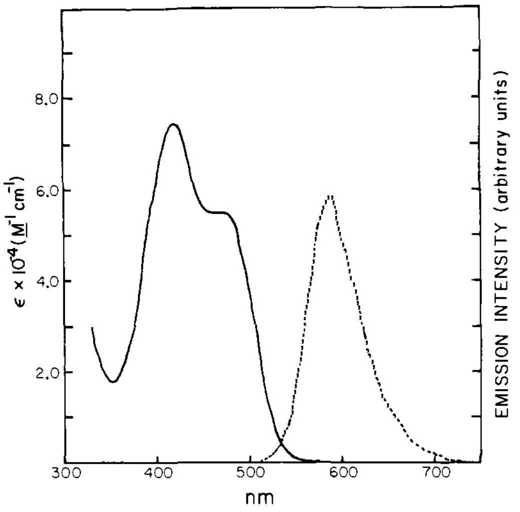

Figure 2. Absorption and emission spectra of $Cr(CNPh)_6$ in 2-MeTHF at 77 K.

gassed chloroform at λ 436 nm gives the one-electron oxidation products $M(CNIph)_6^+$.[7] Complexes of this type containing low-spin d^5 Cr(I) have recently been prepared by thermal routes and characterized by Treichel and Essenmacher.[8] The quantum yield for each of the three complexes is 0.19 ± 0.01. In the presence of oxygen this yield increases dramatically (with M = Cr, the yield at 436 nm is 0.70 ± 0.01 in chloroform saturated with air).[9] Irradiation of $M(CNPh)_6$ (M = Mo, W) produces seven-coordinate, two-electron oxidation products, $[M(CNPh)_6Cl]^+$.[10] Molybdenum(II) complexes of similar composition have been characterized previously by Lippard and co-workers[11] as well as by Bonati and Minghetti.[12]

The above experimental results are consistent with the following mechanistic scheme:

$$\mathrm{ML_6} \xrightarrow{436\ \mathrm{nm}} \mathrm{ML_6}^* \tag{2}$$

$$\mathrm{ML_6}^* + \mathrm{HCCl_3} \rightarrow [\mathrm{ML_6}^+\text{- - -}\mathrm{HCCl_3}\cdot^-] \tag{3}$$

$$[\mathrm{ML_6}^+\text{- - -}\mathrm{HCCl_3}\cdot^-] \rightarrow \mathrm{ML_6}^+ + \mathrm{HCCl_3}\cdot^- \tag{4}$$

$$[\mathrm{ML_6}^+\text{- - -}\mathrm{HCCl_3}\cdot^-] \rightarrow [\mathrm{ML_6Cl}^+\text{- - - - -}\mathrm{HCCl_2}\cdot^-] \tag{5}$$

$$[\mathrm{ML_6Cl}^+\text{- - -}\mathrm{HCCl_2}\cdot^-] \rightarrow [\mathrm{ML_6Cl}]^+ + \mathrm{HCCl_2}\cdot^- \tag{6}$$

The MLCT excited state formed (eq 2) is quenched by chloroform via electron transfer forming the radical pair $[ML_6^+\text{- - -}HCCl_3\cdot^-]$.[13] This species can revert back to starting materials or undergo reaction. For L = CNIph, the $HCCl_3\cdot^-$ radical presumably diffuses away, eventually releasing Cl^-. We propose that this step is rate controlling, thereby giving the constant quantum yield of 0.19 for the three metals.[14] In the complexes containing CNPh, which are much less hindered, we suggest that the chloroform radical anion transfers a chlorine atom to ML_6^+ (eq 5), giving the seven-coordinate products that are observed for M = Mo, W.

Acknowledgments. We thank Edward Cuellar, Nathan Lewis, and Steve Milder for assistance with certain experiments. This research was supported by the National Science Foundation.

