J. Am. Chem. Soc. **1991,** *113,* 2509-2512

The First Structurally Characterized Chiral Rhenium Complex Containing a Metal–Metal Quadruple Bond. Syntheses, Structure, and Spectra of β-Re_2Cl_6[(*S*,*S*)-isodiop]: An Unprecedented Rearrangement of the Diop Ligand

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Abstract: By reaction of $Re_2(O_2CCH_3)_2Cl_4$, $(CH_3)_3SiCl$, and (*S*,*S*)-diop in THF at room temperature, a yellow-green product can be prepared. The pink-red complex β-Re_2Cl_6[(*S*,*S*)-isodiop] was obtained by recrystallizing the yellow-green solid from CH_2Cl_2 solvent. The UV–vis, IR, and CD spectra of β-Re_2Cl_6[(*S*,*S*)-isodiop] have been recorded and the structure has been determined. The crystals of this compound are arranged in the space group $P2_12_12_1$ with four molecules per unit cell. Crystallographic data: $a = 15.039$ (6) Å, $b = 21.056$ (7) Å, $c = 12.299$ (9) Å, $V = 3895$ (6) Å^3. Final residuals: $R = 0.0556$, $R_w = 0.0673$. The structure of this complex has a twist angle of ~0°, and the Re–Re distance is 2.236 Å. It is found in this structure that the diop ligand has been rearranged to give isodiop through a pathway similar to the acid-catalyzed rearrangements of acetals. Isodiop is $Ph_2PCH_2CH(O)R$; $R = \overline{CHOCMe_2PPh_2CH_2}$. Isodiop is a zwitter ion with R′O$^-$ and $PR''_4{}^+$ (R′ and R″ represent alkyl or phenyl groups) components, which coordinates as a bridging ligand through P to one Re atom and O to the other.

Introduction

Several complexes with the formula $Re_2X_6(PR_3)_2$ (X = Cl, Br) have been reported,[1] but until now only two complexes, $Re_2Cl_6(PEt_3)_2$ and $Re_2Cl_6(PMePh_2)_2$, have been structurally characterized.[2,3] No bridged complex of the type $Re_2Cl_6(\mu\text{-PP})$, where PP is a diphosphine ligand, has been shown to exist. Like complexes of the type $Mo_2X_4(\mu\text{-PP})_2$, these complexes would contain quadruple M–M bonds subjected to a twist by the μ-PP ligand and would therefore be expected to show similar CD phenomena.[4]

Two types of chiral complexes of the form $Mo_2X_4(PP)_2$, where PP is a diphosphine ligand and X is Cl, Br, or I have been reported. The first type has "class I" chromophores,[5] that is, inherently chiral chromophores, and their CD spectra can be explained by the CD sign rule,[4] which has been verified with the syntheses and characterization of the complexes[6,7] β-Mo_2Cl_4[(*S*,*S*)-dppb]$_2$ and β-Mo_2Cl_4[(*R*,*R*)-diop]$_2$.

The other type of chiral complexes has "class II" chromophores,[5] that is, an intrinsically achiral chromophore that displays chiroptical effects through perturbation by chiral surroundings. The chiral complex[8] β-Mo_2Cl_4[(*S*,*S*)-bppm]$_2$, which has an approximately 0° torsional angle, appears to belong to this category. The one-electron static coupling mechanism was invoked to explain the CD spectrum for this complex.[8]

Here we report the first chiral complex containing a Re–Re quadruple bond in which the diphosphine ligand bridges the rhenium atoms. However, in this compound the (*S*,*S*)-diop ligand has been rearranged to give (*S*,*S*)-isodiop, a ligand that coordinates through P and O atoms, through a pathway similar to the acid-catalyzed rearrangements of acetals.[9] The preparation, structure, and optical activity of this chiral complex form the subject of this report.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry oxygen-free argon using Schlenk techniques, unless otherwise noted. Solvents were dried and deoxygenated by refluxing over the appropriate reagents before use. THF and *n*-hexane were purified by distillation from sodium–potassium/benzophenone, and dichloromethane was purified by distillation from P_2O_5. The UV–vis and IR absorption spectra were recorded on a Cary 17D spectrophotometer. The CD spectrum was recorded on a Jacso J-600 spectropolarimeter.

Starting Materials. $Re_2(O_2CCH_3)_2Cl_4$ was prepared according to a reported procedure.[10] The ligand (+)-2,3,*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, (*S*,*S*)-diop, and $(CH_3)_3SiCl$ were purchased from Strem Chemicals Inc.

