Synthesis of *P*-Amino-*P*′-benzyltriethylenediphosphonium Dichloride.—To 7.0 g (14.4 mmol) of dibenzyltriethylenediphosphonium dibromide dissolved in 50 ml of tetrahydrofuran was added an excess of lithium aluminum hydride. The stirred mixture was refluxed for 6 hr until it was uniformly gray. The solvent was removed under vacuum and 50 ml of undried ether was carefully added. Hydrolysis was completed by the addition of 20% aqueous sodium potassium tartrate solution. The ether layer was separated under nitrogen, dried, and evaporated to yield a very small amount of waxy solid.

To a benzene solution of this waxy solid was added about 9 mmol of chloramine dissolved in benzene. A white precipitate formed immediately. This precipitate was filtered, washed repeatedly with hot benzene, and dried under vacuum. About 0.42 g of crude product was obtained. It was heated at 100° under high vacuum to remove traces of ammonium chloride; mp 160–165° dec. *Anal.* Calcd for $C_{13}H_{21}P_2NCl_2$: C, 48.17; H, 6.53; N, 4.32; P, 19.11; Cl, 21.87. Found: C, 46.8; H, 6.7; N, 4.8; P, 19.7; Cl, 22.0. Infrared data (Table II) and nmr data (Table III) are consistent with this formulation.

The Reaction of Chloramine with 1,2,5-Triphenylphosphole.—A 1.01-g (3.2-mmol) sample of 1,2,5-triphenylphosphole was dissolved in a mixture of 75 ml of benzene and 25 ml of ether. An ether solution of chloramine (5 ml, 0.93 *M* NH_2Cl) was added rapidly by pipet to the stirred soluton in the dark. A voluminous yellow precipitate formed immediately. Stirring was continued overnight. The precipitate was filtered, dried under vacuum, and heated for 1.5 days at 80–90° under high vacuum to remove ammonium chloride. It was finally washed with benzene and dried; yield 0.96 g (79% of theory); mp 210–211°. *Anal.* Calcd for $C_{22}H_{19}PNCl$: C, 72.63; H, 5.26; N, 3.85; P, 8.51; Cl, 9.75. Found: C, 72.4; H, 5.2; N, 3.8; P, 8.7; Cl, 9.8.

The material is soluble in water and alcohols, reacts with chloroform and dimethyl sulfoxide, and is slightly soluble in benzene and insoluble in ether. Infrared data and nmr data are listed in Tables II and III, respectively.

Reaction of 1,2,5-triphenylphosphole with the ammonia–chloramine mixture from a chloramine generator and exposure of the mixture to light resulted in an as yet uncharacterized product with a P:N ratio of 1:3.

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY,
ATLANTA, GEORGIA 30332

Brillouin Spectra of Solutions. II.[1] Molecular Weights of Acetylacetonate Complexes of Magnesium(II) and Nickel(II)

BY FRANK I. SAN FILIPPO, GEORGE A. MILLER,* AND J. AARON BERTRAND

Received August 23, 1971

Measurement of the intensity of light scattered by a solution relative to the incident beam intensity is a standard procedure for obtaining the weight-average molecular weight of the solute. We have shown previously[1] that one can avoid reference to the incident beam by resolving the scattered light into its Brillouin spectrum of three peaks. If the scattering angle is 90° and the incident light is in the visible region, then the two side peaks are displaced by about 0.1–0.2 cm^{-1} from the unshifted central peak. A highly monochromatic laser is used and the spectrum is resolved with an interferometer. For a dilute, ideal solution, the ratio of intensities of central to side peaks, J, is related to the weight-average molecular weight, M, by the equation $J = J_0 + S(\partial n/\partial c)^2Mc$, where J_0 is the value of J of the pure solvent, n is the refractive index of the solution, and c is the concentration of solute in grams per milliliter. S is a solvent-dependent term given by $S = (J_0 + 1)(\gamma - 1)C_p/\gamma RT^2(\partial n/\partial T)^2$, where γ is the ratio of heat capacities, C_p/C_v, of the solvent, R is the gas constant, T is the absolute temperature, and C_p is the constant-pressure heat capacity of 1 ml of solvent. The quantity S may be determined experimentally using a solute of known molecular weight or calculated using literature values of γ, C_p, and perhaps $\partial n/\partial T$. The molecular weight is calculated from the slope of J *vs.* c. Due to the narrowness of the Brillouin spectrum, adsorption by the solution will attenuate all three peaks equally, and no Beer's law correction is required. We report here the application of this method to the hydrated and anhydrous acetylacetonates of divalent magnesium and nickel.

