axially coordinated. Reaction of $Mo_2(O_2CCF_3)_4$ with PPh_2Me in toluene gave the crystalline product $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ (**3**), which has the same type structure as **2** and an Mo–Mo distance of 2.107 (2) Å. Crystal data for this compound are as follows: space group, $C2/c$; a = 25.898 (4), b = 11.102 (1), c = 17.800 (3) Å; β = 128.55 (1)°; V = 4002 (4) Å^3; Z = 4.

Introduction

The tetrakis(carboxylato)dimolybdenum(II) compounds, especially the acetate, have been widely used intermediates in preparing many other compounds containing the Mo_2^{4+} unit. The extent of reaction varies from the mere weak attachment of axial ligands[1] (eq 1) to the extreme of complete replacement of all carboxylato ligands[2,3] (e.g., eq 2 and 3) with, of course, intermediate degrees of replacement as well[4,5] (eq 4 and 5).

$$Mo_2(O_2CCF_3)_4 + 2py \rightarrow py{\rightarrow}Mo(\mu\text{-}O_2CCF_3)_4Mo{\leftarrow}py \quad (1)$$

$$Mo_2(O_2CCH_3)_4 + \text{excess HCl} \rightarrow [Mo_2Cl_8]^{4-} \quad (2)$$

$Mo_2(O_2CCH_3)_4$ + excess  $\rightarrow Mo_2(mhp)_4$ (3)

Hmhp

$$Mo_2(O_2CCH_3)_4 + HCl + Ph_4AsCl \rightarrow (Ph_4As)_2[Mo_2(O_2CCH_3)_2Cl_4] \quad (4)$$

$$Mo_2(O_2CPh)_4 + HBr + R_3P \rightarrow Mo_2(O_2CPh)_2Br_2(R_3P)_2 \quad (5)$$

$Mo_2(O_2CCF_3)_4$ was first reported in 1971 by Cotton and Norman,[6] who also determined its crystal and molecular structure. Its superiority to the acetate for a variety of physical and chemical purposes, due to its considerable solubility in many organic solvents as well as its volatility, was noted. Indeed, its volatility has even allowed measurment of its structure in the gas phase by the method of electron diffraction.[7]

Since the trifluoroacetate, unlike the acetate, is capable of forming isolable axial adducts, as first demonstrated[1] with the ligand pyridine (eq 1), it was considered of interest to look at reactions of $Mo_2(O_2CCF_3)_4$ with other ligands. In the course of using tertiary phosphines, we found some reactions that did not appear to be simple addition of axial ligands and therefore began X-ray work on some of the products. However, it came to our attention that R. A. Andersen and co-workers at the University of California, Berkely, CA, had already looked at systems of this type. We contacted Andersen and he kindly supplied us with a copy of his manuscript,[8a] which had already been accepted for publication and has since appeared.[8b]

In view of the extensive chemical and spectroscopic work already carried out by Andersen et al., we decided not to extend our own work in these respects but carried on with several X-ray studies intended to give a detailed picture of the novel new compounds which Andersen had been the first to report. It has turned out, however, that things are not quite so straightforward. Some of our findings are not entirely consistent with Andersen's report, although we do fully support his interesting discovery that bridging $CF_3CO_2^-$ ligands can

Table I. Crystallographic Data for Compounds **2** and **3**

parameter	**2**	**3**
formula	$Mo_2(O_2CCF_3)_4(PPhEt_2)_2$	$Mo_2(O_2CCF_3)_4(PPh_2Me)_2$
space group	$P\bar{1}$	$C2/c$
a, Å	8.785 (1)	25.898 (4)
b, Å	11.184 (2)	11.102 (1)
c, Å	11.283 (5)	17.800 (3)
α, deg	120.89 (2)	90
β, deg	103.11 (2)	128.55 (1)
γ, deg	91.50 (1)	90
V, Å^3	912 (1)	4002 (4)
d_x(calcd), g/cm^3	1.776	1.733
Z	1	4
fw	976.36	1044.39
cryst size, mm	0.65 × 0.50 × 0.45	0.25 × 0.25 × 0.35
μ, cm^{-1}	8.766	8.07
range of 2θ, deg	0-50	0-50
no. of unique data	2889	2605
no. of data with $F_o^2 > 3\sigma(F_o^2)$	2762	1740
no. of variables	247	262
R_1	0.042	0.061
R_2	0.058	0.072
esd	1.673	1.691
largest peak, e/Å^3	0.303	0.442

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(3) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.
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(6) Cotton, F. A.; Norman, J. G., Jr. *J. Coord. Chem.* **1971**, *1*, 161.
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(8) (a) Andersen, R. A., private communication, Nov 28, 1979. (b) Girolami, G. S.; Mainz, V. V.; Andersen, R. A. *Inorg. Chem.* **1980**, *19*, 805.
(9) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

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Table II. Table of Positional and Thermal Parameters and Their Estimated Standard Deviations for **2**[a]

