Proton Nuclear Magnetic Resonance Spectra of Tetrabutylammonium Tris(acetylacetonato)cobalt(II) and -nickel(II). Ion Pairing and Magnetic Anisotropy[1a]

William DeW. Horrocks, Jr.,[1b] Ronald H. Fischer,[1b] James R. Hutchison,[1b] and Gerd N. La Mar[1c]

Contribution from the Frick Chemical Laboratory, Princeton University, Princeton, New Jersey, and the Physical Chemistry Laboratory, Swiss Federal Institute of Technology, Zürich, Switzerland. Received November 27, 1965

Abstract: Proton nmr spectra of the octahedrally coordinated cobalt(II) and nickel(II) complexes, $[\mathrm{Bu_4N}][\mathrm{Co(AA)_3}]$ and $[\mathrm{Bu_4N}][\mathrm{Ni(AA)_3}]$, were observed in carbon tetrachloride and deuteriochloroform solutions. The acetylacetonate (AA) ligand proton resonances exhibit isotropic shifts (resonance frequency displacements from the diamagnetic values) indicative of unpaired electron spin delocalization from the metal into the highest filled bonding molecular orbitals of these ligands. Isotropic shifts were also observed for the butyl proton resonances of the cation in the cobalt compound. These latter shifts are attributable to a pseudo-contact interaction due to the magnetic anisotropy of the $[\mathrm{Co(AA)_3}]^-$ anion and the existence of ion pairing in solution. The temperature dependences of the isotropic shifts and the effect on the nmr spectra of adding excess $[\mathrm{AA}]^-$ and $\mathrm{M(AA)_2}$ to the systems were investigated. The present results are consistent with the expected isotropy of the octahedral nickel complex, while an estimate of the magnetic anisotropy of the cobalt complex yields $K_{\parallel} - K_{\perp} = -4280$ cgsu mole^{-1}.

An investigation in these laboratories[2] of the pmr spectra of tetra-*n*-butylammonium $[\mathrm{Bu_4N}]^+$ salts of pseudo-tetrahedrally coordinated paramagnetic anions of the type $[(\mathrm{C_6H_5})_3\mathrm{PMI_3}]^-$, where M = Co(II) or Ni(II), reported isotropic resonance shifts of the tetrabutylammonium protons arising from the dipolar interaction between the proton nuclear moments and the electron spin magnetization in these complexes, which are ion paired in chloroform solution and have anisotropic *g* tensors. Isotropic shifts[3] due to this mechanism, termed the pseudo-contact interaction, are to be distinguished from shifts attributable to the Fermi contact interaction,[4] which are caused by the presence of unpaired electron density at the resonating nuclei. Pseudo-contact shifts will occur only in magnetically anisotropic systems in which the resonating protons have certain preferred orientations with respect to the axes of the *g* tensor as defined by the ligand field of the complex. In the complexes previously studied[2] the tetrabutylammonium ion was situated on the C_3 axis of the paramagnetic anion in the ion-paired configuration. The present study is concerned with isotropic shifts in systems containing the tetrabutylammonium ion and octahedrally coordinated anions containing cobalt(II) and nickel(II). To this end we synthesized the tetrabutylammonium salts of tris(acetylacetonato)-(2,4-pentanedionato)cobalt(II) and nickel(II) anions $[\mathrm{M(AA)_3}]^-$. The radical difference in magnetic anisotropy between octahedral nickel(II) with a d^8 electron configuration and an A_2 ground state, and octahedral cobalt(II) with a d^7 configuration and a T_1 ground state, predicted by theory[5] and confirmed by susceptibility[6] and electron spin resonance experiments,[7] is also evident from our pmr results.

Experimental Section

Preparation of Compounds. $\mathrm{Ni(C_5H_7O_2)_2}$ and $\mathrm{Co(C_5H_7O_2)_2}$. Acetylacetone (2,4-pentanedione) was dissolved in water by the addition of dilute aqueous ammonia until solution was complete. This solution was added to a solution containing a stoichiometric quantity of the appropriate metal chloride. Dilute aqueous ammonia was added until the solution was neutral, precipitating the hydrated complex. The precipitate was recrystallized from methanol and dehydrated by heating *in vacuo* at 57° overnight.

$[(\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{Ni(C_5H_7O_2)_3}]$ and $[(\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{Co(C_5H_7O_2)}]_3$. Stoichiometric quantities of acetylacetone and tetra-*n*-butylammonium hydroxide (25% in methanol; Matheson Coleman and Bell) were added to a suspension of $\mathrm{Ni(C_5H_7O_2)_2}$ or $\mathrm{Co(C_5H_7O_2)_2}$ in methanol. The mixture was heated and stirred until solution was complete. The solution was then evaporated on a rotary flash evaporator. The resulting waxy solid was dissolved in a minimum amount of $\mathrm{CCl_4}$ without heating, and any insoluble residue was removed by filtration. Petroleum ether was added to the filtrate and the product separated as an oil which solidified upon standing overnight. The product was recrystallized from xylene and washed with several small portions of diethyl ether.

For the preparation of the cobalt complex all solvents were made air free by passing in nitrogen prior to use.

$[(\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{Ni(C_5H_7O_2)_3}]$ formed green crystals. *Anal.* Calcd: C, 62.21; H, 9.60; N, 2.34. Found: C, 61.91; H, 9.34; N, 2.45.

$[(\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{Co(C_5H_7O_2)_3}]$ formed dark red crystals. *Anal.* Calcd: C, 62.18; H, 9.60; N, 2.34. Found: C, 62.02; H, 9.75; N, 2.26.

$[(\mathrm{C_4H_9})_4\mathrm{N}][\mathrm{C_5H_7O_2}]$. This compound was prepared by mixing stoichiometric quantities of 25% tetra-*n*-butylammonium hydroxide in methanol with acetylacetone, evaporating the solution to dryness, and recrystallizing from chloroform–ether. A better preparation suggested by Posner, *et al.*,[8] involving recrystallization from methylene chloride–ethyl acetate, was used in later preparations.

