the fundamental nature of the correlation. We believe not only that the reason for the correlation is a fundamental one but also that its origin can be identified with sufficiently and significantly equivalent configurations or essentially in chemistry with conservation of orbital symmetry and that, once its theoretical basis and ramifications are established, it can be incorporated into statistical thermodynamics as a general principle[2] and used not only in the systematics of complex reaction but also in the analysis of systematic errors.[2,7,15,16]

[16] J. R. McCreary, S. A. Rassoul, and R. J. Thorn, *High Temp. Sci.*, **1**, 412 (1969).

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Direct Evaluation of Dipolar Nuclear Magnetic Resonance Shifts from Single-Crystal Magnetic Measurements. Paramagnetic Anisotropy of Bis(2,4-pentanedionato)bis(pyridine)cobalt(II)

Sir:

A fundamental aspect of the study of isotropic nuclear magnetic resonance (nmr) shifts $\Delta\nu^{\text{iso}}$ in paramagnetic systems[1] is the separation of the Fermi contact $\Delta\nu^{\text{con}}$ and dipolar[2] $\Delta\nu^{\text{dip}}$ contributions to these shifts. Contact shifts provide a measure of the unpaired electron spin density at the resonating nucleus, whereas dipolar shifts arise from a through-space dipolar interaction between the electronic magnetic moment and the nuclear spin moment, which does not vanish in magnetically anisotropic systems. In one of the earliest attempts to separate contact and dipolar shifts, Happe and Ward,[3] in 1963, studied the labile pyridine-type base adducts of bis(2,4-pentanedionato)cobalt(II) and -nickel(II), hereafter $Co(acac)_2$ and $Ni(acac)_2$. They observed a difference in the proton isotropic shift ratios between the cobalt and nickel systems and attributed this difference to the presence of a dipolar interaction in the case of the cobalt adducts. They achieved a quantitative separation, assuming that the dipolar shifts conformed to the geometric factors[4] estimated for an axially symmetric system. The method of spin-isolated nuclei was employed wherein it was assumed that the shift of the para proton of 4-phenylpyridine coordinated to $Co(acac)_2$ was purely dipolar in origin. The contact shift ratios for both the cobalt and nickel systems so obtained agree quite well, and the contact shift was attributed to spin delocalization in the σ systems of these heterocyclic amine ligands.

Subsequently, Horrocks and coworkers employed the *ratio method* to achieve the separation in similar systems.[5-8] This latter method has recently been discussed in detail by one of us in an article[9] which also pointed out that dipolar shifts may properly be evaluated from magnetic susceptibility anisotropy data rather than g-tensor anisotropy as had been attempted previously.[10,11] Equations for dipolar shifts, valid for axial symmetry, for the two most probable averaging conditions[10,11] were derived inductively[9] from the analogous expressions involving g-tensor anisotropy.[4,10,11] The validity of one of these equations has recently been verified by independent theoretical derivations.[12,13]

In the present Correspondence we report single-crystal magnetic susceptibility anisotropy data for $Co(acac)_2(py)_2$, py = pyridine, and the direct evaluation of dipolar shifts therefrom. Only for $Co(bipy)_3Br_2 \cdot 6H_2O$, bipy = 2,2′-bipyridyl, has such an evaluation previously been made.[9] The recent publication of ^{13}C isotropic shift data for the $Co(acac)_2(py)_2$[14] and $Ni(acac)_2(py)_2$[14,15] systems renders the present report particularly timely and allows the importance of dipolar shifts for nuclei other than protons to be assessed for the first time.

In their paper,[14] Doddrell and Roberts assume that dipolar shifts are of little importance for ^{13}C nuclei and, on the basis of ratio differences between the cobalt and nickel systems, conclude that the spin delocalization mechanisms are significantly different for the two systems and that a degree of π-spin delocalization is present. Our results indicate that dipolar shifts *do* contribute importantly to ^{13}C isotropic shifts in $Co(acac)_2(py)_2$ and, within the fairly large experimental uncertainties, show that no difference in spin delocalization mechanism is necessary to explain the observed differences between the cobalt and nickel systems.

