indicate that the product is dimethylaminotri-*n*-butylphosphonium bromide. *Anal.* Calcd for $[(CH_3)_2NP(C_4H_9)_3]Br$: C, 51.53; H, 10.18; N, 4.29; P, 9.49; Br, 24.49. Found: C, 51.17; H, 9.83; N, 4.45; P, 9.86; Br, 24.39.

Discussion

The experiments above allow the following conclusions to be drawn.

(1) Bromamine, NH_2Br, can be synthesized in the gas phase by the reaction between bromine and ammonia, but the yield in moles per hour is quite low. The low concentrations are, however, in accord with the findings of Coleman, *et al.*,[6] concerning their inability to obtain high concentrations of bromamine in ether solution. They report yields varying from 0.042 to 0.054 mol/l.

The formation of bromamine in the gas phase was confirmed by comparing the absorption spectra of the product in ethereal and aqueous solutions with the 284- and 278-mμ peaks reported by Johannesson[4] and Morris[5] and by the synthesis and characterization of aminotriphenylphosphonium bromide.

Table III shows the effect of changes in the $Br_2/NH_3/N_2$ ratio on the yield of bromamine. The table indicates that the Br_2/NH_3 ratio is one factor controlling the yield. Generally a small ratio or a large excess of ammonia gives the best yield. Another factor is the total number of moles of gas passing through the generator. A rapid flow through the reaction zone would sweep the bromamine out of the hot zone before it could decompose by

$$3NH_2Br + 2NH_3 \rightarrow 3NH_4Br + N_2$$

The rapid flow is achieved by increasing the nitrogen flow through the system.

(2) Dimethylbromamine, $(CH_3)_2NBr$, can also be synthesized in the gas phase by an analogous reaction using bromine and dimethylamine. Because of the difficulties encountered in attempts to purify reaction products, the effluent gases from the generator were bubbled into a nonhydrogen-bonding solvent and then the mixture was allowed to stand to allow the excess dimethylamine to escape. As the concentration of dimethylamine is reduced, the dissolved dimethylammonium bromide crystallizes out. This procedure is followed because the phosphorus-containing reaction products could not be recrystallized and, therefore, could not be separated from the dimethylammonium bromide.

Table IV indicates that a large excess of dimethylamine is necessary to obtain a reasonable yield of dimethylbromamine. The yields of dimethylbromamine are considerably higher than the yields of bromamine: 0.0092 mol/hr as compared to 0.0033 mol/hr for the highest yields in the two reactions.

(3) Bromamine reacts with triphenylphosphine in a manner similar to that of chloramine to produce the expected aminotriphenylphosphonium bromide, $[H_2NP(C_6H_5)_3]Br$. The infrared spectrum of this material was noted to be essentially the same as the infrared spectrum of the chloride analog.

(4) Dimethylbromamine reacts with triphenylphosphine and tri-*n*-butylphosphine to produce dimethylaminotriphenylphosphonium bromide, $[(CH_3)_2NP(C_6H_5)_3]Br$, and dimethylaminotri-*n*-butylphosphonium bromide, $[(CH_3)_2NP(C_4H_9)_3]Br$, respectively.

The pmr spectra of the compounds synthesized compare favorably with the spectra of similar known compounds. The spectrum of $[H_2NP(C_6H_5)_3]Br$ gives the chemical shift for the NH_2 protons as 2.89 ppm relative to the TMS peak, compared with 2.68 ppm for the chemical shift of the NH_2 protons in $[H_2NP(C_6H_5)_3]Cl$.[7] The spectra of $[(CH_3)_2NP(C_6H_5)_3]Br$ and $[(CH_3)_2NP(C_4H_9)_3]Br$ give the chemical shifts for the N–CH_3 protons as 6.96 and 7.13 ppm, respectively. These values compare favorably with the reported values of 6.96 ppm for $[((CH_3)_2N)_3PBr]Br$[8] and 7.05 ppm for $[(C_6H_5)_2P(N(CH_3)_2)NH_2]Cl$.[7]

