and melts at 208–210 °C. ^{1}H NMR (26 °C, benzene-d_6): δ 2.12 (s, C_5Me_5). Resonances due to coordinated pyridine were not observed. Anal. Calcd for $C_{30}H_{40}N_2Yb$: C, 59.9; H, 6.70; N, 4.66. Found: C, 60.3; H, 6.70; N, 4.47. IR (Nujol): 3092 w, 3063 w, 3037 w, 2720 w, 1594 s, 1486 w, 1213 m, 1159 m, 1107 w, 1069 m, 1033 m, 998 m, 984 w, 942 w, 886 w, 800 w, 759 s, 729 w, 702 s, 662 m, 618 m, 591 m, and 419 m cm^{-1}.

X-ray Data. Crystals of the complex were sealed in quartz capillaries under an atmosphere of argon. A crystal of dimensions 0.06 × 0.22 × 0.22 mm was examined with a Picker FACS-I automated diffractometer equipped with a graphite monochromator and a Mo X-ray tube ($\lambda(K\alpha_1) = 0.709\,30$ Å). Least-squares refinement of the setting angles of 12 manually centered reflections ($45° < 2\theta < 50°$) gave $a = 16.092$ (6) Å, $b = 9.883$ (4) Å, $c = 17.872$ (7) Å, $\beta = 98.46$ (3)°, and $V = 2811.4$ Å^3 at 21 (1) °C. The observed extinctions are unique to space group $P2_1/c$. For $Z = 4$ and a molecular weight of 601.70, the calculated density is 1.42 g cm^{-3}.

Intensity data for two forms ($\pm h,+k,\pm l$) to 50° in 2θ were collected with θ–2θ with a scan speed of 2°/min on 2θ. Three standard reflections, measured after every 150 reflections, decreased in intensity by 2% during data collection, and the measured intensities were corrected accordingly.

An analytical absorption correction was applied[5] ($\mu = 33.3$ cm^{-1}), and the correction factors were varied from 1.27 to 2.42. Intensities of the 10699 reflections measured were also adjusted for the Lorentz and polarization factors,[6] extinctions were removed, and equivalent reflection were averaged to obtain a set of 4985 unique reflections.

Trial coordinates for the ytterbium atom were obtained from a three-dimensional Patterson function and were refined by least squares. An electron density map then revealed all nonhydrogen atoms. In the final cycles of least-squares refinement, all nonhydrogen atoms were refined anisotropically with the pyridine hydrogen atoms included in their calculated positions (with the assumption of a C–H bond distance of 0.95 Å) with a fixed isotropic thermal parameter of 8.0 Å^2. An empirical extinction correction was applied where $F_c = (1 + (4.54 \times 10^{-8})I)F_o$, where F_c and F_o are the corrected and observed structure factors and I is the observed intensity. The refinement converged smoothly to the positions given in Table I with the changes in parameters in the last cycle all less than 0.02σ. Thermal parameters, hydrogen atoms positions, and structure factor amplitudes are included in the supplementary material.

Scattering factors for neutral atoms were those of Doyle and Turner[7] for Yb, N, and C with anomalous dispersion corrections[4] applied; hydrogen scattering factors of Stewart, Davidson, and Simpson[8] were used. Discrepancy indices for 298 parameters varied with 3278 data having $F^2 > 3\sigma(F^2)$ are

$$R = \sum||F_o| - |F_c||/\sum|F_o| = 0.031$$

$$R_w = \sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.037$$

R for all 4985 data is 0.061, and the estimated standard deviation of an observation of unit weight is 1.15. A difference Fourier calculation after the final cycle of least-squares refinement had a maximum electron density of 0.88 e Å^{-3}.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy, under Contract No. W-7405-Eng-48. B.S. was on leave from the Chemistry Department, Beloit College, Beloit, WI. We thank Dr. P. L. Watson for providing us with some of her X-ray structural results in advance of publication.

Registry No. $Yb(C_5Me_5)_2(py)_2$, 81276-72-4; $Yb(C_5Me_5)_2(OEt_2)$, 74282-47-6.

Supplementary Material Available: Listings of anisotropic thermal parameters, calculated hydrogen positions, observed and calculated structure factors, and interatomic distances and angles (23 pages). Ordering information is given on any current masthead page.

