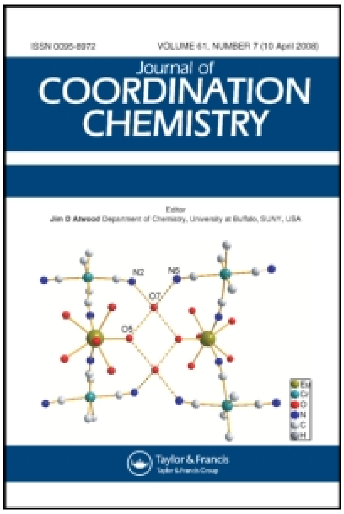

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TRANSITION METAL COMPLEXES OF 1,2-BIS(PHENYLSULFINYL) METHANE AND 1,2-BIS(PHENYLSULFINYL) ETHANE

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TRANSITION METAL COMPLEXES OF 1,2-BIS(PHENYLSULFINYL) METHANE AND 1,2-BIS(PHENYLSULFINYL) ETHANE

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Complexes of the meso and racemic forms of the disulfoxides 1,2-bis(phenylsulfinyl) methane and 1,2-bis (phenylsulfinyl) ethane have been synthesized and characterized. Bond type and ligand field parameters have been determined from infrared and visible-uv diffuse reflectance spectroscopy. There were essentially no observed differences in the properties of complexes of the meso and racemic forms of the ligands.

INTRODUCTION

Interest in sulfoxides as ligands in transition metal complexes began in 1959.[3] Dimethyl sulfoxide complexes of representative transition metal ions were the first to be studied extensively.[4–11] Coordination compounds of several other sulfoxides have been prepared and characterized.[12–18] The coordination chemistry of disulfoxides has received considerably less attention than that of monosulfoxides. Disulfoxides, because of the two sulfoxide groups, function as bidentate ligands. The first known report of the use of a disulfoxide as a ligand was the synthesis of complexes of 2,6-dithia-4-spiroheptane 2,6-dioxide.[19] Recently there have appeared reports of transition metal complexes of 1,2-bis-(methylsulfinyl) methane[15] and bis-(methylsulfinyl) ethane.[20,21,22] The present paper describes the syntheses and spectroscopic study of selected transition metal complexes of 1,2-bis(phenylsulfinyl) methane (PSM)* and 1,2-bis(phenylsulfinyl) ethane (PSE).† This study was undertaken because there are no known reports of complexes of these ligands and because disulfoxides contain two asymmetric centers which yield different isometric forms of the ligands. Specifically, it was of interest to compare complexes formed from the meso and racemic forms of the ligands. Most studies of bidentate ligands containing two asymmetric centers have been done with diamines, such as stilbene diamine[23], where definite differences in properties occur depending upon whether the meso or racemic forms of the ligands are coordinated. We were interested in determining whether or not disulfoxide complexes would show specific differences when the meso or racemic ligands were coordinated.

EXPERIMENTAL

Materials All chemicals used in the syntheses were at least reagent grade. Methanol was dried with Matheson, Coleman and Bell Linde Type 3A molecular sieve for 24–36 hours prior to use. The 2,2-dimethoxypropane was used as received from Aldrich Chemical Company. Metal perchlorates were purchased from G. F. Smith Chemical Company and were dried in vacuo over calcium hydride for 48–72 hours before use. Platinum(II) chloride was used as received from Alfa Inorganics, Inc.

Analyses All analyses were performed by Huffman Laboratories, Inc., 3830 High Court, P.O. Box 350, Wheatridge, Colorado.

Preparation of Compounds

The PSE ligand was synthesized by the procedure of Bell and Bennett[24] except that acetone was used as the solvent for the hydrogen peroxide oxidation of the parent disulfide. The mixture of PSE isomers was separated by multiple fractional crystallizations from acetone. An alpha isomer (m.p. 168°C) and a beta isomer (m.p. 123°C) were isolated.

