3082 *Inorg. Chem.* **1981**, *20*, 3082-3086

Contribution from Ames Laboratory—DOE[1] and Department of Chemistry,
Iowa State University, Ames, Iowa 50011

Lanthanum Monochloride and Lanthanum Sesquichloride

RAFAEL E. ARAUJO and JOHN D. CORBETT*

Received December 31, 1980

Synthesis of LaCl from La and $LaCl_3$ in nearly quantitative yield is attained with powdered La (from LaH_x) and 30-day equilibration periods at 745–820 °C provided either the $LaCl_3$ is first fused to provide intimate contact with the excess La or the reactants in stoichiometric proportions are pressed to ~1000 atm within the welded Ta container prior to reaction. Negligible yields are obtained with La sheet. Data from a single-crystal refinement of the LaCl structure (ZrBr type) are reported ($R\bar{3}m$; a = 4.1026 (6) Å, c = 27.597 (6) Å; R = 0.086; 150 independent reflections with $2\theta < 55°$). LaCl decomposes peritectically at 825–826 °C, close to the eutectic temperature of the binary $LaCl_3$–La system. Needles of La_2Cl_3 (Gd_2Cl_3 type) are also formed in incomplete reactions (a = 15.890 (9) Å, b = 4.404 (2) Å, c = 10.231 (9) Å, β = 119.14 (7)°). The La–La distances in these phases are quite large in comparison with those known for analogous yttrium and terbium phases, and the Pauling bond orders per electron pair summed over all independent distances give a similar picture (LaCl 0.49 vs. YCl 0.94). The large distances and reduced bonding in the expanded La–La arrays relative to the metal may arise from a loss of the significant 4f contribution which has been proposed for the pure metal.

Introduction

In 1961 Keneshea and Cubicciotti[2] published a phase diagram for the system $LaCl_3$–La which indicated only a solution interaction between the components occurred and no new solid phases were formed. Thus the metal was found to dissolve in $LaCl_3$ (mp ~859 °C) to the extent of about 9 mol % at the eutectic temperature (826 °C), and beyond this point the composition of the salt-rich liquid phase in equilibrium with the metal increased only slightly, i.e., to ~11 mol % La at the depressed melting point of the metal (914 °C). Only solid La and $LaCl_3$ were present at lower temperatures. However, they also briefly noted that two additional halts were sometimes seen at ca. 763 and 775 °C, the origin of which could not be determined. Conductivity studies on the melt by Dworkin et al.[3] yielded a similar liquidus limit at 910 °C. But 2 years later Smirnov and co-workers[4] reported a very contrasting result, based on EMF and thermal analysis studies, that melts of a composition corresponding to more than 80 mol % $LaCl_2$ (27 mol % La in $LaCl_3$) could be obtained as low as 850 °C, the product disproportionating to $LaCl_3$ and La on cooling. Thereafter, Polyachenok[5] again directly measured the salt-rich liquidus composition (solubility of La in $LaCl_3$) at 950 °C and confirmed the original data of Keneshea and Cubicciotti. Similar phase results have also been reported for analogous systems of the neighboring yttrium and cerium, but the synthesis of Sc_2Cl_3 and of Gd_2Cl_3 with its novel cluster chain structure provided the first indications that unexpected and unusual phases existed among the reduced rare-earth metal halides.[6]

Very recent studies have amply demonstrated that many highly reduced halides may be obtained from the rare earth metal–metal halide systems when proper recognization is given to the very slow rate of formation of the new phases. This means in particular the use of a large ratio of metal-to-trihalide reactants and long reaction periods, reasonable conditions considering (with hindsight) both the complex and extended structures found for these new phases and their very incongruent formation and decomposition processes. Among the chlorides these approaches led first to both the synthesis of the double-metal-layered GdCl and TbCl[7,8] (ZrCl-type structure[9]) and of Tb_2Cl_3[7,10] (Gd_2Cl_3 type) and the independent discovery of discrete and condensed cluster compounds for scandium in, for example, ScCl[11] (ZrBr type[12]), Sc_7Cl_{10},[13] and, later, Sc_7Cl_{12}.[14] The known array of these novel metal-bonded compounds is expanding very rapidly both with further examples of known structures and with new structure types.[15] Of particular interest for the present work are the recent syntheses of YCl, YBr, Y_2Cl_3, and Y_2Br_3.[16] Although LaBr and PrBr have been prepared in 1–20% yield,[8] the $LaCl_3$–La system has appeared to be devoid of new phases. The present study demonstrates that under certain conditions it is possible to prepare not only LaCl in substantially quantitative yield but also La_2Cl_3 and that the lack of earlier success arose from serious kinetic limitations for the formation reactions coupled with the relatively low decomposition temperatures of the reduced phases.

