were redissolved with 1.5–2.0 ml of H_2O/100 g at 65–70°. The crystals were recovered and redissolved in water at 25°, and the pH was readjusted. The solution was filtered, reconcentrated, and refiltered while warm through Whatman No. 42 paper to remove a haze of insoluble material. Two crops of $LiAsF_6 \cdot 3H_2O$ were recovered at 25 and 0°. The above procedure was repeated and 3456 g of doubly recrystallized product was then further doubly recrystallized from about 7.5×10^{-4} M LiOH solution,[27] yielding 2838 g of hydrated crystals. These were dried in a lyophylizer for several days at 10^{-3} Torr and up to 40° to yield 2130 g of anhydrous $LiAsF_6$ (~50% overall yield). *Anal.* Calcd for $LiAsF_6$: Li, 3.54; As, 38.25; F, 58.21. Found: Li, 3.37, 3.42; As, 37.95, 38.11; F, 58.13, 58.01. Spark source mass spectrometric analysis showed[12] less than 80 ppm of any impurity element except carbon (found 880, 440 ppm) which tended[12] to be erratic in LiF and $LiAsF_6$ by this method. Reanalyses of another sample by four successive sparkings showed a decrease from 490 to 160 ppm C. Combustion train techniques gave <70, 100 ppm (Schwarzkopf Laboratories) and 120 ppm (Galbraith Laboratories). Free fluoride ion was also <100 ppm. Total estimated purity was 99.95% $LiAsF_6$.

Ion-Exchange Method.—Solutions of $KAsF_6$ (98.0% minimum purity, Ozark Mahoning) (0.237–1.00 equiv, 0.96–0.5 M) were passed through columns of Dowex 50W-X8 cation-exchange resin (courtesy of Dow Chemical Co.) in the Li^+ form. Recovery of the $LiAsF_6 \cdot 3H_2O$ generated HF and by-products of low solubility. Recrystallization and drying gave 60% yields of $LiAsF_6$. *Anal.* 0.1% K, >100 ppm each Na, O, and C (Li, F, As, satisfactory).

AsF_5 Method.—Dried LiF (0.127 mol, reagent grade, Baker and Adamson) and redistilled AsF_5 (0.133 mol, Ozark Mahoning Co.) were only 50% reacted after 18 hr at 200°. The solid product had a slightly pinkish color indicative of contamination from the Monel reactor. White $LiAsF_6$ was recovered from an anhydrous ethyl ether extract of the solid. No reaction of LiF and AsF_5 was observed at 25° and only partial conversion occurred in 3 days at 175° or with HF as a solvent at −40°.

Attempted Preparation of $LiAsF_5OH$.—Several variations of the method used for the preparation of $KAsF_5OH$ failed to produce anhydrous $LiAsF_5OH$ from LiH_2AsO_4 and 48% HF. The reaction product eliminated HF upon dehydration, and analysis of recovered solid products indicated mixtures of lithium fluorides and arsenates. Attempts to cause the reaction of LiF, As_2O_5, and excess 48% HF directly up to 100° also failed to yield anhydrous $LiAsF_5OH$.

Properties of $LiAsF_6$.—Anhydrous $LiAsF_6$, a white solid, appears to undergo a crystal transition at 258° (dta, Figure 2A) and loses AsF_5 above 280° under vacuum, as indicated by pyrolysis mass spectrometry (Figure 2B), and at about 350° under dry air, as observed by attack on a sealed glass tube. The $LiAsF_6$ is hygroscopic, forms $LiAsF_6 \cdot H_2O$ (mp 117°) and $LiAsF_6 \cdot 3H_2O$ (mp 58°), becomes deliquescent at 30–35% relative humidity, and dissolves exothermally at about 1.9 g/ml of water at 25°. Its saturated solution concentration is about 6 M (density 1.85 g/ml). $LiAsF_6$–H_2O mixtures at 1:6, 1:7, and 1:8 mole ratios gave dta endotherms at −47°, probably the eutectic. No hydrolysis was observed at 100° in 1 hr. The $LiAsF_6 \cdot 3H_2O$ like $HAsF_6 \cdot 6H_2O$ dissolves endothermally in H_2O. The $LiAsF_6$ is similar[28] to $LiClO_4$ (mp 236°), which forms $LiClO_4 \cdot H_2O$, $LiClO_4 \cdot 3H_2O$ (mp 95°), and a saturated solution approximately 5.6 M at 25°. The $LiAsF_6$ is soluble in ethyl ether (0.55 g/ml) and isopropyl alcohol (0.8 g/ml), forms $LiAsF_6 \cdot 2(C_2H_5)_2O$ at 25°, $LiAsF_6 \cdot 6(C_2H_5)_2O$ at −80°, and a solid solvate with i-C_3H_7OH at −20° (mp <25°).