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Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory,
and Department of Chemistry, University of California, Berkeley, California 94720

Stereochemistry of Bis(carboxylato)dichlorobis(tertiary phosphine)dimolybdenum Complexes. Crystal and Molecular Structure of Two Isomers of $Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$

JOHN D. ARENIVAR, VERA V. MAINZ, HELENA RUBEN, RICHARD A. ANDERSEN,*[1]
and ALLAN ZALKIN*[2]

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Reactions of $Mo_2Cl_4(PEt_3)_4$ with Me_3CCO_2H or $Mo_2(O_2CCMe_3)_4$ with Me_3SiCl and PEt_3 give $Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$. The product of the former reaction yields a red isomer of C_2 symmetry whereas the latter reaction gives an orange isomer of C_{2h} symmetry. The crystal structures of both isomers have been determined by X-ray techniques. The red A isomer, space group $P2_12_12_1$, has the unit cell dimensions $a = 12.542$ (4) Å, $b = 25.344$ (8) Å, $c = 10.437$ (4) Å, $Z = 8$, and $d_x = 1.40$ g/cm^3. The orange B isomer, space group $P\bar{1}$, has the unit cell dimensions $a = 8.989$ (3) Å, $b = 10.640$ (4) Å, $c = 8.978$ (3) Å, $\alpha = 91.46$ (4)°, $\beta = 81.63$ (4)°, $\gamma = 110.10$ (4)°, $Z = 2$, and $d_x = 1.45$ g/cm^3. The Mo–Mo distances are 2.113 and 2.098 Å for the A and B isomers, respectively.

Introduction

Compounds of the type $Mo_2(O_2CR)_2X_2(PR_3)_2$ provide a potentially rich area for investigating stereochemical phenomena in quadruply bonded, binuclear molecules since a variety of isomers are possible. In this paper we describe the synthesis and crystal structure of two such geometrical isomer of $Mo_2(O_2CCMe_3)_2Cl_2(PEt_3)_2$. The preparation and solution spectroscopy of the whole family of isomers of the type $Mo_2(O_2CCMe_3)_2X_2(PR_3)_2$, where X = Cl, Br, and I and PR_3 = PMe_3, PEt_3, and PMe_2Ph, will be described shortly. This is only the second example, in molecules of this general type, in which two structural isomers have been structurally characterized, the others being the two geometrical isomers of $Re_2Cl_4(O_2CMe)_2(H_2O)_2$.[3]

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[2] Lawrence Berkeley Laboratory.

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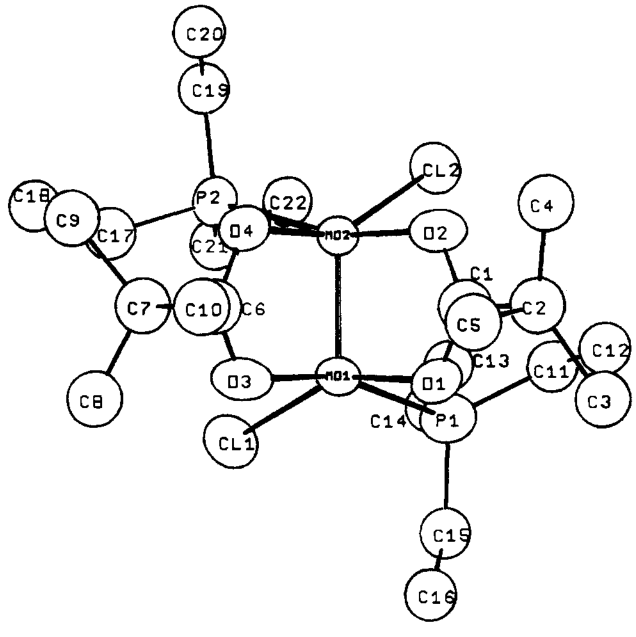


Figure 1. ORTEP drawing of isomer A.

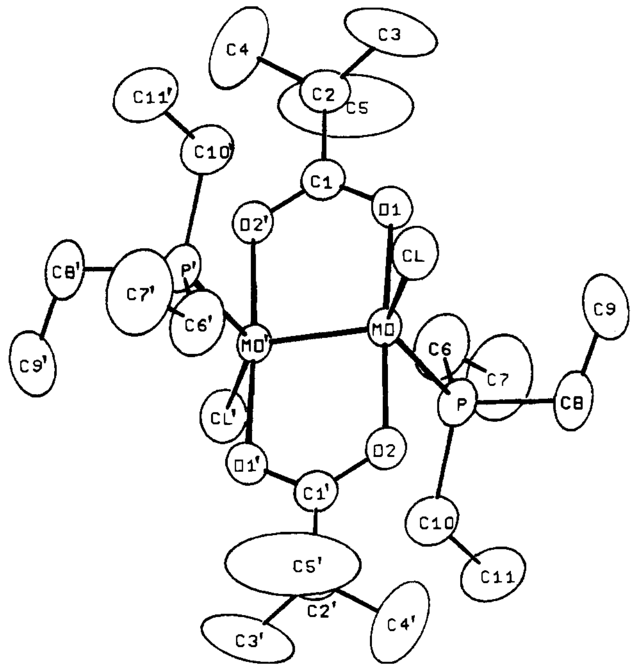
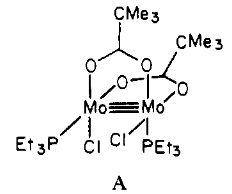


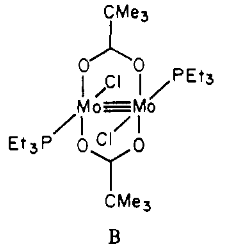
Figure 2. ORTEP drawing of isomer B.