Preparation. (1) $Re_2(O_2CCH_3)_2Cl_4$ (0.07 g, 0.1 mmol), (*S*,*S*)-diop (0.104 g, 0.2 mmol), and $(CH_3)_3SiCl$ (excess, ~0.8 mmol) were placed in a flask containing 15 mL of THF. The mixture was stirred for 20 h, resulting in a yellow-green solution. The solvent was evaporated and the yellow-green solid washed with ether and dried in vacuum. Yield: 0.102 g. UV–vis: 580, 728 nm in CH_2Cl_2 solvent. The pink-red crystals suitable for X-ray crystallographic analysis were obtained from a concentrated CH_2Cl_2 solution of the yellow-green solid, which was kept at 0 °C for several days. UV–vis–IR of the crystals: 350, 480, 790 nm in acetone solvent.

(2) $Re_2(O_2CCH_3)_2Cl_4$ (0.0175 g, 0.025 mmol), (*S*,*S*)-diop (0.026 g, 0.05 mmol), and $(CH_3)_3SiCl$ (excess, ~0.2 mmol) were placed in a flask containing 5 mL of CH_2Cl_2. The mixture was stirred for 20 h, resulting in a yellow-green solution and a pink-red solid. The solid was filtered, washed with ether, and then dried in vacuum. Yield: 0.014 g (46%). The pink-red solid is insoluble in most organic solvents and only partially soluble in acetone. UV–vis–IR: 350, 480, 790 nm in acetone solvent.

X-ray Crystallography. The structure of β-Re_2Cl_6[(*S*,*S*)-isodiop] was determined by a general procedure that has been fully described elsewhere.[11]

A red-pink crystal was mounted inside a capillary with epoxy cement. Crystal quality was confirmed by a rotation photograph. The unit cell constants were determined from 25 reflections with 2θ values in the range from 12° to 26°. These were consistent with an orthorhombic crystal

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Table I. Crystal Data for $Re_2Cl_6[(S,S)\text{-isodiop}]\cdot CH_2Cl_2$

formula	$Re_2Cl_6P_2O_2C_{31}H_{32}\cdot CH_2Cl_2$
formula weight	1166.58
space group	$P2_12_12_1$
a, Å	15.039 (6)
b, Å	21.056 (7)
c, Å	12.299 (9)
V, Å^3	3895 (6)
Z	4
d_{calc}, g/cm^3	1.99
crystal size, mm	0.25 × 0.1 × 0.1
μ(Mo Kα), cm^{-1}	69.61
data collectn instrum	Rigaku AFC5R
radiatn monochromtd in incident beam (Mo Kα), Å	0.71073
no. of orientatn reflctns, range (2θ)	24; $12.73 \leq 2\theta \leq 26.76$
temp, °C	20 ± 1
scan method	$2\theta-\omega$
data collectn range, 2θ, deg	$4 \leq 2\theta \leq 50$
no. of unique data, total with $F_o > 3\sigma(F_o^2)$	3856, 1623
no. of param refined	235 (see text)
transmissn factors, max, min	1.00, 0.94
R^a	0.0556
$R_w{}^b$	0.0673
quality of fit indicator^c	1.244
largest shift/esd, final cycle	0.19
largest peak, e/Å^3	1.407

[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, $[\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{param})]^{1/2}$.

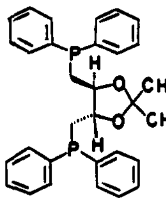

Figure 1. Schematic structure of (S,S)-diop.

system. The diffraction data were collected at 20 ± 1 °C on a Rigaku AFC5R diffractometer equipped with graphite monochromated Mo Kα (λ_α = 0.71037 Å) radiation. Data reduction was carried out by standard methods with the use of well-established computational procedures.[12]

The $\omega-2\theta$ data collection method was used to scan a possible 3856 data points in the range of $4° < 2\theta < 50°$. Three check reflections monitored throughout the data collection displayed no significant gain or loss in intensity. The structure factors were obtained after Lorentz and polarization corrections. Empirical absorption corrections based on azimuthal (ψ) scans of reflections of Eulerian angle χ near 90° were applied to the data.[13]

The Patterson methods program in SHELXS-86[14] led to the location of the positions of the rhenium atoms. The remaining atoms were found in a series of alternating difference Fourier maps and least-squares refinements. Anisotropic thermal parameters were used for the heavier atoms except carbon and oxygen atoms. The positions of two hydrogen atoms were calculated by using the Hydro program to help determine the chiralities of the ligand without further refinement. The final residuals of the first refinement were $R = 0.0624$, $R_w = 0.0753$, corresponding to an R,R configuration for the ligand. A change to the S,S enantiomorph gave much better residuals of 0.0556 and 0.0673. The chiralities of the ligand in this molecule are thus consistent with the S,S ligand used, and we are confident that we have the correct conformer.