The magnitude of the coupling constants J_{PNCH} is in accord with the value of 10.6 ± 1.1 cps reported by earlier workers for a variety of phosphonium compounds.[7] The chemical shifts of $(CH_3)_2N$ protons are reported to be constant (τ 7.11 ± 0.06),[7] being almost unaffected by other substituents on the phosphorus atom. These protons in dimethylaminotriphenylphosphonium bromide, $[(CH_3)_2NP(C_6H_5)_3]Br$, have a chemical shift which is outside the reported range by 0.09 τ unit. However, the $(CH_3)_2N$ protons in the dimethylaminotri-*n*-butylphosphonium bromide are well within the reported range.

Infrared spectra of the new aminophosphonium bromides given in Table I are similar to spectra reported by other workers.

Acknowledgment.—The author gratefully acknowledges receipt of a grant from the donors of the Petroleum Research Fund administered by the American Chemical Society.

---

[6] H. G. Coleman, C. B. Yager, and H. Soroos, *J. Am. Chem. Soc.*, **56**, 965 (1934).

[7] S. R. Jain, W. S. Brey, Jr., and H. H. Sisler, *Inorg. Chem.* **6**, 515 (1967).

[8] H. Nöth and H. J. Vetter, *Ber.*, **98**, 1981 (1965).

CONTRIBUTION FROM LINCOLN LABORATORY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
LEXINGTON, MASSACHUSETTS 02173

A New Series of Rare Earth Garnets $Ln^{3+}{}_3M_2Li^{+}{}_3O_{12}$ (M = Te, W)[1]

BY H. M. KASPER

Received September 9, 1968

The preparation of tellurate garnets $\{A^{2+}{}_3\}[Te_2]\cdot(B^{2+}{}_3)O_{12}$, with A = Ca or Cd and B = Zn or Co, was recently reported.[2] This suggests the possibility of

---

[1] This work was sponsored by the U. S. Air Force.

[2] H. M. Kasper, *Mater. Res. Bull.*, **3**, 765 (1968).

TABLE I

POWDER DIFFRACTION DIAGRAM OF $Gd_3Te_2Li_3O_{12}$

d_{obsd}	d_{calcd}	Intens	*hkl*
5.04	5.06	10	211
4.37	4.38	7	220
3.30	3.31	9	321
3.09	3.10	9	400
2.764	2.770	10	420
2.638	2.641	1	332
2.524	2.529	10	422
2.426	2.430	5	500 430
2.256	2.262	8	521
2.006	2.010	8	611 532
1.957	1.959	3	620
1.823	1.826	3	631
1.786	1.788	2	444
1.716	1.718	7	640
1.684	1.686	6	633 552
1.654	1.656	10	642
1.572	1.573	4	732 651
1.548	1.549	6	800
1.480	1.481	2	653
1.459	1.460	2	822 660
1.401	1.403	1	752
1.384	1.385	7	840
1.351	1.352	6	842
1.335	1.336	3	921 761 655
1.320	1.321	7	664
1.2773	1.2779	3	932 763
1.2639	1.2645	1	844
1.2261	1.2268	1	10,1,1 772
1,2146	1.2149	1	10,2,0 862
1.1809	1.1813	5	10,3,1 952 765
1.1497	1.1504	7	10,4,0 864
1.1402	1.1406	1	10,3,3 961
1.1303	1.1310	8	10,4,2
1.1034	1.1038	5	11,2,1 10,5,1 953
1.0948	1.0951	7	880
1.0700	1.0703	4	11,3,2 10,5,3 972 776
1.0621	1.0624	1	10,6,0 866
1.0395	1.0397	2	965
1.0323	1.0325	6	12,0,0 884
1.0181	1.0185	4	12,2,0
1.0116	1.0116	5	11,5,2 10,7,1 10,5,5
1.0049	1.0050	10	12,2,2 10,6,4
0.9857	0.9857	4	11,6,1 10,7,3
0.9795	0.9795	2	12,4,0