References and Notes

(1) Recent interest in this area, however, has been intense, and it is likely that our understanding of the reactivity of MLCT excited states will develop rapidly. See, for example: (a) J. Van Houten and R. J. Watts, *J. Am. Chem. Soc.*, **98**, 4853 (1976); (b) C. Creutz and N. Sutin, *Inorg. Chem.*, **15**, 496 (1976); (c) R. C. Young, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 286 (1976); (d) M. S. Wrighton, H. B. Abrahamson, and D. L. Morse, *ibid.*, **98**, 4106 (1976); (e) C. T. Lin, W. Böttcher, M. Chou, C. Creutz, and N. Sutin, *ibid.*, **98**, 6536 (1976); (f) C. Creutz and N. Sutin, *ibid.*, **98**, 6385 (1976); (g) C. Lin and N. Sutin, *J. Phys. Chem.*, **80**, 97 (1976); (h) R. E. Hintze and P. C. Ford, *Inorg. Chem.*, **14**, 1211 (1975); (i) G. A. Crosby, K. W. Nipps, and W. H. Elfring, Jr., *J. Am. Chem. Soc.*, **96**, 629 (1974).

(2) K. R. Mann, M. Cimolino, G. L. Geoffroy, G. S. Hammond, A. A. Orio, G. Albertin, and H. B. Gray, *Inorg. Chim. Acta*, **16**, 97 (1976).

(3) In each photoreaction release of one molecule of ligand was observed ($\bar{\nu}$ (CNPh) 2125 cm^{-1}; $\bar{\nu}$ (CNIph) 2115 cm^{-1}) in infrared spectral experiments. Good isosbestic points were obtained in parallel visible absorption measurements.

(4) However, the fact that the quantum yields for the two Cr(0) complexes are the same is consistent with a dissociative pathway for ligand substitution in those cases.

(5) (a) V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, N.Y., 1970, Chapter 17; (b) M. Wrighton, *Chem. Rev.*, **74**, 401 (1974).

(6) For a discussion of the small amount of available evidence for bimolecular excited state processes involving certain substituted metal carbonyl complexes, see A. Vogler in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley-Interscience, New York, N.Y., 1975, Chapter 6.

(7) The $Cr(CNIph)_6^+$ complex was isolated and characterized as a PF_6^- salt. Anal. Calcd: C, 70.94; N, 6.22; H, 7.79. Found: C, 70.57; N, 6.36; H, 7.78. ν(C≡N). Cr, 2065; Mo, 2050; W, 2040 cm^{-1} ($CHCl_3$ solution).

(8) P. M. Treichel and G. J. Essenmacher, *Inorg. Chem.*, **15**, 146 (1976).

(9) Emission from ML_6 complexes was found to be quenched in chloroform.

(10) The $[Mo(CNPh)_6Cl]^+$ complex was isolated and characterized as a Cl^- salt. Anal. Calcd: C, 64.21; N, 10.70; H, 3.85. Found: C, 62.02; N, 10.66; H, 4.09. ν (C≡N). Mo, 2100, 2130 (sh); W, 2100, 2130 (sh) cm^{-1} ($CHCl_3$ solution). Irradiation of $Cr(CNPh)_6$ in degassed chloroform leads to a product which contains Cr(II) but does not correspond to either $Cr(CNPh)_6^{2+}$ or $[Cr(CNPh)_6Cl]^+$. $Cr(CNPh)_6^{2+}$ has been prepared by Treichel and Essenmacher.[7]

(11) (a) D. L. Lewis and S. J. Lippard, *J. Am. Chem. Soc.*, **97**, 2697 (1975); (b) M. Novotny and S. J. Lippard, *J. Chem. Soc., Chem. Commun.*, 202 (1973); (c) D. R. Lewis and S. J. Lippard, *Inorg. Chem.*, **11**, 621 (1972).

(12) F. Bonati and G. Minghetti, *Inorg. Chem.*, **9**, 2642 (1970).

(13) It should be noted that no ML_6 absorptions in $CHCl_3$ solution attributable to metal to solvent transitions were observed in the visible region.

(14) The large increase in yield in oxygenated chloroform solution for $Cr(CNIph)_6^+$ formation could reflect the increased diffusion rate of O_2^-.

