Spin-Hamiltonian Axes of Some Cobalt(II) Schiff Base Complexes from Electron Paramagnetic Resonance in Oriented Nematic Glass

Sir:

We wish to report an epr study of several cobalt Schiff base complexes (Co(SB)) and their monopyridine adducts (Co(SB)py) oriented in frozen "nematic glass."[1] This technique allows an experimental determination of the spin-Hamiltonian (SH) principal axes with respect to the molecular framework which is crucial to the detailed interpretation of our results. These approximately planar (N_2O_2) coordination complexes of cobalt are of interest because of their ability to bind molecular oxygen.[2]

In the nematic mesophase of a liquid crystal a planar solute can be aligned with the normal to the molecular plane normal to the magnetic field. This ordering can be preserved upon freezing and the epr spectrum of such a frozen nematic glass will only show features from magnetic field orientations along the in-plane g and hyperfine tensor directions, with the out-of-plane direction largely or wholly suppressed. Rotation of the frozen nematic solution by 90° will enhance the out-of-plane and diminish the in-plane components.[1] We have used N-(4′-methoxybenzylidene)-4-butylaniline (I) as the nematic solvent, purchased from the Vari-Light Corporation under the trade name VL-1047-N.[3] Epr spectra in frozen CH_2Cl_2 and toluene show that I does not significantly alter the spin-Hamiltonian parameters of either Co(SB) or Co(SB)py.

When randomly oriented in a frozen matrix of I, the various four-coordinate Co(SB) show spectra (Figure 1a) with well-resolved hyperfine interactions with the single cobalt nucleus and a slightly rhombic SH

$$\mathcal{H} = \beta[g_{\parallel}S_{\parallel}H_{\parallel} + (g_2S_2H_2 + g_3S_3H_3)] + [(A_{\parallel}S_{\parallel}I_{\parallel} + A_2S_2I_2 + A_3S_3I_3)]$$

where $g_{\parallel} \gg g_2$ and g_3 and $A_{\parallel} > A_2$ and A_3.

In the frozen nematic glass (Figure 1c) the feature associated with the intermediate $g_{\parallel}$ value, g_2, is almost totally suppressed, and those of the largest and smallest g values ($g_{\parallel}$ and g_3) are enhanced. Upon rotation of the sample by 90° (Figure 1b), g_2 is enhanced relative to the other two. Thus, although the "powder" spectra (Figure 1a) look nearly "axial," the unique g value and hyperfine parameter ($g_{\parallel}$, $A_{\parallel}$) are not associated with the normal to the Co(SB) plane (z axis). Rather, the intermediate g value and hyperfine splitting (g_2, A_2) should be labeled (g_z, A_z) and are associated with the normal direction. We have labeled the direction of largest and smallest g values as x and y, respectively. SH parameters for the Co(SB) are listed in Table I.

This finding that the "parallel" g value lies in the molecular plane is counter to the assignment in a recent powder epr study[4] and similar to the results for $[Co(mnt)_2]^{2-}$ [5] and $Co(mesityl)_2(PEt_2Ph)_2$.[6] What appears to be unique is that the intermediate g value for Co(SB) is $g_z > g_e$. Another recent powder epr measurement of Co(acacen)[7] has correctly assigned the x axis values but not the z axis on the basis of an epr study of Co(salen).[8] Indeed, although Co(salen) is not soluble in I the similarity of its spin-Hamiltonian parameter to those of the Co(SB) studied here leads us to suggest that the assignment of the z axis might require reexamination.

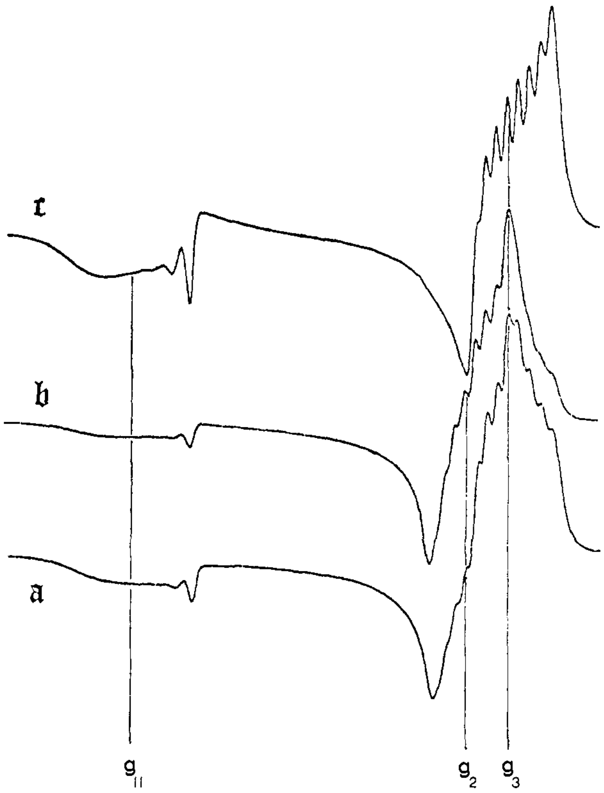

Figure 1. The epr spectra of Co(meacacen) in I at 77°K: (a) unoriented solution, (b) frozen nematic glass rotated by 90°, (c) frozen nematic glass, no rotation. For assignment of molecular axes, see text.