TABLE II

PROPERTIES OF SOME GARNETS

Compn	*a*, Å	Color
$Na_3Te_2Al_3O_{12}$	12.186	White
$Na_3Te_2Ga_3O_{12}$	12.355	White
$Y_3Te_2Li_3O_{12}$	12.265	White
$Pr_3Te_2Li_3O_{12}$	12.607	Green
$Nd_3Te_2Li_3O_{12}$	12.555	Light blue
$Sm_3Te_2Li_3O_{12}$	12.463	Pale yellow
$Eu_3Te_2Li_3O_{12}$	12.426	Light brown
$Gd_3Te_2Li_3O_{12}$	12.390	White
$Tb_3Te_2Li_3O_{12}$	12.346	Pale yellow
$Dy_3Te_2Li_3O_{12}$	12.306	Pale yellow
$Ho_3Te_2Li_3O_{12}$	12.270	Pale orange
$Er_3Te_2Li_3O_{12}$	12.236	Rose
$Tm_3Te_2Li_3O_{12}$	12.203	White
$Yb_3Te_2Li_3O_{12}$	12.172	White
$Lu_3Te_2Li_3O_{12}$	12.148	White
$Pr_3W_2Li_3O_{12}$	12.509	Light green
$Nd_3W_2Li_3O_{12}$	12.463	Light blue

replacing the $A^{2+}{}_3B^{2+}{}_3$ cations by either $A^{+}{}_3B^{3+}{}_3$ or $A^{3+}{}_3B^{+}{}_3$, provided that the A and B ions are not too large. It has been pointed out[2] that the A–B electrostatic repulsive force limits the cation size, since the A–B distance is only $a_0/4 \approx 3$ Å.

This paper reports the preparation of tellurate garnets in which both types of replacement have been made. Stoichiometric amounts of carbonates, hydroxides, and oxides were thoroughly mixed in an agate mortar, transferred to porcelain crucibles, and slowly heated to 700° to oxidize TeO_2. Then the materials were thoroughly reground and refired at the sintering temperature. Two $Na^{+}{}_3B^{3+}{}_3$ compounds, $Na_3Te_2Al_3O_{12}$ and $Na_3Te_2Ga_3O_{12}$, have been obtained by sintering Na_2CO_3, TeO_2, and $Al(OH)_3$ or dried $Ga(NO_3)_3$ at 700° for 12 and 20 hr, respectively. The $A^{3+}{}_3B^{+}{}_3$ substitution has also proved successful, with the small Li^+ ion as B^+ and A = Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, or Lu. These 13 compounds were prepared by sintering Ln_2O_3, TeO_2, and Li_2CO_3 at 850° for 10 hr. In addition, two analogous tungstate garnets, $Pr_3W_2Li_3O_{12}$ and $Nd_3W_2Li_3O_{12}$, were prepared by sintering Ln_2O_3, WO_3, and Li_2CO_3 at 900° for 24 hr. In order to determine whether any significant loss of Na, Li, or Te occurred during the sample preparation, the representative compounds $Na_3Te_2Al_3O_{12}$ and $Pr_3Te_2Li_3O_{12}$ were analyzed chemically. No such loss was detected.

The materials were investigated with X-rays from an iron tube in a Norelco Model 1221510 generator (voltage 40 kV, current 8 mA). Mn-filtered radiation entered a powder camera (360-mm circumference), Model 32056/B, manufactured by North American Philips Corp. The film was arranged in the manner described by Straumanis and Ievinš.[3] The films were measured on a linear scale, and the film length was determined with a computer program[4] (Fortran IV) from those reflections that had a predetermined internal consistency of better than 0.1 mm. The lattice constant was then obtained from high-angle reflections. It is estimated that the accuracy is better than 0.05%. Table I gives the diffraction pattern of $Gd_3Te_2Li_3O_{12}$. Table II lists the lattice parameter and color of each compound.

