derivatized phosphate group at C-2′. Ion 1 (*m*/*e* 103) is also observed, reflecting the absence of the phosphate group at C-5′. Similarly, in 3′,5′-cyclic AMP-$(TMS)_3$,[3e] i, j, and k are unshifted from Figure 1b, while m and l are absent. A peak having no counterpart in 5′-AMP is present at *m*/*e* 310, due to carbons C-2′ through C-5′ of the ribose skeleton, plus their substituents, including the cyclic phosphate trimethylsilyl ester.

Mass spectra of the TMS derivatives of the bases[3c,d] are simple, consisting mainly of M and M − 15,[12] reflecting the resistance of the aromatic nucleus toward fragmentation.[13] While of little use in a detailed structural sense, their spectra appear well suited for analytical applications.[14]

The uncommon elemental compositions of nucleotide, nucleoside, and base TMS derivatives make their high-resolution mass spectra amenable to computer-based identification techniques. We are currently exploring the direct analysis of nucleic acid hydrolysates in this manner,[15] based on the TMS derivatives described above.

(12) For example, % Σ values for M and M − 15: uracil-$(TMS)_2$, 9, 17; thymine-$(TMS)_2$, 8, 17; cytosine-$(TMS)_2$, 10, 12; adenine-$(TMS)_2$, 9, 30; guanine-$(TMS)_3$, 7, 18.

(13) See, for instance: (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1967, pp 585, 592; (b) J. M. Rice and G. O. Dudek, *J. Am. Chem. Soc.*, **89**, 2719 (1967).

(14) P. M. Krueger and J. A. McCloskey, unpublished experiments.

(15) D. M. Desiderio, N. R. Earle, P. M. Krueger, A. M. Lawson, L. C. Smith, R. N. Stillwell, K. Tsuboyama, J. Wijtvliet, and J. A. McCloskey, Sixteenth Annual Conference on Mass Spectrometry and Allied Topics, Pittsburgh, Pa., May 1968.

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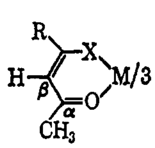
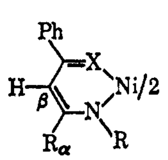
Comparative Stereochemical Effects of Sulfur and Oxygen Donor Atoms in Four- and Six-Coordinate Metal Complexes

Sir:

In complexes of potentially variable stereochemistry, observations from a rapidly growing body of evidence indicate that unsaturated, sulfur-containing, chelating ligands may induce preferential stability of structures which are either unusual or of widespread occurrence. Pertinent examples include the planar structures of bisdithiolene complexes with a variety of metal ions and the trigonal prismatic structures of certain trisdithiolenes.[1] Particular stereochemical consequences of sulfur donor atoms are most clearly recognized and assessed by structural comparisons with complexes identical in constitution except for the donor atom sets. Here are presented two structural comparisons: one of a qualitative nature for six-coordinate complexes (**1**), and the other quantitative for four-coordinate complexes (**2**), which reveal the relative stereochemical effects of sulfur *vs.* oxygen donor atoms.



1, M = Co, V;
X = O, S



2, $Ni(RPhHR_\alpha)_2$; X = O
$Ni(RSPhHR_\alpha)_2$; X = S

cis (facial) and *trans* (meridianal) isomers are possible for complexes **1** with X = O, R ≠ CH_3,[2,3] or X = S. Equilibrium constants for the *trans* ⇌ *cis* reaction of tris(β-diketonato)metal(III) complexes are considerably less than statistical,[2] indicating preferential stability of the *trans* form. In sharp contrast, pmr studies of tris(β-thioketonato)cobalt(III) complexes ($CDCl_3$, ~30°) reveal *exclusive population of the cis isomer* for species with R = CH_3,[4] Ph, *i*-Pr, *t*-Bu; one α-CH_3 or β-H signal is observed consistent with C_3 (or C_{3v}) symmetry. Similarly, only the *cis* isomer was detectable in an analogous series of V(III) complexes (R = CH_3, Ph, *i*-Pr) whose lability ensures equilibrium isomer distributions and whose large contact shifts minimize the possibility of accidental chemical shift degeneracy and an incorrect structural assignment.[3,5] Chemical shift data for a typical pair of tris(β-thioketonates) (R = Ph) are the following: α-CH_3, −141, −4193; β-H, −395, −3507 cps (Co(III), V(III), TMS reference). Heating the thio V(III) complex with R = *i*-Pr in $CDCl_3$ for 24 hr at 118° produced no *trans* rearrangement. Preferential *cis* stability may arise in part from nonbonded S···S interactions in the S_3 unit, similar to those which may assist stabilization of trigonal prismatic coordination.[6]