Conductance Measurements. The equivalent conductances of nitrobenzene solutions of the complexes were obtained with a Serfass conductivity bridge calibrated with 0.0200 *M* aqueous potassium chloride solution. The results were as follows.

---

(1) (a) This work was supported by the National Science Foundation through Grant No. NSF-GP-3397; (b) Princeton University; (c) Swiss Federal Institute of Technology; NSF Postdoctoral Fellow, 1964–1966.

(2) (a) G. N. La Mar, *J. Chem. Phys.*, **41**, 2992 (1964); (b) *ibid.*, **43**, 235 (1965).

(3) For leading references to work in this field, see (a) W. D. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Am. Chem. Soc.*, **86**, 3031 (1964); (b) B. B. Wayland and R. S. Drago, *ibid.*, **87**, 2372 (1965).

(4) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(5) J. S. Griffiths, "The Theory of Transition Metal Ions," Cambridge University Press, New York and London, 1961.

(6) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(7) K. D. Bowers and J. Owen, *Rept. Progr. Phys.* **18**, 304 (1955).

(8) J. C. Posner, D. E. Smith, and D. F. Shriver, private communication.

	Concn, M	Conductivities (25%), cm^2 mole^{-1} ohm^{-1}
$[(C_4H_9)_4N][Ni(C_5H_7O_2)_3]$	1.00×10^{-3}	21.3
$[(C_4H_9)_4N][Co(C_5H_7O_2)_3]$	0.972×10^{-3}	22.3

Ultraviolet, Visible, and Near-Infrared Spectra. The spectra of chloroform solutions of the complexes were obtained with a Cary 14 recording spectrophotometer using 1-cm quartz cells at room temperature. The molar extinction coefficients were reproducible to within about ±2%.

Pmr Spectra. Spectra of deuteriochloroform and carbon tetrachloride solutions were obtained with a Varian A-60 spectrometer at the ambient probe temperature of 34°, and also on a modified Varian HR-60 spectrometer with a 25-kc scan. Frequency calibration was accomplished by the usual side-band techniques. Peak positions are accurate to ±5 cps.

Magnetic Susceptibilities. Powder susceptibilities of the complexes were obtained at room temperature by the standard Gouy method using a Varian 4-in. electromagnet and calibrating with $HgCo(SCN)_4$. Effective magnetic moments of 3.23 and 4.94 BM were obtained for the nickel and cobalt compounds, respectively. A diamagnetic correction of -358×10^{-6} cgs units was made in each case. These values compare fairly well with the literature values[6,9] for the analogous sodium and potassium salts.

Results

Structure of the Complexes. The values found for the equivalent conductances of the complexes in nitrobenzene solution (Experimental Section) fall in the range of uni-univalent electrolytes,[10] although equimolar mixtures of tetra-*n*-butylammonium acetylacetonate and $[M(AA)_2]_x$ would yield similar results. The frequencies of the ultraviolet, visible, and near-infrared absorption maxima and the associated molar extinction coefficients of both complexes measured in chloroform solution are reported in Table I. The spectra are typical of octahedral coordination through oxygen atoms with a spin-free electronic configuration[11] and are quite similar to those of the polymeric octahedrally coordinated divalent metal acetylacetonates themselves.[12,13]

Table I. Absorption Spectra of $[Bu_4N][Co(AA)_3]$ and $[Bu_4N][Ni(AA)_3]$ in Chloroform Solution at Room Temperature[a]

$[(C_4H_9)_4N][Co(C_5H_7O_2)_3]$		$[(C_4H_9)_4N][Ni(C_5H_7O_2)_3]$	
ν_{max}, cm^{-1}	ϵ_{max}, l. mole^{-1} cm^{-1}	ν_{max}, cm^{-1}	ϵ_{max}, l. mole^{-1} cm^{-1}
34,540	2.72×10^4	37,620	2.78×10^4
21,000	45.9	(34,100)	(1.82×10^4)
20,000	48.2	15,600	7.51
(19,600)	(46.8)	(13,200)	(2.53)
(18,700)	(45.1)	9,030	8.98
8,440	6.04		

[a] Values in parentheses indicate shoulders.

The approximate ligand splitting parameter, Δ, for both the cobalt[13] and nickel[14] compounds is ~9000 cm^{-1}. This value is close to those found for the polymeric cobalt(II) and nickel(II) acetylacetonates themselves, the value for $[Ni(AA)_3]^-$ being slightly higher than in the polymeric substance.[15] The symmetry of the complex anions (ignoring the methyl hydrogens) is undoubtedly D_3, with the threefold axis equidistant from all six methyl groups and the three perpendicular twofold axes each passing through the central carbon of a chelate ring and through the central metal atom. Molecular models of the system indicate that for an ion-paired configuration, the closest approach of the tetrabutylammonium cation and the complex anion is along the C_3 axis. The complex anions possess a trigonally distorted octahedral ligand field and the tetrabutylammonium ion, in the ion-paired configuration, is constrained to lie along the threefold axis. Evidence to be presented below suggests that the octahedral anions of the $[M(AA)_3]^-$ type may not be the only species present in these solutions, but they are undoubtedly the predominant species under the conditions of the experiments.

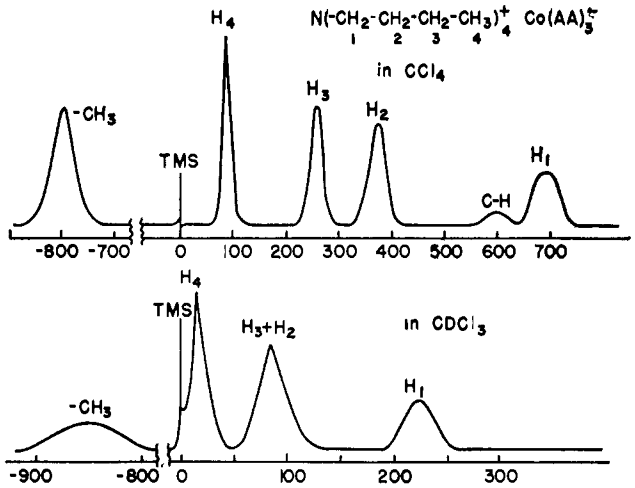

Figure 1. Pmr spectra of $[Bu_4N][Co(AA)_3]$ in carbon tetrachloride and deuteriochloroform solution at 34°.