Magnetic Anisotropy.—Large orthorhombic[16] single crystals of $Co(acac)_2(py)_2$ were grown by slow evaporation of a benzene solution. Single-crystal magnetic anisotropies were measured as a function of temperature from 77 to 293°K by Krishnan's critical-torque method, the technique, theory, and methodology of which is described in detail by us elsewhere.[17] The bulk average susceptibility $\bar{\chi}$ was measured on a powdered sample by the Gouy method, and for both types of measurement a variable-temperature cryostat of published design[18] was employed. The torsion fiber was calibrated with tetragonal nickel sulfate hexahydrate ($\Delta\chi_a$[19] = 80.8 VVk/[20] mol at 27°). The results at 293°K are $\chi_a - \chi_b = 2310$, $\chi_c - \chi_b = 3820$, and $\bar{\chi} = 9569$ VVk/mol,[21] which yielded $\chi_a = 9836$, $\chi_b = 7526$,

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[1] For reviews see (a) E. deBoer and H. van Willingen, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 111 (1967); (b) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

[2] Sometimes referred to as pseudocontact.

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

[4] H. M. McConnell and R. E. Robertson, *ibid.*, **29**, 1361 (1958).

[5] W. DeW. Horrocks, Jr., R. C. Taylor, and G. N. La Mar, *J. Amer. Chem. Soc.*, **86**, 3031 (1964).

[6] R. W. Kluiber and W. DeW. Horrocks, Jr., *ibid.*, **87**, 5350 (1965).

[7] R. W. Kluiber and W. DeW. Horrocks, Jr., *ibid.*, **88**, 1399 (1966).

[8] R. W. Kluiber and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **6**, 166 (1967).

[9] W. DeW. Horrocks, Jr., *ibid.*, **9**, 690 (1970).

[10] J. P. Jesson, *J. Chem. Phys.*, **47**, 579 (1967).

[11] J. P. Jesson, *ibid.*, **47**, 582 (1967).

[12] R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

[13] B. R. McGarvey, *J. Chem. Phys.*, **53**, 86 (1970).

[14] D. Doddrell and J. D. Roberts, *J. Amer. Chem. Soc.*, **92**, 6839 (1970).

[15] I. Morishima, T. Yonezawa, and K. Goto, *ibid.*, **92**, 6651 (1970).

[16] R. C. Elder, *Inorg. Chem.*, **7**, 1117 (1968).

[17] W. DeW. Horrocks, Jr., and D. DeW. Hall, *Coord. Chem. Rev.*, in press.

[18] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 331 (1959).

[19] A. Bose, S. C. Mitra, and S. K. Datta, *Proc. Roy. Soc., Ser. A*, **248**, 153 (1958).

[20] 1 Van Vleck (VVk) = 10^{-6} cgsu; see ref 17.

[21] Includes a diamagnetic correction of −146 VVk/mol.

and χ_c = 11346 VVk/mol. In the crystal $Co(acac)_2(py)_2$ involves a trans geometry with the planes of the two pyridine ligands mutually perpendicular. From the known crystal structure[16] the following simple relationship between the principal crystal and molecular susceptibilities is evident: $\chi_a = \chi_x$, $\chi_b = \chi_z$, and $\chi_c = \chi_y$ as is shown in Figure 1.

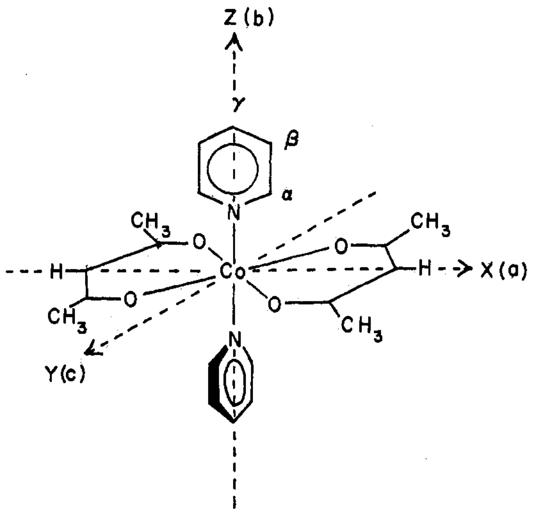

Figure 1.—Coordinate system for $Co(acac)_2(py)_2$.

