

TABLE II. The pressure dependence of the Co^{59} resonance frequency for $\text{Co}(\text{NO}_2)_6^{3-}$ in H_2O [$\sigma(P_0, T) = 0.020$].

$\{[\nu(P, T) - \nu(P_0, T)] / \nu(P_0, T)\} \times 10^5$			
Pressure (kg/cm ²)	$T = 21.4^\circ\text{C}$ $\nu(P_0, T) =$ 8 925 215 cps	$T = 39.4^\circ\text{C}$ $\nu(P_0, T) =$ 8 924 120 cps	
	0	0	0
1000	-4.64	-4.64	
2000	-8.99	-8.99	
3000	-13.08	-13.16	
4000	-16.92	-17.15	
5000	-20.60	-20.92	
6000	-24.17	-24.60	
7000	-27.67	-28.20	
8000	-31.15	-31.72	
9000	-34.52	-35.20	

tablishment of thermal equilibrium. Under these conditions measurements of ν vs T were found to be quite reproducible.

III. EXPERIMENTAL RESULTS

The pressure dependence of the Co^{59} chemical shift was measured in aqueous solutions of $\text{K}_3\text{Co}(\text{CN})_6$, $\text{Na}_3\text{Co}(\text{NO}_2)_6$, $\text{Co}(\text{NH}_3)_6\text{Cl}_3$, and in solutions of $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ in acetone, chloroform, and toluene. In Table I we list the fractional changes in resonance frequency of the Co^{59} nucleus in the $\text{Co}(\text{CN})_6^{3-}$ complex as the pressure is increased from $P_0 = 1$ atm to 10 000 kg/cm² at three different temperatures 20.3°, 68.5°, and 98.1°C. To convert these fractional changes in frequency to changes in chemical shift $[\sigma(P, T) - \sigma(P_0, T)]$ we have only to multiply each entry by the constant factor $[1 + \sigma(P_0, T_0)]$. From Freeman,

TABLE III. The pressure dependence of the Co^{59} resonance frequency for $\text{Co}(\text{NH}_3)_6^{3+}$ in H_2O [$\sigma(P_0, T) = 0.020$].

$\{[\nu(P, T) - \nu(P_0, T)] / \nu(P_0, T)\} \times 10^5$			
Pressure in kg/cm ²	$T_0 = 19.9^\circ\text{C}$ $\nu_0 = 8\,931\,627$ cps	$T_0 = 63.5^\circ\text{C}$ $\nu_0 = 8.9320$ Mc/sec	
	0	0	0
1000	-3.66	-3.66	
2000	-7.11	-7.11	
3000	-10.44	-10.44	
4000	-13.70	-13.70	
5000	-16.80	-16.80	
6000	-19.86	-19.86	
7000	-22.86	-22.86	
8000	-25.77	-25.77	

TABLE IV. The pressure dependence of the Co^{59} resonance frequency in $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ for three solvents.

$\{[\nu(P, T) - \nu(P_0, T_0)] / \nu(P_0, T)\} \times 10^5$			
Pressure (kg/cm ²)	Acetone $T_0 = 22^\circ\text{C}$ $\nu(P_0, T) =$ 8 971 024 cps	Chloroform $T_0 = 22^\circ\text{C}$ $\nu_0 =$ 8 969 671 cps	Toluene $T_0 = 22^\circ\text{C}$ $\nu_0 =$ 8 970 379 cps
	0	0	0
500	-1.51	-1.62	-1.62
1000	-3.01	-3.19	-3.19
2000	-5.92		-6.16
3000	-8.69		-9.00
4000	-11.33		-11.76

Murray, and Richards work, $\sigma = 0.0120$ for this complex. Table II lists similar data for the $\text{Co}(\text{NO}_2)_6^{3-}$ complex; in this case $\sigma = 0.020$. In Table III we list the results for the $\text{Co}(\text{NH}_3)_6$ complex in which $\sigma = 0.020$. Table IV presents the data on the pressure dependence of the resonance frequency for the compound $\text{Co}(\text{C}_5\text{H}_7\text{O}_2)_3$ in three solvents. The linewidth of the cobalt nuclear resonance in $\text{Co}(\text{CN})_6^{3-}$ was determined by the magnetic field inhomogeneity and is less than 10 cps. The cobalt resonances in $\text{Co}(\text{NO}_2)_6^{3-}$ and $\text{Co}(\text{NH}_3)_6^{3+}$ are 60 cps and ~ 200 cps, respectively.

At each pressure point in these tables, the resonance frequency is determined to about ± 2 cps. Thus each entry in the $(\Delta\nu/\nu) \times 10^5$ columns has associated with it an error of ± 0.03 . By combining the data in these tables with our measurements of the temperature dependence of σ at atmospheric pressure we may plot

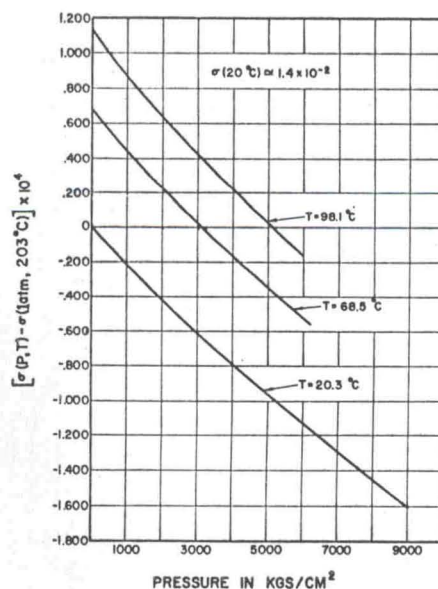


Fig. 2. The pressure dependence of σ at three temperatures for the $\text{Co}(\text{CN})_6^{3-}$ complex.