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Ni(II) and Co(II) Complexes with a Series of Phenyl Methyl Sulfoxides*

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Several new Ni(II) and Co(II) complexes with 4-substituted phenyl methyl sulfoxides have been prepared and characterized. All are six-coordinate and exhibit metal–oxygen bonding as indicated by i.r. spectroscopy. Visible and near i.r. spectral results were used to calculate the ligand field parameters, Dq and B. These suggest that these sulfoxides are somewhat stronger field donors than most of the others which have been studied to date.

Introduction

Almost two decades have passed since the first transition metal complexes of a sulfoxide ligand (dimethylsulfoxide) were reported [1]. Since that time interest in the coordinating ability of the sulfoxide moiety and its potentially ambidentate nature has led to the preparation of a great many compounds of first row transition metals with sulfoxides, including aliphatic [2–5], alicyclic [6–12], aromatic [2, 12, 13], and multidentate [14–17] ones. Despite this extensive activity the effect of electronic factors on the coordinating properties of the sulfoxide group has not been investigated. We wish to report our efforts in this regard, which have entailed the synthesis and characterization of nickel and cobalt complexes of a series of *para*-substituted phenyl methyl sulfoxides.

Experimental

Materials

$Ni(ClO_4)_2\cdot6H_2O$ and $Co(ClO_4)_2\cdot6H_2O$ were obtained from G. F. Smith Chemicals and were used without further purification. The sulfoxides were synthesized by the hydrogen peroxide–acetic acid oxidation of the respective sulfides [18]. The sulfoxides were recovered from the reaction mixture by extracting with $CHCl_3$ after the acetic acid had been neutralized rather than by steam distillation. Those sulfides which were not commercially available were prepared by standard methods, *i.e.*, reacting either an alkyl halide or dimethyl sulfate [19] with the sodium salt of the parent thiophenol. The only exception was p-$CH_3OC_6H_4SCH_3$, which was obtained by reacting dimethyl sulfate with p-$HOC_6H_4SCH_3$. The prepared sulfoxides were purified by recrystallization or distillation *in vacuo*. The boiling/melting points were: $C_6H_5S(O)CH_3$ 136–137 °C (11 torr), p-$CH_3C_6H_4S(O)CH_3$ 138–140 °C (4 torr), p-$CH_3OC_6H_4S(O)CH_3$ 153–155 °C (6 torr), p-$ClC_6H_4S(O)CH_3$ 42 °C, $C_6H_5S(O)C_2H_5$ 118–121 °C (5 torr). All other chemicals were of reagent grade and were used as received.

Preparation of Complexes

The complexes were prepared by mixing warm ethanolic solutions (5 ml) of the appropriate ligand (.006 mol) and a hydrated metal perchlorate (.001 mol) to which 2,2-dimethoxypropane(.01 mol) had been added as a dehydrating agent. The solutions were cooled in ice or evaporated partially at room temperature to obtain solid products which were washed with ethanol and dried *in vacuo*.

Analyses and Physical Measurements

Perchlorates were determined by precipitation with nitron [20]. Carbon and hydrogen analyses were performed by Strauss Microanalytical Laboratory, Oxford, England.

Infra-red spectra were obtained as Nujol mulls in the 4000–500 cm^{-1} region using a Beckman IR-12 spectrophotometer. Near infra-red and visible spectra of the compounds in Nujol mulls spread on filter paper were recorded on a Cary 14 spectrophotometer.

Discussion

All of the complexes prepared appear to be six-coordinate as shown by the analytical data of Table I and the colors and electronic spectra exhibited, which are those expected for O_h symmetry (see below).