Experimental Section

Materials. Vacuum-line, drybox, and high-temperature techniques utilized were as previously described.[11-14] The lanthanum metal was prepared in the Ames Laboratory and had typical major impurities in ppm atomic: O = 295, N = 30, H = 275, C = 128, F = 146, Cu = 10, Fe = 5, Ce = 2, Sc = 1, and Y = 1.4. Lanthanum turnings were obtained from bulk material with a lathe mounted in a drybox and were stored under vacuum. Strips of metal ca. 2.5 × 1 × 0.012 cm were prepared from a slug of metal jacketed in stainless steel which was successively hot rolled to 50% reduction, cold rolled to 0.8-mm thickness, heat treated, and then rolled to final thickness. The strips were electropolished and stored under vacuum. Cleaning the strips in the drybox with fine emery paper just prior to use appeared to have no effect on their reactivity.

Powdered lanthanum metal was prepared by decomposition of the hydride. The metal was hydrogenated at 550 °C and 1 atm to a composition $LaH_{\sim 2.3}$ which was then ground within the drybox and

---

(1) Operated for the U. S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Energy Research, Office of Basic Energy Sciences, WPAS-KC-02-03.

(2) Keneshea, F. J.; Cubicciotti, D. *J. Chem. Eng. Data* **1961**, *6*, 50.

(3) Dworkin, A. S.; Bronstein, H. R.; Bredig, M. A. *Disc. Faraday Soc.* **1961**, *32*, 188.

(4) Smirnov, M. V.; Usov, P. M.; Khazemova, T. F. *Dokl. Akad. Nauk SSSR* **1963**, *151*, 591.

(5) Polyachenok, O. G. *Russ. J. Inorg. Chem.* **1968**, *13*, 104.

(6) Reviewed by: Corbett, J. D. *Rev. Chim. Miner.* **1973**, *10*, 239.

(7) Simon, A.; Mattausch, Hj.; Holzer, N. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 624.

(8) Mattausch, Hj.; Simon, A.; Holzer, N.; Eger, R. *Z. Anorg. Allg. Chem.* **1980**, *466*, 7.

(9) Adolphson, D. G.; Corbett, J. D. *Inorg. Chem.* **1976**, *15*, 1820.

(10) Simon, A.; Holzer, N.; Mattausch, Hj. *Z. Anorg. Allg. Chem.* **1979**, *456*, 207.

(11) Poeppelmeier, K. R.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 294.

(12) Daake, R. L.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 2029.

(13) Poeppelmeier, K. R.; Corbett, J. D. *Inorg. Chem.* **1977**, *16*, 1109.

(14) Corbett, J. D.; Daake, R. L.; Poeppelmeier, K. R.; Guthrie, D. H. *J. Am. Chem. Soc.* **1978**, *100*, 652.

(15) Berroth, K.; Mattausch, Hj.; Simon, A. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 626.

(16) Mattausch, Hj.; Hendricks, J. B.; Eger, R.; Corbett, J. D.; Simon, A. *Inorg. Chem.* **1980**, *19*, 2128.

0020-1669/81/1320-3082$01.25/0

screened to 100 mesh (<0.15-mm diameter). Thin layers of this were decomposed at 560–600 °C in high vacuum to a final pressure of $<10^{-4}$ torr. The final composition was $\sim LaH_{0.08}$ (α phase). The powder begins to sinter at 650 °C. A coarser powder (~50 mesh) was also made by filing metal strips in the drybox.

The trichloride was prepared as described[11,17] by reaction of electronic-grade HCl (Matheson) (plus H_2) with ~20 g of lanthanum turnings at 800–850 °C. The product material was sublimed several times in high vacuum at 860 °C within a tantalum jacket so as to avoid any possible reaction with the silica vessel. Chunks of the product were sealed under vacuum until use.

Reactions. The reactants La and $LaCl_3$ (0.1–0.5 g) were weighed to ±1 mg within the drybox (~3 ppm H_2O) and placed in 0.63- or 0.95-cm diameter Ta tubes ~4–6 cm in length which had been previously cleaned and then crimped and heliarc welded at one end as described elsewhere.[17] The filled tubes were crimped and similarly welded at the other end under ca. $^2/_3$ atm of He and then sealed into evacuated and flamed-fused silica jackets so as to protect the Ta from oxidation during heating. Temperatures were measured with the aid of a thermocouple located on the exterior of the jacket. More accurate measurements of sample temperature were obtained for the purposes of bracketing the decomposition temperature of LaCl. High vacuum lead-throughs in a silica apparatus allowed thermocouples to be fastened directly to small Ta containers which were maintained under active vacuum.