The dynamic planar ⇌ tetrahedral equilibrium has been demonstrated for $Ni(R{-}PhHR_\alpha)_2$ (R_α = H, CH_3) in noncoordinating solvents and thermodynamic data derived from analysis of the temperature dependence of the contact shifts.[7-9] Analogous thio complexes (R_α = H), an unexplored group of compounds,[10] were prepared by nonaqueous chelation[7] employing β-aminothiones obtained by the reaction[11] of 3-phenyl-1,2-dithiolium perchlorate[12] with primary amines. For $Ni(t\text{-}Bu{-}SPhHH)_2$ close correspondence of solution (3.18 BM, $CHCl_3$) and solid-phase (3.20 BM) magnetic moments indicates that, like $Ni(t\text{-}Bu{-}PhHH)_2$,[9] the mole fraction of tetrahedral form (N_t) is equal to 1 in solution. For both, $-\Delta F^{300°}$ >2.8 kcal/mole and no sterochemical differences are observable. However, for the pairs $Ni(R{-}SPhHH)_2$–$Ni(R{-}PhHH)_2$, R = Amp (CH_3CHCH_2Ph), *sec*-Bu, the equilibrium positions in carbon tetrachloride or chloroform solution are such that detectable amounts of both stereoisomers of all

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[1] A. L. Balch, I. G. Dance, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 1139 (1968), and references therein; J. A. McCleverty, *Progr. Inorg. Chem.*, in press.

(2) R. C. Fay and T. S. Piper, *J. Am. Chem. Soc.*, **84**, 2303 (1962); **85**, 500 (1963).

(3) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1315 (1967).

(4) See also A. Yokoyama, S. Kawanishi, M. Chikuma, and H. Tanaka, *Chem. Pharm. Bull.* (Tokyo), **15**, 540 (1967).

(5) F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6**, 1607 (1967); *J. Am. Chem. Soc.*, **89**, 6472 (1967).

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(8) G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968).

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(10) Only several examples have been reported; *cf.* E. Uhlemann, *Z. Naturforsch.*, **21b**, 592 (1966).

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(12) E. Klingsberg, *J. Am. Chem. Soc.*, **83**, 2934 (1961).

complexes are present over the entire temperature range of contact shift measurements (240–360°K). Active [(+,+), (−,−)] and *meso* (+,−) diastereoisomers are generated by the two asymmetric ligand centers; as in other cases[9,13] their pmr signals are clearly resolved and identifiable by preparation of active isomers from resolved amines. Thermodynamic data for comparison, obtained by a procedure described[9] using β-H signals and hyperfine coupling constants ($a_{\beta H}$) from the R = *t*-Bu complexes, are presented in Table I. Two important conclusions applicable within and below the temperature interval of measurement emerge for the pairs A–D compared: (i) $\Delta F_S - \Delta F_O = \Delta\Delta F > 0$, demonstrating that *sulfur effects greater stabilization of planar stereochemistry than oxygen;* (ii) $|\Delta\Delta H| > |T\Delta\Delta S|$, indicating that inequalities in stereochemical populations are due to enthalpy rather than entropy effects. On the basis of arguments developed elsewhere,[8] differences in metal–ligand bonding in the two stereoisomers are considered principally responsible, with a large extent of π bonding in the planar thio complexes a plausible source of the stability differences. Comparison of experimental and calculated spin densities, currently underway, should serve to establish relative degrees of π bonding in the tetrahedral O, S stereoisomers. Finally, conclusions i and ii are unchanged by comparisons in $CDCl_3$ solutions, the following $\Delta\Delta F = \Delta\Delta H - T\Delta\Delta S$ relationships having been obtained for the indicated pairs: A, 5060 − 12.0*T;* B, 3960 − 11.5*T;* C, 3900 − 8.0*T;* D, 3250 − 7.2*T.*

Table I. Thermodynamics of the Planar–Tetrahedral Structural Conversion of Nickel(II) Complexes **2** (X = O, S) in Carbon Tetrachloride Solution[a]

