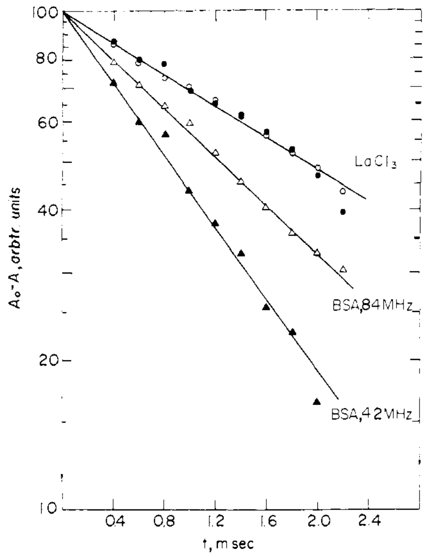

Figure 1. The exponential decay of the magnetization difference (in normalized arbitrary units) of ^{139}La as a function of the time interval, t, between the 180 and 90° pulses in the presence (triangles) and the absence (circles) of BSA at 8.4 (open symbols) and 4.2 MHz (filled symbols).

Table I. Longitudinal Relaxation Rates (in sec^{-1}) of Lanthanum-139 in the Absence and in the Presence of BSA

	8.4 MHz	4.2 MHz
$LaCl_3$	365 ± 8	361 ± 10
$LaCl_3$ + BSA	568 ± 12	835 ± 10
$1/T_{1p}$	203 ± 20	474 ± 20

that lanthanum-139, a nucleus of spin $I = 7/2$ with natural abundance of 99.91% and NMR sensitivity (relative to that of protons) of 5.92% should be a good NMR probe. Presented in this communication are our preliminary results of the relaxation rates of lanthanum-139 in solutions containing bovine serum albumin (BSA). The binding of lanthanides to BSA has previously been established from studies of water proton relaxation rates using Gd^{3+} as a paramagnetic probe and from difference spectra of Nd^{3+}.[7]

The lanthanum-139 magnetic resonance was observed at 8.4 and 4.2 MHz with a Bruker Model 322S Pulsed NMR spectrometer equipped with a Hewlett-Packard Model 5480A signal analyser. Longitudinal relaxation rates, $1/T_1$, were determined by the 180-90° pulse method, by which the magnetization amplitude A is measured as a function of the time interval, t, between the two pulses and the relaxation time obtained from the relation

$$A = A_0[1 - 2\exp(-t/T_1)] \qquad (2)$$

where A_0 is the amplitude in the absence of the 180° pulse.[8] The uncertainty in the $1/T_1$ values obtained in the present work is estimated to be less than ±5%.

All solutions were made in 50 mM MES (2[N-morpholino]ethane sulfonic acid) buffer at pH 6.2 with tetramethylammonium as the cation. The protein solutions contained 0.9 mg/ml BSA (1.3×10^{-5} M) and the $LaCl_3$ concentration was 0.18 M. Measurements were done at the ambient probe temperature of 23 ± 2°.

The differences of the magnetization amplitudes, $A_0 - A$, obtained in solutions of $LaCl_3$ in the presence and in the absence of BSA are shown in Figure 1. The decays are exponential with the time interval, t, between the pulses, as predicted by eq 2. It is seen that the relaxation is faster in the presence of BSA and that the relaxation rate is further enhanced at the lower frequency, whereas the relaxation rate in the absence of protein is frequency independent within the limits of experimental error. The relaxation rates calculated using eq 2 are summarized in Table I.

The observed relaxation rate in the protein solution is the weighted average of the relaxation rates of the free and complexed species, which for a dilute protein solution (in which the concentration of free La^{3+} is very little changed) and rapid chemical exchange is given by[9]

$$1/T_{1,\mathrm{obsd}} = 1/T_{1\mathrm{f}} + P_{\mathrm{b}}/T_{1\mathrm{b}}$$

and by defining the "excess relaxation",

$$1/T_{1\mathrm{p}} \equiv 1/T_{1,\mathrm{obsd}} - 1/T_{1\mathrm{f}}$$

one obtains, $1/T_{1\mathrm{p}} = P_{\mathrm{b}}/T_{1\mathrm{b}}$, where P_{b} is the fraction of complexed species and $1/T_{1\mathrm{b}}$ is their relaxation rate. It is $1/T_{1\mathrm{b}}$ that is related to the correlation time and the resonance frequency by eq 1. Thus the ratio of the $1/T_{1\mathrm{p}}$ values at the two frequencies contains only the correlation time, τ_c, as an unknown, and it can readily be calculated. From the results in Table I we obtain $\tau_c = 2.25 \times 10^{-8}$ sec with an estimated uncertainty of ±10%. At present a small contribution of chemical exchange to the relaxation rates cannot be ruled out and therefore our value of τ_c should be regarded as a lower limit. We note, however, that this value is in excellent agreement with the value of 2.0×10^{-8} sec calculated[3] from the Stokes-Einstein formulas.

