

A 10-g sample of  $[\text{HN}(\text{SO}_2\text{F})_2]_3 \cdot \text{POCl}_3$  was slowly added to 50 ml of ice water. The resulting acid solution was neutralized with  $\text{Cs}_2\text{CO}_3$ . The mixture was filtered and the water removed under vacuum. The residue was recrystallized from ethanol to yield 13.5 g of  $\text{CsN}(\text{SO}_2\text{F})_2$  (mp 116–118°, lit.<sup>7</sup> 115–117°).

A 187-g sample of  $\text{HN}(\text{SO}_2\text{Cl})_2$ <sup>8</sup> and 300 ml of arsenic(III) fluoride were placed in a polyethylene bottle and refluxed for 2 hr. The mixture was treated as described above appropriately scaled by a factor of 6. The residue was distilled to give 132 g of  $\text{HN}(\text{SO}_2\text{F})_2$  (bp 83–84° (25 mm)). Purification and identification of the product were achieved as described in the literature.<sup>6</sup>

**Preparation of  $\text{H}_2\text{NSO}_2\text{F}$ .**—To a 50-g sample of  $\text{PCl}_3=\text{NSO}_2\text{Cl}$  in 50 ml of arsenic(III) fluoride contained in a polyethylene bottle, 4.0 g of  $\text{H}_2\text{O}$  was slowly added. The mixture was refluxed for 1 hr and then cooled. It was worked up as described above and the residue was distilled. A 12.3-g sample of  $\text{H}_2\text{NSO}_2\text{F}$  (bp 71–72° (3 mm), lit.<sup>2</sup> 70° (3 mm); mp 6°, lit.<sup>2</sup> 7–8°) was obtained. The  $\text{F}^{19}$  nmr spectrum contained a single peak at  $\phi = 57.3$ .

**Preparation of  $\text{OSNSO}_2\text{Cl}$ .**—A 25-g sample of  $\text{PCl}_3=\text{NSO}_2\text{Cl}$  was loaded into a 100-ml stainless steel Hoke cylinder equipped with a needle valve. Then 50 ml of  $\text{SO}_2$  was condensed into the bomb with liquid nitrogen. The bomb was heated for 2 hr at 145–150° before being cooled to ambient temperature. The excess  $\text{SO}_2$  was allowed to escape and the residue was washed out of the bomb with  $\text{CH}_2\text{Cl}_2$ . The solvent was removed under vacuum and the residue was distilled. A 2.8-g sample of  $\text{OSNSO}_2\text{Cl}$  (bp 41–42° (1 mm)) was obtained.

*Anal.* Calcd for  $\text{OSNSO}_2\text{Cl}$ : Cl, 22.0; N, 8.67; S, 39.6. Found: Cl, 21.4; N, 8.61; S, 38.9.

**Preparation of  $\text{PCl}_4\text{N}(\text{SO}_2\text{Cl})_2$ .**—A 7.1-g sample of  $\text{PCl}_5$  was added to a solution of 7.3 g of  $\text{HN}(\text{SO}_2\text{Cl})_2$  in 25 ml of  $\text{POCl}_3$ . The mixture was heated to 80° under nitrogen for 2.5 hr. Upon cooling, the product crystallized out. The crystals were removed by filtration in an inert atmosphere to give 8.6 g of  $\text{PCl}_4\text{N}(\text{SO}_2\text{Cl})_2$  (mp 176–188°).

*Anal.* Calcd for  $\text{PCl}_4\text{N}(\text{SO}_2\text{Cl})_2$ : N, 3.66; Cl, 55.2; S, 16.6. Found: N, 3.70; Cl, 54.8; S, 16.2.

The conductivity of  $\text{PCl}_4\text{N}(\text{SO}_2\text{Cl})_2$  was determined in nitromethane using equipment previously described.<sup>9</sup> The concentration ( $M$ ) and equivalent conductance ( $\text{cm}^2/\text{ohm equiv}$ ), respectively, are:  $8.376 \times 10^{-3}$ , 90;  $4.188 \times 10^{-3}$ , 97.3;  $2.094 \times 10^{-3}$ , 102.3; and  $1.047 \times 10^{-3}$ , 105.9. The equivalent conductance at infinite dilution was found to be 114.4. A plot of  $\Omega_{\infty} - \Omega$  vs.  $\sqrt{C}$  had a slope of 250 which is in the range for a 1:1 electrolyte.<sup>10</sup>

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## Nuclear Magnetic Resonance Study of Cobalt and Nickel Tetrafluoroborates

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A number of recent studies have made use of nuclear magnetic resonance spectra to obtain solvation num-

bers, electronic–nuclear coupling constants, and solvent-exchange rates for various metal ions in solution. This type of information is vital to a better understanding of the molecular and electronic structure and of the chemical reactions of these ions in solution. The perchlorate salts of Co(II) and Ni(II) in particular have received considerable attention.<sup>2–9</sup> It was of interest to determine whether the tetrafluoroborate salts of Co(II) and Ni(II) in acetonitrile gave essentially the same results as the perchlorate salts.

