satisfactory by using hfs constants of 74 G and 140 G for **1** and 99 G and 181 G for the $\mathrm{Mn^{2+}/Mn^{3+}}$ species. The line shape of the former complex is not predicted well since the fitting utilizes isoropic line shapes, while the spectrum exhibits axial symmetry. The *g* factors, corrected for the second-order shift of the spectrum,[12] are 2.06 and 2.01, respectively.

Theory predicts that these dimer hfs constants (A^D) can be related to those for the individual Mn ions (A^M) by a scaling factor equal to the projection of the individual Mn ion spin onto the resultant spin of the dimer in the EPR active state, $S_i{\cdot}S/S^2$. The spin coupling formulas for these two cases predict that $|A^D/A^M| = 2$ for $\mathrm{Mn^{3+}}$ and 1 for $\mathrm{Mn^{4+}}$ and $^7/_3$ for $\mathrm{Mn^{2+}}$ and $^4/_3$ for $\mathrm{Mn^{3+}}$, in the respective dimers.[4,12] Applying these to the present data yields hfs constants A^M = 70 G and 74 G for $\mathrm{Mn^{3+}}$ and $\mathrm{Mn^{4+}}$ and 77 G and 75 G for $\mathrm{Mn^{2+}}$ and $\mathrm{Mn^{3+}}$. By comparison, the $^{55}\mathrm{Mn}$ isotropic hfs constant in the mononuclear complex $\mathrm{Mn^{II}(TPP)}$ is 80 G,[9] in $[\mathrm{Mn^{IV}(TPP)Cl)}]^+$ it is 81 G,[13] and in $\mathrm{Mn^{IV}(TPP)Cl_2}$ it is estimated at 73 G.[13] Assignment of both mixed valence spectra to the same oxidation pair leads to unreasonable A^M constants for one pair. Thus the larger EPR spectral width for $\mathrm{Mn^{2+}/Mn^{3+}}$ complexes can serve as a possible means for distinguishing them from $\mathrm{Mn^{3+}/Mn^{4+}}$ complexes having ligands of comparable covalency. The basis for this discrimination is two/fold: the spin-coupling coefficients that multiply the hfs constants are larger for $\mathrm{Mn^{2+}/Mn^{3+}}$ complexes than for $\mathrm{Mn^{3+}/Mn^{4+}}$, and the individual ion hfs constants for Mn^{n+} do not vary much with *n* for ligands having similar covalency. Few $\mathrm{Mn^{2+}/Mn^{3+}}$ complexes have been studied by EPR to test these predictions. Confirmation of a very large multiline EPR spectral width (2000 G) in a $\mathrm{Mn^{2+}/Mn^{3+}}$ complex utilizing pyridine, amine, and acetate ligands has been observed.[14]

A 16-line EPR spectrum for a mixed valence Mn dimer has been reported for the oxidation product of $\mathrm{Mn^{II}}$ (Saldien) with $\mathrm{O_2}$.[15] The magnitude of the observed A^D hfs constants, 165 G and 83 G, was the primary basis for assigning this as a $\mathrm{Mn^{2+}/Mn^{3+}}$ species instead of $\mathrm{Mn^{3+}/Mn^{4+}}$. The predicted A^M hfs constants are then 71 G for $\mathrm{Mn^{2+}}$ and 62 G for $\mathrm{Mn^{3+}}$, considerably smaller than found here for the more covalent TPP ligand. This unexpected difference indicates either a limitation of the theory or an incorrect oxidation state assignment. An alternate formulation of this as a $\mathrm{Mn^{3+}/Mn^{4+}}$ complex leads to A^M hfs constants of 82 G and 83 G; values much closer to those found for mononuclear Mn complexes with these ligands.

Both $\mathrm{O_2}$ and $\mathrm{(TPP)Mn^{II}}$ are required for formation of the $\mathrm{Mn^{2+}/Mn^{3+}}$ complex, suggesting that oxygen forms the bridging group. Exposure of (TPP)MnCl to air does not produce a multiline signal nor does mixing equal molar quantities of $\mathrm{(TPP)Mn^{II}}$ and $\mathrm{(TPP)Mn^{III}Cl}$ in $\mathrm{CH_2Cl_2}$ under anaerobic conditions. One mechanism which is able to account for these observations is as follows.

