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Registry No. I, 110242-22-3; II, 110242-23-4; 1,3-bis[(2-amino-

ethyl)amino]propane, 4741-99-5; *p*-nitrobenzyl malonate, 110270-80-9; cyclic diamide, 97856-33-2.

Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen coordinates (Tables S1-S4) (3 pages); listings of structure factor amplitudes (Tables S5 and S6) (33 pages). Ordering information is given on any current masthead page.

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Preparation, Spectroscopic Properties, and Characterization of *anti*- and *syn*- α - $\text{Mo}_2\text{Cl}_4[(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{p}-\text{CH}_3\text{C}_6\text{H}_4)_2]$ in Solution and in the Solid State

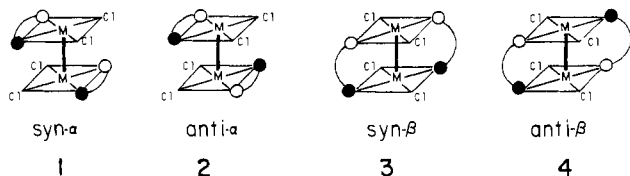
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Dimolybdenum(II) compounds containing the unsymmetrical diphosphine dpdt (1-(diphenylphosphino)-2-(di-*p*-tolylphosphino)ethane) have been synthesized. Each of the two structural isomers (α and β) exists as two geometrical isomers (*syn* and *anti*), as shown schematically by structures 1-4. All isomers can be formed, and all are very soluble in CH_2Cl_2 . The crystal structure of *anti*- α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2 \cdot 2\text{CH}_3\text{OH}$, in which a dpdt ligand chelates to each of the Mo atoms of the dimer, has been determined. The space group is $P2_1/c$ with $a = 12.374$ (4) Å, $b = 9.280$ (2) Å, $c = 24.829$ (5) Å, $\beta = 102.12$ (3)°, $V = 2787$ (2) Å³, and $Z = 2$. The Mo-Mo bond distance is 2.147 (1) Å, similar to that in the dppe compound, while the Mo-P(phenyl) and Mo-P(tolyl) distances are 2.547 (3) and 2.534 (3) Å, respectively. α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ was obtained by slow isomerization of a sample of pure β - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$. The ¹H NMR spectra of the α and β isomers were measured, and the spectra of the *anti* and *syn* isomers of the α form were completely assigned with the aid of aryl ring diamagnetic anisotropy. It has thus been demonstrated that essentially equal amounts of the geometrical isomers are formed in the synthesis of α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ from K_4MoCl_8 . The magnetic anisotropy of the quadruple bond in the α isomers has been estimated to be $-8800 \times 10^{-36} \text{ m}^3/\text{molecule}$.

Introduction

Many quadruply bonded M_2 compounds, $^{1,2} \text{Mo}_2\text{X}_4(\text{LL})_2$, where $\text{X} = \text{Cl}$ and Br and LL is the bridging bidentate phosphine $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$, have been extensively studied in the solid state, with particular attention to how their structural properties relate to the nature of the multiple Mo-Mo bonding. The recent findings³⁻⁵ concerning the isomerization of α - $\text{Mo}_2\text{X}_4(\text{dppe})_2$ to β - $\text{Mo}_2\text{X}_4(\text{dppe})_2$ have added an additional, intriguing dimension to this dimolybdenum chemistry. However, because of the general insolubility of these complexes investigations of their reactions and properties in solution have been quite limited. A complete understanding of this chemistry, especially the isomerization phenomenon, requires detailed characterization of the solution behavior of these compounds, or similar ones. In this paper, we report the successful synthesis of some $\text{Mo}_2\text{Cl}_4(\text{LL})_2$ compounds, which have much greater solubility. As a result, we have been able to make many new observations, including discovery of the reverse isomerization reaction (from the β isomer to the α isomer) and obtain the full characterization of these compounds by ¹H NMR magnetic resonance, including the distinction between geometrical isomers (*syn* and *anti*), which arise because of the unsymmetrical ligand LL' . In the following discussion the terms α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ and β - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ will signify the essentially equimolar mixture of the *syn* and *anti* geometrical isomers.



Experimental Section

All operations were carried out under an atmosphere of purified argon. Solvents were dried by conventional methods and distilled under di-

nitrogen. $\text{K}_4\text{Mo}_2\text{Cl}_8$ and $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ were prepared as described elsewhere.^{6,7} Tri-*p*-tolylphosphine and 1-(diethylphosphino)-2-(diphenylphosphino)ethane (dedp) were purchased from Strem Chemicals. Diphenylvinylphosphine was purchased from Aldrich Chemicals.

Preparation of dpdt. Tri-*p*-tolylphosphine (12 g, 0.039 mol) was treated with Li wire (1.2 g, 0.17 mol) in THF.^{8,9} The resultant dark red solution was hydrolyzed and extracted with ether and the ether extract washed with dilute acid and water. The organic layer was dried over Na_2SO_4 and distilled to give 4.5 g of di-*p*-tolylphosphine (54% yield, bp 124-126 °C (1.2 mmHg)), which was identified by its ¹H NMR spectrum.

A mixture of 4.1 g (0.019 mol) of diphenylvinylphosphine, 4.0 g (0.019 mol) of di-*p*-tolylphosphine, and 0.4 g of potassium *tert*-butoxide in THF was refluxed for 6 h.¹⁰ Evaporation of the solvent gave an orange-yellow residue, which was washed with methanol, and the crude white solid was separated by filtration. This solid was recrystallized from benzene/methanol to give a white crystalline solid: yield 5.7 g (70%); mp 112.0-112.5 °C. Anal. Found: C, 79.31; P, 14.78; H, 6.66. Calcd for $\text{C}_{28}\text{H}_{28}\text{P}_2$: C, 78.86; P, 14.52; H, 6.62.

Preparation of α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$. A mixture of $\text{K}_4\text{Mo}_2\text{Cl}_8$ (0.27 g, 0.43 mmol) and dpdt (0.37 g, 0.87 mmol) in 30 mL of methanol was refluxed for 3 h.¹¹ A precipitated green powder was separated by filtration, washed once with methanol and diethyl ether, and dried in vacuo; yield 0.27 g (55%). This powder contained small amounts of the β form and $\text{K}_4\text{Mo}_2\text{Cl}_8$; the pure α form was obtained from the second CH_2Cl_2 fraction by silica gel column chromatography.