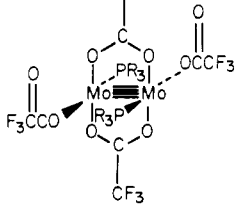
atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.09206 (4)	0.44175 (3)	0.47425 (3)	0.0296 (2)	0.0261 (1)	0.0248 (1)	0.0050 (1)	0.0051 (1)	0.01053 (8)
P	0.1234 (1)	0.4551 (1)	0.2635 (1)	0.0393 (5)	0.0400 (4)	0.0319 (4)	0.0080 (4)	0.0119 (4)	0.0175 (3)
F(1)	0.3331 (8)	0.2722 (4)	0.7741 (4)	0.232 (6)	0.123 (2)	0.078 (2)	0.066 (3)	0.014 (3)	0.070 (1)
F(2)	0.4054 (5)	0.1190 (4)	0.5982 (5)	0.127 (3)	0.139 (2)	0.188 (3)	0.094 (2)	0.077 (2)	0.122 (1)
F(3)	0.1664 (7)	0.1064 (4)	0.6027 (5)	0.107 (4)	0.141 (2)	0.259 (3)	0.006 (2)	0.021 (2)	0.164 (1)
F(4A)	0.4605 (6)	0.8498 (5)	0.8600 (6)	0.059 (3)	0.052 (2)	0.119 (4)	−0.004 (2)	−0.043 (3)	0.007 (2)
F(5A)	0.3866 (8)	0.9229 (5)	0.7259 (5)	0.199 (4)	0.129 (2)	0.083 (2)	−0.123 (2)	−0.022 (2)	0.055 (2)
F(6A)	0.2867 (6)	0.9626 (5)	0.8947 (6)	0.070 (3)	0.058 (3)	0.094 (3)	−0.012 (2)	0.017 (3)	−0.037 (3)
F(4B)	0.461 (2)	0.861 (1)	0.759 (1)	B = 6.1 (3) Å^2					
F(5B)	0.290 (2)	0.978 (1)	0.792 (1)	B = 5.8 (3) Å^2					
F(6B)	0.380 (2)	0.895 (2)	0.912 (2)	B = 8.5 (5) Å^2					
O(1)	0.1638 (4)	0.3627 (3)	0.6119 (3)	0.051 (2)	0.042 (1)	0.040 (1)	0.017 (1)	0.011 (1)	0.0234 (8)
O(2)	0.3132 (6)	0.2551 (4)	0.4666 (4)	0.108 (3)	0.100 (2)	0.088 (2)	0.059 (2)	0.063 (2)	0.059 (1)
O(3)	0.0711 (4)	0.7479 (3)	0.6712 (3)	0.043 (2)	0.027 (1)	0.033 (1)	0.004 (1)	0.007 (1)	0.0111 (8)
O(4)	0.2671 (4)	0.6232 (3)	0.6189 (3)	0.032 (1)	0.036 (1)	0.039 (1)	0.002 (1)	0.005 (1)	0.0157 (8)
C(1)	0.2591 (6)	0.2777 (5)	0.5635 (5)	0.045 (3)	0.041 (2)	0.044 (2)	0.007 (2)	−0.000 (2)	0.021 (1)
C(2)	0.2952 (8)	0.1932 (5)	0.6352 (6)	0.069 (4)	0.060 (2)	0.081 (3)	0.022 (2)	0.006 (3)	0.044 (2)
C(3)	0.2159 (5)	0.7367 (4)	0.6860 (4)	0.039 (2)	0.035 (2)	0.036 (2)	−0.001 (2)	0.004 (2)	0.017 (1)
C(4)	0.3391 (6)	0.8706 (5)	0.7904 (5)	0.047 (3)	0.042 (2)	0.049 (2)	−0.005 (2)	0.004 (2)	0.013 (2)
C(5)	−0.0099 (6)	0.3145 (5)	0.0960 (4)	0.049 (2)	0.047 (2)	0.029 (1)	0.007 (2)	0.011 (2)	0.018 (1)
C(6)	0.0350 (7)	0.1864 (5)	0.0101 (6)	0.075 (3)	0.045 (2)	0.048 (2)	0.014 (2)	0.018 (2)	0.011 (2)
C(7)	−0.0749 (9)	0.0805 (6)	−0.1171 (6)	0.100 (5)	0.053 (3)	0.055 (3)	0.010 (3)	0.025 (3)	0.010 (2)
C(8)	−0.2310 (8)	0.1005 (6)	−0.1580 (5)	0.091 (4)	0.072 (3)	0.041 (2)	−0.017 (3)	0.010 (2)	0.022 (2)
C(9)	−0.2760 (7)	0.2268 (6)	−0.0677 (5)	0.059 (3)	0.082 (3)	0.046 (2)	0.000 (3)	0.003 (2)	0.029 (2)
C(10)	−0.1666 (7)	0.3328 (6)	0.0571 (5)	0.049 (3)	0.070 (2)	0.042 (2)	0.010 (2)	0.008 (2)	0.029 (1)
C(11)	0.3270 (6)	0.4219 (6)	0.2621 (5)	0.040 (2)	0.080 (3)	0.057 (2)	0.015 (2)	0.024 (2)	0.036 (2)
C(12)	0.3859 (7)	0.4232 (7)	0.1413 (6)	0.063 (3)	0.124 (4)	0.091 (2)	0.024 (3)	0.047 (2)	0.067 (2)
C(13)	0.1077 (7)	0.6100 (5)	0.2500 (5)	0.074 (3)	0.046 (2)	0.049 (2)	0.008 (2)	0.019 (2)	0.029 (1)
C(14)	0.2085 (9)	0.7475 (6)	0.3855 (6)	0.116 (5)	0.045 (2)	0.064 (3)	−0.013 (3)	0.015 (3)	0.024 (2)

[a] The form of the anisotropic thermal parameter is $\exp\{-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$. Estimated standard deviations in the least significant digits are shown in parentheses.

be half replaced so as to leave them attached to the molybdenum atoms by only one oxygen atom.

Results and Discussion

The results presented here were obtained by the following sequence of events. At the time we first communicated with Andersen,[8a] we had partially solved the structures of two compounds: $Mo_2(O_2CCF_3)_4(PPh_3)_2$ (**1**) and $Mo_2(O_2CCF_3)_4(PPhEt_2)_2$ (**2**). It was clear that **1** was a simple axial diadduct, as Andersen had already concluded[8] from his evidence. On the other hand, **2** was clearly what he had designated a "class II" compound, that is, one with a structure of type a. Although Andersen had not actually made compound **2**, with its $PPhEt_2$ ligands, this phosphine falls nicely within the field of basicity and cone angle parameters that he proposed to encompass compounds with structures of type a. The structure of compound **2** refined smoothly to convergence at suitably low residuals (Table I) and is fully described below.



a

In the meantime the structure of **1**, which has a very large unit cell, proved troublesome, and the decision was made to seek another example of the axial diadduct type compounds. By this time, we were fully aware of Andersen's results and were guided by them. Accordingly, we chose the phosphine PPh_2Me, which he had reported to give a class I (simple axial adduct) type compound. Following Andersen's procedure, we obtained a crystalline product and undertook a crystallographic study. It was soon apparent that our product contained no phosphine and the crystallography showed it to be $Mo_2(O_2CCF_3)_4\cdot 2Et_2O$ [Anderson has subsequently informed us that it may be necessary to concentrate the ether solution to half (5 mL) the volume stated in his published report (10 mL). This might account for the difference in results.] This structure is not without interest, and the refinement was therefore carried to completion, as will be described elsewhere.

We then attempted to make the PPh_2Me compound by using toluene as the solvent instead of the ether solvent recommended by Andersen. The procedure, as described in the Experimental Section, did give a product of the formula $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ (**3**), but the structure determination shows that **3** *is not an axial diadduct* but instead another compound with a structure of type a. This structure is also reported in detail in this paper.