The reaction containers were usually air quenched after equilibration by removal of the sample and jacket from the furnace, and the products were examined under a low-power microscope in a special drybox. With care, most reaction products were free of the ubiquitous LaOCl both from visual observation and X-ray determination (Guinier technique) unless the temperature had exceeded about 900 °C. Above this temperature region, oxygen impurities are evidently either slowly removed from the Ta or passed through the Ta following degassing of the SiO_2 jacket.

Diffraction Studies. All products were examined by high-resolution Guinier techniques and monochromatized Cu $K\alpha_1$ radiation using samples mounted between pieces of cellophane tape in an evacuable camera, either the Model XDC-700 camera (IRDAB, Stockholm) or the Model FR-552 unit (Enraf-Nonius, Delft, Holland). Lines were measured relative to a high-precision millimeter scale photographically printed on the film. Calibration of the observed diffractions was secured with the use of a quadratic function in position which was fitted to lines of NBS standard Si, a trace of which was included with each sample.

Possible single crystals of products were mounted in thin-walled glass capillaries within the drybox and examined for quality by oscillation photographs. Diffraction data were collected on an automated, four circle diffractometer for a dark blue, pentagonal platelet of LaCl measuring 0.22 × 0.18 × 0.12 mm, the last dimension being parallel to the *c* axis. The crystal gave strong and only slightly broadened maxima with only minor axial streaking so that an ω scan of ±0.75° was sufficient to measure background and the entire peak. The crystal was a very good diffractor and gave reflections at $2\theta > 50°$ with $F_o > 90$. After the *R*-centering condition was verified, a total of 562 integrated intensities were measured for the indicated hexagonal cell over the octants HKL, $\bar{H}KL$, and $\bar{H}K\bar{L}$ in the range $4° < 2\theta < 55°$. An absorption correction was applied based on a ϕ scan of the data crystal at $2\theta = 31.3°$, tuning on the peak every 10° in ϕ. With $\mu = 168.1$ cm^{-1}, the transmission coefficients ranged from 0.54 to 0.98. After this correction, a total of 500 reflections were judged to be observed ($I > 3\sigma(I)$), and these were averaged to 150 independent data ($R = 0.050$ with two reflections with $|F_o - F_A|/F_A > 0.20$ rejected). Lattice constants were determined by least-squares refinement of 14 known reflections, $45° < 2\theta < 55°$, which had been tuned on $\pm\theta$ peaks with the data crystal ($\lambda = 0.71002$ Å).

The diffractometer operation, the programs utilized, and the source of the scattering factors (which included real and imaginary parts of the anomalous dispersion) have been referenced before.[9,18]

Results

LaCl. Several equilibrations of $LaCl_3$ with La metal in the form of thin strips were carried out between 700 and 1000 °C using La:$LaCl_3$ ratios between 2:1 and 9:1 and periods between 42 days at 800 °C and 12 days at 1000 °C. In no case was any new product evident in the Guinier patterns. However, a trace of a dark blue phase was occasionally seen on the metal under the microscope but always in amounts too small for X-ray examination. A clue to a more effective synthesis procedure was provided when a reaction using powdered La suffered an accidental temperature excursion to 1140 °C before it was equilibrated for 30 days at 812 °C. This reaction produced about 5% LaCl as thin, highly reflective, dark blue platelets. Further experiments demonstrated that both an intimate contact between reacting phases and a very high surface area for the metal were necessary for a successful synthesis. Powdered metal prepared from decomposition of LaH_{2+} together with trichloride (5:1 mole ratio) gave ~95% conversion to LaCl after equilibration for ca. 30 days anywhere in the range of 765–820 °C when a short reaction period at ~860 °C was first included in order to melt the $LaCl_3$. The use of metal which had sintered during decomposition of the hydride at 650 °C dropped the yield to a few percent.

Following an observation by Bärnighausen and co-workers,[19] it was found that the same high yield could also be obtained from a *stoichiometric* mixture of powdered metal and $LaCl_3$ if these were first hydraulically pressed within the crimped and welded tantalum tube to ~1000 atm prior to equilibration for 30 days in the range of 745–818 °C. Under these conditions, the Guinier powder patterns of some of the products showed a trace of $LaCl_3$ while others showed only LaCl. A minimum yield of 96–98% is estimated on this basis. The single crystal utilized for the diffraction study came from such a reaction at 818 °C. A 5-day reaction period was found to be sufficient for a 70% yield.