Basic information pertaining to the crystal parameters and the structure refinement are summarized in Table I.

Results and Discussion

(a) Syntheses and Structure of β-$Re_2Cl_6[(S,S)$-isodiop]. The reaction of $Re_2(O_2CCH_3)_2Cl_4$, $(CH_3)_3SiCl$, and (S,S)-diop (Figure 1) in THF at room temperature gave a yellow-green solid. The UV–vis spectrum of the yellow-green solid showed two prominent peaks at 580 and 720 nm, which are consistent with the retention of a Re–Re quadruple bond. The $^{31}P\{^1H\}$ NMR spectrum of the solid showed two sets of peaks at 4.1 (J_{P-P} = 33 Hz) and 16.5 (J_{P-P} = 33 Hz) ppm consistent with the presence of two nonequivalent, coordinated phosphorus atoms that are coupled to each other. From these data we suggest that the structure of the yellow-green solid may be α-$Re_2Cl_6[(S,S)$-diop]. The two phosphorus atoms in this structure are not equivalent due to the lack of symmetry of the entire molecule. In this molecule one rhenium atom is in oxidation state II and the other is in oxidation state IV, a situation that has been found in the complex $Re_2Cl_4(OEt)_2(PPh_3)_2$.[10] Further study will be necessary to determine with certainty the nature of the yellow-green compound. By recrystallization of the yellow-green solid from CH_2Cl_2, the pink-red complex β-$Re_2Cl_6[(S,S)$-isodiop] was obtained. The pink-red complex can also be prepared directly by performing the same reaction in the CH_2Cl_2 solvent.

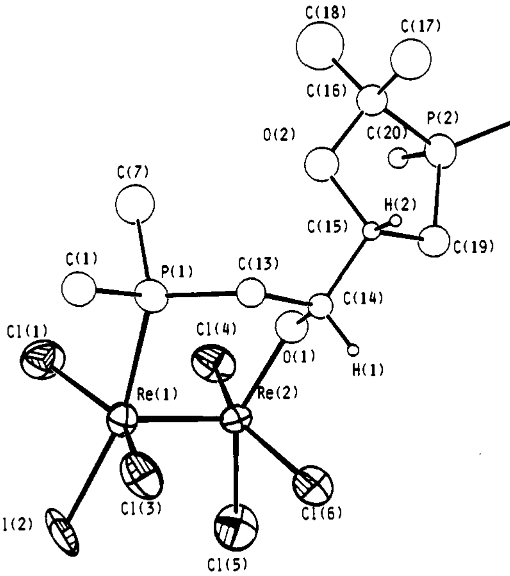

Figure 2. ORTEP drawing of $Re_2Cl_6[(S,S)$-isodiop]. The phenyl rings are represented by their first atoms for clarity.

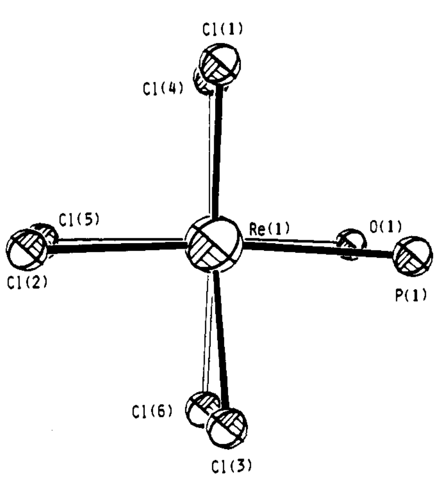

Figure 3. View looking down the Mo–Mo bond, showing only the ten central atoms.