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Crown Ether Model Systems for the Study of Photoexcited State Response to Geometrically Oriented Perturbers. The Effect of Alkali Metal Ions on Emission from Naphthalene Derivatives[1]

Sir:

Compounds **1** and **2** and a number of other new crown ether naphthalene derivatives[1] have been designed and synthesized to facilitate the study of the naphthalene chromophore and its response to a variety of perturbers. An important feature of these molecules is the predetermined orientation of the chromophore and a complexed perturber. In an exploratory study of alkali metal halide perturbation of **1** and **2**[1-4] we have found that these closely related naphthalene derivatives exhibit di-

Table I. Phosphorescence Lifetimes of 2,3-Naphtho-20-crown-6 (**1**) and 1,8-Naphtho-21-crown-6 (**2**) in 95% Ethanol Glass at 77 K with Alkali Chloride Salts Added in 5:1 Molar Excess (crown at 2.00×10^{-4} F)

		τ_p (s)			τ_p (s)
1 +	—	2.9	**2** +	—	2.45
	NaCl	3.4		NaCl	2.3
	KCl	3.1		KCl	1.4
	RbCl	2.7		RbCl	1.3
	CsCl	2.2		CsCl	1.2

Table II. Estimates[a-c] of Rate Constants for Excited State Processes of 2,3-Naphtho-20-crown-6 (**1**) and 1,8-Naphtho-21-crown-6 (**2**) in 95% Ethanol Glass at 77 K with Alkali Chloride Salts Added in 5:1 Molar Excess (crown at 2.00 × 10^{-4} F)

	2,3-Naphtho-20-crown-6 (**1**)			1,8-Naphtho-21-crown-6 (**2**)		
Salt added	$10^{-7}k_{isc}$	$10^{2}k_p$	k_{dt}	$10^{-6}k_{isc}$	$10^{2}k_p$	k_{dt}
none	0.8	1.7	0.32	9.7	3.2	0.37
NaCl	1.4	1.6	0.28	8.5	3.6	0.40
KCl	2.3	1.7	0.30	6.3	3.3	0.70
RbCl	2.5	2.9	0.34	5.5	3.5	0.72
CsCl	6.7	4.6	0.41	7.4	5.9	0.75

[a] All rate constants are in units of s^{-1}. [b] With $\phi_f + \phi_{isc} = 1.0$ assumed,[7] and $k_f = 2 \times 10^6\ s^{-1}$ for **1** and $9 \times 10^5\ s^{-1}$ for 2[9], and $k_{isc} = (1 - \phi_f)k_f\phi_f^{-1}$, $k_p = \phi_p(\tau_p(1 - \phi_f))^{-1}$, $k_{dt} = \tau_p^{-1} - k_p$. [c] Errors in k_{isc} and k_p are at least ±20%, but only about ±5% in k_{dt}.

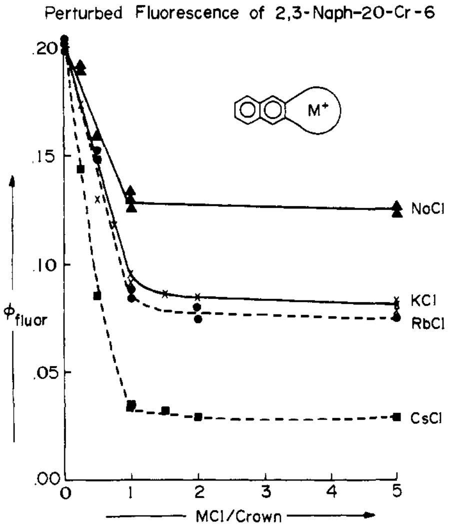


Figure 1. Fluorescence quantum yields[5] of 2.00 × 10^{-4} F 2,3-naphtho-20-crown-6 (**1**) in 95% ethanol glass at 77 K as a function of added alkali metal chlorides (— ▲, NaCl; — ×, KCl; - - ●, RbCl; - - ■, CsCl).