The results presented here indicate that lanthanum-139 should be a useful NMR probe for studying macromolecular dynamics in solution.

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Salt-Molecule Matrix Reactions. Infrared Spectra of the $M^+HCl_2^-$ and $M^+Cl_3^-$ Ion Pairs in Solid Argon

Sir:

In 1968 Noble and Pimentel[1] condensed the microwave discharge products of Ar-HCl-Cl_2 samples and assigned new infrared bands to the HCl_2 radical. Subsequently, Milligan and Jacox[2] observed the same species by vacuum ultraviolet photolysis of HCl and mercury-arc photolysis of alkali atom-HCl samples and suggested the HCl_2^- identification. Similar controversies have arisen over HBr_2 radical[3] or anion.[4] The matrix reaction of an alkali chloride salt and HCl should produce the ion-pair $M^+HCl_2^-$ for investigation of the HCl_2^- spectrum. Nelson and Pimentel[5] observed

Table I. New Infrared Absorptions (cm^{-1}) Observed Following Salt Vapor Matrix Reactions with Cl_2, HCl, and DCl

	Cl_2	HCl	DCl
NaCl	375	658, 709	436
KCl	345	736, 682	498
RbCl	338	729	512
CsCl	327	723	507

an infrared absorption at 374 cm^{-1} following discharge and deposition of chlorine-krypton mixtures which was assigned to the Cl_3 radical. This band has been produced by the matrix reaction of sodium and chlorine.[6] Likewise, the reaction of NaCl and Cl_2 is expected to produce $Na^+Cl_3^-$, which provides a clean synthetic route to the trichloride anion.

Samples of reactant gas and argon (M/R = 400/1) were deposited on a CsI window at 15 K.[7] The alkali chloride salt vapor was produced by evaporation from a Knudsen cell and deposited simultaneously with the gas sample. Approximately 600° was required to produce the necessary vapor pressure of NaCl, while 545° was used for KCl, 520° for RbCl, and 490° for CsCl. Spectra were recorded after 20-30 hr of sample deposition using a Beckman IR-12 infrared spectrophotometer.

NaCl and KCl were each deposited in argon without added reagent, and the spectra were in agreement with the major features previously reported.[8] In addition, a weak new band at 472 cm^{-1}, labeled A in Figure 1, persisted in all of these experiments regardless of reagent. The 472-cm^{-1} feature is believed to be due to a salt-water complex since it was enhanced by adding water to the sample.

A complete salt-reaction study was done with NaCl, KCl, RbCl, and CsCl and the reagent molecules Cl_2, HCl, and DCl. The KCl experiments, illustrated in Figure 1, will be described here; new bands observed in all of the salt studies are listed in Table I. KCl was deposited with a sample of Ar/Cl_2 = 400/1, and the spectrum of this reaction mixture showed one new band at 345 cm^{-1} (0.36 OD) in addition to the 247-cm^{-1} KCl absorption. When KCl was deposited with HCl, two new bands were observed at 736 and 682 cm^{-1} with optical densities of 0.82 and 0.25, respectively. KCl was treated with an HCl-DCl-argon sample and the last spectrum in Figure 1 showed a D/H product ratio of about 2/1. The 736- and 682-cm^{-1} bands were again observed along with an intense new band at 498 cm^{-1}.

The reaction of an alkali chloride with Cl_2 is expected to form the ion pair $M^+Cl_3^-$ on the basis of reaction energetics. This reaction is exothermic for charge separations less than 2.8 Å, and exothermic by 15 kcal/mol for a charge separation of 2.5 Å, as estimated from ionization potentials, electron affinities, and bond strengths of the reactants and products.[9] With the size of the ions formed in these reactions, the reaction to form the alkali-trihalide ion pair is anticipated. In support of this proposal, the crossed-molecular beam reaction of CsI and Cl_2 formed a $Cs^+(ClICl)^-$ collision complex which persisted for many vibrational periods.[10] In the present matrix experiments, the collision complex was stabilized.

The reaction of NaCl with Cl_2 produced a new infrared band at 375 cm^{-1}. In Raman studies on these samples, a very strong band was observed at 275 cm^{-1} with no signal at 375 cm^{-1}.[11] Unfortunately, the strong $(NaCl)_2$ band at 273 cm^{-1} in the infrared spectrum makes it impossible to rule out the presence of infrared absorption at 275 cm^{-1}. Nevertheless, the Raman spectrum of NaCl + Cl_2 products and the previously reported Na + Cl_2 study[6] indicates the linear symmetric ($D_{\infty h}$) structure for Cl_3^- in the $Na^+Cl_3^-$ species. Vibrational assignments of the 375-cm^{-1} infrared band to ν_3 and the 275-cm^{-1} Raman band to ν_1 of Cl_3^- follow.

