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 (23) We are grateful to Professor M. H. Chisholm for suggesting to us the utility of Cp_2Cr as a starting material for the preparation of these and other compounds of divalent chromium.
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 (25) The Enraf-Nonius structure determination package was used on a PDP 11/45 computer at the Molecular Structure Corporation, College Station, Texas. The structure factors and anomalous dispersion corrections were taken from sources previously cited.¹⁴
 (26) This is presumably the same compound formulated by Herzog and Kalies²¹ as $Cr(O_2CH)_2(H_2O)$, the difference being only $1/3 H_2O/Cr$. They reported a magnetic moment, μ_{eff} , at room temperature, per Cr atom of 1.35, which is considerably higher than the moments of ca. 0.5 commonly reported

- for compounds containing Cr only in $Cr_2(O_2CR)_4$ units. This higher value is now qualitatively understandable because of the presence of the isolated Cr(II) ions. It is not clear what significance is to be attached to it quantitatively. An approximate μ_{eff} for the isolated Cr(II) ion may be calculated as $3^{1/2} \times 1.35 = 2.34$, which is too low even for an isolated spin triplet (≥ 2.83) Cr(II) ion, let alone a spin quintet (≥ 4.89).
 (27) The first report of this compound seems to be that of W. Traube, E. Burmeister, and R. Stahn, *Z. Anorg. Allg. Chem.*, **147**, 50 (1925). Herzog and Kalies, *ibid.*, **351**, 237 (1967), report some other $Cr_2(O_2CH)_4$ - $(N\text{-ligand})_2$ compounds, all of which appear to be magnetically normal for dimers.
 (28) It may be noted that the two Cr-Cr vectors per unit cell lie at an angle of 26.4° to each other, thus making this substance a possible candidate for study of spectral polarizations.
 (29) Since there is only one molecule per unit cell, all Cr-Cr vectors are parallel. In agreement with this, the crystals are extremely dichroic; they are generally purple, but virtually colorless in one orientation when viewed in polarized light.

Contribution from the Department of Chemistry,
 Texas A&M University, College Station, Texas 77843

Preparation and Structure of a Quadrupty Bonded Dimolybdenum Compound Containing the 7-Azaindolyl Ligand

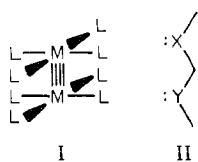
F. ALBERT COTTON,* DENNIS G. LAY, and MICHELLE MILLAR

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The reaction of 7-azaindole with $Mo_2Cl_4(PEt_3)_4$ gives a 29% yield of emerald green $Mo_2Cl_2(PEt_3)_2(C_7H_5N_2)_2$. The compound has been characterized by x-ray crystallography. It crystallizes in space group $P2_1/n$ with $a = 16.077$ (5) Å, $b = 8.936$ (2) Å, $c = 10.976$ (2) Å, $\beta = 94.52$ (2)°, $V = 1571.8$ (6) Å³, and $Z = 2$. The molecules lie on crystallographic inversion centers, and the ligand arrangement is such that there is no additional molecular symmetry possible. Thus, the $Mo_2P_2Cl_2$ atoms are coplanar and the two azaindolyl groups lie above and below this plane oriented in opposite directions. The Mo-Mo distance is 2.125 (1) Å and all other distances are normal. There is some disorder in the PEt_3 group.

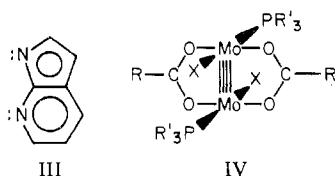
Introduction

The size (i.e., M-M distances usually in the range 2.0–2.4 Å) and square-prismatic geometry (idealized D_{4h} symmetry with M-M-L angles of 90–105°) of typical quadrupty bonded dimetal units, I, result in their having a stereochemical



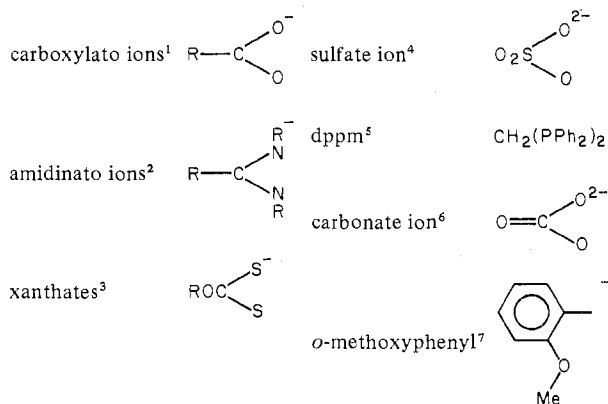
preference for ligands of the class represented schematically by II in which the donor atoms X and Y are separated by ca. 2.2 Å and the axes of their donor orbitals are aligned approximately parallel. The number of potential ligands in this class is very large; those which have already been shown crystallographically to occur in complexes of M-M quadrupty bonded units are shown in Chart I.