$$\mathrm{(TPP)Mn^{II}} + \mathrm{O_2} \rightarrow [\mathrm{(TPP)Mn^{III}}]^+ + \mathrm{O_2}^- \tag{1}$$

$$\mathrm{(TPP)Mn^{II}} + \mathrm{O_2}^- \rightarrow [\mathrm{(TPP)Mn^{III}O_2}]^- \tag{2}$$

$$\mathrm{(TPP)Mn^{II}} + [\mathrm{(TPP)MnO_2}]^- \rightleftarrows [\mathrm{(TPP)Mn^{II}OOMn^{III}(TPP)}]^-\ (\mathbf{2a}) \tag{3}$$

$$[\mathrm{(TPP)Mn^{II}OOMn^{III}(TPP)}]^- \rightleftarrows \mathrm{(TPP)Mn^{IV}O} + [\mathrm{(TPP)Mn^{III}O}]^- \tag{4}$$

$$\mathrm{(TPP)Mn^{II}} + \mathrm{(TPP)Mn^{IV}O} \rightleftarrows \mathrm{(TPP)Mn^{III}OMn^{III}(TPP)} \tag{5}$$

$$\mathrm{(TPP)Mn^{II}} + [\mathrm{(TPP)Mn^{III}O}]^- \rightleftarrows [\mathrm{(TPP)Mn^{II}OMn^{III}(TPP)}]^-\ (\mathbf{2b}) \tag{6}$$

Air oxidation of $\mathrm{(TPP)Mn^{II}}$ to form $[\mathrm{(TPP)Mn^{III}}]^+$ and $\mathrm{O_2}^-$ in step (1) accounts for the loss of $g = 6$ signal and the appearance of a free radical seen by EPR. The superoxide ion reacts with a second $\mathrm{(TPP)Mn^{II}}$ to form the EPR silent peroxide, $[\mathrm{(TPP)Mn^{III}O_2}]^-$ in step (2) (loss of free radical signal). The thermally unstable complex of $[\mathrm{(TPP)Mn^{III}O_2}]^-$ has been shown to form at low temperatures by reaction (2).[16] In step (3) this anion is proposed to react further with excess $\mathrm{(TPP)Mn^{II}}$ to form the μ-peroxo complex $[\mathrm{(TPP)Mn^{II}OOMn^{III}(TPP)}]^-$ (**2a**). This mixed valence species could account for the wide multiline EPR signal in Figure 1B. It is also possible that **2a** undergoes homolytic cleavage of the peroxo bond to form the $[\mathrm{(TPP)Mn^{III}O}]^-$ and $\mathrm{(TPP)Mn^{IV}O}$ species given in step (4). Reaction of the products from step (4) with excess $\mathrm{(TPP)Mn^{II}}$ to form the EPR silent μ-oxo dimer, $\mathrm{(TPP)Mn^{III}OMn^{III}(TPP)}$ in step (5), and the EPR active mixed valence μ-oxo dimer, $\mathrm{(TPP)Mn^{II}OMn^{III}(TPP)}$ (**2b**), in step (6), could also account for the multiline signal in Figure 1B. The present EPR results do not allow us to distinguish which $\mathrm{Mn^{2+}/Mn^{3+}}$ dimer, **2a** or **2b**, is responsible for the wide EPR multiline signal.

Acknowledgment. This work was supported by the National Science Foundation through Grant CHE82-17920.

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(13) Konishi, S.; Hoshino, M.; Imamura, M. *J. Phys. Chem.* **1982**, *86*, 4537.

(14) Isied, S., private communication.

(15) Mabad, B.; Tuchagues, J.-P.; Hwang, Y.-T.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1985**, *107*, 2801.

(16) Van Atta, R. B.; Strouse, C. E.; Hanson, L. K.; Valentine, J. S. *J. Am. Chem. Soc.* **1982**, *109*, 1425.

$\mathrm{Li^+(en)_2{\cdot}Na^-}$: A Simple Crystalline Sodide

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Received August 17, 1987

Since the preparation of the first crystalline sodide, $\mathrm{Na^+[cryptand(2.2.2)]{\cdot}Na^-}$, in 1974,[1,2] we have tried to prepare alkalides that have simpler and less expensive cations. Attempts to use tetraalkylammonium ions, for example, resulted in irreversible decomposition.[3] Recent success in solubilizing sodium by using solutions of lithium in methylamine and the apparent formation of solutions of $\mathrm{Li^+(CH_3NH_2)_4{\cdot}Na^-}$ in various solvents[4] prompted us to try the less volatile complexant, ethylenediamine (en). We report here the synthesis of the simple crystalline sodide, $\mathrm{Li^+(en)_2{\cdot}Na^-}$. Extension of this work to other complexants for the lithium cation and to other anions such as $\mathrm{K^-}$, $\mathrm{Rb^-}$, $\mathrm{Cs^-}$, or $\mathrm{e^-}$ could make available inexpensive, easily prepared alkalides and electrides for use as reductants in synthesis.

