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Lithium Intercalation Compounds of Yttrium and Gadolinium Monochloride: Synthesis and Structure

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The phase Li$_x$YCl is formed in ~10% yield from Y–YCl$_3$–LiCl reactions at 875 °C for 3 weeks. The gadolinium compound Li$_y$GdCl is obtained in low yields from the reaction of powdered KGd$_2$Cl$_7$ with liquid Li at 500 °C and in almost quantitative yield from the Gd–GdCl$_3$–Li reaction at 700 °C, each for 2 weeks. The crystal structures and the compositions of Li$_{0.2}$YCl, Li$_{0.5}$GdCl (from the first preparative route), and for comparison, YCl were solved by single-crystal X-ray methods. All three occur in the ZrBr-type structure (trigonal, $R\bar{3}m$) with lithium evidently randomly distributed in trigonal-antiprismatic interstices between the chlorine layers of adjacent M$_2$Cl$_2$ slabs (the limiting composition is Li$_{0.5}$MCl). The a and c lattice constants (Å), final R and R_w values, and refined lithium occupancies from the single-crystal studies are as follows: YCl, 3.7523 (2), 27.525 (5), 0.039, 0.054, ...; Li$_{0.2}$YCl, 3.7513 (2), 27.803 (2), 0.052, 0.072, 0.15 (8); Li$_{0.5}$GdCl, 3.815 (1), 27.832 (7), 0.082, 0.083, 0.47 (15). The formation of intercalated YCl is accompanied by an appropriate 0.023 (3) Å reduction of the interlayer Y–Y distance. The lower reducibility of YCl through intercalation by Li, the absence of M$^{I}_{x}$YCl products with heavier alkali metals, and the occurrence of an intercalate of only the high-temperature (ZrBr) form of GdCl are discussed.

Introduction

Many of the early transition metals form unusual monohalides in which pairs of metal layers are sheathed with halogen layers to give tightly bound slabs with a X–M–M–X sequence of close-packed layers (X = Cl, Br). Compounds with this type of structure are now known for ZrCl,[3] ZrBr,[4] HfX,[5] many lanthanide chlorides and bromides LnX,[6] ScCl,[7] and YX.[8] The four-layer slabs occur in two stacking sequences, either ···ABC··· in the ZrCl (or low-temperature LnX[6]) type or ··ACB·· in the ZrBr (high-temperature LnX) form, both having characteristic van der Waals gaps between halogen layers of adjacent slabs. Both the d^3 (ZrX) and d^2 (LnX) examples appear to be metallic.[4,6,9]

A significant amount of what may be termed interstitial chemistry can be achieved between the double-metal layers in these, all with retention of the slabs. This includes substitution of small non-metals either in the tetrahedral interstices in the phases ZrXH$_{0.5}$, ZrXH,[10–12] and ZrXO$_y$[13] or in trigonal-antiprismatic sites in MXC$_{0.5}$ phases for M = Sc, Y,[14] and Zr[15] as well as in GdBrC as dicarbon.[16] Several series of experiments designed to intercalate ZrX, ZrClO$_y$, or ZrClC$_{0.5}$ with alkali metal to produce (M$^+$)$_x$(ZrX)$^{x-}$ etc. have all been unsuccessful,[4,13,15] although reactions of this type are quite general with layered dichalcogenides that have empty or partly filled bands centered on a single metal layer.[17] On the other hand, intercalated products of the oxide and carbide derivatives are obtained with the group 3 element yttrium in M$^{I}_{0.1}$YClO and M$^{I}_{0.2}$YClC$_{0.5}$.[14]