Epr spectra for the five-coordinate Co(SB)py complexes are dramatically different from those of the four-coordinate Co(SB),[9] exhibiting substantial rhombic distortions from an axial symmetry with g_2 and $g_3 \gg g_{\parallel} > g_e$. Hyperfine splittings are resolved for cobalt and also, in the parallel direction only, for the single axial nitrogen. This Hamiltonian has previously been assigned to molecular axes with ($g_{\parallel}$, $A_{\parallel}$) = (g_z. A_z).[9] Despite the asymmetry caused by the coordinated pyridine, when Co(SB)py is frozen in a nematic glass $g_{\parallel}$ is indeed suppressed, verifying the assignment. Spin-Hamiltonian parameters are again listed in Table I.

Our description of the electronic structure of these Co(SB) complexes using the (SH) values in Table I begins with application of standard crystal-field perturbation-theory equations based on pure metal d orbitals.[5,6] Disregarding the deviations of g_z from g_e, these equations give reasonable results *only* on the assumption

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[1] (a) J. P. Fackler and J. A. Smith, *J. Amer. Chem. Soc.*, **92**, 5787 (1970); (b) J. P. Fackler, J. D. Levy, and J. A. Smith, *ibid.*, **94**, 2436 (1972).

[2] See, for example, (a) L. H. Vogt, H. M. Faigenbaum, and S. E. Wiberly, *Chem. Rev.*, **63**, 269 (1963); (b) A. L. Crumbliss and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 55 (1970); (c) G. Tauzher, G. Amiconi, E. Antonini, M. Brunori, and G. Costa, *Nature (London)*, **241**, 222 (1973).

[3] D. L. Diemente, Ph.D. Thesis, Northwestern University, 1971.

[4] Y. Nishida and S. Kida, *Chem. Lett.*, 57 (1973).

[5] A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

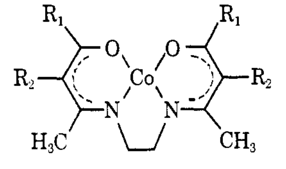
[6] R. Bentley, F. Mabbs, W. Smail, M. Gerlock, and J. Lewis, *J. Chem. Soc. A*, 3003 (1970).

[7] C. Busetto, F. Cariati, P. C. Fantucci, D. Galizzioli, and F. Morazzoni, *Inorg. Nucl. Chem. Lett.*, **9**, 313 (1973).

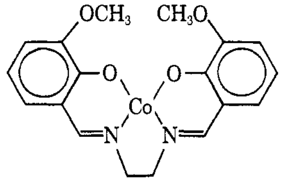
[8] L. M. Engelhardt, J. D. Duncan, and M. Green, *Inorg. Nucl. Chem. Lett.*, **8**, 725 (1972).

[9] (a) B. M. Hoffman, D. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, **92**, 61 (1970); (b) D. Diemente, B. M. Hoffman, and F. Basolo, *J. Chem. Soc. D*, 467 (1970).

Table I. Spin-Hamiltonian Parameters[a] for Some Co(SB) and Co(SB)py Complexes in Nematic Glass at 77°K



Co(acacen) $R_1 = CH_3$, $R_2 = H$
Co(meacacen) $R_1 = R_2 = CH_3$
Co(benacacen) $R_1 = C_6H_5$, $R_2 = H$



Co(MeOsalen)

Compound	$g_x{}^b$	$g_y{}^b$	g_z	$\|a_x{}^{Co}\|^{b,c}$	$\|a_y{}^{Co}\|^{b,c}$	$\|a_z{}^{Co}\|^{c}$	$\|a_z{}^{N}\|^{c}$
Co(acacen)	2.928	1.934	2.01	100.3	32.5	32.8	
Co(meacacen)	2.957	1.952	2.031	73.9	30.7	32.0	
Co(benacacen)	3.084	1.937	2.01	104.1	32.0	32.8	
Co(acacen)py	2.435	2.225[d]	2.012	56.2	12.5[f]	92.3	14.7
Co(benacacen)py	2.428	2.22[f]	2.012	55.2	13.5[f]	92.1	14.9
Co(MeOsalen)py	2.40	2.23[f]	2.015	56[e]	10[f]	89.4	14.7

[a] Errors = 1 in the final digit unless indicated differently. [b] The x and y directions are arbitrarily assigned. These directions are in the average Schiff base plane. [c] Units in $cm^{-1} \times 10^4$. [d] Error is ± 0.003. [e] Error is ± 3. [f] Estimated from computer simulations.