As shown in Figure 1, the lattice constants for the rare earth tellurate garnets are larger than those for the corresponding $Ln_3Al_5O_{12}$ garnets and smaller than those for the corresponding $Ln_3Fe_5O_{12}$ compounds.[5–9] In comparison with the corresponding $Ln_3Ga_5O_{12}$ garnets, the tellurate garnets $Ln_3Te_2Li_3O_{12}$ have larger lattice constants for rare earth ions larger than Tb and smaller constants for smaller rare earth ions. This indicates that the change in Ln ion radius has a greater influence on the lattice constant of a garnet with isolated TeO_6 complexes than in a garnet $Ln_3M_5O_{12}$ with continuous M–O–M linkages, like $Ln_3Ga_5O_{12}$.

The question remains as to why Te^{6+} ions form a much more extended series of garnets than W^{6+} ions. The situation may be compared to that found in the spinels, where Co_5TeO_8 has been obtained,[10] but no spinel with octahedral W^{6+} is known as yet. It is perhaps significant that Te^{6+} ions prefer to form regular octahedral complexes, whereas W^{6+} ions tend to distort

---

(3) M. Straumanis and A. Ievinš, *Z. Physik*, **98**, 461 (1936).

(4) H. Kasper, Dissertation, University of Bonn, 1965; H. Kasper and O. Schmitz-Du Mont, "World List of Crystallographic Computer Programs," 2nd ed, D. P. Shoemaker, Ed., International Union of Crystallography, A. Oosthoek's Uitgevers Mij. N.V., Utrecht, Netherlands, 1966, No. 5058.

(5) S. Geller, *Z Krist*, **125**, 1 (1967).

(6) F. Bertaut and F. Forrat, *Compt. Rend.*, **243**, 2119 (1956).

(7) F. Bertaut and F. Forrat, *ibid.*, **244**, 96 (1957).

(8) G. Espinosa, *J. Chem. Phys.*, **37**, 2344 (1962).

(9) C. B. Rubinstein and R. L. Barns, *Am. Mineralogist*, **49**, 1489 (1964); **50**, 782 (1965).

(10) H. Kasper, *Z. Anorg. Allgem. Chem.*, **354**, 78 (1967).

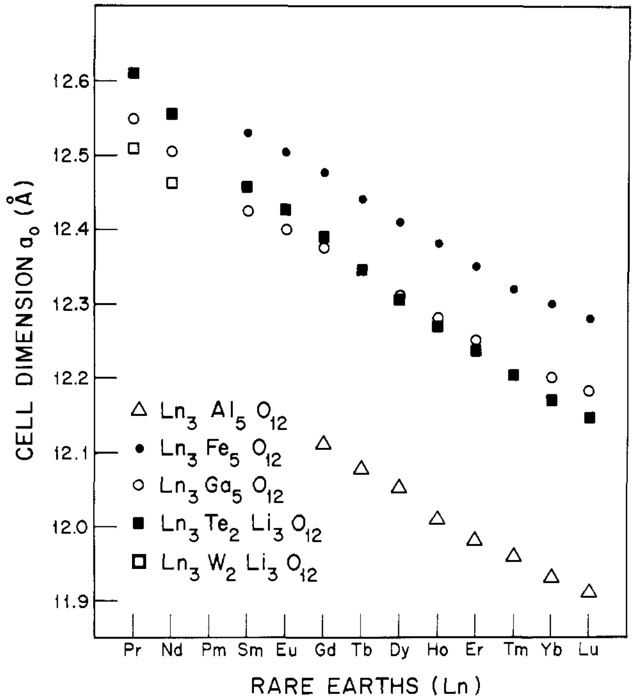


Figure 1.—Lattice constants of rare earth garnets.

octahedral interstices by moving out of the center of symmetry. The octahedral-site coordination has been discussed by Zemann,[11] who pointed out that garnets with very nearly regular octahedra should be possible. This suggests that the TeO_6^{6-} octahedra in the tellurate garnets are regular and that the relative stability of regular octahedra is the reason that there is a much more extended series of rare earth garnets with Te^{6+} ions than with W^{6+} ions.