Experimental Section

The procedure for obtaining the Brillouin spectra with a Ne–He laser (6328 Å) has been described.[1] For colored solutions, a small rectangular fluorimeter cell was used in place of the standard square turbidity cell, and the scattered light was collimated with a spherical lens focused close to one corner of the cell, such that the point from which scattering was observed was about 4 mm from where the incident beam entered and the 90° scattered light left the solution. This represented a balance between minimizing loss of intensity from absorption and minimizing stray scattering from the surfaces of the cell. Extinction coefficients were measured at 6328 Å and the loss in the most concentrated solutions was estimated: NiA_2, 58%; $NiA_2 \cdot 2H_2O$, 40%. Refractive increments were measured on either a Brice-Phoenix differential refractometer or a Bausch and Lomb precision refractometer with the laser as source. The concentration of each solution was determined after the light-scattering measurement by evaporating an aliquot to dryness and weighing. The light-scattering data are given in Table I. A typical spectrum is shown in Figure 1.

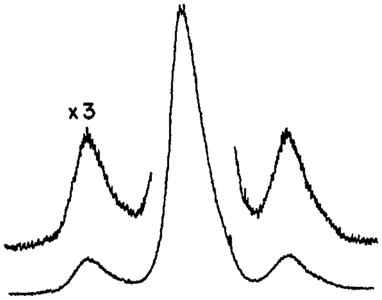

Figure 1.—Spectrum of light scattered by magnesium acetylacetonate in dichloromethane; $c = 2.90 \times 10^{-3}$ g/ml. The central peak is at the incident wavelength, 6328 Å; the side peaks are displaced, 0.05 Å (0.12 cm^{-1}).

Eastman recrystallized naphthalene was used to evaluate S, the solvent parameter, of DMF. Practical 2,4-pentanedione (acetylacetone) was used in the preparations. Otherwise, ACS Certified reagents were used in the preparations and as light-scattering solvents. Nickel(II) acetylacetonate dihydrate ($Ni(C_5H_7O_2)_2 \cdot 2H_2O$) was prepared by a standard procedure.[2] The anhydrous nickel acetylacetonate ($Ni(C_5H_7O_2)_2$) was prepared by heating the dihydrate *in vacuo* at 100° for 12 hr. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Magnesium was analyzed gravimetrically by heating to MgO and volumetrically by EDTA titration. Water of hydration was determined by thermal gravimetric analysis.

Magnesium Acetylacetonate Dihydrate, $Mg(C_5H_7O_2)_2 \cdot 2H_2O$.—A mixture of 6.1 g of magnesium in 100 ml of 2,4-pentanedione was stirred 48 hr at room temperature. Heating to increase the reaction rate also increased the amount of polymeric

---

[1] Part I: G. A. Miller, F. I. San Filippo, and D. K. Carpenter, *Macromolecules*, **3**, 125 (1970).

[2] W. C. Fernelius and B. E. Bryant, *Inorg. Syn.*, **5**, 105 (1957).

TABLE I

EXPERIMENTAL INTENSITY RATIOS, J, AT 25°

10^3c, g/ml	J	10^3c, g/ml	J	10^3c, g/ml	J
—$MgA_2 \cdot 2H_2O$ in CH_3OH—		—$MgA_2 \cdot 2H_2O$ in DMF—		—$C_{10}H_8$ in DMF—	
0	0.25	0	0.38	0	0.38
2.75	0.38	2.39	0.41	53.12	1.24
7.15	0.53	5.76	0.45	58.87	1.31
10.90	0.62	9.55	0.50	68.94	1.45
13.36	0.70	15.27	0.58	80.20	1.62
25.06	1.09	25.17	0.72	94.75	1.87
		36.64	0.88		
—MgA_2 in CH_2Cl_2—		—$NiA_2 \cdot 2H_2O$ in CH_3OH—		—NiA_2 in CCl_4—	
0	0.71	0	0.25	0	0.74
2.47	3.06	3.88	0.43	3.80	0.84
2.90	3.29	5.60	0.48	7.60	0.91
		8.40	0.57	11.40	1.06
		16.80	0.85	15.82	1.22
				24.07	1.52

by-product. The white, solid product was recrystallized several times from methanol. Pumping on the product in a vacuum oven at 100° through a cold trap followed by gas chromatographic analysis of the condensate confirmed that it was hydrated rather than methylated. *Anal.* Calcd: H_2O, 13.9. Found: H_2O, 14.3.

Magnesium Acetylacetonate, $Mg(C_5H_7O_2)_2$.—The dihydrate was heated *in vacuo* at 100° for 12 hr. *Anal.* Calcd: Mg, 10.9; C, 54.0; H, 6.3. Found: Mg, 10.8; C, 5319; H, 6.4.