The LaCl product was been obtained in good yield from reactions at as low as 700 °C. The upper limit of its stability was established by a series of isothermal equilibrations of the phase followed by X-ray examination of the product. The peritectic decomposition of LaCl to metal and $LaCl_3$ occurs at 825–826 °C, that is, close to the eutectic in the binary system $LaCl_3$–La.[2] The phase of course reacts readily with moisture to produce hydrogen.

A possibility existed that hydrogen remaining in the metal powder used for the synthesis was retained in the LaCl product in significant amounts, particularly in view of the low metal–metal bond order found (below). Therefore, LaCl was also prepared with the use of 0.3–0.4-mm diameter metal filings which were prepared in the drybox just prior to use together with the compressed container technique described above and a reaction period of 30 days at 748 °C. Though the yield was only about 3%, a sample of single crystals could be picked out for Guinier examination. As shown in Table I, the lattice constants therefrom are negligently different ($<2\sigma$) from those prepared with powdered metal, and hydrogen is concluded to not be a significant component in the phase. The probable high dissociation pressures of any hydrides and ready loss of H_2 from the metal through the tantalum walls at the temperatures used for the equilibration are thought to be important in this negative result.

LaCl Structure. Comparison of intensities in the Guinier patterns obtained for LaCl with those calculated for the ZrCl and ZrBr prototypes[9,12] made it clear that the latter was correct, so that LaCl is structurally analogous to ScCl, YCl, and the high-temperature forms of GdCl and TbCl. Since well-formed crystals of LaCl were found, diffraction data were collected and the structure refined so that precise metal–metal distances could be compared. Least-squares refinement started with the fractional coordinates of ZrBr and proceeded une-

---

(17) Corbett, J. D. *Inorg. Synth.*, in press.

(18) Adolphson, D. G.; Corbett, J. D.; Merryman, D. J. *J. Am. Chem. Soc.* **1976**, *98*, 7234.

(19) Bärnighausen, H., private communication, **1980**.

(20) Ford, J. E.; Corbett, J. D., unpublished research.

Table I. Refined Lattice Constants (Å, Deg) for LaCl,[a] La_2Cl_3,[b] and Related Phases

compd	metal source	no. of lines refined	lattice const a_h	c_h	c/a
LaCl	hydride pwd	12	4.101 (7)	27.592 (7)	6.73
	filed	22	4.100 (1)	27.577 (9)	6.726
	hydride pwd (single crystal)	14	4.1026 (6)	27.596 (6)	6.726
YCl[c]	hydride pwd	12	3.753 (1)	27.528 (4)	7.335
ScCl[d]	*e*	13	3.473 (2)	26.710 (4)	7.691
GdCl[f]	*e*	14	3.8208 (8)	27.477 (6)	7.191

compd	metal source	no. of lines refined	lattice const *a*	*b*	*c*	*β*
La_2Cl_3	hydride pwd	16	15.890 (9)	4.404 (2)	10.231 (9)	119.14 (7)
Y_2Cl_3[g]	*e*		15.144 (3)	3.825 (1)	10.077 (2)	118.22 (3)
Gd_2Cl_3[h]	*e*		15.237 (4)	3.896 (1)	10.179 (3)	117.66 (3)

[a] Space group $R\bar{3}m$, hexagonal cell. [b] Space group $C2/m$. [c] Single-crystal data;[20] the *c* lattice constant is distinctly different from that published earlier[16] (27.318 (9) Å). [d] Reference 11. [e] High purity sheet or pieces. [f] Reference 8. [g] Reference 16. [h] Reference 10.

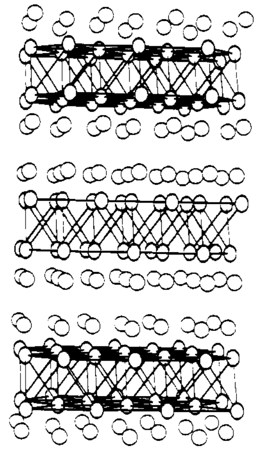


Figure 1. A [110] projection of a portion of the structure of LaCl (ZrBr type) with neighboring lanthanum atoms interconnected (*c* axis vertical). Thermal ellipsoids are at the 90% probability level.