We describe here a compound containing the dinitrogen, monoanionic ligand 7-azaindolyl, III. The compound is



unusual in another respect. There have been only a few compounds reported in which as many as three different kinds of ligands, including one of type II, are present. These are the compounds of type IV, prepared by San Filippo and

Chart I



Sniadoch,⁸ one of which ($R = C_6H_5$, $R' = n\text{-}C_4H_9$, $X = Br$) was structurally characterized by Potenza, Johnson, and San Filippo.⁹ The compound we report here is analogous except that the carboxylato groups are replaced by III, the 7-azaindolyl group.

Experimental Section

Preparation. The entire procedure is carried out under anaerobic conditions with dry, degassed solvents. A mixture of 0.50 g (4.24 mmol) of 7-azaindole and 1.71 g (2.12 mmol) of $Mo_2Cl_4(PEt_3)_4$ ¹⁰ in 50 mL of benzene was heated at reflux for 2 h, cooled to room temperature, and then filtered to give 0.45 g (0.61 mmol) of an emerald green crystalline product. Large black acicular crystals were obtained by slow recrystallization of the product from hot toluene.

X-Ray Structural Characterization. Data Collection. A crystal measuring $0.45 \times 0.32 \times 0.27$ mm was mounted in a sealed glass

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

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	0.01811 (4)	0.10716 (7)	0.46954 (6)	0.00277 (3)	0.00861 (8)	0.00825 (5)	-0.00138 (9)	0.00060 (7)	0.0028 (1)
Cl(1)	-0.0842 (1)	0.2712 (2)	0.3621 (2)	0.0047 (1)	0.0123 (3)	0.0144 (2)	0.0010 (3)	-0.0025 (3)	0.0067 (5)
F(1)	0.1719 (1)	0.1042 (3)	0.5333 (2)	0.00299 (9)	0.0138 (3)	0.0105 (2)	-0.0010 (3)	0.0013 (2)	0.0026 (5)
N(1)	-0.0061 (4)	0.2129 (7)	0.6391 (6)	0.0033 (3)	0.0107 (9)	0.0095 (6)	0.0010 (9)	0.0003 (7)	-0.002 (1)
N(2)	-0.0481 (4)	-0.0250 (7)	0.7049 (6)	0.0032 (3)	0.0134 (10)	0.0083 (6)	-0.0013 (10)	-0.0003 (7)	0.002 (1)
C(1)	0.0032 (6)	0.3605 (9)	0.6814 (8)	0.0043 (4)	0.014 (1)	0.0118 (9)	0.003 (1)	-0.0023 (10)	-0.005 (2)
C(2)	-0.0137 (7)	0.3970 (13)	0.7913 (10)	0.0066 (6)	0.026 (2)	0.0154 (12)	0.006 (2)	-0.0002 (14)	-0.003 (3)
C(3)	-0.0394 (9)	0.3087 (22)	0.8744 (16)	0.0072 (7)	0.058 (4)	0.0262 (20)	0.010 (3)	-0.0053 (20)	-0.017 (6)
C(4)	-0.0844 (6)	0.0145 (16)	0.9084 (9)	0.0040 (4)	0.045 (3)	0.0092 (8)	0.004 (2)	0.0027 (9)	0.011 (3)
C(5)	-0.0762 (5)	-0.0891 (11)	0.8082 (7)	0.0038 (4)	0.024 (2)	0.0089 (7)	-0.000 (1)	0.0010 (9)	0.012 (2)
C(6)	-0.0546 (6)	0.1691 (14)	0.8478 (10)	0.0040 (4)	0.029 (2)	0.0181 (11)	0.008 (2)	-0.0047 (12)	-0.019 (3)
C(7)	-0.0359 (5)	0.1210 (10)	0.7249 (7)	0.0036 (4)	0.016 (1)	0.0087 (7)	0.004 (1)	0.0010 (9)	0.000 (2)

