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Methanesulfonato Complexes of Cobalt, Nickel, and Copper

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Cobalt(II), nickel(II), and copper(II) complexes of the general formula $[ML_4(CH_3SO_3)_2]$ are reported (L = pyridine and 4-methylpyridine). Also prepared was $[Co(py)_2(CH_3SO_3)_2]$. Infrared and electronic spectra and magnetic susceptibility measurements indicate that all are high-spin tetragonally distorted octahedral complexes. Upon evaluation of crystal field parameters, Ds and Dt, it was found that the methanesulfonate anion coordinates more strongly than perchlorate and tetrafluoroborate, but less strongly than chloride and bromide.

Introduction

The coordinating properties of anions of strong acids have been the subject of several recent studies. In particular, the anions of perchloric, tetrafluoroboric, hexafluorophosphoric, and trifluoromethanesulfonic acids have been extensively investigated. A review of the coordinating tendencies of anions of strong acids has been presented by Rosenthal [1].

As the anion of a strong acid, the methanesulfonate group would be expected to coordinate only weakly to metal ions in complex compounds; relatively little, however, is known about the coordinating properties of this group. Paul and coworkers [2] have reported the synthesis and characterization of anhydrous cobalt(II), nickel(II), copper(II), vanadium(III), and chromium(III) methanesulfonates. These compounds were found to be high-spin octahedral complexes and a polymeric structure was proposed. Yeats, Sams, and Aubke [3] have prepared trimethyltin(IV) methanesulfonate which was shown to contain bridging CH_3SO_3 groups. This paper describes the preparation and characterization of some cobalt(II), nickel(II), and copper(II) complexes containing the coordinated CH_3SO_3 group.

Experimental

Reagents

The cobalt, nickel, and copper methanesulfonates were prepared in the same manner. A slurry of the metal carbonate (Baker) was treated with methanesulfonic acid (Eastman). After filtration to remove unreacted carbonate, the solution was evaporated until crystals formed. The hydrated salts were dried at 78 °C for several days. Pyridine (py) was used as received from Fisher Scientific Co. 4-Methylpyridine (4-mepy) was supplied by Eastman Organic Chemicals and was distilled once (b.p. 143–5 °C). Practical grade 2,2-dimethoxypropane (Eastman), methanol and diethyl ether (Fisher) were used as received.

Synthesis

Tetrapyridine complexes, $[ML_4(CH_3SO_3)_2]$

All of the tetrapyridine complexes were prepared in the same general manner. 8×10^{-3} mol (approximately 2 g) of the hydrated metal(II) methanesulfonate was dissolved in a minimal amount of methanol and 2,2-dimethoxypropane. The solution was stirred for one hour, after which an excess of pyridine or 4-methylpyridine (5×10^{-2} mol, approximately 5 ml) was slowly added with stirring. If the complex did not precipitate within 30 minutes, anhydrous ether was added dropwise to force precipitation. Each complex was filtered in a nitrogen atmosphere, dried at 65 °C under reduced pressure for several hours, and stored in a dry box.

Table I summarizes the analytical data and melting points for the $[ML_4(CH_3SO_3)_2]$ complexes.

Bismethanesulfonatobispyridinecobalt(II), $[Co(py)_2(CH_3SO_3)_2]$

Pink bismethanesulfonatotetrapyridinecobalt(II), $[Co(py)_4(CH_3SO_3)_2]$, was heated at 110 °C in an Abderhalden pistol until a uniform purple product was obtained. It decomposed at temperatures above 250 °C. Analytical data are presented in Table I.

Physical Measurements

Infrared spectra were obtained for the solid samples as Nujol mulls spread between sodium chloride plates. Perkin–Elmer model 257 and Beckman IR-5A recording spectrophotometers were

TABLE I. Methanesulfonate Complexes. Analytical Data and Melting Points[a].

Complex	Color	Mp, °C	μ_{eff}, B.M.	Elemental Analyses Calculated (Found), %		
				C	H	N
$[Co(py)_2(CH_3SO_3)_2]$	Purple	250	–	35.38 (35.77)	3.97 (4.29)	6.88 (7.05)
$[Co(py)_4(CH_3SO_3)_2]$	Pink	200[a]	5.25	46.72 (46.63)	4.64 (4.74)	9.91 (9.87)
$[Ni(py)_4(CH_3SO_3)_2]$	Blue	180[a]	3.17	46.74 (46.61)	4.65 (4.69)	9.91 (9.84)
$[Cu(py)_4(CH_3SO_3)_2]$	Dark Blue	190	1.78	46.34 (46.09)	4.61 (4.72)	9.82 (9.70)
$[Co(4\text{-mepy})_4(CH_3SO_3)_2]$	Pink	195–8	5.20	50.23 (50.30)	5.52 (5.44)	9.02 (8.97)
$[Ni(4\text{-mepy})_4(CH_3SO_3)_2]$	Blue	215–7	3.20	50.25 (48.65)	5.52 (5.26)	9.02 (7.73)
$[Cu(4\text{-mepy})_4(CH_3SO_3)_2]$	Dark Blue	173–5	1.88	49.86 (50.30)	5.47 (5.21)	8.95 (7.88)

[a] Decomposition temperature.

used to scan the 4000–625 cm^{-1} region. The spectra were calibrated using polystyrene film.

