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The Cadmium(I) Ion Cd_2^{2+}. Raman Spectrum and Relationship to Hg_2^{2+}[1]

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The Raman spectrum is reported for the system $0.67Cd_2(AlCl_4)_2$–$0.33Cd(AlCl_4)_2$ in the molten state at 250° and, incompletely, as the solid mixture at 70°. In addition to the known transitions of $AlCl_4^-$, the melt exhibits a strong shift of 183 ± 3 cm.$^{-1}$ due to the Cd_2^{2+} ion. The weakness of the bonding in the diatomic cadmium(I) ion is indicated both by the 10-cm.$^{-1}$ line width observed with the melt and by the smallness of the calculated force constant (1.11 mdynes/Å.). The properties of the Cd_2^{2+} ion and related species are contrasted to those of the more stable mercury analogs, and an interpretation is advanced for the anomalous stability of the mercury(I) ion.

Introduction

Previous acid–base interpretation of certain aspects of the solution of some metals in their molten halides,[2] of the nature of $Ga(AlCl_4)$,[3] and of the effect of added salts on metal–salt solutions led to the concept of acid-stabilization of lower oxidation states and to the isolation of the stable cadmium(I) salt $Cd_2(AlCl_4)_2$.[4] In this case substitution for chloride ion of the larger, less basic $AlCl_4^-$ increases the apparent reduction of cadmium(II) in the melt by excess metal from 15.9% at 538° to 65–68% at 230–320°. In addition, a compound of the stoichiometry ($CdAlCl_4$) now is stable below the peritectic temperature of 227°. Since the assignment of the dimeric formula to this compound, in analogy to the mercury(I) state, was based primarily on its diamagnetism, it was considered desirable to identify the ion Cd_2^{2+} by more direct means. This has been accomplished through observation of the Raman spectrum of both the melt and the solid phase.

Experimental

Sample.—Doubly-sublimed $CdCl_2$ and $AlCl_3$ were combined in the proper proportions in an inert atmosphere box and heated *in vacuo* with excess metal to make ~5 cc. (13.7 g.) of a melt corresponding to 66.9% $Cd_2(AlCl_4)_2$, the remainder $Cd(AlCl_4)_2$. The glass container was opened to the Raman cell through a break-seal (with the entire arrangement at ~250° so as to avoid decomposition through volatilization of $AlCl_3$), the sample poured into the cell through an intermediate, medium porosity, sintered glass disk, and the cell sealed off.

Cell.—The cell so filled was of 10.5-mm. o.d. Pyrex tubing with the usual light-blocking kink about two-thirds of the way up from the window so that a 55 to 60 mm. column of melt could be illuminated. In order to minimize self-absorption of scattered light in the blue region by the light green melt, the optical window was sealed to the end of the tube so as to allow irradiation of the melt to within 1 mm. of the window. For this a thin rim of lead glass (Corning 7720) was first fused on the flat end of the sample tube. This was heated upright in a furnace with the circular window resting on this bead until the sealing glass was observed to wet the window (~760°), at which time a slight pressure on the window completed the seal.[5] The result was vacuum tight. As solidification and melting of the reduced mixture usually cause temporary precipitation of small amounts of cadmium metal[4] that would obscure the cell window, the sample always was melted first in a separate furnace with the window upward so that the metal collected at the seal-off. The cell then was inverted and transferred to the preheated furnace container with the Raman source.

Raman Apparatus.—Data were recorded on film with a Lane-Wells Raman spectrograph No. 40-A (aperture f/3). The original excitation unit (No. 60-A2) with two water-cooled, linear Hg lamps in a reflective housing was used in preliminary experiments. This later was altered by installation of the helical "Toronto" Hg source (Applied Research Laboratories) described by Kemp, Jones, and Durkee,[6] with the original housing and control unit appropriately modified for lamp mounting, heaters, blowers, and associated power supply.

The sample tube was positioned vertically along the axis of the source and above the prism directing the emitted light to the spectrograph. For the combined sample support and heater assembly,[7] three 7/32 in., two-hole alumina thermocouple protection tubes were cemented through holes near the outside edges of two 1.5-in.

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[1] Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

[2] J. D. Corbett, S. von Winbush, and F. C. Albers, *J. Am. Chem. Soc.*, **79**, 3020 (1957).

