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Linkage Isomerism of the Sulfinate Ion in Ditoluenesulfinato-Bis(2,2'-bipyridyl) Complexes of Iron(II), Cobalt(II), and Nickel(II)

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Linkage isomers involving the O- and S-bonded unidentate sulfinate ions were prepared. The isomers are of the type $[M(bipy)_2(RSO_2)_2]$ where R = p-toluene and the metal = Fe^{II}, Co^{II}, and Ni^{II}. In the iron(II) compounds, S-bonded sulfinate effects spin-pairing. Thus, Mössbauer spectra of the iron(II) O-bonded (Ia) and S-bonded (Ib) isomers show, at 295°K, quadrupole splittings $\Delta E_Q = 2.65$ and 0.31 mm/sec and isomer shifts $\delta^{IS} = +0.99$ and $+0.31$ mm/sec, for Ia and Ib, serially. These values are characteristic for $^5T_2$ and $^1A_1$ ground states in iron(II) consistent with the magnetic moments, at 292°K, of $\mu_{eff} = 5.27$ and 0.95 BM in Ia and Ib, respectively. From the electronic d–d spectra of nickel(II) O-bonded (IIa) and S-bonded (IIb) isomers, the average values 10Dq = 10,200 and 11,600 cm^{-1} as well as $\beta_{35} = 1.03$ and 0.97 were obtained for IIa and IIb, serially. In the O-bonded cobalt(II) isomer (IIIa), 10Dq = 11,025 cm^{-1} and $\beta_{35} = 0.84$, whereas only the $a^4T_1 \rightarrow {}^4T_2$ transition has been observed in the S-bonded isomer (IIIb) giving the estimate 10Dq ~ 12,300 cm^{-1}. The magnetism of IIa,b, and IIIa,b is consistent with six-coordinated nickel(II) and cobalt(II), respectively. The consequences with regard to the position of the unidentate O- and S-bonded sulfinate ion in the spectrochemical and nephelauxetic series are discussed.

Introduction

The sulfinate ion RSO_2^- is well known for its capability to coordinate to a metal atom as a unidentate ligand in two possible ways, *i.e.* through an O or the S atom. In addition, bidentate coordination through two oxygen atoms has been observed as have bridging sulfinate groups. Infrared spectroscopy provides a convenient means to distinguish between the different possibilities.[2,3]

Recently, we have reported[4] on the electronic absorption and emission spectra, the magnetic susceptibilities, and the ^{57}Fe Mössbauer spectra of the tris-(O,O'-sulfinate) complexes of vanadium(III), chromium(III), and iron(III). The d–d spectra have been employed to establish the position of the bidentate O-bonded sulfinate ligand in the spectrochemical and the nephelauxetic series.

In the present investigation, linkage isomers of the unidentate sulfinate ion were obtained, in transition metal complexes, for the first time. The isomers are of the type $[M(bipy)_2(RSO_2)_2]$ where bipy = 2,2'-bipyridyl, R = p-toluene, and where the metals involved comprise iron(II), cobalt(II), and nickel(II). The electronic ground states of the complexes were established on the basis of magnetic susceptibilities and, in the iron(II) compounds, by the ^{57}Fe Mössbauer spectra. In addition, the d–d bands in the electronic spectra determine the spectrochemical position of both the O- and the S-bonded unidentate sulfinate ligand and, approximately, the position of the ligand in the nephelauxetic series as well.

Experimental Section

(*a*) *Preparation of Di(p-toluenesulfinato)bis2,2'-bipyridyl)metal(II) Complexes.* $[M(bipy)_3](CH_3C_6H_4SO_2)_2$ (M = Fe, Co, Ni) was extracted on a fritted disk with dry acetone (100 ml) under reflux, until the passing acetone appeared colorless. The residue on the disk then consists of the O—bonded isomer $[M(bipy)_2(CH_3C_6H_4OSO)_2]$. In the receiver, the corresponding S—bonded isomer $[M(bipy)_2(CH_3C_6H_4SO_2)_2]$ may be precipitated with ether. The starting materials $[M)bipy)_3](CH_3C_6H_4SO_2)_2$ were easily accessible from $[M(CH_3C_6H_4SO_2)_2(H_2O)_2]$ and 2,2'-bipyridyl in aqueous solution.[3]

Di(p-toluenesulfinato)bis(2,2'-bipyridyl)iron(II). 5.32 g (6.1 mmol) $[Fe(bipy)_3](CH_3C_6H_4SO_2)_2 \cdot 2H_2O$ were extracted for 1 hr as described above to yield 93% of blue-black crystals of the O—bonded isomer. *Anal.* Calcd for $C_{34}H_{30}N_4O_4S_2Fe$: C, 60.25; H, 4.43; N, 8.26; O, 9.45; S, 9.45; Fe, 8.23. Found: C, 60.56; H, 4.36; N, 8.04; O, 10.03; S, 9.12; Fe, 7.99. Mol wt calcd: 678.33. Found: 599 in dmso. In addition, 7% of dark red crystals of the S—bonded isomer were ob-

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[2] E. Lindner and G. Vitzthum, *Chem. Ber.*, *102*, 4062 (1969).