Table II

Atom Parameters in LaCl[a]

	x	*y*	*z*	$B_{11}{}^{b} = B_{22}$	B_{33}
La	0.0	0.0	0.22101 (5)	1.65 (9)	2.62 (10)
Cl	0.0	0.0	0.3843 (3)	2.48 (25)	2.56 (26)

Interatomic Distances (Å) in LaCl

	intralayer	interlayer
La–La	4.1026 (6)	3.823 (2)
Cl–Cl	4.1026 (6)	3.680 (10)
La–Cl		2.911 (3)

Interlayer Angles (Deg) in LaCl

angles defining the antiprismatic coordination of La		angles defining the prismatic coordination of Cl	
La–La–La	64.91 (4)	Cl–Cl–Cl	67.8 (2)
Cl–La–La	101.76 (7)	Cl–Cl–La	85.44 (5)
Cl–La–Cl	89.6 (1)	La–Cl–La	89.6 (1)

[a] Space group $R\bar{3}m$ with $a = 4.1026$ (6) Å, $c = 27.596$ (6) Å, $Z = 6$, $R = 0.086$, and $R_w = 0.109$, for 150 reflections. [b] The thermal parameter expression used is $\exp[-{}^1/_4(B_{11}a^{*2}(h^2 + hk + k^2) + B_{33}l^2c^{*2})]$; $B_{12} = {}^1/_2 B_{11}$; $B_{13} = B_{23} = 0$.

ventfully to $R = 0.095$ and $R_w = 0.148$ (conventional definitions with $w = \sigma_F{}^{-2}$). The reflection data were sorted on F_o and reweighted in 10 groups to more properly assess the significance of the weaker reflections, after which convergence (shift/error < 0.01) was obtained at $R = 0.086$ and $R_w = 0.109$. A difference map calculated at this point contained peaks of 2 e/Å^3 at La positions and was flat to ±1 e/Å^3 elsewhere. The residuals are comparable to those often obtained in these layered structures[8,9] because of intrinsic stacking defects.

The final structural parameters for LaCl together with important distances and angles are given in Table II. Observed and calculated structure factor data are available as supplemental material. A projection of the structure along [110] is shown in Figure 1 with actual thermal ellipsoids at the 90% probability level. The difference between this arrangement (ZrBr type) and that for ZrCl is simply an interchange of the top two, four-layer slabs.

La_2Cl_3. Several incomplete reactions, for example, those using metal filings which had been pressed and equilibrated at 748 or 814 °C for 30 days, also contained bundles of long (~1 mm), black, reflective needles growing from the mixture. Yields were only ~5%. Comparison of the Guinier pattern of selected material with a calculated powder pattern revealed the phase to be La_2Cl_3, isostructural with Gd_2Cl_3 and Y_2Cl_3. The refined lattice constants derived therefrom are also contained in Table I; the 4.404-Å *b* dimension is the repeat distance along the infinite chains. The peritectic decomposition temperature is not known but must be above 814 °C. Additional reduced phases have also been detected in this system and are presently under investigation.

Discussion

The extreme conditions necessary for the synthesis of LaCl and La_2Cl_3 are striking illustrations of what must be pertinent to many other presently undiscovered materials that can be produced only by solid–solid reactions (unless a flux can be utilized). Large excesses of metal in the form of thin sheet or turnings were found to be inadequate for the production of sufficient LaCl for Guinier identification even after reaction periods as long as 30 days at temperatures up to 820 °C. The vapor pressure of $LaCl_3$, 2.4 × 10^{-3} torr at 800 °C,[21] is evidently insufficient to provide the necessary reactivity, and transport reactions appear nonexistent in this system. On the other hand, powdered metal prepared by decomposition of the powdered hydride reduces $LaCl_3$ to LaCl substantially quantitatively after 30 days of equilibration but *only* if this is first brought into intimate contact with the trichloride by either fusion of the salt or the application of ~1000 atm pressure to the sample at room temperature. Solid-state diffusion is

---

(21) Brown, D. "Halides of the Lanthanides and Actinides"; Wiley: New York, 1968; p 155.

presumably the principal means of the reaction.

The necessity of a solid-state reaction in the formation of LaCl is dictated by the fact that it undergoes a very incongruent (peritectic) decomposition to $LaCl_3$(s) or $LaCl_{2.73}$(l) and solid metal at basically the same as the eutectic temperature in the LaCl–La binary system (826 °C). The reduction of $LaCl_3$ activity which occurs in $LaCl_3$–La system on heating above this point may be responsible for the near coincidence of the two temperatures.

Some of the difficulty in preparing LaCl relative to LaBr can now be understood. The melting point of the $LaBr_3$ is 73° below that of $LaCl_3$ and the eutectic with metal 98° lower because of the greater solubility of metal in liquid $LaBr_3$.[22] Thus LaBr may be made in 2 weeks at 747 °C via the more facile reaction of melt with metal foil.[8] Synthesis in 10–20% yield was also accomplished at 667 °C, at which temperature all phases are solid. However, the latter reaction may be aided by the formation of an intermediate phase $LaBr_{2.38}$.[8] No such compound was noted in the chloride system.

