

carbons being reversed on coordination of the hydroxyethyl arm hydroxyl group. Complete line-shape analysis of the reversible coalescence of the two AB quartets (using a density matrix program based on methods similar to those described elsewhere) yields the best-fit line shapes shown in Figure 6, and $k(250.0\text{ K}) = 940 \pm 20\text{ s}^{-1}$, $k(298.2\text{ K}) = 34200 \pm 1800\text{ s}^{-1}$, $\Delta H^\ddagger = 44.00 \pm 0.56\text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = -10.6 \pm 2.2\text{ J K}^{-1}\text{ mol}^{-1}$ for exchange of the hydroxyethyl arms, where the errors represent one standard deviation for the fit of the τ data to the Eyring equation. (The $k(250\text{ K})$ value is the more reliable as it is derived at the midpoint of the spectral coalescence temperature range.) These parameters compare with $k(250.0\text{ K}) = 1530 \pm 200\text{ s}^{-1}$, $k(298.2\text{ K}) = 68000$

$\pm 18000\text{ s}^{-1}$, $\Delta H^\ddagger = 46.6 \pm 4.5\text{ kJ mol}^{-1}$, and $\Delta S^\ddagger = 4 \pm 15\text{ J K}^{-1}\text{ mol}^{-1}$ for exchange of the medial carbons derived through complete line-shape analysis of the medial doublet coalescence seen in Figure 1. Due to a substantially poorer signal to noise ratio characterizing the natural-abundance ^{13}C spectra, the latter data set is subject to higher error, but they are in sufficient agreement with the data derived from the enriched ^{13}C spectra to demonstrate that both coalescence phenomena arise from the same molecular process.

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Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843

Chiroptical Properties of a Compound Containing a Metal-Metal Quadruple Bond. Synthesis, Structure, and Spectra of $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-bppm})_2$, Where S,S-bppm is (2S,4S)-N-(tert-Butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine

Jhy-Der Chen and F. Albert Cotton*

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The complex, $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-bppm})_2$ is prepared by reaction of $\text{K}_4\text{Mo}_2\text{Cl}_8$ with (2S,4S)-tert-butyl 4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-1-pyrrolidinecarboxylate (S,S-bppm). Its UV-vis, CD, IR, and NMR spectra have been recorded, and its structure has been determined. Crystal data: space group $P2_12_12_1$, $a = 19.812(4)\text{ \AA}$, $b = 20.609(2)\text{ \AA}$, $c = 17.815(3)\text{ \AA}$, $V = 7273(2)\text{ \AA}^3$, $Z = 4$, with final residuals $R = 0.0698$ and $R_w = 0.0852$. This complex has a average twist angle of about 0° . The circular dichroism spectrum of this complex shows two prominent bands at 580 and 492 nm which can be assigned to $\delta_{xy} \rightarrow \delta^*_{xy}$ and $\delta_{xy} \rightarrow \delta^*_{x^2-y^2}$ transitions, respectively. The one-electron, static coupling mechanism is used to account for the observation of the circular dichroism bands.

Introduction

Dimetal complexes of the type $\beta\text{-Mo}_2\text{X}_4(\text{PP})_2$, where PP is a diphosphine ligand, have been extensively studied during the last few years.^{1,2} An interesting property of this type of complex is that the molecules adopt a staggered or partially staggered geometry around the metal-metal bond due to ligand constraints. Thus, complexes of this type are configurationally chiral,³ but due to the rapid racemization in solution, these complexes are not optically active and no measureable CD spectrum under the $\delta \rightarrow \delta^*$ transition can be detected, even though the complexes sometimes crystallize as enantiomorphous single crystals. Introducing a chiral ligand of a type that causes the complex to twist preferentially in one direction has become a major method in studying the CD spectra of such complexes.⁴ The conformational preference of the ligand effects an asymmetric synthesis and thereby produces only one of the configurational isomers, and this in turn enables the CD spectrum to be measured. Until now only three^{4,5} complexes of this kind have been structurally characterized, all of which may be classified⁶ as being "case I" chromophores. In this paper, we report the first compound that appears to belong to the "case II" class of chromophore.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry oxygen-free argon by using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. Methanol was purified by distillation from magnesium, *n*-hexane from sodium-potassium/benzophenone, and

dichloromethane from P_2O_5 . The visible absorption spectrum of $\text{Mo}_2\text{Cl}_4(\text{S,S-bppm})_2$ in dichloromethane was recorded on a Beckman DU 70 spectrophotometer. The IR spectrum was recorded on an IBM FTIR/40S spectrometer by pressing the sample in KBr disks. The circular dichroism (CD) spectra were obtained on a Jasco J-600 spectrophotometer. The $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR spectra were recorded on a Varian XL-200 NMR spectrometer.

Starting Materials. $\text{K}_4\text{Mo}_2\text{Cl}_8$ was prepared according to a previously reported⁷ procedure. The ligand (2S,4S)-N-(tert-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (S,S-bppm) was purchased from Aldrich Chemical Co..

Preparation. $\text{K}_4\text{Mo}_2\text{Cl}_8$ (0.1 g, 0.158 mmol) and S,S-bppm (0.18 g, 0.325 mmol), were placed in a flask equipped with a reflux condenser. Methanol (13 mL) was then added. This mixture was refluxed for 3 h to yield a blue solution and a blue solid. The solid was filtered off, washed with methanol and ether, and then dried under reduced pressure. Yield: 0.11 g (48%). IR (KBr disk): 1615 ($\nu_{\text{C=O}}$) cm^{-1} . Solutions of this complex are slightly air-sensitive, but solid samples are air-stable.

Crystals suitable for X-ray diffraction measurement were obtained by hexane-induced crystallization from a dichloromethane solution.

X-ray Crystallography. The structure of $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-bppm})_2$ was determined by general procedures that have been fully described elsewhere.⁸ The diffraction data were collected on a Syntex P3 equivalent diffractometer at $20 \pm 1^\circ\text{C}$, which was equipped with graphite-monochromated Mo $\text{K}\alpha$ ($\lambda_\alpha = 0.71037\text{ \AA}$) radiation. Data reduction was carried out by standard methods with the use of well-established computational procedures.⁹ Basic information pertaining to crystal parameters and structure refinement are summarized in Table I. Tables II and III list positional parameters and selected bond distances and angles, respectively.