Structural Results. As already mentioned the structure of the PPh_3 adduct, **1**, was shown conclusively to be that obtained by axial coordination of a PPh_3 molecule in each axial position of $Mo_2(O_2CCF_3)_4$, with an Mo–P distance of 3.07 ± 0.05 Å, but full refinement was not achieved.

The structures of both **2** and **3** have been solved and refined to convergence in the usual way. The positional and thermal parameters are listed in Tables II and III. The structures are shown in Figures 1 and 2, and the bond lengths and angles are listed in Tables IV–VII. In each compound the molecule resides on a center of inversion and aside from the differences in the phosphine ligands are very similar. The atom numbering schemes have been made as similar as possible to facilitate comparison.

The structure in each case is qualitatively that shown in a, and the point symmetry of the group of atoms consisting of the two metal atoms and the eight ligand atoms is C_{2h}, with the symmetry plane containing the atoms Mo, Mo′, P, P′, O(1), and O(1)′ and with the C_2 axis passing through the C(3)–C(4) and C(3)′–C(4)′ bonds and the center of the Mo–Mo bond. The great similarity of the two structures is emphasized in Table VIII, where a number of key distances and angles are compared in the two molecules. There are only

Table III. Table of Positional and Thermal Parameters and Their Estimated Standard Deviations for **3**[a]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.46155 (4)	0.0319 (1)	−0.00032 (6)	0.0269 (2)	0.0373 (4)	0.0388 (3)	−0.0009 (5)	0.0198 (2)	0.0006 (6)
P	0.4968 (1)	−0.2442 (3)	−0.0485 (2)	0.086 (1)	0.040 (2)	0.146 (2)	−0.013 (1)	0.0960 (8)	−0.019 (2)
F(1)	0.2475 (3)	−0.108 (1)	−0.0741 (6)	0.103 (3)	0.23 (1)	0.263 (5)	−0.075 (5)	0.146 (2)	−0.100 (7)
F(2)	0.2531 (4)	−0.168 (1)	−0.1769 (7)	0.138 (5)	0.38 (1)	0.155 (6)	−0.182 (6)	0.093 (4)	−0.160 (7)
F(3)	0.3059 (4)	−0.244 (1)	−0.0491 (9)	0.136 (4)	0.14 (1)	0.42 (1)	−0.057 (5)	0.193 (4)	−0.032 (9)
F(4)	0.6632 (5)	−0.109 (2)	0.3310 (6)	0.102 (5)	0.48 (2)	0.080 (5)	0.111 (9)	0.047 (3)	0.105 (8)
F(5)	0.5851 (4)	−0.076 (2)	0.3275 (5)	0.172 (5)	0.61 (2)	0.082 (3)	0.193 (9)	0.096 (3)	0.122 (8)
F(6)	0.5931 (7)	−0.227 (2)	0.2804 (7)	0.36 (1)	0.33 (2)	0.135 (6)	0.02 (1)	0.129 (6)	0.136 (7)
O(1)	0.3376 (3)	0.0463 (9)	−0.0433 (6)	0.056 (3)	0.067 (6)	0.103 (4)	0.009 (4)	0.045 (3)	0.011 (5)
O(2)	0.3912 (3)	−0.1086 (8)	−0.0458 (5)	0.063 (3)	0.049 (5)	0.095 (4)	−0.029 (4)	0.054 (2)	−0.027 (4)
O(3)	0.5107 (3)	−0.0251 (9)	0.1420 (4)	0.049 (2)	0.091 (6)	0.047 (3)	0.004 (4)	0.033 (2)	0.007 (4)
O(4)	0.4077 (3)	0.0902 (9)	−0.1422 (4)	0.044 (3)	0.105 (7)	0.041 (3)	0.025 (4)	0.026 (2)	0.027 (4)
C(1)	0.3427 (4)	−0.059 (1)	−0.0555 (6)	0.037 (3)	0.048 (9)	0.064 (4)	−0.006 (4)	0.038 (2)	−0.009 (5)
C(2)	0.2856 (5)	−0.140 (2)	−0.0912 (10)	0.079 (5)	0.10 (1)	0.182 (8)	−0.023 (7)	0.100 (4)	−0.045 (8)
C(3)	0.5658 (5)	−0.073 (1)	0.1811 (7)	0.051 (5)	0.12 (1)	0.046 (5)	0.038 (6)	0.029 (3)	0.027 (6)
C(4)	0.6015 (7)	−0.111 (2)	0.2829 (10)	0.092 (7)	0.32 (3)	0.111 (7)	0.10 (1)	0.073 (5)	0.12 (1)
C(51)	0.4871 (5)	−0.325 (1)	0.0340 (9)	0.219 (5)	0.048 (9)	0.287 (6)	0.020 (6)	0.235 (3)	0.044 (7)
C(61)	0.4216 (5)	−0.262 (1)	−0.1716 (10)	0.069 (5)	0.16 (1)	0.245 (9)	−0.089 (7)	0.109 (4)	−0.174 (7)
C(62)	0.4209 (7)	−0.219 (2)	−0.2435 (10)	0.107 (8)	0.16 (1)	0.135 (8)	0.007 (8)	0.071 (5)	−0.087 (8)
C(63)	0.3594 (8)	−0.237 (2)	−0.3416 (12)	0.089 (9)	0.34 (2)	0.17 (1)	−0.04 (1)	0.060 (6)	−0.18 (1)
C(64)	0.3093 (8)	−0.287 (3)	−0.3534 (14)	0.063 (8)	0.53 (4)	0.27 (1)	−0.07 (2)	0.079 (7)	−0.29 (2)
C(65)	0.3106 (8)	−0.339 (2)	−0.2828 (16)	0.185 (9)	0.38 (2)	0.47 (2)	−0.21 (1)	0.249 (8)	−0.34 (1)
C(66)	0.3680 (7)	−0.325 (2)	−0.1836 (12)	0.163 (7)	0.26 (2)	0.34 (1)	−0.16 (1)	0.204 (5)	−0.25 (1)
C(71)	0.5577 (5)	−0.336 (1)	−0.0418 (9)	0.128 (4)	0.047 (9)	0.202 (6)	0.020 (6)	0.147 (3)	0.027 (7)
C(72)	0.6238 (6)	−0.328 (1)	0.0452 (10)	0.154 (6)	0.08 (1)	0.218 (7)	0.066 (7)	0.160 (4)	0.075 (8)
C(73)	0.6729 (7)	−0.405 (2)	0.0578 (11)	0.207 (7)	0.20 (2)	0.254 (8)	0.13 (1)	0.205 (4)	0.15 (1)
C(74)	0.6574 (8)	−0.481 (2)	−0.0110 (10)	0.393 (9)	0.17 (2)	0.302 (7)	0.18 (1)	0.322 (4)	0.161 (9)
C(75)	0.5945 (7)	−0.489 (2)	−0.0976 (9)	0.396 (8)	0.11 (1)	0.272 (6)	0.115 (9)	0.309 (4)	0.107 (8)
C(76)	0.5403 (6)	−0.417 (1)	−0.1168 (8)	0.266 (6)	0.041 (9)	0.226 (6)	0.038 (6)	0.229 (3)	0.020 (6)