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TABLE I. Analytical Results

L	$NiL_6(ClO_4)_2$					
	%C		%H		$\%ClO_4$	
	Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.
$C_6H_5S(O)CH_3$	45.55	(45.76)	4.21	(4.39)	17.61	(18.05)
$p\text{-}CH_3C_6H_4S(O)CH_3$	48.50	(48.57)	4.84	(5.10)	16.33	(16.76)
$p\text{-}CH_3OC_6H_4S(O)CH_3$	45.16	(44.93)	4.68	(4.71)	14.66	(15.51)
$p\text{-}ClC_6H_4S(O)CH_3$	38.33	(38.64)	3.10	(3.24)	14.66	(15.24)
$C_6H_5S(O)C_2H_5$	48.08	(48.57)	5.25	(5.10)	16.75	(16.76)

L	$CoL_6(ClO_4)_2$					
	%C		%H		$\%ClO_4$	
	Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.
$C_6H_5S(O)CH_3$	45.54	(45.76)	4.59	(4.39)	17.81	(18.05)
$p\text{-}CH_3C_6H_4S(O)CH_3$	48.11	(48.57)	5.19	(5.10)	16.94	(16.76)
$p\text{-}CH_3OC_6H_4S(O)CH_3$	45.03	(44.93)	4.83	(4.71)	15.19	(15.51)
$p\text{-}ClC_6H_4S(O)CH_3$	38.65	(38.64)	3.34	(3.24)	14.96	(15.24)
$C_6H_5S(O)C_2H_5$	48.25	(48.57)	5.22	(5.10)	16.35	(16.76)

TABLE II. Infra-red Data.

$L = C_6H_5S(O)CH_3$	1595s, 1495s, 1095s, 1050vs, 998m, 955s, 810vs, 755s, 690s
$NiL_6(ClO_4)_2$	1100vs, 1005s, 985vs, 950s, 750s, 690s, 620s
$CoL_6(ClO_4)_2$	1100vs, 990vs, 955s, 750s, 690m, 620s
$L = p\text{-}CH_3C_6H_4S(O)CH_3$	1595s, 1495s, 1410s, 1300s, 1205m, 1175m, 1145s, 1085vs, 1045vs, 1015vs, 955s, 810s, 755m, 680s, 615s
$NiL_6(ClO_4)_2$	1090vs, 990vs, 960s, 815s, 730m, 620s
$CoL_6(ClO_4)_2$	1100vs, 990vs, 960s, 815s, 700m, 625s
$L = p\text{-}CH_3OC_6H_4S(O)CH_3$	1600m, 1300s, 1255s, 1172m, 1095s, 1045vs, 1015s, 960s, 830s, 740s, 690m
$NiL_6(ClO_4)_2$	1100vs, 1035s, 985vs, 955s, 836s, 805m, 730m, 695m, 620s
$CoL_6(ClO_4)_2$	1100vs, 1030s, 983vs, 960s, 840s, 808m, 695m, 622s
$L = p\text{-}ClC_6H_4S(O)CH_3$	1580s, 1310s, 1210m, 1172m, 1092vs, 1060s, 1015s, 960s, 818s, 742s, 682m
$NiL_6(ClO_4)_2$	1100vs, 1018m, 990vs, 960s, 840s, 825s, 742s, 690m, 622s
$CoL_6(ClO_4)_2$	1100vs, 1018m, 990vs, 955s, 840s, 822s, 742s, 690m, 622s
$L = C_6H_5S(O)C_2H_5$	1590s, 1420m, 1310m, 1240m, 1150m, 1095s, 1030s, 1005s, 975m
$NiL_6(ClO_4)_2$	1100vs, 980s, 850m, 772m, 752s, 926s, 622s
$CoL_6(ClO_4)_2$	1100vs, 990s, 970s, 772m, 750s, 690s, 622s

The infra-red data obtained are given in Table II. There are only three bands in the spectra of the complexes which do not duplicate those of the free ligands (given here because they have not been reported previously). The three peaks which differ appear at 1100, 990, and 620 cm^{-1}. The first and third of these have been assigned [21] to the antisymmetric stretching and bending vibrations of the perchlorate ion and the unsplit nature of the 1100 cm^{-1} bond can be used as evidence that this species is not coordinated [22]. The remaining band, which appears near 990 cm^{-1}, can be assigned to the sulfur–oxygen stretching frequency (ν_{SO}). The shift in frequency ($\Delta\nu_{SO}$) which this band undergoes upon

TABLE III. Near Infra-red and Visible Spectra (kK).