A deep blue crystal of $\beta\text{-Mo}_2\text{Cl}_4(\text{S,S-bppm})_2$ was mounted on the top of a glass fiber with epoxy cement. A rotational photograph indicated that the crystal diffracted well. The unit cell constants were determined

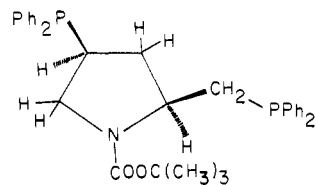
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Table I. Crystal Data for $\text{Mo}_2\text{Cl}_4(\text{S,S-bppm})_2 \cdot 0.75\text{CH}_2\text{Cl}_2$

formula	$\text{Mo}_2\text{Cl}_4\text{P}_4\text{O}_4\text{N}_2\text{C}_{68}\text{H}_{74} \cdot 0.75\text{CH}_2\text{Cl}_2$
fw	1503.93
space group	$P2_12_12_1$
syst absences	$(h00) h \neq 2n; (0k0) k \neq 2n; (00l) l \neq 2n$
$a, \text{\AA}$	19.812 (4)
$b, \text{\AA}$	20.609 (2)
$c, \text{\AA}$	17.815 (3)
$V, \text{\AA}^3$	7273 (2)
Z	4
$d_{\text{calc}}, \text{g/cm}^3$	1.37
cryst size, mm	$0.43 \times 0.55 \times 0.30$
$\mu(\text{Mo K}\alpha), \text{cm}^{-1}$	6.73
data collcn instrum	Syntex P3 equivalent
radiation monochromated in incident beam ($\lambda(\text{Mo K}\alpha), \text{\AA}$)	0.71073
orientation rflcns: no.; range (2θ), deg	25; $20.1 \leq 2\theta < 26.7$
temp., $^\circ\text{C}$	20 ± 1
scan method	$2\theta-\omega$
data collcn range (2θ), deg	$4 \leq 2\theta \leq 55$
no. of unique data; tot. no. with $F_o^3 > 3\sigma(F_o^2)$	8707; 4011
no. of params refined	529
transm factors: max; min	1.00; 0.96
R^a	0.0698
R_w^b	0.0852
quality-of-fit indicator ^c	1.505
largest shift/esd, final cycle	0.23
largest peak, $\text{e}/\text{\AA}^3$	1.2

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

**Figure 1.** Schematic structure of *S,S*-bppm.

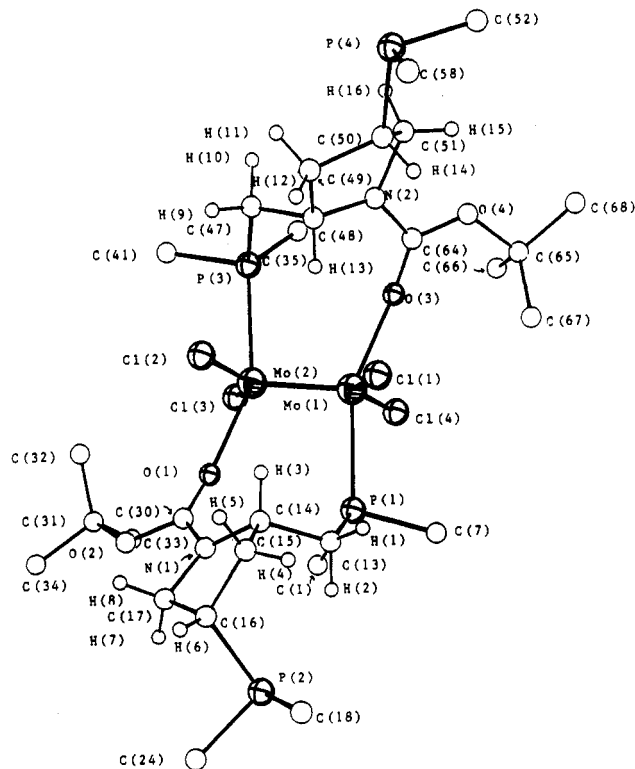
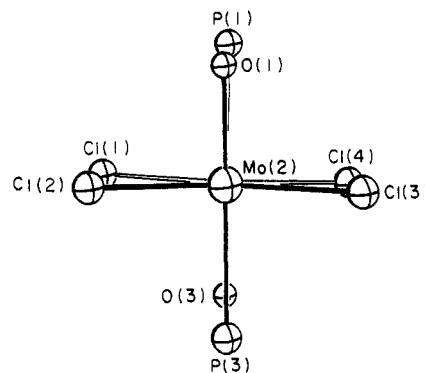
from 25 reflections with 2θ values in the range from 20 to 27°. These were consistent with the orthorhombic crystal system, and the space group was subsequently determined to be $P2_12_12_1$ from the systematic absences.

Routine $2\theta-\omega$ data collection was used to scan a possible 9015 data points in the range $4^\circ < 2\theta < 55^\circ$. Three check reflections monitored throughout the data collection displayed no significant gain or loss in intensity. The structure factors were obtained after a Lorentz and polarization correction. Empirical absorption corrections based on azimuthal (ψ) scans of reflections of Eulerian angle χ near 90° were applied to the data.¹⁰

The direct-methods program in SHELXS-86¹¹ led to the locations of the positions of the molybdenum atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements. Anisotropic thermal parameters were used for all the atoms except those belonging to the phenyl groups. The positions of the hydrogen atoms on the aliphatic carbon atoms (except the methyl groups) were calculated by using the Hydro program to determine the chirality of the ligand without further refinement. The final residuals of the first refinement were $R = 0.0701$, $R_w = 0.0856$, corresponding to a *R,R* configuration for the ligands. A change to the *S,S* enantiomorph gave better residuals of 0.0698 and 0.0852. The chiralities of the ligands in this molecule are consistent with the *S,S* ligand used, and thus we are confident that we have the correct conformer.

Results and Discussion

(a) Structure. Two equivalents of the chiral ligand, *S,S*-bppm, Figure 1, react with 1 equiv of $\text{K}_4\text{Mo}_2\text{Cl}_8$ in boiling methanol to

**Figure 2.** ORTEP drawing of $\text{Mo}_2\text{Cl}_4(\text{S,S-bppm})_2$ in its entirety.**Figure 3.** View looking down the Mo-Mo bond, showing only the 10 central atoms.

give $\text{Mo}_2\text{Cl}_4(\text{S,S-bppm})_2$. Crystals of this compound conform to the space group $P2_12_12_1$ with four molecules per unit cell. The ORTEP diagram, Figure 2, shows that two phosphorus atoms (P(1), P(3)) and two oxygen atoms (O(1), O(3)) from each *S,S*-bppm ligand are coordinated to the molybdenum centers while two other phosphorus atoms (P(2), P(4)) are uncoordinated. In this structure, an inspection of the geometry reveals that two molybdenum, one phosphorus, one oxygen, and four carbon atoms form an eight-membered ring. The conformation of this eight-membered ring can be assigned as λ or δ , if the center of the Mo-Mo bond is supposed to occupy the position of the single atom in a mononuclear complex, just as is the case in the seven-membered ring.¹² It will be seen that this ring has a δ configuration.

