Acknowledgment.—The author wishes to thank Professor D. M. Greenberg for his continued interest in this work and for his help in preparing the manuscript.

Experimental

Material.—α-Keto-γ-methylmercaptobutyric acid was prepared enzymatically by the method described by Meister.[10] All the other α-keto acids were synthesized by Mr. D. C. Morrison of this Laboratory. Other chemicals were obtained from commercial sources.

Methods.—Spectrophotometric measurements were made with a Beckman model DU spectrophotometer at room temperature. Silica cells of 1 cm. length were used.

Silica gel column chromatography was carried out by the method of Kinnory, *et al.*,[11] and paper chromatography of the 2,4-dinitrophenylhydrazones of the α-keto acids according to Altmann, *et al.*[12]

Preparation of Schiff Base.—One hundred μmoles each of pyridoxal–HCl and DL-α-amino-*n*-butyric acid suspended together in 10.0 ml. of absolute ethanol were shaken at room temperature in a tightly stoppered glass vial. A clear yellow solution was obtained in about 15 min. The ethanolic solution of the yellow complex of pyridoxamine–2HCl and sodium α-ketobutyrate was prepared in the same manner. Addition of ether to the alcoholic solution of the Schiff bases precipitated a yellow material and the supernatant liquid became colorless. The precipitated materials, when freed from ether, were strongly hygroscopic, and their analysis was not attempted. Absorption spectra of the Schiff bases were measured on aliquots of the ethanolic solution after appropriate dilution with absolute ethanol, with or without addition of NaOH.

Formation of Amino Acids by Non-enzymatic Transamination between Pyridoxamine and α-Keto Acids.—One ml. of absolute ethanol containing 10 μmoles of pyridoxamine–2HCl and 20 μmoles of NaOH (the precipitate of NaCl was removed by centrifugation) were added to 10 to 40 μmoles of the solid sodium salts of various α-keto acids. After the mixture was shaken for 3 to 10 hr. at room temperature, aliquots were chromatographed on paper with *n*-butanol–acetic acid–water (5:1:2) and/or phenol–water (4:1) as developing solvents. Intense spots of amino acids were revealed on the chromatograms prepared with 2 to 5 μl. of the above mixtures, which represent 0.02 to 0.05 μmole of pyridoxamine initially present. Since the minimum quantity of amino acids detectable under the conditions employed is approximately 0.005 μmole, it is apparent that a significant portion of the added pyridoxamine had participated in the transamination reaction. Determination of pyridoxal and pyridoxamine were not attempted.

Formation of α-Keto Acids by Non-enzymatic Transamination between Pyridoxal and α-Amino Acids.—Fifty μmoles each of α-amino-*n*-butyric acid, pyridoxal–HCl and NaOH were incubated in 10 ml. of absolute ethanol for 8 hr. at room temperature. A portion of this solution was evaporated to dryness with a stream of air, the residue was taken up in small volume of 1 *N* HCl and subjected to silica gel column chromatography. Nine-tenth μmole of α-ketobutyric acid was isolated by this method from an aliquot which represented 10 μmoles of each of the reactants. This suggests that the equilibrium of the tautomerism of the Schiff base favors the aldimine form, at least under the condition employed.

To prepare the 2,4-dinitrophenylhydrazones of α-keto acids formed by transamination between pyridoxal and α-amino acids the ethanolic solution of the Schiff base was dried, and the residue was redissolved in water, acidified with H_2SO_4 to *p*H 2, and this solution was continuously extracted with peroxide-free ether. Ether was removed from the extract by evaporation and the residue was treated with 2,4-dinitrophenylhydrazine in HCl. The step of ether extraction was necessary to remove pyridoxal, the 2,4-dinitrophenylhydrazone of which interferes with the Friedemann–Haugen test.

Pyridoxal Catalysis of Transamination between an Amino Acid and an α-Keto Acid.—Fifty μmoles of pyridoxal–HCl, 100 μmoles of alanine and 200 μmoles of sodium α-ketobutyrate were incubated in 10 ml. of absolute ethanol, in the presence of 50 μmoles of NaOH. After incubating 4 hr. at room temperature 5-μl. aliquots were chromatographed on paper. Spraying the paper with ninhydrin reagent revealed purple spots of alanine and α-amino-*n*-butyrate and a reddish-yellow spot of pyridoxamine. Intensity of the α-amino-*n*-butyrate spot was comparable to or greater than that of the alanine spot, indicating that the transamination reaction had proceeded to a significant extent. Similar results were obtained from experiments with various combinations of amino and keto acids.