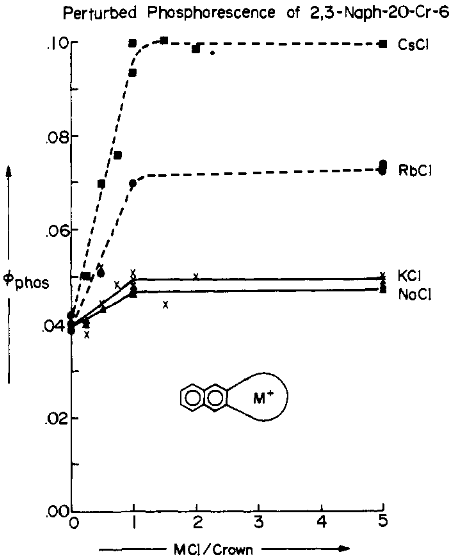


Figure 2. Phosphorescence quantum yields[5] of 2.00 × 10^{-4} F 2,3-naphtho-20-crown-6 (**1**) in 95% ethanol glass at 77 K as a function of added alkali metal chlorides (— ▲, NaCl; — ×, KCl; - - ●, RbCl; - - ■, CsCl).

chotomous behavior. Complexation by **1** of alkali metal chloride salts in 95% ethanol glass at 77 K causes a decrease in fluorescence quantum yield (ϕ_f), an increase in phosphorescence quantum yield (ϕ_p), and a slight decrease in phosphorescence lifetime (τ_p). However, complexation by **2** of potassium, rubidium, or cesium chloride salts causes a perceptible *increase* in ϕ_f, a *decrease* in ϕ_p, and a substantial decrease in τ_p.

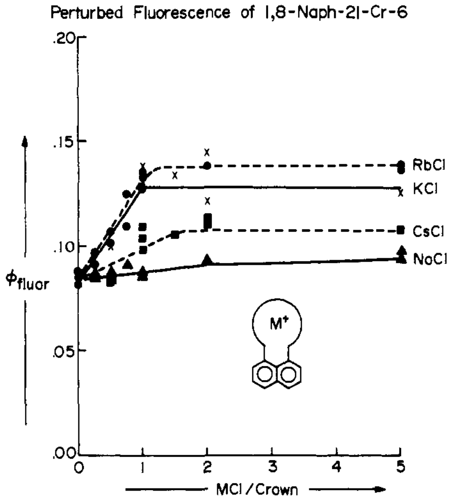
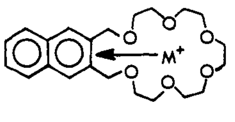
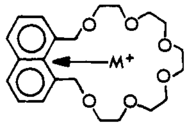


Figure 3. Fluorescence quantum yields[5] of 2.00 × 10^{-4} F 1,8-naphtho-21-crown-6 (**2**) in 95% ethanol glass at 77 K as a function of added alkali metal chlorides (— ▲, NaCl; — ×, KCl; - - ●, RbCl; - - ■, CsCl).



1



2

Quantum yields[5] of fluorescence and phosphorescence of **1** in uncracked 95% ethanol glass at 77 K with various mole-ratios of sodium, potassium, rubidium, and cesium chloride salts are shown in Figures 1 and 2, respectively. Figures 3 and 4 show respectively fluorescence and phosphorescence quantum yields which result when the same salts are added to crown-chromophore **2**. Table I lists phosphorescence lifetimes of **1** and **2** in the presence of fivefold excesses of alkali metal chloride salts in 95% ethanol at 77 K (lithium chloride had no effect on emission or τ_p).[6] Table II lists rate constants for excited state processes calculated assuming $\phi_f + \phi_{isc}$ is unity[7] and k_f (fluorescence rate constant) does not change with the addition of perturber[8] and is 2 × $10^6\ s^{-1}$ for **1** and 9 × $10^5\ s^{-1}$ for **2**.[9] Complexation by **1** of Na^+, K^+, Rb^+, or Cs^+ causes a small (about 25 cm^{-1}) blue shift in phosphorescence, and complexation by **2** of K^+, Rb^+, or Cs^+ (but not Na^+) induces a small (about 25 cm^{-1}) red shift in phosphorescence. Complexation related shifts in fluorescence spectra are smaller.[10]

Perturbation of photoexcited states by alkali metal cations has been reported[3a-d] only a few times, and is not yet well understood. In this case the data in Table II seem to be related to two effects: (1) a complexation induced change in triplet energy relative to ground and excited singlet state energies and, (2) a heavy atom effect operating only for Cs^+ and perhaps Rb^+.