Results

Tetrachlorotetrakis(triethylphosphine)dimolybdenum reacts with 2 molar equiv of pivalic acid, Me_3CCO_2H, to give red, air-stable dichlorobis(triethylphosphine)bis(pivalato)dimolybdenum (A). In contrast, reaction of tetrakis(pivalato)dimolybdenum with trimethylchlorosilane and triethylphosphine gives an orange, air-stable compound (B) of the same empirical formula as A, but it is a different geometrical isomer. The crystal structures of both isomers have been determined by conventional X-ray diffraction methods. A complex of type B, $Mo_2(O_2CPh)_2Br_2(P\text{-}n\text{-}Bu_3)_2$, has been crystallographically characterized previously (ref d in Table VI). However, the structural type A is new. Cell dimensions and other crystal data are given in Table I. Positional parameters are given in Tables II and III. Distances and angles are given in Tables IV and V with atom numbers as in Figures 1 and 2. Tables of thermal parameters and observed structure factors are given in the supplementary material.



A



B

Table I. Summary of Crystal Data Intensity Collection and Least-Squares Refinement Statistics

	isomer A	isomer B
formula wt	348.66	348.66
a, Å	12.542 (4)	8.989 (3)
b, Å	25.334 (8)	10.640 (4)
c, Å	10.437 (4)	8.978 (3)
α, deg	90	91.46 (4)
β, deg	90	81.63 (4)
γ, deg	90	110.10 (4)
V, Å^3	3316	798
space group	$P2_12_12_1$	$P\bar{1}$
Z	8	2
d(calcd), g/cm^3	1.397	1.452
color	red	orange
cryst size, mm	0.25 × 0.27 × 0.30	0.08 × 0.11 × 0.13
cryst vol, mm^3	0.024	0.0012
μ, cm^{-1}	10.2	10.6
T, °C	23	23
no. of scans (including stds)	6398	5544
decay cor range	1.0–1.09	1.0–1.07
no. of unique data	3301	2825
no. of data with $F^2 > 3\sigma(F^2)$ used in least squares	2685	2448
extinctn factor k^a	2.7×10^{-8}	4.3×10^{-8}
ignorance factor, p^b	0.05	0.05
no. of variables in least squares	179	145
$R_w{}^c$	0.083	0.053
R^d	0.053	0.035
R for all data	0.067	0.041
goodness of fit	2.55	1.63

[a] Given by $F_c = (1 + kI)F_o$. [b] Given in the weighting expression $w = (\sigma^2F^2 + (pF^2)^2)^{-1}$. [c] $R_w = [\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$. [d] $R = \Sigma|\Delta F|/\Sigma|F_o|$ ($F^2 > 3\sigma(F^2)$).

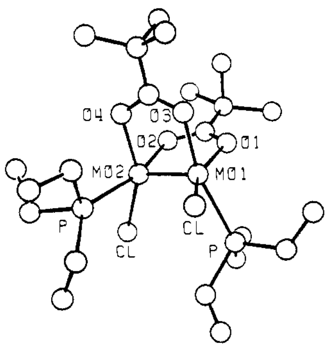


Figure 3. Another view of isomer A, showing the cis orientation.

Discussion

An interesting feature of isomer A is that the two oxygen atoms of each of the carboxylate groups are trans to two different ligands. This type of stereochemistry allows a comparison of the molybdenum–oxygen bond lengths as a function of the trans ligands within the same molecule. The pertinent distances are listed in Table IV. The average molybdenum–oxygen bond distance trans to chloride is 0.07 Å (8σ) shorter than the average molybdenum–oxygen bond trans to phosphine. This difference indicates that phosphine lies higher than

Table II. Positional Parameters for Isomer A[a]