[3] R. K. McMullan and J. D. Corbett, *ibid.*, **80**, 4761 (1958).

[4] J. D. Corbett, W. J. Burkhard, and L. F. Druding, *ibid.*, **83**, 76 (1961).

[5] The author is indebted to W. Bues for this technique.

[6] J. W. Kemp, J. L. Jones, and R. W. Durkee, *J. Opt. Soc. Am.*, **42**, 811 (1952).

[7] Illustrated by J. D. Corbett and F. R. Duke, in "Techniques of Inorganic Chemistry," ed. by H. B. Jonassen, Interscience Publishers, New York, N. Y., in press.

diameter disks of 3/16 in. transite. The lower of these disks was shaped so as to align the cell window over a central hole and the upper, to hold the tube just above the "light kink." Nichrome wire within and around the three alumina tubes comprised the heating elements. The support and heater arrangement was in turn contained within a clear dewar-type vessel with optical windows in the bottom that was supported in the center of the arc and above the prism on a fitted lavite block. A transite cap over the ends of the alumina supports closed the top of the container.

This arrangement provides considerable versatility in operation with volatile or reactive materials without substantial modification of the conventional Raman apparatus. The sample can be withdrawn and inverted before cooling so as to prevent cracking of the window on remelting. The temperature of operation is limited primarily by the glass of construction and by radiation loss at higher temperatures; the latter might be reduced through the use of infrared-reflecting, dichroic filter coatings on the vacuum jacket.

Spectra.—With the arrangement described the more intense shifts from the liquid could be recorded on EK 103D film in 15 sec., using a 100-μ slit and 14.5 amp. through the lamp, and the weakest, in 2 to 3 min. Although the source radiation was not filtered other than by the four intervening layers of Pyrex, no evidence of decomposition in the melt was noted. The calibration of the film scale in the region of 5460.7 Å. (Hg *c*) was established from the positions of the weaker Hg lines between 5318 and 5893 Å.,[8] as measured visually to $<10^{-2}$ mm. on a Sinclair Smith microphotometer, and for scattered radiation from Hg *e* (4358.3 Å.), by the Raman spectrum of benzene[9] from Hg *e,f,g,i,k*. All but the faintest displacements reported are thought to be within ±3 cm.$^{-1}$.

A limited amount of data for the solid was taken in the same apparatus. The sample was solidified with the window up so as to give a cone-shaped surface ("sink-well") about 3 cm. above the window. As the source radiation itself was sufficient to heat the sample to about 165° and thereby give the solid a definite yellow color, a stream of inert gas was blown through the dewar to keep the sample at 75° or less. Unfiltered radiation slowly produced a yellow-brown coloration in the solid but this disappeared on remelting. Exposures were limited to about one-third of those for the liquid due to the increase in Rayleigh scattering. Attempted polarization measurements were not very successful, probably because the incident light was not limited to that normal to the sample axis and the spectra were of poor quality due to the scattered light.

Results and Discussion

Table I summarizes the Raman spectrum obtained for the melt corresponding to $(0.67Cd_2^{2+}, 0.33Cd^{+2})(AlCl_4)_2$ at 245 to 260°. The best data obtained resulted from the green Hg *c* line since the light green color of the melt prevented any but the faintest record of displacements from blue Hg *e*, even with very long exposures.

The assignment given in Table I was made with the aid of the results of Gerding and Houtgraaf[10] for liquid $Na^+AlCl_4^-$, who found 146(2), 180(3), 349(10), and ~575 cm.$^{-1}$ (2b) for the vibrational energy changes (and intensities) for the fundamental vibrations ν_2, ν_4, ν_1, and ν_3, respectively, of the tetrahedral $AlCl_4^-$ ion. The first, third, and fourth of these closely correspond to the $\Delta\bar{\nu}$ values observed here and are so assigned to the anion in the melt. The strongest observed shift, 183 cm.$^{-1}$, is assigned to the Cd_2^{2+} ion, and not to that corresponding to ν_4 of $AlCl_4^-$ at 180 cm.$^{-1}$, on the basis of intensity; that is, the observed displacement, relative to that arising from the symmetric mode ν_1 of $AlCl_4^-$ at 350 cm.$^{-1}$, is 20 ± 4 times stronger than it should be according to the data for $NaAlCl_4$. On the other hand, the agreement between the two sets of data for the relative intensities of the two higher energy shifts for $AlCl_4^-$ is good. The intensity given for 144 cm.$^{-1}$ is uncertain due to halation from the incident radiation.