L	$NiL_6(ClO_4)_2$			
L	ν_1 $^3A_{2g} \rightarrow {}^3T_{2g}$	ν_2 $^3A_{2g} \rightarrow {}^3T_{1g}$ (F)		ν_3 $^3A_{2g} \rightarrow {}^3T_{1g}$ (P)
$C_6H_5S(O)CH_3$	8.29	13.4	(13.8)[a]	24.4
p-$CH_3C_6H_4S(O)CH_3$	8.33	13.1	(13.8)[a]	24.5
p-$CH_3OC_6H_4S(O)CH_3$	8.20	13.4	(13.6)[a]	24.4
p-$ClC_6H_4S(O)CH_3$	8.33	13.3	(13.8)[a]	24.5
$C_6H_5S(O)CH_3$	8.33	13.1	(13.8)[a]	24.4

L	$CoL_6(ClO_4)_2$			
L	ν_1 $^4T_{1g}$ (F) $\rightarrow {}^4T_{2g}$	ν_2 $^4T_{1g}$ (F) $\rightarrow {}^4A_{2g}$	ν_3 $^4T_{1g} \rightarrow {}^4T_{1g}$ (P)	
$C_6H_5(O)CH_3$	8.27	15.8[b]	19.2	(20.7)[c]
p-$CH_3C_6H_4S(O)CH_3$	8.33	16.1[b]	19.2	(20.8)[c]
p-$CH_3OC_6H_4S(O)CH_3$	8.30	15.8[b]	19.1	(21.3)[c]
p-$ClOC_6H_4S(O)CH_3$	8.35	16.2[b]	19.3	(20.7)[c]
$C_6H_5S(O)C_2H_5$	8.40	15.5[b]	19.1	(20.8)[c]

[a] Calculated from Dq, B and ν_3. [b] Estimated peak of broad shoulder. [c] Shoulder.

coordination has become a valuable tool for establishing the identify of the donor atom, with ν_{SO} occurring at lower frequencies (relative to the free sulfoxides) when the oxygen is coordinated and at higher frequencies when the sulfur is the donor atom [1, 23]. Since all of the complexes examined here exhibit lower values of ν_{SO} than do the free sulfoxides it can be concluded that the latter are behaving exclusively as oxygen donors toward Ni(II) and Co(II) ions. This same behavior, with a single exception [24], has been observed for all other sulfoxide complexes with first row transition elements and is consistent with their 'hard acid' behavior [25]. Although it has been suggested that the magnitude of $\Delta\nu_{SO}$ can be used as a measure of the strength of the metal oxygen bond [26], such estimates are precluded in the present study due to coupling between the S–O stretching and methyl rocking vibrations [27] and the appearance of aromatic vibrations in this region, both of which make the exact assignment of ν_{SO} difficult.

The visible and near infra-red spectra are similar to those expected for octahedral Ni(II) and Co(II) complexes in weak field environments, consisting of 2 broad bands (near 7600 and 12000 Å for Ni(II) and 6500 and 12000 Å for Co(II), and one sharper peak which appears at about 4000 Å for Ni(II) and near 5000 Å with a shoulder at ~4800 Å for Co(II). The peak energy values, which are shown in Table III with their respective assignments, were used to calculate the ligand field parameters, Dq and B, which are listed in Table IV. Because of the difficulty encountered in establishing the wavelength maximum of the middle band for both series of compounds, the first and third bands were employed in this calculation and a graphical method [28] was used to obtain the values for Co(II).

