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Lithium Hexafluoroarsenate and Hexafluoroarsenic Acid[1]

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Lithium hexafluoroarsenate recently became of interest as an electrolyte in high-energy density batteries but was commercially unavailable. $LiAsF_6$ was first synthesized by Cox[2] and later by Kemmitt, Russell, and Sharp[3] using the reaction[4] of the metal fluoride and As_2O_3 with liquid BrF_3. Atkinson and Hallada[5] apparently prepared $LiAsF_6$ of good purity from $KAsF_6$ by a batch cation-exchange technique. Solutions of $LiAsF_6$ and solid $LiAsF_6$ have been prepared, respectively, by metathetical reactions in methyl formate[6,7] and liquid ammonia.[6] Structural[2,3] and electrochemical[5-8] data for $LiAsF_6$ have been reported. We have investigated four potential methods for the preparation of high-purity $LiAsF_6$: (1) neutralization of the known[9] $HAsF_6$ with LiOH, (2) ion exchange[5] with $KAsF_6$; (3) reaction of LiF and AsF_5,[10] and (4) fluorination of LiH_2AsO_4 with HF *via* the AsF_5OH^- ion.[9,11] We report here an improved method for the synthesis of $LiAsF_6$, some of its properties, and some observations on commerical hexafluoroarsenic acid.

Results and Discussion

The $LiAsF_6$ was successfully prepared[12] by all but the AsF_5OH^- ion method, in which the intermediate $LiAsF_5OH$ was not obtained. The acid neutralization method was used with a multiple recrystallization and drying procedure to prepare 2 kg of anhydrous $LiAsF_6$ which contained not more than a 100-ppm impurity of any element and had an overall purity of 99.95%.

The neutralization of commerical hexafluoroarsenic acid required over twice as much LiOH as expected and gave only a 65–70% yield of $LiAsF_6$ (based on nominal $HAsF_6$ content). By-products of low solubility (largely LiF and lithium arsenates) were produced upon neutralization and, in smaller amounts, during concentration, recrystallization, and drying of crude $LiAsF_6$. The development of these latter precipitates was accompanied by the regeneration of small amounts of HF, indicative of hydrolysis reactions in these highly concentrated solutions. The $LiAsF_6$ solutions eventually became pH stable and purification by recrystallization could then be accomplished. Double recrystallization of the $HAsF_6$ reduced, but did not eliminate, the excess base required for neutralization and the formation of by-products. Preparation of $LiAsF_6$ by ion exchange with commercial $KAsF_6$ was also accompanied by generation of HF and small amounts of precipitate. These results, together with the hydrolytic stability of pure $LiAsF_6$ and the apparent instability of $LiAsF_5OH$ compared to other AsF_5OH^- salts, suggest the presence of other fluoroarsenate species in $HAsF_6$ and $KAsF_6$.

The fluorination of KH_2AsO_4 proceeds to $KAsF_4(OH)_2$ in 40% aqueous HF,[11] to $KAsF_5OH$ in 48% aqueous HF,[9,11] and to $KAsF_6$ in anhydrous HF.[9,11] The Na^+, Rb^+, Cs^+, Zn^{2+}, and $C_{20}H_{17}N_4^+$ salts of AsF_5OH^- and $AsF_4(OH)_2^-$ have also been prepared and studied.[13-16] In contrast to the AsF_6^- ion, the AsF_5OH^- ion hydrolyzes[9,11,17] relatively rapidly in water[18] and the $AsF_4(OH)_2^-$ ion still more easily.[11] At about 140° the AsF_5OH^- salts lose HF and form linear polymeric anions[19] $(-AsF_4O-)_n^{n-}$ which can rearrange at about 250° to cyclic dimer[20-22] anions $(-AsF_4O-)_2^{2-}$ (not the trimers[13-15]). These anions are much more hydrolytically stable than AsF_5OH^-; *e.g.*, $K_2(AsF_4O)_2$ could be recrystallized from water. The Li^+ salts have not been reported for any of these four complex fluoroarsenate anions. Our unsuccessful attempts to prepare anhydrous $LiAsF_5OH$ suggest that it (like the Li^+ salt of PF_6^-) is less stable than the Na^+ and K^+ salts and the order of stability for the other fluoroarsenate salts may be similar.