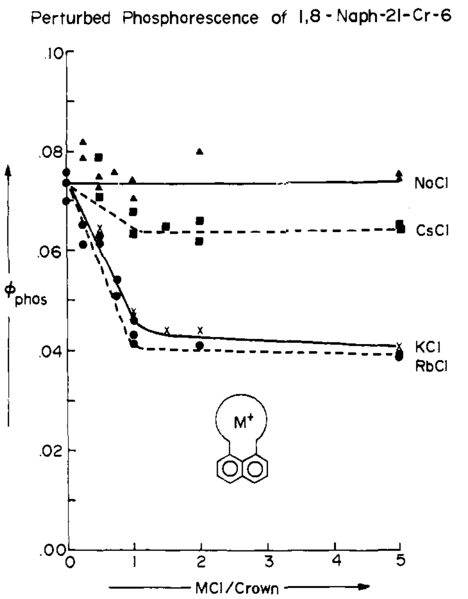


Figure 4. Phosphorescence quantum yields[5] of 2.0×10^{-4} F 1,8-naphtho-21-crown-6 (**2**) in 95% ethanol glass at 77 K as a function of added alkali metal chlorides (— ▲, NaCl; — ×, KCl; - - ●, RbCl; - - ■, CsCl).

Considering the lighter cations first, Table II shows complexation by **1** of Na^+ or K^+ increases the rate constant for intersystem crossing of S_1 to T_1 (k_{isc}) and slightly decreases the rate constant for radiationless decay of the triplet (k_{dt}). A narrowing of the S_1-T_1 energy gap and an increase in the T_1-S_0 energy difference is also observed. This correlation is to be expected since rates of T_1-S_0 radiationless decay depend strongly on the T_1-S_0 energy separation,[11] and S_1-T_1 intersystem crossing rates should be increased by decreasing S_1-T_1, energy separation[12] (and vice versa). Complexation of K^+ by **2** increases the S_1-T_1, energy gap and decreases the T_1-S_0 energy separation (Na^+ causes little change). This observation coincides with the decrease in k_{isc} and the increase in k_{dt} noted in Table II for perturbation by K^+ (Na^+ causes little change).[13] The lack of change in phosphorescence rate constants (k_p) for **1** and **2** with light cation complexation apparently indicates less dependence of k_p on the T_1-S_0 energy separation. Similar energy level arguments have been used by Song[3b] to rationalize Li^+, Na^+, and K^+ induced increases in ϕ_f for *all-trans*-retinal in ethanol glass at 77 K. Further experiments are required to determine if this directionally dependent light cation effect is due to (1) direct cation–chromophore interaction, (2) conformational changes in the chromophore enforced by crown-metal complexation, (3) conformational changes in the chromophore enforced by solvent orientation about the complexed cation,[14] or other interactions.

The effect of complexation of heavy cations (Cs^+ and perhaps Rb^+) by **1** and **2** can be rationalized as a superposition of (1) a normal heavy atom effect tending to increase k_{isc}, k_p, and k_{dt}, and (2) complexation induced changes in triplet energy levels as seen with lighter cations (see above). Recently, quenching of the fluorescence of aromatic hydrocarbons by concentrated cesium chloride solutions has been attributed[3d] to an external heavy atom effect of cesium ion. The results in Table II for **1** and **2** show the tendency of Rb^+ and Cs^+ to increase each rate constant relative to the values observed with Na^+ and K^+ complexation.

Molecules **1** and **2** provide a relatively well-known orientation of perturber and chromophore, especially when compared to external heavy atom studies in which the orientation is usually indeterminant. Comparison of the effects of K^+ with Cs^+ for **1** and **2** suggests that heavy cation perturbation may be slightly more effective from the end of the naphthalene chromophore (as in **1**). This would agree with a suggestion by Berlman[15a] based on external heavy atom quenching of fluorescence of substituted naphthalenes. A comparison with results from studies of the directional dependence of internal heavy atom effects, using brominated naphthonorbornenes, for example,[15c] is not meaningful since the complications caused by through-bond vibrational-spin-orbit interactions in those systems[15c] make simple analysis difficult.

