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Solvent Dependence of Ambidentate Equilibria in Octahedral Systems

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The position of the equilibrium (t-Bupy)Co(DH)$_2$SCN $\rightleftarrows$ (t-Bupy)Co(DH)$_2$NCS in both protic and aprotic solvents of varying dielectric constant, ϵ 2.3–165, has been measured by utilizing the difference in chemical shift of the methyl resonances in the pmr spectra of the two isomers. In aprotic solvents the equilibrium lies to the left or right in solvent having low (ϵ <10) or high (ϵ >30) dielectric constants, respectively. In protic solvents with high dielectric constants, the S-bonded isomer was unexpectedly stable. The dependence of the equilibrium position on dielectric constant found here for these octahedral complexes is opposite to that found for several square-planar complexes. This difference is explained as resulting from the relatively greater importance of the solvent interaction (such as H bonding) with the nonbonding N or S in SCN in octahedral complexes as compared to square-planar complexes.

It has been found[1,2] that several square-planar complexes containing metal–CNS bonds (CNS refers to the SCN group but does not imply bonding mode) were exclusively S-bonded in DMF and DMSO (type A solvents) and either N- and S- or exclusively N-bonded in solvents such as benzene or methylene chloride (type B solvents).[3] This solvent dependence was explained using Klopman's treatise[4] which demonstrates theoretically that S bonding is favored in high-dielectric medium and N bonding favored in low dielectric medium. However, the equilibria of the square-planar complexes could also be partly correlated with coordinating ability of the solvent,[1] and for this reason, a study of coordinatively saturated octahedral complexes is worthwhile.

We now report our results on one of the first octahedral systems for which a solvent dependence of an ambidentate isomerism has been measured in a range of solvents.[5-8] This effect was observed for the isomers of (t-Bupy)Co(DH)$_2$CNS (where t-Bupy = 4-*tert*-butylpyridine and DH = monoanion of dimethylglyoxime).

We have found that the usual preparations of complexes of the type LCo(DH)$_2$X although analytically pure usually contain trace cobalt(II) impurities (<0.1%) which catalyze many reactions of these complexes in nonaqueous solvents.[9,10] Using this information, we have been able to clarify the interpretation of the chemical and spectral properties of the isomers of (t-Bupy)Co(DH)$_2$CNS in type A solvents containing 1–2% BrCCl$_3$ (an oxidant capable of removing the catalysts).[9] No equilibration occurred spontaneously in DMF and DMSO in the absence of catalysts but otherwise equilibration was relatively rapid ($t_{1/2}$ *ca.* 10–15 min). Since no reaction was taking place in the presence of BrCCl$_3$, the resonances in the pmr spectra of the N- and S-bonded isomers were readily identified and the areas of these resonances could be utilized to determine the equilibrium ratio of isomers in solutions containing no oxidants.

Solutions of the N- and of the S-bonded isomer in class B solvents even in the absence of BrCCl$_3$ did not undergo spectral changes readily[10] in agreement with Burmeister's findings on the pyridine complexes.[8] Burmeister has recently detected the presence of paramagnetic impurities in freshly prepared samples of the isomers of (py)Co(DH)$_2$CNS by using the Faraday technique.[11]

Equilibration of the (t-Bupy)Co(DH)$_2$CNS in type A solvents could be effected immediately by addition of small amounts of cobalt(II) catalysts.[10] These catalysts produced considerable line broadening in type B solvents preventing the determination of the equilibrium ratio of isomers in such solvents by the pmr method. This problem has been overcome by adding sufficient BrCCl$_3$ to oxidize the paramagnetic species.

