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Complexes of Sulfoxides. I. Octahedral Complexes of Manganese(II), Iron(II), Cobalt(II), Nickel(II), and Zinc(II)

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Eighteen octahedral manganese(II), iron(II), cobalt(II), nickel(II), and zinc(II) complexes of RR′SO (where R and R′ are phenyl, phenyl and methyl, *n*-propyl, and *n*-butyl) have been synthesized. The manganese(II), cobalt(II), and nickel(II) complexes exhibit normal high-spin magnetic behavior. From infrared spectra it is inferred that all of the ligands coordinate through the oxygen. The S–O stretching vibration frequency of 1055 to 1011 cm^{-1} in the ligand is reduced to 990–968 cm^{-1} in the complexes. The downward shift relative to the free ligand is 28–58 cm^{-1}. Selected infrared bands in the ligands and complexes are assigned.

Introduction

Since 1960 a considerable amount of literature[2–13] has been published on dimethyl sulfoxide and tetramethylene sulfoxide complexes of the first transition series, platinum(II), and palladium(II). A recent preliminary report[14] includes the synthesis of octahedral complexes of diphenyl sulfoxide with members of the first transition series. Early general agreement based on infrared studies that oxygen acts as a donor atom toward members of the first transition series and that sulfur is the donor atom in platinum(II) and palladium(II) complexes has been verified. Bennett, Cotton, and Weaver[12] found that the conclusions from infrared studies are correct for *trans*-$[FeCl_2((CH_3)_2SO)_4][FeCl_4]$ and *trans*-$[PdCl_2((CH_3)_2SO)_2]$.

There is some disagreement regarding the assignment of the S–O stretching and CH_3 rocking vibrations in dimethyl sulfoxide oxygen-bonded complexes. Some authors[5,6] assign the S–O stretching fundamental to a band near 1000 cm^{-1} and the CH_3 rocking vibration to a band near 930 cm^{-1}. Other authors[4,8,11] reverse the assignments. Because the S–O stretching fundamental and the methyl group vibrations are coupled in dimethyl sulfoxide,[15] the assignments are uncertain.

It has been suggested[3] that the frequency shift of the S–O stretching vibration upon oxygen coordination is proportional to the strength of the metal–oxygen bond. Based on this assumption, the following stability order[6] has been proposed for dimethyl sulfoxide complexes with perchlorate anions: copper(II) > lead(II) > iron(II) > cobalt(II) > manganese(II) > nickel(II).

Experimental Section

The synthetic methods of 18 complexes representing five different metals with various sulfoxide ligands are listed in Table I along with their colors, melting points, and elemental analyses.

Chemicals.—The following chemicals were obtained from the Aldrich Chemical Co., Inc.: di-*n*-propyl sulfoxide, di-*n*-butyl sulfoxide, and diphenyl sulfoxide. Dimethyl sulfoxide was obtained from the Crown Zellerbach Chemical Products Division and phenyl methyl sulfoxide was a gift from Dr. K. K. Andersen.[16] The hydrated metal perchlorate salts were obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio. All other chemicals were of reagent grade quality. Liquid sulfoxides were dried over barium oxide and in some cases were vacuum distilled.

Synthetic Method A.—This was based on the procedure given by Meek, Drago, and Piper.[10] The appropriate hydrated perchlorate salt (0.002 mole) was dissolved in a minimum amount of methanol. A 0.02 molar quantity of 2,2-dimethoxypropane was added to this solution and to a second flask containing the appropriate ligand (0.012 mole). Both flasks were stoppered and stirred at 40° for 2.5 hr. The ligand solution was added to the metal ion solution and the resulting mixture was stirred for an additional 30–60 min. In the instances where crystalli-

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[1] (a) This report is based on a thesis submitted by William F. Currier to the Graduate School of the University of New Hampshire in partial fulfillment of the requirements of the Master of Science degree; (b) author to whom correspondence should be addressed.

