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Contact Shift Studies of the Square-Planar Complex Bis(dithioacetylacetonato)cobalt(II)[1]

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The synthesis, magnetic moment, and the proton nmr contact shift data for the square-planar complex bis(dithioacetylacetonato)cobalt(II) are reported. Our results indicate that the unpaired electron resides in the d_{z^2} orbital in agreement with some previous studies on square-planar cobalt(II) complexes. Possible electron delocalization mechanisms and dipolar contributions to the observed contact shifts are discussed.

Introduction

Although a square-planar geometry is relatively unusual for cobalt(II) complexes, this stereochemistry is prevalent in a number of biologically significant systems such as the phthalocyanines[2] and the porphyrins.[3]

Beckett and Hoskins[4] have used X-ray crystallography to show that the compound $Co(sacsac)_2$ (sacsac = dithioacetylacetonato) possesses a square-planar geometry as had been suggested in an earlier report of the synthesis by Martin and Stewart.[5]

We report details of the synthesis of $Co(sacsac)_2$ and have decided to investigate this interesting and unusual compound by means of nmr contact shifts.

Electron spin resonance has been used to study square-planar cobalt(II) complexes, but we are unaware of any previous proton contact shift data reported for complexes of this type. The general theory and interpretation of nmr contact shifts has been discussed in several recent review articles.[6,7] Because this technique potentially offers a method of studying the metal–ligand bonding in detail, we have decided to use it to investigate the bonding and electronic structure in this complex.

Experimental Section

Apparatus. (a) **Nmr Spectra.**—The nmr spectra were obtained on Varian Models A-60 and DA-60 spectrometers. All nmr spectra were referenced relative to TMS as an internal standard.

(b) **Magnetic Susceptibility Measurements.**—The solution moment was determined by nmr at 38°, using a method first reported by Evans.[8] The measured susceptibility was corrected for diamagnetism by the use of Pascal's constants.[9]

Synthesis of Bis(dithioacetylacetonato)cobalt(II).—Though the synthesis of bis(dithioacetylacetonato)cobalt(II) is relatively straightforward, effective ventilation is required to remove the toxic and obnoxious excess of hydrogen sulfide required for the reaction. The reaction is carried out in a gas washing bottle (Kontes K-657250 or the equivalent) in which hydrogen chloride and hydrogen sulfide displace oxygen sufficiently to prevent extensive oxidation of the cobalt(II) ion. Hydrogen sulfide is passed through a hydrogen chloride saturated solution of 11.9 g (0.05 mol) of $CoCl_2 \cdot 6H_2O$ and 10 g (0.10 mol) of 2,4-pentanedione in 200 ml of anhydrous methanol until red-brown crystals separate from the green mother liquor. The product is filtered under a blanket of dry nitrogen, washed with anhydrous methanol until the washings are colorless, and dried in a stream of dry nitrogen. The complex is stable to air when dry, but it is readily oxidized in the presence of coordinating solvents such as pyridine, N,N-dimethylformamide, and dimethyl sulfoxide. *Anal.* Calcd for $CoC_{10}H_{14}S$: Co, 18.35; C, 37.37; H, 4.40. Found: Co, 18.14; C, 37.35; H, 4.29.

Treatment of the Nmr Data.—The complex was studied at a ~0.05 *M* concentration in chloroform solution at 28°. The contact shifts, $\Delta\nu$, were referenced relative to the isomorphous, diamagnetic analog $Ni(sacsac)_2$. The relationship between the contact shift, $\Delta\nu$, and the hyperfine coupling constant, A, in gauss, is then given by the modified Bloembergen equation[10]

$$\frac{\Delta\nu}{\nu_0} = \frac{-A g_{av}^2 \beta_e^2 S(S+1)}{g_N \beta_N (3kT)} \qquad (1)$$

where $g_N - 5.58$, $\beta_N = 5.05 \times 10^{-24}$ erg/G, $g_{av} = \mu_{eff}/\sqrt{S(S+1)}$, $\beta_e = 9.27 \times 10^{-21}$ erg/G, S is the total sum of the electron spin, A is the hyperfine coupling constant in gauss, $\Delta\nu$ is the contact shift relative to the analogous diamagnetic complex, and ν_0 is the probe frequency (both in Hz).

Results

Nmr Data.—All of the complexed ligand signals appeared as broadened singlets in the nmr spectra. The methyl protons were identified by integration of the spectra. The nmr data for $Co(sacsac)_2$ are given in Table I.

TABLE I
NMR RESULTS

Group	δ,[a] Hz	$\Delta\nu$,[b] Hz	g_{av}	10^3A, G
CH	−223	+218	2.54	−30.96
CH_3	−78	+64	2.54	−9.09

[a] The chemical shifts are relative to TMS at 28°. [b] The contact shift is relative to the diamagnetic complex $Ni(sacsac)_2$ at 28°. The hyperfine coupling constants were calculated from $\Delta\nu$ and g_{av} using eq 1.