Pmr Spectra. The spectra of carbon tetrachloride and deuteriochloroform solutions of the two complexes are shown in Figure 1. The butyl proton resonances are labeled according to the convention used previously.[2]

$$[N(\overset{1}{C}H_2—\overset{2}{C}H_2—\overset{3}{C}H_2—\overset{4}{C}H_3)_4]$$

Spectrum of $[Bu_4N][Co(AA)_3]$ in Carbon Tetrachloride Solution. The spectrum at 34° shows four peaks, labeled H_1–H_4 in Figure 1, which are due to the butyl protons shifted upfield from their positions in diamagnetic tetrabutylammonium iodide by a pseudo-contact interaction (*vide infra*). This behavior is qualitatively similar to butyl resonances of the ionic compounds studied in ref 2, although the ratios of the isotropic shifts are somewhat different and they are larger in absolute magnitude. Addition of excess tetrabutylammonium ions to the solution in the form of the iodide causes the butyl peaks to shift downfield toward their diamagnetic positions, indicating that these resonances represent a time average of tetrabutylammonium protons in ion-paired and nonion-paired configurations. The butyl peaks have approximately the expected intensity ratios (reading upfield, 3:2:2:2) and are assigned respectively to protons H_4, H_3, H_2, H_1. A weak, broad peak appears as a shoulder on the H_1 resonance in the pure complex and, although difficult to

(9) F. P. Dwyer and A. M. Sargeson, *Proc. Roy. Soc. New South Wales*, 90, 29 (1956).

(10) C. M. Harris and R. S. Nyholm, *J. Chem. Soc.*, 4375 (1956).

(11) C. K. Jorgensen, "Absorption, Spectra and Chemical Bonding in Complexes," Pergamon Press, Ltd., Oxford, 1962.

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

(13) A. D. Liehr, *J. Phys. Chem.*, 67, 1314 (1963).

(14) A. D. Liehr, *Ann. Phys.*, 2, 134 (1959).

(15) F. A. Cotton and J. P. Fackler, Jr., *J. Am. Chem. Soc.*, 83, 2818 (1961).

Table II. Chemical Shifts of $[Bu_4N][Co(AA)_3]$ in Carbon Tetrachloride and Deuteriochloroform at Various Concentrations and with Added $[Bu_4N][I]$ at 34°[a]

Solvent	Concn of complex, mole/l.	Concn of $[(C_4H_9)_4N]$ [I], mole/l.	Butyl protons H_1	H_2	H_3	H_4	Ligand protons CH_3	3-H[b]
CCl_4	0.0282	0	650	358	248	83	−794	592
	0.0549	0	663	365	251	83	−790	591
	0.0862	0	690	375	259	90	−796	608
	0.0549	0.0549	190	110	67	7	−818	572
$CDCl_3$	0.0412	0	188	68		10	−845	. . .
	0.0804	0	227	86		16	−855	. . .
	0.552	0	330	144		34	−858	. . .
	0.0412	0.0662	45	22		0	−850	. . .

[a] In cps from TMS. [b] Uncertainty ±20 cps for this resonance.

locate precisely, has a position relatively insensitive to the concentration of complex or added tetrabutylammonium iodide (Table II). The much larger peak at about −795 cps from TMS is also relatively independent of complex or added cation concentration. This downfield peak is assigned to the methyl groups on the acetylacetonate ligands, while the upfield peak at about +600 cps from TMS must be due to the single hydrogen at the 3-position of the ligand. The relative intensities of the −795 cps peak and the butyl proton resonances agree with this assignment. No other signals were observed over a 25,000-cps scan centered at TMS. The chemical shifts of the various resonances of $[Bu_4N][Co(AA)_3]$ at several concentrations of complex and with added $[Bu_4N][I]$ are given in Table II for both carbon tetrachloride and deuteriochloroform solutions.

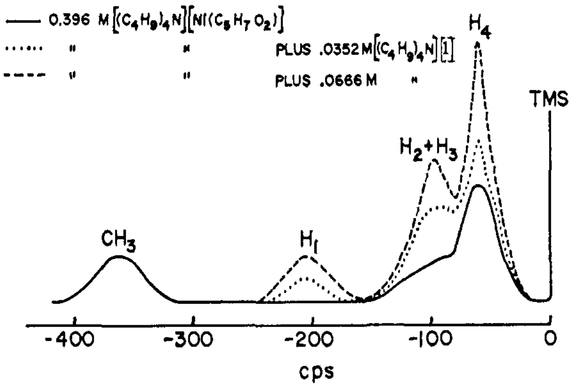

Figure 2. Pmr spectra of $[Bu_4N][Ni(AA)_3]$ in deuteriochloroform solution at 34° showing the effect of added $[Bu_4N][I]$.

The temperature dependences of the ligand methyl and cation butyl proton isotropic shifts in carbon tetrachloride are qualitatively similar to those in deuteriochloroform which are shown in Figure 3.

Spectrum of $[Bu_4N][Co(AA)_3]$ in Deuteriochloroform Solution. The butyl proton resonances of this compound in deuteriochloroform show a difference (Figure 1) from the carbon tetrachloride spectra and the compounds studied in ref 2 and 4. Only three peaks are observed at 34° with intensity ratios, reading upfield, 3:4:2, and are therefore assigned respectively to protons H_4, $H_3 + H_2$, H_1. The concentration dependences of these resonances and the effect of adding $[Bu_4N][I]$ are given in Table II. The peaks assigned to the butyl protons collapse toward the diamagnetic position as the concentration of cation is increased, while the peak at about −850 cps from TMS remains fairly constant in position and intensity. This latter peak is assigned to the ligand methyl groups on the basis of its relative intensity with respect to the butyl protons. The 3-hydrogen resonance has not been definitely identified in deuteriochloroform solutions. The temperature dependences of the isotropic shifts are give in Figure 3.

