$[CoL_6][CdBr_4]$. X-Ray powder patterns (data presented in Table I) for CoL_3Br_2 and for $[CoL_6][CdBr_4]$ were found to be almost identical in both peak position and intensity, and the compounds thus appear to be isomorphous; the CoL_3X_2 compounds, therefore, contain both tetrahedral and octahedral cobalt(II) complexes.

TABLE I

X-RAY POWDER PATTERNS[a]

$[CoL_6][CdBr_4]$ d, Å.	I	CoL_3Br_2 d, Å.	I
14.243	m	14.243	m
8.665	w	8.665	w
7.431	s	7.493	s
6.857	vs	6.857	vs
6.320	w	6.276	w
6.021	m	5.981	m
5.862	m	5.862	m
5.273	w	5.273	w
4.818	s	4.818	s
4.149	m	4.149	m
4.055	s	4.037	s
3.966	s	3.948	m
3.218	w	3.206	w
3.162	m	3.129	m
3.066	s	3.046	m

[a] The symbols used to designate intensities are: s, strong; m, medium; w, weak; and v, very.

A similar structure was recently assigned to the cobalt(II) halide complex of the chelate ligand, bis(diisopropoxyphosphinyl)methane, on the basis of its spectrum.[6]

Attempts were made to obtain the spectrum of $[CoL_6][CdBr_4]$ as a mull, but due to the low extinction coefficients of octahedral bands and the background noise encountered with the mull technique, very poor results were obtained. Attempts were also made to obtain the spectrum of this compound in dimethylformamide and in acetonitrile; in both solvents, the compound gave deep blue solutions and the spectra were identical, with respect to absorption positions, with the spectra of CoL_3Br_2 in the same solvents; molar extinction coefficients were much lower than those of CoL_3Br_2.

These spectral results indicate that the solution measurements previously reported, such as conductivity and molecular weight, are not directly related to the species present in the solid since reaction apparently occurs on dissolving. These results also raise the question as to what species are present in solution. In an attempt to answer this, we dissolved cobalt(II) bromide in dimethylformamide and observed the spectrum as the concentration of pyridine N-oxide was increased; no appreciable change in any visible band was noted although the tail of an ultraviolet band did increase in intensity. The only explanations are that: (1) there is no coordination by pyridine N-oxide in these solutions, or (2) pyridine N-oxide and dimethylformamide have identical ligand field parameters.

Studies of the octahedral nickel(II) complexes of these two ligands[7,8] support the latter explanation; the fact that the spectrum of the pyridine N-oxide complex of nickel(II) was obtained in dimethylformamide does not rule out the possibility of solvent exchange. The spectrum of the same complex in acetonitrile[9] is similar to, though not identical with, the spectrum in dimethylformamide.

Although we cannot identify the species present, the solution spectra of CoL_3X_2 and $[CoL_6][CdBr_4]$ indicate that the cobalt(II) is present predominantly as tetrahedral species in solution.

Experimental

Tris(pyridine N-oxide)cobalt(II) Halides.—The bromide and chloride were prepared by methods in the literature.[1,2]

Anal. Calcd. for $Co(C_5H_5NO)_3Cl_2$: C, 43.39; H, 3.64. Found: C, 43.45; H, 3.89. Calcd. for $Co(C_5H_5NO)_3Br_2$: C, 35.74; H, 3.00. Found: C, 35.98; H, 3.08.

Hexakis(pyridine N-oxide)cobalt(II) Tetrabromocadmiate.—A hot ethanol solution of anhydrous $CoBr_2$, anhydrous $CdBr_2$, and pyridine N-oxide, in mole ratios of 1:1:6, was prepared and allowed to cool. The blue solution yielded an orange-red solid on standing; the solid was filtered, washed, and dried.

Anal. Calcd. for $[Co(C_5H_5NO)_6][CdBr_4]$: C, 33.94; H, 2.85; Co, 5.55. Found: C, 33.88; H, 2.95; Co, 5.50.