### Experimental Section

The nmr spectra were obtained with a Varian A-60 spectrometer equipped with a V-6040 nmr variable-temperature controller. Temperatures were measured to  $\pm 1^\circ$  by means of an iron–constantan thermocouple.

The salts were prepared in anhydrous acetonitrile solution under a dry nitrogen atmosphere. The acetonitrile was purified by successive distillations from phosphorus pentoxide. The solutions were analyzed for cobalt by EDTA titration and for nickel by the gravimetric dimethylglyoximate method.

### Results and Discussion

The  $\Delta\nu_M$  shifts were obtained using the fast-exchange form of eq 8 of Swift and Connick<sup>10</sup>

$$\Delta\nu_{\text{obsd}} = P_M \Delta\nu_M \quad (1)$$

where  $\Delta\nu_{\text{obsd}}$  is the observed shift of the solvent peak,  $P_M$  is the mole fraction of bound sites assuming a coordination number of six, and  $\Delta\nu_M$  is the shift for unit mole fraction of coordinated sites. The results are given in Table I. The values of  $\Delta\nu_M$  showed a linear dependence on  $1/T$  with a nonzero intercept as also found by Matwiyoff and Hooker<sup>6</sup> and by Ravage, Stengle, and Langford.<sup>7</sup> A least-squares treatment of the Co(II) data gave a slope of  $(5.88 \pm 0.32) \times 10^5$  cps deg and an intercept of  $-1440 \pm 100$  cps. Since  $\mu_{\text{eff}}$  was equal to 5.18 BM<sup>11</sup> at room temperature for  $\text{Co}(\text{CH}_3\text{CN})_6^{2+}$  and was assumed to be temperature independent,<sup>6</sup> the coupling constant,  $A$ , was calculated to be  $-(1.85 \pm 0.10) \times 10^5$  cps from eq 8 of Matwiyoff and Hooker.<sup>6</sup> A similar least-squares treatment for the Ni(II) data gave a coupling constant of  $-(5.21 \pm 0.41) \times 10^5$  cps and an intercept of  $-910 \pm 170$  cps. The value used for  $\mu_{\text{eff}}$  was 3.22 BM.<sup>11</sup> It too was assumed to be temperature independent.<sup>7</sup> The results obtained are listed in Table II, together with values previously reported.<sup>6,7</sup> The value of the Co(II) coupling constant is larger than that of Matwiyoff and Hooker,<sup>6</sup> the Ni(II) coupling constant is also larger than that obtained by Matwiyoff and Hooker,<sup>6</sup> but smaller than that of Ravage, Stengle, and Langford.<sup>7</sup>

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TABLE I  
 $\Delta\nu_M$  VALUES (CPS) AT VARIOUS TEMPERATURES  
 FOR Co(II) AND Ni(II)

	Temp., °C						
	50	55	60	65	70	75	80
$\Delta\nu_M(\text{Co(II)})$	384	348	313	307	272	245	211
$\Delta\nu_M(\text{Ni(II)})$	...	...	...	1310	1270	1240	1210

TABLE II  
 SUMMARY AND COMPARISON OF RESULTS

Ion	$10^{-5}A$ , cps	$\Delta H^\ddagger$ , kcal/mole	$\Delta S^\ddagger$ , eu	$10^{-4}k$ , sec <sup>-1</sup>	Ref
Ni(II)	$-5.21 \pm 0.41$	$11.8 \pm 0.8$	$-0.2 \pm 2.5$	1.24	This work
Ni(II)	-2.63	10.9	-8.8	0.39	6
Ni(II)	$-8.1 \pm 0.5$	$11.7 \pm 0.1$	$-3.6 \pm 1.0$	0.24	7
Co(II)	$-1.85 \pm 0.10$	$8.4 \pm 0.6$	$-7 \pm 2$	15	This work
Co(II)	-0.228	$8.1 \pm 0.5$	$-7.5 \pm 2$	15	6

The reasons for the differences, especially between the nickel(II) perchlorate salts, are not known.