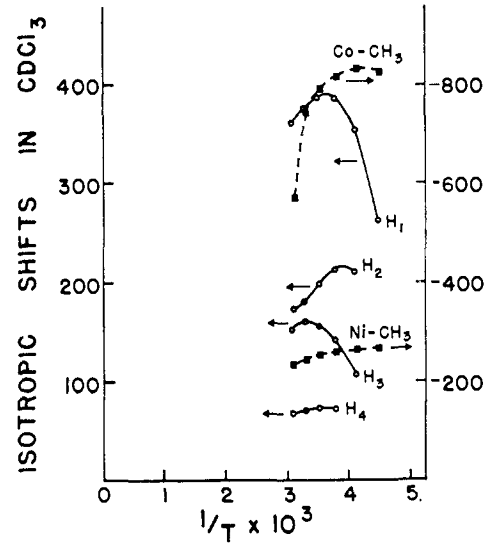

Figure 3. Plot of the temperature dependences of the isotropic shifts of the methyl and butyl protons of $[Co(AA)_3]^-$ and of the methyl protons of $[Ni(AA)_3]^-$ in deuteriochloroform solution.

Spectra of $[Bu_4N][Ni(AA)_3]$ in Carbon Tetrachloride and Deuteriochloroform Solution. The spectra in these solvents are quite similar. The latter (A-60 spectrometer, 34°) is shown in Figure 2. The butyl protons appear unshifted from their diamagnetic positions, but are extremely broad due to a fairly efficient relaxation attributable to the proximity of the paramagnetic anions. The broadening increases markedly in the order $H_4 < H_2$ and $H_3 < H_1$. Indeed, in the pure compound the H_1 proton resonance is unobservable. Upon addition of $[Bu_4N][I]$, a broad peak grows in at the unshifted H_1 position (see Figure 2) and the other butyl peaks gain in intensity and, of course, do not shift. The broad peak at about −310 cps from TMS in carbon tetrachloride solution and −363 cps in deuteriochloroform solution is unaffected either in position or intensity by addition of $[Bu_4N][I]$ and is therefore assigned to the methyl groups of the ligands. The intensity of this peak is far too large to be the ligand 3-hydrogen signal. Carbon tetrachloride solutions show a broad peak at +640 cps, best detected with a DP-60 spectrometer, of intensity approximately one-sixth that of the methyl resonance and it is assigned to the 3-hydrogen. In deuteriochloroform an extremely weak peak at about +650 was detected; however, the intensity of the peak seems insufficient for the 3-hydrogen signal. It was also observed that the chloroform proton resonance grows in intensity with time in these solutions. A speculative explanation for the low intensity of the 3-hydrogen signal is that this proton is exchanging with the deuterium of the solvent. This mechanism, is, of course, inoperative in carbon tetrachloride solutions.

Ligand (acetylacetonate) proton resonance isotropic shifts for both the cobalt and nickel compounds in carbon tetrachloride and deuteriochloroform are given in Table III.

Table III. Isotropic Shifts of Ligand Proton Resonances[a]

	$[Co(AA)_3]^-$		$[Ni(AA)_3]^-$	
	CCl_4	$CDCl_3$	CCl_4	$CDCl_3$
Methyl	−675	−730	−190	−240
3-Hydrogen	+915	...	+960	...

[a] Measured in cps at 34° from diamagnetic chemical shifts of $Al(AA)_3$ taken as −120 (methyl) and −320 cps (3-hydrogen) from TMS.

Effect of Adding $[Bu_4N][AA]$ and $M(AA)_2$. The solvent sensitivity of the methyl resonances, as well as the unusual temperature dependence of the spectra to be discussed in a later section, suggests that there may be some sort of labile equilibrium occurring in these solutions. Possible equilibria such as the following may be envisaged.

$$[M(AA)_3]^- \rightleftharpoons M(AA)_2 + [AA]^- \qquad (I)$$

or

$$2[M(AA)_3]^- \rightleftharpoons [M_2(AA)_5]^- + [AA]^- \qquad (II)$$

It should be kept in mind that the divalent metal acetylacetonates are themselves polymeric species, $Co(AA)_2$ existing as a complex mixture of oligomers[12] while $Ni(AA)_2$ is almost exclusively trimeric in benzene at room temperature.[16] Adding diamagnetic $[Bu_4N][AA]$ to a deuteriochloroform solution of $[Bu_4N][Co(AA)_3]$ at 40° caused the methyl resonance assigned to the complex anion to move downfield about 30–40 cps upon a small addition with no further effect upon further addition. As more $[Bu_4N][AA]$ was added, a peak at −125 cps grew in, characteristic of the methyl resonance of diamagnetic $[AA]^-$. The same experiment at 25° caused no appreciable shift in the methyl resonance of $[Co(AA)_3]^-$. These results indicate that there is no rapid exchange between coordinated and uncoordinated $[AA]^-$ in these solutions and are consistent with addition of excess $[AA]^-$ driving any equilibrium such as (I) or (II) to the left. The butyl proton resonances were of course shifted downfield toward their diamagnetic positions in the above experiments.