Spectral Measurements.—All spectral measurements were made using a Bausch and Lomb Spectronic 505. Solid spectra were obtained by the mull technique, using hexachlorobutadiene as mulling liquid.

X-Ray Powder Patterns.—X-Ray powder patterns were obtained with a Phillips diffractometer, using Cu Kα radiation. Several packings were run, and some preferred orientation was observed. The results are presented in Table I.

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Ternary Perovskite Phases in Systems of Lithium Hydride with Barium, Strontium, and Calcium Hydrides

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As part of a series of studies on lithium hydride phase equilibria, these systems have been investigated by X-ray powder crystallography. No previous work has been reported on the systems lithium hydride–barium hydride and lithium hydride–strontium hydride.

Thermal analysis of the system lithium hydride–calcium hydride showed simple eutectic behavior at the melting point.[1]

In the closely analogous fluoride systems, the compound $LiBaF_3$, of cubic inverse perovskite structure, has been reported, with lattice constant values of 3.988[2] and 3.995 Å.[3] Roy[3] attempted the preparation of the corresponding strontium and calcium compounds without success. $LiBaF_3$ has also been reported as an incongruently melting compound in the system LiF–BaF_2,[4] while the systems LiF–SrF_2[5] and LiF–CaF_2[6] seem to show simple eutectic behavior.

Experimental

The lithium metal was obtained from the Foote Mineral Company, with a stated purity of 99.98%. The barium and strontium metals were Dominion Magnesium, Ltd., 99+% grade, with other alkaline earths as major impurities. The calcium metal was Dominion Magnesium, Ltd., 99.9% Ca.

All manipulations of metals were carried out in an argon drybox. The hydride samples were prepared by treating weighed mixtures of the metals, in stainless steel boats in a stainless steel bomb, with catalytically purified hydrogen. After maximum uptake of hydrogen at 700–750° and 1 atm. pressure for 20–30 min., the samples were held for 2–3 hr. at 500–600° before cooling. The amounts of hydrogen reacted were determined by *PVT* measurements.

Each original preparation was ground in an agate mortar in the drybox. A small sample (the A sample) was taken for X-ray crystallography, and the rest was returned to the hydriding system for a second thermal cycle (simulating the times and temperatures in the hydriding) under 1 atm. of hydrogen. The principal X-ray sample (the B sample) was then taken. In the case of Ba sample I, a third thermal cycle was run.

Lithium–barium mixture I (see Table I) began to absorb hydrogen on heating at 200°. Mixture II took up 59% of its total hydrogen overnight at room temperature. After hydriding, both preparations took on the gross shapes of the original barium lumps. The preparations were gray to yellow before grinding, and nearly white after.

The lithium–strontium mixtures began reacting at 250–300°, and the hydrided preparations appeared partially or completely fused. They were chocolate-brown before grinding, and tan-yellow after.

The X-ray powder diffraction patterns were taken in part with a General Electric XRD-4 unit and 143.2-mm. camera, and in part (Sr sample II) with a Norelco X-ray diffractometer, Type 12045, and 114.6-mm. camera. Cu Kα radiation, 0.3–0.5-mm. glass capillaries, and 2–4 hr. exposure times were used. Intensities were estimated visually. The lattice constants of the perovskite phases were determined by extrapolation, using the Nelson–Riley function,[7] after correction for film shrinkage. In a few cases the variation of lattice constants with angle was so small that the arithmetic average of the last eight to ten reflections could be used.

Results

In each of the powder patterns except that of the LiH–CaH_2 mixture, a series of 21–27 sharp, well-defined lines was found, which could be indexed on the basis of a primitive cubic unit cell of Ba or Sr. These, by analogy with $LiBaF_3$, were interpreted in terms of inverse perovskite lattices of $LiBaH_3$ and $LiSrH_3$. Neutron diffraction studies would of course be required to establish the positions of the lithium and hydrogen atoms and define the structures.