The PSM ligand was prepared by modifying a method reported by Shriner, Struck and Jorison.[25] Sixty-six grams (0.30 moles) of thiophenol and fifty-

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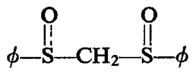
$\phi{-}\overset{\displaystyle O}{\overset{\|}{S}}{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{S}}{-}\phi$

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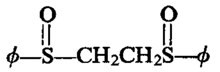
$\phi{-}\overset{\displaystyle O}{\overset{\|}{S}}{-}CH_2CH_2\overset{\displaystyle O}{\overset{\|}{S}}{-}\phi$

five grams (0.97 moles) of potassium hydroxide were dissolved in 200 milliliters of 95% ethanol. Then fifty-two grams (0.15 moles) of methylene bromide were added, with stirring, over a period of thirty minutes. The resulting mixture was heated on a steam bath for 3–4 hours. The disulfide product was then extracted into 500 milliliters of ether. The solution was evaporated to *ca.* 150 milliliters and cooled to precipitate the white crystalline disulfide (m.p. 32°C). The product was washed with ether and air dried. Yield—95%. The oxidation of the disulfide was essentially the same as that of Shriner *et al.*, except that it was carried out at room temperature. If the solution is heated during oxidation the beta isomer is decomposed. The mixture of PSM isomers was separated by fractional crystallization from acetone yielding an alpha isomer (m.p. 196°C) and a beta isomer (m.p. 104°C). The beta isomer has not been previously reported, therefore an elemental analysis was obtained. Calc. for $C_{13}H_{12}O_2S_2$: C, 59.06; H, 4.58; S, 24.25. Found: C, 58.33; H, 4.70; S, 23.44.

All tris(disulfoxide) complexes of Co(II), Ni(II), and Cu(II) with both isomers of PSE and the meso isomer of PSM were prepared as follows. Exactly 0.001 mole of the hydrated metal perchlorate was dissolved in 2.0 milliliters of methanol and dehydrated by addition of 2.0 milliliters of 2,2-dimethoxypropane.[26] Dehydration was effected by mild heating (40°C) and stirring for 2–3 hours. Then 0.003 moles of the respective ligand were dissolved in a minimum amount of 1:1 methanol—2,2-dimethoxypropane and the metal ion and ligand solutions were mixed and stirred for 2–3 hours at 30°C. After stirring, 50 milliliters of dry benzene was added and the volume reduced to cloud point by aspiration. The solution was then cooled in an ice bath and the resulting crystals were dried *in vacuo* over $CaCl_2$ for 12–15 hours.

Precaution

Transition metal complexes of organic ligands in which perchlorate ion is the anion, are known to be explosive. Sulfoxide complexes of the type studied here have been observed to decompose violently.[9] In this study a "mild" explosion occurred during transfer of a dried complex from a fritted glass filter funnel. For this reason, no melting or decomposition temperatures are reported in this paper.

Physical Measurements

Near infrared and visible diffuse reflectance spectra were obtained with a Cary, Model 14, recording spectrophotometer equipped with a Cell-Space Total Diffuse Reflectance Accessory, Model 1411750 and 151100. Near I.R. and visible solution spectra were obtained with the Cary 14 using 10 cm matched cells.

Infrared spectra were obtained as Nujol mulls between sodium chloride plates using a Perkin–Elmer Grating Infrared Spectrophotometer.

Nuclear Magnetic Resonance Spectra were recorded on a Varian A–60 NMR Spectrometer using deuterochloroform as solvent and tetramethylsilane as an internal standard. All NMR spectra were recorded at 24°C.

RESULTS

NMR Spectra

The alpha form of the PSM ligand gave a singlet at 4.00 ppm while the beta form gave a closely spaced multiplet centered at 4.13 ppm. The alpha form of PSE gave a singlet at 3.1 ppm and the beta form gave an A_2B_2 type multiplet centered at 3.1 ppm.

Analytical and Physical Data

Analytical and other data pertaining to the meso and racemic forms of PSE and PSM complexes are listed in Table I.

Infrared Spectra

Pertinent infrared data for the free ligands and the complexes are listed in Table II.

Visible and Near-Infrared Spectra

Diffuse reflectance spectra, transition assignments, and relative band intensities for the complexes are presented in Table III.