Far-infrared spectra (700–150 cm^{-1} region) were obtained as Nujol mulls sandwiched between polyethylene plates using a Digilab FTS-IR20 spectrometer.

Spectra of the complexes in the visible and near-infrared region were obtained using a Cary 17I recording spectrophotometer manufactured by the Applied Physics Corporation. The spectra of solid samples were obtained as Nujol mulls spread on a piece of Kimwipe. The mull was prepared in a nitrogen atmosphere. Kimwipe saturated with Nujol was placed in the reference beam to equilize light scattering.

Solution spectra of the methanesulfonate complexes were obtained in dichloromethane. The spectra were run in 5- and 10-cm matched quartz cells with solvent in the reference beam.

Magnetic susceptibilities of the compounds were measured using a Gouy balance, consisting of an electromagnet, power supply, and current regulator (Alpha Scientific Laboratories) and a semi-micro balance (Mettler). $HgCo(SCN)_4$ was used as a calibrant. All measurements were made at 23 ± 2 °C.

Results and Discussion

The magnetic moments of the new compounds are listed in Table I. The values for the cobalt(II) and nickel(II) compounds are typical of high-spin octahedral stereochemistries. Because the magnetic moments for monomeric (magnetically dilute) copper(II) complexes occur in the range of 1.8–2.0 BM regardless of stereochemistry about the copper atom, these data do not provide a means of determining whether or not the methanesulfonate anion is coordinated.

The infrared spectral features associated with the methanesulfonate group for the complexes prepared in this study are presented in Table II.

The methanesulfonate anion has a tetrahedral structure and belongs to the C_{3v} point group. If the anion is represented as XSO_3^- (where $X = CH_3$), there should be six normal modes of vibration [5], all of which would be active in both the Raman and infrared spectrum. The three totally symmetric (A_1) vibrations include an SO_3 symmetric stretch, an SX stretch, and an SO_3 symmetric bend. The asymmetric (E) vibrations can be described as an SO_3 asymmetric stretch, an SX wag, and an SO_3 asymmetric bend. Upon coordination through an oxygen atom (as in $X{-}SO_2{-}O^*$, where X represents CH_3 and O* represents the coordinating oxygen atom), the symmetry is lowered to C_s. No degeneracy exists in this point group and nine fundamental vibrations are expected. These vibrations [5] may be described as SO_2 symmetric and asymmetric stretches, an SO_2 bending mode, SX and SO* stretches, an SO_2 rock, an SX wag, an SO* wag and a torsion. All vibrations for C_s symmetry are infrared and Raman active.

Assignments made in this work are based upon comparison of the vibrational frequencies of ionic KCH_3SO_3 [5] with those of the coordinated CH_3SO_3 group [6, 7]. The anionic SO_3 symmetric stretch

TABLE II. CH_3SO_3 Vibrational Frequencies (cm^{-1}) in Complexes.

$[M(py)_4(CH_3SO_3)_2]$			$[M(4\text{-mepy})_4(CH_3SO_3)_2]$			$[Co(py)_2(CH_3SO_3)_2]$	Assignment
Co	Ni	Cu	Co	Ni	Cu		
1255	1248	1235	1252	1249	1245	1258 broad 1200	SO_2 asymmetric stretching
1172	1170	1183 1144	1170	1170	1187	1170 broad	SO_2 symmetric stretching
1051	1051	1045	1050	1043	1048	1045 broad	S–O* stretching
774	770	772	780	770	770	770 725	S–CH_3 stretching
550	550	552	550	552	551		SO_2 bend
532	531	527	535	534	525	575–510 broad	SO_2 rock
516	516		517	517			S–O* wag
364	360		350	360		350 broad	torsion
340	340	343	341	340	340		S–CH_3 wag

at 1049 cm^{-1} is observed to shift to higher frequency (by approximately 120 cm^{-1}) upon coordination as would be expected due to the increased double bond character of the SO bonds. The SO_3 asymmetric stretch at 1183 for the anion splits on complexation to give a new band at 1250 cm^{-1} and another band at 1050 cm^{-1}; a greater splitting is observed for the parent acid [6]. This band splitting is consistent with the fact that upon coordination the degeneracy of the asymmetric stretching mode is lifted. Similar splitting effects are observed on coordination for the degenerate SO_3 asymmetric bend and the degenerate SX wag (523 and 346 cm^{-1}, respectively) in the anion. Thus, based upon these observations, it is concluded that only one type of CH_3SO_3 group is present and that the spectral data are consistent with monodentate coordination in the tetrapyridine and tetrakis (4-methylpyridine) cobalt(II) and nickel(II) compounds.