The Dq values calculated for the ligands in the current study indicate stronger fields than those found for the majority of the other sulfoxides studied to date, including bidentate species, some of which are listed in Table IV for comparison. It is noteworthy that the Dq values for phenyl methyl sulfoxide and its derivatives are greater than those for either dimethyl- or diphenyl-sulfoxide. Apparently the factors which contribute to the donor strength of the sulfoxide moiety (*e.g.*, size and electronic nature of the attached groups) are optimized in the alkaryl compound, rather than being intermediate between the dialkyl and diaryl cases. A similar anomaly has been reported for the basicities of these three compounds in aqueous and non-aqueous media [29]. The Dq value for phenyl methyl sulfoxide is also greater than those for the corresponding bidentate species; 1,1-bis(phenylsulfinyl)methane (PSM) and 1,2-bis(phenylsulfinyl)ethane (PSE). Although chelating ligands frequently exhibit higher Dq values than their monodentate counterparts, *e.g.*, 1,2'bis(methylsulfinyl)ethane (860 cm^{-1}) [14] *vs.* dimethylsulfoxide (773 cm^{-1}) [6]; 2,2'bipyridine (1150 cm^{-1}) [30] *vs. pyridine (1010* cm^{-1}) [31]; 2,2'bipyridine 1,1-dioxide (875 cm^{-1}) [32] *vs.* pyridine N-oxide (840 cm^{-1}) [6]; ethylenediamine (1150 cm^{-1}) [33] *vs.* methylamine (993 cm^{-1}) [34], it may be that the internal strain of the 6-membered PSM and the 7-membered PSE complexes [15] offset this effect.

TABLE IV. Calculated Ligand Field Parameters.

L		$NiL_6(ClO_4)_2$		
		Dq (cm^{-1})	B (cm^{-1})	Ref.
$C_6H_5S(O)CH_3$		829	886	This work
p-$CH_3C_6H_4S(O)CH_3$		833	890	This work
p-$CH_3OC_6H_4S(O)CH_3$		820	896	This work
p-$ClC_6H_4S(O)CH_3$		833	890	This work
$C_6H_5S(O)C_2H_5$		833	882	This work
$C_6H_5S(O)C_6H_5$		796	908	8
$CH_3S(O)CH_3$		800	887	6
$C_4H_8S(O)$		823	885	8
$C_5H_{10}S(O)$		851	887	8
$[C_6H_5S(O)CH_2]_2$	*racemic*	809	899	15
	meso	792	901	15
$[C_6H_5S(O)]_2CH_2$	*racemic*	812	863	15
	meso	799	885	15

L		$CoL_6(ClO_4)_2$		
		Dq (cm^{-1})	B (cm^{-1})	Ref.
$C_6H_5S(O)CH_3$		929	802	This work
p-$CH_3C_6H_4S(O)CH_3$		945	799	This work
p-$CH_3OC_6H_4S(O)CH_3$		939	796	This work
p-$ClC_6H_4S(O)CH_3$		945	807	This work
$C_6H_5S(O)C_2H_5$		952	780	This work
$C_6H_5S(O)C_6H_5$		862	821	8
$CH_3S(O)CH_3$		830	826	6
$C_4H_8S(O)$		830	826	6
$[C_6H_5S(O)CH_2]_2$	*racemic*	862	759	15
	meso	869	802	15
$[C_6H_5S(O)]_2CH_2$	*racemic*	869	797	15
	meso	863	800	15

One of the original goals of this work was to determine whether a relationship between Dq and the electronic properties of the ligands as determined by the *para*-substituents could be found. As can be seen, however, the similarity of the values do not suggest such a trend, in contrast to the results obtained for a series of 4-substituted pyridine N-oxides [35]. The absence of such a relationship is somewhat surprising, particularly in view of the fact that the pK_a s of these sulfoxides are governed by the nature of the *para* substituents [36], but may be due to the greater steric requirements introduced by placing 6 ligands around the metal ion.

The B values are also very similar for each set of compounds and indicate a moderate degree of covalent character in the metal oxygen bond [37]. Not surprisingly, the B values for the d^8 Ni(II) ion are somewhat larger than those for the d^7 Co(II) species.