Figure 3 shows a view of the inner part of this molecule looking down the Mo-Mo bond. The average torsional angle is approximately 0° , and the Mo-P and Mo-O bonds are almost eclipsed.

A question pertaining to the ligand arrangement is of interest: why do the oxygen atoms of the carbonyl groups coordinate to the two metal centers rather than the two uncoordinated phosphorus atoms? This is an interesting and important question, since we can draw 10 possible isomers for this molecule by changing

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Table II. Positional and Isotropic Equivalent Thermal Parameters (\AA^2) and Their Estimated Standard Deviations for Mo₂Cl₄(S,S-bppm)₂·0.75CH₂Cl₂

atom	x	y	z	B, \AA^2	atom	x	y	z	B, \AA^2
Mo(1)	0.09822 (7)	0.98828 (7)	0.66068 (8)	2.25 (2)	C(37)	-0.195 (1)	1.090 (1)	0.686 (1)	6.0 (6)*
Mo(2)	0.11502 (7)	1.08198 (7)	0.61418 (9)	2.37 (3)	C(38)	-0.178 (1)	1.090 (1)	0.760 (1)	5.5 (5)*
Cl(1)	0.1117 (2)	0.9089 (2)	0.5605 (2)	3.32 (9)	C(39)	-0.115 (1)	1.095 (1)	0.780 (1)	4.6 (4)*
Cl(2)	0.1313 (2)	1.0682 (2)	0.4802 (3)	3.7 (1)	C(40)	-0.061 (1)	1.099 (1)	0.731 (1)	4.0 (4)*
Cl(3)	0.1027 (3)	1.1591 (2)	0.7144 (3)	4.0 (1)	C(41)	-0.0054 (9)	1.1952 (9)	0.557 (1)	2.9 (4)*
Cl(4)	0.0795 (2)	1.0003 (3)	0.7934 (2)	3.7 (1)	C(42)	-0.042 (1)	1.237 (1)	0.601 (1)	4.0 (4)*
P(1)	0.2201 (2)	0.9676 (2)	0.6929 (3)	2.5 (1)	C(43)	-0.035 (1)	1.306 (1)	0.586 (1)	4.6 (5)*
P(2)	0.4464 (3)	0.9503 (3)	0.5688 (3)	3.5 (1)	C(44)	0.005 (1)	1.323 (1)	0.524 (1)	5.6 (6)*
P(3)	-0.0062 (2)	1.1069 (2)	0.5841 (3)	2.7 (1)	C(45)	0.040 (1)	1.279 (1)	0.480 (1)	5.0 (5)*
P(4)	-0.1504 (3)	0.8778 (3)	0.3645 (3)	4.6 (1)	C(46)	0.035 (1)	1.212 (1)	0.497 (1)	4.8 (5)*
O(1)	0.2190 (6)	1.1048 (6)	0.6161 (7)	3.1 (3)	C(47)	-0.0371 (9)	1.067 (1)	0.497 (1)	3.4 (4)
O(2)	0.3121 (6)	1.1597 (6)	0.5765 (8)	3.9 (3)	C(48)	-0.0282 (8)	0.992 (1)	0.499 (1)	3.5 (4)
O(3)	-0.0079 (5)	0.9657 (6)	0.6555 (7)	3.2 (3)	C(49)	-0.047 (1)	0.965 (1)	0.421 (1)	4.7 (5)
O(4)	-0.1009 (6)	0.9043 (6)	0.6547 (7)	3.6 (3)	C(50)	-0.090 (1)	0.9030 (9)	0.436 (1)	4.0 (5)
N(1)	0.3099 (6)	1.0532 (7)	0.5617 (8)	2.6 (3)	C(51)	-0.1287 (9)	0.923 (1)	0.511 (1)	3.9 (4)
N(2)	-0.0745 (7)	0.9605 (7)	0.5548 (9)	3.3 (3)	C(52)	-0.205 (1)	0.825 (1)	0.417 (1)	5.7 (6)*
C(1)	0.2709 (9)	1.0235 (9)	0.751 (1)	2.9 (4)*	C(53)	-0.180 (1)	0.766 (1)	0.447 (2)	7.4 (7)*
C(2)	0.343 (1)	1.011 (1)	0.749 (1)	5.0 (5)*	C(54)	-0.225 (2)	0.729 (2)	0.499 (2)	8.9 (9)*
C(3)	0.380 (1)	1.052 (1)	0.799 (1)	6.1 (6)*	C(55)	-0.295 (2)	0.752 (2)	0.500 (2)	11 (1)*
C(4)	0.349 (1)	1.100 (1)	0.841 (1)	5.1 (5)*	C(56)	-0.317 (2)	0.809 (2)	0.482 (2)	13 (1)*
C(5)	0.280 (1)	1.111 (1)	0.839 (1)	5.3 (5)*	C(57)	-0.224 (2)	1.151 (2)	0.926 (2)	11 (1)*
C(6)	0.241 (1)	1.069 (1)	0.791 (1)	4.1 (4)*	C(58)	-0.401 (1)	1.179 (1)	0.807 (1)	4.9 (5)*
C(7)	0.2195 (9)	0.8943 (9)	0.749 (1)	2.9 (4)*	C(59)	-0.466 (1)	1.168 (1)	0.796 (1)	5.3 (5)*
C(8)	0.245 (1)	0.895 (1)	0.822 (1)	4.7 (5)*	C(60)	-0.004 (2)	1.295 (2)	0.253 (2)	9.2 (9)*
C(9)	0.242 (1)	0.838 (1)	0.865 (1)	5.8 (6)*	C(61)	0.026 (2)	1.235 (1)	0.282 (2)	8.2 (8)*
C(10)	0.214 (1)	0.781 (1)	0.835 (1)	5.8 (5)*	C(62)	0.098 (2)	1.231 (2)	0.273 (2)	10 (1)*
C(11)	0.186 (1)	0.784 (1)	0.763 (1)	4.8 (5)*	C(63)	0.136 (1)	1.273 (1)	0.226 (2)	7.9 (7)*
C(12)	0.193 (1)	0.838 (1)	0.717 (1)	3.8 (4)*	C(64)	-0.0587 (8)	0.9437 (9)	0.6232 (9)	2.4 (4)
C(13)	0.2739 (9)	0.9436 (9)	0.618 (1)	3.5 (4)	C(65)	-0.089 (1)	0.871 (1)	0.725 (1)	4.3 (5)
C(14)	0.2784 (8)	0.9906 (8)	0.5484 (9)	2.6 (3)	C(66)	-0.093 (1)	0.922 (1)	0.789 (1)	4.9 (5)
C(15)	0.3232 (9)	0.962 (1)	0.487 (1)	3.7 (5)	C(67)	-0.017 (1)	0.837 (1)	0.724 (1)	5.7 (6)
C(16)	0.3927 (9)	0.9923 (8)	0.4965 (8)	3.2 (4)	C(68)	-0.148 (1)	0.823 (1)	0.731 (1)	5.7 (6)
C(17)	0.3762 (9)	1.0618 (8)	0.525 (1)	2.9 (4)	C(69)	0.314 (3)	0.439 (3)	0.767 (3)	12 (2)*
C(18)	0.467 (1)	0.874 (1)	0.519 (1)	3.9 (4)*	Cl(5)	0.291 (1)	0.433 (1)	0.674 (1)	20.1 (8)*
C(19)	0.463 (1)	0.863 (1)	0.441 (1)	5.0 (5)*	C6(6)	0.391 (1)	0.406 (1)	0.750 (2)	25 (1)*
C(20)	0.483 (1)	0.804 (1)	0.413 (1)	5.0 (5)*	H(1)	0.2603	0.9019	0.5994	4.5*
C(21)	0.512 (1)	0.754 (1)	0.458 (1)	6.0 (6)*	H(2)	0.3196	0.9387	0.6370	4.5*
C(22)	0.516 (1)	0.766 (1)	0.537 (1)	5.7 (6)*	H(3)	0.2314	0.9964	0.5356	3.6*
C(23)	0.495 (1)	0.825 (1)	0.567 (1)	5.3 (5)*	H(4)	0.3265	0.9148	0.4901	4.5*
C(24)	0.5269 (9)	0.997 (1)	0.557 (1)	4.1 (4)*	H(5)	0.3060	0.9710	0.4368	4.5*
C(25)	0.545 (1)	1.035 (1)	0.619 (1)	6.1 (6)*	H(6)	0.4179	0.9904	0.4517	4.0*
C(26)	0.605 (1)	1.075 (1)	0.614 (1)	6.8 (6)*	H(7)	0.4103	1.0778	0.5585	3.8*
C(27)	0.644 (1)	1.068 (1)	0.552 (1)	7.1 (7)*	H(8)	0.3743	1.0923	0.4830	3.8*
C(28)	0.630 (1)	1.027 (1)	0.492 (1)	6.3 (6)*	H(9)	-0.0146	1.0850	0.4540	4.4*
C(29)	0.567 (1)	0.993 (1)	0.494 (1)	5.8 (5)*	H(10)	-0.0852	1.0773	0.4906	4.4*
C(30)	0.2765 (9)	1.1045 (9)	0.5871 (8)	2.6 (4)	H(11)	-0.0732	0.9958	0.3930	6.2*
C(31)	0.288 (1)	1.226 (1)	0.605 (1)	4.2 (5)	H(12)	-0.0078	0.9544	0.3929	6.2*
C(32)	0.224 (1)	1.244 (1)	0.571 (1)	5.1 (6)	H(13)	0.0177	0.9842	0.5131	4.6*
C(33)	0.284 (1)	1.226 (1)	0.687 (1)	5.5 (6)	H(14)	-0.0603	0.8664	0.4479	5.0*
C(34)	0.349 (1)	1.265 (1)	0.577 (2)	7.6 (7)	H(15)	-0.1443	0.8859	0.5386	5.0*
C(35)	-0.0735 (9)	1.1001 (9)	0.654 (1)	3.1 (4)*	H(16)	-0.1675	0.9495	0.5001	5.0*
C(36)	-0.143 (1)	1.099 (1)	0.631 (1)	5.2 (5)*					