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Table I

Synthetic Methods and Characterization of Metal Sulfoxide Complexes

Compound	Syn method	Color	Mp,[a] °C	Analyses, %						Magnetic susceptibility data		
				Calcd			Found			Temp, °C	χ_M,[b,c] cgs × 10^6	Magnetic moment, BM
				H	C	S	H	C	S			
$[Co((C_6H_5)(CH_3)SO)_6](ClO_4)_2$	A	Pink	196–198	4.37	45.91	17.51	4.64	45.87	17.69	16	10,610	4.97
										17	10,200	4.89
$[Ni((C_6H_5)(CH_3)SO)_6](ClO_4)_2$	A	Pale green	214–216	4.37	45.92	17.51	4.48	45.39	17.18	16	4,820	3.35
								45.60		19	4,630	3.29
$[Mn((C_6H_5)(CH_3)SO)_6](ClO_4)_2$	A	White	150.5–152	4.39	46.08	17.57	4.39	45.08	17.73	18	16,000	6.13
							4.20	45.16		17	15,130	5.94
$[Fe((C_6H_5)(CH_3)SO)_6](ClO_4)_2$	B	Pale yellow	152–154	4.38	46.04	17.56	4.44	45.41	17.16			
$[Zn((C_6H_5)(CH_3)SO)_6](ClO_4)_2$	B	White	174.5–176	4.34	45.65	17.41	4.30	45.79	17.34			
$[Co((C_6H_5)_2SO)_6](ClO_4)_2$	A	Pink	193–194	4.08	58.79	13.10	4.18	58.43	12.61	13	10,780	5.11
									12.74	18	10,570	5.00
$[Ni((C_6H_5)_2SO)_6](ClO_4)_2$	A	Pale green	197–199	4.08	58.80	13.08	4.20	58.66	12.80	14	4,970	3.41
										19	4,700	3.32
$[Mn((C_6H_5)_2SO)_6](ClO_4)_2$	A	White	169–171	4.09	58.95	13.11	4.31	59.25	13.40	17	15,530	6.02
										17	15,120	5.94
$[Fe((C_6H_5)_2SO)_6](ClO_4)_2$	B	Pale yellow	159–160	4.09	58.91	13.11	4.20	58.83	12.96			
$[Zn((C_6H_5)_2SO)_6](ClO_4)_2$	B	White	176–178	4.06	58.53	13.02	4.16	57.70	13.08			
$[Co((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$	A	Pink	114–116	7.91	40.69	18.10	7.79	40.47	18.18	16	11,920	5.25
										19	11,350	5.17
$[Ni((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$	A	Pale yellow	159–161	7.91	40.70	18.11	7.89	41.06	18.09	16	5,130	3.46
										19	5,120	3.46
$[Mn((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$	A	White	109–111.5	7.94	40.84	18.17	8.02	41.05	18.28	16	16,300	6.16
										18	15,380	6.02
$[Fe((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$	B	Pale yellow	105–107.5	7.93	40.81	18.16	8.00	40.92	18.24			
$[Zn((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$	A	White	74–76	7.86	40.45	17.99	7.80	40.44	18.22			
$[Co((n\text{-}C_4H_9)_2SO)_6](ClO_4)_2$	C	Pink	82.5–84	8.78	46.84	15.63	8.81	46.87	15.69	18	10,730	5.03
										17	10,470	4.94
$[Ni((n\text{-}C_4H_9)_2SO)_6](ClO_4)_2$	C	Pale yellow	95–97	8.78	46.85	15.63	8.66	46.89	15.63	18	4,870	3.39
										18	4,940	3.41
$[Mn((n\text{-}C_4H_9)_2SO)_6](ClO_4)_2$	C	White	53–56	8.70	47.00	15.68	8.70	46.80	15.58			
$Zn(ClO_4)_2 \cdot 5(CH_3)_2SO$	A	White	192–194	4.62	18.34		4.66	18.20				

[a] Uncorrected. [b] Molar susceptibility corrected for total diamagnetism. [c] The first value for each complex was obtained at 8.6 kgauss; the second at 5.6 kgauss.

zation did not immediately occur, the solution was concentrated and approximately 5 ml of anhydrous ethyl ether was added. Crystals formed immediately; they were filtered, pressed between filter paper, and dried *in vacuo* over calcium chloride for 10–15 hr. The complexes obtained from this procedure required no further purification.