Atom	x	y	z	B, Å ²	Atom	x	y	z	B, Å ²
C(11)	0.2178 (12)	0.252 (2)	0.431 (2)	5.4 (4)	C(32)	0.3239 (21)	-0.059 (4)	0.475 (3)	12.6 (10)
C(12)	0.1729 (8)	0.391 (1)	0.422 (1)	7.8 (3)	C(41)	0.2045 (14)	0.302 (3)	0.534 (2)	7.4 (5)
C(21)	0.2054 (11)	0.174 (2)	0.687 (2)	5.3 (4)	C(51)	0.2212 (11)	0.050 (2)	0.685 (2)	5.3 (4)
C(22)	0.1795 (7)	0.090 (1)	0.792 (1)	6.4 (2)	C(61)	0.2376 (17)	-0.001 (3)	0.420 (2)	9.5 (7)
C(31)	0.2344 (15)	-0.061 (3)	0.512 (2)	7.8 (6)	C(62)	0.2390 (11)	-0.135 (2)	0.415 (2)	4.6 (4)

^a The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

capillary and examined on a Syntex $P\bar{1}$ four-circle automated diffractometer equipped with a graphite-crystal incident-beam monochromator. Precise unit cell dimensions were obtained by centering on 15 strong reflections in the range $20^\circ < 2\theta < 30^\circ$. The crystal was found to be of good quality with ω scan widths at half-height of less than 0.15° for several strong reflections. The operation of the diffractometer and other details of data collection have been described elsewhere¹¹ and only deviations from that procedure are noted here.

The crystal was found to be monoclinic with cell constants $a = 16.077$ (5) Å, $b = 8.936$ (2) Å, $c = 10.976$ (2) Å, $\beta = 94.52$ (2)°, and $V = 1571.8$ (6) Å³. The volume indicates the presence of two molecules per unit cell, one-half molecule per asymmetric unit, with a calculated density for $Z = 2$ of 1.51 g cm⁻³. Data were collected at $23 \pm 1^\circ\text{C}$ employing a θ - 2θ variable-scan technique with a scan rate ranging from 3.5 to $24.0^\circ/\text{min}$, depending upon the intensity of the reflection. Standard reflections, collected every 100 reflections, showed no evidence of crystal decomposition or crystal movement. A symmetric scan range of 1.1° below $K\alpha_1$ to 1.1° above $K\alpha_2$ was used to measure 2547 unique reflections up to a maximum 2θ value of 46.0° . Background measurements were made at both limits of each scan. A total of 1446 reflections having $|F_o|^2 > 3\sigma(F_o^2)$ were used for refinement of the structure. Lorentz and polarization corrections were applied. The linear absorption coefficient for the compound is 10.74 cm⁻¹ and no absorption correction was applied.

An examination of the intensity data indicated the following systematic absences: $0k0, k = 2n + 1$; $h0l, h + l = 2n + 1$. The space group was taken to be $P2_1/n$, a nonstandard setting, and this choice was proven correct by the successful structure solution and refinement described next.

Solution and Refinement of Structure. The Enraf-Nonius structure determination package with a PDP 11/45 computer was used to solve and refine the structure. The position of the molybdenum atom was obtained from a three-dimensional Patterson map. The first electron density map clearly indicated the positions of the phosphorus and chlorine atoms and a subsequent map showed the positions of the remaining nitrogen and carbon atoms. Least-squares refinement of these atom positions and associated isotropic thermal parameters yielded discrepancy factors of

$$R_1 = (\sum ||F_o| - |F_c||) / \sum |F_o| = 0.136$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.189$$

Atomic scattering factors were those of Cromer and Waber.¹² Anomalous dispersion effects were included in the scattering factors of molybdenum.¹³

High thermal parameters were found for several carbon atoms in the phosphine group suggesting a disorder problem. A difference electron density map at this point revealed peaks at distances 1.0 – 0.6 Å from those atoms with high thermal parameters (C(11), C(21), C(31), and C(32), the three α -carbon atoms, and one of the β -carbon atoms). These peaks (C(41), C(51), C(61), and C(62)) were refined as half-atoms as were the first four. The discrepancy factors at this point were $R_1 = 0.102$ and $R_2 = 0.151$.