atom	*x*	*y*	*z*
Mo(1)	0.08938 (9)	0.12469 (4)	0.14225 (7)
Mo(2)	0.08896 (8)	0.12204 (4)	0.34460 (7)
Cl(1)	−0.0590 (3)	0.1716 (2)	0.0482 (3)
Cl(2)	0.1921 (3)	0.1886 (2)	0.4534 (3)
P(1)	0.2059 (4)	0.2025 (2)	0.0836 (4)
P(2)	−0.0794 (3)	0.1734 (2)	0.4044 (3)
O(1)	0.2201 (7)	0.0762 (4)	0.1318 (8)
O(2)	0.2242 (7)	0.0708 (4)	0.3435 (7)
O(3)	−0.0051 (7)	0.0560 (4)	0.1354 (9)
O(4)	−0.0041 (7)	0.0549 (4)	0.3454 (9)
C(1)	0.260 (1)	0.0581 (5)	0.237 (1)
C(2)	0.345 (1)	0.0147 (7)	0.233 (2)
C(3)	0.425 (2)	0.024 (1)	0.112 (2)
C(4)	0.393 (2)	−0.002 (1)	0.362 (3)
C(5)	0.285 (2)	−0.036 (1)	0.191 (3)
C(6)	−0.0296 (9)	0.0357 (5)	0.235 (1)
C(7)	−0.097 (1)	−0.0158 (7)	0.235 (2)
C(8)	−0.168 (3)	−0.023 (1)	0.107 (3)
C(9)	−0.155 (2)	−0.0282 (9)	0.359 (2)
C(10)	−0.010 (3)	−0.061 (1)	0.230 (3)
C(11)	0.326 (2)	0.226 (1)	0.160 (3)
C(12)	0.398 (2)	0.179 (1)	0.184 (3)
C(13)	0.112 (2)	0.255 (1)	0.133 (3)
C(14)	0.164 (3)	0.309 (1)	0.119 (3)
C(15)	0.214 (2)	0.2130 (9)	−0.087 (1)
C(16)	0.186 (2)	0.1685 (8)	−0.180 (2)
C(17)	−0.203 (1)	0.1399 (6)	0.347 (1)
C(18)	−0.306 (1)	0.1643 (8)	0.403 (2)
C(19)	−0.091 (1)	0.1785 (5)	0.576 (1)
C(20)	−0.073 (2)	0.1245 (6)	0.642 (2)
C(21)	−0.102 (1)	0.2412 (6)	0.355 (2)
C(22)	−0.031 (1)	0.2833 (7)	0.421 (2)

[a] In this and in the following tables the numbers in parentheses are the estimated standard deviations in the least significant digits.

Table III. Positional Parameters for Isomer B

atom	*x*	*y*	*z*
Mo(1)	0.11261 (4)	0.00692 (4)	0.02587 (4)
Cl(1)	0.1210 (2)	−0.1189 (1)	0.2444 (1)
P(1)	0.2896 (1)	0.1580 (1)	−0.1881 (1)
O(1)	0.1239 (4)	0.1749 (3)	0.1587 (4)
O(2)	0.1171 (4)	−0.1559 (3)	−0.1106 (3)
C(1)	0.0038 (5)	0.2132 (4)	0.1750 (5)
C(2)	0.0058 (6)	0.3337 (5)	0.2720 (6)
C(3)	0.106 (2)	0.342 (1)	0.396 (1)
C(4)	−0.159 (1)	0.320 (1)	0.345 (2)
C(5)	0.070 (2)	0.4554 (8)	0.179 (1)
C(6)	0.2797 (7)	0.3289 (6)	−0.1855 (8)
C(7)	0.409 (1)	0.4338 (7)	−0.291 (1)
C(8)	0.4954 (6)	0.1742 (6)	−0.1685 (7)
C(9)	0.5341 (8)	0.2164 (9)	−0.0076 (9)
C(10)	0.2654 (7)	0.0917 (7)	−0.3803 (6)
C(11)	0.3999 (9)	0.1545 (9)	−0.5073 (8)

chloride in a trans-influence series in Mo(II) chemistry. A related bond length trend is observed in $Re_2Cl_6(PEt_3)_2$, and ascribed to a trans influence,[4] and is in agreement with the extensive data available for platinum(II) complexes.[5]

A structural comparison between the two isomers is revealing since isomer A has chloride ligands trans to a carboxylate group whereas isomer B has chloride ligands trans to triethylphosphine. The average molybdenum–chloride bond length in isomer A is 0.02 Å (4σ) shorter than the average molybdenum–chloride distance in isomer B. This suggests that phosphine lies higher on a trans-influence series than a carboxylate group. By combination of this result with the one developed above, two inequalities may be written: $Et_3P > Me_3CCO_2$ and $Et_3P > Cl$. In a similar fashion, comparison of molybdenum–oxygen bond lengths between the two isomers yields the inequality $Me_3CCO_2 \geq Cl$. Thus a trans series, based upon bond length changes in the two isomers, may be written: $Et_3P > M_3CCO_2 \geq Cl$. Since no Pt–X bond lengths have been determined for X trans to carboxylate, this part of the series cannot be directly compared with the Pt(II)-derived scale. However, in Pt(II) chemistry, a phosphine ligand lengthens a bond trans to it more than does a chloride ligand.