This communication apparently reports the first study of excited states to use perturbers which are held in a predetermined orientation without the use of covalent binding. The alkali metal salt enhancement of fluorescence of an aromatic hydrocarbon system is also previously unreported. Alkali metals were selected as perturbers, but clearly many other metal ions, alkyl ammonium ions, and other species can be investigated.

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(1) L. R. Sousa and J. M. Larson, presented in part at the 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 1975.

(2) Synthesized from bis(hydroxymethyl)naphthalenes and appropriate polyethylene glycol ditosylates (**1**, mp 58.0–58.5 °C; **2**, mp 53.5–54.5 °C; spectral data and elemental analyses agree with structures proposed).

(3) For examples of excited state perturbation attributed to alkali halides see (a) H. Rau and L. Augenstein, *J. Chem. Phys.*, **46**, 1773 (1967); (b) P.-S. Song, Q. Chae, M. Fujita, and H. Baba, *J. Am. Chem. Soc.*, **98**, 819 (1976); (c) F. Bishai, E. Kuntz, and L. Augenstein, *Biochim. Biophys. Acta*, **140**, 381 (1967); (d) L. K. Patterson and S. J. Rzad, *Chem. Phys. Lett.*, **31**, 254 (1975); (e) G. Porter and M. R. Wright, *Discuss. Faraday Soc.*, **27**, 18 (1959); (f) R. H. Hofeldt, R. Sahai, and S. H. Lin, *J. Chem. Phys.*, **53**, 4512 (1970); (g) B. R. Henry and M. Kasha, *J. Mol. Spectrosc.*, **26**, 536 (1968). References 3e through 3 g and others cited therein involve perturbations attributed to the halide anion of alkali halide salts.

(4) For some reviews of crown ether chemistry see (a) C. J. Pedersen and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972); (b) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974); (c) D. J. Cram and J. M. Cram, *Science*, **183**, 803 (1974); (d) J.-M. Lehn, *Struct. Bonding (Berlin)*, **16** (1973).

(5) Quantum yields are relative to naphthalene taken as $\phi_f = 0.30$ and $\phi_p = 0.03$, V. L. Ermolaev, *Sov. Phys.-Usp. (Engl. Transl.)*, 333 1963, and references cited.

(6) In control experiments 10^{-2} M cesium chloride had no effect on the emission of the bismethyl ethers corresponding to **1** and **2**. Also sodium fluoride and bromide gave results identical with those shown for sodium chloride in figures 1–4 (sodium iodide gave different results).

(7) (a) V. L. Ermolaev and E. B. Sueshnikova, *Opt. Spectrosc.*, **16**, 320 (1964); (b) A. R. Horrocks and F. Wilkinson, *Proc. R. Soc. London, Ser. A*, **306**, 257 (1968).

(8) This assumption is based on the lack of change in the UV absorption of **1** and **2** as salt is added (room temperature).

(9) Based on preliminary fluorescence lifetime measurements.

(10) Complexation induced shifts in fluorescence spectra were less than 8 cm^{-1} toward the blue for **1** and less than 15 cm^{-1} toward the red for **2**. Shifts in fluorescence are probably real, but are near the value of experimental error. The longer wavelength phosphorescence shifts noted in the text are more reliably determined. It is possible, but less likely, that apparent phosphorescence shifts could be due to 0–0 bands which are greatly enhanced (for **1**) or diminished (for **2**) by complexation. Spectra will be published in a later report.

(11) R. E. Kellogg and N. C. Wyeth, *J. Chem. Phys.*, **45**, 315 (1966).

(12) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969; Chapters 5 and 6.