The commercial $HAsF_6$ is prepared[23] by the reaction of HF with H_3AsO_4 in the presence of sufficient water to give the approximate composition $HAsF_6 \cdot 6H_2O$ and the commercial $KAsF_6$ is prepared[23] from the $HAsF_6$. The results of the present investigation suggest that in addition to the AsF_6^- ion, the commercial hexafluoroarsenic acid contains several per cent of fluoroarsenate species (probably AsF_5OH^- and $AsF_4(OH)_2^-$) which hydrolyze readily upon neutralization and smaller amounts of other fluoroarsenate species (possibly the dimeric or polymeric anions) which hydrolyze slowly upon concentration or dehydration of the $LiAsF_6$. The K^+ salts of these latter impurities appear to be more hydrolytically stable and appear to be present in commercial $KAsF_6$. Infrared and nmr spectra (Figure 1) of the 65% $HAsF_6$, recrystallized $HAsF_6$, and the

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(1) This work was supported by the National Aeronautics and Space Administration under Contract NAS3-12979.

(2) B. Cox, *J. Chem. Soc.*, 876 (1956). The reported analysis indicates an approximate composition of $LiAsF_6 \cdot 0.4LiF$.

(3) R. D. W. Kemmitt, D. R. Russell, and D. W. A. Sharp, *ibid.*, 4408 (1963).

(4) A. A. Wolf and H. J. Emeléus, *ibid.*, 1050 (1950).

(5) G. Atkinson and C. J. Hallada, *J. Phys. Chem.*, **64**, 1487 (1960).

(6) Honeywell, Inc., Contract NAS3-10613, Final Report (for the period May 31, 1967–April 30, 1968); Report NASA CR-72535, National Aeronautics and Space Administration, Office of Scientific and Technical Information.

(7) Monsanto Research Corp., Contract NAS3-9431, Final Report (Sept 1968); Report NASA CR-72464, National Aeronautics and Space Administration, Office of Scientific and Technical Information.

(8) Rocketdyne, A Division of North American Rockwell Corp., Contract NAS3-8521, Final Report (Dec 1968); Report NASA CR-72803, National Aeronautics and Space Administration, Office of Scientific and Technical Information.

(9) H. M. Dess and R. W. Parry, *J. Amer. Chem. Soc.*, **79**, 1589 (1957).

(10) Analogous to the reaction of NOF and AsF_5 to give $NOAsF_6$ as reported by O. Ruff, K. Stauber, and H. Graf, *Z. Anorg. Allg. Chem.*, **58**, 325 (1908).

(11) L. Kolditz and W. Röhnsch, *ibid.*, **79**, 1589 (1957).

(12) Midwest Research Institute, Contract NAS3-12979, Final Report (June 1970); Report NASA CR-72640, National Aeronautics and Space Administration, Office of Scientific and Technical Information.

(13) L. Kolditz and B. Nussbücker, *Z. Anorg. Chem.*, **312**, 20 (1961).

(14) L. Kolditz and D. Renno, *ibid.*, **315**, 46 (1962).

(15) L. Kolditz, *Z. Chem.*, **2**, 186 (1962).

(16) L. Kolditz and J. Wendt, *ibid.*, **3**, 312 (1963).

(17) W. L. Johnson and M. M. Jones, *Inorg. Chem.*, **5**, 1345 (1966).

(18) Hydrolysis of $KAsF_5OH$ in 9 *M* H_2SO_4 has also been reported by W. L. Lockhardt, Jr., M. M. Jones, and D. O. Johnston, *J. Inorg. Nucl. Chem.*, **31**, 407 (1969).

(19) L. Kolditz and K. Haage, *Z. Anorg. Allg. Chem.*, **301**, 36 (1959). The $AsF_4(OH)_2^-$ salts give two- or three-dimensional polymers.

(20) H. Dunken and W. Haase, *Z. Chem.*, **3**, 433 (1963).

(21) W. Haase, *Chem. Zvesti*, **19**, 167 (1965).

(22) L. Kolditz and B. Nussbücker, *Z. Anorg. Allg. Chem.*, **337**, 191 (1965).

(23) Dr. Wayne White, private communication, Ozark Mahoning Co., 1969.