that the unpaired electron occupies the d_{z^2} orbital.[10] The spin–orbit parameters of Co(meacacen), for example, are found to be $b_1 = \lambda/(E_{yz} - E_{z^2}) = -0.159$, $b_2 = \lambda/(E_{xz} - E_{z^2}) = -0.001$; for both SB = meacacen and benacacen, hyperfine parameters are $P \simeq 140$ ($\times 10^{-4}$ cm^{-1}) and $\kappa \simeq 0.1$–0.12. A somewhat larger value of P is required for Co(acacen), and the magnitude of the hyperfine anisotropy ($|A_x| - |A_y|$) is not quite as well reproduced as for the other two complexes.

Comparing b_1 and b_2 shows that the large in-plane g anisotropy arises from a large splitting of the (d_{xz}, d_{yz}) orbitals, with the d_{yz} lying closely below the half-filled d_{z^2} and d_{xz} far lower. Of the other two d orbitals, the in-plane orbital, pointing directly at the ligand atoms (d_{xy} in our coordinates[10]), must be the highest lying empty orbital; the other in-plane orbital ($d_{x^2-y^2}$) must be below d_{z^2} and filled.

The finding that $g_z > g_e > g_y$ for the four-coordinate Co(SB), however, prevents a complete fit to the g factors using a pure d-electron ground-state configuration. An electron in a pure d_{z^2} orbital has no first-order contributions to g_z and second-order corrections ($-3b_1{}^2$) must tend to decrease g_z below g_e.

It does not appear that mixing of cobalt d orbitals[5] in the low-symmetry environment of the Co(SB) can account for $g_z > g_e$. The Co(SB) probably exhibit an out-of-plane puckering which reduces their overall symmetry to C_2—with twofold rotation about the x axis. In this symmetry d_{z^2}, $d_{x^2-y^2}$ and d_{yz} are all of a symmetry, and it is possible to mix the latter two orbitals with d_{z^2}, forming

$$|z^2\rangle = \alpha(d_{z^2}) + \beta(d_{x^2-y^2}) + \gamma(d_{yz})$$

with $(\alpha^2 + \beta^2 + \gamma^2) = 1$ and where we expect $\alpha^2 \gg \beta^2$ and γ^2. This hybrid orbital has first-order contributions to g_z. However, the contribution from mixing d_{yz} is $(-2\gamma^2 b_2)$ which is positive but much too small to counterbalance the negative second-order contribution to g_z.

The contribution to g_z from admixture of $d_{x^2-y^2}$ is $(-8\beta^2 b_3)$, where $b_3 = \lambda/(E_{d_{xy}} - E_{d_{z^2}})$. To fit g_z by use of this term would require b_3 to be large and negative, implying that the d_{xy} orbital lies below $|z^2\rangle$ and is doubly occupied and therefore that the unoccupied orbital is $d_{x^2-y^2}$. But this ordering contradicts our above conclusions regarding the placing of these two levels.

A possible simple solution to this contradiction is to postulate the existence of filled predominantly ligand σ orbitals of b (xy) symmetry[6] or, alternatively, filled predominantly ligand π orbitals of b symmetry which could couple, respectively, through the $d_{x^2-y^2}$ or the d_{yz} components of $|z^2\rangle$ to give positive contributions to g_z.

Despite the qualitative difference between resonance spectra of the Co(SB) and Co(SB)py complexes, the results in the latter are also rationalized by placing the odd electron in the d_{z^2} orbital. Complexation by pyridine reduces the splitting between the d_{xz}–d_{yz} orbitals, presumably by reducing the out-of-plane "puckering," and creates the pattern g_x and $g_y > g_z$. The result $g_z > g_e$, however, leads to the same contradictions as in the four-coordinate Co(SB). Cobalt porphyrin complexes also have $g_z > g_e$.[11]

Acknowledgment. This work was supported by the National Institutes of Health and by the donors of the Petroleum Research Fund, administered by the American Chemical Society. B. M. H. wishes to acknowledge Professor R. G. Pearson for a helpful discussion on the symmetry properties of Co(SB).

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[10] We choose the x axis to pass through Co and the center of the C–C bond of the ethylenediamine and the z axis to be normal to the mean SB plane.

[11] F. A. Walker, *J. Amer. Chem. Soc.*, **92,** 4235 (1970).

[12] Alfred P. Sloan Foundation Fellow, and recipient of a NIH Career Development Award.

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Received April 13, 1973

^{31}P Nuclear Magnetic Resonance Spectrum of Pentamethylcyclopentaphosphine. Evidence for a Large Stereochemical Dependence of the $^1J(PP)$ Spin–Spin Coupling

Sir:

The influence of lone-pair orientation on the nuclear spin–spin coupling constant values has long been