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[10] A. Meister, *J. Biol. Chem.*, **197**, 309 (1952).

[11] D. S. Kinnory, Y. Takeda and D. M. Greenberg, *ibid*, **212**, 379 (1955).

[12] S. M. Altmann, E. M. Crook and S. P. Datta, *Biochem. J.*, **49**, lxiii (1951).

COMMUNICATIONS TO THE EDITOR

HEAT CAPACITY OF ORDERED Mg_3Cd BETWEEN 4 AND 15°K.[1]

Sir:

Heat capacity data for ordered Mg_3Cd between 12 and 320°K. were presented in THIS JOURNAL several years ago.[2] This paper contains results extending those measurements into the liquid helium range.

The sample employed was a portion of the material used in the earlier study.[2] It had been heat treated to assure that it was in the ordered state. The composition of the sample was 24.98 ± 0.04 atomic % cadmium. 308.53 g. or 6.66 g. atoms of this material were used in the study. The apparatus, described elsewhere,[3,4] used a gas thermometer as the working thermometer. The constant of this gas thermometer was essentially determined by a calibration against the 1955 liquid helium vapor pressure scale.

The measurements were carried out in two series, of 25 and 23 experiments, respectively, both covering the range 4.5 to 16°K. After the first series the

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[1] This work was supported by a grant from the National Science Foundation.

[2] L. W. Coffer, R. S. Craig, C. A Krier and W. E. Wallace, THIS JOURNAL, **76**, 241 (1954).

[3] M. H. Aven, Ph.D. Dissertation, University of Pittsburgh, 1955.

[4] M. H. Aven, R. S. Craig and W. E. Wallace, *Rev. Sci. Instruments*, **27**, 623 (1956).

gas thermometer was evacuated, filled with helium gas and recalibrated.

Smoothed values of C_p are given in Table I. A plot of C_p/T *versus* T^2 is presented (Fig. 1). Such a plot is, of course, linear over the region in which the T^3 law is obeyed.

TABLE I

HEAT CAPACITY OF ORDERED Mg_3Cd AT ROUNDED TEMPERATURES

T, °K.	C_p, joules/ °K. g. atom	T, °K.	C_p, joules/ °K. g. atom
4	0.008	9	0.0829
5	.0145	10	.021
6	.0237	12	.239
7	.0370	14	.421
8	.0560	16	.638

The pronounced curvature in the plot in Fig. 1 makes the electronic specific heat coefficient as determined from the intercept somewhat uncertain. A provisional value of 0.8×10^{-3} joule/mole deg.[2] is obtained from the present data. This may be compared with 1.32×10^{-3} and 0.6×10^{-3} which have been obtained for magnesium[5] and cadmium,[6] respectively.

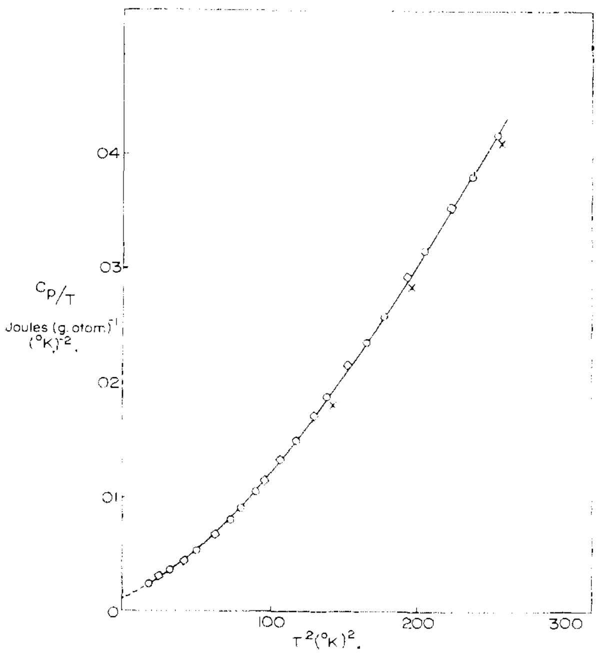

Fig. 1.—Heat capacities of ordered Mg_3Cd: This study. ○, 1st series; □, 2nd series; × data from ref. 4.