[3] E. Lindner, I.P. Lorenz, and G. Vitzthum, *Angew. Chem.*, *83*, 213 (1971); *ibid., Internat. Ed.*, *10*, 193 (1971).

[4] E. König, E. Lindner, I.P. Lorenz, G. Ritter, and H. Gausmann, *J. Inorg. Nucl. Chem.*, *33*, 3305 (1971).

tained. *Anal.* Calcd for $C_{34}H_{30}N_4O_4S_2Fe \cdot 2H_2O$: C, 57.10; H, 4.76; N, 7.84; O, 13.44; S, 8.98; Fe, 7.81. Found: C, 57.24; H, 4.63; N, 8.09; O, 13.76; S, 9.08; Fe, 8.02. Two moles of H_2O were determined by the weight loss over P_2O_5.

Di(p-toluenesulfinato)bis(2,2′-bipyridyl)cobalt(II) 2.1 g (2.51 mmol) $[Co(bipy)_3](CH_3C_6H_4SO_2)_2$ were extracted for 12 hr as described above to yield 91% of the orange O—bonded isomer. *Anal.* Calcd for $C_{34}H_{30}N_4O_4S_2Co$: C, 59.85; H, 4.41; N, 8.22; O, 9.40; S, 9.40; Co, 8.65. Found: C, 59.66; H, 4.44; N, 8.02; S, 9.61; Co, 8.78. In addition, 8% of the yellow S—bonded isomer resulted. *Anal.* Found: C, 59.10; H, 4.38; N, 8.68; S, 9.69; Co, 8.52.

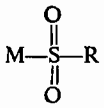
Di(p-toluenesulfinato)bis(2,2′-bipyridyl)nickel(II). 2.33 g (2.86 mmol) $[Ni(bipy)_3](CH_3C_6H_4SO_2)_2$ were extracted for 6 hr as described above. Yield: 95% of the green O-bonded isomer. *Anal.* Calcd for $C_{34}H_{30}N_4O_4S_2$-Ni: C, 59.90; H, 4.41; N, 8.22; O, 9.40; S, 9.40; Ni, 8.63. Found: C, 59.96; H, 4.44; N, 8.50; S, 9.29; Ni, 8.52. In addition, 5% of the pink S-bonded isomer were obtained. *Anal.* Found: C, 60.28; H, 4.52; N, 8.74; S, 9.17; Ni, 8.41.

(*b*) *Microanalyses and Molecular Weight.* Analyses of C, H, N, O, Fe, Co, and Ni were carried out at the Institute of Inorganic Chemistry II, University of Erlangen-Nürnberg, and, in part, by Dr. F. Pascher, Microanalytical Laboratory, Bonn. Molecular weights were determined by vapor pressure osmometry.

(*c*) *Physical Measurements.* Infrared spectra were recorded in KBr pellets on a Beckman IR 7 spectrophotometer. Static magnetic susceptibilities were measured by the Faraday method on solid samples. The magnetic balance employes a Varian 6" magnet equipped with Henry type pole caps and a Cahn RG electrobalance. $HgCo(NCS)_4$ was used as calibrant. All measurements were made at the field strengths of 5, 7, and 9 kGauss and no field dependence was observed. The diamagnetic corrections used are: Fe^{2+}, −13; Co^{2+}, −12; Ni^{2+}, −11; bipy, −105; $CH_3C_6H_4SO_2$, −88; H_2O, −13 (all values in 10^{-6} cgs/mol). The effective magnetic moment μ_{eff} was determined according to $\mu_{eff} = 2.84(\chi'_m \cdot T)^{1/2}$, χ'_m being the corrected molar susceptibility and T the temperature in °K. ^{57}Fe Mössbauer spectra were measured with a Frieseke and Höpfner FHT800A constant-acceleration spectrometer operating in the multiscaler mode. The output of the multichannel analyzer was punched onto paper tape, processed by a LGP 21 computer, and the normalized spectra were plotted by a Calcomp 565 plotter. Cobalt-57 diffused into copper was used as source. The isomer shifts δ^{IS} are corrected for the source temperature and measured relative to the midpoint of the spectrum of an iron foil absorber at 295°K. To convert to the nitroprusside scale, add +0.257 mm sec^{-1}. Movement of the source toward the absorber corresponds to positive velocities. Electronic spectra of solid samples were measured with a Cary 14 spectrophotometer equipped with the model 1411 diffuse reflectance accessory. LiF was used both as standard and diluent.