We herein report the synthesis of the lithium intercalation compounds of the double-metal-layered YCl and GdCl from the corresponding LiCl–MCl$_3$–M reactions and also the second by lithium reduction of molten KGd$_2$Cl$_7$ as part of a general study of reduced ternary phases of the lanthanide elements.[18] Single-crystal structural determinations and Guinier powder patterns are the principal means of characterization of these two phases. The crystal structure of YCl has also been refined for comparison since it had previously been identified only by powder diffraction.[9] These lithium derivatives represent the first examples of intercalated rare-earth metal compounds and the first of a halide of the more electropositive transition elements where intercalated chalcogenides are well-known. The new products are also among the few examples of simple layered intercalates that have been structurally characterized by single-crystal rather than powder X-ray methods. Recently Schöllhorn and co-workers[19] have briefly reported the room-temperature intercalation of other types of halides, namely α-RuCl$_3$ (layered YCl$_3$ type) and β-RuBr$_3$ (chains, TiI$_3$ type) with several univalent metal ions by both electrochemical and chemical reductive means.

Experimental Section

Materials. As has been detailed before, all compounds were handled by drybox techniques and all reactions were run in welded tantalum or niobium containers. The YCl$_3$ was prepared as before[20] from metal and high-purity HCl and sublimed under high vacuum. Powdered yttrium was prepared by thermal decomposition of ground (<150 μm) YH$_{2-x}$ under high vacuum, slowly heating the sample to 750 °C and until the pressure dropped below discharge. The LiCl (Fisher Scientific) was carefully dehydrated by slowly heating under a high vacuum until it sublimed. The starting material KGd$_2$Cl$_7$[21] was prepared by the aqueous HCl route followed by careful dehydration under a stream of gaseous HCl[22] and was simple phase according to Guinier powder diffraction. The lithium was obtained from Merck.

Syntheses. Guinier patterns of reaction products and the lattice constant data deduced therefrom were generally important in following

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reactions and identifying phases.[4,13] Thin black plates of YCl are obtained in 10–20% yield as the only product of the reaction of excess Y powder with YCl_3 at 850 °C for a few weeks followed by quenching. Slow cooling or equilibrium at ≤825 °C gives about a 50:50 mixture with Y_2Cl_3. Fluxed reactions between Y powder and 10–40 mol % of LiCl in YCl_3 at 500–650 °C yield 10– (usually) 50% YCl, the remainder Y_2Cl_3 (and Li_3YCl_6). The use of yttrium in the form of rolled strips generally does not produce any YCl, only Y_2Cl_3, and such a reaction in the presence of a comparable amount of KCl and excess Y will produce greater than 95% Y_2Cl_3 (based on YCl_3). A reaction of KCl:YCl_3 (1:4) with strips at 950 °C did produce YCl. These ternary systems of course give problems as far as the separation of pure product from the flux.

Reactions in Y/YBr_3 system at 830 °C have also given good yields of YBr in the ZrBr structure type (a = 3.8080 (4) Å, c = 29.168 (9) Å), as distinguished from the ZrCl form by the intensity distributions observed in both Guinier and Weissenberg patterns. Previously only the ZrCl type had been identified.[8]

Li_xYCl is obtained in 5–15% yield from the ternary reaction

$$3x\mathrm{LiCl(l)} + (2 + x)\mathrm{Y(s)} + (1 - x)\mathrm{YCl_3(l)} \rightarrow 3\mathrm{Li}_x\mathrm{YCl(s)} \qquad (1)$$

using powdered metal plus 25–50 mol % of LiCl in YCl_3, but *only* when this is run at higher temperatures, ≥875 °C, for ca. 3 weeks. The black hexagonal platelets are found growing on sintered clumps of metal. The phase is easily identified by its expanded YCl-type pattern. The intercalate has not been made by the direct reductions of YCl because of the difficulty in first obtaining YCl in good yield. Unless very clean conditions are maintained 3R-$Li_{0.1}YClO$ and 1T-$Li_{0.2}YClC_{0.5}$ may also be obtained,[14] and their separation from Li_xYCl is difficult since all three phases have similar morphologies. No evidence was found for the existence of comparable compounds of sodium or potassium. Numerous reactions of powdered metal with YCl_3 and NaCl or KCl at 900–950 °C yielded no like products on the metal, but 10–15% of $M^{I}_{0.1}YClO$ or $M^{I}_{0.2}YClC_{0.5}$ was found on occasion in other parts of the container. All reduced products were utilized in the mounting of samples for Guiner examination so it is not likely that a new phase in any significant quantity would have been missed.