Preparation of β - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$. $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ (0.16 mg, 0.25 mmol) was dissolved in 20 mL of THF, and Me_3SiCl (0.2 mL) was added. This solution was stirred for 12 h,¹² and then 216 mg of dpdt (0.51 mmol) was added. After 10 h, a brown solution was obtained. No precipitates were observed. The solvent was evaporated, and the brown residue was washed with methanol and cold ether. The light brown powder was dried in vacuo; yield 0.17 g (60%). This powder was not yet the pure β form and was redissolved in CH_2Cl_2 and then separated by silica gel chromatography. The first brown fraction was collected, and the CH_2Cl_2 was evaporated to give the light brown, pure β form. The α - and β - $\text{Mo}_2\text{Cl}_4(\text{dedp})_2$ compounds were prepared in a similar way.

- (1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.
- (2) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* 1985, 62, 99.
- (3) Agaskar, P. A.; Cotton, F. A.; Fraser, I. F.; Peacock, R. D. *J. Am. Chem. Soc.* 1984, 106, 1851.
- (4) Agaskar, P. A.; Cotton, F. A.; Derringer, D. R.; Powell, G. L.; Root, D. R.; Smith, T. J. *Inorg. Chem.* 1985, 24, 2786.
- (5) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* 1986, 25, 15.

- (6) Cotton, F. A.; Norman, J. G., Jr. *Coord. Chem.* 1972, 1, 161.
- (7) Cotton, F. A.; Brencic, J. V. *Inorg. Chem.* 1970, 9, 351.
- (8) Wittenberg, D.; Gilman, H. *J. Org. Chem.* 1958, 23, 1063.
- (9) Grim, S. O.; Molenda, R. P. *Phosphorus Relat. Group V Elem.* 1974, 4, 189.
- (10) Kapoor, P. N.; Pathak, D. D.; Gaur, G.; Kutty, M. *J. Organomet. Chem.* 1984, 276, 167.
- (11) Best, S. A.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* 1978, 17, 99.
- (12) Agaskar, P. A.; Cotton, F. A. *Inorg. Chem.* 1984, 23, 3383.

Table I. Summary of Crystallographic Data and Data Collection Procedures

formula	Mo ₂ Cl ₄ P ₄ C ₃₈ H ₆₄ O
fw	1250.65
space group	<i>P</i> 2 ₁ / <i>c</i>
systematic absences	<i>h</i> 0 <i>l</i> , <i>l</i> ≠ 2 <i>n</i> ; 0 <i>k</i> 0, <i>k</i> ≠ 2 <i>n</i>
<i>a</i> , Å	12.374 (4)
<i>b</i> , Å	9.280 (2)
<i>c</i> , Å	24.829 (5)
β, deg	102.12 (3)
<i>V</i> , Å ³	2787 (2)
<i>Z</i>	2
<i>d</i> _{calcd.} , g/cm ³	1.416
cryst size, mm	0.4 × 0.4 × 0.2
μ(Mo Kα), cm ⁻¹	6.68
data collectn instrument	CAD-4S
radiation (monochromated in incident beam)	Mo Kα (λ _K = 0.71073 Å)
orientation reflns: no.; range (2θ), deg	25; 20–32
temp, °C	22 ± 3
scan method	ω scan
data collectn range, 2θ, deg	4–45
no. of unique data, total with <i>F</i> _o ² > 3σ(<i>F</i> _o ²)	4109, 2136
no. of params refined	318
transmission factors: max, min	100%, 79.8%
<i>R</i> ^a	0.051
<i>R</i> _w ^b	0.068
quality-of-fit indicator ^c	1.969
largest shift/esd, final cycle	0.16
largest peak, e/Å ³	0.950

^a $R = \sum(|F_o| - |F_c|) / \sum|F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. ^c Quality of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observns}} - N_{\text{params}})]^{1/2}$.

Preparation of Crystals. The pure α form was dissolved in dichloromethane, and a layer of methanol was gently introduced over the green solution. The two layers were kept below 0 °C for several days. Two kinds of green crystals, plate- and needle-shaped, were obtained. The needle-shaped crystals were too small to collect X-ray diffraction data. A two-layer preparation for crystallization of the β form was set up in a similar manner. However, the crystals obtained were not those of the β form but those of the green α form. One of these crystals was used for X-ray diffraction.

X-ray Diffraction Procedures. Data Collection. The crystal was placed in a thin-walled glass capillary and surrounded by mother liquid. This was examined on an Enraf-Nonius CAD-4 automated diffractometer. Unit cell constants were determined from the geometric parameters of 25 well-centered reflections with 2θ values in the range of 20° ≤ 2θ ≤ 32° and are listed in Table I. The space group *P*2₁/*c* was chosen on the basis of the unit cell parameters and observed systematic absences of *hkl* reflections with *h*0*l* for *l* ≠ 2*n* and 0*k*0 for *k* ≠ 2*n*. No decay correction was done, because the intensity standards showed no decay. An empirical absorption correction was applied on the basis of a transmission function derived from azimuthal scans of six reflections with values of the χ angle around 90°. The maximum and minimum relative transmission factors are given in Table I.

Solution and Refinement of the Structure of α-Mo₂Cl₄(dpdt)₂·2CH₃OH. The position of the molybdenum atom was obtained from a three-dimensional Patterson map and then refined by full-matrix least-squares calculations. The other non-hydrogen atoms were found in a series of alternating refinements and difference maps. Anisotropic displacement parameters were used for all atoms except those of the methanol molecules. Toward the end of the development of the structure, substantial difference peaks were observed in positions that could be occupied by the molybdenum atoms of a cocrystallized molecule of β-Mo₂Cl₄(dpdt)₂. This site was modeled as a molybdenum atom with an isotropic displacement parameter, and the site occupancies of the two molybdenum atoms were refined, leading to values near 98% and 2% for the α and β sites, respectively. For the final refinement the multiplicities were fixed at those values. The significance of the minor site is verified by its stable refinement and by the fact that modeling this site led to significant lowering of the *R* factors and the quality of fit. The derived parameters for the minor (β) molecule are within acceptable ranges, although one derived distance (Mo(2)–Cl(1) = 2.61 (4) Å) deviates by ca. 0.2 Å from its expected value. In any event, we have not attempted to derive accurate geometrical calculations regarding the β structure, from this study. The final refinement parameters are given in Table I,