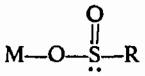
Results and Discussion

Infrared Spectra. It has been shown previously by one of the present authors [2,3] that S— and O—bonded sulfinate ligands may be distinguished by their symmetric and asymmetric stretching frequencies. Thus, for S—bonded unidentate sulfinate ligands (*viz.* type I), $\nu_{as}(SO_2)$ = 1100 – 1250 cm^{-1} and $\nu_s(SO_2)$ = 1000 –1100 cm^{-1}. For O—bonded unidentate sulfinate (*viz.* type II), the ν(SO) frequency involving the uncoordinated oxygen atom occurs in the range 1050-1100 cm^{-1}, whereas ν_{as}(SOM) of the S-O-M bond is shifted to lower frequencies relative to $\nu_s(SO_2)$ of the free sulfinate ion, *viz.* 979 cm^{-1} (in sodium *p*-toluenesulfinate). The sulfinate stretching frequencies of the $[M(bipy)_2(CH_3C_6H_4SO_2)_2]$ complexes are listed in Table I. The type of linkage involved has been established by comparison with the characteristic properties summarized above.



$M{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}{-}R$

(I)



$M{-}O{-}\overset{\overset{O}{\|}}{\underset{\cdot\cdot}{S}}{-}R$

(II)

Magnetism and ^{57}Fe Mössbauer Effect. The results of magnetic measurements at four different temperatures are presented in Table II in terms of the molar magnetic susceptibility χ_m and the magnetic moment μ_{eff}. Values of the Weiss constant Θ are included for all those compounds where the susceptibility is following the Curie-Weiss law, $\chi_m = C_m/(T-\Theta)$, over the temperature range 77-293°K. Since all the values of Θ are rather small, significant metal-metal interaction is not involved. The magnetic moments for the $[Fe(bipy)_2(CH_3C_6H_4SO_2)_2]$ isomer containing O-bonded sulfinate ligands are typical of $^5T_2$ ground states in iron(II).[5] On the other hand, a $^1A_1$ iron(II) ground state is implied in the S-bonded isomer by μ_{eff}-values varying, over the range of temperatures studied, between 0.77 and 0.95 BM. Indeed, magnetic moments of this magnitude and of comparable temperature-dependence were recently calculated[6] for the $^1A_1(t_2^6)$ ground state if complete configuration interaction is included.

The inference of two different ground states in the O—and the S—bonded isomers is further supported by the results of ^{57}Fe Mössbauer effect studies listed in Table III. The values of the isomer shift δ^{IS} and the quadrupole splitting ΔE_Q of the O-bonded isomer are both typical of a $^5T_2$ ground term (high-spin iron (II)), those of the S-bonded isomer are typical of a $^1A_1$ ground term (low-spin iron(II)).[7] There is an appreciable temperature dependence of ΔE_Q in the O-bonded isomer which may be rationalized in terms of an axial ligand field. A relevant plot based on calculations of the temperature and distortion dependence of ΔE_Q for high-spin iron(II) has been presented elsewhere.[8] From a comparison with the present

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Table I. Stretching Frequencies of the Sulfinate Ligand (in cm^{-1}) in the Linkage Isomers $[M(bipy)_2(CH_3C_6H_4SO_2)_2]$, M=$Fe^{II}$, Co^{II}, Ni^{II}.

Compound	$\nu_{as}(SO_2)$ or $\nu(SO)$	$\nu_s(SO_2)$ or $\nu_{as}(SOM)$	Structure
$Fe(bipy)_2(CH_3C_6H_4SO_2)_2$,	1219 vs	1034 m	S-sulfinate
red isomer	1199 vs	1012 m	
$Fe(bipy)_2(CH_3C_6H_4OSO)_2$,	1054 vs	918 vs	O-sulfinate
blue-black isomer			
$Co(bipy)_2(CH_3C_6H_4SO_2)_2$,	1215 vs	1034 m	S-sulfinate
yellow isomer	1202 vs	1012 m	
$Co(bipy)_2(CH_3C_6H_4OSO)_2$,	1056 vs	944 m	O-sulfinate
orange isomer		920 s	
$Ni(bipy)_2(CH_3C_6H_4SO_2)_2$,	1219 vs	1035 vs	S-sulfinate
pink isomer	1204 vs	1013 s	
$Ni(bipy)_2(CH_3C_6H_4OSO)_2$,	1055 vs	958 m	O-sulfinate
green isomer		943 m	

Table II. Magnetic Data for $[M(bipy)_2(CH_3C_6H_4SO_2)_2]$ Complexes, M=Fe^{II}, Co^{II}, Ni^{II}.