Synthetic Method B.—These complexes were prepared according to the procedure outlined by Selbin, *et al.*[6] The hydrated perchlorate salt (0.002 mole) was dried over calcium chloride in a vacuum desiccator. It and the appropriate ligand (0.012 mole) were separately dissolved in a minimum amount of acetone and stirred at 30° for 30 min. The ligand solution was added to the metal ion solution, and the resulting solution was stirred at 30° for 30 min. The solvent was evaporated by means of an aspirator until the solution became cloudy. Upon the addition of approximately 5 ml of dry ethyl ether, fine crystals formed. The crystals were filtered, pressed between filter paper, and dried *in vacuo* over calcium chloride for 10–15 hr. No further purification was required for these complexes.

Synthetic Method C.—The hydrated metal perchlorate salt (0.002 mole) was dissolved in a minimum amount of methanol. To this solution 2,2-dimethoxypropane (0.02 mole) was added and the flask was stoppered and stirred at 50° for 2.5 hr. The ligand (0.013 mole) was also dissolved in 2,2-dimethoxypropane and stirred for 2.5 hr at 50°. The two solutions were mixed and stirred for 30–60 min at a temperature of 50°. The solvent was then evaporated until a heavy oil was obtained. The oil was then dissolved in dichloromethane, placed in a hood, and allowed to evaporate at room temperature to a solid residue. To recrystallize the complex it was dissolved in a minimum amount of methanol. Approximately 5 ml of 2,2-dimethoxypropane and 1 ml of ligand were added. The resulting solution was placed on a magnetic stirrer for 30 min at a temperature of 50°. The solvent was then evaporated and dry ethyl ether was added. Crystals were formed, then were filtered and dried *in vacuo* over calcium chloride for 10–15 hr.

Melting Point Determination.—Melting points were obtained with a Thomas-Hoover capillary melting point apparatus.

Infrared Spectra.—Infrared spectra of all complexes were obtained from a Perkin-Elmer Model 337 grating infrared spectrophotometer. Solid spectra were obtained from Nujol and Halocarbon mulls employing sodium chloride salt plates. Solution spectra were obtained from solutions in Spectrograde nitromethane using 0.100-mm matched sodium chloride liquid cells. Polystyrene was used to calibrate each spectrum. Frequency assignments are accurate within ±5 cm^{-1}.

Magnetic Susceptibility Measurements.—Magnetic susceptibility measurements were performed by the Gouy method[17] on a Varian Associates V-4004 magnet system in conjunction with a Mettler H16 semimicro balance. A Gouy tube with a standard taper stopper was used. The standard sample used was Hg-

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[17] B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 400.

TABLE II

INFRARED ABSORPTION DATA OF RR'SO AND THEIR COMPLEXES[g]

Compound	ν_{CH_3}, cm^{-1} [f]	ν_{SO}, cm^{-1} [f]	$\Delta\nu_{SO}$,[a] cm^{-1}	ν_{C-S}, cm^{-1}
$(CH_3)(C_6H_5)SO$	950 s[c] [955 s][d]	1050 vs [1045 vs]	...	670 w [670 w]
$[Ni((CH_3)(C_6H_5)SO)_6](ClO_4)_2$	950 s [960 s]	982 vs [983 vs]	...	720 w [719 w]
$[Fe((CH_3)(C_6H_5)SO)_6](ClO_4)_2$	947 s	983 vs	...	720 w
$[Co((CH_3)(C_6H_5)SO)_6](ClO_4)_2$	950 s [945 s]	984 vs [984 vs]	...	720 w [718 w]
$[Zn((CH_3)(C_6H_5)SO)_6](ClO_4)_2$	949 s	987 vs	...	720 w
$[Mn((CH_3)(C_6H_5)SO)_6](ClO_4)_2$	950 s [960 s]	991 vs [990 vs]	...	720 w [720 w]
$(CH_3)_2SO$[b]	954 s	1055 vs [1045 vs]	...	698 m, 675 m
$[Ni((CH_3)_2SO)_6](ClO_4)_2$	950 s [950 s]	1000 vs [995 vs]	...	715 m [715 m]
$[Fe((CH_3)_2SO)_6](ClO_4)_2$	950 s	985 vs	...	720 m
$[Co((CH_3)_2SO)_6](ClO_4)_2$	948 s [945 s]	1000 vs [995 vs]	...	715 m [715 m]
$Zn(ClO_4)_2 \cdot 5(CH_3)_2SO$[e]	947 s	997 vs	...	718 m
$[Mn((CH_3)_2SO)_6](ClO_4)_2$	955 s [950 s]	1000 vs [998 vs]	...	720 m [720 m]
$(n\text{-}C_4H_9)_2SO$		1030 vs [1019 vs]	...	685 vw
$[Ni((n\text{-}C_4H_9)_2SO)_6](ClO_4)_2$		974 vs [970 vs]	56 [49]	NO
$[Co((n\text{-}C_4H_9)_2SO)_6](ClO_4)_2$		973 vs [972 vs]	57 [47]	NO
$[Mn((n\text{-}C_4H_9)_2SO)_6](ClO_4)_2$		972 vs [985 vs]	58 [34]	NO
$(C_6H_5)_2SO$		1035 vs [1020 vs]	...	670 vw
$[Ni((C_6H_5)_2SO)_6](ClO_4)_2$		979 vs [978 vs]	56 [42]	720 vw [720 vw]
$[Fe((C_6H_5)_2SO)_6)](ClO_4)_2$		985 vs	50	720 vw
$[Co((C_6H_5)_2SO)_6](ClO_4)_2$		982 vs [980 vs]	53 [40]	720 vw [720 vw]
$[Zn((C_6H_5)_2SO)_6](ClO_4)_2$		989 vs	46	718 vw
$[Mn((C_6H_5)_2SO)_6](ClO_4)_2$		990 vs [990 vs]	45 [30]	720 vw [720 vw]
$(n\text{-}C_3H_7)_2SO$		1017 vs [1011 vs]	...	685 vw
$[Ni((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$		968 vs [970 vs]	49 [41]	NO
$[Fe((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$		975 vs	42	NO
$(Co((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$		972 vs [972 vs]	45 [39]	NO
$[Zn((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$		976 vs	41	NO
$[Mn((n\text{-}C_3H_7)_2SO)_6](ClO_4)_2$		982 vs [983 vs]	35 [28]	NO