Results and Discussion

The evaluation of the solvent parameters is summarized in Table II; the results are given in Table III.

TABLE II

SOLVENT PARAMETERS AT 25°

	J_0	γ	C_p, cal/ml deg[a]	$10^4\partial n/\partial T$	S, mol/ml
Methanol	0.25	1.205[b]	0.4760[c]	−3.90[d]	3.75
Methylene chloride	0.71	1.521[e]	0.3748[e]	−6.0[f]	3.43
Carbon tetrachloride	0.74	1.440[b]	0.3243[g]	−5.74[d]	2.95
Dimethylformamide					4.42[h]

[a] Densities for converting to these units came from the reference in footnote *f*. [b] E. B. Freyer, J. C. Hubbard, and D. H. Andrews, *J. Amer. Chem. Soc.*, **51,** 759 (1929). [c] H. G. Carlson and E. F. Westrum, Jr., *J. Chem. Phys.*, **54,** 1464 (1971). [d] Measured in this laboratory at 6328 Å. [e] J. L. Hunter and H. D. Dardy, *J. Chem. Phys.*, **42,** 2961 (1965). [f] "Selected Values of Properties of Chemical Compounds," Manufacturing Chemists Association Research Project, Thermodynamics Research Center, Texas A & M University, College Station, Texas. [g] J. F. G. Hicks, J. G. Hooley, and C. C. Stephenson, *J. Amer. Chem. Soc.*, **66,** 1064 (1944). [h] Determined experimentally using naphthalene: $\partial n/\partial c = 0.166$, $J - J_0 = 15.6c$, $M = 128.17$.

TABLE III

SOLUTION PARAMETERS AND WEIGHT-AVERAGE MOLECULAR WEIGHTS AT 25°

Complex[a]	Formula wt	Solvent	$\partial n/\partial c$	dJ/dc[b]	M
$MgA_2 \cdot 2H_2O$	258.6	CH_3OH	0.190	32.6	241
$MgA_2 \cdot 2H_2O$	258.6	DMF	0.104	13.7	287
MgA_2	222.5	CH_2Cl_2	0.0966	911	28,500
$NiA_2 \cdot 2H_2O$	293.0	CH_3OH	0.182	34.8	280
NiA_2	256.9	CCl_4	0.0708	32.8	2,220

[a] A = acetylacetonate ligand ($C_5H_7O_2$). [b] From a linear least-squares fit to the data in Table I.

The hydrates, which are monomeric as expected, bind their water strongly and may be recrystallized unchanged from the coordinating solvents in which they were studied. Not surprisingly, we found the molecular weight of MgA_2 in CH_2Cl_2 to be quite sensitive to traces of water. The solubility of water in CH_2Cl_2[3] is such that, at the highest concentration of MgA_2, there would be enough water to hydrate 39% of the MgA_2 if the solvent were previously saturated with water. We removed traces of water by dissolving MgA_2 in hot CH_2Cl_2 and cooling to 0° to precipitate essentially all the complex. Because of the much lower solubility of water in CCl_4,[3] we did not attempt to dry this solvent.

Our results for NiA_2 are not necessarily incompatible with earlier ebullioscopic results in CCl_4,[4] which yielded a number-average molecular weight equivalent to that of the trimer, but only point to a broad distribution of oligomers. This situation has been already suggested for the analogous cobalt complex, CoA_2.[5] As a simple example of the effect of a broad distribution, equal-weight fractions of $(NiA_2)_2$ and $(NiA_2)_{14}$ would yield a number-average molecular weight of 900 and a weight-average value of 2056.

Acknowledgment.—This research was supported in part by a grant from the National Science Foundation (GP-9224).

---

(3) C. Marsen and S. Mann, "Solvents Guide," Interscience, New York, N. Y., 1963.

(4) J. P. Fackler and F. A. Cotton, *J. Amer. Chem. Soc.*, **83,** 3775 (1961).

(5) F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3,** 1 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA,
AND THE INORGANIC MATERIALS RESEARCH DIVISION,
LAWRENCE BERKELEY LABORATORY,
BERKELEY, CALIFORNIA 94720

Nitrogen 1s Binding Energies of Some Azide, Dinitrogen, and Nitride Complexes of Transition Metals

BY PATRICIA FINN AND WILLIAM L. JOLLY*

Received October 1, 1971

We have used X-ray photoelectron spectroscopy to determine the nitrogen 1s binding energies of azide, dinitrogen, and nitride complexes of several transition metals. Such data are of interest because the binding