[a] The form of the anisotropic thermal parameter is $\exp\{-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$. Estimated standard deviations in the least significant digits are shown in parentheses.

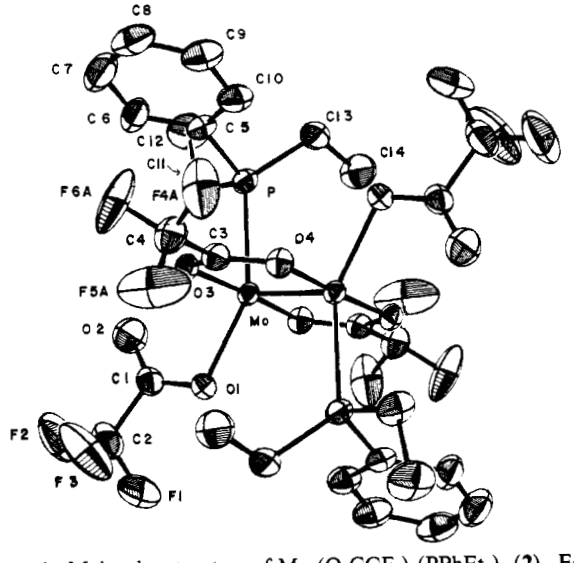


Figure 1. Molecular structure of $Mo_2(O_2CCF_3)_4(PPhEt_2)_2$ (**2**). Each atom is represented by its ellipsoid of thermal vibration scaled to enclose 30% of the electron density. Each unlabeled atom is related to a labeled one by the crystallographic inversion center at the midpoint of the Mo–Mo′ bond.

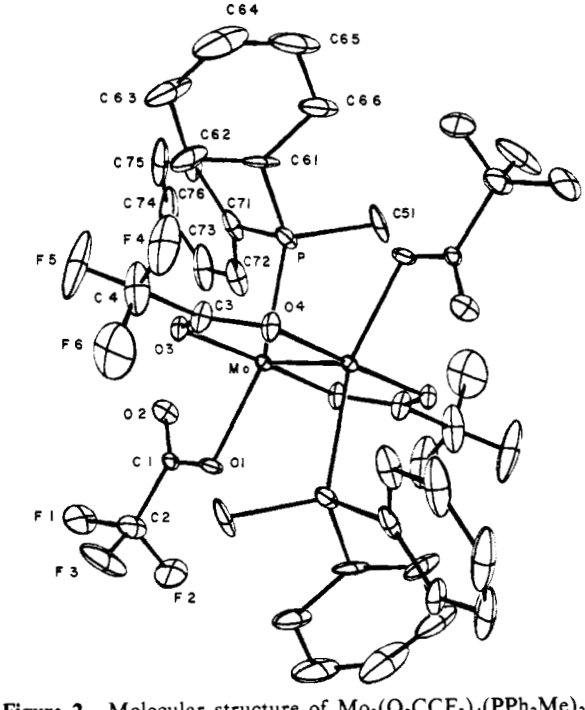


Figure 2. Molecular structure of $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ (**3**). Unlabeled atoms are related to labeled ones by an inversion center at the midpoint of the Mo–Mo′ bond. Each atom is represented by its ellipsoid of thermal vibration, scaled to enclose 30% of the electron density.

five differences that might be significantly outside of the experimental uncertainties, and these are given in the last column of the table. Presumably the two differences in angles simply reflect slightly different nonbonded repulsions and are of no chemical significance. The slightly shorter Mo–P distance for PPh_2Me, which is associated with a slightly longer Mo–Mo bond might indicate that PPh_2Me is a slightly better π acceptor (from the Mo–Mo π and δ bonds) than is $PPhEt_2$, thus strengthening the Mo–P bond while weakening the Mo–Mo bond. However, there is also a difference in the long axial O(2)···Mo distance such that a slightly stronger axial bond in **3** could be responsible for weakening the Mo–Mo bond. All these effects are so small, however, that, even if real, they are of minor importance.

It is noteworthy that the unidentate CF_3CO_2 ligand shows a considerable difference between the two C–O distances, in the direction expected if the bonding is as described by b, in

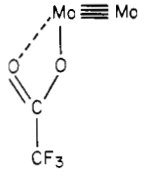
Table IV. Bond Lengths (Å) in $Mo_2(O_2CCF_3)_4(PPhEt_2)_2$ (2)

Mo-Mo′	2.100 (1)	C(2)-F(2)	1.292 (6)
Mo-P	2.532 (1)	C(2)-F(3)	1.322 (7)
Mo-O(1)	2.142 (3)	C(4)-F(4A)	1.277 (7)
Mo-O(2)	2.871 (8)	C(4)-F(4B)	1.198 (15)
Mo-O(3)	2.109 (2)	C(4)-F(5A)	1.268 (7)
Mo-O(4)	2.108 (2)	C(4)-F(5B)	1.280 (15)
P-C(5)	1.806 (4)	C(4)-F(6A)	1.298 (7)
P-C(11)	1.838 (4)	C(4)-F(6B)	1.213 (19)
P-C(13)	1.821 (4)	C(5)-C(6)	1.387 (6)
O(1)-C(1)	1.273 (5)	C(6)-C(7)	1.400 (7)
O(2)-C(1)	1.202 (5)	C(7)-C(8)	1.407 (9)
O(3)-C(3)	1.263 (5)	C(8)-C(9)	1.387 (8)
O(4)-C(3)	1.258 (5)	C(9)-C(10)	1.387 (6)
C(1)-C(2)	1.526 (6)	C(10)-C(5)	1.401 (6)
C(3)-C(4)	1.525 (5)	C(11)-C(12)	1.570 (7)
C(2)-F(1)	1.294 (7)	C(13)-C(14)	1.545 (7)

