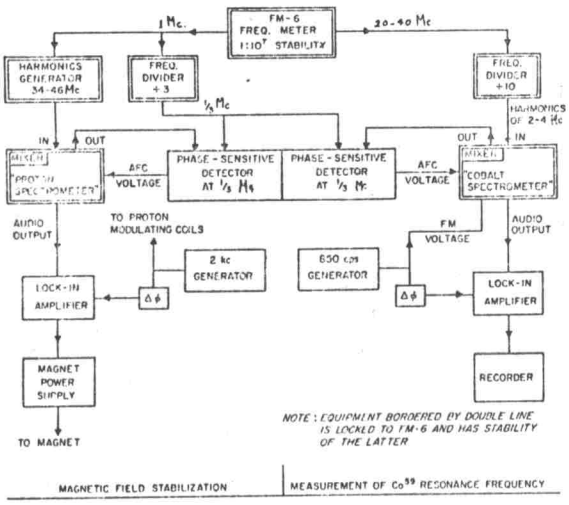

FIG. 1. Block diagram of field and frequency stabilization system.

orbital moment is given by $\sigma_p = \Delta H/H \approx 6\beta^2 \langle 1/r^3 \rangle / \Delta$. By carrying out this line of argument rigorously using Ramsey's[5] general formula for the chemical shift Orgel and Griffith[4] find

$$\sigma_p = 32\beta^2 \langle 1/r^3 \rangle_{3d} (1/\Delta), \tag{2}$$

where Δ is the splitting between the $^1A_{1g}$ ground state and $^1T_{1g}$ excited state using the strong field limit of crystal-field theory. There is, of course, a diamagnetic contribution (σ_d) to σ from the Larmor circulation. However, in the case of the Co^{3+} complexes $\sigma_d \sim 0.1\%$ while $\sigma_p \sim 1\%$.

Freeman, Murray, and Richards studied the chemical shift of a number of cobalt complexes in aqueous solution, and also determined Δ for each complex. By plotting σ vs $(1/\Delta)$ they were able to show that Eq. (1) correctly describes the chemical shift in the sense that $\langle 1/r^3 \rangle_{3d}$ was essentially independent of the nature of the ligand, and its magnitude is in fairly good agreement with estimates of this quantity from paramagnetic resonance data.[4] These results were confirmed by Dharmatti and Kanekar[6] on a large number of Co^{3+} complexes.

The present work consists first of a study of the pressure dependence of the chemical shift σ of the Co^{59} nuclear resonance frequency in aqueous solutions of the complexes $[Co(CN)_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)_6]^{3-}$, and solutions of $Co(C_5H_7O_2)_3$ in acetone, chloroform, and toluene. In carrying out these measurements we took advantage of the precision which is attainable in measurements of changes in σ. In our experiments it was possible to detect variations ($\delta\sigma$) in σ which were as small as $\delta\sigma/\sigma \sim \pm 2\times 10^{-5}$. From our measurements of σ vs pressure we have been able to estimate the dependence of the crystal-field splitting parameter Δ on the Co–ligand distance (R). As a second part of our study, we re-examined,[3] with our highly precise system, the temperature dependence of σ and have clearly observed a nonlinear dependence of σ on T for the $[Co(NH_3)_6]^{3+}$ and $[Co(NO_2)_6]^{3-}$ complexes. We have also developed an explicit theory for the temperature dependence of the chemical shift. The fundamental parameters which enter into the theory are the vibration frequencies of the normal modes of the complex when the $3d$ electrons are in their ground and their excited states. While the ground-state vibration frequencies are known it is difficult to determine the excited state frequencies either theoretically or experimentally. Nevertheless, fairly reasonable choices for the ratio of excited to ground vibrational frequencies can explain the observed values of $(d\sigma/dT)$. We have also considered the implicit dependence of σ on the temperature through the thermal expansion of the complex.

II. EXPERIMENTAL METHODS

The experimental methods for generation, containment, and measurement of high pressure while magnetic resonance experiments are being conducted have been described previously in the literature.[7] In the present work the sample is a liquid and has to be isolated from the petrol ether used to transmit the pressure. To accomplish this the sample is contained in a small cylindrical vial of Teflon whose wall thickness is 0.010 in. A Teflon cap was cemented on to this vial with epoxy resin after etching the contacting Teflon surfaces. The walls of this container are flexible and transmit the pressure to the sample without breakage or leak.

The method required to detect changes in σ as small as a few parts in 10^5 can be anticipated by means of the following considerations. In a field of about 8.85 kG the resonance frequency of the Co^{59} nucleus is about 9 Mc/sec. Since $\sigma \sim 1\%$, the chemical shift contributes $\sim$90 kc/sec to the resonance frequency. Since the resonance lines are $\sim$50 cps, the center should be locatable to within ± 2 cps, and hence one should be able to detect changes in σ as small as ± 2 cps/90×10^3 cps$\sim \pm 2\times 10^{-5}$. From these considerations two important criteria emerge. First, one must have a means of stabilizing and measuring the frequency of the Co^{59} resonance spectrometer to ± 2 cps out of 9 Mc/sec, i.e., $(\delta\nu/\nu) \sim 2\times 10^{-7}$. Second, one must also be able to stabilize the external magnetic field to the same precision or better during the 8 to 10 h period of a pressure run. Thus the field must be stable to within $\delta H/H \sim 2\times 10^{-7}$. These requirements are met by the system whose block diagram is shown in Fig. 1.

The heart of the system is a Gertsch F.M.-6 frequency meter, which generates fundamental frequencies between 20 and 40 Mc/sec from a 1-Mc/sec tempera-

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[7] T. Kushida, G. Benedek, and N. Bloembergen, Phys. Rev. **104**, 1364 (1956).