Addition of $Co(AA)_2$ to a deuteriochloroform solution of $[Bu_4N][Co(AA)_3]$ causes the methyl resonance of the complex anion to move rapidly upfield with increasing $Co(AA)_2$ concentration. This indicates that some species is being formed which is in labile equilibrium with $[Co(AA)_3]^-$. It is impossible to determine whether $Co(AA)_2$ is itself a partner in this rapid equilibrium since the spectrum of pure $Co(AA)_2$ shows only an extremely broad ($\Delta H_{1/2}$ = ~200 cps) peak centered under TMS, and changes in the spectrum of this species in the presence of $[Bu_4N][Co(AA)_3]$ cannot, of course, be detected. These observations are in accord with the presence of a labile equilibrium in which intermediates exist such as $[Co_2(AA)_5]^-$ which has a methyl proton chemical shift upfield (the methyl resonance shift is 115 cps for equal mole ratios of $[Co(AA)_3]^-$ and $Co(AA)_2$) from that of $[Co(AA)_3]^-$. Upon addition of $Co(AA)_2$ to the solution, the butyl proton resonances move upfield abruptly upon the initial addition by about 15 cps. This observation is again compatible with an equilibrium in solution in which more $[Co(AA)_3]^-$ is formed, and hence the proportion of ion-paired $[Bu_4N]^+$ ions is increased.

The corresponding experiments were performed with $[Bu_4N][Ni(AA)_3]$ where, upon addition of $[Bu_4N][AA]$, no change in the position of the $[Ni(AA)_3]^-$ methyl resonance was observed, and a sharp peak at −125 cps grew in indicating slow exchange of the added $[AA]^-$ ligands with those in the complex. Addition of $Ni(AA)_2$ produced spectra which correspond to a superposition of pure $[Bu_4N][Ni(AA)_3]$ and that of $Ni(AA)_2$ itself. The latter species has a broad methyl resonance at −286 cps. This behavior contrasts with the corresponding cobalt case where addition of $Co(AA)_2$ causes a shift in the observed methyl resonance position. This difference is perhaps related to the fact that $Ni(AA)_2$ exists in fairly stable trimeric units in solution while $Co(AA)_2$ does not.

Discussion

Pseudo-Contact Shifts of Butyl Protons in $[Bu_4N][Co(AA)_3]$. The isotropic shifts observed for the butyl proton resonances of the cobalt compound must, in the absence of any unpaired electron spin density on the tetrabutylammonium ion, be due to the dipolar pseudo-contact interaction. For a solid this is given by[17]

$$(\Delta\nu/\nu)_i = -\frac{1}{3N}(K_\parallel - K_\perp)\frac{3\cos^2\chi_i - 1}{r_i^3} \qquad (1)$$

where $(\Delta\nu/\nu)_i$ is the fractional pseudo-contact shift for the ith resonating proton, N is Avogadro's number, $K_\parallel$ and $K_\perp$ are the principal molar susceptibilities parallel and perpendicular to the ligand field axes, respectively, χ_i is the angle between this axis and a radius vector to the proton of interest, and r_i is the length of this vector. Equation 1 is applicable to situations wherein some unquenched orbital angular momentum remains in the ground state, and the magnetic susceptibility does not obey the Curie law. In such cases (octahedral cobalt(II) with a $^4T_1$ ground

---

(16) J. P. Fackler, Jr., and F. A. Cotton, *J. Am. Chem. Soc.*, **83**, 3775 (1961).

(17) For systems with no residual orbital angular momentum where the molar susceptibility, K_M, is given for $K_M = Ng^2_{av}\beta^2S(S+1)/3kT$, eq 1 reduces to the equation[4] for the pseudo-contact shift in a *solid* expressed in terms of *g* tensor anisotropy. The equation appropriate for pseudo-contact shifts in solution for systems with residual orbital angular momentum cannot be expressed in simple terms.

term is an example) neither χ nor $\Delta\nu/\nu$ can be stated in a simple form in terms of the total spin quantum number, S, and a function of g-tensor components and the equations previously given[4,18] are not strictly applicable. Quantitative application of eq 1 to the present data is complicated by several factors: (i) the observed proton resonances represent an average of the tetrabutylammonium proton resonances in the ion-paired configuration where the cation is experiencing a large pseudo-contact interaction and the resonances of the same protons in non-ion-paired and hence pseudo-contact free environments; (ii) $K_{\parallel}$ and $K_{\perp}$ are unknown; (iii) the average values of $[(3\cos^2\chi_i - 1)/r_i^3]$ for the various butyl protons are unknown; (iv) the unusual Curie plots and solvent sensitivity of the butyl proton isotropic shifts indicate that these systems are not as simple as might have been expected, and species other than $[Bu_4N]^+$ and $[Co(AA)_3]^-$ are probably present in solution; and (v) ours is solution data. For the present discussion we will assume that the simple ionic species are predominant.