The lattice dimensions of LaCl and La_2Cl_3 (Table I) as well as the lanthanum–lanthanum distances found in LaCl are significant in their magnitudes. Between TbCl and LaCl, the two rare-earth metal monochlorides with refined structures, there is an increase in M–M distances both within and between the metal layers of 8.3%, distinctly greater than the 5.3% increase in the distances in the metals themselves[23] (or 5.9% in their single-bond metallic radii[24]). Similarly, the increase in the interlayer M–M distance on progressing from ScCl[11] to YCl to LaCl is in each step close to 9%, and within the layers, 8.1 and 9.4%, respectively, but an increase in the interatomic separation of 9.8% between Sc to Y metals contrasts with only 4.2% from Y to La (10.9 and 4.7%, respectively, for the single-bond metallic radii).

It appears that metal–metal distances in LaBr may be similarly affected. The intralayer distance (*a* dimension), well-known from Guinier data, is quite close to that for LaCl, 4.133 (Br) vs. 4.103 (Cl) Å. The LaBr structure has also been refined but only from powder data, and the more important interlayer distances are not known nearly as precisely. The value computed from the LaBr results,[8] 3.71 Å with an estimated standard deviation of 0.05 Å, is probably not distinguishable from that in the chloride, 3.823 (2) Å. The *a* dimension of LaBr is also noted to be about 0.044 Å larger than expected from an extrapolation of the *a* parameters[8] of the heavier rare-earth metal monobromides (all ZrCl type). The increase in the *a* parameter from YBr[16] to LaBr is also similar to that noted above for the chlorides.

The changes in lattice dimensions between Y_2Cl_3 and La_2Cl_3 (Table I) are substantial and more or less in proportion according to the degree to which each dimension reflects changes in the metal–metal distances. Particularly striking is the 15.1% increase in the *b* lattice constant, the greatest dimension of the distorted metal octahedra which share trans edges to form chains. In none of the above cases can the changes be blamed on metal–metal bonding constraints provided by Cl–Cl repulsions (matrix effects); rather just the opposite pertains, the reduced bonding occurs with the largest M–M and Cl–Cl separations. The problem appears to focus quite clearly on a marked contrast between the La–La distances in the metal and the relatively much longer ones found in the reduced lanthanum chlorides and bromide.

A useful means for comparing the total amount of metal–metal bonding for a collection of different distances and for different metals and compounds has been developed recently[24] in terms of the Pauling[25] bond order per electron pair (PBO/e). The bond order *n* is defined in terms of the empirical equation $D_n = D_1 - 0.60 \log n$, where D_1 is similarly calculated from the known valence of and distances in the pure metal. The bond order sum is carried over all independent distances in compounds, and a PBO/e value of 1.0 corresponds to a degree of bonding per electron pair which is exactly equivalent to that in the metal. Many examples of "good" metal–metal bonding are found to occur in metal-rich halides and chalcogenides of transition groups 3–6 (where $1.0 \geq \mathrm{PBO/e} \geq 0.8$ is defined as "good"). All occur in structures where nonmetal–nonmetal contacts do not limit metal–metal approaches, and vice versa, low PBO/e values are always found when the nonmetal atoms severely restrict the metal–metal bonding, e.g., in most M_6X_{12} clusters. The success of the bond order approach appears to lie in the sensitivity of d bands mainly to nearest-neighbor interactions together with only a moderate dependence of the band on distance. In most of the well-bonded examples in groups 3 and 4, the M–M distances are within ±0.3 Å of those in the pure metals. As a consequence of the foregoing the dimensionality of the metal-bonded array makes little difference, the "good" examples ranging from clusters, chains, and sheets to three-dimensional structures.

Scandium and yttrium have many nearly ideal examples: ScCl, PBO/e = 0.84; Sc_5Cl_8, 1.04; YCl, 0.94; Y_2Cl_3, 0.96. Only TbCl has a somewhat lower value (0.75) for which no explanation is at hand. Still these all stand out with respect to a PBO/e value of only 0.49 for LaCl, this number representing more precisely how disparate the sum of all La–La separations is relative to the metal. It should also be noted that the above bond order comparison already allows for the fact that the average distance in lanthanum metal, and therefore its value of D_1 as well, is ~0.06 Å larger than that obtained by extrapolation of the values for the heavier lanthanides. Similar though smaller deviations also occur for gadolinium and lutetium, and all three have been attributed to the absence of crystal field effects with these spherical configurations.[26] The observation of such a low bond order in LaCl relative to that in the trivalent metal is one of the very few cases in which a matrix effect is clearly not responsible so that a failure of the bond order equation must be assumed.