Compound	T °K	χ_m 10^{-6}cgs mol^{-1}	μ_{eff} [a] BM	Θ [b] °K
$[Fe(bipy)_2(CH_3C_6H_4OSO)_2]$,	292	11,380	5.27	—6
O-bonded isomer	273	12,142	5.25	
	195	16,711	5.19	
	77	41,614	5.11	
$[Fe(bipy)_2(CH_3C_6H_4SO_2)_2] \cdot 2H_2O$,	294	—47.278	0.95	...
S-bonded isomer	273	—22.113	0.94	
	195	75.192	0.89	
	77	538.20	0.77	
$[Co(bipy)_2(CH_3C_6H_4OSO)_2]$,	293	9170.5	4.77	—18
O-bonded isomer	273	9796.5	4.74	
	195	13,254	4.63	
	77	30,826	4.40	
$[Co(bipy)_2(CH_3C_6H_4SO_2)_2]$,	293	6822.2	4.13	—25
S-bonded isomer	273	7327.5	4.12	
	195	10,024	4.05	
	77	23,129	3.82	
$[Ni(bipy)_2(CH_3C_6H_4OSO)_2]$,	293	3931.1	3.20	—10
O-bonded isomer	273	4159.7	3.17	
	195	5834.7	3.13	
	77	14,760	3.07	
$[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$,	293	3532.4	3.05	—22
S-bonded isomer	273	3720.4	3.01	
	195	4887.9	2.88	
	77	11,713	2.74	

[a] Experimental uncertainty ±0.05 BM. [b] Experimental uncertainty ±5°K.

Table III. Isomer Shifts δ^{IS} and Quadrupole Splittings ΔE_Q from ^{57}Fe Mössbauer Spectra of $[Fe(bipy)_2(CH_3C_6H_4SO_2)_2]$ Complexes

Compound	T °K	δ^{IS} [a] mm sec^{-1}	ΔE_Q mm sec^{-1}
$[Fe(bipy)_2(CH_3C_6H_4OSO)_2]$,	295	$+0.99\pm0.03$	2.65 ± 0.02
O-bonded isomer	77	$+0.98\pm0.03$	3.37 ± 0.02
$[Fe(bipy)_2(CH_3C_6H_4SO_2)_2] \cdot 2H_2O$,	295	$+0.31\pm0.04$	0.31 ± 0.03
S-bonded isomer	77	$+0.25\pm0.04$	0.33 ± 0.03

[a] Isomer shifts δ^{IS} are relative to the center of the spectrum of an iron foil absorber at 295°K. Following convention, δ^{IS} is taken as positive when the source is moved toward the absorber.

results, an axial field splitting of the $^5T_2$ term of $\delta = -1450\pm70$ cm^{-1} has been estimated. The splitting involved being according to $^5T_2 \rightarrow {^5B_2} + {^5E}$, the ground state is $^5B_2$ within the approximation of an axial ligand field.

The present results on the compounds $[Fe(bipy)_2(CH_3C_6H_4SO_2)_2]$ may be compared with investigations on the extended series of $[Fe(phen)_2X_2]$ complexes containing the related ligand 1,10-phenanthroline (phen).[9] In general, the data reported above fit well with those in the latter series. It should be observed, however, that a $^1A_1$ ground state has been obtained in $[Fe(phen)_2X_2]$ complexes only if X=(½)phen, NO_2, CNO, or CN. In the corresponding $[Fe(bipy)_2X_2]$

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(8) E. König, G. Ritter, H. Spiering, S. Kremer, K. Madeja, and A. Rosenkranz, *J. Chem. Phys.*, in the press.

(9) E. König, *Coord. Chem. Rev.*, 3, 471 (1968).

series, the only low-spin compounds hitherto known are for X=(½)bipy, CNO, and CN.[9] Thus it may be concluded that, on a relative scale, the ligand field introduced by the S–bonded sulfinate ion must be rather strong. A more reliable estimate of the ligand fields of the O– and the S–bonded sulfinate ligand will be discussed below.