[a] $\nu_{RR'SO} - \nu_{complex}$. [b] See ref 6 for synthesis of dimethyl sulfoxide complexes. [c] Nujol mull or neat. [d] Values in brackets refer to nitromethane solutions. [e] Infrared shows no uncomplexed $(CH_3)_2SO$. [f] ν_{CH_3} and ν_{SO} are coupled in dimethyl sulfoxide, phenyl methyl sulfoxide, and their complexes. [g] Abbreviations: s, strong; m, medium; w, weak; vw, very weak; NO, not observed.

$[Co(SCN)_4]$. Susceptibility measurements were obtained at 8.6 and 5.6 kgauss. The susceptibility values were corrected for the ligand and anion using the method described by Figgis and Lewis.[17]

Carbon, Hydrogen, and Sulfur Analyses.—Analyses for carbon, hydrogen, and sulfur were performed and reported by Galbraith Laboratories, Inc., Knoxville, Tenn.

Discussion

Magnetic Susceptibility.—The magnetic moments of the sulfoxide complexes in Table I are in the expected range for octahedral high-spin cobalt(II), nickel(II), and manganese(II) complexes.[18] The magnetic moments of the octahedral cobalt(II) sulfoxide complexes fall in the expected range of 4.9–5.2 BM. The values of octahedral cobalt(II) dimethyl sulfoxide[2] and tetramethylene sulfoxide[9] complexes are also within this range. Octahedral cobalt(II) complexes exhibit magnetic moments much higher than the spin-only value of 3.9 BM because of orbital contributions from the $^4T_{1g}(F)$ ground state and the ^4T excited states.

The nickel(II) sulfoxide complexes, as expected for octahedral complexes, exhibit magnetic moment values of 3.3–3.5 BM. This compares to hexakis(dimethyl sulfoxide)nickel(II) perchlorate which has a value of 3.4 BM.[2] Octahedral nickel(II) complexes are closer to their spin-only value than the corresponding cobalt(II) complexes. The spin-only value of 2.8 BM for nickel(II) complexes is seldom exceeded by more than 0.7 BM. The reason for this is that orbital contributions cannot arise from the $^3A_{2g}$ ground state, but only from the ^3T excited state.

The hexakis(dialkyl sulfoxide)manganese(II) complexes exhibit magnetic moments from 5.9 to 6.2 BM. The values differ only slightly from the spin-only value of 5.9 BM because no orbital contribution occurs in the $^4A_{1g}$ ground state and because there are no excited states with a multiplicity of six. The values of the magnetic moments of the manganese(II) complexes are not as reproducible as desired because they are difficult to pack. In fact, the di-*n*-butyl sulfoxide complex forms an oil upon grinding.