TABLE I

RAMAN SPECTRUM OF THE MELT $Cd_2(AlCl_4)_2 + Cd(AlCl_4)_2$ (67:33) AT ~250°

$\Delta\bar{\nu}$, cm.$^{-1}$	Source[a]	Intensity	Assignment
~144	$+a, +e$	≈0.5	ν_2, $AlCl_4^-$
183	$\pm a, \pm b, \pm c(\pm e)$	10(±2)b	ν_1, Cd_2^{2+} [b]
350	$+a, -b, \pm c$	1.7s	ν_1, $AlCl_4^-$
~587	$+c$	0.4	ν_3, $AlCl_4^-$

[a] $a = 5790.7$, $b = 5769.6$, $c = 5460.7$, $e = 5358.3$ Å. Weaker source lines interfere with 144, $+b$ and 350, $-a, +b$. [b] See text.

The incomplete Raman spectrum of the solid cadmium tetrachloroaluminate mixture at 60 to 75° also exhibited the displacement due to Cd_2^{2+}, in this case at 177 ± 6 cm.$^{-1}$. The poor quality of the data prevented definite observation of other lines.

Both the magnitude and the character of the 183-cm.$^{-1}$ shift in the liquid confirm the weakness of the homopolar bond in Cd_2^{2+} that is suggested by its chemical properties.[4] An unusually small force constant of 1.11 mdynes/Å. is computed[11] for Cd_2^{2+}, which may be compared to

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[8] K. W. F. Kohlrausch, "Raman Spektren," Vol. 9, part 6 of 'Hand- und Jahrbuch der Chemischen Physik," ed. by A. Eucken and K. L. Wolf, Akademische Verlagsgesellshaft, Leipzig, Germany, 1943, p. 34.

[9] W. R. Angus, C. K. Ingold, and A. H. Leckie, *J. Chem. Soc.*, 925 (1936).

[10] H. Gerding and H. Houtgraaf, *Rec. trav. chim.*, **72**, 21 (1953).

[11] Anharmonicity corrections, although unavailable, probably are not negligible for the bonds in M_2^{2+} species. Force constants computed thus relate to the actual vibration state and will be smaller than k_e for infinitesimal displacement.

0.98 for K_2 and 1.72 for Na_2 and I_2.[12] As a consequence of this small restoring force the spectrum of Cd_2^{2+} is that of a rather uniform band about 10 cm.$^{-1}$ in width rather than a fairly sharp line such as is observed for ν_1 of $AlCl_4^-$. The existence of such a range of vibrational energies in Cd_2^{2+} in the melt is considered to result from the effect of a distribution of neighboring ions appropriate to a liquid on the particularly weak and compliant bond; in other words, a 10% range in the apparent force constant is caused by an effective anharmonicity induced by the varying environment. A generous allowance for the normal isotopic distribution in cadmium accounts for one-third or less of the effect, in agreement with the sharper line observed in the spectrum of the solid at 70°.

Before the cadmium result can be compared with that for mercury, the sensitivity of the bond distance to the anionic environment even in the more stable Hg_2^{2+} should be noted. Crystal structure studies show that the Hg_2^{2+} bond length decreases more or less uniformly from 2.69 Å. in the iodide[13] to 2.43 ± 0.04 Å. in the fluoride,[14] while a distance of 2.54 ± 0.01 Å. has been reported in the arrangement $Hg_2^{2+}(OH_2)_2(NO_3^-)_2$[14] (and a remarkable 2.90 Å. in the diacethydrazide[15]). Thus with halide anions the bond length decreases, and the bond strength presumably increases, with decreasing tendency for covalent bonding by the anion. This is substantially the same effect as considered in the stabilization of cadmium(I) salts, that is, the necessity of having an anion with a low tendency for complex formation.[4] Similarly, the formation of chelates of Hg_2^{2+} with pyrophosphate, oxalate, etc., but disproportionation with most nitrogen bases, cyanide, etc., has been interpreted in terms of the need for strongly "ionic" ligands to prevent decomposition.[16]

