

shift has been noted previously with certain borane adducts.⁹ It has also been postulated that organoboranes form the unstable intermediate R_3BCO in certain solvents containing water followed by shifts of two R groups from boron to carbon.^{10,11} It is possible that the mechanism of this shift is similar to that involved in our work.

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Complexes of Sulfinamides

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We have recently initiated a study of the chemistry of alkanesulfinamides, $RS(O)NR_2$, which as might be expected show a number of properties similar to those of corresponding sulfoxides.¹⁻⁴ The ligand of primary interest in this work is *N,N*-dimethylmethanesulfinamide (DMMS), although the nickel(II) perchlorate complexes of *N*-methylmethanesulfinamide (NMMS) and methanesulfinamide (MS) are also included.

Sulfinamides might also be considered as similar to carboxylic acid amides in that coordination to a metal ion could occur through oxygen or nitrogen. Infrared spectra of the free ligands and the complexes were studied in order to determine the site of coordination which was found to be oxygen for all complexes reported in this paper. The general characterization of the complexes was obtained by a combination of elemental analysis, spectral studies, conductivity studies, and studies of magnetic susceptibilities.

Experimental Section

Reagents and Solvents.—The sulfinamides were prepared by the aminolysis of methanesulfinyl chloride which had been prepared by the chlorination of methyl disulfide in glacial acetic acid.⁵ The preparation of DMMS, $CH_3S(O)N(CH_3)_2$, was accomplished by dropwise addition of methanesulfinyl chloride to dimethylamine in ether at -10 to -20° .⁶ After removal of the ammonium salts and ether the product was obtained as a colorless liquid by vacuum distillation (bp 38° (2.0 mm)). The compound NMMS, $CH_3S(O)NHCH_3$, was prepared in the same manner by combining a 2:1 mole ratio of monomethylamine and

methanesulfinyl chloride. The pure product was obtained as a colorless liquid by vacuum distillation from a small amount of anhydrous $CoCl_2$ (bp 63° (0.15 mm)). Both of these sulfinamides were very hygroscopic. The compound MS, $CH_3S(O)NH_2$, was prepared by dropwise addition of methanesulfinyl chloride in ether to an excess of ammonia in ether at -78° . After refluxing for 10 hr the ammonium salts and the solid product were separated from the ether. The product was extracted from the ammonium salts with methyl ethyl ketone and recrystallized from chloroform (mp $70-73^\circ$). This sulfinamide is not hygroscopic. The analytical data are found in Table I.

Fisher reagent grade nitromethane was used without further purification. Pure dry acetonitrile was obtained by distilling Fisher reagent grade materials from phosphorus pentoxide. Eastman 2,2-dimethoxypropane was used without purification.

Hydrated metal perchlorates were obtained from G. F. Smith Chemical Co. Hydrated nickel(II) tetrafluoroborate was obtained from Alfa Inorganics, Inc.

Preparation of the Complexes.—All of the complexes were prepared by the same method. The hydrated metal perchlorate or tetrafluoroborate (0.002 mole) was dehydrated by stirring with 10 ml of *N,N*-dimethoxypropane and 4 ml of methanol for 1.5–2 hr. The volume of solvent was reduced by half before adding >0.014 mole of DMMS, NMMS, or MS. The ligand MS was added as solute in chloroform. After stirring for 10 min ether was added to complete the precipitation of the complexes which were then filtered, washed with anhydrous ether, and dried under vacuum for 30 min. The DMMS complexes of Mn(II), Co(II), Ni(II), and Zn(II) were only slightly hygroscopic while $[Ni(NMMS)_6](ClO_4)_2$ and the Cu(II) complexes were sufficiently hygroscopic to cause difficulty in weighing. The iron complex $[Fe(DMMS)_6](ClO_4)_2$, which is not very hygroscopic, changed from a pale yellow-brown to brown while standing several weeks in a desiccator. The other compounds showed no changes. The four-coordinate Cu(II) complex was obtained by heating the six-coordinate complex under vacuum at 60° for 20 hr. The analytical data and yields are recorded in Table I.