Li_yGdCl was first obtained from the reaction of powdered KGd_2Cl_7 with an equimolar amount of liquid Li at 500 °C for 20 days. The black platelets of Li_yGdCl appear to grow on large plates of KGd_2Cl_7. The yield is a few percent, with crystals of KGd_2Cl_7 and K_2GdCl_5 as the other main products. Its more direct synthesis from Li, Gd powder, and $GdCl_3$ in the ideal 3:4:2 molar proportion (for y = 0.5) at 700 °C for 2 weeks is also successful (>90% yield, with no Gd_2Cl_3), but the very thin platelets obtained are of very poor quality as far as single-crystal diffraction.

Structure Solution. Powder patterns clearly indicate that the R-centered trigonal cell of YCl (ZrBr-type[4] or high-temperature GdCl[6]) applies to all our products of these syntheses.[23] Crystals of the yttrium compounds were selected in a glovebox under dry N_2 and mounted in thin-walled capillaries that were then sealed off. The correctness of the chosen cell and symmetry for Li_xYCl was also confirmed by Weissenberg photographs, which showed sharp spots and no twinning. Crystals of Li_yGdCl were selected under a stream of dry Ar and mounted in thin-walled capillaries without grease and sealed off under Ar. The crystal quality was checked by using oscillation and zero-level Weissenberg photographs.

All data sets were collected with monochromatic Mo Kα radiation on four-circle diffractometers using the usual standard reflections; no evidence of decay was noted. Details regarding the data collection and structure solution are summarized in Table I. The absorption coefficient of yttrium for Mo radiation is particularly large since it lies on the absorption edge (μ = 277 cm^{-1} for YCl) so the YCl and Li_xYCl data sets were corrected for absorption by using a ϕ-scan method where the reflection was tuned every 10° in ϕ.[24] Two scans at 2θ = 34.2 and 58.0° were used for Li_xYCl. The R-centering condition $-h+k+l = 3n$ was not imposed during data collection on Li_xYCl, and 28 violations were found among 808 observed reflections in the total set. However, none exhibited a reasonable profile, and all originated from overlap or streaking of an adjacent strong reflection.

Table I. Diffraction and Refinement Data

	YCl	Li_xYCl	Li_yGdCl
size, mm	0.2 × 0.2 × 0.1	0.2 × 0.2 × 0.1	0.3 × 0.25 × 0.1
octants measd	4^a	4	4
2θ max, deg	50	60	60
reflcn data			
checked	546^a	2604	2364
obsd (>$3\sigma(I)$)	523	808	
indep	101	156	167
R(av)	0.038	0.039	0.12
struct soln^b			
R	0.039	0.052	0.082
R_w	0.054	0.072	0.083

[a] The complete set of reflections allowed for the R-centered cell was first collected for an equivalent triclinic cell and then converted to the correct indexing. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Both studies utilized neutral-atom scattering factors (although the effect of Li^+ factors was also explored), and these included corrections for the real and imaginary parts of anomalous scattering of the heavier atoms. The structural solution of YCl started with positional parameters for the isostructural ScCl[7] while that for its intercalate utilized those refined for YCl. Least-squares refinement and Fourier synthesis steps for the yttrium salts employed the programs ALLS[25] FOUR[26] respectively. A Fourier map for Li_xYCl based on just refined heavy-atom positions indicated two possible positions between the chlorine layers for a lithium atom that were approximately tetrahedral and trigaonl antiprismatic with respect to chlorine neighbors. Only the latter could be refined, both the occupancy and isotropic temperature factor being varied simultaneously to yield 0.15 (8) and 1.4 (40) at R = 0.052, R_w = 0.072. (Values of 0.09, 1.1, and R = 0.056 reported earlier[14] originated with a less satisfactory data averaging method.) Final difference maps were flat everywhere to <1 e/Å^3.