One of the earliest proofs of the dimeric nature of the mercury(I) ion was similarly the observation by Woodward[17] in an aqueous solution of mercury(I) nitrate of the Raman line due to Hg_2^{2+} at 169 cm.$^{-1}$. Inasmuch as the bond distance is found to be markedly dependent on the anion or solvent (above), comparison of the force constant for cadmium with that for Hg_2^{2+} might better be done for a mercury system with an anion with a similar low tendency for covalent bonding. In the absence of Raman data for $Hg_2(AlCl_4)_2$, the force constant for Hg_2^{2+} in aqueous solution (1.68 mdynes/Å.), with a bond length presumably comparable to that in solid $Hg_2(H_2O)_2(NO_3)_2$, therefore has been converted to that appropriate to the shorter distance in the more ionic Hg_2F_2 by means of Badger's rule.[18] Although the result, 2.52 mdynes/Å., is necessarily approximate, it is in striking contrast to the 1.11 quantity obtained for Cd_2^{2+}; the relative bond strengths can be expected to vary in roughly the same manner. Thus relative to mercury, the instability of the cadmium(I) ion in the solid state with the more basic anions appears to result not only from the relative magnitudes of the lattice energies of the compounds in the two oxidation states, plus other fixed terms in the Born-Haber cycle,[4] but also from the somewhat weaker Cd–Cd bond itself.

The almost unique character of the Hg_2^{2+} ion emphasized by the above results and by the generally greater stability of the mercury(I) state with respect to disproportionation may be considered to be unusual in view of the usual decrease in stability of catenated compounds of the representative elements with increasing atomic number within the group. As this aspect does not appear to have been discussed previously, it is instructive to consider first further evidence for a like relationship in other related systems and then a possible explanation for this behavior.

Several pairs of diatomic molecules or ions comparable to Cd_2^{2+} and Hg_2^{2+} are found to show the same order of stability. For example, trends in bond properties in the M_2^{2+} ions for the zinc family elements might be expected to be reflected in the respective MH^+ compounds, as the M–H bond in these can be considered to be roughly comparable to a simple sigma bond in M^+–M^+. In this case HgH^+ is indeed found to have a notably larger force constant than CdH^+ (2.44 *vs.* 1.85 mdynes/Å.) and, although the data here are only approximate, apparently a higher dissociation energy (~53 *vs.* ~46 kcal./mole).[12] The suitability of these compounds for the present comparison appears to be substantiated by the agree-

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[12] G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1950, Table 39, p. 502ff.

[13] R. Wyckoff, "Crystal Structures," Vol. I, Interscience Publishers, Inc., New York, N. Y., chap. 3, p. 43.

[14] D. Grdenić, *J. Chem. Soc.*, 1316, 1312 (1956).

[15] K. Broderson and L. Kunkel, *Chem. Ber.*, **91,** 2698 (1958).

[16] T. Yamane and N. Davidson, *J. Am. Chem. Soc.*, **82,** 2123 (1960).

[17] L. A. Woodward, *Phil. Mag.*, **18,** 823 (1934).

[18] L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N. Y., 1960, p. 231. The quantities 2.0 and 2.32 were used in Badger's rule for a_{ij} for M_2^{2+} and MH^+, respectively, to evaluate the more important b_{ij}.

ment between the covalent radius of Hg^+ calculated from HgH^+ with that in Hg_2^{2+}. With 0.37 Å. (0.5 d_{H_2}) as the radius of hydrogen, the bond length of 2.45 Å. calculated for Hg_2^{2+} compares very well with the 2.43 ± 0.04 Å. reported[14] in the fluoride. Since d_{HgH^+} is 0.07 Å. *less* than d_{CdH^+},[12] the same calculation gives 2.59 Å. for the bond in Cd_2^{2+}, in qualitative agreement with the lower force constant for the lighter ion. Alternatively, a distance of *ca.* 2.64 Å. in Cd_2^{2+} can be estimated by means of Badger's rule from the experimental force constant and data for MH^+ and Hg_2^{2+}.[18]