Examination of bond lengths in related binuclear molybdenum compounds suggest a possible generalization of the structural trans-influence series. Table VI lists representative bond lengths as a function of the trans ligand. This list is not exhaustive but it includes a cross section of accurate structures that have been reported on neutral molybdenum(II) dimers with pseudo-square-planar ligand arrays. Inspection of Table VI shows that the molybdenum–oxygen bond length depends upon the ligand trans to it in the same general way that was deduced by comparison of the two isomers A and B, viz., P > O ≥ Cl. Similarly, the molybdenum–chloride bond distances (see Table VII) follow the general trend, P > O, Cl. Hence, phosphine is higher on a trans-influence series than chloride is mononuclear Pt(II) and binuclear Mo(II) and Re(III) molecules. Thus, the postulate of a trans-influence series in Mo(II) that is analogous to that found in Pt(II) appears to be a reasonable generalization. Arguments similar to those advanced here have been used recently to rationalize W–P and W–Cl bond lengths in two isomers of $W_2Cl_4(dppe)_2$, where dppe is 1,2-bis(diphenylphosphino)ethane.[6]

The isolation of two isomers, beginning from different starting materials, has not been observed before in quadruply bonded molybdenum systems. The solution properties of each isomer and their rates and mechanisms of interconversion will be addressed in a later paper.

Experimental Section

All operations were performed under argon. Analyses were done by the microanalytical laboratory of this department.

Dichlorobis(2,2-dimethylpropionato)bis(triethylphosphine)dimolybdenum(II). (A) The Red, C_2 Isomer. Pivalic acid (0.57 g, 0.0056 mol) in benzene (2 mL) was added to tetrachlorotetrakis(triethylphosphine)dimolybdenum[7] (2.25 g, 0.00279 mol) in benzene (20 mL). After 4 h of refluxing, the benzene was evaporated, and the red-violet gummy residue was extracted with pentane (3 × 50 mL). The combined extracts were concentrated under reduced pressure to ca. 50 mL and cooled to −15 °C. The red prisms were collected and dried under reduced pressure. The mother liquor yielded two more crops of complex, the total yield being 1.35 g (69%); mp 162–165 °C. Anal. Calcd for $C_{22}H_{48}Cl_2Mo_2O_4P_2$: C, 37.7; H, 6.90; Cl, 10.1. Found: C, 38.5; H, 7.07; Cl, 10.0. The $\nu_{asy}(CO_2)$ was at 1490 cm^{-1} in the infrared spectrum.

(B) The Orange, C_{2h} Isomer. Triethylphosphine (0.42 g, 0.0036 mol) was added to tetrakis(2,2-dimethylpropionato)dimolybdenum (1.05 g, 0.00176 mol) in diethyl ether (25 mL). Trimethylchlorosilane (0.35 g, 0.0035 mol) was added, and the orange solution was stirred for 30 min and then cooled (−15 °C). The microcrystals were isolated and crystallized from diethyl ether (ca. 10 mL, −15 °C) as orange prisms: mp 178–180 °C; yield 1.1 g (90%). Anal. Calcd for $C_{22}H_{48}Cl_2Mo_2O_4P_2$: C, 37.7; H, 6.90; Cl, 10.1. Found: C, 38.1; H, 6.98; Cl, 10.2. The $\nu_{asy}(CO_2)$ was at 1480 cm^{-1} in the infrared spectrum.

X-ray Diffraction. Red crystals of isomer A and orange crystals of isomer B were glued to Pyrex fibers and subjected to Weissenberg photography for the preliminary examination. A Picker FACS-1 automated diffractometer, equipped with a graphite monochromator and a molybdenum X-ray tube, was used to collect the intensity data for the crystal structure determinations. Setting angles of 12 reflections

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Table IV. Interatomic Distances (Å)

isomer A				isomer B	
Mo(1)-Mo(2)	2.113 (1)			Mo-Mo'[a]	2.0984 (4)
-O(1)	2.051 (8)	Mo(2)-O(2)	2.136 (8)	-O(1)	2.105 (5)
-O(3)	2.106 (9)	-O(4)	2.063 (9)	-O(2)	2.105 (5)
-Cl(1)	2.415 (4)	-Cl(2)	2.410 (4)	-Cl	2.428 (5)
-P(1)	2.529 (4)	-P(2)	2.558 (4)	-P	2.513 (4)
P(1)-C(11)	1.81 (2)[b]	P(2)-C(17)	1.86 (2)[b]	P-C(6)	1.850 (8)
-C(13)	1.86 (2)[b]	-C(19)	1.80 (2)[b]	-C(8)	1.832 (7)
-C(15)	1.81 (2)[b]	-C(21)	1.82 (2)[b]	-C(10)	1.861 (7)
O(1)-C(1)	1.29 (2)	O(3)-C(6)	1.20 (2)	O(1)-C(1)	1.267 (6)
O(2)-C(1)	1.24 (2)	O(4)-C(6)	1.29 (2)	O(2)-C(1)	1.264 (6)
C(1)-C(2)	1.54 (2)	C(6)-C(7)	1.55 (2)	C(1)-C(2)	1.529 (7)
C(2)-C(3)	1.63 (3)	C(7)-C(8)	1.61 (4)	C(2)-C(3)	1.51 (1)
-C(4)	1.54 (3)	-C(9)	1.53 (3)	-C(4)	1.49 (1)
-C(5)	1.55 (3)	-C(10)	1.57 (3)	-C(5)	1.45 (1)
C(11)-C(12)	1.52 (2)[b]	C(17)-C(18)	1.55 (2)[b]	C(6)-C(7)	1.53 (1)
C(13)-C(14)	1.52 (2)[b]	C(19)-C(20)	1.55 (2)[b]	C(8)-C(9)	1.55 (1)
C(15)-C(16)	1.53 (2)[b]	C(21)-C(22)	1.55 (2)[b]	C(10)-C(11)	1.51 (1)

[a] Atom at $-x$, $-y$, $-z$. [b] These distances were restrained in the least-squares refinement, and the numbers in parentheses do not represent the true error.