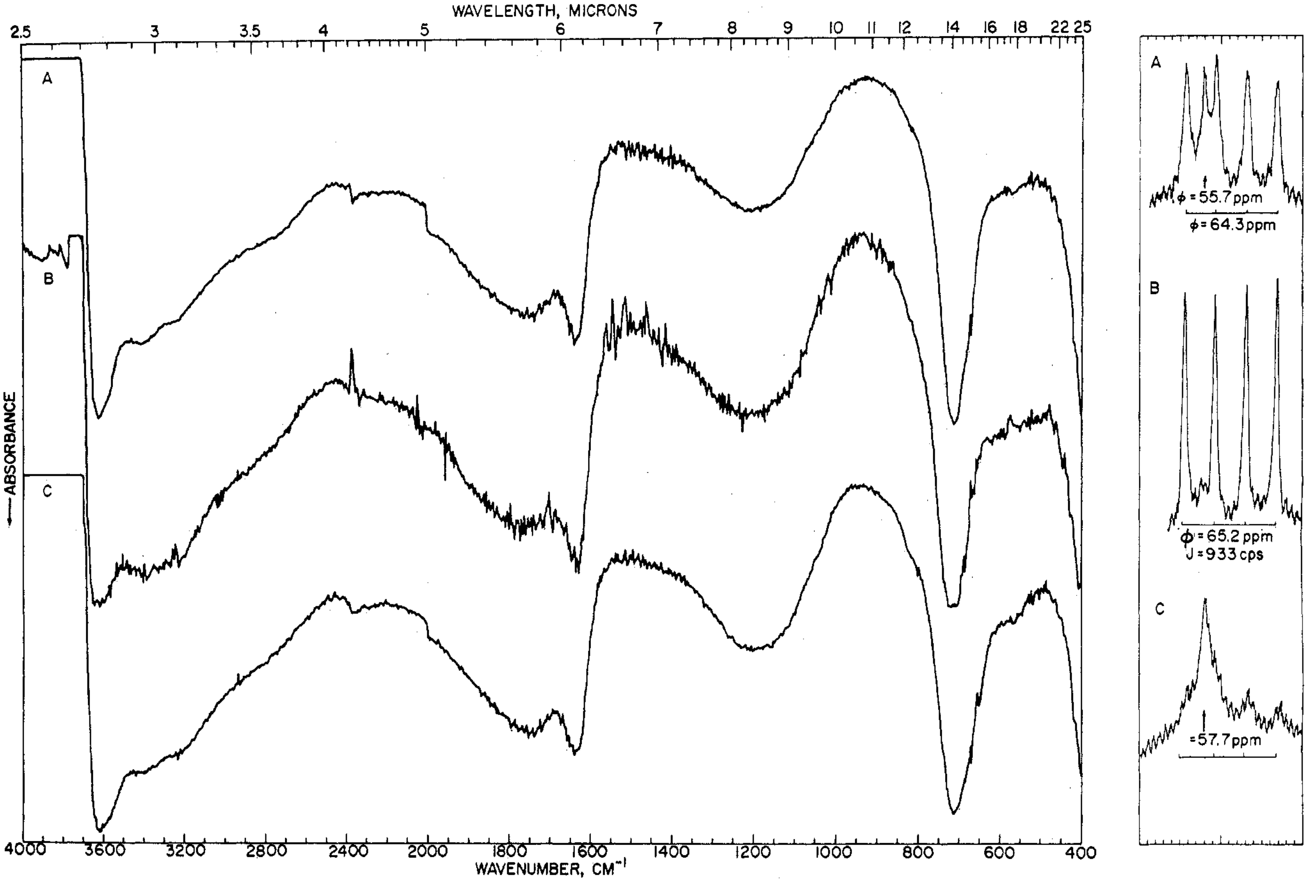

Figure 1.—Infrared and nmr spectra of $HAsF_6$ fractions: (A) stock 65% $HAsF_6$ solution (greenish); (B) twice-recrystallized $HAsF_6$ (faint green); (C) mother liquor from recrystallization (dark green).

residual mother liquor support these conclusions. The infrared spectra showed very little difference between the three, indicating a generally similar chemical composition. The nmr spectra are markedly different and clearly show that the 65% $HAsF_6$ is a mixture of AsF_6^- and one or more impurities which appear to be fluoroarsenates and are concentrated in the mother liquor. These results are in agreement with the neutralization studies.

Experimental Section

Analyses.—Major constituent analyses were performed primarily by Schwarzkopf Microanalytical Laboratories. Impurity analyses for all elements were performed by the spark source mass spectrometric method at Bell and Howell Reearch Laboratories. Supplemental analyses for carbon and certain metallic elements were also performed. Extensive prior analyses of standard samples by emission, atomic absorption, and spark source mass spectrometries and by other methods were used to evaluate the analytical procedures.[12] A Varian Associates Model HA-100 spectrometer was used to obtain nmr spectra. Pyrex tubes with Teflon inserts were used for $HAsF_6$. All ^{19}F chemical shifts are relative to external $CFCl_3$. Infrared spectra were obtained on a Beckman IR-12 spectrometer, using the KBr sandwich technique[24] for $LiAsF_6$ and AgCl windows for $HAsF_6$. An Atlas CH-4B mass spectrometer equipped with a direct-inlet probe for solids and a Du Pont Model 900 differential thermal analyzer were used to determine thermal characteristics.

