Solvent and Cation Dependence of the Tetrahydroborate, BH_4^-, Raman Spectrum

A. E. Shirk and D. F. Shriver*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

Received January 27, 1973

Abstract: Raman spectral data were collected in the B–H stretching region of tetrahydroborate in a variety of solvents: $LiBH_4$ and $NaBH_4$ in pyridine, H_2O ($NaBH_4$ only), isopropyl alcohol, 1,2-dimethoxyethane (glyme), and bis(2-methoxyethyl) ether (diglyme). The $LiBH_4$ spectrum was observed for tetrahydrofuran (THF) and diethyl ether (Et_2O) solutions. Spectra for the $LiBH_4$–Et_2O system, which are unique, indicate strong Li–BH_4 interaction through hydride bridges. The other systems appear to involve weaker cation–anion interaction. For $LiBH_4$ in diglyme the presence of two types of species is demonstrated by the temperature dependence of the Raman spectrum. Data in aqueous solution gave no striking evidence for H···H hydrogen bonding. All of the fundamentals for BH_4^- and BD_4^- in aqueous media are presented, along with the corresponding force constants.

Based on the variation of rate for BH_4^- reductions of organic compounds as a function of solvent and cation, Brown and coworkers have suggested that the degree of cation–anion interaction is chemically quite important.[1] In the present work we explore whether or not such cation–anion interactions are manifested in the BH_4^- Raman spectrum. This study is part of a general vibrational spectroscopic investigation of group III tetrahydride anions, BH_4^-, AlH_4^-, and GaH_4^-, in solution.[2]

Assignments for the tetrahedral BH_4^- anion are available from comprehensive Raman studies of isotopically substituted tetrahydroborates in liquid ammonia solution, by Emery and Taylor. Their vibrational frequencies are generally considered to be representative of free BH_4^-, since the vibrations are not appreciably cation dependent.[3] Emery and Taylor did note a 25 cm^{-1} change in ν_1 of tetrahydroborate between the solvents liquid ammonia and water, and Volkov, *et al.*, reported some infrared results for other solvents.[4] However, there has been no comprehensive vibrational study on the nature of BH_4^- salts in solution.

Results and Discussion

Solvent and Cation Dependence. The Raman spectra of the lithium and sodium tetrahydroborate solutions are, in general, complex in the region of B–H stretching vibrations (*ca.* 2300 cm^{-1}) owing to numerous overtone and combination bands of the deformation vibrations of BH_4^-. In addition weak solvent bands are usually present in this region and more intense solvent bands mask the deformation region (1050–1250 cm^{-1}). Therefore the intense, totally symmetric stretching frequencies were employed for comparison of solvent and cation effects. Our parallel work on $MAlH_4$ salts indicated that these totally symmetric modes should be highly sensitive to environment.[2] The stretching frequencies, which are listed in Table I, vary with changes in both solvent and cation. All of the ν_1 frequencies are within the region 2280–2307 cm^{-1} except for those of the liquid ammonia and diethyl ether solutions.

Table I. Tetrahydroborate Vibrations in the Region of B–H Stretch in Various Solvents

Cation	Solvent	Concn, M	Frequency, cm^{-1}
Li[a]	NH_3	2–4	2265
Na[a]	NH_3	2–4	2264
Li	Pyridine	0.2	2298
Na	Pyridine	0.3	2282
Li	H_2O–NaOH		Reacts
Na	H_2O–NaOH	0.8	2294
Li	Isopropyl alcohol	0.2	2297, 2286
Na	Isopropyl alcohol	0.2	2294, 2282
Li	Diglyme	0.3	2307 (2248)[b]
Na	Diglyme	0.3	2287
Li	Glyme	1.2	2304 (2207)[c]
Na	Glyme	0.2	2292 (2206)[c]
Li	THF	0.8	2305 (2217)[c]
Na	THF		Practically insoluble
Li	Et_2O	0.4	2367, 2247
Na	Et_2O		Insoluble

[a] Reference 3; frequencies are for $^{11}BH_4^-$. [b] Present at lower temperatures. [c] Polarized band of medium intensity which appears to sharpen at lower temperatures.