Infrared Spectra.—The data observed for the infrared absorption bands of the sulfoxide complexes prepared in this study are given in Table II. Only the C–S and S–O stretching vibrational frequencies, along with the methyl rocking vibrational frequency, will be considered in detail. Infrared spectra in the 4000–1400-cm^{-1} range were also obtained but are not reported. The purpose for viewing the upper region is to demonstrate the absence of water.

During the course of the infrared investigation two bands were found to occur at nearly constant frequencies throughout the spectrum of all complexes studied. The first absorption was found to be very broad and intense occurring in the region 1060–1090 cm^{-1}. The second absorption, occurring at 620 cm^{-1}, was sharp but of considerably less intensity than the band found in the range 1060–1090 cm^{-1}. On the basis of the ex-

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[18] B. N. Figgis, "Introduction to Ligand Fields," Interscience Publishers, Inc., New York, N. Y., 1966, p 278 ff.

periments performed by Wickenden and Krause[19] on acetonitrile complexes of nickel(II) perchlorates, it can be stated that these two bands are due to the perchlorate anion. The absence of any splitting of the broad band in the region 1060–1090 cm^{-1} would seem to rule out the possibility of perchlorate coordination.

The S–O stretching vibrational frequency of all uncomplexed sulfoxides of this study occurs in the range 1011–1055 cm^{-1}. This range includes mull spectra as well as spectra in nitromethane solutions. The values of this work agree with those of other workers,[20,21] who assign the S–O stretching frequency to a range of 1020–1096 cm^{-1} in solutions with a corresponding reduction of 10–20 cm^{-1} in the mull spectra. The assignment of the S–O stretching vibration is complicated by aromatic ring vibrations in diphenyl sulfoxide and methyl phenyl sulfoxide and their complexes. Included in Figure 1 are the mull spectra from 1150 to 900 cm^{-1} of the aromatic sulfoxides and their hexakis nickel(II) complexes. It is observed that the frequency of the ligand bands (or shoulders) near 1080, 1070, 1020, and 995 cm^{-1} is relatively insensitive to complex formation. The same effect has been observed when aromatic sulfoxides are complexed with ICN[22] or are studied in different solvents.[21] For this reason the four bands are assigned to aromatic vibrations. The band at 1035 cm^{-1} in diphenyl sulfoxide is assigned to the S–O stretching vibration. The S–O stretching vibration occurs at frequencies of 1017 and 1030 cm^{-1} in mull spectra of di-*n*-propyl sulfoxide and di-*n*-butyl sulfoxide, respectively. Strong coupling between the S–O stretching and methyl rocking vibrations make it difficult to assign the S–O stretching vibration in dimethyl sulfoxide[15] or phenyl methyl sulfoxide.

It has been stated[2,4,23] that it is possible to determine from $\Delta\nu_{\mathrm{SO}}$ (ν_{SO}(ligand) $-$ ν_{SO}(complex)) whether coordination in sulfoxide complexes occurs *via* the oxygen or the sulfur atom. This view has very recently received direct support from the work of Bennett, Cotton, and Weaver.[12] Their X-ray results on an iron(III) and a palladium(II) complex with dimethyl sulfoxide definitely confirm that O-bonded and S-bonded complexes of dimethyl sulfoxide are formed, respectively, as predicted from infrared spectra. From Table II it can be seen that in all of the complexes prepared in this study the frequency shift upon complexation of the sulfoxide was toward lower frequency values. The magnitude of this shift ranged from 35 to 58 cm^{-1} in the mull infrared data. It is concluded from the direction of the S–O shift that in all of the complexes prepared and investigated in this study, coordination occurs through the oxygen atom of the sulfoxide.