Table II. Positional and Thermal Parameters for α-Mo₂Cl₄(dpdt)₂·2CH₃OH^a

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> , Å ²
Mo(1)	0.05381 (7)	-0.02101 (8)	0.03917 (3)	3.34 (2)
Mo(2)	0.080 (4)	0.016 (5)	-0.017 (2)	4.3 (9)*
Cl(1)	-0.0085 (2)	-0.2297 (3)	0.0830 (1)	4.82 (6)
Cl(2)	0.2126 (2)	-0.1617 (3)	0.0287 (1)	4.89 (6)
P(1)	-0.0315 (2)	0.1537 (3)	0.0976 (1)	3.91 (6)
P(2)	0.1779 (2)	0.1992 (3)	0.0505 (1)	3.90 (6)
C(1)	-0.1720 (8)	0.143 (1)	0.1079 (4)	4.6 (2)
C(2)	-0.2265 (9)	0.009 (1)	0.1042 (4)	5.8 (3)
C(3)	-0.3311 (9)	-0.002 (1)	0.1184 (4)	6.3 (3)
C(4)	-0.380 (1)	0.118 (1)	0.1371 (4)	6.7 (3)
C(5)	-0.324 (1)	0.252 (1)	0.1408 (5)	7.0 (3)
C(6)	-0.2214 (8)	0.266 (1)	0.1264 (4)	5.4 (3)
C(7)	0.0407 (7)	0.152 (1)	0.1708 (4)	4.2 (2)
C(8)	0.0394 (8)	0.022 (1)	0.1994 (4)	5.2 (3)
C(9)	0.087 (1)	0.019 (1)	0.2554 (5)	6.6 (3)
C(10)	0.1392 (9)	0.141 (1)	0.2837 (4)	6.3 (3)
C(11)	0.140 (1)	0.267 (1)	0.2532 (4)	6.9 (3)
C(12)	0.0925 (8)	0.276 (1)	0.1965 (4)	5.2 (3)
C(13)	0.2795 (8)	0.247 (1)	0.0101 (4)	4.1 (2)
C(14)	0.2644 (9)	0.365 (1)	-0.0263 (4)	5.9 (3)
C(15)	0.3506 (9)	0.406 (1)	-0.0518 (4)	6.4 (3)
C(16)	0.4512 (8)	0.331 (1)	-0.0414 (4)	4.9 (2)
C(17)	0.4635 (9)	0.212 (1)	-0.0062 (4)	5.5 (3)
C(18)	0.3788 (8)	0.172 (1)	0.0203 (4)	4.8 (2)
C(19)	0.2679 (7)	0.1910 (9)	0.1198 (3)	3.6 (2)
C(20)	0.2838 (8)	0.063 (1)	0.1496 (4)	4.5 (2)
C(21)	0.3458 (8)	0.063 (1)	0.2027 (4)	5.3 (3)
C(22)	0.3958 (9)	0.190 (1)	0.2264 (4)	5.6 (3)
C(23)	0.3850 (9)	0.317 (1)	0.1957 (4)	6.2 (3)
C(24)	0.3218 (9)	0.317 (1)	0.1421 (4)	5.2 (3)
C(25)	0.5410 (9)	0.381 (1)	-0.0685 (5)	7.5 (3)
C(26)	0.460 (1)	0.190 (2)	0.2879 (5)	8.8 (4)
C(27)	0.0929 (8)	0.364 (1)	0.0524 (4)	4.9 (3)
C(28)	-0.0185 (8)	0.3383 (9)	0.0711 (4)	4.7 (2)
O(1)	0.208 (2)	0.627 (2)	0.1616 (8)	9.8 (5)*
O(2)	0.737 (1)	0.169 (2)	0.3463 (7)	8.1 (4)*
C(29)	0.187 (2)	0.657 (3)	0.2081 (9)	6.9 (6)*
C(30)	0.778 (2)	0.183 (3)	0.296 (1)	6.9 (6)*

^a Starred values indicate atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{1}{3}[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

and the final positional and thermal parameters are presented in Table II.

Physical Measurements. Electronic absorption spectra were obtained with a Cary 14 spectrophotometer, for dichloromethane solutions in 1-cm quartz cells. Infrared spectra were recorded as Nujol mulls with a Perkin-Elmer 783 spectrometer. ¹H NMR spectra were obtained on a Varian XL-400 NMR spectrometer operating in the Fourier transform mode (64K data points transform of 5300-Hz spectral width after 61–158 pulses) at 22, -25, and -90 °C.

Results and Discussion

Both α- and β-Mo₂Cl₄(dpdt)₂ are fairly soluble in CH₂Cl₂ and slightly soluble in CH₃OH. This is in direct contrast with the insolubility of α- and β-Mo₂Cl₄(dppe)₂.¹¹ The *p*-methyl groups of the dpdt ligands thus play a surprisingly important role in enhancing the solubility of the compounds. The α-Mo₂Cl₄(R₂PCH₂CH₂PR₂)₂ (R = CH₃ and C₂H₅) compounds also have good solubility^{13,14} but are air-sensitive¹⁴ in solution, while α-Mo₂Cl₄(dpdt)₂ is not air-sensitive and thus is well-suited for investigation of the solution behavior of this type of compound.

Owing to the good solubility of α-Mo₂Cl₄(dpdt)₂ in toluene, its synthesis from Mo₂(O₂CCF₃)₂/CH₃SiCl/dpdt/toluene provides a mixture of α and β forms since the reversible isomerization reaction^{3–5} proceeds in solution. The system K₄Mo₂Cl₈/dpdt/CH₃OH was therefore used to synthesize the α isomer. On the other hand, β-Mo₂Cl₄(dpdt)₂ was prepared from a mixture of

(13) α- and β-Mo₂Cl₄(depe)₂, which have been synthesized, are quite soluble in CH₂Cl₂.

(14) San Filippo, J., Jr.; Sniadoch, H. J.; Grayson, R. L. *Inorg. Chem.* **1974**, *13*, 2121.