TABLE I
ANALYSIS AND YIELDS OF SULFINAMIDE COMPLEXES

Compound	% C		% H		% N		Yield, %
	Calcd	Found	Calcd	Found	Calcd	Found	
$CH_3S(O)N(CH_3)_2$	33.63	34.40	8.47	8.69	13.08	13.29	...
$CH_3S(O)NHCH_3$	25.80	26.36	7.60	7.64	15.05	14.83	...
$CH_3S(O)NH_2$	15.19	15.20	6.38	5.14	17.72	17.80	...
$[Mn(DMMS)_6](ClO_4)_2$	24.11	24.16	6.03	6.15	9.37	9.33	89
$[Fe(DMMS)_6](ClO_4)_2$	24.08	24.05	6.02	6.29	9.36	9.23	76
$[Co(DMMS)_6](ClO_4)_2$	24.00	23.90	6.00	6.08	9.33	9.20	94
$[Ni(DMMS)_6](ClO_4)_2$	24.00	23.93	6.00	6.21	9.33	9.04	98
$[Ni(DMMS)_6](BF_4)_2$	24.71	24.35	6.22	6.39	9.60	8.89	95
$[Ni(NMMS)_6](ClO_4)_2$	17.65	17.36	5.19	4.99	10.29	10.34	95
$[Ni(MS)_6](ClO_4)_2$	9.84	10.04	4.10	4.30	11.48	11.22	90
$[Cu(DMMS)_6](ClO_4)_2$	23.89	23.69	5.97	6.25	9.29	9.05	81
$[Cu(DMMS)_4](ClO_4)_2$	20.89	20.58	5.22	5.28	8.12	8.49	...
$[Zn(DMMS)_6](ClO_4)_2$	23.82	23.70	5.96	6.08	9.27	9.40	95

Physical Measurements.—Infrared spectra of the ligands and the complexes were obtained using a Perkin-Elmer Model 21 spectrophotometer. Near-infrared and visible spectra of complexes in solution and in Nujol mulls were obtained using a Beckman DK-2 spectrophotometer. The solution spectra were measured in 1.0- and 5.0-cm quartz cells using the ligand proper as a solvent with the same solvent as a reference. The mull spectra were obtained using smears on filter paper. Magnetic susceptibilities were measured using the Faraday method with a Spectromagnetic Industries power source and magnet. The measurements were made at 22° using $Hg[Co(CNS)_4]$ as a calibration standard. The electrolytic conductance measurements were made at 27° in nitromethane and acetonitrile using an Industrial Instruments, Inc., conductivity bridge and a calibrated cell.

Analysis.—The carbon and hydrogen analyses were obtained using a Coleman carbon-hydrogen analyzer. The nitrogen analyses were obtained using a Coleman nitrogen analyzer.

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Results and Discussion

The spectral properties of the ligands and the complexes are recorded in Table II. These include the sulfur-oxygen stretching frequency, ν_{s-o} , the visible and near-infrared spectra of the complexes, and the colors of the complexes. The magnetic properties of the complexes are given in Table III.

$\pm 10 \text{ cm}^2 \text{ mole}^{-1} \text{ ohm}^{-1}$ at $2 \times 10^{-3} M$ in CH_3CN) are indicative of uni-divalent electrolytes.^{7,8}

The sulfur-oxygen stretching frequencies of the sulfinamides, ν_{s-o} , and their respective complexes were assigned by comparing the infrared spectra of these compounds with those of similar sulfinyl and thionyl compounds.⁹ These frequencies are recorded in Table II.

TABLE II
SPECTRAL DATA

Compound	Infrared ν_{s-o} , cm^{-1}	Visible and near-infrared		Color
		λ_{max} , $\text{m}\mu$ (cm^{-1})	ϵ_{max}^a	
$\text{CH}_3\text{S}(\text{O})\text{N}(\text{CH}_3)_2$	1073, 1078 ^b	Colorless
$\text{CH}_3\text{C}(\text{O})\text{NHCH}_3$	1054, 1084 ^b	Colorless
$\text{CH}_3\text{S}(\text{O})\text{NH}_2$	1018, 1067 ^c	White
$[\text{Mn}(\text{DMMS})_6](\text{ClO}_4)_2$	996	White
$[\text{Fe}(\text{DMMS})_6](\text{ClO}_4)_2$	993	1075 (9,305) ^d	2.4	Yellow-brown
$[\text{Co}(\text{DMMS})_6](\text{ClO}_4)_2$	992	487 (20,530) ^d	1.2	Lavender
		544 (18,380)	1.7	
		675 (14,810)	4.7	
		1327 (7,540)	2.5	
$[\text{Ni}(\text{DMMS})_6](\text{ClO}_4)_2$	988	420 (23,810) ^d	14.1	Pale green
		710 (14,080)	0.6	
		782 (12,790)	4.7	
		1307 (7,650)	3.9	
		415 (24,100) ^e	...	
		704 (14,200)	...	
		752 (13,300)	...	
		1188 (8,420)	...	
$[\text{Ni}(\text{DMMS})_6](\text{BF}_4)_2$	989	Pale green
$[\text{Ni}(\text{NMMS})_6](\text{ClO}_4)_2$	991	420 (23,810) ^f	17.1	Pale green
		702 (14,240)	0.9	
		778 (12,850)	5.9	
		1295 (7,720)	5.6	
		414 (24,160) ^e	...	
		700 (14,290)	...	
		755 (13,240)	...	
		1192 (8,390)	...	
$[\text{Ni}(\text{MS})_6](\text{ClO}_4)_2$	997	410 (24,390) ^e	...	Pale green
		700 (14,290)	...	
		760 (13,160)	...	
		1200 (8,330)	...	
$[\text{Cu}(\text{DMMS})_6](\text{ClO}_4)_2$	975, 1023	816 (12,260) ^d	40.0	Blue-green
$[\text{Cu}(\text{DMMS})_4](\text{ClO}_4)_2$	971	Pale green
$[\text{Zn}(\text{DMMS})_6](\text{ClO}_4)_2$	992	White