From the association studies reported to date, it appears that the MBH_4 salts are rarely completely dissociated into discrete cations and anions in solution. $NaBH_4$ in liquid ammonia solution is reported to be an ion pair from vapor pressure depression studies[5] and $LiBH_4$ is a dimer (ion quadruplet) in diethyl ether solution.[6] Conductivity data on $LiBH_4$ show dissociation into ions to be negligible in diethyl ether and tetrahydrofuran solutions (equivalent conductivity $<10^{-4}$ ohm^{-1} cm^{-1}).[6]

Among the various spectra, those of $LiBH_4$ in diethyl ether (Table II) are unique. Two intense, polarized, and widely separated B–H stretching frequencies are observed at 2247 and 2367 cm^{-1}. This spectrum is somewhat reminiscent of covalent borohydrides, where the high-frequency terminal ν_{BH} is well-separated from the low-frequency bridging ν_{BH}. The possibility that these two features arise from different species in solution seems remote in view of the lack of appreciable

---

(1) H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 77, 6209 (1955); H. C. Brown and K. Ichikawa, *ibid.*, **83**, 4372 (1961).

(2) A. E. Shirk and D. F. Shriver, *ibid.*, **95**, 5904 (1973).

(3) A. R. Emery and R. C. Taylor, *J. Chem. Phys.*, **28**, 1029 (1958).

(4) V. V. Volkov, E. V. Sobolev, Z. A. Grankina, and I. S. Kalinina, *Russ. J. Inorg. Chem.*, **13**, 343 (1968).

(5) R. W. Parry, G. Kodama, and D. R. Schultz, *J. Amer. Chem. Soc.*, **80**, 24 (1958).

(6) H. Nöth, *Angew. Chem.*, 73, 371 (1961).

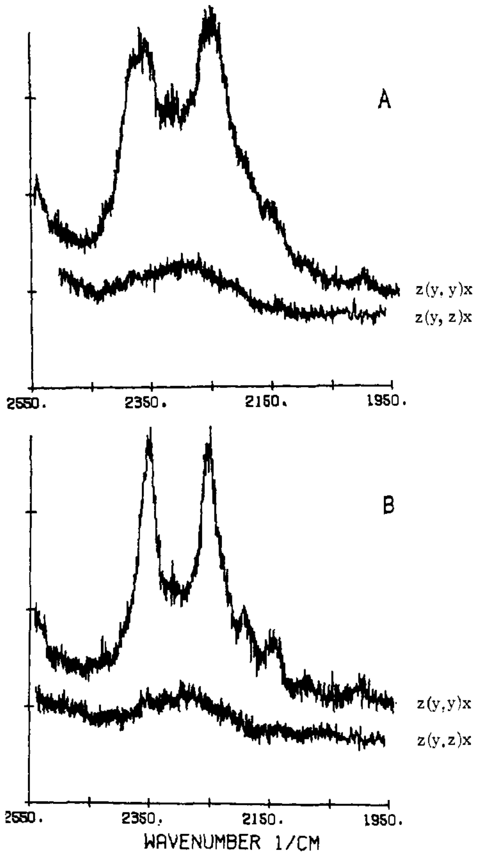


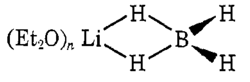
Figure 1. Raman spectra of the B-H stretch region of 0.6 *M* $LiBH_4$ in Et_2O, $z(y,y)x$ and $z(y,z)x$ orientations: (A) 24°, (B) −60°.

Table II. Infrared and Raman Data for $LiBH_4$ in Diethyl Ether Solution (in cm^{-1})[a]

Infrared[b] *ca.* 18°	Raman 24°	Raman −60°
	2144 w	2148 w
2227 sh, m (2225 sh)		2220 w
	2247 s, p	2258 s, p
2271 s (2270 s)		
2311 sh	2311 w	2310 w
2349 m (2350 sh)		
2373 m	2367 s, p	2360 s, p

[a] Key: s = strong, m = medium, w = weak, sh = shoulder, p = polarized, dp = depolarized. [b] Values in parentheses from ref 4.

change in relative intensity with cooling (Figure 1) or with concentration (0.25–0.4 *M* for the ir and 0.4–0.6 for Raman). Since the rest of the spectrum is not available a variety of structural possibilities can be entertained including a double hydrogen bridged species I which might undergo further weak association



I

into aggregates. Because the rest of the spectrum is obscured by solvent bands, it is not possible to critically examine this and/or other Li–BH_4 bonding modes such as single or triple hydride bridges.