The μ_{eff}–values of the $[Co(bipy)_2(CH_3C_6H_4SO_2)_2]$ complexes are indicative of six-coordinated high-spin cobalt(II) having an $a^4T_1(t_2^5e^2)$ ground state. The somewhat low moment of the S–bonded isomer may be affected by the presence of an impurity. This compound is extremely difficult to prepare and decomposition is observed once it is isolated from solution (*cf.* below).

The magnetic moments of the complexes $[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$ are within the range (*viz.* 2.80-3.50 BM) commonly encountered in six-covalent octahedral nickel(II). The ground term being $^3A_2(t_2^6e^2)$, strictly octahedral complexes of nickel(II) should show moments which are determined according to[10]

$$\mu_{eff}=2.83(1-4\lambda/10Dq) \qquad (1)$$

In eq (1), λ is the spin-orbit coupling constant, λ = -315 cm^{-1} in the free Ni^{2+} ion, and 10Dq denotes the octahedral ligand field splitting parameter. It follows that, in general, moment values somewhat higher than the spin-only value for $S = 1$ (2.83 BM) should be expected. In addition, μ_{eff} should be the smaller, the higher 10Dq. This inference is well documented by the present compounds (*cf.* μ_{eff} in Table II and 10Dq in Table VII), although the symmetry is certainly lower than octahedral.

Electronic Spectra. The d-d spectrum of the O–bonded isomer of $[Fe(bipy)_2(CH_3C_6H_4SO_2)_2]$ consists of a single broad band with maximum at 10,800 cm^{-1} (*cf.* Table IV) which we assign to the $^5T_2 \rightarrow {}^5E$ transition of a high-spin iron(II) ion. In strictly octahedral complexes of iron(II), *e.g.* the $Fe(H_2O)_6^{2+}$ ion, the excited ^5E state is split by the Jahn-Teller effect,[11] whereas in high-spin compounds of the $[Fe(diimine)_2X_2]$ type, the splitting is caused by static fields of lower symmetry.[9] Although no splitting of the $^5T_2 \rightarrow {}^5E$ band is observed in the present case, this may be due to the raising background of the intense charge-transfer band at 16,000 cm^{-1} and to low resolution of the broad d-d band. In the S–bonded isomer of $[Fe(bipy)_2(CH_3C_6H_4SO_2)_2]$, d-d bands were not observed.

Table IV. Absorption Maxima in the Electronic Spectra of $[Fe(bipy)_2(CH_3C_6H_4SO_2)_2]$ Complexes (in cm^{-1}).

$[Fe(bipy)_2(CH_3C_6H_4SO_2)_2]$		
O-bonded isomer	S-bonded isomer	Assignment
10,800	. . .	$^5T_2(t_2^4e^2) \rightarrow {}^5E(t_2^3e^3)$
16,000	18,520	$(core)\pi^2t_2^ne^m \rightarrow$ $(core)\pi^2t_2^{n-1}e^m\pi^*$
18.180	20,830	
. . .	27,030	
32,260	32,260	$^1A_1(bipy) \rightarrow {}^1B_1(bipy)$
33,330	33,330	
39,220	39,220	$^1A_1(bipy) \rightarrow {}^1A_1(bipy)$

There are two bands of high intensity at 16,000 cm^{-1} and 18,180 cm^{-1} in the O-bonded isomer and at 18,520 cm^{-1} and 20,830 cm^{-1} in the S–bonded isomer of $[Fe(bipy)_2(CH_3C_6H_4SO_2)_2]$ (*cf.* Table IV) which are usually assigned to charge transfer of the metal-to-ligand type. To shorter wavelengths, these bands are followed by internal $\pi \rightarrow \pi^*$ transitions of the 2,2'-bipyridyl ligands showing a small shift to lower energy due to the reversed crystal-field effect of the central ion.[12,13]

Table V. Absorption Maxima in the Electronic Spectra of $[Co(bipy)_2(CH_3C_6H_4SO_2)_2]$ Complexes (in cm^{-1}) [a].

$[Co(bipy)_2(CH_3C_6H_4SO_2)_2]$		
O-bonded isomer	S-bonded isomer	Assignment
9800	11,000	$a^4T_1(t_2^5e^2) \rightarrow {}^4T_2(t_2^4e^3)$
. . .	. . .	$a^4T_1(t_2^5e^2) \rightarrow {}^4A_2(t_2^3e^4)$
20,830	. . .	$a^4T_1(t_2^5e^2) \rightarrow b^4T_1(t_2^4e^3)$
(27,780)	(29,410)	charge transfer
32,260	32,470	$^1A_1(bipy) \rightarrow {}^1B_1(bipy)$
33,330	33,330	
39,680	40,480	$^1A_1(bipy) \rightarrow {}^1A_1(bipy)$

[a] Shoulders in parentheses.