Table III. Spectroscopic Properties of Molybdenum(II) Complexes

complex	IR $\nu_{\text{Mo-Cl}}$, cm^{-1}	electronic abs ^a λ , nm (ϵ , $\text{M}^{-1} \text{cm}^{-1}$)
α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$	301, 285	345 (6340), 390 sh, 475 (365), 675 (2940)
β - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$	335, 295	345 (2920), 470 (730), 550 sh, 762 (870)
α - $\text{Mo}_2\text{Cl}_4(\text{dedp})_2$	302, 280	327 (5780), 375 sh, 475 (330), 665 (2250)

complex		obsd ^1H NMR chem shifts, ^b ppm							
		phenyl			tolyl		ethylene		CH_3
		o	m	p	α	β	prox	dist	
$\text{anti-}\alpha$ - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$	parallel	7.625	7.057	7.288	7.535	6.953			2.334
	upright	6.593 ^c	6.538 ^c	6.745 ^c	6.422 ^c	6.309	4.68 ^d	3.32 ^d	1.881
$\text{syn-}\alpha$ - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$	parallel	7.647	7.122	7.304	7.518	6.892			2.329
	upright	6.593 ^c	6.538 ^c	6.745 ^c	6.422 ^c	6.309	4.68 ^d	3.32 ^d	1.881
β - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$		7.32 ^e	7.14 ^e	7.37 ^e	7.60 ^e	7.48 ^e	3.40 ^f		2.336

^a CH_2Cl_2 solution. ^b Shifts referenced to $(\text{CH}_3)_4\text{Si}$; observed at -25°C . Error limits are ± 0.001 ppm. The numbering of phenyl protons is the usual one, and that of tolyl protons is done by the use of α and β characters. "Prox" and "dist" denote proximal and distal, respectively. ^c Error limits, ± 0.005 ppm, due to overlapping of signals. ^d Broad signal due to multiplets; error limits ± 0.01 ppm. ^e Averaged broad signals. ^f Error limits ± 0.005 ppm.

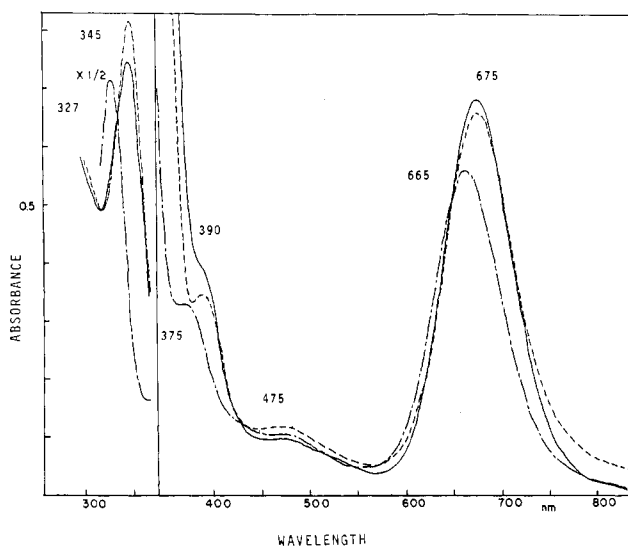


Figure 1. Electronic absorption spectra of α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ (—, 2.35×10^{-4} M), α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$ (---, 2.37×10^{-4} M), and α - $\text{Mo}_2\text{Cl}_4(\text{dedp})_2$ (-.-., 2.46×10^{-4} M) in dichloromethane solution.

$\text{Mo}_2(\text{O}_2\text{CCF}_3)_4/\text{CH}_3\text{SiCl}/\text{dpdt}/\text{THF}$, where no precipitation of the β form occurred, and thus THF was completely evaporated. This procedure is different from the method reported previously.¹² In both syntheses, column chromatography was employed to obtain highly pure α and β forms.

Figure 1 displays the electronic absorption spectra of α - $\text{Mo}_2\text{Cl}_4(\text{LL}')_2$ ($\text{LL}' = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ (dppe), dpdt, and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PET}_2$ (dedp)). The compounds of dppe¹¹ and dpdt give nearly identical spectra, showing that the CH_3 group has only a very weak spectrophotometric perturbation on the parent dppe compound, while the dedp compound exhibits a greater difference, as shown in Table III and Figure 1. The δ - δ^* transition energies increase in the order dppe (675 nm, 14800 cm^{-1}) = dpdt < dedp (665 nm, 15000 cm^{-1}) < depe (654 nm, 15300 cm^{-1}).¹³ Thus, although dpdt has an unsymmetrical structure, α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ has electronic properties very close to those of α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$. The only major difference is found in the solubility, which makes $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ a good model of $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$, but much more tractable for experimental study.

Structure of anti- α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$. The entire molecule is shown in Figure 2, where the atom-numbering scheme is also given. The C_i symmetry of the molecule is clearly seen. Table IV provides a list of important bond distances and angles. The Mo-Mo bond distance of 2.147 (1) Å is slightly longer than that observed in α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$ (2.140 (2) Å).⁵ The average Mo-Cl and Mo-P bond distances, 2.421 (2) and 2.541 (2) Å, are similar to the corresponding distances in the dppe compound. However, the unsymmetrical character of the bisphosphine dpdt manifests itself in the Mo-P bond distances; the Mo-P(2) (tolyl phosphorus atom)

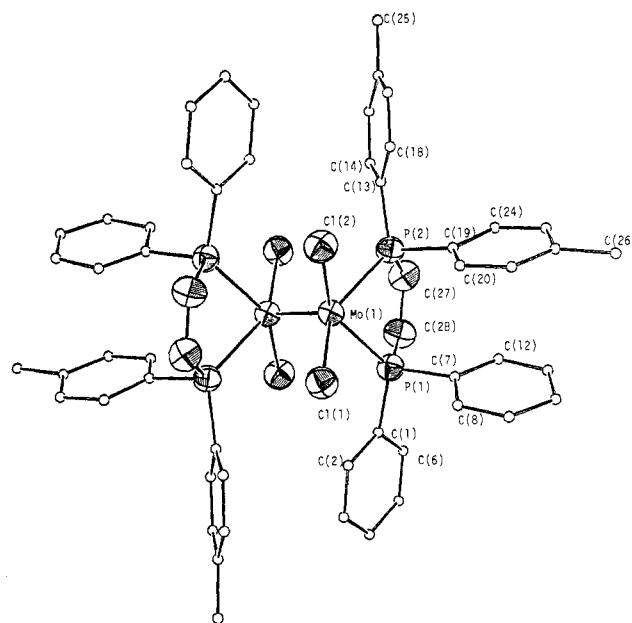


Figure 2. ORTEP drawing of the entire molecule of $\text{anti-}\alpha$ - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ with thermal ellipsoids at the 50% level for Mo, Cl, and P atoms and C(27) and C(28). Ellipsoids of the atoms in the phenyl rings have been arbitrarily reduced. The numbers of unlabeled phenyl carbon atoms follow from those given. Only half the atoms are labeled; the others are related by a center of inversion at the midpoint of the Mo-Mo bond.