Experimental Section

The details of the preparation of these and other dimethylglyoxime complexes containing thiocyanate will be published shortly.[12] Analytically pure samples of (t-Bupy)Co(DH)$_2$SCN (containing *ca.* 7% (t-Bupy)Co(DH)$_2$NCS, which was difficult to remove completely) were dissolved in the solvents indicated in Table I but containing *ca.* 2% BrCCl$_3$. The relative chemical shifts of the methyl and butyl resonances of the N- and S-bonded isomer could readily be identified by their relative sizes (Varian A60 instrument). Next *ca.* 0.1 *M* solutions of this same sample were prepared in the solvent of interest and a small amount of P(C$_6$H$_5$)$_3$Co(DH)$_2$ added. Although equilibration was probably immediate, BrCCl$_3$ (1 drop) was not added to the solution to quench the reaction until at least 5 min had elapsed. The spectral region of interest was expanded (1 cps/cm) and the relative areas of the methyl resonances determined by integration. The N-bonded isomer, being less soluble than its isomer, could be obtained isomerically pure but was usually too insoluble for the quantitative measurement of relative peak area. However, qualitatively the same equilibrium ratios were found using this isomer. As might be expected, no dependence of the equilibrium ratio on total Co(III) concentration was found for any solvent.

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[1] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Inorg. Chem.*, **10**, 2032 (1971).

[2] J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Commun.*, 679 (1970).

[3] Bridging CNS groups were also found in type B solvents especially for complexes of triphenylarsine and triphenylstibine.

[4] G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).

[5] Other octahedral systems of this type have been studied[6-8] but true attainment of equilibrium in nonpolar solvents can be questioned[8] in one study,[7] and in another study[8] the N-bonded isomer was reported to predominate in all solvents. However, recent results have shown that S-bonding predominates in type B solvents after equilibration (personal communication, J. L. Burmeister).

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[10] L. A. Epps and L. G. Marzilli, *J. Chem. Soc., Chem. Commun.*, 109 (1972).

[11] J. L. Burmeister, personal communication.

[12] These samples were kindly supplied by Mr. Leon A. Epps. *Anal.* Calcd for CoC$_{19}$H$_{27}$N$_6$O$_4$S: Co, 12.2; C, 44.8; H, 5.6. Found (S-bonded): Co, 12.2; C, 45.0; H, 6.0. Found (N-bonded): Co, 12.1; C, 44.5; H, 6.0.

TABLE I

SOLVENT DEPENDENCE OF THE EQUILIBRIUM RATIO [(t-Bupy)Co(DH)$_2$NCS]/[(t-Bupy)Co(DH)$_2$SCN]

Solvent[a]	Type[b]	Dielectric constant (T, °C)[c]	Ratio (T, °C)[d]
	Aprotic Solvents		
DMSO	A	47 (25)	1.7
Furfural	A[e]	42 (20)[f]	1.3
DMF	A	37 (25)	1.2
Nitrobenzene	B	35 (30)	1.1
Nitrobenzene	B	25 (90)[f]	0.76 (100)
Acetone	A	21 (25)	1.0
Methylene chloride	B	9.1 (20)[f]	0.72
Benzene	B	2.3 (25)	0.77
Benzene	B		0.33 (77)
	Protic Solvents		
N-Methylformamide	A[e]	165 (40)	1.0
Formamide	A	110 (25)	<1[g]
Methanol	C	33 (25)	0.29[h]

[a] Reagent grade solvents were used. Furfural was distilled just prior to use. [b] References 1 and 8. [c] E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 269. [d] At 33° except as noted, estimated accuracy ±15%. [e] These were assigned in keeping with the Burmeister classification.[1] [f] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, pp E61–E71. [g] The solubility of the complexes was too low to allow an accurate determination, but the S-bonded isomer definitely had a larger signal. [h] Determined from the area of the butyl resonances which were better separated than the methyl signals.

Results and Discussion

The equilibrium ratios of N-bonded to S-bonded isomers in various solvents are presented in Table I. The methyl resonances of the two isomers centered around τ 7.6 could be resolved in all solvents examined except chloroform and were usually separated by at least 1.5 cps. Except for the aromatic solvents, the methyl resonance of the N-bonded isomer was found downfield to that of the S-bonded isomer.

The following points can be made regarding the trend of the results obtained at 33°: (1) the solvent effect on this octahedral system is small compared to that found for square-planar complexes; (2) the solvent dependence for aprotic solvents is opposite to that found previously;[1,2] (3) the coordinating ability of the solvent has no obvious influence; and (4) in protic solvents (type C),[1] the S-bonded isomer is unexpectedly stable.