Table V. Bond Angles (Deg) in $Mo_2(O_2CCF_3)_4(PPhEt_2)_2$ (2)

Mo′-Mo-P	100.83 (3)	C(9)-C(10)-C(5)	121.2 (5)
Mo′-Mo-O(1)	111.05 (7)	O(1)-C(1)-O(2)	126.7 (4)
Mo′-Mo-O(2)	160.2 (5)	O(1)-C(1)-C(2)	113.2 (4)
Mo′-Mo-O(3)	91.58 (7)	O(2)-C(1)-C(2)	119.9 (4)
Mo′-Mo-O(4)	92.09 (7)	C(1)-C(2)-F(1)	112.6 (4)
P-Mo-O(1)	148.09 (8)	C(1)-C(2)-F(2)	113.3 (5)
P-Mo-O(3)	89.18 (7)	C(1)-C(2)-F(3)	110.4 (4)
P-Mo-O(4)	91.02 (7)	F(1)-C(2)-F(2)	108.7 (5)
O(1)-Mo-O(3)	88.6 (1)	F(1)-C(2)-F(3)	103.4 (6)
O(1)-Mo-O(4)	89.3 (1)	F(2)-C(2)-F(3)	108.0 (5)
O(3)-Mo-O(4)	176.2 (1)	O(3)-C(3)-O(4)	124.9 (3)
Mo-P-C(5)	111.3 (1)	O(3)-C(3)-C(4)	118.0 (4)
Mo-P-C(11)	102.2 (2)	O(4)-C(3)-C(4)	117.0 (4)
Mo-P-C(13)	124.8 (2)	C(3)-C(4)-F(4A)	112.8 (4)
Mo-O(1)-C(1)	108.1 (3)	C(3)-C(4)-F(4B)	112.1 (8)
Mo-O(3)-C(3)	115.9 (2)	C(3)-C(4)-F(5A)	111.6 (4)
Mo-O(4)-C(3)	115.5 (2)	C(3)-C(4)-F(5B)	111.4 (7)
P-C(5)-C(6)	122.2 (4)	C(3)-C(4)-F(6A)	111.5 (4)
P-C(5)-C(10)	118.5 (3)	C(3)-C(4)-F(6B)	113.5 (10)
P-C(11)-C(12)	115.4 (4)	F(4A)-C(4)-F(5A)	107.9 (6)
P-C(13)-C(14)	113.3 (3)	F(4A)-C(4)-F(6A)	100.9 (5)
C(5)-C(6)-C(7)	119.4 (5)	F(5A)-C(4)-F(6A)	111.7 (6)
C(6)-C(7)-C(8)	121.2 (5)	F(4B)-C(4)-F(5B)	107 (1)
C(7)-C(8)-C(9)	118.6 (5)	F(4B)-C(4)-F(6B)	103 (1)
C(8)-C(9)-C(10)	120.2 (5)	F(5B)-C(4)-F(6B)	110 (1)

which the C–O bond orders are considered to differ significantly, as in an ester.



b

Spectroscopic Results for 3. Because the structure of the product we obtained with PPh_2Me was not that assigned on spectroscopic evidence by Andersen et al.,[8b] we carried out some spectroscopic studies to see if we could resolve the apparent discrepancy.

The infrared criterion of structure is, in principle, a simple one. When an RCO_2^- ion is bridging, the two C–O bonds are equivalent and the frequencies of the symmetric and antisymmetric stretching modes are found at 1400–1440 cm^{-1} (medium) and ca. 1600 cm^{-1} (strong). This pattern is well exemplified by $Mo_2(O_2CCF_3)_4$ itself; its spectra in the pertinent region are shown for both $CHCl_3$ solution and a KBr pellet in Figure 3. For monodentate RCO_2^- ligand (see b) the symmetric and antisymmetric C–O stretching modes are expected to be much more widely separated; the former will still occur at 1400–1440 cm^{-1}, but the latter should be in the range 1675–1700 cm^{-1}. Thus, for a structure of type a, which contains both bridging and monodentate $CF_3CO_2^-$ ligands, we would expect a spectrum with a band in the 1675–1700-cm^{-1} range, a strong band at ca. 1600 cm^{-1}, and multiple absorptions in the 1400–1450-cm^{-1} range. As Figure 4 shows this is what we observe for our compound **3**. Thus, the infrared spectra we observe, for both the solid and the $CHCl_3$ solution, are diagnostic of the structure found by X-ray crystallography.

Table VI. Bond Lengths (Å) in $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ (3)

Mo-Mo′	2.107 (2)	C(2)-F(3)	1.30 (2)
Mo-P	2.511 (3)	C(4)-F(4)	1.26 (2)
Mo-O(1)	2.137 (6)	C(4)-F(5)	1.17 (3)
Mo-O(2)	2.803 (7)	C(4)-F(6)	1.30 (4)
Mo-O(3)	2.102 (6)	C(61)-C(62)	1.36 (3)
Mo-O(4)	2.086 (6)	C(62)-C(63)	1.47 (2)
P-C(51)	1.87 (1)	C(63)-C(64)	1.30 (4)
P-C(61)	1.82 (2)	C(64)-C(65)	1.37 (7)
P-C(71)	1.82 (1)	C(65)-C(66)	1.44 (4)
O(1)-C(1)	1.28 (1)	C(66)-C(61)	1.44 (2)
O(2)-C(1)	1.21 (1)	C(71)-C(72)	1.43 (2)
O(3)-C(3)	1.25 (1)	C(72)-C(73)	1.43 (2)
O(4)-C(3)	1.26 (1)	C(73)-C(74)	1.33 (4)
C(1)-C(2)	1.49 (2)	C(74)-C(75)	1.38 (5)
C(3)-C(4)	1.49 (2)	C(75)-C(76)	1.46 (3)
C(2)-F(1)	1.25 (2)	C(76)-C(71)	1.43 (2)
C(2)-F(2)	1.24 (2)		