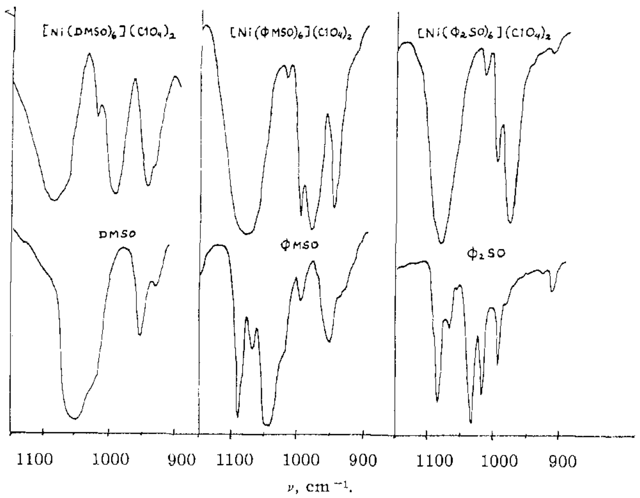

Figure 1.—Mull infrared spectra of $(CH_3)_2SO$ (DMSO), $(C_6H_5)(CH_3)SO$ (ϕMSO), $(C_6H_5)_2SO$ (ϕ_2SO), and their hexakis nickel(II) perchlorate complexes.

Cotton and co-workers[4] in a study of dimethyl sulfoxide complexes have assigned the S–O stretching vibrational frequency to the bands occurring around 950 cm^{-1}. They observed a band at approximately 1000 cm^{-1} and attributed this absorption to a methyl rocking mode of vibration. Drago, *et al.*,[5] however, reversed this assignment. In all of the complexes of dimethyl sulfoxide and phenyl methyl sulfoxide the two bands in question were observed (Figure 1). The higher energy absorption was observed as a strong band near 990 cm^{-1} and the second band near 950 cm^{-1}. In the dimethyl sulfoxide and phenyl methyl sulfoxide complexes it is difficult because of coupling to identify the S–O stretching vibration. Thus $\Delta\nu_{\mathrm{SO}}$ has no meaning with these two ligands. The band near 950 cm^{-1} does not occur in the complexes of diphenyl sulfoxide, and the band near 985 cm^{-1} is assigned to the S–O stretching vibration. The S–O stretching vibration frequency in the hexakis complexes of di-*n*-propyl and di-*n*-butyl sulfoxide is near 975 cm^{-1} in all cases. There is no evidence that the S–O stretching vibration is coupled with another vibration when the ligands contain no methyl groups.

The C–S stretching vibration in sulfoxides, as reported by Bellamy,[24] is a weak absorption occurring in the region 600–700 cm^{-1}. Because of the weak intensity of this absorption, a definite assignment is difficult. Selbin, *et al.*,[6] have assigned a value of 697 cm^{-1} for the C–S stretching vibrational band of dimethyl sulfoxide and a range of 707–737 cm^{-1} for this band upon complexation. In agreement, the complexes in this study have a C–S stretching vibration near 720 cm^{-1}. There are, however, two C–S stretching vibrations in dimethyl sulfoxide: an asymmetric one near 697 cm^{-1} and a symmetric one near 675

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(19) A. E. Wickenden and R. A. Krause, *Inorg. Chem.*, **4**, 404 (1965).

(20) A. D. Cross, "Introduction to Practical Infrared Spectroscopy," 2nd ed., Butterworth Inc., Washington, D. C., 1964, p 78.

(21) T. Cairns, G. Eglinton, and D. T. Gibson, *Spectrochim. Acta*, **20**, 31 (1964).

(22) E. Augdahl and P. Klaboe, *Acta Chem. Scand.*, **18**, 18 (1964).

(23) F. A. Cotton, R. D. Barnes, and E. Bannister, *J. Chem. Soc.*, 2199 (1960).

(24) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p 353 ff.

cm^{-1}.[15] Assignment of the C–S stretching vibration in sulfoxides with an aryl substituent is more difficult.

According to Bellamy[24] the C–S stretching vibration of aryl sulfoxides occurs in the 702–607-cm^{-1} region. A very weak bond near 670 cm^{-1} is assigned to the C–S stretching vibration in diphenyl sulfoxide and phenyl methyl sulfoxide. In their complexes the assignment is even more difficult because of the very intense bands of the C–H out-of-plane deformation modes of vibration which occur near 750 and 700 cm^{-1}. A weak band observed near 720 cm^{-1} in all diphenyl sulfoxide and phenyl methyl sulfoxide complexes is tentatively assigned to the C–S stretching vibration. A weak absorption near 685 cm^{-1} might be the C–S stretching vibration in di-*n*-propyl sulfoxide and di-*n*-butyl sulfoxide, but that vibration is not observed in any of their complexes.