The crystals of β-$Re_2Cl_6[(S,S)$-isodiop] belong to space group $P2_12_12_1$ with four molecules per unit cell. Figure 2 shows an ORTEP diagram of β-$Re_2Cl_6[(S,S)$-isodiop]. It is seen from this diagram that one oxygen atom (O(1)) and one phosphorus atom (P(1)) of the ligand are coordinated to the rhenium centers. This is the first structurally characterized example of a rhenium complex containing a Re–Re quadruple bond and a bridging bidentate ligand. The ligands in the complex[8] β-$Mo_2Cl_4[(S,S)$-bppm$]_2$ also bridge the metal centers through one oxygen atom and one

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Table II. Selected Bond Distances (Å) and Angles (deg) for $Re_2Cl_6[(S,S)$-isodiop$]\cdot CH_2Cl_2$[a]

atom 1	atom 2	distance	atom 1	atom 2	distance
Re(1)	Re(2)	2.224 (2)	P(2)	C(16)	1.87 (4)
Re(1)	Cl(1)	2.297 (12)	P(2)	C(19)	1.81 (4)
Re(1)	Cl(2)	2.349 (12)	P(2)	C(20)	1.77 (3)
Re(1)	Cl(3)	2.326 (11)	P(2)	C(26)	1.76 (4)
Re(1)	P(1)	2.447 (11)	O(1)	C(14)	1.40 (4)
Re(2)	Cl(4)	2.284 (11)	O(2)	C(15)	1.49 (4)
Re(2)	Cl(5)	2.345 (13)	O(2)	C(16)	1.42 (4)
Re(2)	Cl(6)	2.315 (12)	C(13)	C(14)	1.59 (5)
Re(2)	O(1)	1.94 (3)	C(14)	C(15)	1.53 (4)
P(1)	C(1)	1.82 (4)	C(15)	C(19)	1.52 (5)
P(1)	C(7)	1.88 (4)	C(16)	C(17)	1.51 (6)
P(1)	C(13)	1.79 (4)	C(16)	C(18)	1.67 (7)

atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
Re(2)	Re(1)	Cl(1)	107.2 (3)	C(1)	P(1)	C(13)	105 (2)
Re(2)	Re(1)	Cl(2)	108.0 (3)	C(7)	P(1)	C(13)	109 (2)
Re(2)	Re(1)	Cl(3)	105.4 (3)	C(16)	P(2)	C(19)	93 (2)
Re(2)	Re(1)	P(1)	91.1 (3)	C(16)	P(2)	C(20)	109 (2)
Cl(1)	Re(1)	Cl(2)	87.5 (4)	C(16)	P(2)	C(26)	113 (2)
Cl(1)	Re(1)	Cl(3)	147.0 (4)	C(19)	P(2)	C(20)	113 (2)
Cl(1)	Re(1)	P(1)	91.6 (4)	C(19)	P(2)	C(26)	112 (2)
Cl(2)	Re(1)	Cl(3)	87.6 (4)	C(20)	P(2)	C(26)	115 (2)
Cl(2)	Re(1)	P(1)	160.3 (4)	Re(2)	O(1)	C(14)	125 (2)
Cl(3)	Re(1)	P(1)	82.4 (4)	C(15)	O(2)	C(16)	109 (2)
Re(1)	Re(2)	Cl(4)	104.6 (3)	P(1)	C(13)	C(14)	114 (2)
Re(1)	Re(2)	Cl(5)	103.7 (3)	O(1)	C(14)	C(13)	115 (3)
Re(1)	Re(2)	Cl(6)	100.4 (3)	O(1)	C(14)	C(15)	111 (3)
Re(1)	Re(2)	O(1)	108.2 (7)	C(13)	C(14)	C(15)	109 (3)
Cl(4)	Re(2)	Cl(5)	86.7 (4)	O(2)	C(15)	C(14)	110 (2)
Cl(4)	Re(2)	Cl(6)	154.9 (4)	O(2)	C(15)	C(19)	107 (3)
Cl(4)	Re(2)	O(1)	86.8 (8)	C(14)	C(15)	C(19)	112 (3)
Cl(5)	Re(2)	Cl(6)	84.9 (4)	P(2)	C(16)	O(2)	100 (2)
Cl(5)	Re(2)	O(1)	148.0 (8)	P(2)	C(16)	C(17)	115 (3)
Cl(6)	Re(2)	O(1)	88.0 (8)	P(2)	C(16)	C(18)	107 (3)
Re(1)	P(1)	C(1)	105 (1)	O(2)	C(16)	C(17)	111 (3)
Re(1)	P(1)	C(7)	119 (1)	O(2)	C(16)	C(18)	106 (3)
Re(1)	P(1)	C(13)	113 (1)	C(17)	C(16)	C(18)	116 (3)
C(1)	P(1)	C(7)	105 (2)	P(2)	C(19)	C(15)	106 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

phosphorus atom. A view down the Re(1)–Re(2) axis is shown in Figure 3. It is seen from this projection that this molecule has an approximately eclipsed configuration and thus has nonchiral C_s symmetry in the central portion. β-$Re_2Cl_6[(S,S)$-isodiop$]$ shows no evidence of disorder in the metal atoms.