(13) (a) It is possible that the correlations of changes in rate constants k_{isc} and k_{dt} with energy separations is only coincidental, and that the rate constant changes are due to complexation induced distortions in the naphthalene chromophore. Out-of-plane distortions are important to intersystem crossing in naphthalene (M. A. El-Sayed, W. R. Moomaw, and J. B. Chodak, *Chem. Phys. Lett.*, **20**, 11, (1973)), and a change in an important out-of-plane naphthalene normal mode might account for the results with **1**. A directionally dependent combination of normal mode disruption and enhancement would be required to rationalize the behavior of **2**. (b) Rate constants

can be decreased by complexation which does not alter energy levels. Xenon is reported to lengthen the triplet lifetime of naphthalene by forming a xenon–naphthalene complex which induces no energy change (D. A. Head, A. Singh, M. G. Cook, and M. J. Quinn, *Can. J. Chem.*, **51**, 1624 (1973)).

(14) In ref 3a the authors attribute an ionic strength dependent decrease in ϕ_f (τ_p decreased and ϕ_p increased) for aromatic amino acids in water–sucrose glasses at 77 K to a salt-induced solvent structure change which perturbs the chromophore.

(15) (a) I. B. Berlman, *J. Phys. Chem.*, **77**, 562 (1973); (b) T. Pavlopoulos and M. A. El-Sayed, *J. Chem. Phys.*, **41**, 1082 (1964); (c) N. J. Turro, G. Kavarnos, V. Fung, A. L. Lyons, Jr., and T. Cole, Jr., *J. Am. Chem. Soc.*, **94**, 1392 (1972).

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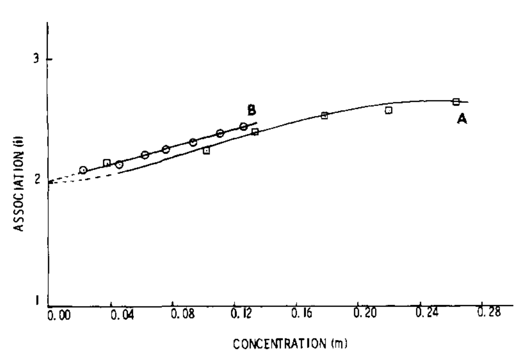


Figure 1, Molecular association studies of HMgCl (A) and HMgBr (B) in tetrahydrofuran.

The Preparation of HMgX Compounds

Sir:

Hydridomagnesium halides (HMgX, where X = halogen) represent a novel new class of compounds which have been highly sought after and which presumably can function as selective reducing agents toward organic substrates[1] and as intermediates in the preparation of novel complex magnesium hydrides. Wiberg and Strebel[2] in 1957 reported the preparation of THF soluble HMgCl and HMgBr by the reaction of ethyl Grignard reagents with diborane. However, we showed later[3] that such compounds are not formed under the conditions described. Sometime later, Dymova and Eliseeva[4] reported that HMgX compounds could be prepared in diethyl ether as insoluble solids by the hydrogenolysis of ethylmagnesium halides. They also reported that these compounds disproportionated to MgH_2 and MgX_2 when THF was added. We have also repeated this work in detail and have shown that the solid products obtained in these reactions involving diethyl ether as a solvent are actually physical mixtures of MgH_2 and MgX_2 as determined by x-ray powder diffraction analysis.[5] A third route reported by Rice and co-workers[6] for the preparation of nonsolvated HMgBr, involved the pyrolysis of ethylmagnesium bromide. This report was supported by x-ray powder pattern data. However, when we desolvated $MgBr_2 \cdot Et_2O$ to correspond to the exact amount of ether present in $HMgBr \cdot 0.27Et_2O$, then the powder diffraction patterns were the same showing that the $HMgBr \cdot 0.27Et_2O$ was actually a physical mixture of MgH_2 and $MgBr_2 \cdot 0.54OEt_2$.[7]