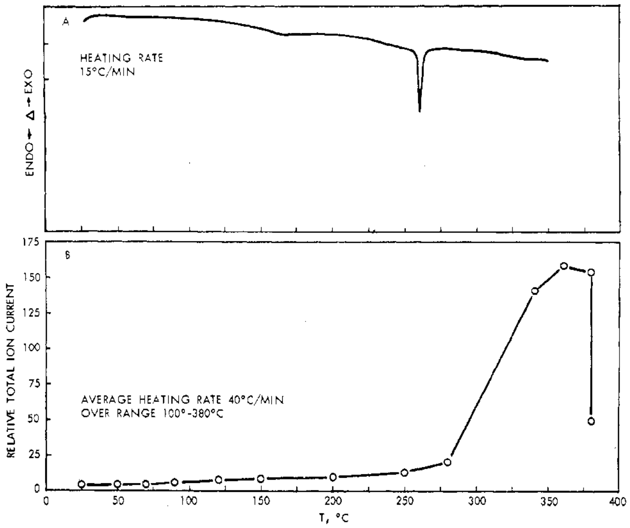

Figure 2.—Thermal stability of $LiAsF_6$: (A) differential thermal analysis; (B) pyrolysis mass spectrometry.

Acknowledgments.—The nmr spectra, mass spectra, and differential thermal analyses were obtained by Mrs. Hope Miller, Mr. George Vaughn, and Dr. Evelyn Murrill, respectively.

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[27] Samples of $LiAsF_6 \cdot 3H_2O$ recovered from acidic solutions developed a gray color upon vacuum drying. $HAsF_6 \cdot 6H_2O$ gave a black oil.

[28] "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Company, Cleveland, Ohio, 1969–1970.

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Proton Nuclear Magnetic Resonance Contact Shifts of Some Tris(1,10-phenanthroline)nickel(II) Complexes[1]

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In two previous communications[2,3] we reported the proton nmr contact shifts of some nickel(II)- and cobalt(II)-2,2′-bipyridine (bipy) complexes. These studies showed that the mechanism of spin delocalization for $Ni(bipy)_3^{2+}$ was different from that of $Co(bipy)_3^{2+}$ and that a mechanism of spin delocalization for $Ni(bipy)_3^{2+}$ could be proposed. We have now extended this study to include the tris octahedral nickel(II) complexes of the very similar ligand 1,10-phenanthroline (phen) and some methyl-substituted derivatives.

Since our preliminary report of the nmr spectra of some tris(1,10-phenanthroline)nickel(II) complexes,[1] a recent paper[4] has discussed possible spin delocalization mechanisms in this system based on nickel(II) complexes using some unsymmetrically substituted phen ligands in which substitution is at the 3,8 and 4,7 ring positions. Since the use of methyl-substituted ligands greatly aids in elucidating the mechanism of spin delocalization for complexes having aromatic rings, we feel it is of value to have contact shift data for the Ni(II)–phen complexes having methyl substituents at each of the four ligand positions.

Experimental Section

Materials and Analyses.—1,10-Phenanthroline monohydrate was purchased from Eastman Organic Chemicals while the methyl-substituted phenanthrolines were purchased from G.