The Raman spectrum of $LiBH_4$ in diglyme contains two polarized bands in the range usually associated with ionic tetrahydroborates, 2306 and 2248 cm^{-1}. Apparently these represent two generally different species as the 2248-cm^{-1} feature gains in relative intensity at lower temperatures (Figure 2). Two polarized bands also are observed in the $LiBH_4$–THF, $LiBH_4$–glyme, and $NaBH_4$–glyme systems. The lack of clear-cut temperature dependence in these latter spectra makes it impossible to be sure that two general species are present in each of these solutions; however, this interpretation does seem reasonable. The second feature observed in these systems does not appear to be a Fermi doublet.

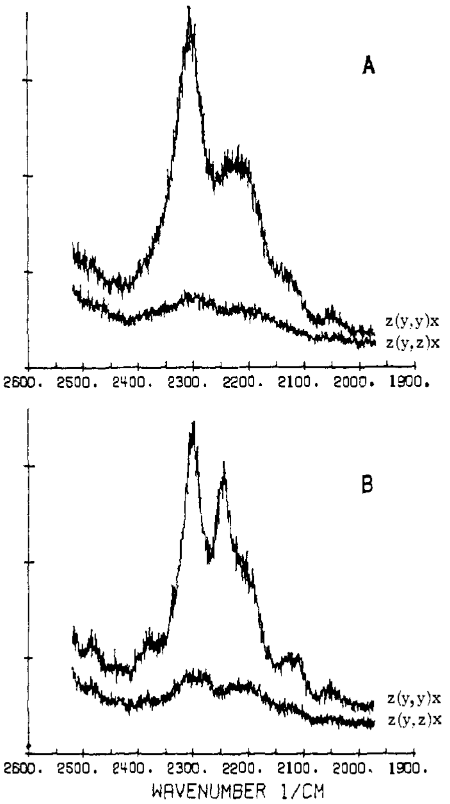


Figure 2. Raman spectra of the B–H stretch region of 0.3 *M* $LiBH_4$ in diglyme, $z(y,y)x$ and $z(y,z)x$ orientations: (A) 23°, (B) −60°.

Because of the lack of solvent interference, all of the tetrahydroborate fundamentals were observed for $NaBH_4$ in NaOH–H_2O and $NaBD_4$ in NaOD–D_2O, Table III.

The possibility of a hydrogen bond between the hydrogen atoms of different molecules has been mentioned in the literature.[7,8] By comparison with the systems previously studied, one might expect particularly strong H···H hydrogen bonds between BH_4^- and H_2O. From the similarity between the aqueous and nonaqueous BH_4^- spectra (excluding of course diethyl ether solutions) we conclude that if this type of hydrogen bonding does exist, it does not have large effect on ν_1 (BH_4^-).

Assignments and Vibrational Analysis. The symmetric stretch $\nu_1(A_1)$ is assigned to the intense and polarized band in the Raman spectrum in the region of B–H (B–D) stretch at 2294 cm^{-1} (1585), see Figure 3.

---

(7) E. R. Alton, R. D. Brown, J. C. Carter, and R. C. Taylor, *J. Amer. Chem. Soc.*, **81**, 3550 (1959).

(8) M. P. Brown, R. W. Heseltine, P. A. Smith, and P. J. Walker, *J. Chem. Soc. A*, 410 (1970).

Table III. Raman and Infrared[a] Frequencies (in cm^{-1}) and Assignments of $NaBH_4$ and $NaBD_4$ in Solution

Assignment	Basic aqueous solution BH_4^- [b]	Basic aqueous solution BD_4^-	Ammonia solution[c] BH_4^-	Ammonia solution[c] BD_4^-
Impurity, prob CO_3^{2-} or BO_3^{3-}	1066 w			
ν_4	1097 w	842 vw (843 w)	1080	823
ν_2	1246 w	890 w	1210	855
Solvent	1641 m	1212 m		
$2\nu_4(A_1)$?	2146 mw, p	1694 m, p	2146	1668
$2\nu_4$(E or F_2) ?	2196 w, dp (2200 sh)	1675 w, dp (1666 sh)		1636
ν_3	2266 w, dp (2272 s)	1723 w, dp (1721 s)	2244	1696
ν_1	2294 s, p	1585 vs, p	2264	1570
$\nu_2 + \nu_4$	2340 w, sh, dp			
$2\nu_2$	2460 w, p		2398	
Solvent	3200–3700 vvs	2200–2800 vvs		

[a] Infrared data in parentheses. [b] Infrared data from ref 4. [c] Raman data and assignments from ref 3.