Table VII. Bond Angles (Deg) in $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ (3)

Mo′-Mo-P	96.5 (1)	C(64)-C(65)-C(66)	120 (3)
Mo′-Mo-O(1)	109.6 (2)	C(65)-C(66)-C(61)	113 (3)
-O(2)	159.8 (2)	C(66)-C(61)-C(62)	126 (2)
-O(3)	91.8 (2)	C(71)-C(72)-C(73)	119 (2)
-O(4)	91.6 (2)	C(72)-C(73)-C(74)	120 (3)
P-Mo-O(1)	153.8 (2)	C(73)-C(74)-C(75)	123 (3)
-O(3)	93.3 (2)	C(74)-C(75)-C(76)	121 (3)
-O(4)	87.0 (2)	C(75)-C(76)-C(71)	115 (2)
O(1)-Mo-O(3)	88.3 (3)	C(76)-C(71)-C(72)	122 (1)
-O(4)	89.9 (3)	O(1)-C(1)-O(2)	127 (1)
O(3)-Mo-O(4)	176.6 (3)	O(1)-C(1)-C(2)	118 (1)
Mo-P-C(51)	114.6 (6)	O(2)-C(1)-C(2)	115 (1)
-C(61)	115.3 (7)	C(1)-C(2)-F(1)	117 (1)
-C(71)	109.6 (5)	C(1)-C(2)-F(2)	114 (2)
Mo-O(1)-C(1)	105.4 (6)	C(1)-C(2)-F(3)	111 (2)
Mo-O(3)-C(3)	115.0 (6)	F(1)-C(2)-F(2)	110 (2)
Mo-O(4)-C(3)	115.8 (6)	F(1)-C(2)-F(3)	102 (2)
P-C(61)-C(62)	118 (1)	F(2)-C(2)-F(3)	102 (2)
P-C(61)-C(66)	116 (2)	O(3)-C(3)-O(4)	126 (1)
P-C(71)-C(72)	116 (1)	O(3)-C(3)-C(4)	115 (1)
P-C(71)-C(76)	122 (1)	O(4)-C(3)-C(4)	119 (1)
C(51)-P-C(61)	109.0 (8)	C(3)-C(4)-F(4)	113 (2)
C(61)-P-C(71)	104.5 (8)	C(3)-C(4)-F(5)	121 (2)
C(51)-P-C(71)	102.6 (6)	C(3)-C(4)-F(6)	106 (3)
C(61)-C(62)-C(63)	116 (2)	F(4)-C(4)-F(5)	112 (3)
C(62)-C(63)-C(64)	119 (3)	F(4)-C(4)-F(6)	98 (2)
C(63)-C(64)-C(65)	126 (4)	F(5)-C(4)-F(6)	103 (2)

Table VIII. Comparison of Key Bond Lengths and Angles in **2** and **3**

bond length or angle	2	3	difference[a]
Mo-Mo, Å	2.100 (1)	2.107 (2)	0.007 (2)?
Mo-P, Å	2.532 (1)	2.511 (3)	0.021 (3)
Mo-O(1), Å	2.142 (3)	2.137 (6)	
Mo-O(2), Å	2.871 (8)	2.803 (7)	0.068 (11)
Mo-O(3)/O(4) (av), Å	2.108 (2)	2.094 (7)	
C(1)-O(1), Å	1.273 (5)	1.28 (1)	
C(1)-O(2), Å	1.202 (5)	1.21 (1)	
C(3)-O(3)/O(4) (av), Å	1.260 (4)	1.26 (1)	
C(1)-C(2), Å	1.526 (6)	1.49 (2)	
C(3)-C(4), Å	1.525 (5)	1.49 (2)	
P-C(alkyl) (av), Å	1.83 (1)	1.87 (1)	
P-C(aryl) (av), Å	1.806 (4)	1.82 (2)	
Mo′-Mo-O(1), deg	111.05 (7)	109.6 (2)	1.5 (2)
Mo′-Mo-P, deg	100.83 (3)	96.5 (1)	4.3 (1)
Mo′-Mo-O(2), deg	160.2 (5)	159.8 (2)	

[a] If significant.

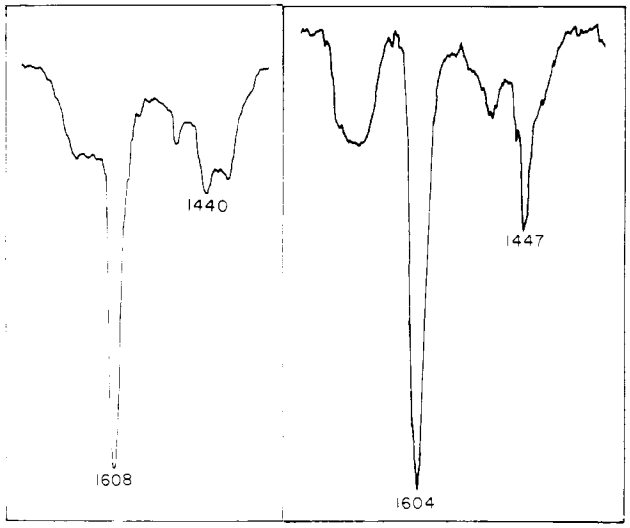


Figure 3. Infrared spectra in a KBr disk (left) and $CHCl_3$ solution (right) for $Mo_2(O_2CCF_3)_4$.

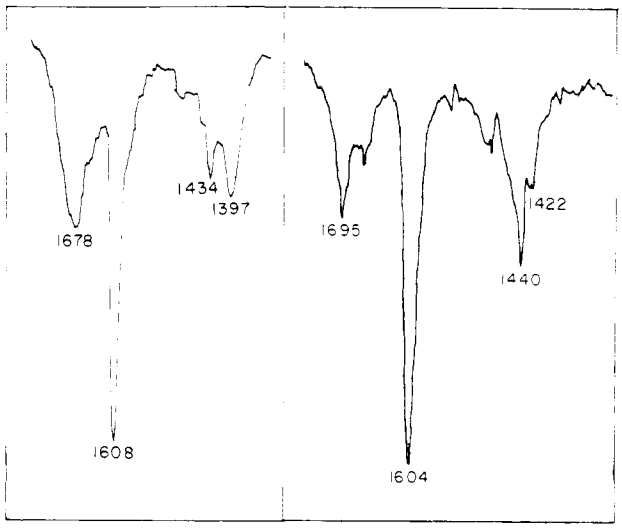


Figure 4. Infrared spectra in a KBr disk (left) and $CHCl_3$ solution (right) for $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ (**3**).