The validity of the above conclusions regarding the unusually tight binding in Hg_2^{2+} and HgH^+ *vs.* the respective cadmium species appears to be supported by the properties known for the isoelectronic counterparts of these compounds found with the copper family elements. Thus, for Au_2 and Ag_2, the force constants are 2.11 and 1.18 mdynes/Å.[19] (comparable to those cited here for M_2^{2+}), while the D_0^0 values are 2.18 and 1.63 e.v., respectively.[20] Similarly, k_e and D_0^0 for AuH are 73 and 24% greater, respectively, than those recorded for AgH, and the bond in the latter is reported to be about 0.09 Å. longer.[12] The disproportionate stability of Au_2 with respect to its position in the periodic table has been noted by Drowart and Honig.[20]

Returning to the M_2^{2+} ions, it is a remarkable fact that formation of ions of this type in condensed states apparently is limited to ions of the zinc family with the configuration $(n - 1)d^{10}ns^1$, and furthermore, that the diatomic mercury(I) example is almost singular in its stability and is in fact totally unique under more familiar conditions. This behavior is worthy of further comment, for in spite of the long-standing knowledge of the existence of this ion, an explicit explanation for it has not been noted. It appears that this may be accomplished in terms of more fundamental effects manifested in the ionization energies and in other related properties of the representative elements in group II.

A useful interpretation of trends in the strength of covalent bonding by a series of ions of the same charge has been given[21] in terms of the variation in energy for the last ionization step leading to the ion in question. This relationship is based on the observation that the inverse of this ionization step is somewhat related to the process accompanying the formation of a covalent bond. In the present case, the electron affinity of M^+, *i.e.*, the negative of the ionization energy leading to M^+, for the elements mercury and cadmium may be considered to relate to the energy derived through attainment of a roughly analogous configuration by the reaction $2M^+ \rightarrow M_2^{2+}$. It is noteworthy that the first ionization potential of mercury, 10.4 e.v., is 1.4 e.v. greater than that for cadmium and is, in fact, at least 1 e.v. greater than that for any other metal. Thus, when considered according to the above relationship, the prominence of the Hg_2^{2+} ion is qualitatively in accord with the unusually large electron affinity of Hg^+. The source of this energy anomaly doubtless arises from the poor nuclear shielding by the 5d and, particularly, the additional 4f electrons, an effect that is especially important in Hg_2^{2+} (HgH^+ and Au_2) where the bonding electrons presumably have a large amount of s character and hence are highly penetrating. This also gives more explicit interpretation of the "inert pair effect" as applied to the unique properties of elemental mercury.[22] The covalent proclivities of the more common mercury(II) state also can be attributed to the high effective field on bonding electrons.[23] Thus in this case the effect of the "lanthanide contraction" is manifested in a different manner that serves to make the sixth period elements markedly different from, rather than more similar to, those in the fifth period as found among the transition groups.

Finally, the species ZnH^+, CuH, and Cu_2 have force constants, bond strengths, etc., that are in between those of the corresponding compounds of the fifth and sixth period elements already considered. There is, however, no direct evidence for the homoatomic ion Zn_2^{2+}. The effect of the anion in the liquid system is particularly important in this case. The apparent reduction of the associated $ZnCl_2$(l) by zinc metal is relatively slight,[2] and attempted substitution of less basic anions for chloride through addition of the acids such as $AlCl_3$ and $BeCl_2$ does not have a substantial effect on the magnitude of the reduction.[24]

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(19) B. Kleman and S. Lindkvist, *Arkiv Fysik*, **9**, 385 (1955); B. Kleman, S. Lindkvist, and L. E. Selin, *ibid.*, **8**, 595 (1954).

(20) J. Drowart and R. E. Honig, *J. Phys. Chem.*, **61**, 980 (1957).

(21) H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953); A. E. Martell and M. Calvin, "Chemistry of Metal Chelate Compounds," Prentice Hall, Inc., New York, N. Y., 1952, p. 188.

(22) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Oxford University Press, London, 1950, p. 286.

(23) D. F. C. Morris and L. H. Ahrens, *J. Inorg. Nucl. Chem.*, **3**, 263 (1956).

(24) W. J. Burkhard, S. von Winbush, and J. D. Corbett, unpublished research.