Table IV. Observed and Calculated Frequencies for the Fundamental Vibrations of $NaBH_4$ and $NaBD_4$ in Basic Aqueous Solution (in cm^{-1})[a]

Fundamental	BH_4^- Obsd	BH_4^- Calcd	BD_4^- Obsd	BD_4^- Calcd
$\nu_1(A_1)$	2294	2275.7	1585	1609.8
	(2244)	2254.1	(1609)	1594.5
$\nu_2(E)$	1246	1251.1	890	885.0
$\nu_3(F_2)$	2266	2271.4	1722	1714.8
$\nu_4(F_2)$	1097	1107.9	842	826.7
Average error:	A_1 Class, 21.5 cm^{-1} or 1.18%			
	12.3 0.68%			
	E Class 5.0 cm^{-1} or 0.48%			
	F_2 Class 9.7 cm^{-1} or 0.86%			

[a] Second set of data for the A_1 class calculated from ν_1 frequencies corrected for Fermi resonance.

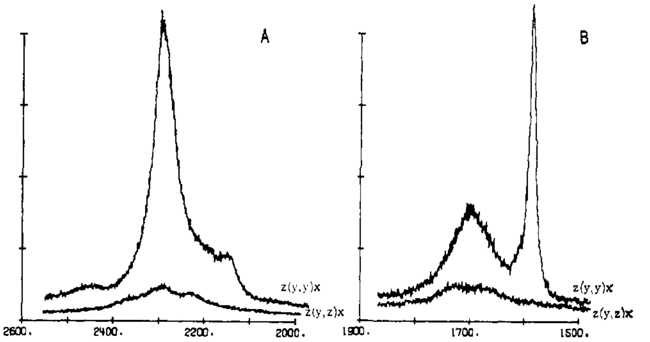


Figure 3. Raman spectra of (A) B–H stretch region of 0.8 *M* $NaBH_4$ in NaOH–H_2O and (B) B–D stretch region of 0.8 *M* $NaBD_4$ in NaOD–D_2O, $z(y,y)x$ and $z(y,z)x$ orientations.

The symmetric deformation $\nu_2(E)$ is assigned as the 1246-cm^{-1} (890) band in the deformation region of the Raman spectrum. Both values for ν_2 fall slightly higher than that observed in liquid ammonia solution,[3] at 1210 cm^{-1} (855); this trend holds for the frequencies of all the fundamental vibrations. The asymmetric stretch $\nu_3(F_2)$ is assigned to the strong 2272-cm^{-1} feature in the infrared spectrum and the corresponding depolarized and weak band in the Raman spectrum at 2266 cm^{-1} (1723 cm^{-1} in the Raman for BD_4^-, 1721 cm^{-1} in the infrared). The asymmetric deformation $\nu_4(F_2)$ is assigned to the band at 1097 cm^{-1} in the Raman spectrum. The ν_4 of BD_4^- is assigned to the weak 842-cm^{-1} band in the Raman and 843 cm^{-1} in the infrared. Assignment of the overtone and combination bands was straightforward except for the 2146-cm^{-1} and the 1694-cm^{-1} polarized features in the Raman spectra of BH_4^- and BD_4^-, respectively. These are attributed to the A_1 components of $2\nu_4$ which are in Fermi resonance with their respective $\nu_1(A_1)$ vibrations. The unaffected E or F_2 components of $2\nu_4$ are assigned to the features at 2196 (BH_4^-) and 1675 cm^{-1} (BD_4^-). The presence of two components for $2\nu_4$ facilitates the correction of ν_1 for Fermi resonance. Assuming the shift of ν_1 to be equal to the magnitude of the shift ($2\nu_4(A_1)$ − $2\nu_4$(E or F_2)), the corrected ν_1 values are 2244 for BH_4^- and 1609 cm^{-1} for BD_4^-. Fermi resonance of this type has been observed previously in the Raman spectra of other tetrahydroborates.[3,9,10]