Since GdCl is known from powder data to crystallize with both ZrCl- and ZrBr-type structures,[6] the first refinements on Li_yGdCl started with the atomic positions reported for both types of TbCl.[6] Only a few cycles of the program[27] were necessary to produce R = 0.14 for the ZrBr-type model while the ZrCl-like arrangement hung up at R = 0.51. Introduction of anisotropic thermal parameters for Gd and Cl dropped the R factor to 0.087, which appeared quite satisfactory in view of R(av) of only 0.12. A Fourier difference map showed a small electron density in the trigonal-antiprismatic interstices between the chlorine layers, and this could be refined well but not with simultaneous variation of the isotropic B and the site occupation. A fixed isotropic B of 0.79 Å^2 for Li (U = 0.01, approximately equivalent to the isotropic B's refined for Gd and Cl) yielded a Li site occupancy y = 0.46 (15) and R = 0.082 and R_w = 0.083. A fixed 0.5 occupancy for Li yielded poorer R values, 0.087 and 0.088. The final difference map was flat everywhere to <1 e/Å^3 except for a residue of ~0.1 Gd at the metal site.

Results and Discussion

Parametric data for the YCl, $Li_{0.2}YCl$, and $Li_{0.5}GdCl$ structures are given in Table II together with lattice constants for these and GdCl. All occur in the ZrBr-type ($R\bar{3}m$) structure. Residuals for the refinements were given in Table I. Figure 1 shows (110) sections of YCl and $Li_{0.2}YCl$ drawn with experimental thermal ellipsoids at the 95% probability level, and Table III gives some distance comparisons.

The refinement of both intercalate structures was sufficiently well conditioned that the occupancies of the lithium atom could

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(23) An earlier report on YCl[8] in the ZrBr structure with a smaller c lattice constant, 27.381 Å (misprinted 27.318 Å), correctly pertains to the ZrCl (low-temperature LnX) modification, for which a recent redetermination gives a = 3.753 (1) and c = 27.359 (2) Å.[16] Values of c for YCl (ZrBr type) have ranged from 27.473 (3) to 27.525 (5) Å for samples prepared in both Ames and Stuttgart with or without KCl flux as well as with either powdered or bulk metal. Residual hydrogen in powdered Y is therefore not responsible for this small range.

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Table II. Positional and Thermal Parameters and Lattice Constants for YCl, $Li_{0.2}YCl$, and $Li_{0.5}GdCl$[a]

Structural Parameters

	z[b]		occup	B_{11}[c]		B_{33}		
	M	Cl	Li	M	Cl	M	Cl	B(Li), Å^2
YCl	0.21683 (5)	0.3883 (1)		1.08 (6)	1.5 (1)	1.31 (9)	1.2 (1)	
$Li_{0.2}YCl$	0.21583 (4)	0.3884 (1)	0.15 (8)	1.05 (5)	1.31 (8)	1.24 (6)	1.1 (1)	1.1 (40)
$Li_{0.5}GdCl$	0.21710 (6)	0.3876 (3)	0.47 (15)	0.24 (6)	0.8 (2)	1.49 (9)	1.1 (3)	0.8[d]

Lattice Constants

	diffractometer		Guinier	
	a, Å	c, Å	a, Å	c, Å
YCl	3.7523 (2)	27.525 (5)	3.753 (1)[e]	27.500 (16)[e]
$Li_{0.2}YCl$	3.7513 (2)	27.803 (2)	3.7481 (3)	27.796 (7)
GdCl[f]			3.819 (1)	27.482 (6)
$Li_{0.5}GdCl$	3.815 (1)	27.832 (7)	3.823 (1)	27.904 (10)[g]

[a] $R\bar{3}m$ space group. [b] $x = y = 0; z(\text{Li}) = 0.0$. [c] $\exp[-\frac{1}{4}(B_{11}a^{*2}(h^2 + hk + k^2) + B_{33}l^2c^{*2})]$ for M and Cl; isotropic for Li. [d] Fixed. [e] Average from four different meprations, with the average deviation in parentheses.[22] [f] From ref 6. [g] For a sample prepared by a different route (Li, Gd, $GdCl_3$) and with a possibly higher Li content.