The picture is slightly blurred by the fact that even $Mo_2(O_2CCF_3)_4$ has weak to medium, but broad, absorption from 1680–1700 cm^{-1}. However, the sharp absorption bands in the spectra of **3** are quite different in appearance and seem rather clearly to be indicative of new, genuine vibrations.

These results appear to be inconsistent with the infrared results tabulated by Andersen et al., who report "ν_{as}" bands at 1600 ($CHCl_3$ solution) and 1596 cm^{-1} (Nujol mull). It does not seem likely that they could have failed to notice (or to mention) the bands seen in Figure 4 at 1695 and 1678 cm^{-1}.

We are not certain how to explain the differences between the two sets of infrared spectra. They would seem to suggest that perhaps two forms of $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ exist, one being obtained (though not in our hands) by reaction under very mild conditions in diethyl ether solvent, while the other (with structure a) is obtained under more strenuous reaction conditions. The latter is, then, evidently stable (probably thermodynamically) in $CHCl_3$ solution as well as in the solid state. It is pertinent that PPh_2Me is a phosphine that lies close to the borderline proposed by Andersen to divide the phosphines into the classes that give the two types of adduct, and this is naturally where any uncertainty, any error, or any possibility of ambivalent character would be most likely to occur in the classification.

We have also examined the ^{19}F NMR spectrum of our compound **3**. For their $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ compound and several others to which they assigned a simple axial adduct structure, Andersen et al. report a single line at 69.8–70.6 ppm below the resonance for $CFCl_3$ in $CDCl_3$ solutions at −55 °C.

For compounds to which they assigned structure a, they reported two or three lines from 69.7 to 73.7 ppm for $CDCl_3$ solutions at −55 °C. Our results for **3** are quite different from all of these.

At 22 °C we find a single sharp line at 61.5 ppm. At −18 °C there is still a strong sharp line at 61.4 ppm, but it now has very weak (ca. 5% intensity) sharp satellites at 60.6 and 63.8 ppm. At −37 °C the main line at 61.4 ppm has now broadened by about a factor of 2 but, the satellites are still sharp. At −50 °C the central line is about half as wide as the separation between the satellites, which are still sharp, and at −59 °C the central line has virtually disappeared into the base line.

We do not know how to account for these ^{19}F NMR results other than to suggest that (1) several isomeric forms must coexist and (2), if a structure of type a predominates as suggested by the infrared data, the two types of CF_3 group must be exchanging rapidly at 22 °C but slowly at ca. −50 °C. It is not at all clear why the results of Andersen et al. for several compounds to which they assigned an a type structure and ours for **3** are so different in chemical shift.

Experimental Section

Infrared spectra of solutions were recorded on a Pye Unicam SP1100 infrared spectrometer; solid-state spectra were recorded on a Beckman 4260 spectrometer using KBr pellets. NMR spectra were measured on a Jeol PF7-100 Nicolet 1080 Fourier transform spectrometer at 92.659 MHz. ^{19}F chemical shifts are reported relative to $CFCl_3$. Reactions and most manipulations were routinely carried out under nitrogen, but crystals were selected and mounted with use of a layer of mineral oil for protection from the atmosphere. The crystals of the phosphine complexes are attacked by air over a period of days but seem to be stable indefinitely in a nitrogen atmosphere.

$Mo_2(O_2CCF_3)_4(PPh_3)_2$ (1) and $Mo_2(O_2CCF_3)_4(PPhEt_2)_2$ (2). These were prepared following the methods reported for **1** and for compounds similar to **2** by Anderson et al.[8b] Crystals of **2** suitable for X-ray work were obtained by dissolving the red-orange microcrystalline product initially obtained in the minimal quantity of diethyl ether at room temperature and setting the solution aside to cool slowly over a period of 2 days in a cold chest at −10 °C.

$Mo_2(O_2CCF_3)_4(Et_2O)_2$. We obtained this substance by following the directions of Andersen et al.[8b] for the preparation of $Mo_2(O_2CCF_3)_4(PPh_2Me)_2$. There was no visual indication of a reaction upon addition of the phosphine to a diethyl ether solution of $Mo_2(O_2CCF_3)_4$ at room temperature. The solution was filtered and cooled to 0 °C, and after 30 min yellow crystals had formed and were collected.

$Mo_2(O_2CCF_3)_4(PPh_2Me)_2$ (3). Methyldiphenylphosphine (0.34 g, 1.7 mmol) was added to a solution of $Mo_2(O_2CCF_3)_4$ (0.54 g, 0.84 mmol) in 50 mL of warm (60 °C) toluene. The solution was stirred for 12 h and then filtered, and the filtrate was evaporated to a volume of about 10 mL by vacuum distillation. Red-orange crystals were obtained by suspending a 25-mL flask containing the filtrate over dry ice and allowing convection cooling to occur. Blocks of various sizes formed over a period of 2 days.

X-ray Procedures. In all cases crystals were mounted on glass fibers and protected from the atmoshere by a light coating of epoxy cement.

Data were collected on an Enraf-Nonius CAD4-F autodiffractometer at 25 ■ 2 °C using Mo Kα radiation monochromated by a graphite crystal mounted in the incident beam. Details of crystallographic procedures have been described previously.[9] Usually 25 high-angle reflections in the range $25° < 2\theta < 35°$ were used to obtain precise cell constants. During data collection three intensity standards were measured after every hour of exposure. No decay was observed for any of the compounds.

Crystallographic data for the two compounds, **2** and **3**, whose structures were solved, are given in Table I. For each crystal the data were corrected for Lorentz and polarization effects, but because of the low linear absorption coefficients, absorption corrections were omitted.

The heavy-atom positions in all three compounds were obtained from three dimensional Patterson functions, and the structure for **3** was refined to convergence by using anisotropic thermal parameters for all nonhydrogen atoms. The refinement proceeded straightforwardly for this structure.

For compound **2** the structure refinement also proceeded uneventfully with all atoms being found and refined isotropically with $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.099$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.138$.