Table VI. Absorption Maxima in the Electronic Spectra of $[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$ Complexes (in cm^{-1}) [a].

$[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$		
O-bonded isomer	S-bonded isomer	Assignment
10,200	11,600	$^3A_2(t_2^6e^2) \rightarrow {}^3T_2(t_2^5e^3)$
12,800	12,800	$^3A_2(t_2^6e^2) \rightarrow {}^1E(t_2^6e^2)$
(16,000)	18,800	$^3A_2(t_2^6e^2) \rightarrow a^3T_1(t_2^5e^3)$
17,200	. . .	
(26,000)	(27,000)	charge transfer
32,260	32,260	$^1A_1(bipy) \rightarrow {}^1B_1(bipy)$
33,330	33,330	
39,220	39,680	$^1A_1(bipy) \rightarrow {}^1A_1(bipy)$

[a] Shoulders in parentheses.

The d-d spectrum of the O–bonded isomer of $[Co(bipy)_2(CH_3C_6H_4SO_2)_2]$ shows two bands, *viz.* $a^4T_1 \rightarrow {}^4T_2$ at 9800 cm^{-1} and $a^4T_1 \rightarrow b^4T_1$ at 20,830 cm^{-1} *cf.* Table V). From these data, 10Dq and B_{35} were calculated on the basis of procedure (b)[14] of the usual first-order perturbation treatment, the resulting values being listed in Table VII. It follows that the second spin-allowed band ($a^4T_1 \rightarrow {}^4A_2$) should occur at 20,825 cm^{-1}. Since this is almost accurately the energy of the $a^4T_1 \rightarrow b^4T_1$ transition, it is not surprising that this band which usually shows weak intensity has not been observed. This inference is immediately apparent by reference to the empirical energy-level diagram of Reedijk *et al.*[15] assuming $Dq/B = 1.35$. In the S–bonded isomer, the $a^4T_1 \rightarrow {}^4T_2$ band is shifted to higher energy by ~1200 cm^{-1}. Unfortunately, in the wavelength region where the $a^4T_1 \rightarrow b^4T_1$ transition is expected, only a slowly rising background absorption was observed. This seems to be due to the absorption of some unidentified de-

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Table VII. Spectral Parameters of the Averaged Field in Ditoluenesulfinato-bis(2,2′-bipyridyl) Complexes of Nickel(II) and Cobalt(II)

Complex	10Dq cm^{-1}	B_{35} [a] cm^{-1}	β_{35} [a,b]	B_{33} [c] cm^{-1}	β_{33} [b,c]
$[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$,					
O-bonded isomer	10,200	1070.8	1.03	825.0	0.79
S-bonded isomer	11,600	1015.4	0.97	821.8	0.79
$[Co(bipy)_2(CH_3C_6H_4SO_2)_2]$,					
O-bonded isomer	11,025	817.0	0.84		
S-bonded isomer [d]	~12,300	~820	~0.85		

[a] Subject to uncertainties discussed in reference (14). [b] $B_{free}(Ni^{2+}) = 1041$ cm^{-1}; $B_{free}(Co^{2+}) = 971$ cm^{-1}. [c] Determined from the band energy of $^3A_2(t_2^6e^2) \rightarrow {}^1E(t_2^6e^2)$. [d] Values estimated (see text for details).

composition product. The compound is photo-sensitive and changes color to brown on exposure to the monochromator beam. However, if a shift by ~1200 cm^{-1} to higher energy is tentatively assumed for the $a^4T_1 \rightarrow b^4T_1$ transition, the parameter values listed in Table VII are obtained. In this case, the $a^4T_1 \rightarrow {}^4A_2$ band is calculated at 23,300 cm^{-1} and thus would again be obscured. At higher energies, charge-transfer and internal $\pi \rightarrow \pi^*$ transitions of 2,2′-bipyridyl are encountered, *viz.* Table V.

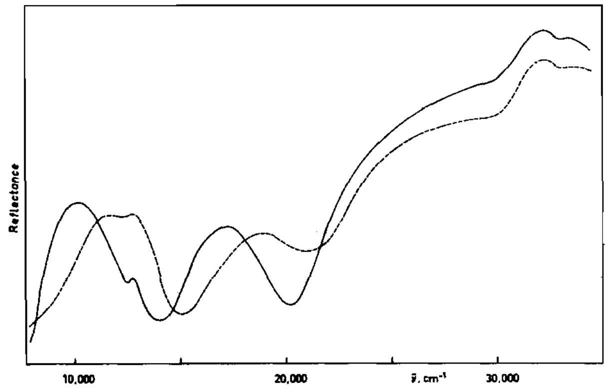

Figure 1. Electronic reflectance spectra of $[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$ complexes containing O-bonded (full line) and S-bonded (broken line) sulfinate ion.