Table V. Force Constants (mdyn/Å) and F_2 Potential Energy Distribution for BH_4^- and BD_4^-

Symmetry force constant	Aqueous solution	NH_3 solution[a]
F_{11}	3.073 (3.015)[b]	3.051
F_{22}	0.310	0.290
F_{33}	2.666	2.674
F_{44}	0.308	0.290
F_{34}	0.068	−0.015

Valence force constant	Aqueous solution	NH_3 solution[a]
f_r	2.768 (2.753)[b]	2.768
f_{rr}	0.102 (0.087)[b]	0.094
$r^2 (f_\alpha - f_{\alpha\alpha})$	0.309	0.290
$r^2 (f_\alpha - f_{\alpha\alpha'})$	0.308	0.291
$r (f_{r\alpha'} - f_{r\alpha})$	0.048	−0.011

	BH_4^- V_{33}	BH_4^- V_{44}	BH_4^- V_{34}	BD_4^- V_{33}	BD_4^- V_{44}	BD_4^- V_{34}
ν_3	0.968	0.014	0.018	0.934	0.038	0.028
ν_4	0.038	0.991	−0.029	0.071	0.968	−0.039

[a] Data from ref 3. [b] Value from calculation using ν_1 corrected for Fermi resonance.

Using the above assignments, observed and (calculated) frequency ratios from the Teller–Redlich product rule are A_1, 1.447 (1.414); E, 1.40 (1.414); and F_2, 1.71 (1.76). Only the observed value for the A_1 block is unreasonable but an acceptable value, 1.395, is obtained from the corrected ν_1 values mentioned above.

(9) K. B. Harvey and N. R. McQuaker, *Can. J. Chem.*, **49**, 3272 (1971).

(10) J. W. Nibler, D. F. Shriver, and T. H. Cook, *J. Chem. Phys.*, **54**, 5257 (1971).

Vibrational analysis of the tetrahydroborate and tetradeuterioborate anions, using the data from aqueous solutions, were carried out by the methods outlined in the accompanying paper.[2] The B–H bond length adopted for these calculations, 1.255 Å, has been determined by broad-line nmr.[11] The results, which are summarized in Tables IV and V, show close agreement with those obtained for BH$_4^-$ in liquid ammonia. Apparently either set of force constants may be taken as a reasonable representation of the BH$_4^-$ anion.

Experimental Section

The sensitivity of the compounds to air and moisture required that all manipulations be done in an inert atmosphere of dry N$_2$, in a drybox, Schlenk line, or in a chemical vacuum line. Most of the sampling and spectroscopic techniques have been described in the accompanying paper,[2] but where differences exist the procedure is given below.

LiBH$_4$ (Alfa Inorganics and ROC/RIC, 99% D) was used without further purification. Diethyl ether (Allied Chemical, anhydrous), tetrahydrofuran (Matheson Coleman and Bell and Fisher Scientific), 1,2-dimethoxyethane (Mallinckrodt) and bis(2-methoxyethyl) ether (Aldrich) were dried and distilled from LiAlH$_4$ or benzophenone ketyl and stored over LiH or Na metal. Pyridine (Baker) was dried and distilled from CaH$_2$ and isopropyl alcohol (Matheson Coleman and Bell) was similarly purified from Mg metal. D$_2$O (Bio-Rad) and deionized H$_2$O were used for the aqueous samples for Raman and infrared work; aqueous NaOD solutions were made by dissolving Na metal into D$_2$O. Infrared spectra of aqueous solutions were run as thin films on IRtran-2 plates prepared in a glove bag under N$_2$.

Acknowledgment. This research was initially supported by a grant from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and more recently by a grant from the NSF. Amy Shirk was an NIH Predoctoral Fellow.

---

[11] P. T. Ford and R. E. Richards, *Discuss. Faraday Soc.*, **19**, 230 (1955).