Table V. Selected Angles (Deg)

isomer A				isomer B	
O(1)-Mo(1)-O(3)	87.3 (4)	O(4)-Mo(2)-O(2)	87.0 (4)	O(1)-Mo-O(2)	88.6 (2)
O(3)-Mo(1)-Cl(1)	87.6 (3)	O(2)-Mo(2)-Cl(2)	90.1 (3)	O(1)-Mo-Cl	90.6 (2)
Cl(1)-Mo(1)-P(1)	87.9 (2)	Cl(2)-Mo(2)-P(2)	88.4 (1)	Cl-Mo-P	142.2 (2)
P(1)-Mo(1)-O(1)	89.6 (3)	P(2)-Mo(2)-O(4)	87.2 (3)	P-Mo-O(1)	90.0 (2)
O(1)-Mo(1)-Cl(1)	152.6 (3)	O(4)-Mo(2)-Cl(2)	151.5 (3)	O(2)-Mo-Cl	89.7 (2)
O(3)-Mo(1)-P(1)	163.9 (3)	O(2)-Mo(2)-P(2)	165.0 (3)	O(2)-Mo-P	87.5 (2)
Mo(2)-Mo(1)-O(1)	92.1 (2)	Mo(1)-Mo(2)-O(2)	90.7 (2)	Mo-Mo-O(1)	91.4 (1)
-O(3)	90.3 (3)	-O(4)	91.8 (3)	-O(2)	91.7 (1)
-P(1)	105.6 (10)	-P(2)	103.3 (1)	-P	99.8 (1)
-Cl(1)	114.8 (1)	-Cl(2)	116.6 (1)	-Cl	117.9 (1)
Mo(1)-O(1)-C(1)	118.3 (8)	Mo(2)-O(2)-C(1)	116.6 (8)	Mo-O(1)-C(1)	117.6 (3)
Mo(1)-O(3)-C(6)	117.9 (9)	Mo(2)-O(4)-C(6)	116.6 (8)	Mo-O(2)-C(1)	117.5 (3)
O(1)-C(1)-O(2)	122 (1)	O(3)-C(6)-O(4)	123 (1)	O(1)-C(1)-O(2)	121.8 (4)
Mo(1)-P(1)-C(11)	129 (1)[a]	Mo(2)-P(2)-C(17)	112 (1)[a]	Mo-P-C(6)	114.2 (2)
-C(13)	98 (1)[a]	-C(19)	110 (1)[a]	-C(8)	106.3 (2)
-C(15)	113 (1)[a]	-C(21)	123 (1)[a]	-C(10)	115.8 (3)
O(1)-C(1)-C(2)	120 (1)	O(3)-C(6)-C(7)	120 (1)	O(1)-C(1)-C(2)	119.5 (4)
O(2)-C(1)-C(2)	118 (1)	O(4)-C(6)-C(7)	117 (1)	O(2)-C(1)'-C(2)'	118.7 (4)

[a] Angles calculated from restrained distances in the least-squares refinement; the numbers in parentheses do not represent true error.

Table VI. Molybdenum-Oxygen Bond Lengths (Å) as a Function of the Trans Ligand

compd	Mo-O	trans group	ref
$Mo_2(O_2CMe)_4$	2.119 ± 0.010	O	*a*
$Mo_2(O_2CCMe_3)_4$	2.111 ± 0.007	O	*b*
$Mo_2(O_2CPh)_4$	2.106 ± 0.013	O	*b*
$Mo_2(CH_2SiMe_3)_2(O_2CMe)_2(PMe_3)_2$	2.114 ± 0.005	O	*c*
$Mo_2Br_2(O_2CPh)_2[P(n\text{-}Bu)_3]_2$	2.105 ± 0.005	O	*d*
$Mo_2Cl_2(O_2CCMe_3)_2(PEt_3)_2$ (C_{2h})	2.105 ± 0.002	O	*e*
$Mo_2Cl_2(O_2CCMe_3)_2(PEt_3)_2$ (C_2)	2.136 ± 0.008	P	*e*
$Mo_2Cl_2(O_2CCMe_3)_2(PEt_3)_2$ (C_2)	2.063 ± 0.009	Cl	*e*

[a] Cotton, F. A.; Mester, Z. C.; Webb, T. R. *Acta Crystallogr., Sect. B* 1974, *B30*, 2768. [b] Cotton, F. A.; Extine, M.; Gage, L. D. *Inorg. Chem.* **1978**, *17*, 172. [c] Hursthouse, M. B.; Malik, K. M. A. *Acta Crystallogr.*, **1979**, *B35*, 2709. [d] Potenza, J. A.; Johnson, R. J.; San Fillipo, J. *Inorg. Chem.* 1976, *15*, 2215. [e] This work.