Crystal Field Parameters

Some crystal field parameters and calculated vs. observed absorption frequencies are listed in Table IV. Derivations and interpretation of these results are included in the Discussion section.

DISCUSSION

Differences in NMR spectra of meso and racemic PSM were used to assign configurations.[20] Only the meso PSM could have diastereotopic methlyene hydrogens which are non-equivalent, whereas, the

TABLE I

Analytical and Other Data of Meso and Racemic PSM and PSE Complexes

Compound	Color	Calculated C	Calculated H	Calculated S	Found C	Found H	Found S
Cu(*meso*-PSE)$_3$ (ClO$_4$)$_2$	green	45.96	3.85	17.53	46.56	3.72	16.99
Ni(*meso*-PSE)$_3$ (ClO$_4$)$_2$[a]	green	46.16	3.87	17.60	45.75	3.88	16.99
Co(*meso*-PSE)$_3$ (ClO$_4$)$_2$	pink	46.15	3.87	17.60	45.95	3.65	17.69
Pt(*meso*-PSE)Cl$_2$	brown	30.89	2.59		30.42	2.80	
Cu(*rac*-PSE)$_3$ (ClO$_4$)$_2$	white	45.96	3.85	17.53	45.80	3.77	17.20
Ni(*rac*-PSE)$_3$ (ClO$_4$)$_2$[a]	green	46.16	3.87	17.60	47.00	4.23	16.83
Co(*rac*-PSE)$_3$ (ClO$_4$)$_2$	pink	46.15	3.87	17.60	45.94	3.99	17.33
Pt(*rac*-PSE)Cl$_2$	brown	30.89	2.59		30.36	2.56	
Cu(*meso*-PSM)$_3$ (ClO$_4$)$_2$	green	44.42	3.44	18.24	44.76	3.74	18.67
Ni(*meso*-PSM)$_3$ (ClO$_4$)$_2$[a]	green	44.58	3.45	18.31	44.72	4.05	17.27
Co(*meso*-PSM)$_3$ (ClO$_4$)$_2$	pink	44.57	3.45	18.31	44.15	3.71	18.74
Cu(*rac*-PSM)$_3$ (ClO$_4$)$_2$	green	44.42	3.44	18.24	38.87	3.56	14.52
Ni(*rac*-PSM)$_3$ (ClO$_4$)$_2$[a]	green	44.58	3.45	18.31	44.08	4.42	17.03
Co(*rac*-PSM)$_3$ (ClO$_4$)$_2$	pink	44.57	3.45	18.31	46.33	4.03	16.75

[a] hygroscopic

TABLE II

Infrared Data

Compound	V_{so}(cm^{-1})	ΔV_{so}(cm^{-1})	V_{cs}(cm^{-1})
meso-PSE	$1042^{\text{s, sh}}$		735^{w}
Pt(*meso*-PSE)Cl$_2$	$1156^{\text{s, sh}}$	-114	N.O.[b]
Cu(*meso*-PSE)$_3$ (ClO$_4$)$_2$	$952^{\text{s, b}}$, $966^{\text{s, sh}}$	90, 76	760^{vw}
Co(*meso*-PSE)$_3$ (ClO$_4$)$_2$	$980^{\text{s, b}}$	62	752^{vw}
Ni(*meso*-PSE)$_3$ (ClO$_4$)$_2$	$980^{\text{s, b}}$	62	757^{vw}
rac-PSE	$1042^{\text{s, sh}}$		725^{w}
Pt(*rac*-PSE)Cl$_2$	$1156^{\text{s, sh}}$	-114	N.O.
Cu(*rac*-PSE)$_3$ (ClO$_4$)$_2$	$961^{\text{s, sh}}$, $971^{\text{a, m}}$	81, 71	766^{m}
Co(*rac*-PSE)$_3$ (ClO$_4$)$_2$	$980^{\text{s, vb}}$, $990^{\text{a, m}}$	62, 52	763^{m}
Ni(*rac*-PSE)$_3$ (ClO$_4$)$_2$	$980^{\text{s, vb}}$	62	N.O.
meso-PSM	$1047^{\text{s, sh}}$		725^{m}
Cu(*meso*-PSM)$_3$ (ClO$_4$)$_2$	$952^{\text{a, s}}$,$980^{\text{s, sh}}$	90, 66	N.O.
Co(*meso*-PSM)$_3$ (ClO$_4$)$_2$	995^{s}	52	N.O.
Ni(*meso*-PSM)$_3$ (ClO$_4$)$_2$	990^{s}	57	N.O.
rac-PSM	$1047^{\text{s(sh}}$		725^{m}
Cu(*rac*-PSM)$_3$ (ClO$_4$)$_2$	$985^{\text{s, b}}$, $1047^{\text{s, sh}}$	62, 0	N.O.
Co(*rac*-PSM)$_3$ (ClO$_4$)$_2$	$995^{\text{s, b}}$, $1047^{\text{s, sh}}$	52, 0	N.O.
Ni(*rac*-PSM)$_3$ (ClO$_4$)$_2$	$990^{\text{s, b}}$, $1047^{\text{s, sh}}$	57, 0	N.O.