Table II

Geometric Factors and Shifts for Acetylacetonate Protons at 293°K

Proton	$G(\theta,r)^a$	$G'(\theta,\Omega,r)^a$	$\Delta\nu_{Ni}^{iso\ b}$	$\Delta\nu_{Co}^{iso\ b}$	$\Delta\nu_{Co}^{dip}(G)^c$	$\Delta\nu_{Co}^{dip}(G')^d$	$\Delta\nu_{Co}^{dip}$(total)	$\Delta\nu_{Co}^{con}$
CH	-1.19×10^{-2}	1.19×10^{-2}	+19.1	−17.9	−20.2	+15.0	−5.2	−12.7
CH_3	-8.47×10^{-3}	5.04×10^{-3}	−3.0	−24.9	−14.4	+6.3	−8.1	−16.8

[a] In $Å^{-3}$; estimated from X-ray data of ref 16. [b] Data from ref 24 corrected to 293°K. [c] Calculated from first term of eq 1. [d] Calculated from second term of eq 1.

Evaluation of Dipolar Shifts.—For the case of rhombic ligand field symmetry appropriate to $Co(acac)_2(py)_2$, dipolar shifts are calculable from eq 1,[9,12,13] where the geometric factors ($G(\theta,r) = \langle(3\cos^2\theta - 1)r^{-3}\rangle_{av}$, $G'(\theta,\Omega,r) = \langle(\sin^2\theta\cos 2\Omega)r^{-3}\rangle_{av}$, Ω is the angle made between the x axis and the projection of vector r on the xy plane, and the averaging conditions are those appropriate to eq 10 of ref 9, wherein the other symbols are defined. For coordinated pyridine, effective axial symmetry is likely since the $G'(\theta,\Omega,r)$ terms contribute equally and oppositely for the ligands in the xz and yz planes (Figure 1). The occurrence of these two configurations in the solid state suggests effective free rotation about the Co–N axis in solution which would cause the $G'(\theta,\Omega,r)$ terms to average to zero. Thus, as has been previously assumed for adducts of this type, dipolar shifts for monodentate ligand nuclei are expected to be proportional to the $G(\theta,r)$ values which are listed in Table I along with the derived dipolar shifts. Also listed in Table I are the isotropic shifts which were placed on an absolute scale using the ratios of Doddrell and Roberts[14] and a quantitative study of the proton shifts in our laboratory. For systems undergoing rapid ligand exchange, $\Delta\nu^{iso} = \Delta\nu^{obsd}/P_m$, where

$$\frac{\Delta\nu^{dip}}{\nu} = -\frac{1}{3N}\left[\chi_z - \frac{\chi_x}{2} - \frac{\chi_y}{2}\right]G(\theta,r) - \frac{1}{2N}[\chi_x - \chi_y] \times G'(\theta,\Omega,r) \qquad (1)$$

Table I

Geometric Factors and Isotropic, Dipolar, and Contact Shifts for $M(acac)_2(py)_2$ Systems at 293°K

Atom or ratio	$G(\theta,r)^a$	$\Delta\nu_{Ni}^{iso\ b,c}$	$\Delta\nu_{Co}^{iso\ b,c}$	$\Delta\nu_{Co}^{dip\ b,d}$	$\Delta\nu_{Co}^{con\ b}$
α-H	2.33×10^{-2}	−87.7	-32.9^e	39.5	−72.4
β-H	1.06×10^{-2}	-26.6^e	−5.0	18.1	−23.1
γ-H	9.20×10^{-3}	−8.0	9.4	15.6	−6.2
α-C	5.48×10^{-2}	93.0	199	92.5	106
β-C	2.10×10^{-2}	−344	−229	35.7	−265
γ-C	1.67×10^{-2}	34.5	73.8	28.3	45.5
β-H/α-H		0.30	0.15		0.32
γ-H/α-H		0.09	−0.29		0.09
γ-H/β-H		0.30	−0.32		0.27
β-C/α-C		$-3.7(-1.7)^f$	−1.2		−2.5
γ-C/α-C		$0.37(0.45)^f$	0.37		0.43
γ-C/β-C		$-0.10(-0.27)^f$	−0.32		−0.17

[a] In $Å^{-3}$; evaluated from the X-ray data of ref 16, with the protons placed at their calculated positions 1.08 Å from the appropriate carbon atoms. [b] In ppm. [c] Data obtained from ratios of ref 14. [d] Calculated using eq 1 from susceptibility anisotropy data; see text. [e] Datum used to place ratios of ref 14 on an absolute scale based on present proton shift measurements. [f] Ratios in parentheses are those of ref 15.