The different coordination geometry between the octahedral complexes reported here and the square-planar complexes studied earlier most likely explains the small dependence on dielectric constant. Solvent molecules can approach more closely the vicinity of the metal–CNS bond in square-planar complexes than the same bond in octahedral complexes. Therefore, it is not unexpected that the influence of solvent on bonding mode is smaller for these octahedral complexes than for the square-planar complexes.[1,2]

If the complexes studied here exhibited the same solvent dependence as the square-planar systems examined by Burmeister, then the S-bonded isomer would be relatively more stable in high dielectric constant solvents, but it was found that the S-bonded isomer was not more stable relative to the N-bonded isomer in any *aprotic* solvent with $\epsilon > 20$. Furthermore, the S-bonded isomer was relatively more stable in every low dielectric constant solvent examined. These trends were not altered by raising the solvent temperature except that the S-bonded isomer becomes relatively more stable. The increased relative stability of the S-bonded isomer is most likely a consequence of a positive enthalpy change favoring the S-bonded isomer. Alternatively, the increased relative stability of the S-bonded isomer may simply reflect the lower dielectric constants of the solvents at the elevated temperatures.

Norbury and his coworkers have suggested[7] that since cobalt(III) centers are classified as hard, one might expect a solvent behavior different from that found for soft metal centers.[1,2] This explanation seems unlikely for two reasons. First, as pointed out previously,[8] trends predicted by Klopman's treatise[4] are the same for both hard and soft metal centers. Secondly, several types of evidence, both kinetic[13,14] and thermodynamic,[9] suggest that the metal centers in these dimethylglyoxime complexes are relatively soft.

One aspect of Klopman's treatment of solvent dependence may present an explanation for the solvent dependence found here. His calculations show that the "softness" of a metal center increases with $1/\epsilon$ and that this dependence becomes relatively more important as the oxidation state of the metal is increased.[4] As solvent dielectric constant is decreased, the cobalt(III) center studied here should become softer relative to the Pt(II) and Pd(II) centers studied earlier[1,2] and except for the protic solvents, and perhaps DMSO, the solvent effect can be understood.

It is likely that, for these sterically crowded octahedral complexes, the interaction of the solvent with the uncoordinated S or N atom is sufficiently large to influence the relative stability of the two isomers. For example, N bonding may be highly favored in DMSO not only because of the high ϵ of this solvent but also because of favorable interaction between the soft S atom of the CNS group and the soft solvent molecules. The stability of the S-bonded isomer in protic solvents probably reflects the favorable interaction between the nonbonded N of the CNS group and the protons of the solvent.[15] These types of arguments have been detailed for organic systems by Parker,[16] and the same line of reasoning applies here. As for the square-planar complexes studied by Burmeister,[1,2] it is likely that the influence of the solvent on the metal–ligand bond strength is of primary importance.

The stability of the X-bonded isomer of $Co(CN)_5XCN^{3-}$ (X = S,[17] Se[2]) in water and the N-bonded isomer in CH_2Cl_2 has been explained[2,8] using Klopman's theory.[18] Klopman-like solvent effects are expected to be greater on these pentacyano complexes than on the more sterically hindered DH complexes reported here. Favorable nonbonded atom solvent interactions cannot be ignored since the type C solvent (H_2O) would promote X bonding whereas in the absence of such interaction (such as in CH_2Cl_2) the N-bonded isomer may be

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(17) D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **91**, 3105 (1969).

(18) NOTE ADDED IN PROOF.—In ref 17 and in a later paper [D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3364 (1971)], Gutterman and Gray have pointed out that enviromental effects could possibly obscure hard–soft relationships.

more stable. The need for the study of more octahedral complexes of differing steric requirements and containing metals in differing oxidation states is clear.