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Magnetic Susceptibility Data.—The magnetic susceptibility data for Co(sacsac)$_2$ are given in Table II.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA FOR Co(sacsac)$_2$[a]

Compound	$10^6\chi_M$	χ_{diamag}	$10^6\chi_{M(cor)}$	μ_{eff}, BM
Co(sacsac)$_2$	1739	−174	1913	2.19 ± 0.05

[a] The moment was determined at 38° in CHCl$_3$.

Discussion

Before discussing the implications for the bonding deduced from the contact shift data, we must show the effects of pseudocontact shifts that arise from a dipolar coupling of the moments.

Pseudocontact shifts occur under conditions where there is a proper combination of magnetic anisotropy and geometric factors. Since the crystal structure of Co(sacsac)$_2$ is known,[4] we can compute the necessary geometric factors. However, the magnetic anisotropy in this compound is unknown.

The observation of relatively narrow lines in the nmr spectra of Co(sacsac)$_2$ at room temperature is indicative of an extremely short electronic relaxation time. This is consistent with the fact that we have observed no signal in the esr spectrum at room temperature. In general, these two techniques tend to be complementary and mutually exclusive because of differing requirements of the relaxation times for the observation of spectra. Eaton[11] has demonstrated this experimentally for a large series of transition metal–acetylacetonate complexes. Thus, as would be expected, the previously reported esr work[3,12] on the cobalt(II)–phthalocyanine complexes was done at low temperatures. Therefore, we must find some way of approximating the magnetic anisotropy. To us, the esr data for the cobalt(II)–phthalocyanine complexes seem to be the most reasonable choice.

Assour and Kahn[13] have shown that the g-tensor anisotropy for the cobalt(II)–phthalocyanine complex is extremely sensitive to its polymorphic form. Earlier esr studies[3,12] had been on the β-cobalt phthalocyanine. In this polymorph the cobalt ion lies at the center of a second more distant array of nitrogen atoms in addition to the primary square-planar configuration of nitrogen donors. Second-order contributions to the anisotropy must be included and the experimental g values[3,12] are $g_\parallel = 1.92$ and $g_\perp = 2.90$. The magnetic susceptibility data of Figgis and Nyholm[14] provide additional proof of the large orbital angular momentum contribution to the ground state of the β polymorph. At room temperature $\mu_{eff} = 2.72$ BM which is substantially above the spin-only value. However, in the α-cobalt phthalocyanine, where there is only a square-planar field of nitrogen atoms, at room temperature[13] $\mu_{eff} = 2.38$ BM. The measured g values are $g_\parallel = 2.01$ and $g_\perp = 2.42$.

Our magnetic moment at room temperature is $\mu_{eff} = 2.19$ BM. Although low solubility in chloroform-*d* prevented accurate measurements in this solvent, we would not expect z-axis solvation in chloroform to be appreciable; this together with our lower value for the magnetic moment and the location of the unpaired electron in the d_{z^2} orbital (*vide infra*) suggests to us that the anisotropies in Co(sacsac)$_2$ ought to resemble those of the α-cobalt phthalocyanine most closely.

As mentioned previously, we can calculate the appropriate geometric factors and using the anisotropy for α-cobalt phthalocyanine we can calculate the probable pseudocontact contribution using the Jesson[15] equation

$$\frac{\Delta\nu}{\nu_0} = \frac{-\beta_e^2 S(S+1)(3\cos^2\chi - 1)(3g_\parallel + 4g_\perp)(g_\parallel - g_\perp)}{45kTr^3} \qquad (2)$$

where r is the radius vector from the metal ion to the appropriate proton, χ is the angle between the pseudo C_4 axis and the radius vector, $g_\parallel$ and $g_\perp$ are the parallel and perpendicular g factors, respectively, and the other symbols have been defined previously. The data necessary for the calculation of the pseudocontact shift in Co(sacsac)$_2$ are given in Table III.

TABLE III

PSEUDOCONTACT SHIFT DATA FOR Co(sacsac)$_2$

Group	χ_i, deg	r_i, Å	$g_\parallel$	$g_\perp$	$\Delta\nu_i$, Hz
CH	90.0	4.83	2.01	2.42	−119
CH$_3$	78.7	7.09	2.01	2.42	−33

Substitution of the appropriate factors into eq 2 gives the values −119 Hz for β-CH and −33 Hz for the methyl groups. Thus, although it is impossible to assess the *exact* magnitude of the dipolar contribution, we emphasize the important point that *isotropic* contact shifts are *upfield* and the observed upfield shifts are not the result of a pseudocontact contribution. Also, the sign of the hyperfine coupling constant is the same for both the β-CH and the methyl groups. Although different anisotropies would change the magnitude of the pseudocontact contribution, they would not affect its direction. Only in what we consider to be the unlikely event that the anisotropy lies in the xy plane, as in the cobalt–maleonitriledithiolato complex,[16] would our conclusions be altered.

In the D_{2h} point group the $3d_{z^2}$, $3d_{x^2-y^2}$, and the 4s orbitals are of appropriate symmetry for σ bonding and transform as A_g. The $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$ orbitals are of appropriate symmetry for π bonding and transform as B_{1g}, B_{2g}, and B_{3g}, respectively.