P_m is the ratio of coordinated py to total py in the system. $\Delta\nu^{obsd}$ values were obtained on deuteriochloroform solutions 0.4 and 0.8 M in py which the py:$M(acac)_2$ ratio was varied from 11 to 3. Plots of chemical shifts *vs.* P_m were linear and the slopes yielded $\Delta\nu^{iso}$ values. The contact shifts for cobalt $\Delta\nu_{Co}^{con}$ were obtained by subtraction of $\Delta\nu_{Co}^{dip}$ from $\Delta\nu_{Co}^{iso}$. These and ratios of various quantities are shown in Table I. For both ^1H and ^{13}C nuclei the ratios of $\Delta\nu_{Ni}^{iso}$ and $\Delta\nu_{Co}^{iso}$ within the respective complexes are in considerable disagreement, however the ratios of the $\Delta\nu_{Co}^{con}$ values compare reasonably well with the $\Delta\nu_{Ni}^{iso}$ ratios, which are contact in origin. The ^{13}C ratios are in less satisfactory agreement than those for the proton data; however, there is considerable discrepancy between the $\Delta\nu_{Ni}^{iso}$ ratios reported by two different laboratories[14,15] (see Table I). The present results show that differences in isotropic shift ratios for nuclei of coordinated pyridine-type ligands in $M(acac)_2$ systems can be quantitatively accounted for by the dipolar shift present in $Co(acac)_2$ complexes. This implies that the dominant mode of spin delocalization is the same for both the cobalt and nickel complexes. Indeed, the isotropic shifts for ^1H and ^{13}C nuclei of py and 2-, 3-, and 4-picoline coordinated to $Ni(acac)_2$ have been adequately accounted for by INDO/2 calculations[22] involving σ-spin delocalization *alone*. As in the case of the $Co(bipy)_3^{2+}$ ion,[9] the conditions necessary for the application of the *ratio method*[9] are shown to apply.[23] Further support for the validity of the present analysis is provided by the fact that the ratio $\Delta\nu_{Ni}^{iso}/\Delta\nu_{Co}^{con}$ for corresponding protons is 1.15 in the case of the $M(bipy)_3^{2+}$ ions[9] and 1.21 for the present $M(acac)_2(py)_2$ systems.

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(22) W. DeW. Horrocks, Jr., and D. L. Johnston, *Inorg. Chem.*, **10**, 1835 (1971).

(23) For the latest attack on this method see J. I. Zink and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 5339 (1970).

Acetylacetonate Protons.—For these resonances[24] both the $G(\theta,r)$ and $G'(\theta,\Omega,r)$ terms contribute to the dipolar shifts as is indicated in Table II. Inspection of the derived values of $\Delta\nu_{\mathrm{Co}}{}^{\mathrm{con}}$ shows that they do not even qualitatively agree with the $\Delta\nu_{\mathrm{Ni}}{}^{\mathrm{iso}}$ values. This implies that the mode of spin delocalization does differ for the acetylacetonato moiety between the cobalt and nickel systems. Such variation with a change in metal has been discussed by Eaton.[25]

Finally, it should be pointed out that a degree of non-Curie behavior is predicted for the dipolar shifts, based on the temperature variations of the principal molecular susceptibilities; however, the predicted deviations from a $1/T$ behavior for $\Delta\nu_{\mathrm{Co}}{}^{\mathrm{iso}}$ are small for the acac H and CH_3 protons over the temperature range accessible to solution measurements. Complications from the slowing of ligand exchange[26] render an experimental verification impossible for the pyridine nuclei.

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[24] G. N. La Mar, *J. Magn. Resonance*, **1**, 185 (1969).

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

[26] R. W. Kluiber, R. Kukla, and W. DeW. Horrocks, Jr., *Inorg. Chem.*, **9**, 1319 (1970).