The d-d spectra of $[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$ are characterized by two medium intensity bands (*viz.* Figure 1), one in the 10,000 – 12,000 cm^{-1} range assigned to the $^3A_2 \rightarrow {}^3T_2$ transition, the other in the region of 17,000 – 19,000 cm^{-1} due to $^3A_2 \rightarrow a^3T_1$. In the O–bonded isomer, the latter band shows a shoulder at ~ 16,000 cm^{-1} probably due to a splitting according to $^3T_1 \rightarrow {}^3A_2 + {}^3E$. The center of gravity of the band is estimated at ~16,900 cm^{-1}. In the S–bonded isomer, the two bands are shifted by ~1500 cm^{-1} to higher energy as compared to the O–bonded isomer. The $^3A_2(t_2^6e^2) \rightarrow {}^1E(t_2^6e^2)$ transition is observed, in both isomers, at 12,800 cm^{-1}. The $^3A_2(t_2^6e^2) \rightarrow b^3T_1(t_2^4e^4)$ transition is apparently masked by a moderately intense charge-transfer band at ~26,000 cm^{-1}. Similar to the iron(II) compounds discussed above, internal $\pi \rightarrow \pi^*$ transitions of 2,2′-bipyridyl follow at higher energies. A complete listing of band energies and assignments is presented in Table VI. The values of 10Dq, B_{35}, and β_{35} resulting from these data are compiled in Table VII. Since only two spin-allowed bands were observed, B_{35} was calculated according to procedure (a)[14] of the usual first-order perturbation treatment. The values of B_{33} were determined fron the energy of the $^3A_2 \rightarrow {}^1E$ band, employing the expressions corrected for subshell intermixing.[16] Also, β_{35} and β_{33} are the corresponding nephelauxetic ratios, *e.g.* $\beta_{35} = B_{35,\ complex}/B_{free\ ion}$.

Spectrochemical Position of the O– and the S–bonded Sulfinate Ion. To obtain an estimate of the octahedral ligand field splitting parameter Δ = 10Dq of the O– and the S–bonded unidentate p–toluenesulfinate ion, the rule of average environment[17] will be applied. According to this rule as applied to the present nickel(II) complexes,

$$\Delta\{Ni(bipy)_2(RSO_2)_2\} = {}^2/_3\Delta\{Ni(bipy)_3{}^{2+}\} + {}^1/_3\Delta\{Ni(RSO_2)_6{}^{4-}\} \qquad (2)$$

where R = p-$CH_3C_6H_4$. In the $[Ni(bipy)_3]^{2+}$ ion, 10Dq = 12,200 cm^{-1} has been reported.[18] Employing the values of 10Dq for the two isomers listed in Table VII we obtained 10Dq}Ni,O–sulf} = 6200 cm^{-1} and 10Dq}Ni,S–sulf} = 10,400 cm^{-1} for the hypothetical $[Ni(CH_3C_6H_4SO_2)_6]^{4-}$ ion containing O– and S–bonded sulfinate ligands, respectively. The ligand field strength of the S–bonded sulfinate ion is thus comparable to that of triethylamine (10Dq = 10,500 cm^{-1} in $[Ni(N\}C_2H_5\{_3)_6]^{2+}$).[14] Using the empirical relation 10Dq = f(ligand) · g(central ion) due to Jørgensen[17] and g(Ni^{II}) = 8.9, one arrives at f = 1.17 for the S–bonded sulfinate ion. This value seems to be reasonable, although it is difficult to estimate the inaccuracy introduced by application of eq (2). On the other hand, the value for 10Dq of the O–bonded sulfinate ion is certainly much too low. The lowest splitting parameters in octahedral nickel (II), *viz.* 10Dq ~ 7250 cm^{-1}, were reported for fluoride coordination.[19] In $NiBr_2$, 10Dq = 6800 cm^{-1}.[20] However, this value is probaly caused by a lower than octahedral symmetry around the nickel(II) ion.[20] We assume, therefore, that in $[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$ containing O–bonded sulfinate ligands the value of 10Dq is likewise affected by a distorted octahedral ligand arrangement. This assertion is supported by the large axial field observed in the analogous iron(II) complex on the basis of the quadrupole