*Starred values denote atoms that were refined isotropically. Values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

the coordination atoms but retaining the bridging role for the ligand (the schematic figures of these isomers are available as supplementary material). Some of these isomers can be immediately excluded by consideration of steric factors that can be deduced from a molecular model set. This is true for those isomers that involve the ligand bridging via an oxygen atom and the phosphorus atom, which is bonded directly to the five-membered ring on the ligand. More difficult to exclude are those four isomers involving coordination of the two phosphorus atoms from each ligand. In order to accommodate this sort of bridging, it is required to have a torsional angle on the order of 80° . This would result in a weaker δ bond. The best overlap is achieved (stronger bond) when the twist angle is 0° . This type of arrangement also entails steric interactions between a CH₂ group in the five-membered ring of the bridging ligand and a chloride ligand. We are then left to consider two possibilities, one of which has the two oxygens coordinated to the same molybdenum atom and the other to different ones (the compound we obtained). The latter could be

more stable than the former since the latter has higher symmetry and thus better crystal packing.

The lone pair of electrons on the nitrogen atom might play an important role after the oxygen atoms have coordinated to the molybdenum atoms. A partial positive charge on the oxygen atoms is created after coordination, and this lone pair could then be partially delocalized among the N-C-O bonds to stabilize this positive charge.

(b) Spectroscopic Studies. (1) Absorption Spectrum. The absorption spectrum (Figure 4) is typical for compounds with a Mo-Mo quadruple bond. The lowest energy band at 585 nm (17094 cm^{-1}) can be assigned to the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition.⁴ The energy of this transition is much higher than those of the other β complexes. This is due to the very small twist angle of the molecule resulting in a stronger overlap of the d_{xy} orbitals. The other band at 492 nm (20325 cm^{-1}) is due to a forbidden transition, and with the help of the CD spectrum (see below), can be assigned to the $\delta_{xy} \rightarrow \delta^*_{x^2-y^2}$ transition.⁴

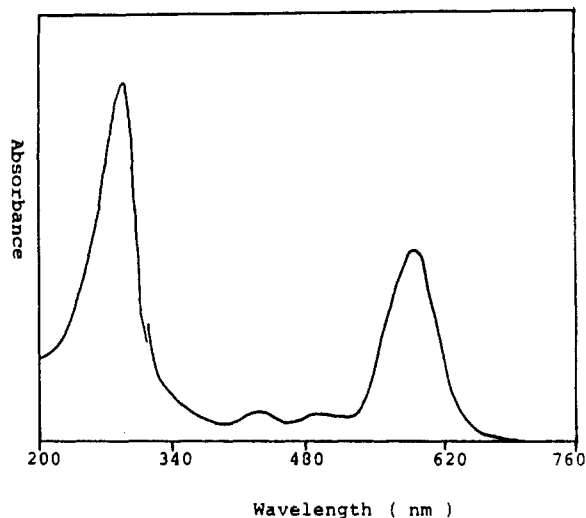
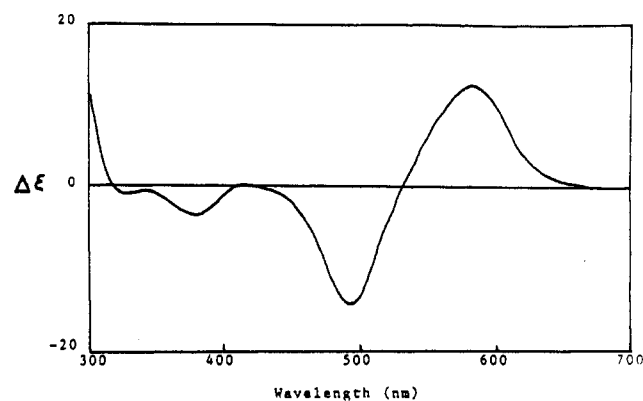
Table III. Selected Bond Distances (Å) and Angles (deg) for $\text{Mo}_2\text{Cl}_4(\text{S},\text{S}-\text{bppm})_2 \cdot 0.75\text{CH}_2\text{Cl}_2^a$