References

1 F. A. Cotton and R. Francis, *J. Am. Chem. Soc., 82,* 2986 (1960).
2 W. F. Currier and J. H. Weber, *Inorg. Chem., 6,* 1539 (1967).
3 J. Gopalakrishnan and C. C. Patel, *J. Sci. Ind. Res., 27,* 475 (1968).
4 J. H. Weber, *Inorg. Chem., 8,* 2813 (1969).
5 E. Giesbrecht and V. K. Lakatos Osorio, *J. Inorg. Nucl. Chem., 37,* 1409 (1975).
6 D. W. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem., 1,* 285 (1961).
7 P. W. N. M. van Leeuwen and W. L. Groeneveld, *Rec. Trav. Chim. Pays Bas, 86,* 721 (1967).
8 P. W. N. M. van Leeuwen and W. L. Groeneveld, *ibid., 86,* 1219 (1967).
9 J. J. Reedijk, A. H. M. Fleur and W. L. Groeneveld, *ibid., 88,* 1115 (1969).
10 A. H. M. Fleur and W. L. Groeneveld, *ibid., 91,* 317 (1972).
11 A. H. M. Driessen Fleur and W. L. Groeneveld, *Inorg. Chim. Acta, 7,* 139 (1973).

12 P. W. N. M. van Leeuwen and W. L. Groeneveld, *Rec. Trav. Chim. Pays Bas, 85,* 1173 (1963).
13 P. W. N. M. van Leeuwen, *ibid., 86,* 201 (1967).
14 S. K. Madan, C. M. Hull and L. J. Herman, *Inorg. Chem., 7,* 491 (1968).
15 T. R. Musgrave and G. D. Kent, *J. Coord. Chem., 2,* 23 (1972).
16 E. Weber and F. Foegtle, *Justus Liebig's Ann. Chim.,* 891 (1976).
17 A. P. Zipp and S. K. Madan, *Inorg. Chim Acta, 22,* 49 (1977).
18 E. V. Bell and G. M. Bennett, *J. Chem. Soc.,* 1798 (1927).
19 B. J. Hazzard, "Organicum: Practical Handbook of Organic Chemistry", Addison–Wesley, Reading, Mass., 1973, p. 202.
20 F. J. Welcher, "Organic Analytical Reagents", Pergamon Press, New York, N.Y., 1959.
21 B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.,* 3091 (1961).
22 S. F. Parkovic and D. W. Meek, *Inorg. Chem., 4,* 109 (1965).
23 M. J. Bennett, F. A. Cotton and D. L. Weaver, *Nature, 212,* 286 (1966).
24 H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem., 12,* 2084 (1973).
25 J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity", 2nd Ed. Harper and Row, Phila., Pa. 1978, p. 276 *et seq.*
26 D. W. Meek, D. K. Straub and R. S. Drago, *J. Am. Chem. Soc., 82,* 6013 (1960).
27 W. D. Horrocks, Jr. and F. A. Cotton, *Spectrochim. Acta, 17,* 134 (1961).
28 A. B. P. Lever, *J. Chem. Ed., 45,* 711 (1968).
29 D. Landini, G. Modena, G. Scorrano and F. Taddei, *J. Am. Chem. Soc., 91,* 6703 (1969).
30 C. K. Jϕrgensen, *Acta Chem. Scand., 10,* 887 (1956).
31 W. E. Bull and L. E. Moore, *J. Inorg. Nucl. Chem., 27,* 1341 (1965).
32 F. A. Cotton, R. Francis and W. D. Horrocks, *J. Phys. Chem., 64,* 1534 (1960).
33 C. K. Jϕrgensen, "Absorption Spectra and Chemical Bonding in Complexes", Addison–Wesley, Reading, Mass., 1962, p. 111.
34 R. S. Drago, D. W. Meek, R. Longhi and M. D. Joesten, *Inorg. Chem., 2,* 1056 (1963).
35 D. W. Herlocker, R. S. Drago and V. I. Meek, *Inorg. Chem., 5,* 2009 (1966).
36 G. Modena, *Int. J. Sulfur Chem., C, 7,* 95 (1972) and references therein.
37 K. F. Purcell and J. C. Kotz, "Inorganic Chemistry", Saunders, Philadelphia, Pa., 1977, p. 568.