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[1] Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[2] M. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2196 (1968).

[3] M. Wicholas and R. S. Drago, *ibid.*, **90**, 6946 (1968).

[4] G. N. La Mar and G. R. Van Hecke, *Inorg. Chem.*, **9**, 1546 (1970).

Frederick Smith Co. All solvents used were reagent grade and were commercially available. Analyses were performed under the supervision of Mr. J. Nemeth of the University of Illinois Microanalytical Laboratory and also by Galbraith Laboratories.

Preparation of the Complexes.—In the following syntheses and throughout the text the substituted phenanthroline ligands shall be abbreviated as follows: 1,10-phenanthroline, phen; 4,7-dimethyl-1,10-phenanthroline, 4,7-dmp; 3,4,7,8-tetramethyl-1,10-phenanthroline, 3,4,7,8-tmp, etc.

All the tris complexes mentioned herein were prepared from the hydrated metal chlorides and appropriate ligands in a tetrahydrofuran (THF)-methanol solvent as was previously described in the preparation of some analogous 2,2'-bipyridine complexes.[3] $Ni(2,9\text{-dmp})_2(NO_3)_2 \cdot H_2O$ was made by the method of Hall, *et al.*,[5] who prepared the analogous complex with 4,4',6,6'-tetramethylbipyridine. Analyses for these complexes are presented in Table I.

TABLE I

ANALYTICAL DATA

Compd	% calcd C	% calcd H	% calcd N	% found C	% found H	% found N
$Ni(phen)_3Cl_2 \cdot 3H_2O$	59.52	4.16	11.57	59.03	4.14	10.88
$Ni(4,7\text{-dmp})_3Cl_2 \cdot 3H_2O$	62.41	5.24	10.40	62.78	5.20	10.28
$Ni(5,6\text{-dmp})_3Cl_2 \cdot H_2O$	65.32	4.96	10.88	64.77	5.27	10.86
$Ni(3,4,7,8\text{-tmp})_3Cl_2 \cdot 5H_2O$	62.08	6.30		61.87	6.04	
$Ni(2,9\text{-dmp})_2(NO_3)_2 \cdot H_2O$	54.48	4.25		54.22	4.17	

Spectral Measurements.—The nmr spectra were obtained at approximately 28° with Varian DP-60 and T-60 spectrometers. All shifts in D_2O were measured relative to the high-field multiplet of THF which was used as an internal reference.

Results and Discussion

The isotropic shifts of the 1,10-phenanthroline complexes prepared here are listed in Table II. For $Ni(phen)_3^{2+}$ in D_2O, the 2,9 and 3,8 proton resonances were unambiguously assigned on the basis of their half-widths. Of these the 2,9 proton resonance was extremely broad and could be located at best on the oscilloscope. The 4,7 and 5,6 proton resonances have approximately the same half-widths, and therefore the 4,7- and 5,6-dimethyl-substituted complexes were synthesized in order to identify these two resonances unequivocally. The contact shifts for $Ni(phen)_3^{2+}$ are remarkably similar to those of $Ni(bipy)_3^{2+}$ [2] and further illustrate the similarity of these two ligands.

TABLE II

CONTACT SHIFTS OF THE PHENANTHROLINE COMPLEXES

Compd[a]	Solvent	$\Delta\nu_{2,9}$	$\Delta\nu_{3,8}$	$\Delta\nu_{4,7}$	$\Delta\nu_{5,6}$
$Ni(phen)_3Cl_2 \cdot 3H_2O$	D_2O	−8800[b]	−2496	−537	−998
$Ni(2,9\text{-dmp})_2(NO_3)_2 \cdot H_2O$[c]	CD_3NO_2	(+949)	−2813	−582	−891
$Ni(4,7\text{-dmp})_3Cl_2 \cdot 3H_2O$	D_2O		−2253	(+705)	−1102
$Ni(5,6\text{-dmp})_3Cl_2 \cdot H_2O$	D_2O		−2426	−498	(−57)
$Ni(3,4,7,8\text{-tmp})_3Cl_2 \cdot 5H_2O$	D_2O		(−405)	(+733)	−1060