BaH_2, SrH_2, and CaH_2 were identified in certain samples by comparison with the published patterns of Zintl and Harder.[8] BaH_2 or SrH_2 was present in the final samples, after final heat treatment, only when the atomic ratio Ba/Li or Sr/Li was greater than unity.

The crystallographic constants of the perovskite phases were: $LiBaH_3$ $a_0 = 4.023 \pm 0.001$ Å., $\rho = 3.756$ g. cm.$^{-3}$; $LiSrH_3$ $a_0 = 3.833 \pm 0.001$ Å., $\rho = 2.877$ g. cm.$^{-3}$. Within these limits, the lattice constants were independent of Ba/Li or Sr/Li ratio and also independent of the number of heat treatment cycles.

Table I gives the compositions and crystallographic results for the individual samples. In all cases except possibly Sr sample II the cubic phase was the major phase present. The amount of MH_2 is based upon the visually estimated intensities of the strongest MH_2 lines.

TABLE I

COMPOSITIONS AND CRYSTALLOGRAPHIC RESULTS

Metal	Sample[a]	Mole % M in orig. M–Li	H_2 absorbed, % of theor.	Amt. MH_2, visual est.	Lattice constant $LiMH_3$ a_0, Å.
Ba	IA	43.0	95.0	None	4.0230 ± 0.0005
Ba	IB	43.0	95.0	Moderate	4.023 ± 0.001
Ba	IC	43.0	95.0	None	4.0232 ± 0.0005
Ba	IIA	55.2	93.6	Moderate	4.023 ± 0.001
Ba	IIB	55.2	93.6	Slight	4.0230 ± 0.0005
Sr	IA	38.6	95.9	Slight	3.833 ± 0.001
Sr	IB	38.6	95.9	None	3.8325 ± 0.0005
Sr	IIA	55.4	81.4	Considerable	3.8330 ± 0.0005
Sr	IIB	55.4	81.4	Considerable	3.834 ± 0.001
Sr	IIIA	52.1	96.1	Moderate	3.833 ± 0.001
Sr	IIIB	52.1	96.1	Slight	3.834 ± 0.001
Ca	I	46.4	Not detd.	Large	No perovskite

[a] Roman numerals denote separate preparations. A, B, and C denote increasing numbers of heat treatment cycles.

Two unexplained anomalies were noted in the preparations. First, barium hydride was found after the second heat treatment of Ba sample I, when it was not present in the original preparation. It was eliminated by a third overnight heat treatment. Second, Sr sample II absorbed only 81.8% of the theoretical hydrogen.

No nonhydride lines were found in the barium samples or in Sr sample I. In the Ca sample, CaO lines, and two of the strongest LiH lines, were found.

In the Sr samples II and III and the Ca preparation certain other lines were found, which were all weak to very, very weak in intensity, and which could not be attributed to any impurity ordinarily to be expected.

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The Sr preparations contained six such lines; the Ca preparation eight. The *d*-spacings of four of the Sr lines agreed very roughly with the *d*-spacings of certain stronger lines common to γ-Sr[9] and to both tetragonal and hexagonal "Sr_8Li."[9] The Ca lines agreed very roughly with certain of the stronger lines of Laves-phase $CaLi_2$.[10] Hence, it is possible that these lines were due to small amounts of α-phase slightly hydrided metal.

The interionic distances in the perovskite phases have been calculated and are given in Table II along with the distances in related binary hydrides and fluorides.