Table III. Comparative Distances in YCl, $Li_{0.2}YCl$, and $Li_{0.5}GdCl$ and Estimated Values for GdCl (Å)

	YCl	$Li_{0.2}YCl$	GdCl[a]	$Li_{0.5}GdCl$
		Intralayer		
M-M, Cl-Cl (6×)	3.7523 (2)	3.7513 (2)	3.819 (1)	3.815 (1)
		Interlayer		
M-M (3×)	3.511 (2)	3.488 (2)	⩾3.57[b]	3.567 (3)
M-Cl (3×)	2.750 (2)	2.777 (2)	2.787[b]	2.800 (2)
Cl-Cl (3×)	3.722 (5)	3.747 (5)	3.689 (6)[c]	3.734 (6)
Li-Cl (6×)		2.651 (2)		2.669 (1)

[a] From ref 6. [b] Estimated from TbCl value. [c] Value for TbCl.

be determined directly although not with high precision. These gave 0.15 (8) and 0.46 (15) for the Y and Gd phases, respectively, which will be rounded off to 0.2 and 0.5 hereafter. The same values were secured with scattering factors for either neutral or ionized lithium and no significant differences could be discerned even among the low-angle reflections where the scattering factors do differ. The limiting composition for these phases would be $Li_{0.5}MCl$, and in the absence of any evidence for ordering, the lithium must be randomly distributed over about 30% (Y) and 90% (Gd) of the available trigonal-antiprismatic (TAP) sites.

The structure solution for YCl (ZrBr type) is unremarkable save for the evident quality of the crystal employed, as attested to by the uniformity of the thermal ellipsoids and the low residuals. The $Li_{0.2}YCl$ result appears to be comparable (Table II and Figure 1). Both results are unusual for layered compounds of this sort, particularly for the intercalation derivative, perhaps because single-crystal examples of the latter have often been obtained by low-temperature routes[17] that give crystals containing a greater number of layering defects. In the present case the intercalation step would require only a small expansion of the parent YCl structure without a change in the layering sequence although we have no reason to believe that the synthesis actually occurs with the prior formation of YCl.

Of course, for such a small amount of scattering matter it might be argued that the refinement of lithium is illusory and that the apparent electron density is actually the reflection of errors in the data that accumulated at a point of high symmetry. However, the refined metal-metal distances in YCl vs. $Li_{0.2}YCl$ (Table III) do show differences that clearly support the occurrence of a real reduction of the metal substrate. The apparent reaction causes a significant decrease in the Y-Y distances between the metal layers, 0.023 (3) Å, while an insignificant change occurs in the longer intralayer separation, perhaps because this is determined more by Cl-Cl repulsions. In addition, there are significant and appropriate increases in the Y-Cl distance (0.027 (3) Å), evidently reflecting the counterpolarization of chlorine by the lithium ion in binding between slabs, and in d(Cl-Cl) across this gap (0.025 (7) Å) in order to accommodate lithium and perhaps because of an increased charge on the chlorine layers (see below). The overall result of intercalation on lattice dimensions, a substantial increase in the c axis of 0.29 Å (1%), originates with the latter two changes, especially with the Y-Cl distances that occur with twice the frequency, and the increases in Y-Cl and Cl-Cl separations quite obscure the noteworthy decrease in the Y-Y interlayer distance. Lithium intercalation into YClO and $YClC_{0.5}$ produce very similar increases in the c-axis lengths.[14,28]