La Mar has recently been able to estimate values of $[(3\cos^2 \mathrm{Q}_1 - 1)/r_1^3]_{av}$ for tetrabutylammonium protons in the ion-paired configurations as a function of interionic distance.[2] Using the observed ratios of the H_1/H_2 proton isotropic shifts of $[Bu_4N][Co(AA)_2]$ at 34° and the results of La Mar's calculations, the Co–N interionic distance in the ion pair is estimated to be about 3.6 A from the data in deuteriochloroform and about 3.7 A from the carbon tetrachloride data. These interionic distances are slightly shorter than those estimated for the $[Bu_4N][(C_6H_5)_3PMI_3]$ systems with M = Co or Ni. A study of space filling molecular models shows that the tetrabutylammonium ion can approach the complex anion quite closely along the threefold axis; however, the models indicate that 3.6 or 3.7 A is too short an interionic distance and 4 to 6 A would seem more reasonable. In the ion-paired configuration of most intimate approach, there is extensive steric interaction between the butyl chains of the cation and the methyl groups of the complex anion. This interaction prevents the protons of the tetrabutylammonium ion from occupying, with equal probability, a spherical distribution with respect to the nitrogen while involved in ion pairing. An appreciable interaction of this sort, of course, invalidates the use of La Mar's model to determine the interionic distance in this case. Isotropic shifts for the various butyl protons were calculated, taking the chemical shifts of the protons in diamagnetic $[Bu_4N][I]$ to be $H_1 = -205$, $H_2 = -115$, $H_3 = -90$, $H_4 = -65$, all in cps from TMS. The magnitude of the isotropic shift for the H_1 proton is quite similar in $[Bu_4N][(Co(AA)_3]$ and in $[Bu_4N][(C_6H_5)_3PCoI_3]$ in deuteriochloroform solution, but there is a significant difference in the shift pattern (ratios of isotropic shifts) such that the H_2 and H_3 signals are not resolved at 34° in solutions of the former compound in this solvent. The butyl proton isotropic shifts observed for carbon tetrachloride solutions of $[Bu_4N][Co(AA)_3]$ at 34° are almost twice as large as for the same compound dissolved in deuteriochloroform, and the pattern is again somewhat different. The H_2 and H_3 proton signals are well separated in this case. The difference between the shift patterns of the compounds studied in ref 2 and those in the present case, as well as the failure of the H_1/H_2 ratio to yield a reasonable interionic distance, is to be expected in view of the unusual temperature and solvent dependences of the butyl proton resonances (Figures 1 and 3). It is clear from these Curie plots that the isotropic shifts and their ratios are extremely sensitive to changes in solvent and temperature. Deviations from Curie law behavior are expected owing to the following causes: (i) changes in extent of ion pairing with temperature; (ii) changes in the average geometry of the ion-paired configuration with temperature and solvent; and (iii) changes in the nature and relative quantities of the anionic species in solution. For instance, formation of $[Co_2(AA)_5]^-$ or $[AA]^-$ at the expense of $[Co(AA)_3]^-$ would have a profound influence on the average isotropic shifts of the butyl protons. It is interesting that the maxima in the isotropic shifts of the various butyl protons (H_1, H_2, H_3, H_4) occur at different temperatures. Such behavior would not be expected for a mechanism which simply reduced the number of ion pairs in solution, but might very well occur if some of the $[Bu_4N]^+$ ions were ion paired to a different anionic species such as $[Co_2(AA)_5]^-$, which would have different anisotropy and geometrical properties. Further speculation on the cause for the decrease in butyl proton isotropic shifts at low temperatures is not in order at present. The greater magnitude of the isotropic shifts in carbon tetrachloride compared with deuteriochloroform solution is probably due to the higher percentage of ion pairs in the solvent of lower dielectric constant.

The shifts increase slightly with increasing concentration, indicating a higher percentage of ion pairs in the more concentrated solutions. This contrasts with the behavior of the $[Bu_4N][(C_6H_5)_3PMI_3]$ systems where the shifts are observed to decrease with increasing concentration.[19] This latter behavior may be attributable to the presence of aggregates higher than ion pairs. Indeed, such higher aggregates are to be expected[20,21] at these concentrations in a solvent of so low a dielectric constant as chloroform.

Ligand Proton Resonances. Ligand proton isotropic shifts (Table III) may be attributed to one or more of the following causes: (i) Fermi contact interaction due to unpaired electron spin delocalized in the π system of the ligands, either the highest filled bonding level (π_b) or the lowest empty antibonding level (π_a); (ii) a contact interaction due to spin delocalization in the σ system; (iii) the pseudo-contact interaction.

The method of separation of contact and pseudo-contact shifts used elsewhere,[3a,22] based on comparisons of isotropic shift ratios, cannot be used with confidence in the present case since there are only two observed proton resonances. As expected, the immobility of the butyl proton resonances in $[Bu_4N][Ni(AA)_3]$ indicates that the pseudo-contact interaction is either extremely small or absent in this compound. The methyl shift is therefore attributable to a contact interaction of the

---

[18] (a) G. N. La Mar, *J. Phys. Chem.*, **69**, 3212 (1965); (b) *J. Chem. Phys.*, **43**, 1085 (1965).

[19] R. H. Fischer, unpublished observations.

[20] C. W. Davis, "Ion Association," Butterworths Scientific Publications, Ltd., London, 1962.

[21] R. M. Fuoss and F. Accascina, "Electrolytic Conductance," Interscience Publishers, Inc., New York, N. Y., 1959, Chapter 16.

[22] G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *J. Chem. Phys.*, **41**, 2126 (1964).

σ or π type or a combination of both. Spin delocalization in σ orbitals leads to downfield resonance shifts.[23] In the case of coordinated acetylacetonate ligands, both the methyl and 3-position protons are removed from the metal by four bonds with a double path for σ spin density being available to the 3-position proton in these chelates. The fact that the 3-hydrogen resonance is shifted upfield while the methyl resonance is shifted downfield militates against a dominant σ-spin-delocalization cause for the observed isotropic shifts. Spin delocalization by a π mechanism in octahedrally coordinated acetylacetonate complexes has recently been discussed by Eaton.[24] In an attempt to decide whether spin is delocalized in the highest filled π-bonding molecular orbital (π_b) or the lowest vacant π-antibonding orbital (π_a) of the acetylacetonate ligand, he presents the results of a Hückel MO calculation corrected for spin correlation by the method of McLachlan.[25] These calculations yield, for one unpaired electron delocalized in π_b, spin densities of $+0.064$ and $+0.729$ at the 2- and 3-position carbons, respectively, while for delocalization into π_a the spin densities are $+0.498$ and -0.166 at the same two carbons. Positive spin density at a carbon atom of an aromatic system gives rise to an upfield isotropic shift of an attached proton and generally a downfield shift for an attached methyl group. The results for $[\mathrm{Ni(AA)_3}]^-$ are in qualitative agreement with spin delocalization in π_b where a sizeable upfield shift is predicted for the 3-hydrogen resonance and a much smaller shift of opposite sign for the methyl resonance. This is consistent with the conclusion of Eaton that spin delocalization in π_b becomes more important as one progresses across the periodic table from left to right in the transition series.