[a] V_{so} (free disulfoxide) − V_{so}(complexes).

[b] V_{cs} is not observed because phenyl rings bands overlap the V_{cs} bands.

Abbreviations: a, shoulder; b, broad; sh, sharp; s, strong; m, medium; w, weak.

**

TABLE III

Diffuse Reflectance Spectra, Band Assignments and Relative Intensities

Compound	λmax(cm^{-1})		Assignment	R.I.[a]
Co(*meso*-PSM)$_3$(ClO$_4$)$_2$	7,460	V$_1$	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	.57
	14,290[c]	V2	$\rightarrow {}^4A_{2g}(F)$	.20
	18,520	V$_3$	$\rightarrow {}^4T_{1g}(P)$	1.00
	20,580[d]			.70
Co(*rac*-PSM)$_3$(ClO$_4$)$_2$[b]	7,630	V1	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	.39
	14,700[c]	V$_2$	$\rightarrow {}^4A_{2g}(F)$	.18
	18,850	V^3	$\rightarrow {}^4T_{1g}(P)$	1.00
	20,410[d]			.76
Co(*meso*-PSE)$_3$(ClO$_4$)$_2$	7,630	V1	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	.54
	14,800[c]	V$_2$	$\rightarrow {}^4A_{2g}(F)$	.32
	18,590	V$_3$	$\rightarrow {}^4T_{1g}(P)$	1.00
	20,410[d]			.68
Co(*rac*-PSE)$_3$(ClO$_4$)$_2$	7,580	V$_1$	$^4T_{1g} \rightarrow {}^4T_{2g}(F)$	.73
	14,800[c]	V$_2$	$\rightarrow {}^4A_{2g}(F)$	.18
	17,920	V$_3$	$\rightarrow {}^4T_{1g}(P)$	1.00
	19,760[d]			.67
Ni(*meso*-PSM)$_3$(ClO$_4$)$_2$	7,630[c]	V$_1$	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	.53
	13,360	V$_2$	$\rightarrow {}^3T_{1g}(F)$	.58
	14,490[d]			.47
	23,920	V$_3$	$\rightarrow {}^3T_{1g}(P)$	1.00
Ni(*rac*-PSM)$_3$(ClO$_4$)$_2$	8,030[c]	V$_1$	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	.44
	12,660			.52
	13,460[d]	V$_2$	$\rightarrow {}^3T_{1g}(F)$	.42
	23,810	V$_3$	$\rightarrow {}^3T_{1g}(P)$	1.00
Ni(*meso*-PSE)$_3$(ClO$_4$)$_2$	7,600[c]	V$_1$	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$	.79
	13,160	V$_2$	$\rightarrow {}^3T_{1g}(F)$	.71
	14,290[d]			.57
	23,920	V$_3$	$\rightarrow {}^3T_{1g}(P)$	1.00
Ni(*rac*-PSE)$_3$(ClO$_4$)$_2$	7,650[c]	V^1	$^3A_g \rightarrow {}^3T_{2g}(F)$	.59
	13,480	V$_2$	$\rightarrow {}^3T_{1g}(F)$	.61
	14,490[d]			.51
	24,270	V^3	$\rightarrow {}^3T_{1g}(P)$	1.00
Cu(*meso*-PSM)$_3$(ClO$_4$)$_2$	10,000[c, d]			.59
	12,470		$^2E_g \rightarrow {}^2T_{2g}$	1.00
Cu(*rac*-PSM)$_3$(ClO$_4$)$_2$[b]	9,800[c, d]			.71
	12,350		$^2E_g \rightarrow {}^2T_{2g}$	1.00
Cu(*meso*-PSE)$_3$(ClO$_4$)$_2$	12,630		$^2E_g \rightarrow {}^2T_{2g}$	1.00
Cu(*rac*-PSE)$_3$(ClO$_4$)$_2$	9,620[c, d]			.61
	12,660		$^2E_g \rightarrow {}^2T_{2g}$	1.00