La Mar's data[17] on the heteroatom-substituted bis(acetylacetonate)–nickel(II) adducts indicate that if the unpaired electron spin resides in orbitals containing

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substantial amounts of π character, the contact shifts for the methyl group and β-CH will be of opposite sign and have a magnitude of several thousand hertz. Eaton's data[11] on the closely related transition metal acetylacetonates also show large isotropic contact shifts and delocalization in molecular orbitals of π symmetry. Thus, although π delocalization was least when the heteroatom was S in La Mar's system,[17] we would still expect contact shifts of substantial magnitude if the unpaired electron was located in the d_{xy} orbital.

If one chooses our coordinate system, so that the x and y axes intersect the corners of the square-plane, the $d_{x^2-y^2}$ orbital is usually considered the "bonding orbital" in a square-planar geometry,[18] and the $\sigma_{a_g}{}^*$ orbital, which is mainly $d_{x^2-y^2}$ in character, should be strongly antibonding. If the unpaired electron resided in this orbital, large contact shifts should occur. In Co(sacsac)$_2$, the hyperfine coupling constants for the methyl group are of the same sign. This, together with the observation of relatively small contact shifts, leads us to conclude that the unpaired electron resides in the $3d_{z^2}$ metal orbital—rather than the $3d_{xy}$ orbital. This conclusion is in agreement with esr studies of the square-planar cobalt(II)–phthalocyanine complex[2,10,11] which also showed that the unpaired electron was located in the $3d_{z^2}$ orbital. If the extended Hückel molecular orbital calculations of Cotton, *et al.*,[19] on the square-planar (D_{2h}) bis(β-ketoenolate) complexes of nickel(II) and copper(II) can be extrapolated to Co(sacsac)$_2$, then for a d^7 case the unpaired electron would also be in a σ_{a_g} (d_{z^2}) orbital.

Finally, we need to discuss the mechanism by which the unpaired electron spin density reaches the ligand protons. There are two probable mechanisms by which this may occur. The first is an admixture of the 4s and $3d_{z^2}$ orbitals which is possible since they both transform as A_g in the D_{2h} point group. Ingram, *et al.*,[3] had calculated this admixture to be 4% in the β-cobalt(II)–phthalocyanine complex. However, this mechanism would place *positive* spin density in the σ_{a_g} (4s) molecular orbital and would result in a *downfield* contact shift for the protons. The second is a "core polarization" mechanism that has been invoked by Watson and Freeman[20] to explain the hyperfine splitting observed in the atomic spectra of transition metal ions and atoms that contain no unpaired "s" electrons. Here, the unpaired electrons in the d orbitals contribute indirectly by polarizing the formally paired electron spins in the s orbitals, thus leading to negative spin density at the metal nucleus. Garito and Wayland[21] have recently used such a mechanism to account for the observed negative hyperfine coupling constants in Cu(t-Bu(oac))$_2$ (t-Bu(oac) = t-butyl acetoacetate) and its 1:1 substituted pyridine type adducts.

Apparently, this indirect mechanism is dominant and negative spin density from the metal is mixed into the σ_{a_g} (4s) molecular orbital. Such a mechanism would lead to the observed negative hyperfine coupling constants and upfield contact shifts.

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The Hydrolysis of Phosphatopentaamminecobalt(III) in Aqueous Solution

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The kinetic parameters of the hydrolysis of phosphatopentaamminecobalt(III) in aqueous solution at unit ionic strength have been measured. The following hydrolysis constants were determined: for $Co(NH_3)_5PO_4{}^0$, $k(60°) = 2.0 \times 10^{-6}$ sec^{-1}, $\Delta H^{\ddagger} = 39.6 \pm 1.4$, $\Delta S^{\ddagger} = 33.7 \pm 4.5$; for $Co(NH_3)_5HPO_4{}^+$, $k(60°) = 1.05 \times 10^{-6}$ sec^{-1}, $\Delta H^{\ddagger} = 26.8 \pm 0.5$, $\Delta S^{\ddagger} = -6.6 \pm 1.5$; for $Co(NH_3)_5PO_4H_2{}^{2+}$, $k(60°) = 1.57 \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 23.3 \pm 0.3$, $\Delta S^{\ddagger} = -11.2 \pm 1.0$; for the base-catalyzed hydrolysis of $Co(NH_3)_5PO_4{}^0$, $k(60°) = 4.0 \times 10^{-4}$ M^{-1} sec^{-1}, $\Delta H^{\ddagger} = 36.8 \pm 0.7$, $\Delta S^{\ddagger} = 36.0 \pm 2.0$, where the units of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are kcal mol^{-1} and cal deg^{-1} mol^{-1}, respectively.

Introduction

In aqueous solution phosphatopentaamminecobalt(III) exhibits four stages of protonation[2,3] such that n varies from 0 to 4 in the formula $Co(NH_3)_5PO_4H_n{}^{n+}$. This complex is eminently suited for a study of the effect of protonation upon the hydrolysis rate of the phosphato ligand from the cobalt moiety. Previous kinetic studies of this system have been mainly concerned with the species for which $n = 4$ and 3 and also with the base-catalyzed hydrolysis.[3,4]

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