In both copper complexes, the methanesulfonate group is considered to be only weakly coordinated or "semi-coordinated". The degeneracy of the SO_3 asymmetric stretch vibration is lifted to give new bands around 1240 and 1045 cm^{-1} as would be expected on coordination. However, neither of the degenerate modes for the anion in the far-infrared is split.

The infrared spectrum of $[Co(py)_2(CH_3SO_3)_2]$ in the 1400–900 cm^{-1} region consists of very broad bands which could not be completely resolved. The absorptions are listed in Table II. It appears as though more than one type of CH_3SO_3 group is present. The overlapping of absorptions associated with two different environments for the methanesulfonate group could give rise to the observed spectrum. One CH_3SO_3 group might be bidentate with the second ionic. Another possibility which is preferred by the authors is that one CH_3SO_3 is bridging between cobalt centers while the second CH_3SO_3 is associated with only one cobalt. This latter suggestion is consistent with the low solubility of the compound in non-coordinating solvents.

The pyridine and 4-methylpyridine absorption bands were typical of previously reported coordination compounds containing these nitrogen bases [8–10].

One infrared active metal–nitrogen vibration is expected for octahedral or tetragonal (D_{4h} symmetry) compounds [11]. This vibration for the methanesulfonate complexes is listed in Table III and is consistent with coordination of all pyridine and 4-methylpyridine molecules to the metal ion. The metal–nitrogen vibration is split in some of the complexes, presumably due to solid state effects or distortion from octahedral symmetry.

TABLE III. Infrared Absorptions of Metal–Ligand Vibrations. (cm^{-1})

Compound	M–N	M–O
$[Co(py)_4(CH_3SO_3)_2]$	233	170
$[Ni(py)_4(CH_3SO_3)_2]$	248	180
$[Cu(py)_4(CH_3SO_3)_2]$	268	237
$[Co(4\text{-mepy})_4(CH_3SO_3)_2]$	210 260	
$[Ni(4\text{-mepy})_4(CH_3SO_3)_2]$	225 265	
$[Cu(4\text{-mepy})_4(CH_3SO_3)_2]$	240 285	215
$[Co(py)_2(CH_3SO_3)_2]$	225, broad	180

The metal–oxygen vibrational frequencies of the bismethanesulfonatotetrapyridine complexes follow the trend found in their metal–nitrogen vibrations: Cu > Ni > Co. That a metal–oxygen frequency was observed for only bismethanesulfonatotetrakis(4-methylpyridine)copper(II) suggests that the metal–oxygen vibrations for the corresponding cobalt(II) and nickel(II) complexes occur below 170 cm^{-1} and

TABLE IV. Visible and Near-infrared Spectral Data[a].

Absorption Maxima[b,c] (cm^{-1}) and Assignments						
Compound	$^3B_{1g} \rightarrow {}^3E_g$	$\rightarrow {}^3B_{2g}$	$\rightarrow {}^3B_{2g}$	$\rightarrow {}^3E_g$	$\rightarrow {}^3A_{2g}$	$\rightarrow {}^3E_g$
$[Ni(py)_4(CH_3SO_3)_2]$	8330m	11,900w	13,600w (14,240)	16,800s	21,700sh (25,640)	27,000vs
$[Ni(4\text{-}mepy)_4(CH_3SO_3)_2]$	8330m	10,900w	13,300w (12,000)	16,000s	20,400sh (23,200)	26,300vs
	$^4T_{1g} \rightarrow {}^4T_{2g}$		$\rightarrow {}^4T_{1g}({}^4P)$			
$[Co(py)_4(CH_3SO_3)_2]$	9000m		19,200s	21,100vs		
$[Co(4\text{-}mepy)_4(CH_3SO_3)_2]$	8330m		19,000sh	19,400vs	20,600sh	
$[Co(py)_2(CH_3SO_3)_2]$	7940m	14,900m	18,900vs			
$[Cu(py)_4(CH_3SO_3)_2]$	17,900s[d]					
$[Cu(4\text{-}mepy)_4(CH_3SO_3)_2]$	17,000s[d]					

[a] Nujol mull spectra. [b] Calculated values in parentheses. [c] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder. [d] The three expected transitions occur under this broad band envelope.

supports the trend found in the tetrapyridine complexes. Metal–oxygen frequencies are listed in Table III.