At this stage it was noted that the thermal parameters for the fluorine atoms in the bidentate trifluoroacetato group were unexpectedly high, suggesting a possible disorder problem. An electron density map at this point revealed three high peaks at distances of 0.45, 0.70, and 0.74 Å from F(4), F(5), and F(6) and the three additional peaks were refined, treating them as fluorine atoms. This produced occupancy factors of approximately 0.75 for the original fluorine atoms and 0.25 for the three additional peaks. The occupancy factors were fixed at these values, and all nonhydrogen atoms except for the three lower-occupancy fluorine atoms were henceforth treated anisotropically. The final agreement factors were $R_1 = 0.042$ and $R_2 = 0.058$. No attempt was made to locate any hydrogen atoms.

Compound **1** crystallized in the space group $P\bar{1}$ with cell constants of $a = 9.083$ (2) Å, $b = 19.897$ (6) Å, $c = 18.828$ (3) Å, $\alpha = 134.62$ (3)°, $\beta = 98.34$ (2)°, $\gamma = 94.12$ (2)°, $V = 2323$ (3) Å^3, and $Z = 2$ with one molecule as the asymmetric unit. The two independent molybdenum atoms were located from a three-dimensional Patterson function, and the coordination sphere about the Mo_2^{4+} unit was found in the first electron density map. Alternate refinement and electron density map steps revealed positions for 63 of the 68 atoms, and the discrepancy indices at this point were $R_1 = 0.194$ and $R_2 = 0.285$. The missing atoms belonged to phenyl groups, and further effort, using additional electron density maps, did not provide any clear evidence for them. Moreover, the already complete phenyl groups were found to be badly distorted. In view of the time and cost involved in each stage of computation for such a large structure (253 variables and 6131 observations), together with the fact that qualitative demonstration that the phosphine ligands are axially coordinated fulfilled our main purpose in conducting a crystallographic study of this compound, we decided not to continue the work with this structure.

Acknowledgment. We thank the National Science Foundation for support.

Registry No. **1**, 41772-59-2; **2**, 76036-80-1; **3**, 76036-79-8; $Mo_2(O_2CCF_3)_4$, 35489-62-4; $Mo_2(O_2CCF_3)_4(Et_2O)_2$, 76036-78-7.

Supplementary Material Available: Tables of observed and calculated structure factors for compounds **2** and **3** (20 pages). Ordering information is given on any current masthead page.

Notes

Contribution from Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87545

^{15}N NMR Study of Complexation of 1-Methylimidazole by Zinc(II) and Cadmium(II) in Aqueous Solution[1]

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Received July 10, 1980

In prior publications we have reported on ^{15}N NMR studies of complexation of doubly ^{15}N-labeled imidazole (Im) by Zn(II)[2] and Cd(II)[3] in aqueous solution. In those systems, rapid N–H proton exchange between imidazole species and rapid Im exchange between all metal ion–imidazole complexes ($M(Im)_i^{2+}$, $1 \le i \le 6$) allows observation of only a single ^{15}N resonance in any given solution. In treating the experimental data to extract the ^{15}N shift produced by complexation of Im with Zn^{2+} or Cd^{2+}, we were thus limited to determination of the average shift over both imidazole nitrogens ($^{15}N_1$ and $^{15}N_3$). To measure the effect of metal ion complexation on each nitrogen, we felt it would be useful to do a similar study with doubly ^{15}N-labeled 1-methylimidazole (1-MeIm) which displays separate $^{15}N_1$ and $^{15}N_3$ resonances. Since metal ion complexation occurs at $^{15}N_3$, it is expected to produce a large shift at that nitrogen and a much smaller shift at $^{15}N_1$, with the average being comparable to the shift observed for the ^{15}N resonance of Im when complexed by the same ion. The results of such a study should enable us to predict more accurately the effects of metal ion complexation on imidazole-ring ^{15}N shifts in biological systems where the two nitrogens are usually distinguishable.

Experimental Section

Doubly ^{15}N-labeled 1-MeIm was prepared as described in an earlier publication.[4] Preparation of the metal ion–1-MeIm solutions and acquisition of ^{15}N NMR data were also as described earlier[2] with the exception that in the present work constant ionic strength of 0.2 was maintained for all solutions. The pH of each solution was measured with an Orion combination electrode and Corning Digital 110 pH meter. Samples were thermostated at 25.0 ± 0.1 °C and flushed with argon to exclude atmospheric CO_2 during the pH measurement. Since Avdeef and Bucher[5] have found a significant difference between true hydrogen ion concentration and measured pH on a Beckman combination electrode, we have used their expressions to correct our measured pH (at ionic strength of 0.2, the true pH is 0.15 unit less than measured pH for all the solutions used in this work). The corrected pH values are listed in Table I.

Table I. ^{15}N Shifts for 1-MeIm in Aqueous $Zn(NO_3)_2$ or $Cd(NO_3)_2$ Solutions

sample	[TL],[a] mol/L	[TA],[b] mol/L	[TM],[c] mol/L	pH[d]	δ_{obsd}[e] $^{15}N_3$	δ_{obsd}[e] $^{15}N_1$
			Zn(II)			
A	0.0787	0.0501	0.0498	5.66	59.0	−6.1
B	0.1121	0.0501	0.0495	5.90	52.1	−5.4
C	0.1334	0.0500	0.0495	6.09	49.8	−5.3
D	0.1649	0.0497	0.0494	6.22	47.9	−5.2
E	0.2188	0.0496	0.0492	6.51	46.0	−5.2
F	0.2489	0.0493	0.0492	6.70	44.6	−5.2
G	0.3220	0.0491	0.0488	7.25	37.0	−4.4
H	0.3544	0.0490	0.0486	7.34	33.8	−4.1
			Cd(II)			
A	0.0768	0.0503	0.0493	5.62	58.3	−6.1
B	0.1299	0.0499	0.0492	6.29	44.4	−4.7
C	0.1565	0.0499	0.0490	6.60	38.6	−4.1
D	0.2391	0.0495	0.0486	7.14	28.7	−3.1
E	0.3997	0.0487	0.0481	7.61	18.4	−2.1

[a] Total 1-MeIm concentration. [b] Total added HNO_3 concentration. [c] Total $Zn(NO_3)_2$ or $Cd(NO_3)_2$ concentration. [d] Uncertainty ≤±0.05 pH unit. [e] All $^{15}N_3$ shifts are *upfield* and all $^{15}N_1$ shifts *downfield* relative to their respective positions in aqueous 1-MeIm at pH >10.

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