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Pentacoordinated Molecules. XVII.[1] Molecular Structure of HPF_4 and H_2PF_3 in the Gas, Liquid, and Solid States from Infrared and Laser Raman Spectroscopy

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The vapor-phase and solid-state infrared spectra (4000–33 cm^{-1}) of HPF_4 and H_2PF_3 are reported along with laser Raman spectra for these substances in the liquid and solid states. Polarization measurements were obtained on the liquid states. Complete analysis of the vibrational data supports the trigonal-bipyramidal conformation for the vapor state with the protons residing in equatorial sites for both HPF_4 and H_2PF_3. In contrast to earlier literature on H_2PF_3, the data further suggest retention of the gas-phase structure in the liquid and solid states. The same holds true for HPF_4. With the aid of band-shape analysis on the highly structured infrared spectra, detailed spectral assignments are made supporting the C_{2v} point group. Intramolecular exchange mechanisms consistent with the vibrational assignments are presented.

Introduction

A microwave study of HPF_4[2] has established its vapor-state structure as a trigonal bipyramid with an equatorially positioned proton. This is consistent with a similar structure established for CH_3PF_4 by electron diffraction[3] and other monosubstituted derivatives of PF_5 indicated by vibrational analysis to have this conformation with the unique ligand in an equatorial site. These derivatives are CCl_3PF_4,[4a] $(CH_3)_3CPF_4$,[4b] CF_3PF_4,[5] $ClPF_4$,[6] and CH_3PF_4.[7]

An infrared and Raman study of H_2PF_3[8,9] suggested a trigonal bipyramid for the vapor with the hydrogen atoms again in equatorial sites as expected. However, association to a fluorine bridge dimer was reported[9] to occur in the liquid and solid states.

In contrast to these results, ^{19}F nmr data[10] for the liquid at −46° are consistent with the structure reported for the vapor. Because of the difficulties in handling[8,10] these highly reactive species, reproducible nmr spectra were not easy to obtain. Broad fluorine resonances in the intensity ratio of about 2:1 were observed[10] having a doublet character (P–F spin coupling). On the other hand the ^1H and ^{31}P splitting patterns were consistent with the presence of three equivalent fluorine atoms and, hence, indicative of the presence of intramolecular exchange at low temperature. At higher temperatures (−15°), the ^{19}F pattern[10] also pointed to the onset of positional exchange.

In view of the discrepancies between the vibrational interpretation[9] and the nmr findings,[10] a more detailed study of the structure of H_2PF_3 was undertaken by infrared and laser Raman spectroscopy. In addition, clarification of the condensed-state structure is needed in order to properly interpret intramolecular exchange phenomena observed[10] here. As with H_2PF_3, HPF_4 has been studied previously;[8,10] however, no definitive vibrational analysis has been carried out. To ascertain if HPF_4 behaved analogously and as an aid in assignments, its spectra were also investigated in the gas, liquid, and solid states.

Experimental Section

Materials.—Both HPF_4 and H_2PF_3 were prepared as before[8] from the reaction of hydrogen fluoride with the respective phosphorous acid in a copper vacuum system containing Kel-F U traps. The products were purified by trap-to-trap distillation. The starting materials, anhydrous hydrogen fluoride (Matheson, 99.9%) and phosphorous acid (Fisher Certified reagent, 98.9%), were used without further purification. Hypophosphorous acid (Fisher, purified) needed for the preparation of H_2PF_3 was purified as described previously.[8]

Since the compounds are highly reactive with Pyrex and quartz, H_2PF_3 more so than HPF_4, subsequent handling for spectral determinations made use of glass-free systems. Samples were fractionated just prior to use. During the course of any of the spectral measurements, no changes in band intensities were observed. It was determined that samples of HPF_4 contained in Monel infrared cells partially decomposed into HF and PF_3 during a 24-hr period. The latter were detected from their characteristic infrared spectra. The samples could be stored at −78° in Kel-F, stainless steel, or Monel ampoules for prolonged periods with no noticeable decomposition.

Spectral Measurements.—Infrared spectra were recorded with a Beckman IR 11-12 spectrophotometer. In all runs the instrument was purged with dry nitrogen. The far-infrared region was calibrated with HF, HCl, and H_2O vapor. The higher region was calibrated with CO_2 and H_2O vapor. Samples for gas-phase

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