^a ϵ_{max} is expressed in units of $\text{l. mole}^{-1} \text{ cm}^{-1}$. ^b Infinite dilution in CCl_4 . ^c Maximum observable shift in CHBr_3 before solvent cutoff. ^d In DMMS at solvent. ^e Nujol mull. ^f In NMMS as solvent.

TABLE III

MAGNETIC PROPERTIES

Compound	$10\chi_m'$, cgs^a	μ_{eff} , BM^b
$[\text{Mn}(\text{DMMS})_6](\text{ClO}_4)_2$	15,308	6.03
$[\text{Fe}(\text{DMMS})_6](\text{ClO}_4)_2$	12,475	5.45
$[\text{Co}(\text{DMMS})_6](\text{ClO}_4)_2$	10,273	4.94
$[\text{Ni}(\text{DMMS})_6](\text{ClO}_4)_2$	4,734	3.36
$[\text{Ni}(\text{NMMS})_6](\text{ClO}_4)_2$	4,799	3.38
$[\text{Cu}(\text{DMMS})_6](\text{ClO}_4)_2$	1,586	1.94

^a Corrected for diamagnetic susceptibility using 432×10^{-6} cgs/mole for DMMS and 361×10^{-6} cgs/mole for NMMS: B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 403.

^b $\mu_{\text{eff}} = 2.84 \sqrt{\chi_m' T}$ BM, average of three determinations.

The analytical data for all of the complexes are consistent with the stoichiometry $[\text{ML}_6](\text{ClO}_4)_2$. The product obtained by heating $[\text{Cu}(\text{DMMS})_6](\text{ClO}_4)_2$ *in vacuo* gives an analysis consistent with the formula $[\text{Cu}(\text{DMMS})_4](\text{ClO}_4)_2$. The observed conductivities (300

In order to ensure the proper assignment and to remove the possibility of confusion of ν_{s-o} with a perchlorate band, the complex $[\text{Ni}(\text{DMMS})_6](\text{BF}_4)_2$ was prepared and its infrared spectrum was recorded. It is found that for each of the sulfinamides ν_{s-o} shifts to lower frequency upon coordination. As was first proposed by Cotton¹ for dimethyl sulfoxide complexes, coordination at the oxygen site of the sulfinamide should also result in a shift of ν_{s-o} to lower frequencies. It is concluded that the coordination site of the sulfinamide is the oxygen atom for the sulfinamide complexes reported in this paper. A consideration of the relative steric requirements imposed for oxygen or nitrogen coordination might suggest that oxygen coordination would be favored. Conversely, interaction of sulfinamides with

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an acid with small or no steric requirements should indicate which site, oxygen or nitrogen, is the more basic. The proton of water or another hydrogen-bonding acid such as phenol should differentiate. When DMMS is exposed to moist air for 5–10 min, ν_{s-o} undergoes a shift of approximately 36 cm^{-1} to lower frequencies. The phenol adduct of DMMS in carbon tetrachloride has an ν_{s-o} of 1051 cm^{-1} , 27 cm^{-1} less than that of DMMS in CCl_4 . It has also been observed that ν_{s-o} is shifted to lower frequency upon interaction with trimethylalane, a Lewis acid of relatively low steric requirements.¹⁰ Each of these facts suggests that the lone pair of electrons on the nitrogen atom is not nearly as available for donation as in an amine. This observation could be explained by considering the inductive effect of the methanesulfinyl group or by invoking sulfur–nitrogen $p\pi-d\pi$ bonding.

The rather wide variation in the shifts of ν_{s-o} of the three sulfinamides upon coordination to Ni(II) can be explained by considering the nature of the pure sulfinamides. In the series DMMS, NMMS, and MS there is increasing hydrogen bonding. The effect of hydrogen bonding is shown by comparing the ν_{s-o} of DMMS (1073 cm^{-1}) and NMMS (1054 cm^{-1}) as pure liquids with the corresponding values of 1078 and 1084 cm^{-1} at infinite dilution in carbon tetrachloride. Thus the unassociated sulfinamides show similar shifts of ν_{s-o} when complexed to Ni(II). In MS where hydrogen bonding would be most extensive, insolubility prevented a dilution study in CCl_4 ; however, the ν_{s-o} did shift to 1067 cm^{-1} in CHBr_3 before solvent cutoff prevented further observable shift. The variation of the observed sulfur–oxygen stretching frequency shift, $\Delta\nu_{s-o}$, in the DMMS complexes is in the sequence predicted by the Irving–Williams order of metal–ligand interaction (*i.e.*, $\text{Mn} < \text{Fe} < \text{Co} < \text{Ni} < \text{Cu} > \text{Zn}$).