A plausible source for this difficulty is an additional contribution of a 4f orbital to the conduction band and binding of the lightest rare earths, especially lanthanum. This process has been invoked or suggested several times, in most detail by Gschneidner in terms of the apparent effect of a 4f contribution on both the structure of the rare-earth metals under pressure or with alloying[26] and their melting points and sublimation enthalpies.[27] Both proximity of the 4f levels to the Fermi level and the 4f radial extentions fall off rapidly with increasing atomic number in this region and appear to be relatively small beyond about cerium. The participation of 4f in a largely 5d–6s band in lanthanum metal would be also expected to diminish rapidly with expansion of the metal structure, basically what happens during the formation of the reduced halide phases. Thus the disproportionately long distances in and low bond order observed for the reduced lanthanum chlorides arise from this loss of binding and the fact that the bond order equation contains no reflection of the uncommon and highly distant-dependent 4f contribution.

Acknowledgment. R.E.A. is indebted to the Universidad de Los Andes, Mérida, Venezuela, for the support of a scholarship during this investigation. The authors also

---

[22] Sallach, R. A.; Corbett, J. D. *Inorg. Chem.*, **1963**, *2*, 457.

[23] Pearson, W. B. "The Crystal Chemistry and Physics of Metals and Alloys", Wiley-Interscience: New York, 1972; p 151.

[24] Corbett, J. D. *J. Solid State Chem.* **1981**, *37*, 335.

[25] Pauling L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 400.

[26] Gschneidner, K. A., Jr.; Valletta, R. M. *Acta Metall.* **1968**, *16*, 1968.

[27] Gschneidner, K. A., Jr. *J. Less-Common Metals* **1971**, *25*, 405.

gratefully acknowledge J. E. Ford for assistance in the structure determination, Professor H. Bärnighausen for information on the effects of pressure on rare earth metal–metal iodide reactivity in the solid state, and Professors S. Liu and K. Gschneidner for helpful discussions.

Registry No. LaCl, 17655-42-4; La_2Cl_3, 78392-92-4; La, 7439-91-0; $LaCl_3$, 10099-58-8.

Supplementary Material Available: A listing of structure factor amplitudes for LaCl (1 page). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and the Materials and Molecular Research Division,
Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720

Bis[π-(cyclobutenocyclooctatetraene)]uranium(IV)

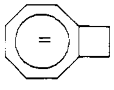
WAYNE D. LUKE, STUART R. BERRYHILL, and ANDREW STREITWIESER, JR.*[1]

Received December 8, 1980

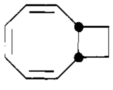
The title compound **3** was prepared by reaction of cyclobutenocyclooctatetraene dianion **1** with UCl_4 and characterized by visible, IR, NMR, and mass spectra. The magnetic susceptibility shows Curie–Weiss dependence to 15 K and is temperature independent between 15 and 4.2 K. Variable-temperature ^1H NMR from −80 to +70 °C as well as chemical trapping experiments show no evidence for opening of the cyclobutene ring to a quinodimethane moiety. The ^1H NMR spectrum is analyzed in terms of pseudocontact and contact contributions. It is shown that $\mu_\perp^2 \neq 0$ and that $\mu_\parallel^2 - \mu_\perp^2 = 12.5\ \mu_B^2$.

Introduction

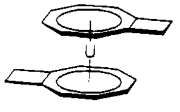
The substituent effects of a wide variety of alkyl and heteroatom substituents on the physical properties of uranocene are well documented.[2-4] We now wish to report the synthesis of the first annulated uranocene and the effects of annulation on the uranocene skeleton. Recently, Staley and co-workers have investigated the preparation of the annulated cyclooctatetraene dianion **1** by dideprotonation of the corresponding *cis*-bicyclooctatriene **2**.[5,6] They showed that treatment of **2** with potassium amide in liquid ammonia leads to **1** in high yield. The availability of **1** prompted us to investigate its use in the synthesis of an annulated uranocene. In this paper we report the conversion of **1** into the first annulated uranocene, dicyclobutenouranocene (**3**).[7]



1



2



3

Synthesis and Physical Properties of Dicyclobutenouranocene. The bicyclooctatriene **2** was prepared as described by Staley and Henry[8] and further purified through its silver nitrate adduct. Attempted deprotonation of **2** with either *n*-butyllithium/TMEDA or lithium diisopropylamide in THF was unsuccessful; however, treatment of **2** with potassium amide in liquid ammonia according to the Staley procedure[9] afforded **1** as a grey-green solid after evaporation of the solvent. Reaction with UCl_4 in THF gave an air-sensitive dark green crystalline solid which was purified by Soxhlet extraction with pentane.