It is well known that  $\sigma$  and  $\pi$  electrons of a central metal ion in a complex may affect resonance signals of ligand nuclei in different ways. This is true because  $\sigma$  and  $\pi$  metal orbitals interact with ligand orbitals of their own symmetry. A consideration of electron delocalization and spin polarization in metal-acetonitrile complexes leads one to expect that  $\sigma$  electrons in metal  $e_g$  orbitals will cause an upfield shift and that  $\pi$  electrons in metal  $t_{2g}$  orbitals will cause a downfield shift of the metal proton signal. The observed shifts are in agreement with this expectation. Thus the upfield shift in the Ni(II) solutions is due to the two unpaired  $e_g$  electrons, whereas the smaller upfield shift in the Co(II) solutions is the net result of an upfield shift from the two unpaired  $e_g$  electrons and a downfield shift from the unpaired  $t_{2g}$  electron.

The Co(II) rate constants were evaluated using eq 10b of Swift and Connick.<sup>10</sup> The activation parameters were evaluated from a least-squares treatment of the equation

$$\log \frac{6}{\tau_M} - \log T = \log \frac{k}{h} + \frac{\Delta S^\ddagger}{2.303R} - \frac{\Delta H^\ddagger}{2.303RT} \quad (2)$$

where  $6/\tau_M$  is the rate constant for the exchange of a solvent molecule of the hexacoordinated complex, and the other symbols have their usual meanings. For Co(II) the enthalpy of activation was found to be  $8.4 \pm 0.6$  kcal mole<sup>-1</sup> and the entropy of activation was  $-7 \pm 2$  cal deg<sup>-1</sup> mole<sup>-1</sup>. The data for a  $1.72 \times 10^{-2}$  M solution of Co(II) are given in Table III. Data from three other concentrations gave identical results.

The Ni(II) rate constants were evaluated in the temperature range from 65 to 80° using eq 10b of Swift and Connick.<sup>10</sup> Use of this equation involves the assumption that  $(1/\tau_M)^2 \gg \Delta\nu_M^2$ . At 65° this assumption introduces an error smaller than 3%. At the temperatures 60 and 55° the rate constants were determined using the equation

$$\frac{1}{T_{2p}} = \frac{P_M \tau_M \Delta\nu_M^2}{1 + \tau_M^2 \Delta\nu_M^2} \quad (3)$$

TABLE III  
 DATA FOR Co(CH<sub>3</sub>CN)<sup>2+</sup>-SOLVENT EXCHANGE FOR  
 $1.72 \times 10^{-2}$  M Co(II)

$10^5/T$	$\Delta\nu_{1/2}$ , cps	$\Delta\nu_M$ , cps	Log (6/ $\tau_M$ )
3.55	0.25	643	4.757
3.60	0.28	673	4.738
3.66	0.45	712	4.572
3.72	0.58	744	4.502
3.77	0.85	777	4.396
3.88	1.62	837	4.155
3.97	2.18	891	4.084

and obtaining  $\Delta\nu_M$  values from extrapolation of the least-squares treatment of  $\Delta\nu_M$  vs.  $1/T$  to the desired temperatures. The activation parameters were evaluated by a least-squares treatment of eq 2 using the Ni(II) data. The values obtained were  $\Delta H^\ddagger = 11.8 \pm 0.8$  kcal mole<sup>-1</sup> and  $\Delta S^\ddagger = -0.2 \pm 2.8$  cal mole<sup>-1</sup> deg<sup>-1</sup>.

The rate constants and activation enthalpies and entropies are listed in Table II together with those previously obtained.<sup>6,7</sup> The reported activation enthalpies for both ions are in agreement within experimental error; the  $\Delta H^\ddagger$  values reported here and by Ravage, Stengle, and Langford for Ni(II) are in especially good agreement, as are those reported here and by Matwiyoff and Hooker for Co(II). The agreement indicates that the Co(II) and Ni(II) cations are most likely not complexed by the anions of the two different salts and that the assumption of complete dissociation of these salts in acetonitrile is probably justified. If the perchlorate and tetrafluoroborate salts are completely ionized, the differences noted for the reported coupling constants cannot be explained on the basis of partial complexing of the cations by one or both of the anions.

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## Dimeric Copper(II) Levulinate Hydrate

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Copper(II) alkanoates form an interesting class of compounds, whose magnetic susceptibility at room temperature is lower than that required for one unpaired spin.<sup>1</sup> The molecular structure of cupric acetate,<sup>2</sup> cupric succinate,<sup>3</sup> cupric acetate monopyridine,<sup>4</sup> and similar compounds, as determined by X-ray diffraction, consists of a dimeric unit with four carboxylate groups bridging the two copper atoms. The close approach of the two metal atoms in the dimer (2.64 Å) implies the

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