[a] The contact shifts are reported in hertz at 60 MHz. The diamagnetic references are the respective tris iron(II) complexes except for $Ni(2,9\text{-dmp})_2(NO_3)_2$ where the free ligand is used. Methyl proton resonances are enclosed in parentheses. [b] This resonance was measured on the oscilloscope and is accurate to only ±1000 Hz. [c] Only one set of resonances was found for this complex and this would imply that a rapid racemization process is occurring in solution.

Since octahedrally coordinated nickel(II) should be orbitally nondegenerate in D_3 symmetry, the observed isotropic shifts of the tris complexes are entirely due to a contact interaction.[6] Any pseudocontact contribution to the isotropic shifts is expected to be negligible. On this basis the isotropic shifts should provide direct evidence of the mechanism of spin delocalization in $Ni(phen)_3^{2+}$. Also for the complex $Ni(2,9\text{-dmp})_2(NO_3)_2$, which has coordinated nitrate and is most likely octahedrally coordinated,[7] no sizable pseudocontact shifts are expected.

As shown previously the contact shifts of $Ni(phen)_3^{2+}$ and its methyl-substituted analogs[2,4] reflect the dominance of a σ-delocalization mechanism presumably caused by delocalization of positive spin density in the highest filled ligand σ MO, along with some participation from π delocalization which need not necessarily be related to metal–ligand π bonding.[8] The problem is now to relate this π delocalization to a specific ligand π MO and to propose a reasonable π spin delocalization mechanism; however, using the Hückel π spin densities recently reported for 1,10-phenanthroline,[9] we can find no simple π-delocalization mechanism which will properly explain the observed methyl proton contact shifts in these substituted phen complexes. As an example spin delocalization into either the highest filled π MO or lowest empty π^* MO of the methyl-substituted phenanthroline ligands predicts[4] positive contact shifts for the 2,9-CH_3, 4,7-CH_3, and *5,6-CH_3* protons whereas it is observed that $\Delta\nu_{5,6}$ in $Ni(5,6\text{-dmp})_3^{2+}$ is negative. At the present time, it is then not yet possible to relate this π spin delocalization in $Ni(phen)_3^{2+}$ to any particular ligand π MO or simple combination of π MO's. The exact mechanism by which positive methyl proton contact shifts are observed in these complexes is still unknown and might, as suggested by La Mar and Van Hecke,[4] be due to some indirect spin polarization mechanism rather than to spin delocalization *via* metal–ligand π bonding.

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(5) J. R. Hall, M. R. Litzow, and R. A. Plowman, *Aust. J. Chem.*, **19**, 201 (1966).

(6) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(7) This complex is anlogous to $Ni(4,4',6,6'\text{-tmb})_2(NO_3)_2 \cdot H_2O$ (tmb = tetramethylbipyridine) which was characterized by Hall, *et al.*,[5] and has identical properties.

(8) A. D. McLachlan, *Mol. Phys.*, **1**, 233 (1958).

(9) G. N. La Mar and G. R. Van Hecke, *J. Amer. Chem. Soc.*, **91**, 3442 (1969).

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Contact Shifts in Octahedral Nickel(II) and Cobalt(II) Complexes of 4-Methylpyridine *N*-Oxide

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In recent years,[1-4] we have been interested in the use of isotropic shifts of paramagnetic transition metal ion complexes to obtain information on bonding and structure. If the complexes are magnetically isotropic, as in

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(1) M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, **91**, 1361 (1969).

(2) M. F. Rettig and R. S. Drago, *ibid.*, **91**, 3432 (1969).

(3) R. E. Cramer and R. S. Drago, *ibid.*, **92**, 66 (1970).

(4) R. E. DeSimone and R. S. Drago, *ibid.*, **92**, 2343 (1970).