Properties of $HAsF_6$.—Hexafluoroarsenic acid was obtained (Ozark Mahoning Co.) as a greenish solution stated to contain 65% $HAsF_6$ and 1–3% HF and also as slightly wet, off-white crystals stated to be the hexahydrate[9] (mp 25–30°). Preliminary experiments[12] showed that both of these materials required more base than expected and produced by-products of low solubility (mostly LiF and lithium arsenates[25]) as follows: 65% solution: equiv wt 128, precipitate 0.2 g/g; stock crystals: equiv wt 140, precipitate 0.15 g/g; calcd for $HAsF_6 \cdot 6H_2O$: equiv wt 298. Double recrystallization of 65% solution gave somewhat better crystals (equiv wt 270–280, precipitate 0.05–0.1 g/g) and concentrated the impurities in the dark green liquor (equiv wt 73, copious amounts of precipitate). Infrared and nmr spectra of recrystallization fractions, Figure 1, were as follows: ir: AsF_6^- bands[26] at 708 and 395 cm^{-1} plus unidentified broad bands in 65% solution; nmr: AsF_6^- quartet[26] at 64.3 ppm, singlet at 55.7 ppm in 65% solution; quartet at 65.2 ppm and singlet much reduced in purified acid; singlet at 55.7 ppm and weak broad resonance at 40–90 ppm in mother liquor. The singlet and broad resonances probably arise from unidentified fluoroarsenates, the collapsed structure resulting from fluoride ion exchange, coupling with hydrogen, and/or a multiplicity of fluoride environments.

Preparation of $LiAsF_6$ from $HAsF_6$.—The purification procedure was based on recrystallization of $LiAsF_6 \cdot 3H_2O$ from water. Recrystallization of the $HAsF_6 \cdot 6H_2O$ from water or of the $LiAsF_6 \cdot 3H_2O$ of $LiAsF_6$ from the lower alcohols, acetone, or ethyl ether did not appear advantageous. About 8000 g of hexafluoroarsenic acid in polyethylene containers were neutralized to pH 8–10 with prefiltered 5 *M* LiOH solution (reagent $LiOH \cdot H_2O$, Matheson Coleman and Bell). Each portion was held at 100° for several hours and then filtered to remove solid by-product (largely LiF and Li_2HAsO_4, estimated weight 1400 g, dry basis). The solutions were concentrated in a rotary flash evaporator at 55–60° and readjusted to pH 8 (to reduce contamination by LiH_2AsO_4), and insoluble by-product was removed (10–15 g). The crude $LiAsF_6 \cdot 3H_2O$ crystals were recovered from the yellowish liquor on a coarsely fritted polyethylene funnel. (Considerable reworking of filtrates was required throughout because of the salt's high solubility.) To help complete hydrolysis of unstable fluoroarsenates, the crystals

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(24) E. W. Lawless, *Anal. Lett.*, **1**, 153 (1967).

(25) Greenish by-product. One small sample of white acid crystals gave a white by-product. *Anal.* Found: Li, 17.00; F, 66.72; As, 16.28.

(26) $KAsF_6$ ir (KBr pellet): two strong bands at 703 and 410–390 (db) cm^{-1}; ^{19}F nmr (1 *M* solution): quartet, ϕ 64.7 ppm, J = 933 cps.

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°).

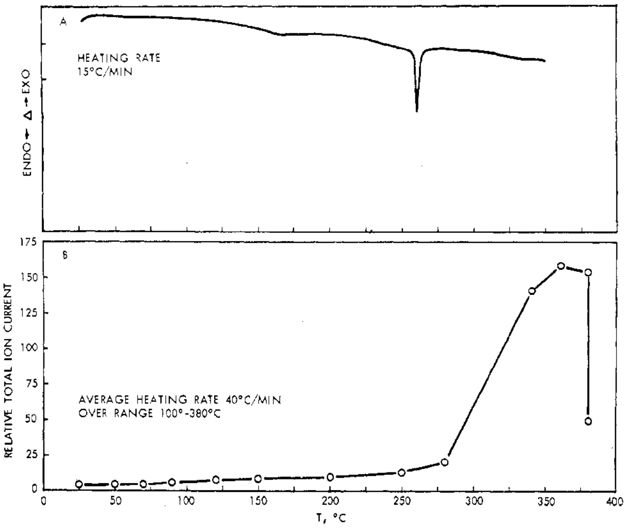

Figure 2.—Thermal stability of $LiAsF_6$: (A) differential thermal analysis; (B) pyrolysis mass spectrometry.

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).