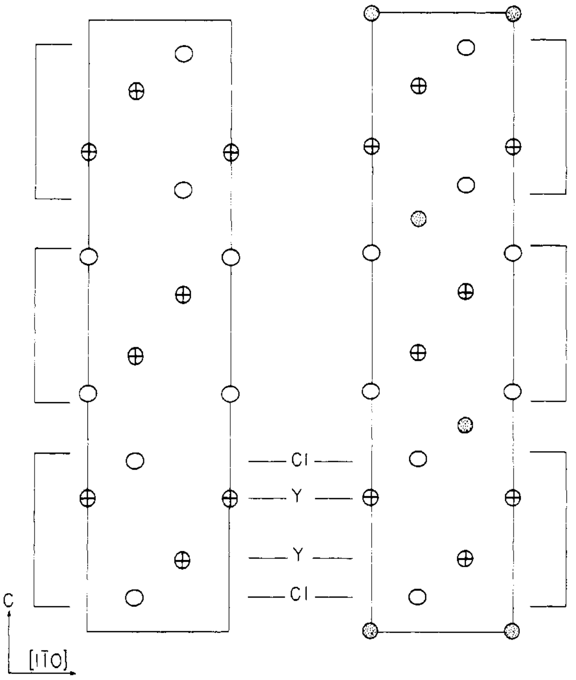

Figure 1. (110) sections of the unit cells of YCl (left) and $Li_{0.2}YCl$ (right), with brackets defining the Cl-Y-Y-Cl slabs: open circles, Cl; crossed circles, Y; shaded circles, Li. Thermal ellipsoids shown are at the 95% probability level.

The observed decrease in Y-Y distances may also be correlated in an empirical but plausible way to the concentration of lithium and the consequent number of electrons added to the predominantly yttrium band. In pure YCl the net amount

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[28] Ford, J. E.; Corbett, J. D., to be submitted for publication.

of metal–metal bonding as represented by the Pauling bond order sum per electron pair is 0.95; that is, the metal–metal bonding achieved in the compound is 95% of that in the hcp yttrium metal calibrant when the difference in electron count is taken into consideration.[29] The same 95% result for the intercalated YCl would correspond to 2.11 electrons/yttrium in the substrate or a composition $Li_{0.11}YCl$, in good agreement with the X-ray results and in further support of a complete electron transfer.

Obviously the crystal of $Li_{0.5}GdCl$ did not have the same high degree of perfection as the yttrium derivative although it is still moderately good. The elongation of the gadolinium "thermal" ellipsoids [001] is somewhat unusual in that the effect is not shared by chlorine, suggesting an absorption effect or something like an aperiodic displacement of only Gd that might be associated with electron localization on it rather than some stacking disorder that should also affect the halogen. The same effect has been seen in 3R-$Na_{0.16}YClO$ even after an absorption correction.[14,28]

Some of the trouble with $Li_{0.5}GdCl$ is probably associated with crystal imperfections resulting from the relatively low temperature (500 °C) used in its synthesis by lithium reduction of KGd_2Cl_7. The success of this gadolinium synthesis is especially noteworthy since no evidence of the formation of $Li_{0.2}YCl$ could be found in the LiCl-fluxed reactions of powdered yttrium and the trichloride at 500–650 °C; rather, a temperature near 875 °C or above is required (see Experimental Section). The lithium reductant used in the former case may first produce gadolinium metal and LiCl, the finely divided and highly reactive metal so obtained being responsible for a more effective synthesis at lower temperature. But the direct synthesis of the intercalated GdCl from Gd, $GdCl_3$, and Li at 700 °C is also more facile than the analogous yttrium route, and YCl likewise appears considerably more difficult to make in respectable yields than is GdCl.[6] Interestingly, the Li_zGdCl prepared in >90% yield by the latter route in the presence of a higher and more suitable lithium ion activity has lattice constants that are greater than for $Li_{0.46(15)}GdCl$ (5.6σ in c, Table II), a feature that may indicate an appreciable nonstoichiometry. A systematic investigation of the more direct route ($3Li + 4Gd + 2GdCl_3$) seems worthwhile as a route to better crystals in high yield.