Table IV. Principal Bond Distances (Å) and Bond Angles (deg)

Bond Distances			
Mo(1)-Mo(1)'	2.147 (1)	Mo(1)-P(1)	2.547 (3)
-Cl(1)	2.424 (3)	-P(2)	2.534 (3)
-Cl(2)	2.417 (3)		

Bond Angles			
Mo(1)-Mo(1)-Cl(1)	110.89 (6)	Cl(1)-Mo(1)-P(1)	92.45 (9)
-Cl(2)	111.27 (7)	-P(2)	146.69 (8)
-P(1)	98.53 (6)	-Cl(2)	87.72 (9)
-P(2)	101.50 (6)	Cl(2)-Mo(1)-P(1)	140.01 (8)
P(1)-Mo(1)-P(2)	74.82 (9)	-P(2)	87.70 (9)

distance is shorter by 0.013 Å than Mo-P(1) (phenyl phosphorus atom). The difference may be attributed to the electron-donating nature of the methyl group, which increases the basicity of one phosphorus atom. The structure of $\text{anti-}\alpha$ - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ nicely demonstrates the sensitivity of the Mo-P bond distance to the basicity of the phosphorus atom. It is interesting that this difference between the two Mo-P bond distances, as well as a slightly longer Mo-Mo bond distance, has no measurable effect on the δ - δ^* transition compared with that in α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$.

NMR Spectra of Anti and Syn Isomers of α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$. Because of the high solubility of α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ in CD_2Cl_2 , a

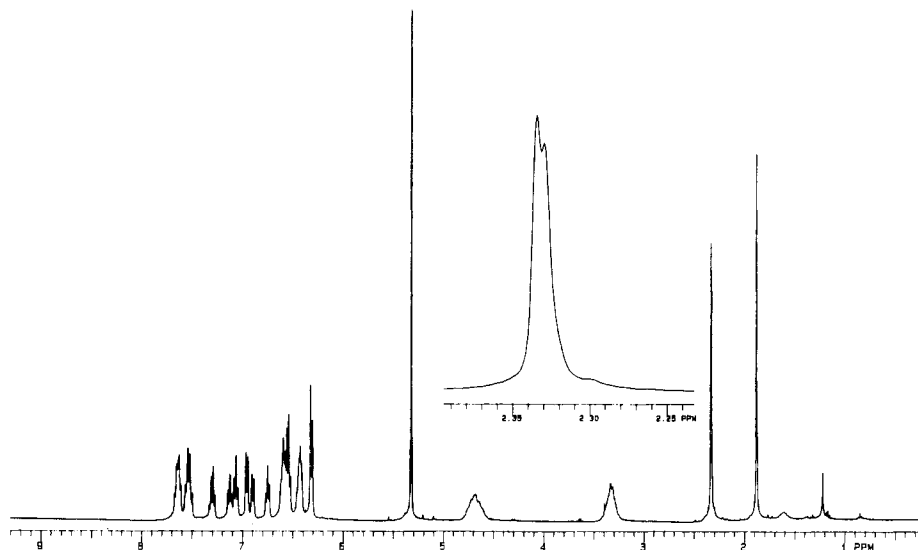


Figure 3. ^1H NMR spectrum at -25°C of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ obtained in CD_2Cl_2 at 400 MHz. An enlargement of one methyl signal is also shown.

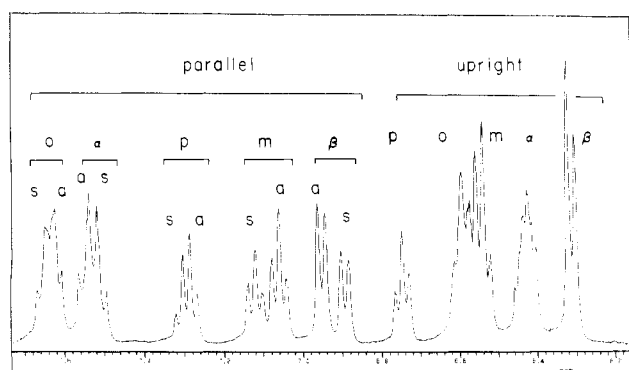
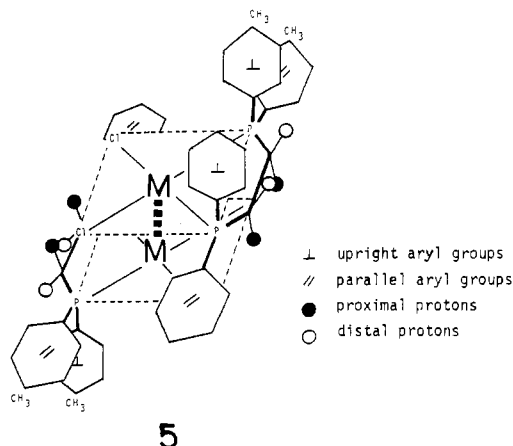


Figure 4. Expansion of the aromatic region of the $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ ^1H NMR spectrum. The characters a and s denote *anti*- and *syn*- $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$, respectively.

well-resolved spectrum was obtainable at -25°C . This is the first ^1H NMR spectrum reported for this type of compound. Because of the excellent signal to noise ratio and resolution, the spectra of the anti and syn isomers were observed and, from stereochemical reasoning (*vide infra*), separately assigned. Figure 3 shows the entire ^1H NMR spectrum of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$, while Figure 4 presents an expanded view of the spectrum in the aromatic region. It is evident that the large number of lines implies the presence of both geometric isomers in comparable amounts. We turn now to the problem of the assignment.