Raman and Infrared Spectra of Tetrahydroaluminate, AlH$_4^-$, and Tetrahydrogallate, GaH$_4^-$, Salts

A. E. Shirk and D. F. Shriver*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received January 27, 1973*

Abstract: Raman and infrared data of MH$_4^-$ (M = Al, Ga) with monovalent cations Li$^+$, Na$^+$, and (C$_2$H$_5$)$_4$N$^+$ for the aluminum salts and Li$^+$, Na$^+$, and K$^+$ for the gallium salts are reported. The data were collected on samples in the solid state and/or ether solutions (diethyl ether, dimethyl ether, tetrahydrofuran, 1,2-dimethoxyethane). Solution data for AlH$_4^-$ are interpreted in terms of three distinct species existing in the various solutions, tightly and loosely bound aggregates and ion pairs. In some solutions, the latter two species exist together in a temperature- and concentration-dependent equilibrium. There is strong evidence against solvent coordination to the AlH$_4^-$ moiety as previously postulated. The previous assignment of ν_2(E) of AlH$_4^-$ in diethyl ether is discounted and alternative assignments for it are considered. Tentative assignments for the remaining three vibrational modes are made, and a vibrational analysis was carried out. The A$_1$ stretching frequencies and associated force constants for the group IIIa tetrahydrides show an unusual trend: BH$_4^-$ > GaH$_4^-$ > AlH$_4^-$.

The present work on the vibrational spectra of AlH$_4^-$ and GaH$_4^-$ was designed to elucidate trends in bonding for main group III hydrides. The vibrational spectrum of GaH$_4^-$ has not been studied except for one brief mention of infrared data[1] while that of AlH$_4^-$ has been considered by several workers.[2–6] However, the variation in the AlH$_4^-$ vibrations in the different solvent systems has led to contradictory interpretations in the literature. From the work of Lippincott[2] and of D'Or and Fuger[3] it is known that AlH$_4^-$ is essentially tetrahedral; the Raman and infrared spectra of LiAlH$_4$ in diethyl ether (Et$_2$O) confirmed such an assignment. By contrast, infrared studies of AlH$_4^-$ in more strongly coordinating ethers such as tetrahydrofuran (THF) and dimethoxydiethyl ether (diglyme) have been interpreted in terms of a six-coordinated AlH$_4$(OR$_2$)$_2^-$ moiety.[4,5] Even with LiAlH$_4$ in diethyl ether solution it has been proposed that a five-coordinate species AlH$_4$(OR$_2$)$_2^-$ exists.[4] In the Russian work[5] the argument in favor of ether coordination to aluminum is based on the idea that LiAlH$_4$ in diethyl ether displays a spectrum most characteristic of AlH$_4^-$, and, therefore, the lower Al–H stretching frequencies observed in other solvents arise from ether coordinated AlH$_4^-$. The German group,[4] however, uses $\nu_{\mathrm{Al-H}}$ of amine–AlH$_3$ complexes as a standard for four-coordinated aluminum hydrides.

In the solid state, a single-crystal X-ray diffraction study of LiAlH$_4$[7] shows that the AlH$_4^-$ tetrahedra are slightly distorted. This is in agreement with the splittings observed in the vibrational spectrum of the solid.[5] Claims for a tetrahedral AlH$_4^-$ moiety in the solid state have been made by Semenenko, *et al.*,[6] from the Raman and infrared data for [R$_4$N][AlH$_4$], where R = CH$_3$ and C$_2$H$_5$.

---

[1] (a) L. I. Zakharkin, V. V. Gavrilenko, and Yu. N. Karaksin, *Syn. Inorg. Metal-Org. Chem.*, **1**, 37 (1971); (b) L. I. Zakharkin, V. V. Gavrilenko, and Yu. N. Karaksin, *J. Gen. Chem. USSR*, **41**, 2722 (1971).

[2] E. R. Lippincott, *J. Chem. Phys.*, **17**, 1351 (1949).

[3] L. D'Or and J. Fuger, *Bull. Soc. Roy. Sci. Liege*, **25**, 14 (1956).

[4] R. Dautel and W. Zeil, *Z. Elektrochem.*, **64**, 1234 (1960).

[5] T. G. Adiks, V. V. Gavrilenko, L. I. Zakharkin, and L. A. Ingat'eva, *Zh. Prikl. Spektrosk.*, **6**, 806 (1967).

[6] K. N. Semenenko, A. P. Chavgun, V. B. Polyakova, A. L. Dorosinskii, and A. A. Plakhtii, *Russ. J. Inorg. Chem.*, **15**, 1504 (1970).

[7] N. Sklar and B. Post, *Inorg. Chem.*, **6**, 669 (1967).