As is customary in work of this nature the effective Debye temperature θ is calculated from the experimental results. With help of data from reference 2 it is found that the Debye θ has a minimum of 226°K. at a temperature of 18°K. and approaches 292°K. at absolute zero. The curve of θ *versus* T is very similar to the same curve for Cd given by Smith and Wolcott. They have observed that both zinc and cadmium show a pronounced minimum in the θ-curve whereas magnesium does not. They have suggested that the minimum may originate with the same factors that produce the anomalous axial ratio in zinc and cadmium. It is of interest to note that Mg_3Cd also exhibits the minimum, despite the fact that it has a normal axial ratio.[7,8]

The authors wish to acknowledge the assistance of Mr. Kay F. Sterrett and Mr. Guido Galli in making the measurements contained in this communication.

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[5] P. L. Smith, *Phil. Mag.*, [7] **46**, 744 (1955).

[6] P. L. Smith and N. M. Wolcott, *ibid.*, 1 [8] 854 (1956).

[7] D. A. Edwards, W. E. Wallace and R. S. Craig, THIS JOURNAL, **74**, 5256 (1952).

[8] W. E. Wallace, *J. Chem. Phys.*, **23**, 2281 (1955).

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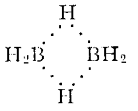
RECEIVED DECEMBER 22, 1956

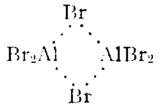
SINGLY-BRIDGED COMPOUNDS OF THE BORON HALIDES AND BORON HYDRIDES

Sir:

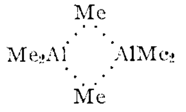
The existence of dimeric molecules in the hydride of boron, $(BH_3)_2$, the halides of aluminum and gallium, $(AlBr_3)_2$ and $(GaCl_3)_2$, and in the alkyls of aluminum, $(AlMe_3)_2$, has long provided a difficult hurdle for valency theory.[1] It is now accepted that these dimeric molecules involve doubly-bridged structures (I–III).



I



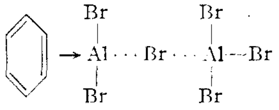
II



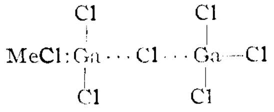
III

The precise interpretation of the electronic bonding in these bridged structures has been the subject of numerous discussion.[2]

Aluminum bromide reacts with aromatic hydrocarbons to form molecular species with the composition $ArH \cdot Al_2Br_6$ and $ArH \cdot AlBr_3$.[3] Likewise methyl chloride forms addition compounds with gallium chloride, $MeCl:Ga_2Cl_6$ and $MeCl:GaCl_3$.[4] The species $ArH \cdot Al_2Br_5$ and $MeCl \cdot Ga_2Cl_6$ were interpreted[3,4] as involving a single halogen bridge (IV, V).



IV



V

The boron halides are monomeric and exhibit no tendency to form doubly-bridged dimers. However, we have observed that 1:1 addition compounds of the boron halides with triethylamine and with pyridine are capable of absorbing a second equivalent of boron halide at temperatures from −78 to 0° to form relatively unstable 1:2 addition compounds. The following products have been synthesized: $Et_3N:2BF_3$, $Et_3N:2BCl_3$, $Et_3N:2BBr_3$, $Py:2BF_3$, $Py:2BBr_3$. At −78° triethylamine

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[1] See E. Cartmell and G. W. A. Fowles, "Valency and Molecular Structure," Academic Press, Inc., New York, N. Y., 1956, Chapter 13, for a summary and pertinent references.

[2] K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945); R. E. Rundle, *ibid.*, **69**, 1327, 2075 (1947); W. N. Lipscomb, *J. Chem. Phys.*, **22**, 985 (1954).

[3] H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6265 (1953). Unpublished work with Dr. Sang Up Choi.

[4] H. C. Brown, L. P. Eddy and R. Wong, *ibid.*, **75**, 2675 (1953).