The detailed crystal structure of *anti*- $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ (Figure 2) provides a basis for the schematic representation 5, to which we shall now refer in developing our assignments. In the prep-



aration of 5, the least-squares planes for the phenyl and tolyl

groups and the MoCl_2P_2 group were calculated from the coordinates in Table II. It is evident in 5 that the aryl groups in $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ are of two kinds. On each dpdt ligand one phenyl group and one tolyl group are "upright" while the other two are "parallel", taking as the plane of reference the mean plane of the MoCl_2P_2 coordination unit. The terms "upright" and "parallel" are only approximate but nonetheless useful in a practical way. The upright phenyl and tolyl groups make dihedral angles of ca. 101° with the MoCl_2P_2 mean plane rather than 90° , and the parallel tolyl group actually tilts by 42° from the ideal parallel position. The parallel phenyl group, however, is only 11° away from being perfectly parallel. The distance between the centers of the two upright aryl groups is 3.5 \AA , which is small enough for their protons to experience ring current effects from each other. The signals from upright rings are therefore all shifted upfield from those for parallel rings. The nearest-neighbor parallel aryl groups also interact with each other, but the ring current effect is weaker than that between the upright aryl groups, because of the greater distance (4.7 \AA). This ring current shift of protons for the parallel pair is responsible for our ability to recognize the anti and syn isomers of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$.

The ^1H NMR spectrum in Figure 3 is composed of three characteristic regions: the most upfield region contains the methyl group signals of the tolyl groups, while the ethylene protons resonate in the region of 3–5 ppm. The complicated pattern of aryl proton signals appears in the most downfield region and is shown in detail in Figure 4. The methyl signals at 1.88 and 2.33 ppm are assigned to upright and parallel tolyl methyl groups, respectively, on the basis of the ring current effects. The downfield methyl signal is split into two signals, separated by 0.005 ppm, as also shown in Figure 3. These two signals are ascribed to the parallel tolyl methyl groups of the anti and syn isomers, since the interaction between upright phenyl and tolyl groups in dpdt is essentially the same in both isomers, while that between the nearest-neighbor parallel aryl groups depends on how they are paired, namely as tolyl–tolyl in the syn isomer and tolyl–phenyl in the anti isomer.

The complex pattern of aryl proton signals clearly demonstrates that all the protons experience ring current effects, causing them to resonate at different frequencies. All the signals were completely assigned by use of the homonuclear double-resonance technique and on the basis of integrated intensities of each signal. Detailed assignments will be mentioned in the following section and are indicated in Figure 4. Among these signals, well-separated β -proton signals of parallel tolyl groups give the ratio of anti to syn isomers. Figure 4 is a spectrum of the chromatographic first fraction of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$, and the intense signals are attributable to the anti form, whose ratio to the syn form is 1.4. On the other hand, the ratio for the initial reaction product of α -

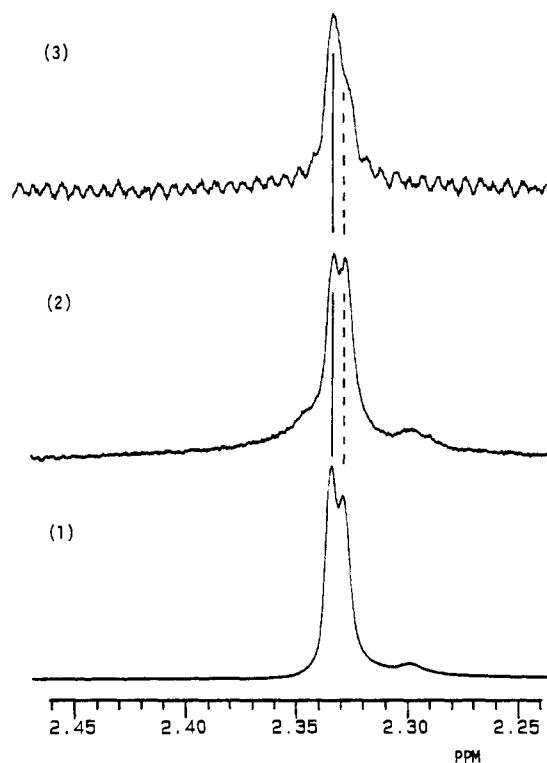


Figure 5. Methyl signal region of ^1H NMR spectra at -25°C of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$: (1) solution of the column chromatographic first fraction; (2) solution of the column chromatographic second fraction; (3) solution of green plate crystals separated mechanically. The low signal-to-noise ratio in spectrum 3 is attributable to the concentration being much lower than in the case of the other two.

$\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ is nearly 1, indicating no preference during synthesis for the formation of syn or anti forms. In this aromatic region anti and syn forms are still distinguished by ^1H NMR spectroscopy at 22°C , but the methyl signals of the two isomers are accidentally superimposed and appear as a single signal due to a very small difference in shift.

The situation for $\beta\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ is much more complicated than for the α isomer. Its ^1H NMR spectrum at 22°C gives sharp signals, as if only one species were present, due to complete line averaging. Even at -90°C , this chemical exchange does not cease but becomes slower, and one observes quite broad signals, which show a barely resolved splitting. On this basis, $\beta\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ must be assumed to have a low-energy fluxional process. According to the solid-state structure of the analogous $\beta\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$,¹² two rotational isomers, a principal (87%) and minor (13%) one, exist, which are distinguished by having different conformations for the six-membered rings of the $\text{Mo}_2\text{P}_2\text{C}_2$ moiety. With conformational isomers of this type, there could be at least four isomers in solution, because there are anti and syn isomers for each conformational isomer. If the fluxional interconversion between the conformational isomers could be completely frozen, anti and syn isomers might be observed by ^1H NMR spectroscopy. This possibility is now under investigation with use of temperatures lower than -90°C .