It is also noteworthy that the structure found for $Li_{0.5}GdCl$ is based on the ZrBr-type (high-temperature LnX) arrangement even though the compound was synthesized at 500 °C in the regime of the low-temperature form of GdCl (ZrCl type). Mattausch et al.[6] observed a 720 °C transition between the two forms of GdCl in thermal analysis studies (on heating) and always obtained the low-temperature form from long-term synthetic reactions run below that temperature. However, the low-temperature (ZrCl) type of GdCl, which can be obtained (in reverse orientation) by interchanging the top two slabs in Figure 1, would place two Gd atoms along c as second-nearest neighbors to each TAP site in the gap. Preference for the ZrBr arrangement very likely arises from the absence of these neighbors, as seen in Figure 1.[30]

Although comparative structural parameters are not available for GdCl, the results for $Li_{0.5}GdCl$ appear qualitatively comparable to those for $Li_{0.2}YCl$ (Table III). In addition, the M–Cl and Cl–Cl distances seem to show very much the same trend in the intercalation product, those in GdCl being estimated with some credibility from the values in the neighboring TbCl.[6] The Li–Cl distances of 2.65 and 2.67 Å for the yttrium and gadolinium compounds, respectively, are similar to but somewhat larger than Shannon's[31] crystal radius sum, 2.57 Å, which is also d(Li–Cl) in LiCl. Actually, the expansions observed in the van der Waals gap are greater than necessary to accommodate an ideal Li^+ ion. Similarly oversized increases are found in the lithium intercalates of dichalcogenides, the TAP sites in TiS_2 and especially in VSe_2, for example, being large enough to accommodate Li^+ with no expansion. In these cases it has been concluded that the increase in distances across the gap is not associated with lithium propping open the layers (as it is with the larger alkali metals) but rather with an increased repulsion between the anion layers that arises from an increase in charge on these non-metal atoms as a result of the reductive intercalation.[32,33]

It is interesting that variations in M–M and M–Cl distances between the yttrium and gadolinium intercalates (Table III) reflect a significant difference between the effective metallic and crystal (core) radii for yttrium and gadolinium. Thus, the two types of M–M separations differ by 0.064 Å (intralayer) and 0.079 Å (interlayer), which is well more than twice the 0.023-Å difference in d(M–Cl) that is quite appropriate to the difference in crystal radii between these two cations.[31] The former values must reflect substantial differences in orbital composition and bond strength in the metal band for elements that have nearly the same core size. This effect has also been noted in Y_2Cl_3 vs. Gd_2Cl_3.[8]

Property studies of $Li_{0.2}YCl$ have been very much limited by the low yields that have been achieved, apparently because of the crystal nucleation and growth limitations that also pertain to the preparation of YCl itself. Intercalates of YCl with alkali metals heavier than lithium do not appear to be stable at ~950 °C judging from negative results in many attempts at their synthesis from YCl_3, Y and NaCl, KCl, or CsCl (see Experimental Section). A lower stability of the intercalated M^I_xYCl phases for $M^I \neq Li$ appears plausible when one considers the limiting decomposition reaction (2).

$$M_xYCl = (1 - x)YCl + xY + xMCl \qquad (2)$$

Binding of the alkali metal ion between chlorine layers in the intercalate should logically decrease with increasing size of the cation, and this trend is reinforced by a parallel increase in the enthalpies of formation of the MCl product. In practice the synthesis of M_xYCl was attempted with excess YCl_3 and Y rather than YCl as the reactants, so reaction 2 would actually involve the formation of a solid or liquid double salt between YCl_3 and the product M^ICl. However, this does not appear to alter the foregoing conclusions since the stabilities of these compounds generally increase with increasing size of M, for example, for $M^I_3YCl_6$ with M = Li, Na, and K judging from the melting points. Many other $MCl–YCl_3$ compositions are not even known for M = Li or Na.[34]

Another striking feature of these results is the inherently much lower reducibility of the YCl matrix since only the composition $Li_{0.2}YCl$ is achieved in presumed equilibrium with Y and LiCl (eq 2), while gadolinium readily forms $Li_{0.5}GdCl$ in high yields. It is likely that monohalides of many other lanthanides will also form reduced intercalates, and possibly with other alkali metals as well.