Selbin, *et al.*,[6] have proposed the following stability series for dimethyl sulfoxide metal(II) perchlorate complexes: copper(II) > lead(II) > iron(II) > cobalt(II) > manganese(II) > nickel(II). Their order is based on the assumption that the magnitude of the decrease in the S–O stretching vibrational frequency ($\Delta\nu_{SO}$) of the ligand is a measure of the strength of the metal–oxygen bond. Because of the coupling between ν_{SO} and $\nu_{CH_3\,rock}$ in the complexes of dimethyl sulfoxide and phenyl methyl sulfoxide, a stability order based on $\Delta\nu_{SO}$ is meaningless in these two series of complexes. No coupling of the S–O stretching frequency has been demonstrated in di-*n*-propyl sulfoxide, diphenyl sulfoxide, and di-*n*-butyl sulfoxide. An average metal ion stability series based on $\Delta\nu_{SO}$ of these three ligands is: nickel(II) $\sim$ cobalt(II) > iron(II) $\sim$ manganese(II) $\geq$ zinc(II). This order is in basic agreement with the Irving–Williams series. If the average $\Delta\nu_{SO}$ for all metal ions is considered, the average stability order for the ligands is: $(n\text{-}C_4H_9)_2SO > (C_6H_5)_2SO > (n\text{-}C_3H_7)_2SO$. This order is not easily rationalized. It does not agree with the order expected from a consideration of inductive effects alone: $(n\text{-}C_4H_9)_2SO > (n\text{-}C_3H_7)_2SO > (C_6H_5)_2SO$; nor does it agree with a stability order expected from consideration of steric effects: $(C_6H_5)_2SO > (n\text{-}C_3H_7)_2SO > (n\text{-}C_4H_9)_2SO$. A combination of inductive and steric effects is probably responsible for the observed order. The use of $\Delta\nu_{SO}$ for determining stability series in hexakis-sulfoxide complexes is at best a gross approximation.

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Five-Coordination. VII. Diamagnetic Nickel(II) Complexes with Polydentate Phosphines Containing Sulfur and Selenium Donor Atoms[1,2]

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The tridentate ligand bis(*o*-methylthiophenyl)phenylphosphine (DSP, I) forms three types of five-coordinate nickel(II) complexes illustrated by the formulas $[Ni(DSP)X_2]$, $[Ni(DSP)_2](ClO_4)_2$, and $[Ni(DSP)(bidentate)](ClO_4)_2$. The bidentate ligand diphenyl(*o*-methylthiophenyl)phosphine (SP, II) gives four-, five-, and six-coordinate nickel(II) complexes, exemplified by the formulas $[Ni(SP)Cl_2]$, $[Ni(SP)_2Br]ClO_4$, and $[Ni(SP)_2Cl_2]$, respectively. The analogous selenium–phosphine ligand diphenyl(*o*-methylselenophenyl)phosphine (SeP, III) functions similarly. The properties of the SP and SeP complexes, especially the electronic absorption spectra, are compared with those of the phosphorus–arsenic ligand, diphenyl(*o*-diphenylarsinophenyl)phosphine. The spectrochemical series for the different donor groups is established as $R_2Se < R_2S < R_3As < R_3P$, whereas the absorption band intensities, which may be related to the covalent character of the nickel–ligand bond, produce a different order: $S < Se < As$.

Introduction

Five-coordinate nickel(II) complexes containing polydentate ligands have become quite numerous during the past 3 years. For example, all of the "tripod-like" tetradentate ligands $P(o\text{-}C_6H_4P(C_6H_5)_2)_3$,[4] $As(o\text{-}C_6H_4As(C_6H_5)_2)_3$,[5–6] $P(o\text{-}C_6H_4SCH_3)_3$,[7] $P(o\text{-}C_6H_4SeCH_3)_3$,[8] $P(CH_2CH_2CH_2As(CH_3)_2)_3$,[9] $As(CH_2CH_2CH_2As(CH_3)_2)_3$,[10] and $N(CH_2CH_2N(CH_3)_2)_3$[11] form trigonal-bipyramidal nickel(II) complexes. With $As(o\text{-}C_6H_4As(C_6H_5)_2)_3$ and

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