Important bond distances and angles are presented in Table II. The dimensions of the central Re_2Cl_6PO portion of the molecule are quite similar to those of $Re_2Cl_6(PEt_3)_2$ and $Re_2Cl_6(PMePh_2)_2$, except that this molecule has a Re–O distance of 1.94 (3) Å. The Re–Re distance in this molecule, 2.224 (2) Å, is completely normal for the Re–Re quadruple bond. The Re–Re distances in $Re_2Cl_6(PEt_3)_2$ and $Re_2Cl_6(PMePh_2)_2$ are 2.222 (3) and 2.227 (1) Å, respectively. The Re–Cl distances of β-$Re_2Cl_6[(S,S)$-isodiop$]$ show a slight trans influence by both the phosphorus atom and the oxygen atom. The Re–Cl bond distances in which the Cl is trans to the P or O atom are 2.345 (13) and 2.349 (12) Å, whereas the other four range from 2.284 (11) to 2.326 (11) Å with an average of 2.306 Å.

(b) Rearrangement of the (*S*,*S*)-diop Ligand. Figure 1 is a schematic drawing of the free ligand (*S*,*S*)-diop. Comparison of the structures of this free ligand and of the one coordinated to the complex shows that the (*S*,*S*)-diop ligand has been rearranged to give what we call (*S*,*S*)-isodiop. The complex β-$Mo_2Cl_4[(R,R)$-diop$]_2$ has been synthesized recently.[7] In this molecule the diop ligand retains its configuration, with the two phosphorus atoms coordinated to the molybdenum atoms, and the principal isomer of this complex was found to have a twist angle of ~78°. The oxidation states of the molybdenum metal centers are 2+ in this complex. The diop ligand has also been used intensively in the study of stereoselective catalytic reduction reactions by coordinating it to a transition metal in a low oxidation state,[15] e.g., Rh^{1+}. No change in the structure of the diop ligand has ever before been reported, so far as we can discover.

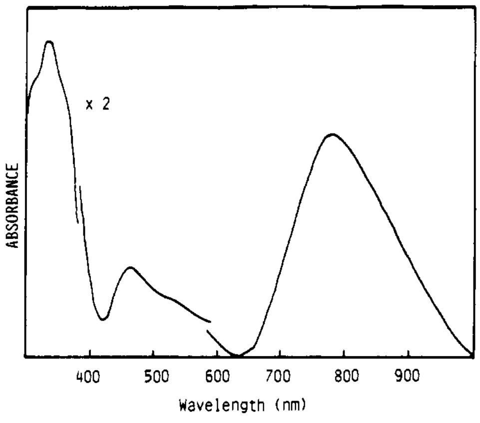
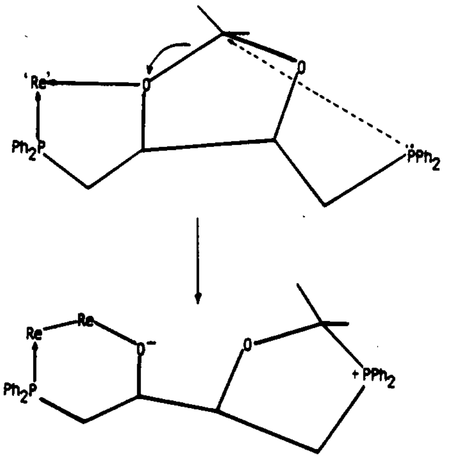


Figure 4. UV-vis-IR spectrum of $Re_2Cl_6[(S,S)$-isodiop$]$ in acetone solvent.