The ligand isotropic shifts in $[\mathrm{Bu_4N}][\mathrm{Co(AA)_3}]$ undoubtedly contain both contact and pseudo-contact contributions. It is possible to gain some insight into the pseudo-contact contribution by inspection of eq 1. The upfield shifts of the butyl proton resonances in the cobalt compound indicate that $\Delta\nu/\nu$ is positive for these protons. The geometry of the situation, with the ions approaching one another along the C_3 axis, dictates that the tetrabutylammonium protons will occupy positions in space where $[(3\cos^2\chi - 1)/r^3]$ is positive. Indeed, calculations show that $[(3\cos^2\chi - 1)/r^3]_{\mathrm{av}} \equiv G(\chi)_{\mathrm{av}}$ for the $\mathrm{H_1}$ butyl protons varies from $+0.0290$ A^{-3} at an interionic distance of 4.0 A to $+0.0150$ A^{-3} at 5.0 A.[2] Of all the butyl protons, the estimate of the average value of the geometric factor for the $\mathrm{H_1}$ protons using the spherical model should be least affected by the steric factors mentioned in an earlier section. The magnetic anisotropy function $(k_\parallel - k_\perp)$ must thus be negative. Assuming a regular octahedral coordination of oxygens about the cobalt and D_3 symmetry for the complex anion as a whole and using the structural parameters of Bullen for $\mathrm{Co(AA)_2\cdot 2H_2O}$,[26] the geometric factors $G(\chi)_{\mathrm{av}}$ for the methyl protons and 3-hydrogen were calculated. The average was taken over all possible rotations of the equivalent methyl groups about their axes. A value of -0.00251 A^{-3} was obtained for the methyl protons and -0.0122 A^{-3} for the 3-hydrogen. These calculated geometric factors are of opposite sign from those estimated for the tetrabutylammonium protons and this, along with the observation of an upfield pseudo-contact shift for the butyl protons, leads us to expect a downfield pseudo-contact shift for the ligand protons with the larger shift being experienced by the 3-hydrogen. A lower limit for the pseudo-contact shift of the methyl and 3-hydrogen protons can be estimated in the following manner. A reasonable lower limit for $G(\chi)_{\mathrm{av}}$ for the $\mathrm{H_1}$ butyl protons is 0.01 A^{-3}, and it is not a particularly sensitive function of interionic distance at reasonable (5 to 7 A) values of this parameter.[2b] The observed isotropic shift for the $\mathrm{H_1}$ butyl proton resonance in carbon tetrachloride solution is $+895$ cps at 34°. This may be taken as a lower limit of the pseudo-contact shift for a proton with this $G(\chi)_{\mathrm{av}}$ since the presence of any non-ion-paired tetrabutylammonium ions will decrease the observed shifts. From the calculated $G(\chi)$'s for the methyl and 3-hydrogen protons, lower limits of the pseudo-contact contribution to the isotropic shifts of these resonances can be estimated as -225 and -1090 cps, respectively, the negative sign indicating downfield shifts. Although the relative contributions of the π_a and π_b MO's in delocalization of spin in the cobalt and nickel complexes are not expected to be identical (Eaton's analysis[24] would indicate a greater π_a contribution in cobalt than in nickel), the reasonableness of the above estimation of pseudo-contact shifts may be evaluated by assuming that the spin density distribution ratios between ligand carbons 2 and 3 are identical in the two complexes. With this assumption the ratio of 3-hydrogen contact shift $\Delta\nu_{\mathrm{H}}^{\mathrm{cont}}$, to the methyl contact shift, $\Delta\nu_{\mathrm{CH_3}}^{\mathrm{cont}}$, should be equal in the two compounds, and an estimation of the pseudo-contact shifts in $[\mathrm{M(AA)_3}]^-$ can be obtained from eq 2 as described previously,[3a,22] where $\Delta\nu$ without

$$\frac{\Delta\nu_{\mathrm{H}}^{\mathrm{cont}}}{\Delta\nu_{\mathrm{CH_3}}^{\mathrm{cont}}} = \frac{(\Delta\nu_{\mathrm{H}})_{\mathrm{Ni}}}{(\Delta\nu_{\mathrm{CH_3}})_{\mathrm{Ni}}} = \frac{(\Delta\nu_{\mathrm{H}}^{\mathrm{cont}})_{\mathrm{Co}}}{(\Delta\nu_{\mathrm{CH_3}}^{\mathrm{cont}})_{\mathrm{Co}}} = \frac{(\Delta\nu_{\mathrm{H}})_{\mathrm{Co}} - 4.86X_{\mathrm{o}}}{(\Delta\nu_{\mathrm{CH_3}})_{\mathrm{Co}} - X_{\mathrm{o}}} \tag{2}$$

a superscript stands for the observed isotropic shift, X_{o} is the pseudo-contact shift experienced by the methyl group, and 4.86 is the ratio of $G(\chi)$ for the 3-hydrogen to that of the methyl group. Solution of eq 2 using the observed isotropic shifts yields an X_0 of -252 cps, and -1220 cps for the pseudo-contact contribution to the 3-hydrogen isotropic shift. The excellent agreement of this calculation with the above independent estimate based on the butyl proton shifts lends support to our model. It should be pointed out that pseudo-contact shifts are not negligible compared with the contact shifts in this octahedral cobalt(II) complex. With the above assumptions the contact shifts for the methyl and 3-hydrogen of the cobalt complex become -423 and $+2135$ cps, respectively. This implies that the percentage of total spin delocalization in the cobalt complex is about 1.19 times that in the nickel.

Magnetic Anisotropy. $[\mathrm{Bu_4N}][\mathrm{Ni(AA)_3}]$. The tetrabutylammonium protons in this compound show no isotropic shifts under the same conditions in which the butyl resonances of the cobalt compound undergo large displacements. This indicates that $(K_\parallel - K_\perp)$ must be zero or quite small. This behavior of the

---

[23] J. A. Happe and R. L. Ward, *J. Chem. Phys.*, **39**, 1211 (1963).

[24] D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).