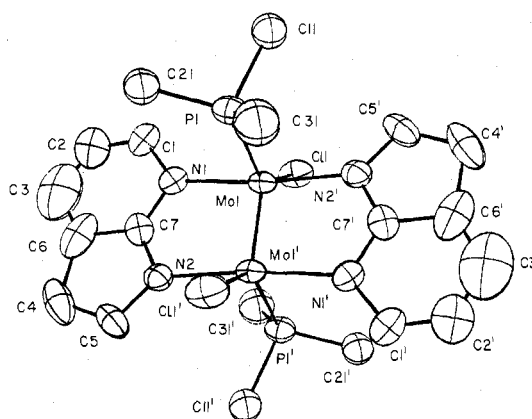


Figure 1. ORTEP drawing of the molecule. Atoms are represented by ellipsoids or spheres of thermal vibration scaled to enclose half of the electron density. The atom numbering scheme is defined; primed numbers designate atoms related by inversion to those with the corresponding unprimed numbers.

Anisotropic refinement of the molybdenum, phosphorus, chlorine, and ring carbon atoms led to discrepancy factors of $R_1 = 0.053$ and $R_2 = 0.080$. The structure was converged by 5 cycles of full-matrix least squares with final agreement factors of $R_1 = 0.046$ and $R_2 = 0.066$. No attempt was made to locate any hydrogen atoms.

The error in an observation of unit weight was 1.57. The final data/parameter ratio was 9.7. In the final cycle of refinement no parameter varied by more than 0.5 times its estimated standard deviation. A final difference Fourier map yielded one peak of height 0.914 e Å⁻³ at a distance of 1.7 Å from the phosphorus atom. All remaining peaks were less than 0.58 e Å⁻³ where the smallest peak for a carbon half-atom appeared on a previous difference map at 1.84 e Å⁻³.

Results and Discussion

The final positional and thermal parameters are listed in Table I. It is to be noted that each α -carbon atom of the ethyl groups in the PEt_3 ligand and one of the β -carbon atoms are represented by two half-atoms in order to make allowance for disorder in the orientation of this ligand. For the α -carbon atoms we thus have the pairs of half-atoms C(11) and C(41), C(21) and C(51), C(31) and C(61), and for one of the β -carbon atoms C(32) and C(62).

Figure 1 depicts the centrosymmetric molecule and shows the atom numbering scheme. For clarity only one set of the disordered α -carbon atoms is shown. Aside from the crystallographic inversion center at the midpoint of the Mo–Mo bond, there is no other element of symmetry possible in view

Table II. Bond Lengths (Å)^a

Mo(1)-Mo(1)'	2.125 (1)	P(1)-C(11)	1.91 (2)
Mo(1)-P(1)	2.516 (2)	P(1)-C(21)	1.84 (2)
Mo(1)-Cl(1)	2.436 (2)	P(1)-C(31)	1.81 (2)
Mo(1)-N(1)	2.15 (1)	P(1)-C(41)	1.84 (2)
Mo(1)-N(2)'	2.14 (1)	P(1)-C(51)	1.85 (2)
N(1)-C(1)	1.40 (1)	P(1)-C(61)	1.93 (2)
C(1)-C(2)	1.30 (1)	C(11)-C(12)	1.44 (2)
C(2)-C(3)	1.30 (2)	C(21)-C(22)	1.46 (2)
C(3)-C(6)	1.30 (2)	C(31)-C(32)	1.53 (3)
C(6)-C(7)	1.47 (1)	C(41)-C(12)	1.51 (2)
C(6)-C(4)	1.62 (1)	C(51)-C(22)	1.45 (2)
C(4)-C(5)	1.45 (1)	C(61)-C(32)	1.56 (4)
C(5)-N(2)	1.38 (1)	C(31)-C(62)	1.27 (3)
C(7)-N(1)	1.36 (1)	C(61)-C(62)	1.21 (3)
C(7)-N(2)	1.33 (1)		

^a Figures in parentheses are estimated standard deviations occurring in the least significant figure in each parameter.