Separation of anti- and syn- $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$. The CH_2Cl_2 solution was layered with CH_3OH , whereby both needle and plate types of green crystals of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ were obtained. The plate crystals, used for X-ray crystallography, contain the anti- α form, while the nature of the needle crystals is unknown since they were too small for X-ray crystallography. The crystals were collected and mechanically separated from each other. The plates were dissolved in CD_2Cl_2 , and their ^1H NMR spectrum was recorded. The methyl region is shown as part 3 in Figure 5. A signal at 2.334 ppm is dominant over the upfield one, indicating that the downfield methyl signal is to be assigned to the anti- α form. The upfield signal still remains as a shoulder on the main methyl signal. This is because complete separation is very difficult

and a small amount of needle-type crystals remain attached to the plate-type crystals. On the basis of this absolute identification, assignments of aryl proton signals were unambiguously confirmed as in Figure 4.

We tried to separate the two isomers of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ by silica gel chromatography but failed to get well-separated fractions by any of various combinations of solvents. Evidently, the physicochemical nature of a tolyl group is too similar to that of a phenyl group to permit full chromatographic separation. In Figure 5, parts 1 and 2 are the spectra for two different chromatographic fractions; the methyl signals of the anti and syn forms appear in both fractions. The first fraction contains more anti form than syn form (the ratio of anti/syn = 1.4 was estimated from the aryl region). This is because the anti form is slightly less polar than the corresponding syn form and elutes slightly faster.

Reverse Reaction from β to α Form. The isomerization of the α to the β form occurs in $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ as well as $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$,⁵ indicating that $\beta\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ is more thermally stable than the corresponding α form. This process was followed as a function of time at 23°C by monitoring the absorbance at the maximum of the $\delta\text{-}\delta^*$ transition for the α form (675 nm) and analyzed according to a previously published method.⁵ The isosbestic behavior of the time-dependent spectra indicated a single equilibrium. The forward (k_1) and reverse (k_{-1}) reaction constants are $(1.1 \pm 0.1) \times 10^{-5}$ and $(1.7 \pm 0.9) \times 10^{-6} \text{ s}^{-1}$, respectively, which are very close to those for $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$. By use of the rate constants, the equilibrium constant $K (=k_1/k_{-1} = [\beta]/[\alpha])$ is estimated to be $K \approx 10$. K is large enough to prevent the detection of the α isomer in equilibrium with the β isomer by use of the electronic absorption spectrum.

We have obtained the α isomer from the β isomer by altering their relative solubilities, thereby obtaining experimental proof of the reverse (i.e., $\beta \rightarrow \alpha$) reaction. While a significant amount of α form is not obtainable from a solution of $\beta\text{-Mo}_2\text{Cl}_4(\text{dpdt})_2$ in pure CH_2Cl_2 , the use of a mixed solvent, CH_3OH and CH_2Cl_2 (1/2 v/v), makes this possible. This is because the α form is less soluble in the mixed solvent than is the β form, and selective precipitation of the α form takes place. From this reverse reaction, a plate-shaped green crystal was obtained, and an X-ray diffraction structure determination revealed the anti- α form (Figure 2). The mass of crystals obtained here also contained some microcrystalline material in addition to the plate crystal. They were all collected and dissolved in CD_2Cl_2 for ^1H NMR measurements. This spectrum shows that the anti form is dominant but that the syn form is still present.

In the case of dppe, appreciable amounts of $\alpha\text{-Mo}_2\text{Cl}_4(\text{dppe})_2$ could not be obtained from the pure β form, because it was primarily the β form that precipitated from $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ solution. The good yield of the α form of $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ is associated with the relative solubilities of the two forms.

Magnetic Anisotropy of Quadruple Bond. Figure 3 shows that there is a remarkable shift difference (1.36 ppm) between the two ethylene bridge signals. Because the tolyl and phenyl groups are chemically so similar to each other, this difference in shifts cannot be attributed to the different CH_2 groups in the unsymmetrical ligand. The difference must be attributed to the fact that, within each CH_2 unit, one hydrogen atom is distal and the other proximal with respect to the midpoint of the $\text{Mo}^4\text{-Mo}$ bond. The chemical shift difference is thus caused primarily by the diamagnetic anisotropy of the metal-metal bond, as in other previously studied cases.^{1,15-18} The observed shift difference, together with our knowledge of the molecular structure, affords a method for estimating the diamagnetic anisotropy of the Mo-Mo quadruple

(15) San Filippo, J., Jr. *Inorg. Chem.* **1972**, *11*, 3140.

(16) Chisholm, M. H.; Cotton, F. A.; Frenz, B. A.; Reichert, W. W.; Shive, L. W.; Stults, B. R. *J. Am. Chem. Soc.* **1976**, *98*, 4469.

(17) (a) McGlinchey, M. J. *Inorg. Chem.* **1980**, *19*, 1392. (b) McGlinchey, M. J.; Burns, R. C.; Hofer, R.; Top, S.; Jaouen, G. *Organometallics* **1986**, *5*, 104.

(18) Agaskar, P. A.; Cotton, F. A. *Polyhedron* **1986**, *5*, 899.

Table V. Geometric Factors for Proximal ($H_{1,3}$) and Distal ($H_{2,4}$) Protons^a of α - $\text{Mo}_2\text{Cl}_4(\text{LL}')_2$

LL'		$r, \text{\AA}$	θ, deg	$10^{-27}G_i^b, \text{m}^3$	$10^{-27}G_{\text{av}}^b, \text{m}^3$
dppe	H ₁	3.72	105.7	5.03	4.39
	H ₃	3.98	71.8	3.75	
	H ₂	4.73	104.1	2.59	
	H ₄	4.77	76.8	2.59	
dpdt	H ₁	3.88	107.6	4.14	4.76
	H ₃	3.63	73.9	5.37	
	H ₂	4.64	102.9	2.85	
	H ₄	4.59	75.6	2.81	

^aThe C-H distance is 1.0 \AA , and the C-C-H angle is 109°. ^b $G = (1 - 3 \cos^2 \theta)/3r^3$.

bond. The opportunity here is actually superior to those in other cases in the sense that there need be no concern with averaging over the rotational space available to the methyl group, as was the case in all earlier estimates of Mo-Mo bond anisotropies.