Scheme I. Transformation of the (*S*,*S*)-diop Ligand to the (*S*,*S*)-isodiop Ligand by Coordinating to the Re^{3+} Metal Centers



We believe that the rearrangement of diop to isodiop in the present case is attributable to Lewis acidity of the Re^{3+} metal centers (better Lewis acid than Mo^{2+}). As shown in Scheme I (where 'Re' may be all or part of the Re_2^{6+} core), the attack of the Re^{3+} ion on the oxygen atom promotes C–O bond breaking, and the high basicity of the uncoordinated phosphorus atom ensures the overlap of electrons on the phosphorus atom with the developing charge on the carbon, resulting in the formation of a stabilized phosphonium–oxo zwitterion. This process is similar to Lewis acid promoted ring openings of cyclic acetals that are well known in synthetic organic chemistry.[9] It will be clear in Scheme I that the rearrangement leaves the two chiral centers unchanged.

(c) Spectroscopic Studies. (1) UV–vis–IR Spectrum. Figure 4 shows the absorption spectrum of the β-$Re_2Cl_6[(S,S)$-isodiop$]$ in acetone solvent. The lowest energy band at 790 nm (12658 cm^{-1}) can be assigned to the $\delta \rightarrow \delta^*$ transition on the basis of detailed single-crystal polarized spectral studies[16] on $(Bu_4N)_2Re_2Cl_8$ and $Re_2Cl_6(PEt_3)_2$ and the results from a SCF-Xα-SW calculation for $Re_2Cl_8^{2-}$ ion.[17] A very weak band at 580 nm might be assigned to the $\delta \rightarrow \pi^*$ or $\pi \rightarrow \delta^*$ transition and the band at 480 nm might be assigned to a $\pi \rightarrow \pi^*$ transition. The other peaks are due to ligand to metal charge transfer (LMCT) transitions. The absorption spectra of complexes of the type $Re_2X_6(PR_3)_2$ (X = Cl, Br) also show their lowest energy electronic transition between 700 and 760 nm, together with several additional bands between 580 and 340 nm.[18]

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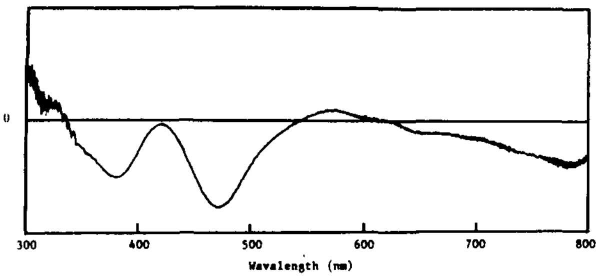

Figure 5. CD spectrum of $Re_2Cl_6[(S,S)$-isodiop] in acetone solvent.

(2) CD Spectrum. Circular dichroism (CD) can occur only if the electronic transition entails not only a charge translation but also a charge rotation, such that the two moments are not orthogonal.[19] If the chromophore is chiral, all allowed electronic transitions have both electric and magnetic moments that are not orthogonal and enable the CD spectrum to be measured. In the case of $Re_2Cl_6[(S,S)$-isodiop], however, the Re_2Cl_6PO core has a symmetry very closely approximating to C_s. In this symmetry all the transitions are both electrically and magnetically allowed, but the vectors are orthogonal, and no CD should occur for this molecule. In fact a CD spectrum has been recorded. Figure 5 shows the CD spectrum of the complex, $Re_2Cl_6[(S,S)$-isodiop] in acetone solvent. This CD spectrum has negative signs for the transitions at 790, 480, and 380 nm, and a positive sign for the one at 580 nm.

In order to explain the CD of this compound, we invoke the one-electron, static coupling mechanism. On the basis of the classification by Moscowitz,[5] the complex β-$Re_2Cl_6[(S,S)$-isodiop] falls into the "class II" category, that is, an intrinsically achiral chromophore, which gives rise to chiroptical effects through perturbation by chiral surroundings. The one-electron, static coupling mechanism has been discussed by Mason[19] and by Schellman.[20,21] This mechanism has also been used to account for the chiroptical properties of $Rh_2[(S)$-mandelate$]_4(EtOH)_2$ and $Rh_2[(R)$-α-methoxy-α-phenylacetate$]_4(THF)_2$,[22] and the $Mo_2Cl_4[(S,S)$-bppm$]_2$ complex.[8] The one-electron static coupling 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 1 and 2.[22]

$$|M_eL_o\rangle' = |M_eL_o\rangle + \langle M_mL_o|V|M_eL_o\rangle|M_mL_o\rangle(E_e - E_m)^{-1} \quad (1)$$

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

The function $|M_eL_o\rangle$ represents the state in which the chromophore (M) is in an electric dipole accessible state, and the surroundings (L) are in the ground state, while $|M_mL_o\rangle$ 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 $V = \sum e_ie_j/r_{ij}$. 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 1) or by the mixing of an electric dipole accessible excited state with a magnetically accessible one (eq 2). A transition from the ground state to one of the perturbed states will therefore be both electrically and magnetically allowed and a corresponding CD band should have nonzero intensity.