Table III. Bond Angles (deg)^a

Mo(1)-Mo(1)-N(1)	92.9 (2)	C(4)-C(5)-N(2)	114 (1)
Mo(1)-Mo(1)-N(2)'	93.4 (2)	C(5)-N(2)-C(7)	109 (1)
Mo(1)-Mo(1)-Cl(1)	120.2 (1)	C(6)-C(7)-N(2)	113 (1)
Mo(1)-Mo(1)-P(1)	101.0 (1)	Mo(1)-P(1)-C(11)	104 (1)
N(1)-Mo(1)-N(2)'	173.7 (2)	Mo(1)-P(1)-C(21)	117 (1)
N(1)-Mo(1)-P(1)	90.3 (2)	Mo(1)-P(1)-C(31)	121 (1)
N(1)-Mo(1)-Cl(1)	89.6 (1)	Mo(1)-P(1)-C(41)	105 (1)
Cl(1)-Mo(1)-N(2)'	87.9 (2)	Mo(1)-P(1)-C(51)	127 (1)
P(1)-Mo(1)-N(2)'	87.7 (2)	Mo(1)-P(1)-C(61)	113 (1)
P(1)-Mo(1)-Cl(1)	138.7 (1)	C(11)-P(1)-C(21)	102 (1)
Mo(1)-N(1)-C(1)	132 (1)	C(11)-P(1)-C(31)	104 (1)
Mo(1)-N(1)-C(7)	115 (1)	C(21)-P(1)-C(31)	105 (1)
Mo(1)-N(2)'-C(7)	116 (1)	C(41)-P(1)-C(51)	98 (1)
Mo(1)-N(2)'-C(5)'	135 (1)	C(41)-P(1)-C(61)	107 (1)
C(1)-N(1)-C(7)	112 (1)	C(51)-P(1)-C(61)	104 (1)
C(2)-C(1)-N(1)	121 (1)	P(1)-C(11)-C(12)	115 (1)
C(3)-C(2)-C(1)	127 (1)	P(1)-C(21)-C(22)	118 (1)
C(6)-C(3)-C(2)	119 (1)	P(1)-C(31)-C(32)	124 (2)
C(3)-C(6)-C(7)	116 (1)	P(1)-C(41)-C(12)	115 (1)
C(6)-C(7)-N(1)	124 (1)	P(1)-C(51)-C(22)	118 (1)
C(7)-C(6)-C(4)	102 (1)	P(1)-C(61)-C(62)	122 (2)
C(6)-C(4)-C(5)	101 (1)		

^a Figures in parentheses are estimated standard deviations occurring in the least significant figure in each parameter.

of the unsymmetrical nature of the 7-azaindolyl ligand. In the carboxylato analogue, the symmetric nature of the RCO₂ groups allows them to lie on a (virtual) twofold axis so that the virtual molecular symmetry is C_{2h}. Here we have an example of the somewhat uncommon situation in which the sole element of symmetry is an inversion center.

The bond distances and angles are listed in Tables II and III, respectively. The Mo-Mo quadruple bond distance is among the longer ones known, 2.125 (1) Å; it is, notably, longer than that found in compound IV, 2.091 (3) Å. There is no obvious reason for this. Other distances involving the

metal atoms are as expected. The Mo-P distance, 2.516 (2) Å, is essentially the same as that in IV, 2.526 Å, and the Mo-Cl distance, 2.436 (2) Å, agrees well with the value 2.45 Å obtained from the Mo-Br distance in IV by subtracting 0.12 Å, the normal difference in the single-bond radii¹⁴ of Cl and Br.

The average of the P-C distances, 1.86 Å, agrees well with the sum of single-bond radii,¹⁴ 1.87 Å, although individual values, involving the six carbon half-atoms, are badly scattered from 1.81 to 1.93 Å. The situation is similar with respect to the C-C distances. Evidently the model used for the disorder is imperfect, but it is adequate in view of our objective of characterizing the geometry and dimensions of the Mo₂ unit and its bonding to ligand atoms.

The Mo-Mo-L angles vary considerably from one another and thus the coordination geometry of the Mo₂ unit and its eight bond vectors deviates markedly from the prototypal D_{4h} symmetry. The Mo-Mo-N angles are virtually equal with a mean value of 93.2 ± 0.2°, while the Mo-Mo-P angle is larger, 101.0 (1)°, and the Mo-Mo-Cl distance is the largest of this type, 120.2 (1)°. This is similar to the pattern observed in IV, where the corresponding angles are Mo-Mo-O = 90.2°, Mo-Mo-P = 101.9°, and Mo-Mo-Br = 115.9°. These patterns are, in turn, similar to that first observed¹⁵ a long time ago in Re₂(O₂CPh₂)₄ where the Re-Re-I angles are quite large, namely, 110°.

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Registry No. Mo₂Cl₂(PEt₃)₂(C₇H₅N₂)₂, 64440-59-1.

Supplementary Material Available: A table of observed and final calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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