The visible and near-infrared mull spectral data for the $[ML_4(CH_3SO_3)_2]$ complexes are presented in Table IV. The band positions and intensities are consistent with those in the literature for octahedral complexes with moderate tetragonal distortion.

From the close agreement of absorption bands for mull and dichloromethane solution spectra of the cobalt and nickel tetrapyridine and tetrakis(4-methylpyridine) complexes, it seemed that no significant dissociation occurs on dissolution in dichloromethane. A shift of the absorption band to lower frequency for the copper complexes in non-coordinating dichloromethane indicates that the weakly-coordinating methanesulfonate anion is probably liberated in solution.

Absorption maxima for the $[Co(py)_2(CH_3SO_3)_2]$ mull spectrum are given in Table IV. From the broad nearly symmetrical bands at 7940 and 20,000 - 18,000 cm^{-1}, it is inferred that tetragonal distortion is small.

The spectra of the nickel(II) complexes are characterized by four main absorption areas. There is a very broad medium intensity band in the near-infrared region having a maximum at 8330 cm^{-1}. Near 11,500 and 13,500 cm^{-1} are found low intensity absorptions. The band near 16,500 cm^{-1} is rather intense and almost symmetrical. The highest intensity band has a maximum around 26,500 cm^{-1}.

Expressions relating the observed transition energies to the parameters Ds, Dt, Dq_{xy}, Dq_z, and the Racah B′ term have been developed for the nickel(II) ion [15] in a *trans*-$[NiL_4X_2]$ type complex. The parameters as well as values for the two $^3B_{1g} \rightarrow {}^3A_{2g}$ transitions were evaluated using a least-squares computer program and are listed in Table V. The calculated values for the transitions do not fit the observed energies in all cases, particularly the higher energy transitions. The lack of agreement is due partly to the difficulty associated with estimating the position of a band maximum that appears as a shoulder on a more intense absorption. However, quite reasonable B′ values (near 860) were obtained.

TABLE V. Electronic Spectral Parameters for $[NiL_4(CH_3SO_3)_2]$ (cm^{-1}).

Parameter[a]	L = py	L = 4-mepy
Dq_{xy}	1190	1090
Dq_z	557	628
Ds	741	622
Dt	363	264
B′	862	867
Δ_1	355	547
Δ_2	11,900	10,900
Δ_3	4730	3809
$d\sigma$	−1793	−1428
$d\pi$	−204	−273

[a] All values include configurational interaction.

McClure [16] has given expressions which relate the crystal field parameters to molecular orbital parameters. These expressions are applicable only to high-spin *trans*-$[M(L)_4(X)_2]$ complexes derived from O_h $M(L)_6$ compounds [16]. The quantity $d\sigma$ is defined as $d\sigma = \sigma_z - \sigma_{xy}$. Here σ_z and σ_{xy} represent the sigma antibonding ability of ligands along the z-axis and the ligands in the xy-plane. A large positive dσ-value represents strong σ-donor strength of the axial ligands when compared to the equatorial ligands. The quantity dπ represents the π-antibonding character and is defined as $d\pi = d\pi_z - d\pi_{xy}$. Thus, the quantities d$\sigma$ and dπ give a quantitative comparison of differences in bonding strength of the CH_3SO_3 group and the pyridine or 4-methylpyridine base.

Referring to Table V, it is seen that in the nickel(II) compounds, pyridine and 4-methylpyridine are stronger σ-donors than the methanesulfonate ion. It is also evident from the sign of dπ that the π-antibonding interaction is greater in the xy-plane than along the z-axis.

Comparison of Dt values calculated from the electronic spectral data for various pyridine complexes [8, 17] indicates that the methanesulfonate ion coordinates more strongly than the perchlorate (577 cm^{-1}) and the tetrafluoroborate (625 cm^{-1}), and less strongly than the chloride (307 cm^{-1}) and bromide (349 cm^{-1}) anions. The methanesulfonate ion has a Dt value very close to those for the perrhenate (368 cm^{-1}) and the trifluoromethanesulfonate (353 cm^{-1}) ions.

It has been shown that in $Co(L)_4(X)_2$ complexes [18], two peaks are frequently observed in the visible region. In addition, the separation of these two peaks in *trans* compounds should be much greater than in those with *cis* structures. The *cis* compounds normally have a very broad band while *trans* compounds have a distinct separation in the two bands. Since at least two peaks are evident in the visible band, it seems that the CH_3SO_3 groups occupy the *trans* positions. This further supports a D_{4h} assignment to the compounds.

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