Table VII. Molybdenum-Chloride Bond Lengths (Å) as a Function of the Trans Ligand

compd	Mo-Cl	trans group	ref
$Mo_2Cl_4(SEt_2)_4$	2.411 ± 0.004	Cl	*a*
$Mo_2Cl_4(Ph_2PCH_2PPh_2)_2$	2.394 ± 0.006	Cl	*b*
$Mo_2Cl_4(PEt_3)_2(MeOH)_2$	2.404 ± 0.002	Cl	*c*
$Mo_2Cl_2(O_2CCMe_3)_2(PEt_3)_2$ (C_2)	2.428 ± 0.005	P	*d*
$Mo_2Cl_2(PEt_3)_2$(azaindolyl)$_2$	2.436 ± 0.002	P	*e*
$Mo_2Cl_2(O_2CCMe_3)_2(PEt_3)_2$ (C_{2h})	2.410 ± 0.004	O	*d*

[a] Cotton, F. A.; Fanwick, P. E. *Acta Crystallogr., Sect. B* 1980, *B36*, 457. [b] Abbott, E. H.; Bose, K. S.; Cotton, F. A.; Hall, W. T.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 3240. [c] McGinnis, R. N.; Ryan, T. R.; McCarley, R. E. *J. Am. Chem. Soc.* **1978**, *100*, 7900. [d] This work. [e] Cotton, F. A.; Lay, D. G.; Millar, M. *Inorg. Chem.* **1978**, *17*, 186.

where $40 < 2\theta < 57°$ (for isomer A) and $40 < 2\theta < 46°$ (for isomer B), ($\lambda(\text{Mo K}\alpha_1) = 0.70930$ Å) were used for least-squares adjustments of the cell dimensions. Cell dimensions and other crystal data are given in Table I.

A θ–2θ scan technique with a scan speed of 2°/min was used to collect the intensities in the range $4° < 2\theta < 50°$; backgrounds were measured for 10 s at the beginning and end of each scan. ω scans of several low-angle reflections showed widths at half-peak height of 0.16 (isomer A) and 0.10 (isomer B). Three standard reflections were measured after each 250 scans to monitor for crystal decay, instrumental stability, and crystal alignment. Decays of 9% (isomer A) and 7% (isomer B) were observed in the intensities of the standards, and the data were adjusted accordingly. Corrections for absorption were made by an analytical integration method.[8] During refinement, effects of extinction were evident in the data, and an empirical isotropic

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(8) Templeton, L. K.; Templeton, D. H. "Abstracts, American Crystallographic Association Proceedings"; American Crystallographic Association: Storrs, CT, 1973; Series 2, Vol. 1, p 143.

correction was applied (see Table I). Atomic scattering factors of Doyle and Turner[9] were used, and anomalous scattering corrections[10] were applied.

Three-dimensional Patterson maps indicated the positions of the Mo atoms. Subsequent least-squares refinements and difference Fourier maps revealed all of the nonhydrogen atoms. Most of the hydrogen atom peaks were not resolved in the Fourier maps, and none were included in the least-squares refinements. All of the atoms with the exception of the carbon atoms in isomer A were assigned anisotropic thermal parameters in the final refinements. Because of the poor resolution of the ethyl groups in the A isomer, restraints were imposed on the geometry of the triethylphosphine groups by a procedure suggested by Waser,[11] and described in a previous paper.[12] For the A isomer, the C–C and P–C bond distances were restrained to 1.54 and 1.82 Å, respectively. The full-matrix least-squares program minimizes the function $\sum w(\Delta F)^2/\sum wF_o^2$. After the last cycle of refinement, the largest shift of the parameter was 0.03 and 0.01 of its esd for the A and B isomer, respectively. *R* factors and other statistical results of the least-squares refinement are given in Table I.

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Registry No. *C*$_2$-Mo$_2$Cl$_2$(O$_2$CCMe$_3$)$_2$(PEt$_3$)$_2$, 81276-73-5; *C*$_{2h}$-Mo$_2$Cl$_2$(O$_2$CCMe$_3$)$_2$(PEt$_3$)$_2$, 81339-50-6; Mo$_2$Cl$_4$(PEt$_3$)$_4$, 59780-36-8; Mo$_2$(O$_2$CCMe$_3$)$_4$, 55946-68-4; Me$_3$SiCl, 75-77-4.