TABLE II

INTERIONIC DISTANCES IN HYDRIDE AND FLUORIDE PHASES

X = H or F; M = Ca, Sr, or Ba

	d_{Li-H}, Å.	d_{M-H}, Å.	d_{Li-F}, Å.	d_{M-F}, Å.
LiX	2.04^a	...	2.01^f	...
CaX_2	...	$2.32^{b,c}$	...	2.36^h
SrX_2	...	$2.49^{c,d}$	...	2.51^h
$LiSrX_3$	1.92	2.71	...	...
BaX_2	...	$2.67^{c,e}$	...	2.69^h
$LiBaX_3$	2.01	2.84	2.00^g	2.82^g

[a] E. Staritzsky and D. J. Walker, *Anal. Chem.*, **28**, 1055 (1956). [b] J. Bergsma and B. O. Loopstra, *Acta Cryst.*, **15**, 92 (1962). [c] The distance given is that of the seven nearest H^- neighbors of a Ca^{+2} in the proposed structure.[b] [d] Assuming the H^- parameters to be the same as in CaH_2[b] and the lattice constant ratio of 1.074 ± 0.002 for SrH_2 to CaH_2[8] to hold for interatomic distances within the cell as well as for a_0, b_0, and c_0. [e] With similar assumptions; ratio 1.150 ± 0.008 for BaH_2 to CaH_2. [f] H. E. Swanson and E. Tatge, "Standard X-Ray Diffraction Patterns," National Bureau of Standards Circular 539, Vol. 1, U. S. Government Printing Office, Washington, D. C., 1953, p. 92. [g] Reference 2. [h] R. G. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, New York, N. Y., 1948, Chapter IV, Table p. 14c.

The M–H distances are considerably higher in the perovskites than in the binary hydrides. This is probably the effect of the change in coordination number of H^- around M^{+2} from 7 in MH_2 to 12 in $LiMH_3$. This same effect is noted in the corresponding fluorides.

The Li–H distance in $LiBaH_3$ is close to that in LiH, but is considerably shorter in $LiSrH_3$. The Li–F distance is "normal" in $LiBaF_3$. This shortened distance in $LiSrH_3$, and the fact that $LiSrF_3$ could not be readily prepared,[3] may be attributed to the high polarizability of H^- relative to F^-. The rigid fluoride ions cannot adapt to the shortened distance requirements with strontium in this lattice; the deformable hydride ions can.

The uniformity of the lattice constant values of $LiBaH_3$ and $LiSrH_3$ suggests that departures from stoichiometry in these phases cannot be very large, at least not at room temperature.

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Boron-Nitrogen Compounds. XV.[1,2] Preparation of Vinylated Aminoboranes

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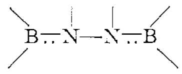
Recent investigations have demonstrated that hindered rotation about the B–N linkage of an aminoborane, $R_2N–BR_2'$, is possible and appears to result from the participation of the free electron pair of the nitrogen in the B–N bond.[3] This behavior substantiates the analogy drawn between aminoboranes and their corresponding olefins as postulated by Wiberg.[4] On the other hand, considerable differences in the chemical behavior of both types of compounds have been observed; therefore an interpretation of physicochemical data has to be treated with extreme caution as has recently been illustrated by a detailed investigation of (methylphenylamino)methylphenylborane.[5] New interesting results contributing to the understanding of the boron–nitrogen bond should be realized through a study of (formal) inorganic dienic structures. Of the pure B–N combination, three structures can be formulated involving conjugated B–N π-bonding in addition to a normal covalent bond (I–III). Likewise two semi-inorganic structures illustrate a conjugation of formal bonds with B–N π-bonding (IV and V).



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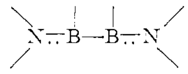

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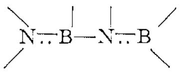

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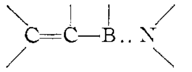

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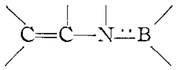

V

Compounds containing the basic grouping as illustrated in structures I and II have recently been synthesized.[6,7] The route for the preparation of type III has recently been described[8] and the preparation of some B-vinylated boron–nitrogen compounds has been reported.[1,9] In the present paper, the syntheses of some representative compounds of types IV and V are described.

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