Bond Distances			
Mo(1)–Mo(2)	2.128 (2)	P(4)–C(52)	1.80 (3)
Mo(1)–Cl(1)	2.436 (5)	O(1)–C(30)	1.25 (2)
Mo(1)–Cl(4)	2.407 (5)	O(2)–C(30)	1.35 (2)
Mo(1)–P(1)	2.518 (5)	O(2)–C(31)	1.53 (2)
Mo(1)–O(3)	2.156 (11)	O(3)–C(64)	1.24 (2)
Mo(2)–Cl(2)	2.426 (5)	O(4)–C(64)	1.29 (2)
Mo(2)–Cl(3)	2.403 (5)	O(4)–C(65)	1.45 (2)
Mo(2)–P(3)	2.513 (5)	N(1)–C(14)	1.45 (2)
Mo(2)–O(1)	2.113 (11)	N(1)–C(17)	1.48 (2)
P(1)–C(1)	1.84 (2)	N(1)–C(30)	1.33 (2)
P(1)–C(7)	1.81 (2)	N(2)–C(48)	1.51 (2)
P(1)–C(13)	1.78 (2)	N(2)–C(51)	1.53 (2)
P(2)–C(16)	1.88 (2)	N(2)–C(64)	1.31 (2)
P(2)–C(18)	1.86 (2)	C(1)–C(2)	1.44 (3)
P(2)–C(24)	1.87 (2)	C(1)–C(6)	1.32 (3)
P(3)–C(35)	1.83 (2)	C(7)–C(8)	1.39(3)
P(3)–C(41)	1.88 (2)	C(13)–C(14)	1.57 (3)
P(3)–C(47)	1.85 (2)	C(18)–C(19)	1.40 (3)
P(4)–C(50)	1.83 (2)	C(31)–C(32)	1.46 (3)

Bond Angles			
Mo(2)–Mo(1)–Cl(1)	107.9 (1)	Mo(1)–O(3)–C(64)	153 (1)
Mo(2)–Mo(1)–Cl(4)	108.3 (1)	C(64)–O(4)–C(65)	124 (1)
Mo(2)–Mo(1)–P(1)	95.3 (1)	C(14)–N(1)–C(17)	115 (1)
Mo(2)–Mo(1)–O(3)	109.3 (3)	C(14)–N(1)–C(30)	123 (1)
Cl(1)–Mo(1)–Cl(4)	143.7 (2)	C(17)–N(1)–C(30)	120 (1)
Cl(1)–Mo(1)–P(1)	87.0 (2)	C(48)–N(2)–C(51)	108 (1)
Cl(1)–Mo(1)–O(3)	86.0 (3)	N(1)–C(14)–C(13)	116 (1)
Cl(4)–Mo(1)–P(1)	86.6 (2)	P(2)–C(16)–C(15)	114 (1)
Cl(4)–Mo(1)–O(3)	85.1 (4)	P(2)–C(16)–C(17)	109 (1)
P(1)–Mo(1)–O(3)	155.3 (3)	N(1)–C(17)–C(16)	103 (1)
Mo(1)–Mo(2)–Cl(2)	107.3 (1)	P(2)–C(18)–C(19)	126 (2)
Mo(1)–Mo(2)–Cl(3)	107.2 (1)	P(2)–C(24)–C(25)	114 (2)
Mo(1)–Mo(2)–P(3)	96.9(1)	P(2)–C(24)–C(29)	123 (2)
Mo(1)–Mo(2)–O(1)	110.4 (3)	O(1)–C(30)–O(2)	122 (2)
Cl(2)–Mo(2)–Cl(3)	145.3 (2)	O(1)–C(30)–N(1)	127 (2)
Cl(2)–Mo(2)–P(3)	86.6 (2)	O(2)–C(30)–N(1)	111 (2)
Cl(2)–Mo(2)–O(1)	85.0 (3)	O(2)–C(31)–C(32)	112 (2)
Cl(3)–Mo(2)–P(3)	85.8 (2)	P(3)–C(35)–C(36)	121 (2)
Cl(3)–Mo(2)–O(1)	86.5 (3)	P(3)–C(35)–C(40)	123 (1)
P(3)–Mo(2)–O(1)	152.8 (4)	P(3)–C(41)–C(42)	118 (1)
Mo(1)–P(1)–C(1)	123.0 (6)	P(3)–C(41)–C(46)	117 (2)
Mo(1)–P(1)–C(7)	105.1 (6)	P(3)–C(47)–C(48)	113 (1)
Mo(1)–P(1)–C(13)	116.7 (7)	N(2)–C(48)–C(47)	112 (1)
C(1)–P(1)–C(7)	102.4 (8)	P(4)–C(50)–C(49)	118 (1)
C(1)–P(1)–C(13)	105.5 (8)	C(48)–N(2)–C(64)	126 (1)
C(7)–P(1)–C(13)	101.0 (9)	C(51)–N(2)–C(64)	121 (2)
C(16)–P(2)–C(18)	100.9 (8)	P(1)–C(1)–C(2)	114 (1)
C(16)–P(2)–C(24)	99.8 (9)	P(1)–C(1)–C(6)	120 (1)
C(18)–P(2)–C(24)	101.2 (9)	P(1)–C(7)–C(8)	121 (2)
Mo(2)–P(3)–C(35)	122.4 (6)	P(1)–C(7)–C(12)	117 (1)
Mo(2)–P(3)–C(41)	104.1 (6)	P(1)–C(13)–C(14)	117 (1)
Mo(2)–P(3)–C(47)	113.8 (6)	P(1)–C(13)–H(1)	110 (2)
C(35)–P(3)–C(41)	104.6 (8)	N(2)–C(51)–C(50)	103 (1)
C(35)–P(3)–C(47)	107.0 (8)	P(4)–C(52)–C(53)	121 (2)
C(41)–P(3)–C(47)	102.6 (9)	O(3)–C(64)–O(4)	123 (2)
C(50)–P(4)–C(52)	102. (1)	O(3)–C(64)–N(2)	122 (2)
Mo(2)–O(1)–C(30)	152 (1)	O(4)–C(64)–N(2)	115 (1)
C(30)–O(2)–C(31)	123 (1)	O(4)–C(65)–C(66)	108 (2)

^a Numbers in parentheses are estimated standard deviations in the last significant digits.