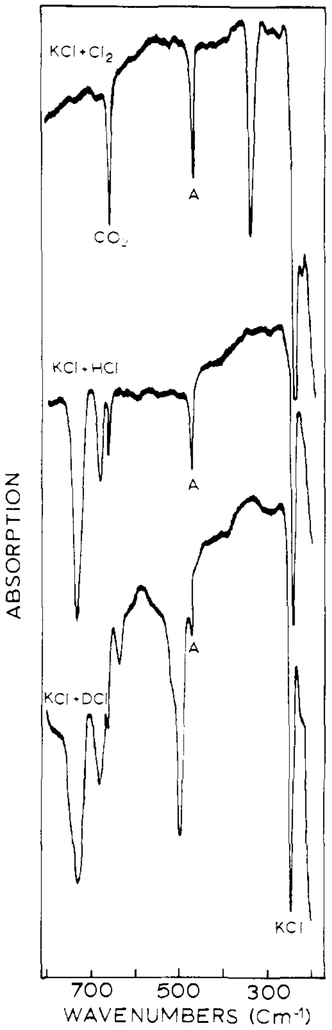

Figure 1. Infrared spectra of the products of matrix reactions of KCl with Cl_2, HCl, and DCl. The top trace represents the spectrum of the reaction mixture of KCl with Ar/Cl_2 = 400/1, over the spectral range 200–800 cm^{-1}. The middle spectrum shows the reaction of KCl with HCl and the bottom trace shows the reaction of KCl with DCl and HCl, with D/H = 2, and M/R = 400/1. The label A denotes a KCl-H_2O complex.

Nelson and Pimentel[5] observed a structured 374-cm^{-1} absorption from a species formed by glow discharge of krypton-chlorine samples. In subsequent experiments by Noble using more dilute samples, the mixed isotopic splittings were removed; these data indicate that a $D_{\infty h}$ trichlorine species was trapped in the matrix.[12] In view of the observation of the 375-cm^{-1} band in Na and NaCl matrix reactions with chlorine[6] and in proton radiolysis of argon-chlorine samples,[13] it is necessary to reassign the band of Nelson and Pimentel to Cl_3^-. Recent work has indicated that the geometry of the microwave discharge apparatus is crucial to the nature of the products.[13] When the glow of the discharge extends almost to the cold surface,[1,3] ions may be trapped, while if the glow is kept a considerable distance (4-5 cm) from the cold surface, only radicals are trapped.[14]

Distortion of the well-known triiodide ion from $D_{\infty h}$ to $C_{\infty v}$ symmetry, as a function of crystal environment and cation size, is well known.[15-17] It is suggested here that trichloride ion in the K^+, Rb^+, and $Cs^+Cl_3^-$ species is linear asymmetric, which accounts for the decrease in the ν_3 trichloride frequency in the direction of 232 cm^{-1} found for the asymmetric Cl_3^- ion in benzene solution in the presence of tetra-*n*-butylammonium cation.[18]

The reaction of KCl and HCl produced a very intense band at 736 cm^{-1} and a weak absorption at 682 cm^{-1}. The ν_3 antisymmetric vibration of linear, symmetric HCl_2^- in crystals with large cations has been observed in this spectral region,[19] and matrix-isolated $M^+HCl_2^-$ should give a similar absorption. The 736-cm^{-1} band is, therefore, assigned to ν_3 of HCl_2^- in the $K^+HCl_2^-$ species; the weaker 682 cm^{-1} feature is presumably due to the same species in a different matrix site. The 736-cm^{-1} band shifted to 498 cm^{-1} when DCl was employed. The intense doublet in Figure 1 indicates that only a single hydrogen is involved in the vibration, which supports the assignment to HCl_2^-. Also, the H/D frequency ratio is 1.48, while the anticipated harmonic ratio is only 1.41. This is due to dominance of the anharmonicity by a positive quartic term in the potential function, and the absence of a cubic term, which requires a linear, centrosymmetric structure for the HCl_2^- species, as discussed by Noble and Pimentel.[1] Raman spectra of the $Rb^+HCl_2^-$ species produced a weak, reproducible signal at 250 cm^{-1}.[11] This band, attributed to ν_1 of HCl_2^-, is near the 260-cm^{-1} value deduced from the 956-cm^{-1} assignment to $\nu_1 + \nu_3$ of isolated HCl_2^-.[2]