[25] A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

[26] G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

nickel complex is consistent with the low-temperature esr results[27] for benzene and *p*-dioxane clathrates of $NaNi(AA)_3$ which contain the same complex anion. The magnetic anisotropy of octahedral nickel(II) with an orbitally nondegenerate ground state is expected to be small.[5] This has been amply confirmed experimentally.[6,28]

$[Bu_4N][Co(AA)_3]$. Although the isotropic shifts for the tetrabutylammonium protons in this complex arise solely from the pseudo-contact interaction (eq 1), the labile equilibrium involved, as well as uncertainty in the relevant geometric factors, prevents an absolute evaluation of the anisotropy from the observed butyl proton resonance displacements. Qualitatively, results for both the cation and ligand pseudo-contact shifts indicate that $(K_{\parallel} - K_{\perp})$ is negative (*vide supra*), and therefore $K_{\perp} > K_{\parallel}$ in this compound. A rough quantitative evaluation of the susceptibility tensor anisotropy can be made from the estimated ligand proton pseudo-contact shifts using eq 1 and the calculated geometric factors. From a pseudo-contact shift of −1220 cps for the 3-hydrogen, a value of $K_{\parallel} - K_{\perp}$ of -3010×10^{-6} cgsu mole^{-1} at 34° is obtained. Since eq 1 applies to solids perhaps a better method, with some precedent,[29] is to compute g_{av} from the measured molar susceptibility with the equation given in ref 17 and then to use the equation,[4,18] $(\Delta\nu/\nu)_i = [-\beta^2 S(S + 1)/45kT][(3 \cos^2 \chi_i - 1)/r_i^3][3g_{\parallel}^2 + g_{\parallel}g_{\perp} - 4g_{\perp}^2]$ to compute $g_{\parallel}$ and $g_{\perp}$. By this procedure we obtain $g_{av} = (^1/_3)(g_{\parallel} + 2g_{\perp}) = 2.55$, $g_{\parallel} - g_{\perp} = -0.57$ which yields $K_{\parallel} - K_{\perp} = -4280 \times 10^{-6}$ cgsu mole^{-1}. It should be emphasized that *g* tensor components obtained by this method are not comparable with those obtained from esr measurements at liquid helium temperatures where values of g_{av} near 4.5 are generally observed.[5,7] The magnetic susceptibility of octahedral cobalt(II) complexes does not obey the simple expression given in ref 17. Neither esr nor magnetic anisotropy measurements are available for compounds containing the $[Co(AA)_3]$ anion; however, our estimate is of the order of magnitude observed[30] for the magnitude anisotropy of cobalt(II) in Tutton salts at room temperature.

---

[27] M. Peter, *Phys. Rev.*, **116**, 1432 (1959).

[28] J. H. Van Vleck, *Discussions Faraday Soc.*, **26**, 96 (1958).

[29] R. G. Shulman, H. Sternlicht, and B. J. Wyluda, *J. Chem. Phys.*, **43**, 3116 (1965).

[30] K. Kambe, S. Koide, and T. Usui, *Progr. Theoret. Phys.* (Kyoto), **17**, 15 (1952).

Studies of the Planar–Tetrahedral Configurational Equilibrium in Solutions of Bis(β-ketoamino)cobalt(II) Complexes

G. W. Everett, Jr.,[1a] and R. H. Holm[1b]

Contribution from the Departments of Chemistry, Harvard University, Cambridge, Massachusetts, and the University of Wisconsin, Madison, Wisconsin.

Received December 27, 1965

Abstract: A series of bis(β-ketoamino)Co(II) complexes of general formulation $Co[R_\gamma COCR_\beta C(NR)R_\alpha]_2$ has been synthesized by a nonaqueous chelation reaction. Only the tetrahedral stereoisomeric form is measurably populated in the solid and solution phases by complexes having $R_\alpha = CH_3$, $R_\beta = H$, $R_\gamma = CH_3$ and C_6H_5, and $R = CH_3$, *n*-C_3H_7, and C_6H_5. However, when R = H, three complexes having the following sets of substituents are low spin and planar in the solid but in solution exhibit magnetic and spectral properties indicative of the presence of both planar and tetrahedral forms: $R_\alpha = R_\gamma = CH_3$, $R_\beta = H$; $R_\alpha = CH_3$, $R_\beta = H$, $R_\gamma = C_6H_5$; $R_\alpha = H$, $R_\beta = R_\gamma = CH_3$. By a detailed study of spectral and magnetic properties over temperature and/or concentration ranges and consequent elimination of other solution equilibria known for bis(chelate)Co(II) complexes, it is concluded that these complexes are implicated in a planar ($S = {^1/_2}$) $\rightleftharpoons$ tetrahedral ($S = {^3/_2}$) configurational equilibrium similar to that already established for several classes of Ni(II) complexes but previously unknown for any other metal. Analysis of the temperature dependence of the magnetic moments has yielded ΔF, ΔH, and ΔS values characterizing the structural change for the three complexes. The formation of the tetrahedral stereoisomer is found to be endothermic in each case. Ni(II) complexes with R = H and having the same ligand systems are found to be 100% planar up to 80° in solution. Similar Ni(II) complexes with $R = CH_3$ are less than 5% tetrahedral at 25° whereas under the same conditions the corresponding Co(II) complexes are ~100% tetrahedral. The most important conclusions drawn from the data at hand are (i) ligands which stabilize a measurable amount of tetrahedral Ni(II) induce ~100% tetrahedral Co(II), and (ii) ligands which stabilize a measurable amount of planar Co(II) induce ~100% planar Ni(II). A brief comparison of thermodynamic data for the planar–tetrahedral conversion of Co(II) and Ni(II) complexes with R = H and CH_3 is presented.

The stereochemistry of complexes of cobalt(II) which are four coordinate on the basis of simplest formulation is frequently complicated in both the solution and solid phases by intermolecular association or additional intramolecular chelation. In solutions of noncoordinating solvents these effects are sometimes manifested by various types of structural equilibria involving high ($S = 3/2$) or low spin ($S = 1/2$) cobalt(II) which may be categorized as follows. The most

$$\text{octahedral polymer(s) (high spin)} \rightleftharpoons \text{tetrahedral (high spin)} \qquad (1)$$

---

[1] (a) National Science Foundation Predoctoral Fellow, 1962–1966; (b) Alfred P. Sloan Foundation Fellow, 1964–1967.