(2) CD Spectrum. Circular dichroism (CD) can occur only if the electron is associated not only with a charge translation but also with a charge rotation such that the two moments are not orthogonal.¹³ The “rotational strength” of a transition is the scalar product of the magnetic and electric moments,¹⁴ as shown in the equation $R = \text{Im} \langle a|P|b \rangle \langle b|M|a \rangle = \mu m \cos \theta$, in which Im signifies the imaginary part, P and M are electric and magnetic operators, respectively, a and b represent the orbitals involved in the transition, μ and m are the electric dipole and magnetic dipole moments

**Figure 4.** UV-vis spectra of $\text{Mo}_2\text{Cl}_4(\text{S},\text{S}-\text{bppm})_2$ in CH_2Cl_2 solvent.**Figure 5.** CD spectrum of $\text{Mo}_2\text{Cl}_4(\text{S},\text{S}-\text{bppm})_2$ in CH_2Cl_2 solvent.

associated with the transition, and θ is the angle between the two moments. Experimentally, the rotational strength of an electronic transition is calculated by measuring the area under the corresponding CD band in the spectrum. The relationship¹⁵ can be expressed as

$$R = 0.248 \int (\Delta\epsilon / \bar{\nu}^2) d\bar{\nu} \quad (1)$$

where $\Delta\epsilon$ is the differential molar extinction coefficient, and β is the Lorentz field correction $[(n^2 + 2)/3]$ for the refractivity, n , of the solvent at the radiation wavenumber $\bar{\nu}$ (cm^{-1}). The rotational strength also has the symmetry properties of a pseudoscalar quantity with a sign depending on the parallel or antiparallel orientation between the electric and magnetic moments.

If the chromophore is chiral, all allowed electronic transitions have both electric and magnetic moments, enabling the CD spectrum to be measured. In the case of $\text{Mo}_2\text{Cl}_4(\text{S},\text{S}-\text{bppm})_2$, however, the $\text{Mo}_2\text{Cl}_4\text{P}_2\text{O}_2$ chromophore has symmetry very closely approximating to C_{2h} . In this symmetry, no transition can be strictly allowed both electrically and magnetically. Accordingly, no CD should occur for this molecule, but in fact a CD spectrum has been recorded. Figure 5 shows the CD spectrum of the complex $\text{Mo}_2\text{Cl}_4(\text{S},\text{S}-\text{bppm})_2$ in dichloromethane solution. This CD spectrum has a positive sign for the $\delta_{xy} \rightarrow \delta_{xy}^*$ transition (580 nm) and a negative sign for the $\delta_{x^2-y^2} \rightarrow \delta_{x^2-y^2}^*$ transition (492 nm).

In order to explain the CD of this compound, we must invoke the one-electron, static-coupling mechanism. On the basis of the classification by Moscovitz,⁶ this molecule falls into the “case II” category, that is, an intrinsically achiral chromophore which gives rise to chirality effects through perturbation by chiral sur-

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roundings. This one-electron, static-coupling mechanism has been discussed by Mason¹⁵ and by Schellman.^{16,17} The mechanism has also been used to account for the chiroptical properties of $\text{Rh}_2[(\text{S})\text{-mandelate}]_4(\text{EOH})_2$ and $\text{Rh}_2[(\text{R})\text{-}\alpha\text{-methoxy-}\alpha\text{-phenylacetate}]_4(\text{THF})_2$.¹⁴ The one-electron mechanism assumes that while the chromophore is soft and perturbable, the substituent is hard and remains in its ground state during the excitation process. This mechanism comprises a first-order perturbation mixing of a magnetically accessible excited state into an electric dipole accessible excited state and vice versa. The perturbation mixing can be described by eqs 2 and 3.¹⁴

$$|M_e L_0\rangle' = |M_e L_0\rangle + \langle M_m L_0 | V | M_e L_0 \rangle |M_m L_0\rangle (E_e - E_m)^{-1} \quad (2)$$

$$|M_m L_0\rangle' = |M_m L_0\rangle + \langle M_e L_0 | V | M_m L_0 \rangle |M_e L_0\rangle (E_m - E_e)^{-1} \quad (3)$$

The function $|M_e L_0\rangle$ represents the state in which the chromophore (M) is in an electric dipole accessible state and the surroundings (L) are in the ground state, and $|M_m L_0\rangle$ represents the state in which the chromophore is in the magnetically accessible state. E_e and E_m are the energies of the excited states of the chromophore relative to the ground state. V is the Coulombic potential between the charges e_i of the chromophore M and the charges e_j of the surroundings L. If the distances between the charges are r_{ij} , this potential can be expressed as $V = \sum e_i e_j / r_{ij}$. Thus the optical activity of a symmetric chromophore is induced by a static potential, i.e., by the mixing of a magnetically accessible excited state with an electric dipole accessible state (eq 2) or by the mixing of an electric dipole accessible excited state with a magnetically accessible one (eq 3). Thus a transition from the ground state to one of the perturbed states will be both electrically and magnetically allowed, and a corresponding CD band should have nonzero intensity.

After the mixing, the electric moment, μ_{0e} of the chromophore transition, which is taken to have its first-order value, acquires a magnetic moment, m_{e0} , by first order mixing, which can be described by eq 4,¹⁴ where m_{m0} is the magnetic moment of the

$$m_{e0} = m_{m0} \langle M_m L_0 | V | M_e L_0 \rangle (E_e - E_m)^{-1} \quad (4)$$

magnetically allowed transition, which is mixed with the electric dipole allowed transition. At the same time, the magnetic dipole moment acquires an electric moment as described in eq 5.¹⁷

$$\mu_{0m} = \mu_{0e} \langle M_e L_0 | V | M_m L_0 \rangle (E_m - E_e)^{-1} \quad (5)$$

If the zero-order moments, μ_{0e} and m_{m0} , have a common polarization, e.g., x and R_x , the two transitions will acquire rotational strengths that are equal in magnitude but opposite in sign, as shown in eq 6.¹⁵

$$R_{0m} = -R_{0e} = i\mu_{0e} m_{m0} \langle M_e L_0 | V | M_m L_0 \rangle (E_e - E_m)^{-1} \quad (6)$$