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An Erroneous Conclusion Based on a Misinterpretation of the IUPAC Rules for Designating Absolute Configurations

Sir:

Unfortunately in a recent review article[1] on absolute configurations of transition metal complexes it was concluded that the suggested IUPAC rules for designating absolute configurations[2] did not appear to apply to polydentate ligand complexes. As an example it was pointed out that for the three isomers (+)-Co(en)$_3{}^{3+}$, (+)-Co(en)$_2$(NH$_3$)$_2{}^{3+}$, and (−)-Co(penten)$^{3+}$ (penten = *N*,*N*,′,*N*′-tetrakis(2′-aminoethyl)-1,2-diaminoethane), shown in Figure 1, which should be configurationally related according to the reviewers,[3] the IUPAC nomenclature indicated that the designations for the three isomers should be Λ, Λ and Δ, respectively. Therefore, the last was not configurationally related to the first two. This is a misinterpretation of the IUPAC rules. The rules simply stated that in a case where a multidentate ligand is involved, all the Δ's and Λ's belonging to all the "skew-line pairs" be given. Thus, (−)-Co(penten)$^{3+}$ should be designated ΔΔΛ. What, in fact, was referred to in this review article was the "ring-pairing" scheme upon which the IUPAC nomenclature is based.[4] In this scheme the complex would have been designated Δ since Δ pairs predominate over Λ pairs.[5]

More importantly, however, is that experimental evidence, both X-ray[6] and circular dichroism studies,[7] shows clearly that (+)-Co(en)$_3{}^{3+}$ and (+)-Co(en)$_2$(NH$_3$)$_2{}^{3+}$ are *not* configurationally related to (−)-Co(penten)$^{3+}$ as stated by the review article but to (+)-Co(penten)$^{3+}$, Figure 1.

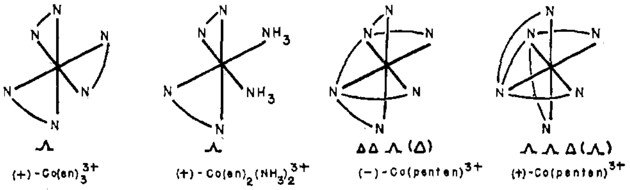

Figure 1.—Absolute configurations of complexes discussed in the text. Designation is that suggested by IUPAC. Designation in parentheses is that obtained by applying the "ring-pairing" scheme. (See text.)

It is important to note, then, that the IUPAC rules still appear to be useful[8] contrary to what was concluded.[1] It is clear that the rules leave something to be desired; but until a better scheme is developed, it is strongly urged that a serious effort be made to follow the IUPAC rules.

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[1] R. D. Gillard and P. R. Mitchell, *Struct. Bonding* (*Berlin*), **7**, 46 (1970).

[2] *Inorg. Chem.*, **9**, 1 (1970).

[3] The reviewers confused this issue by intermixing nomenclatures at this point and in the review in general although some attempt was made to justify this when nomenclatures were discussed.

[4] J. I. Legg and B. E. Douglas, *J. Amer. Chem. Soc.*, **88**, 2697 (1966).

[5] Note that the suggested IUPAC nomenclature is equivalent to selecting the C_3 axis defined by three chelate rings as in Co(en)$_3{}^{3+}$ whereas ref 4 used the C_2 axis defined by the two chelate rings constituting the ring pair. Designations change in going from one reference axis to the other. See ref 4 for clarification.

[6] F. Muto, F. Marumo, and Y. Saito, *Inorg. Nucl. Chem. Lett.*, **5**, 85 (1969).

[7] S. F. Mason and B. J. Peart, *ibid.*, **5**, 491 (1969).

[8] A recent crystallographic study of $(+)_{5461}$-Co(TRI)$_2$I$_3$ (TRI = tribenzo[*b*,*f*,*j*][1,5,9]triazocycloduodecine), a complex which cannot be "configurationally related" to Co(en)$_3{}^{3+}$ (it has no "ring pairs") but yet has a CD spectrum very similar to that of Co(en)$_3{}^{3+}$ (R. M. Wing and R. Eiss, *J. Amer. Chem. Soc.*, **92**, 1929 (1970)), strongly supports the trigonal twist model (T. S. Piper and A. G. Karipides, *Inorg. Chem.*, **4**, 923 (1965)) and suggests that the "ring-pairing" scheme and consequently the IUPAC rules may be limited to complexes with constraining ligands (*i.e.*, those for which ligand–metal–ligand bond angles are expected to be less than 90° such as for five-membered ring systems which are the most commonly encountered chelates).

[9] Acknowledgment is made to the donors of the Petroleum Research Fund (Grant No. 3153-A3), administered by the American Chemical Society, for partial support of this research. A grant provided for biological and medical research by State of Washington Initiative Measure No. 171 is also gratefully acknowledged.

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