It is clear that the 736-cm^{-1} band observed from the reaction of KCl with HCl is due to ν_3 of HCl_2^- in $K^+HCl_2^-$ with a linear symmetric geometry for the anion. The band assigned to ν_3 of the HCl_2 radical by Noble and Pimentel[1] was observed at 696 cm^{-1}, and the same band was assigned to the HCl_2^- anion by Milligan and Jacox.[2] While the $M^+HCl_2^-$ frequencies listed in Table I do not exactly match their observed frequency, the agreement is substantial, and we must conclude that the band at 696 cm^{-1} in these earlier works was in fact due to the isolated HCl_2^- anion. Noble and Pimentel formed this species using a microwave discharge, and it is apparent that the position of their discharge tube led to the trapping of ionic species. In fact, recent quantum mechanical calculations predict linear symmetric FHF to be unstable and infer that ClHCl is likewise unstable.[20]

Reactions of salt molecules and hydrogen chloride in argon matrices have led to the HCl_2^- anion in the species $M^+HCl_2^-$. Comparison of the ν_3 frequencies and deuterium shifts observed here and those observed in microwave and photolysis work has led to the conclusion that the species assigned to the HCl_2 radical by Noble and Pimentel[1] is in fact the isolated anion HCl_2^-, as assigned by Milligan and Jacox.[2] Similar salt-chlorine reactions have produced the $M^+Cl_3^-$ species and identified ν_3 of the trichloride anion. It is clear that the salt-molecule matrix reaction, in essence an ion-molecule reaction, is an effective method of preparing polyatomic ionic molecules for spectroscopic study.

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Unusually Large Platinum-Phosphorus Coupling Constants in Platinum(0) Tetraphosphine Complexes

Sir:

Owing to the tendency of $Pt(PR_3)_4$ compounds (R = aryl or alkyl groups) to dissociate in solution and to the synthetic difficulties of preparing mixed complexes of the type $Pt(PR_3)_2(PR'_3)_2$, very little data are available in the literature concerning the magnitudes of Pt-P and P-P couplings for platinum(0) complexes.[1] Using the triphosphine ligand $CH_3C(CH_2PPh_2)_3$, we have isolated and characterized a series of *dissociatively stable* platinum(0)-tetraphosphine complexes of the type Pt(triphosphine)PR_3.[2]

For these complexes the Fourier transform ^{31}P pattern is essentially first order and consists of a doublet (intensity 3) with platinum-195 satellites and a quartet (intensity 1) with its platinum satellites. The Pt-P coupling observed for the triphosphine ligand (Table I) decreases systematically from 3098 ± 2.4 to 2867 ± 2.4 Hz as the monodentate phosphine changes from $(p\text{-tolyl})_3P$ to PF_3, whereas the Pt-P coupling for the monodentate phosphine increases dramatically in the series $PPh_3 < P(OCH_2)_3CCH_3 < PF_2NMe_2 < P(OPh)_3$. The magnitudes of the Pt-P couplings for the monodentate phosphines are approximately *double* the Pt-P values observed in trans Pt(II) complexes and approximately *55%* larger than the Pt-P couplings in *cis*-$PtCl_2(PR_3)_2$ complexes of the corresponding PR_3 phosphines.[1] Although there are few examples available for direct comparison of the Pt-P and P-P couplings in Pt(II) and Pt(0) complexes of the same ligand, the data for the Me_2NPF_2 complex illustrate the increased Pt-P couplings to the monodentate ligand in our mixed Pt(triphosphine)(PR_3) compounds. The Pt-P coupling in *cis*-$PtCl_2(PF_2NMe_2)_2$ is ~5690 Hz,[3] whereas the Pt-P coupling in Pt(triphosphine)(PF_2NMe_2) is 8838 Hz. Also, the $^2J_{P-P}$ values are considerably larger than found in *cis*-$PtCl_2(PR_3)_2$ complexes. The larger coupling constants do not arise from the different oxidation state of platinum, as the $^1J_{Pt-P}$ and $^2J_{Pt-F}$ values for $Pt(PF_3)_4$ are 6480 and 421 Hz, respectively.[3]

In the few cases where the same PR_3 ligand has been used on both zero-valent platinum and tungsten, a plot of $^1J_{Pt-P}$ against $^1J_{W-P}$ is nearly linear.[4] For example, the phosphite and PF_3 complexes always exhibit the largest values of $^1J_{M-P}$ and $^2J_{P-M-P}$ within their respective series. Except for the ligand Me_2NPF_2, the increasing $^2J_{P-P}$ values are linearly related to the increasing values of $^1J_{Pt-P}$. Unusual $^2J_{P-P}$ values have been observed previously[4-6] for a number of phosphine ligands containing dialkylamino groups.

Using the complex $Pt(Ph_2PCH_2CH_2CH_2PPh_2)_2$[2] (which has four equivalent nonexchanging phosphorus nuclei over