We are now in a position to assign the peaks at 580 and 492 nm in the CD spectrum. In the discussion of the UV-vis spectrum, we have stated that the band at 585 nm is electric dipole allowed and can be assigned to the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition. The transition at 492 nm is electric dipole forbidden but magnetically allowed and can be assigned to the $\delta_{xy} \rightarrow \delta^*_{x^2-y^2}$ transition. If we consider only the $\text{Mo}_2\text{Cl}_4(\text{PO})_2$ chromophore, which has C_{2h} symmetry, the δ_{xy} orbital transforms as B_g , the δ^*_{xy} orbital transforms as A_u , and the $\delta^*_{x^2-y^2}$ orbital transforms as A_g , assuming that the z axis is parallel to the Mo-Mo bond and the x axis coincides with the C_2 axis of symmetry. From these symmetries, it follows that the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition is electric dipole allowed with z polarization and the $\delta_{xy} \rightarrow \delta^*_{x^2-y^2}$ transition is only magnetically allowed via $R_z(B_g)$. We assign the CD transition at 580 nm to the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition ($B_g \rightarrow A_u$), which obtains rotational strength by mixing of the electronic excited state into the magnetic excited state of the $\delta_{xy} \rightarrow \delta^*_{x^2-y^2}$ transition. The reverse mixing explains the CD peak at 490 nm. This assignment is consistent with the prediction that, after being mixed, these two transitions will acquire rotational

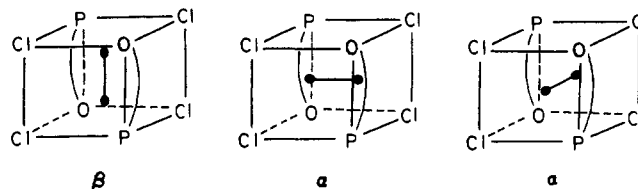


Figure 6. Drawing showing the result of reorienting the Mo_2 unit within the ligand cage, thereby converting the β isomer to two equivalent α isomers.

strengths that are equal in magnitude but opposite in sign. From the CD spectrum, we can see that the $\delta_{xy} \rightarrow \delta^*_{xy}$ has a positive sign and the $\delta_{xy} \rightarrow \delta^*_{x^2-y^2}$ transition has a negative sign. Moreover, the ratio of the areas under these two bands is about 0.85, which approximately satisfies the prediction that the magnitudes of the rotational strengths should be equal.

(3) **NMR Spectroscopic Studies.** The proton NMR spectrum only shows one type of molecule in solution: 0.65 (9 H), 1.92 (1 H), 2.75–3.3 (5 H), 3.75 (1 H), 6.4 (1 H), and 6.8–8.8 ppm (20 H). The signal at 6.4 ppm can be easily assigned to H(3) (or H(13)) without ambiguity, since it is close to the Mo-Mo bond and nearly over its midpoint. Compared with the chemical shift of this proton in the free ligand, which is 3.8 ppm, it can be seen that this proton has shifted 2.6 ppm downfield. This is due to the diamagnetic anisotropy of the Mo-Mo quadruple bond. The diamagnetic anisotropy of quadruple and triple bonds between atoms has been the subject of several publications.^{18–21} For molecules having axial symmetry, the simple McConnell equation, eq 7, can be used to calculate the diamagnetic anisotropy. θ is

$$\Delta\delta = 1/3r^3[(\chi_{\parallel} - \chi_{\perp})(1 - 3\cos^2\theta)]/4\pi \quad (7)$$

the angle between r and the z axis (parallel to the Mo-Mo bond), where r is the distance from the hydrogen to the center of the Mo-Mo bond.

On the basis of the hydrogen atoms H(3) and H(13), which are shifted from 3.8 to 6.4 ppm, the diamagnetic anisotropy of this complex is calculated to be $(2915 \pm 523) \times 10^{-36} \text{ m}^3/\text{molecule}$.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of this complex shows two peaks at 32.5 and -7.8 ppm. When these are compared with the chemical shifts of the free ligand at -8.4 and -22.7 ppm, we can assign the peak at 32.5 ppm to P(2) and P(4), which are coordinated to the metal center, and the peak at -7.8 ppm to P(1) and P(3), which are uncoordinated. The low-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR experiment has also been carried out to see the possibility of isomerization of this complex in solution. No change was observed from room temperature to -80 °C.

(c) **Mo-Mo Bond Distance vs Twist Angle.** It has been recognized that the strength of the δ component of a quadruple metal-metal bond depends inversely on the angle of rotation away from the eclipsed conformation.¹ The δ bond strength varies according to $\cos 2\chi$, where χ is the average of the four smallest torsional angles about the Mo-Mo quadruple bond. This linear relationship has been demonstrated.² In the case of β - $\text{Mo}_2\text{Cl}_4(\text{S,S-bppm})_2$, the χ angle is 0° and the metal-metal bond distance is 2.128 Å. This combination is consistent with the prediction that a molecule with no twist angle, i.e., eclipsed, will have a short quadruple metal-metal bond.

(d) **Lack of Isomers or Disorder.** In β - $\text{M}_2\text{X}_4(\text{LL})_2$ molecules generally, it has been found that there is a crystallographic disorder such that the M-M unit is found with two approximately perpendicular orientations relative to a roughly constant array of ligands.⁴ This is equivalent to having two β isomers, which differ in their ring conformations, whose gross shapes are similar enough to allow them to pack together in the same crystal. In one case,⁵ it has been shown that these two isomers are also present in

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solution, although not in the same molar ratio as in the crystal. In the present case there is no second isomer in the solution or in the crystal (i.e., no disorder in the crystal). Why should this be so?

Inspection of Figure 6 will reveal the answer. Neither of the two molecules that can be obtained from the one that is found by changing the orientation of the Mo_2 within the ligand cage is a β isomer. Both are α isomers, and in fact, they are identical. Evidently the energy difference between the β and α isomers is

so great as to disfavor the α isomer altogether.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Complete tables of anisotropic thermal parameters, bond distances, bond angles, and torsional angles for the central portion of the molecule and schematic figures of the 10 possible isomers (11 pages); listings of observed and calculated structure factors (21 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

Tertiary Phosphine Complexes of Chromium(III): Syntheses, Magnetic Properties, and Single-Crystal Structure Studies on $\text{Cr}_2\text{Cl}_6(\text{PMe}_3)_4$, $\text{Cr}_2\text{Cl}_6(\text{PET}_3)_4$, and $\text{Cr}_2\text{Cl}_6(\text{dmpm})_2$