Acknowledgments.—The advice and assistance of J. B. Goodenough, A. Ferretti, J. M. Longo, E. B. Owens, Mary C. Finn, and A. J. Strauss are gratefully acknowledged.

[11] J. Zemann, *Beitr. Mineral. Petrog.*, **8**, 180 (1962).

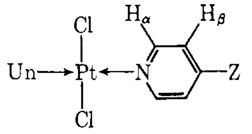
Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

Solvent Displacement of Ligands from Carbonyl Complexes of Platinum (II)

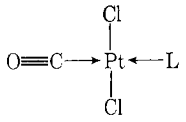
By Thomas A. Weil, Paul Schmidt,
Mark Rycheck, and Milton Orchin

Received September 16, 1968

Earlier work in this laboratory has shown that the nmr spectra of pyridine complexes of structure **1** may not show the expected $^{195}Pt-H_\alpha$ spin coupling because of rapid exchange of the pyridine ligand with solvent molecules until the exchange rate is slowed by low temperatures.[1,2]



1 (Un = unsaturated ligand)



2

(a) L = 4-Z-PyO
(b) L = 4-Z-Py
(c) L = 4-Z-An

The temperature at which such coupling is observed depends upon the solvent and the nature of Un and Z. Thus, for example, when Z = CN and Un is varied in the series: ethylene, *trans*-2-butene, *cis*-2-butene, and carbon monoxide, the temperatures at which coupling is observed in chloroform solution are respectively: −51, −25, 3, and 30°. This order of ligands may thus be construed to be the order of *trans*-labilizing ability: ethylene >> *trans*-2-butene > *cis*-2-butene > CO. When Un is held constant, the temperature for coupling is a function of the nature of Z: the strongest electron-withdrawing substituents require the lowest temperature for coupling to be observed. Finally, it has also been shown that when the nmr spectrum of any particular complex **1** is taken in several solvents, the solutions made from coordinating solvents such as acetone must be cooled to lower temperatures to observe coupling than when solvents such as chloroform are employed. In the present study, we examined the infrared spectra of a series of carbonyl complexes **2** in order to determine whether the labilizing effects of solvent determined by nmr spectra could also be demonstrated by the infrared spectra.

Experimental Section

The complexes **2a** and **2b** were prepared by the displacement of ethylene by carbon monoxide from the corresponding complexes **1** (Un = ethylene) by a procedure similar to that previously reported.[3,4] The ethylene complex, which was prepared from Zeise's salt and the appropriate pyridine, was dissolved in 10 ml of dry $CHCl_3$ and CO bubbled through the yellow solution until most of the original color had disappeared. The volume of the solution was reduced by evaporation and hexane added with cooling. The precipitated complex was filtered, washed with hexane, and dried. The product was then redissolved in dry chloroform and the above precipitation repeated to assure pure complexes.

The aniline carbonyl complexes **2c** were prepared by the reaction of the appropriate aniline with the carbonyl analog of Zeise's salt, $[(CO)PtCl_3]K$, in acetone. After the precipitated KCl was removed, the solution was concentrated and hexane added to induce precipitation of the product.

Most of the complexes have been previously reported.[3,4] All infrared spectra were determined with a Perkin-Elmer Model 337 grating spectrophotometer with expanded scale and polystyrene calibration using 0.05-mm KBr cells unless otherwise noted. The spectra were determined in spectral grade acetone, chloroform, and acetonitrile, dried over Linde 4A molecular seives.

Results and Discussion

The carbonyl stretching frequencies of complexes with structure **2** are listed in Table I for the three

---

[1] P. D. Kaplan, P. Schmidt, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 4537 (1967).

[2] P. D. Kaplan, P. Schmidt, and M. Orchin, *ibid.*, **91**, 85 (1969).

[3] W. H. Clement and M. Orchin, *J. Organometal. Chem.*, **3**, 98 (1965).

[4] A. R. Brause, M. Rycheck, and M. Orchin, *J. Amer. Chem. Soc.*, **89**, 6500 (1967).