We would now like to report that hydridomagnesium halides (HMgX, where X = Cl and Br) have been prepared by the reaction of magnesium halides with an active form of magnesium hydride slurried in THF (eq 1). The active form of magnesium hydride was prepared by the reaction of Ph_2Mg or Et_2Mg with equimolar amounts of $LiAlH_4$ in diethyl ether (eq 2). The MgH_2 is insoluble in ether

$$MgH_2 + MgX_2 \xrightarrow[\text{room temp}]{\text{THF}} 2HMgX \tag{1}$$

$$R_2Mg + LiAlH_4 \xrightarrow{Et_2O} MgH_2 + LiAlH_2R_2 \tag{2}$$

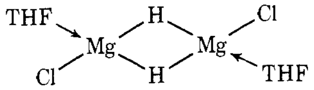
and was isolated from the soluble $LiAlH_2R_2$ by filtration. A slurry of this MgH_2 in freshly distilled THF was then allowed to react at room temperature with a THF solution of MgX_2 (where X = Cl or Br). The reaction is exothermic and results in the formation of a clear solution within a few minutes. Analysis of the resulting solution of HMgBr in THF showed a Mg:H:Br ratio of 1.00:0.97:1.02 and for HMgCl a Mg:H:Cl ratio of 1.00:0.98:1.04.

No reaction was observed when the THF solvent was replaced by diethyl ether, probably because of the insoluble nature of HMgX compounds in diethyl ether. Interestingly, HMgCl and HMgBr are both soluble and quite stable in THF contrary to earlier reports. A 1.5 M solution of HMgCl and a 0.5 M solution of HMgBr in THF could be prepared. Ebullioscopic molecular weight studies on HMgCl and HMgBr in THF showed both compounds to be dimeric in dilute solution and gave some indication of associating further in more concentrated solution to form trimers (Figure 1). Infrared spectra have been recorded in THF solution (HMgCl: 1380 m, 1345 m, 1320 m, 1290 mb, 1120 s, 990 vs, 800 sh, 710 vs, 600 m, 580 m, 550 m, 396 m; HMgBr: 1410 m, 1380 m, 1345 m, 1260 mb, 1118 s, 1010 vs, 800 vs, 700 s, 670 vs, 570 mb, 390 m). NMR spectra of HMgCl and HMgBr in THF did not give any fruitful information regarding the Mg-H proton.

The Mg-H stretching band in HMgBr and HMgCl was determined by preparing DMgBr and DMgCl by the method above (eq 1-2) using $LiAlD_4$ and comparing the infrared spectra of the HMgX and DMgX compounds. The bands at 1260 and 1290 cm^{-1} observed for HMgBr and HMgCl in THF were shifted to ~940 cm^{-1} in the case of DMgBr and DMgCl indicating 1260 and 1290 cm^{-1} as the Mg-H stretching bands for HMgBr and HMgCl, respectively.[8]

When the THF solvent was removed from HMgCl, a solid of empirical formula HMgCl·THF was formed. The x-ray powder diffraction pattern of this solid was identical with that of $MgCl_2 \cdot 2THF$. However, the solid redissolved immediately when THF was added. DTA-TGA studies of this solid showed decomposition at 300 °C with hydrogen evolution. The x-ray powder pattern for HMgBr·1.5THF formed on removal of THF from the solution prepared above, gave lines identical with $MgBr_2 \cdot 3THF$ indicating disproportionation of HMgBr to MgH_2 and $MgBr_2$ in the solid state.

On the basis of molecular weight and spectroscopic studies, the molecular structure of HMgCl in THF is suggested to be that represented below:



Because of the insoluble nature of MgI_2 in THF, an attempt was made to prepare HMgI by addition of a solution of MgI_2 in diethyl ether to MgH_2 slurry in diethyl ether and in THF. An x-ray powder pattern of the solid isolated after the removal of the solvent under vacuum showed strong lines due to $MgI_2 \cdot 6THF$ rather than the expected product HMgI·3THF. The nonreactivity of MgH_2 toward MgI_2 in THF is probably due to the insoluble nature of MgI_2 in THF. Interestingly, the DTA-TGA of this so-called mixture gave no hydrogen evolution at 310 °C as expected for MgH_2 decomposition, but instead showed extensive THF cleavage.

Both HMgBr and HMgCl in THF have been shown to reduce ketones such as benzophenone and 4-*tert*-butycyclohexanone to the corresponding alcohols. More importantly,