Vacuum-line synthesis methods, solvent purification, alkali metal handling, and analytical techniques are described elsewhere.[5-8] To prepare the title compound it is only necessary to combine lithium metal, sodium metal, and ethylenediamine in stoichiometric amounts with the aid of a suitable solvent and then remove the solvent slowly by low-temperature distillation. A

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(1) Dye, J. L.; Ceraso, J. M.; Lok, M. T.; Barnett, B. L.; Tehan, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 608-609.

(2) Tehan, F. J.; Barnett, B. L.; Dye, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 7203-7208.

(3) DaGue, M. G. Ph.D. Dissertation, Michigan State University, East Lansing, MI, 1979.

(4) Faber, M. K.; Fussa', O.; Skowyra, J.; Hill, L.; Dye, J. L., unpublished work, this laboratory.

(5) Dye, J. L.; Andrews, C. W.; Mathews, S. E. *J. Phys. Chem.* **1975**, *79*, 3065-3070.

(6) Dye, J. L. *J. Phys. Chem.* **1980**, *84*, 1084-1090.

(7) Van Eck, B.; Le, L. D.; Issa, D.; Dye, J. L. *Inorg. Chem.* **1982**, *21*, 1966-1970.

(8) Dye, J. L. *J. Phys. Chem.* **1984**, *88*, 3842-3846.

0002-7863/87/1509-7203$01.50/0

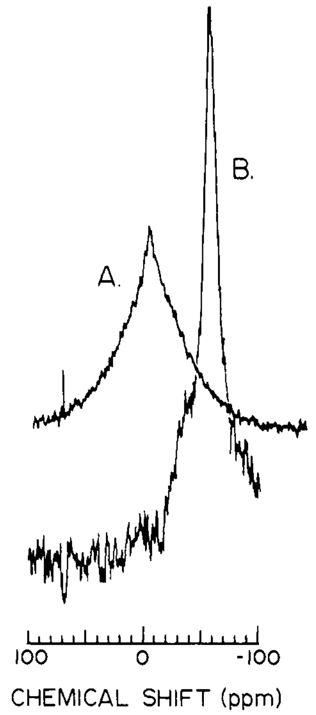

Figure 1. MAS-NMR spectra of solid Li$^+$(en)$_2$·Na$^-$ ($t \approx -70$ °C): (A) ^{7}Li NMR spectrum; (B) ^{23}Na NMR spectrum. Chemical shifts are relative to the aqueous cations at infinite dilution.

procedure that gave pure stoichiometric samples, stable to decomposition during preparation, is described here. Although less rigorous methods can also be used, especially to prepare solutions, they can lead to some decomposition.

Weighed equimolar amounts of sodium and lithium (typically 3–5 mmol of each) were introduced into one arm of an evacuable H-cell[9] in a helium-filled glovebox. Stoichiometric amounts of anhydrous ethylenediamine were contained in a break-seal tube that had been previously attached with Teflon heat-shrinkable tubing to a distillation sidearm on the other side of the H-cell. After evacuation to $<10^{-5}$ Torr, anhydrous ammonia was condensed on the metals to form a solution and then evaporated to leave a metal film in the H-cell. About 20 mL of anhydrous methylamine was condensed onto the metal film at −78 °C, forming a dark blue solution that was poured through the glass frit into the other arm of the H-cell. This solution was frozen in a liquid nitrogen bath, the break-seal was broken, and the ethylenediamine was distilled into the H-cell, followed by a seal-off of the sidearm. A homogeneous solution formed upon standing at −30 °C. All of the methylamine was then removed by distillation, leaving a gold-colored shiny film. In initial experiments designed to check the stoichiometry, the film was repeatedly washed with *n*-pentane to remove any excess ethylenediamine. In later preparations, this step was eliminated by careful control of the initial amounts of lithium, sodium, and ethylenediamine. About 20 mL of anhydrous ethylamine was then condensed onto the film, forming a deep blue, apparently homogeneous solution. Condensation of 10–15 mL of *n*-pentane, followed by standing for 12–20 h at −78 °C and slow removal of the solvents by distillation at temperatures below −50 °C, resulted in the formation of a gold-bronze powder. To remove traces of solvent, the H-cell was evacuated to $\sim 10^{-6}$ Torr for 12–24 h with the cell temperature kept at −35 to −78 °C. The powder was transferred while cold to a storage vessel in a nitrogen-filled glove bag. Recrystallization from ethylamine by addition of *n*-pentane was used to prepare samples for analysis and NMR studies. Analysis[7] by pH titration, dc plasma emission spectroscopy, and quantitative ^{1}H NMR spectroscopy confirmed the stoichiometry Li$^+$(en)$_2$·Na$^-$. Initial experiments showed that it is important to keep the solutions below −50 °C during solvent evaporation to avoid loss of ethylenediamine.