After mixing, the electric moment, μ_{oe} of the chromophore transition, which is taken to have its first-order value, acquires a magnetic moment, m_{eo} by first-order mixing, which can be described by eq 3,[22] where m_{mo} is the magnetic moment of the

$$m_{eo} = m_{mo}\langle M_mL_o|V|M_eL_o\rangle(E_e - E_m)^{-1} \quad (3)$$

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 4.[22]

$$\mu_{om} = \mu_{oe}\langle M_eL_o|V|M_mL_o\rangle(E_m - E_e)^{-1} \quad (4)$$

If the zero-order moments, μ_{oe} and m_{mo}, 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 5.[19]

$$R_{om} = -R_{oe} = i\mu_{oe}m_{mo}\langle M_eL_o|V|M_mL_o\rangle(E_e - E_m)^{-1} \quad (5)$$

We are now in a position to assign the peak at 790 nm in the CD spectrum. In the study of the UV-vis-IR spectrum we have argued that the peak at 790 nm can be assigned to the $\delta \rightarrow \delta^*$ transition. To assign this transition in the CD spectrum, we shall first assume that the main effect of the electrostatic perturbation, V, is the admixture of the higher Re(1)- and Re(2)-centered atomic orbitals ϕ to the δ^* orbital. A similar assumption has been used by Wagnière to discuss the optical activity for asymmetric ketones.[23] If we consider only the $Re_2Cl_6(PO)$ chromophore, which has C_s symmetry, the δ_{xy} orbital transforms as A″ and the δ^*_{xy} orbital also transforms as A″, assuming that the z axis is parallel to the Re–Re bond and the yz plane coincides with the symmetry plane. From these symmetries, it follows that the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition has the symmetry of A′, which is electric dipole allowed along the z axis.

To allow a nonorthogonal component of the magnetic dipole moment, ϕ must itself transform as A′, because R_z transforms as A″. Consequently, ϕ may be one of the linear combinations of p_y, p_z, $d_{x^2-y^2}$, d_{z^2} and d_{yz} orbitals. According to a calculation for the $Re_2Cl_8^{2-}$ ion,[17] the possible combinations that have energies greater than that of the δ^*_{xy} orbital are π^*_{yz}, $\sigma^*_{z^2}$, and $d_{x^2-y^2}$. Thus, we assign the CD transition at 790 nm to the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition, which obtains rotational strength by mixing of the electronic excited state into the magnetic excited state of one of the three transitions, $\delta_{xy} \rightarrow \pi^*_{yz}$, $\delta_{xy} \rightarrow \sigma^*_{z^2}$, and $\delta_{xy} \rightarrow d_{x^2-y^2}$. We think that the mixing is most probably due to the $\delta_{xy} \rightarrow \pi^*_{yz}$ transition. In the discussion of the UV-vis-IR spectrum we have stated that the weak band beside the one due to the $\delta \rightarrow \delta^*$ transition might be assigned to the $\delta \rightarrow \pi^*$ transition. This transition is also found in the CD spectrum at the same energy, and it has a positive sign, which is opposite to that of the $\delta_{xy} \rightarrow \delta^*_{xy}$ transition. This assignment is consistent with the prediction that after mixing the two transitions will acquire rotational strengths that have opposite signs, although the magnitudes of the rotational strengths are not equal.

It is interesting to note that although the causal process for the CD at the $\delta \rightarrow \delta^*$ transition is different in this case from what it was in the case of $[Re_2Cl_4[(S,S)$-dppb$]_2]^+$, we find the $\Delta\epsilon/\epsilon$ value to be approximately -2.5×10^{-3} while that reported[4] for the other compound is -6.0×10^{-3}.

Acknowledgment. We are grateful to the National Science Foundation for support. We also thank Professor David Giedroc of the Department of Biochemistry for very graciously allowing us to use his Jasco (J-600) CD spectrometer.

Supplementary Material Available: Complete table of positional and isotropic equivalent thermal parameters, bond distances, bond angles and torsional angles for the central portion of the molecule (8 pages); listings of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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