Table I. Infrared Spectrum (cm^{-1}) of Dicyclobutenouranocene (**3**) in Nujol Compared with That of Uranocene

uranocene[a,b]	**3**[a]
1730 (w)	
1262 (s)[c]	1262 (m), 1195 (w), 1165 (w)
1018 (s)[c]	1120 (s), 979 (s), 918 (s)
799 (s)	820 (m), 818 (s), 795 (w), 791 (s), 780 (m)
720 (s)	718 (vs)

[a] Key: w = weak, m = medium, s = strong, vs = very strong. [b] For assignments of the IR bands of uranocene, see: Hocks, L.; Goffart, J.; Duyckaerts, G.; Teyssie, P. *Spectrochim. Acta, Part A* 1974, *30A*, 907. [c] Broad.

Mass spectral analysis showed a molecular ion of 498 and principal fragments of 368 (loss of $C_{10}H_{10}$) and 130 ($C_{10}H_{10}$), confirming the dicyclobutenouranocene (**3**) structure. Furthermore, controlled air oxidation of **3** produced bicyclo[6.2.0]deca-1,3,5,7-tetraene, which was identified by its ^1H NMR spectrum.[10] The visible spectrum of **3** shows the expected bathochromic shift for an alkyl-substituted uranocene with λ_{max} at 623 nm (ε 610). A comparison of the IR spectrum of **3** with that of uranocene is shown in Table I.

At 30 °C the ^1H NMR spectrum of **3** consists of three singlets with line widths of about 35 Hz at δ −27.7, −35.9, and −43.8 ppm (upfield from Me_4Si) and two sharp doublets (J_{H-H} = 9.64 Hz) at −26.75 and 19.65 ppm. From the line widths and the splitting pattern, the three singlets can be assigned to the three ring protons and the two doublets to the methylene protons, indicating that the methylene groups are fixed with the protons distinguishable as a diastereotopic pair with a remarkable shift difference of 46.4 ppm. Although the chemical shifts for the ring protons fall within the region given by various substituted uranocenes, the range from −27.7 to −43.8 ppm is somewhat larger than usual.[11]

---

(1) To whom correspondence should be addressed at the Department of Chemistry.
(2) Streitwieser, A., Jr.; Harmon, C. A. *Inorg. Chem.* **1973**, *12*, 1102.
(3) Harmon, C. A.; Bauer, D. P.; Berryhill, S. R.; Hagiwara, K.; Streitwieser, A., Jr. *Inorg. Chem.* **1977**, *16*, 2143.
(4) Streitwieser, A., Jr.; Burghard, H. P. G.; Morrell, D. G.; Luke, W. D. *Inorg. Chem.* **1980**, *19*, 1863.
(5) (a) Staley, S. W.; Cramer, G. M.; Orvedal, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 7499. (b) Staley, S. W.; Linkowski, G. E.; Heyn, A. S. *Tetrahedron* **1975**, *31*, 1131. (c) Staley, S. W.; Cramer, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 5051.
(6) Compare: (a) Osborn, C. L.; Shields, T. C.; Shoulders, B. A.; Krause, J. T.; Cortez, H. V.; Gardner, P. D. *J. Am. Chem. Soc.* **1965**, *87*, 3158. (b) La Lancette, E. A.; Benson, R. E. *Ibid.* **1965**, *87*, 1941. (c) Staley, S. W.; Linkowski, G. E. *Ibid.* **1976**, *98*, 5010. (d) Staley, S. W.; Linkowski, G. E.; Fox, M. A. *Ibid.* **1978**, *100*, 4818.
(7) By analogy with ferrocene nomenclature, we have named this compound as an annulated derivative of the parent uranocene skeleton.
(8) Staley, S. W.; Henry, T. J. *J. Am. Chem. Soc.* **1970**, *92*, 7612. See also: Cotton, F. A.; Degasello, A. *Ibid.* **1972**, *94*, 2142.
(9) Staley, S. W.; Cramer, G. M.; Orvedal, A. W. *J. Am. Chem. Soc.* **1974**, *96*, 7433.
(10) Elix, J. A.; Sargent, M. V.; Sondheimer, F. *J. Am. Chem. Soc.* **1967**, *89*, 180.