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for the tantalum tubing employed in the gadolinium reduction reactions.

Registry No. YCl, 14530-75-7; Y, 7440-65-5; YCl_3, 10361-92-9; LiCl, 7447-41-8; YBr_3, 13469-98-2; KGd_2Cl_7, 71619-19-7; Li, 7439-93-2; Gd, 7440-54-2; $GdCl_3$, 10138-52-0; YBr, 17655-40-2.

Supplementary Material Available: Observed and calculated structure factor amplitudes for the three structures (3 pages). Ordering information is given on any current masthead page.

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Solvent Dependence of Metal-to-Ligand Charge-Transfer Transitions. Evidence for Initial Electron Localization in MLCT Excited States of 2,2′-Bipyridine Complexes of Ruthenium(II) and Osmium(II)

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Metal-to-ligand charge-transfer (MLCT) absorption bands for the complexes $Ru(bpy)_3^{2+}$, $Os(bpy)_3^{2+}$, $Os(bpy)_2(py)_2^{2+}$, $Os(bpy)_2(CH_3CN)_2^{2+}$, and $Os(bpy)_2(1,2\text{-}(Ph_2P)_2C_6H_4)^{2+}$ (bpy is 2,2′-bipyridine; py is pyridine) are solvent dependent. The dependence can be interpreted with use of dielectric continuum theory but for the D_3 ions $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ only if in the excited state the excited electron is localized on a single ligand rather than delocalized over all three.

Introduction

Although metal-to-ligand charge-transfer (MLCT) excited states of molecules such as $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ (bpy is 2,2′-bipyridine) have found extensive use as redox photosensitizers,[1] a number of questions remain concerning the electronic structures of the excited states. A particularly troublesome one has been that of whether the MLCT excited states are better described as being localized or delocalized (having the promoted electron confined to the π^* orbital over all *three* bpy ligands). An electronic structural model has been presented that assumes that both the absorbing and emitting MLCT states are delocalized,[2] but the available experimental evidence is in disagreement with the predictions of this model.[3-7] In fact, in dealing with the problem of localized vs. delocalized descriptions, there are two different types of excited states to consider that are probed by two different spectroscopic techniques. Optical absorption, which interconverts the thermally equilibrated ground and nonequilibrium excited states, is dominated by transitions to states largely singlet in character. Emission from vibrationally equilibrated excited states to nonequilibrium ground states occurs from states largely triplet in character.[6,7]

For the equilibrated excited states, evidence has accumulated in favor of a localized description. It has been noted that polarization ratio data are inconsistent with excited states having rigorous D_3 symmetry as do the tris chelates $M(bpy)_3^{2+}$ ($M = Fe^{II}, Ru^{II}, Os^{II}$) in their ground states, and it was suggested that this may be due to a static environmental inhomogeneity.[3,6] A more exhaustive study argues that only localized emitting states could account for the observed polarization data.[4] The temperature dependence of the EPR signals and the observation of a broad low-energy absorption band assignable as a bpy → bpy intervalence charge-transfer transition of the related ligand-reduced species $Ru(bpy)_3^{+/0/-}$ have been interpreted as implying that each of the added electrons is localized in the π^* orbital of one of the bpy ligands.[8] Finally, time-resolved resonance Raman spectra of the emitting excited state(s) of $Ru(bpy)_3^{2+}$ have been interpreted as being consistent with the formulation of a localized excited state, i.e., $Ru^{III}(bpy)_2(bpy^{-}\cdot)^{2+}$, on a time scale ranging from a few hundred picoseconds to 10 ns after excitation.[9]

It has previously been argued that in the absence of specific polarization effects, the dipole moment of an excited state can be determined from the solvent dependence of the energy of the electronic absorption band.[10-13] The prediction concerning dipole moment has been verified quantitatively for several system.[13-15] Considering the expense of specialized equipment

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