[a] Relative intensity using the maximum absorption = 1.00.
[b] impure sample.
[c] broad band, value given is estimate.
[d] shoulder.

racemic mixture of the active form would have equivalent methylene hydrogen atoms. Therefore, the alpha isomer, which gave a singlet, must be the racemic mixture and the beta isomer is assigned the meso configuration.

Configurational assignment is not as straight forward for PSE as for PSM. Molecular models would lead one to predict that both isomers should give multiplets for the methylene hydrogens and, in fact, both isomers of 1,2-bis(*methyl*sulfinyl) ethane do give multiplets. The lack of multiplicity for tha alpha isomer can only be ascribed to an accidental degeneracy of the methylene hydrogens. Fortunately, Taddei[27] resolved the alpha isomer into its optically active components, hence the alpha isomer must be the racemic mixture and the beta isomer is the meso configuration.

The differences in NMR spectra were useful in

TABLE IV

Calculated Crystal Field Parameters

Compound	Dq(cm^{-1})	B(cm^{-1})	$V_{1\,exp.}$(cm^{-1})	$V_{1\,cal.}$(cm^{-1})
Ni(*rac*-PSE)$_3$(ClO$_4$)$_2$	809	899	7600	8090
Ni(*meso*-PSE)$_3$(ClO$_4$)$_2$	792	901	7550	7920
Ni(*rac*-PSM)$_3$(ClO$_4$)$_2$	812	863	8030	8120
Ni(*meso*-PSM)$_3$(ClO$_4$)$_2$	799	884	7630	7990
			$V_{2\,exp.}$(cm^{-1})	$V_{2\,cal.}$(cm^{-1})
Co(*rac*-PSE)$_3$(ClO$_4$)$_2$	862	759	14,800	16,200
Co(*meso*-PSE)$_3$(ClO$_4$)$_2$	869	802	14,800	16,300
Co(*rac*-PSM)$_3$(ClO$_4$)$_2$	869	797	14,700	16,330
Co(*meso*-PSM)$_3$(ClO$_4$)$_2$	863	800	14,290	16,500

determining purity of each form of the ligands. Recrystallizations were continued until NMR signals indicated 99–100% purity for a given form of a ligand.

All complexes listed in Table I were prepared at least twice and results were completely reproducible except for the complexes of racemic PSM. Data presented later (I.R. spectra) indicate that complexes prepared with racemic PSM (as well as the platinum complexes of both meso and racemic PSM) have some uncoordinated S = O groups as well as some water and/or solvent impurities. The reasons for this are not entirely clear, although studies of molecular models indicate that pure tris (racemic PSM) complexes would be sterically strained using any combination of isomer coordination.