The ν_{s-o} region of the infrared spectrum of $[\text{Cu}(\text{DMMS})_6](\text{ClO}_4)_2$ shows two bands at 975 and 1023 cm^{-1} with the former being more intense. When the complex is heated *in vacuo* to give $[\text{Cu}(\text{DMMS})_4](\text{ClO}_4)_2$, the band at 1023 cm^{-1} disappears and the band at 975 cm^{-1} shifts to 971 cm^{-1} . Similar behavior was reported by Cotton¹ for $\text{CuCl}_2 \cdot 3\text{DMSO}$ (DMSO = dimethyl sulfoxide). The spectrum of $[\text{Cu}(\text{CMMS})_6](\text{ClO}_4)_2$ is interpreted in terms of four DMMS bonded to Cu(II) giving rise to the more intense 975-cm^{-1} band and two more weakly bonded ligands resulting in the 1023-cm^{-1} band. The shift of the 975-cm^{-1} band to lower frequency as the two weakly bound DMMS are lost is consistent with the expected increased metal–ligand interaction in going from six to four coordination. Since all of the other six-coordinate DMMS complexes reported here show only one ν_{s-o} and are presumably nearly octahedral with respect to the six-coordinated oxygen atoms and since all of these species would be expected to be isomorphous in the crystalline state in the absence of any metal ion electronic effects, the tetragonal distortion in the Cu(II) complex is probably due to the Jahn–Teller effect.

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The colors and the visible and near-infrared solution spectra of the DMMS complexes of Fe(II), Co(II), Ni(II), and Cu(II) are typical of six-coordinate complexes of these ions. The spectra of $[\text{Ni}(\text{DMMS})_6](\text{ClO}_4)_2$ in DMMS and of $[\text{Ni}(\text{NMMS})_6](\text{ClO}_4)_2$ in NMMS show only small differences. The ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ bands of these spectra indicate Dq values of 765 cm^{-1} for DMMS and 772 cm^{-1} for NMMS. Attempts to evaluate the Dq parameter for MS by dissolving $[\text{Ni}(\text{MS})_6](\text{ClO}_4)_2$ and excess MS in another solvent were unsuccessful because of the insolubility of the MS. However, the absorption spectra of the milled Ni(II) complexes of DMMS, NMMS, and MS are very similar and it is concluded that Dq values are probably nearly the same for each of these ligands. In the absence of a significant difference in steric requirements in the complexes, DMMS would be expected on the basis of inductive consideration to have a Dq larger than that of NMMS. The similarity of the Dq values suggests that there is either no effect induced by substituting a methyl for hydrogen or the increased steric requirement of the methyl negates the inductive effect. The reported Dq values for acetamide, N-methylacetamide, and N,N-dimethylacetamide toward Ni(II) indicate that in the six-coordinate complexes inductive effects are important but steric effects predominate in determining the metal–ligand interaction.¹¹ It was found that acetamide had the highest Dq . Consideration of the large size of the sulfur atom suggests that the steric effects in sulfinamide complexes should be less severe than that observed in the acetamide complexes. In the absence of steric effects or with nearly equal steric effects in the sulfinamide complexes, the invariance of Dq with methyl substitution indicates that the nitrogen–sulfur–oxygen bonding system does not efficiently propagate the inductive influence of substituents on nitrogen.

The calculated ν_{max} values of the middle bands in the visible and near-infrared solution spectra of the Ni(II) complexes are $12,837\text{ cm}^{-1}$ for DMMS and $12,934\text{ cm}^{-1}$ for NMMS. When compared to the average of the middle bands (*i.e.*, $13,435\text{ cm}^{-1}$ for DMMS and $13,549\text{ cm}^{-1}$ for NMMS) a deviation of approximately 600 cm^{-1} is observed. This suggests that both complexes have some distortion from octahedral symmetry.¹²

Using the equation $[6Dqp - 16(Dq)^2] + [-6Dq - p]E + E^2 = 0$, the splittings of the ${}^3\text{P}$ and ${}^3\text{F}$ terms in the Ni(II) complexes were calculated to be $13,697\text{ cm}^{-1}$ for DMMS and $13,584\text{ cm}^{-1}$ for NMMS to give the B values 913 and 916 , respectively. The percentage lowering of this splitting relative to that found for Ni(II) in the gas phase is 13.5% for DMMS and 14.2% for NMMS. These values which measure the nephelauxetic effect of the ligands are almost the same as that reported for dimethyl sulfoxide (*i.e.*, 12.7%).⁴

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