We wish to apply eq 1, which pertains to the case of axial symmetry.^{17,19} Here r is the distance of the test nucleus from

$$\Delta\sigma = \chi(4\pi)(1 - 3 \cos^2 \theta)/3r^3 \quad (1)$$

the center of the Mo-Mo bond and θ is the angle between the r vector and C_2 axis perpendicular to the Mo-Mo axis. To do this, we had to calculate the positions of the ethylene protons, which could not be accurately determined by X-ray crystallography. This was done by using conventional crystallographic computer codes for calculating the positions of methylene hydrogen atoms. The calculated geometric factors are listed in Table V. From eq 1 and Table V, the observed $\Delta\sigma$ gives $\chi = (-9680 \pm 250) \times 10^{-36} \text{ m}^3/\text{molecule}$ for α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$. Because of the similarity of α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ to α - $\text{Mo}_2\text{Cl}_4(\text{dppe})_2$, χ is estimated by assuming C_{2h} symmetry, resulting in $\chi = (-8800 \pm 250) \times 10^{-36} \text{ m}^3/\text{molecule}$.

An additional point to consider is that both dppe and dpdt have aryl groups which potentially could exert ring current effects on the ethylene hydrogen atoms. On the basis of the structure of

anti- α - $\text{Mo}_2\text{Cl}_4(\text{dpdt})_2$ as observed in the crystal, this effect has been estimated. A ring current shift diagram for a phenyl group²⁰ was used, and calculated coordinates of protons relative to each aryl ring allowed us to calculate the ring current shift. It was found that one upright aryl group influences only one nearest-neighbor distal proton to give a 0.16 ppm downfield shift (structure 5). Consequently, even if this effect contributes to the observed shift, the overestimation of the magnetic anisotropy, as given above, is only 12%, and the χ value is still at least $(-7540 \pm 250) \times 10^{-36} \text{ m}^3/\text{molecule}$.

There have been previous attempts to estimate χ for the Mo-Mo bond. McGlinchey¹⁷ proffered a rough estimate of -7500×10^{-36} to $-12600 \times 10^{-36} \text{ m}^3/\text{molecule}$, employing chemical shifts for the ring protons of $\text{Mo}_2\text{Br}_2(\text{O}_2\text{CPh})_2[\text{P}(n\text{-C}_4\text{H}_9)_3]_2$. Later, Agaskar and Cotton¹⁸ used data for $\text{Mo}_2(\text{O}_2\text{CR})_4$ molecules, with the shifts in the free acids, RCO_2H , as reference, and calculated much lower values, viz., $(-2640 \pm 380) \times 10^{-36} \text{ m}^3/\text{molecule}$. The problem with the latter method of estimation is that the reference may not be entirely valid. In all cases, lack of complete rigidity of the structure may be a source of uncertainty, as may also be the small anisotropies of other structural units besides the M-M bond that are near the test nuclei. In the present work, we believe that the problem of a suitable reference has been eliminated since it was possible to compare the chemical shift difference for two groups that were in identical chemical environments *except* only for their spatial position. We therefore believe that the values obtained in this study are the best available. The χ value of ca. $-8800 \times 10^{-36} \text{ m}^3/\text{molecule}$ is the largest among multiple-bond systems, indicating that the Mo-Mo bond itself is highly electronically anisotropic.

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Supplementary Material Available: Full listings of bond angles, bond distances, and anisotropic displacement parameters (4 pages); a table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

(19) McConnell, H. M. *J. Chem. Phys.* 1957, 27, 226.

(20) Johnson, C. E., Jr.; Bovey, F. A. *J. Chem. Phys.* 1958, 29, 1012.

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Structural and Spectroscopic Characterization of the Dirhenium Octakis(isothiocyanato) Salt $(\text{Ph}_4\text{As})_2\text{Re}_2(\text{NCS})_8 \cdot 2\text{L}$ ($\text{L} = (\text{CH}_3)_2\text{CO}, \text{C}_5\text{H}_5\text{N}$). A Unique Case of Axial Coordination in M_2X_8 Compounds

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Molecular structures of two dirhenium(III) octakis(isothiocyanato) compounds, $(\text{Ph}_4\text{As})_2\text{Re}_2(\text{NCS})_8 \cdot 2(\text{CH}_3)_2\text{CO}$ (**1**) and $(\text{Ph}_4\text{As})_2\text{Re}_2(\text{NCS})_8 \cdot 2\text{C}_5\text{H}_5\text{N}$ (**2**), have been established by X-ray crystallography. They were prepared in high yield from $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ by a ligand-exchange reaction. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with unit cell dimensions $a = 14.697$ (3) \AA , $b = 10.949$ (3) \AA , $c = 23.617$ (5) \AA , $\beta = 99.67$ (2)°, $V = 3746$ (1) \AA^3 , and $Z = 2$. The $[\text{Re}_2(\text{NCS})_8]^{2-}$ anions reside on a crystallographic inversion center and are therefore rigorously eclipsed. The Ph_4As^+ cations reside on a general position. Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell dimensions: $a = 12.823$ (4) \AA , $b = 13.153$ (2) \AA , $c = 12.762$ (3) \AA , $\alpha = 95.81$ (2)°, $\beta = 108.91$ (2)°, $\gamma = 118.80$ (2)°, $V = 1696$ (1) \AA^3 , and $Z = 1$. The $[\text{Re}_2(\text{NCS})_8]^{2-}$ anions reside on a crystallographic inversion center, while the Ph_4As^+ cations reside on general positions. Two distinct bands are observed in the electronic spectrum of $\text{Re}_2(\text{NCS})_8^{2-}$ salts. The band at 990 nm ($10.1 \times 10^3 \text{ cm}^{-1}$; $\epsilon = 3980 \text{ M}^{-1} \text{ cm}^{-1}$) is assigned to the δ - δ^* transition, while the intense band at 465 nm ($\epsilon = 21500 \text{ M}^{-1} \text{ cm}^{-1}$) is most probably a charge-transfer band from the ligand to the empty metal orbitals.

Introduction

Homoleptic, multiply bonded dimers of the $[\text{M}_2\text{X}_8]^{n-}$ type have been extensively studied in the past. For $\text{X} =$ halogen there are numerous examples of Mo, W, Re, Tc, and Os multiply bonded compounds.¹⁻³ Very little attention has been paid to M_2X_8

complexes with ligands other than halide ions, viz., SCN^- , OCN^- , N_3^- , etc. Only thiocyanato complexes have received limited at-

(1) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*; Wiley: New York, 1982.