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splitting (*cf.* above). In addition, it is consistent with X-ray structure results on the high-spin and low-spin forms of $[Fe(bipy)_2(NCS)_2]$.[21] On the other hand, employing 10Dq = 12,670 cm^{-1} for the $[Co(bipy)_3]^{2+}$ ion,[22] we obtained 10Dq{Co,O—sulf} = 7735 cm^{-1} for the hypothetical ion $[Co(CH_3C_6H_4OSO)_6]^{4-}$ on the basis of eq. (2). This result yields, in conjunction with $g(Co^{II}) = 9.3$,[18] the value f = 0.83 for the O—bonded sulfinate ion. This value for f places O—bonded sulfinate close to the chloride ion in the spectrochemical series which seems reasonable. In any case, the values deduced above clearly demonstrate the considerably higher ligand field strength of the S—bonded sulfinate as compared to the O—bonded sulfinate ion.

Nephelauxetic Effect of O— and S—bonded Sulfinate. With respect to the nephelauxetic ratio β there is no simple relationship in mixed complexes comparable to eq (2). In addition, it was recently demonstrated[14] that the accuracy of the parameters B_{35} and β_{35} is subject to certain limitations depending on the band energies used in the fit. Since, in the nickel(II) complexes studied at present, B_{35} was determined from the energy of the second band (*i.e.* the $^3A_2 \rightarrow a^3T_1$ transition), values resulting from the same procedure (*viz.* method (a) in reference (14)) should be applied for comparative purposes. It then follows that the average values of β_{35} listed in Table VII, *viz.* $\beta = 1.03$ and 0.97, compare well with those in $[Ni(en)_3]^{2+}$ ($\beta_{35} = 1.03$ with method (a)) and $[Ni(den)_2]^{2+}$ $\beta_{35} = 0.99$ with method (a)), respectively. On the other hand, application of method (a) to the spectral data of $[Ni(bipy)_3]^{2+}$ [22] results in $B_{35} = 746.1$ cm^{-1} and $\beta_{35} = 0.72$. Likewise, $[Ni(bipy)_3]^{2+}$ yields $B_{33} = 760.9$ cm^{-1} and $\beta_{33} = 0.73$. Thus the decrease of the Racah parameter B of interelectronic repulsion is much less in the $[Ni(bipy)_2(CH_3C_6H_4SO_2)_2]$ complexes than in the $[Ni(bipy)_3]^{2+}$ ion. This result implies a less covalent average metal-ligand interaction in the mixed complexes as compared to that in $[Ni(bipy)_3]^{2+}$. Less pronounced but similar results are produced in the cobalt(II) analogues. Thus, $[Co(bipy)_3]^{2+}$ yields[22] $B_{35} = 791$ cm^{-1} and $\beta_{35} = 0.81$, whereas $B_{35} = 817$ cm^{-1} and $\beta_{35} = 0.84$ are obtained from the $[Co(bipy)_2(CH_3C_6H_4SO_2)_2]$ complexes. It should be kept in mind that any comparison of spectral parameters which were obtained by method (a) in nickel(II) may be affected by experimental uncertainties[14] and the same applies to a lesser degree to method (b) in cobalt(II). However, the β-values observed in nickel(II) are strikingly different which gives weight to the above conclusion.

Summary and Conclusions

The present investigation provides evidence for the considerably larger ligand field strength of the S—bonded over that of the O—bonded sulfinate ion. This is exemplified by the 10Dq values for the average field in the $[M(bipy)_2(RSO_2)_2]$ isomers, M = cobalt(II) and nickel(II), which were determined from d-d spectra. A consequence of this property is the spin-pairing introduced by the S—bonded sulfinate ligand in the iron(II) complex, $[Fe(bipy)_2(RSO_2)_2]$, R = *p*-toluene.

According to available chemical experience,[3] the S—bonded sulfinate is likely to be considered as a soft Lewis base,[23] whereas O—bonded sulfinate is a hard base comparable to other oxygen containing anions. Similar to metal-N and metal-S bonding in complexes involving the thiocyanate ion,[24] hard metals (class A metals according to the Ahrland-Chatt-Davies classification[25]) form M-O bonds with sulfinate ligands, whereas M-S bonds are prefered by soft metals (class B). Thus it is surprising at first sight that linkage isomers of the sulfinate ion may be prepared in the first transition metal series with metals like Fe^{II}, Co^{II} and Ni^{II}. However, it is well known that the softness of a metal is dependent on other ligands present. 2,2'-Bipyridyl as the other ligand certainly favors the softness of a metal by increasing the π-back-bonding capability of the central ion. In addition, the small yields of the S—bonded isomers during the preparation may serve to demonstrate that, even in the present compounds, the formation of the O—bonded isomer is prefered.

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