With coordination via the sulfur atom, the platinum complexes of PSE would have 5 membered chelate rings while PSM would chelate so as to give a four membered ring. The inherent instability of four membered ring chelates coupled with the bulky steric hindrance of phenyl groups undoubtedly explains the inability of platinum to form pure PSM complexes.[28, 29]

Pertinent infrared data for the ligands and complexes are listed in Table II. The intense band around 1000 cm^{-1} is assigned to the S = O stretch[30, 31], and the band at about 750 cm^{-1} to the C–S stretch.[32] Infrared spectra of the PSM and PSE complexes are similar to those of other transition metal complexes of mono- and disulfoxides.[3-11, 21, 22] Upon coordination the sulfur-oxygen stretch of sulfoxides is shifted relative to the frequency in a free sulfoxide. It has been demonstrated[5, 10] and verified by X-ray studies[11] that the shift in the S = O stretching frequency can be used to determine whether coordination in a sulfoxide complex is through the oxygen or the sulfur atom. In all complexes, except those of platinum, the S = O band is shifted to frequencies lower than that for the free disulfoxide (see ΔV_{so} in Table II). For the platinum complexes the shifts are to higher frequencies. Therefore, it is concluded that coordination is through the oxygen in all complexes except the platinum(II) compounds where coordination is via the sulfur atom. All complexes (except platinum) also showed intense bands at *ca.* 1100 cm^{-1} and 625 cm^{-1} which are assigned to uncoordinated perchlorate ion.[32, 33]

Complexes prepared with racemic PSM and platinum complexes of both meso and racemic PSM have infrared bands identical to that of the free ligand S = O infrared frequency. This fact indicates that the PSM is not completely bidentially chelated but coordinates, at least partially, as a monodentate ligand. In addition, the Co(II), Ni(II) and Cu(II) racemic PSM complexes display weak absorption bands in the 3200–3000 cm^{-1} and 1700–1500 cm^{-1} region indicative of the presence of water and/or solvent. These complexes are probably mixtures of tris bidentate compounds and complexes in which the disulfoxides function as monodentate ligands with water or solvent at the other coordination site(s).

There are surprisingly small differences in the infrared spectra of complexes of meso and racemic forms of PSE. The copper complexes show the greatest difference, but nothing outstanding. In the spectrum of [Cu(meso-PSE)$_3$](ClO$_4$)$_2$ the S = O band is sharp with a shoulder at higher frequency while in the complex of racemic PSE there are two distinct sharp peaks separated by *ca.* 14 cm^{-1}. The peak doubling would indicate distortion from O_h symmetry with a greater degree of distortion for the complex of racemic PSE.

Diffuse reflectance spectra and transition assignments are presented in Table III. The absorption maxima and intensities are typical of octahedral complexes of weak field ligands and are similar to other sulfoxide complexes possessing at least approximate O_h symmetry.[7,21] The $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ transition for nickel(II) complexes appears as a very broad band at *ca.* 7600 cm^{-1}. The $^4T_{1g}(F) \rightarrow {}^4T_{1g}(F)$ transition for cobalt (II) complexes is a shoulder at *ca.* 14,800 cm^{-1}. The difficulty in accurate determination of the maxima of these bands severely limits their use in calculation of ligand field parameters.[34] For this reason, v_2 and v_3 were used to evaluate the ligand field parameters Dq and B for the nickel complexes and v_1 and v_3 were used to calculate the parameters for the cobalt complexes. The graphic method of Lever was used to calculate values of Dq and B, and the position of the other spin allowed transition (v_1 for Ni(II), and v_2 for Co(II)).[35] The results are given in Table IV.

The magnitude of the Racah parameters, B, indicate a fairly high degree of covalency in the ligand-metal bonds.[36,37] The Dq values for PSM and PSE are larger than have been observed for monodentate sulfoxide complexes, probably due in part to the bidentate nature of the disulfoxides. It may be expected that PSM, which gives 6 membered chelate rings, would have a significantly higher Dq value than PSE which yields 7 membered chelate rings. The fact that the Dq values of both ligands are approximately identical supports the supposition that there is considerable steric strain in the complexes of PSM.

The data indicate that there is very little difference in the properties of the complexes of the meso and racemic forms of the two disulfoxides studied. In fact, there is even little observed difference between the two disulfoxides. This is in contrast to what has been found for diamines. The explanation for this is probably twofold: (1) the disulfoxides are "weaker" ligands and the metal-ligand bond distances may be sufficiently large as to diminish stereochemical influences of the ligands, and (2), the stereochemical effects of the six and seven membered chelate rings formed in these complexes may be negligible when compared to the five membered ring systems inherent in most studies of diamine complexes.

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