Supplementary Material Available: Listings of thermal parameters and observed structure factors (26 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, University of California, and the
Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California 94720

Organouranium Complexes of Pyrazole and Pyrazolate. Synthesis and X-ray Structures of $U(C_5Me_5)_2Cl_2(C_3H_4N_2)$, $U(C_5Me_5)_2Cl(C_3H_4N_2)$, and $U(C_5Me_5)(C_3H_3N_2)_2$

CHARLES W. EIGENBROT, JR., and KENNETH N. RAYMOND*

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The title compounds have been prepared by the reaction between U(C$_5$Me$_5$)$_2$Cl$_2$ and pyrazole (C$_3$H$_4$N$_2$), or sodium pyrazolate (NaC$_3$H$_3$N$_2$), in THF. The new compounds are characterized by their infrared, ^{1}H NMR visible–near-IR, and mass spectra and by single-crystal X-ray diffraction (monochromatic Mo Kα radiation). The molecular structure of U(C$_5$Me$_5$)$_2$Cl$_2$(C$_3$H$_4$N$_2$) consists of discrete mononuclear units at positions of *mm* (C_{2v}) symmetry. The U^{4+} ion is coordinated by two η^5-pentamethylcyclopentadienide rings, two chloride ions, and one nitrogen atom from the neutral pyrazole ring, for a total coordination number of 9. Red-brown crystals from toluene conform to space group *Cmcm* with a = 13.697 (4) Å, b = 11.496 (2) Å, c = 15.555 (2) Å, and four molecules per unit cell. For the 924 independent reflections with $F^2 > 3\sigma(F^2)$, the final weighted and unweighted *R* factors are 3.48 and 2.45%, respectively. The average U–C bond distance is 2.74 (2) Å, the U–N bond distance is 2.607 (8) Å, and the U–Cl distance is 2.696 (2) Å. This compound exhibits Curie–Weiss behavior with C = 1.46, Θ = 43.3 K, and μ_{eff} (from the slope of $1/\chi$ vs. T) = 3.24 μ_B. The molecular structure of U(C$_5$Me$_5$)$_2$Cl(C$_3$H$_3$N$_2$) consists of discrete U^{4+} ions coordinated by two η^5-pentamethylcyclopentadienide rings, one chloride ion, and both nitrogen atoms from the pyrazolate anion, for a total coordination number of 9. Red-brown crystals from toluene conform to space group $P2_1/n$ with a = 8.737 (1) Å, b = 18.068 (1) Å, c = 15.229 (1) Å, β = 92.38 (1)°, and four molecules per unit cell. For the 2566 independent reflections with $F^2 > 3\sigma(F^2)$, the final weighted and unweighted *R* factors are 4.50 and 3.27%, respectively. The average U–C bond distance is 2.73 (3) Å, the U–N distances are 2.351 (5) and 2.349 (5) Å, and the U–Cl distance is 2.611 (2) Å. This compound exhibits Curie–Weiss behavior with C = 0.73, Θ = 5.95 K, and μ_{eff} = 2.42 μ_B. The molecular structure of U(C$_5$Me$_5$)$_2$(C$_3$H$_3$N$_2$)$_2$ consists of discrete mononuclear U^{4+} ions coordinated by two η^5-pentamethylcyclopentadienide rings and four nitrogen atoms from the two pyrazolate anions, for a total coordination number of 10. Red-brown crystals from toluene conform to space group $C2/c$ with a = 33.326 (2) Å, b = 10.450 (2) Å, c = 16.646 (1) Å, β = 117.09 (1)°, and eight molecules per unit cell. For the 2706 independent reflections with $F^2 > 3\sigma(F^2)$, the final weighted and unweighted *R* factors are 3.31 and 2.43%, respectively. The average U–C bond distance is 2.75 (2) Å, and the U–N distances are 2.403 (4), 2.360 (5), 2.363 (5), and 2.405 (5) Å. This compound does not exhibit simple magnetic behavior.

Introduction

As part of our effort to create, examine, and explain structural[1] and magnetic[2] probes of the bonding in organolanthanide and actinide compounds, we have sought the synthesis and magnetic characterization of an appropriate dimeric uranium complex. Our recent report of the synthesis and structure of UCp$_3$(pz$^-$)[3] (pz$^-$ = pyrazolate) revealed that our attempt to form a dimer (based on a precedent in titanium chemistry, [TiCp$_2$(pz$^-$)]$_2$)[4] resulted instead in the formation of a monomeric species, allowing us to characterize a new mode of pyrazolate bonding. To investigate what role, if any, steric factors played in the formation of the monomeric compound, and to learn more about the pyrazolate ion as a ligand, we have adjusted the size and number of the Cp (C$_5$H$_5$) ligands. We anticipated that a reduction in the total steric bulk of the other ligands might lead to the formation of one or more dimeric species. The compound UCp″$_2$Cl$_2$ (Cp″ = C$_5$Me$_5$) has proven to be a useful starting material for other studies[5,6]

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* To whom correspondence should be addressed at the University of California.

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