The polycrystalline compound melts at −23 °C to form a gold-colored liquid that is stable at this temperature. Upon raising the temperature to ~0 °C the solution becomes dark blue and appears to contain a precipitate (probably the metals). The gold material is *not* reformed upon cooling. Raising the temperature to ~30 °C causes irreversible decomposition. Differential scanning calorimetry shows an endotherm at −30 to −20 °C, a second and larger endotherm at −5 to +5 °C, and an exotherm at +30 to +40 °C. We interpret these changes as melting, decomplexation, and decomposition, respectively.

The solid compound at low temperatures (<−70 °C) shows ^{7}Li and ^{23}Na MAS-NMR peaks of both Li$^+$ ($\delta = 0.1$ ppm, $\Delta\nu_{1/2} = 3$ KHz) and Na$^-$ ($\delta = -59$ ppm, $\Delta\nu_{1/2} = 720$ Hz) as shown in Figure 1. Its solution in ethylamine also shows these two peaks at $\delta = 1.8$ ppm (Li$^+$) and $\delta = -61$ ppm (Na$^-$) but with line widths of only 50 Hz. A thin solvent-free film of the material, produced by rapid evaporation of methylamine, shows the characteristic optical absorption peak of Na$^-$ at 650 nm.

The compound is soluble to at least 0.1 M in methylamine and ethylamine at −5 °C, forming gold-colored films in contact with dark blue solutions at lower temperatures. Its solubility in tetrahydrofuran, dimethyl ether, and 2-aminopropane is lower, but it was possible to prepare 0.01 M solutions in all of these solvents at −30 °C. Decomplexation to metal and ethylenediamine occurs in diethyl ether. The compound is insoluble in *n*-pentane and trimethylamine. Although the powdered samples described here are polycrystalline, we have thus far been unable to grow single crystals for structure determination.

Acknowledgment. This work was supported by National Science Foundation Solid State Chemistry Grant DMR 84-14154. Some of the equipment was provided by the M.S.U. Center for Fundamental Materials Research. R.C. is grateful to the Council for International Exchange of Scholars for a Fulbright Grant for this research. We acknowledge the help of Mark Kuchenmeister, Jineun Kim, Lauren Hill, and Long Le with some of the measurements.

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(9) Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 327-441.

Pyridine Complexes of Chlorine Atoms

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Received July 9, 1987

The use of pyridine ester templates to direct selective steroid chlorinations has been described.[3] The results indicate that a chlorine atom coordinates to the pyridine nitrogen and is then relayed to a geometrically accessible substrate hydrogen. Although many studies have been reported on chlorine atom complexes to benzene and its derivatives,[4-7] pyridine raises some unique questions. Is the chlorine σ bonded to N or π bonded? Is it a

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(1) Columbia University.

(2) Rutgers University.

(3) Breslow, R.; Brandl, M.; Hunger, J.; Adams, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 3799-3801.

(4) Russell, G. A. *J. Am. Chem. Soc.* **1957**, *79*, 2977-2978. Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 4987-4996. Walling, C.; Mayahi, M. F. *J. Am. Chem. Soc.* **1958**, *81*, 1485-1489.

(5) Skell, P. S.; Baxter, H. N., III; Taylor, C, K. *J. Am. Chem. Soc.* **1983**, *105*, 120-121. Skell, P. S.; Baxter, H. N., III; Tanko, J. M.; Chebolu, V. *J. Am. Chem. Soc.* **1986**, *108*, 6300-6311.

(6) Bunce, N. J.; Ingold, K. U.; Landers, J. P.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5464-5472. Bunce, N. J.; Joy, R. B.; Landers, J. P.; Nakai, J. S. *J. Org. Chem.* **1987**, *52*, 1155-1156.

(7) Bühler, R. E.; Ebert, M. *Nature (London)* **1967**, *214*, 1220-1221. Bühler, R. E. *Helv. Chim. Acta* **1968**, *51*, 1558-1571.

0002-7863/87/1509-7204$01.50/0