F. A. Cotton,*[†] Judith L. Eglin,[‡] Rudy L. Luck,[†] and Kyung-ae Son[†]

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Anhydrous chromium(III) chloride reacts, in appropriate solvents at reflux temperatures, with each of the monodentate tertiary phosphines PMe_3 and PET_3 and with the bidentate tertiary phosphine bis(dimethylphosphino)methane (dmpm) to form $\text{Cr}_2\text{Cl}_6(\text{PMe}_3)_4$ (1), $\text{Cr}_2\text{Cl}_6(\text{PET}_3)_4$ (2) and $\text{Cr}_2\text{Cl}_6(\text{dmpm})_2$ (3), respectively. Complex 1 was also obtained from the reaction of $\text{Cr}_2(\text{OAc})_4$, Me_3SiCl , and PMe_3 . The magnetic susceptibility of 2 varies with temperature in the range 5–300 K, in agreement with the Curie–Weiss law, and this indicates no significant interaction between the Cr atoms. However, the magnetic properties of 3 suggest that there may be an antiferromagnetic interaction between the Cr atoms at low temperatures (1.3–10 K). The Cr...Cr distances are as follows: 1, 3.587 (5) Å; 2, 3.637 (2) Å; 3, 3.480 (1) Å. Crystal data: $\text{Cr}_2\text{Cl}_6(\text{PMe}_3)_4$ (1), orthorhombic, space group $Pm\bar{c}n$, $a = 13.452$ (3) Å, $b = 18.292$ (3) Å, $c = 11.317$ (2) Å, $V = 2784.7$ (9) Å³, $Z = 4$, $R = 0.064$ ($R_w = 0.092$) for 877 data with $F_o^2 > 3\sigma(F_o^2)$; $\text{Cr}_2\text{Cl}_6(\text{PET}_3)_4$ (2), orthorhombic, space group $Pnma$, $a = 20.184$ (3) Å, $b = 19.066$ (2) Å, $c = 10.642$ (1) Å, $V = 4095.3$ (9) Å³, $Z = 4$, $R = 0.0498$ ($R_w = 0.072$) for 1889 data with $F_o^2 = 3\sigma(F_o^2)$; $\text{Cr}_2\text{Cl}_6(\text{dmpm})_2$ (3), monoclinic, space group $P2_1/a$, $a = 8.505$ (2) Å, $b = 20.574$ (2) Å, $c = 8.481$ (1) Å, $\beta = 92.66^\circ$, $V = 1482.4$ (3) Å³, $Z = 2$, $R = 0.0332$ ($R_w = 0.0423$) for 2099 data with $F_o^2 > 3\sigma(F_o^2)$.

Introduction

Chromium(III) complexes containing monodentate tertiary phosphines have been known for quite some time. These include the dimers $[\text{CrX}_3(\text{PR}_3)_2]_2$ ($X = \text{Cl}$, $R = \text{Et}$, Bu^n ; $X = \text{Br}$, $R = \text{Et}$),^{1,2} several polymers $[\text{CrCl}_3(\text{PR}_3)]_n$ ($R = \text{Et}$, Bu^n , Ph), and the monodentate anionic complex $[\text{PPh}_4][\text{CrCl}_4(\text{PR}_3)_2]$ ($R = \text{Et}$).² However, there have not been any prior reports of binuclear chromium(III) complexes containing bidentate tertiary phosphines. In addition, the structures of the binuclear Cr(III) complexes containing P donor atoms have generally been inferred from conductance and molecular weight measurements,¹ and IR and electronic spectra.² No single-crystal X-ray data have been reported previously for these Cr dimers.

We report here the preparation and the single-crystal structure determinations of binuclear Cr(III) complexes containing mono- $[\text{Cr}_2\text{Cl}_6(\text{PMe}_3)_4$ (1) and $\text{Cr}_2\text{Cl}_6(\text{PET}_3)_4$ (2)] and bidentate tertiary phosphines $[\text{Cr}_2\text{Cl}_6(\text{dmpm})_2$ (3)] and the variable-temperature magnetic susceptibilities of complexes 2 and 3. The purpose of this work was to see what sort of Cr–Cr interactions might occur in these bridged binuclear systems, as well as to have well-characterized dichromium(III) species as potential synthetic precursors for the preparation of dichromium(II) compounds.

Experimental Section

All operations were carried out under an atmosphere of prepurified argon. Solvents were dried by conventional methods and distilled under dinitrogen. Electronic spectra were measured in dichloromethane and benzene solutions with a Cary 17D spectrophotometer. The elemental analysis was done by Galbraith Laboratories, Knoxville, TN. PMe_3 , PET_3 , dmpm, and CrCl_3 were purchased from Strem Chemicals, and $(\text{CH}_3)_3\text{SiCl}$ was purchased from Aldrich Chemicals Co.

Preparation of $\text{Cr}_2\text{Cl}_6(\text{PMe}_3)_4$ (1). The complex $\text{Cr}_2\text{Cl}_6(\text{PMe}_3)_4$ (1) was obtained as a byproduct from the reaction of a mixture of $\text{Cr}_2(\text{O-}$

Table I. Crystallographic Data for Compounds 1–3

	1	2	3
formula	$\text{C}_{12}\text{H}_{36}\text{Cl}_6\text{Cr}_2\text{P}_4$	$\text{C}_{24}\text{H}_{60}\text{Cl}_6\text{Cr}_2\text{P}_4$	$\text{C}_{10}\text{H}_{28}\text{Cl}_6\text{Cr}_2\text{P}_4 \cdot 2\text{CH}_2\text{Cl}_2$
fw	621.0	789.35	758.81
space group	$Pm\bar{c}n$ (No. 62)	$Pnma$ (No. 62)	$P2_1/a$ (No. 14)
a , Å	13.452 (3)	20.184 (3)	8.505 (3)
b , Å	18.292 (3)	19.066 (2)	20.574 (5)
c , Å	11.317 (3)	10.642 (3)	8.481 (1)
α , deg	90	90	90
β , deg	90	90	94.66 (2)
γ , deg	90	90	90
V , Å ³	2784.7 (9)	4095.3 (9)	1482.4 (3)
Z	4	4	2
T , °C	21	20	–80
λ , Å	0.71073	0.71073	0.71073
ρ_{obs} , g/cm ³	1.487	1.285	1.706
μ , cm ^{–1}	15.705	10.819	18.445
trans coeff	1.00–0.77	1.00–0.82	1.00–0.83
$R(F_o)^a$	0.064	0.050	0.033
$R_w(F_o)^b$	0.092	0.072	0.042

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

$\text{Ac})_4$,³ 4 equiv of PMe_3 , and excess Me_3SiCl in THF.⁴ Crystals suitable for the X-ray analysis were obtained by the slow diffusion of hexane into a THF solution of the residue from the above reaction. A high yield of compound 1 can be obtained by reacting CrCl_3 with PMe_3 .¹

Preparation of $\text{Cr}_2\text{Cl}_6(\text{PET}_3)_4$ (2). This was prepared by the method of Issleib and Froehlich.^{1,2} A 0.64-g (4.0-mmol) sample of anhydrous chromium(III) chloride was reacted with 1.1 mL (7.6 mmol) of PET_3 in

* Texas A&M University.

† Michigan State University.

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