	Pair	Isomer	ΔH, cal/mole	ΔS, eu	$\Delta F^{323°}$,[b] cal/mole	$N_t^{323°}$ [b]
A	Ni(Amp–PhHH)$_2$	active	−320	3.06	−1310	0.89
	Ni(Amp–SPhHH)$_2$		3580	11.4	−98	0.54
B	Ni(Amp–PhHH)$_2$	*meso*	399	4.70	−1120	0.85
	Ni(Amp–SPhHH)$_2$		2910	11.4	−784	0.77
C	Ni(*sec*-Bu–PhHH)$_2$	active	892	5.98	−1040	0.83
	Ni(*sec*-Bu–SPhHH)$_2$		3490	10.1	221	0.41
D	Ni(*sec*-Bu–PhHH)$_2$	*meso*	1230	6.82	−969	0.82
	Ni(*sec*-Bu–SPhHH)$_2$		3120	9.98	−106	0.54

[a] Data calculated from measured proton contact shifts (240–360°K) and eq 3 in ref 9 using $a_{\beta H}$ (X = O) = −0.884 G (from Ni(*t*-Bu–PhHH)$_2$) and $a_{\beta H}$ (X = S) = −0.717 G (from Ni(*t*-Bu–SPhHH)$_2$). [b] Given at the indicated temperature for comparison with data in ref 9.

Acknowledgment. This research was supported by National Science Foundation Grant GP-7576X.

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(14) National Science Foundation Predoctoral Fellow 1966 to present.

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Restricted Rotation Around Phosphorus-Nitrogen Bonds[1]

Sir:

We wish to report the first measurement of a rotational barrier around a P–N bond. The ^1H nmr spectrum of chloro(dimethylamino)phenylphosphine (**1**), $C_6H_5P(Cl)N(CH_3)_2$, displayed the expected doublet in the methyl region at ambient temperature with J_{PNCH} = 12.6 Hz and τ 7.4.[2] On cooling, the methyl doublet broaded (Figure 1b) and eventually coalesced. Below −60° (Figures 1d, e) two clearly defined doublets developed. At −80° the low-field doublet (τ 7.22) had J_{PNCH} = 19.2 Hz and the high-field doublet (τ 7.75) had

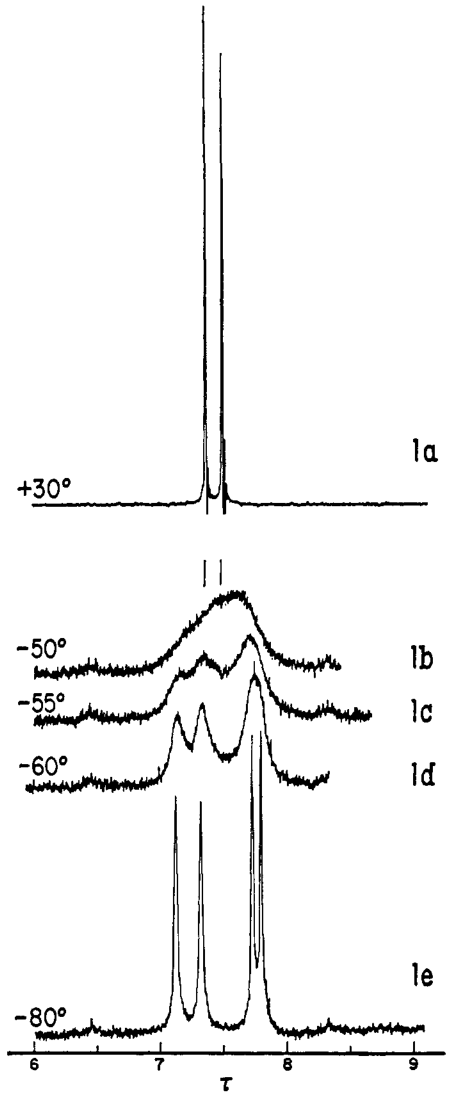

Figure 1.

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(1) This work was supported by the Air Force Office of Scientific Research, through Grant No. AF-AFOSR-1050-67, and the Robert A. Welch Foundation.

(2) All spectra were measured by Mr. E. J. Burshnick on a Varian Associates HA-100 spectrometer equipped with a calibrated variable-temperature accessory. Approximately 15% solutions of the (dialkylamino)phosphines in CCl_3F were sealed *in vacuo* along with a few per cent TMS as internal standard. Chloro(dibenzylamino)phenylphosphine was dissolved in $CDCl_3$ (5% solution) with CH_2Cl_2 internal standard.