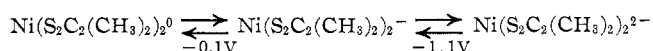The occurrence of uncommon lower oxidation states (*e.g.*, Ir(II), Co(I), Ni(I), ...) which are stable, on the polarographic time scale at least, no doubt reflects the ability of the dithioacetylacetonate ligand to delocalize electronic charge otherwise accumulated on the metal.

Comparisons with the electron-transfer properties of the dithiolenes[3] must be drawn carefully. The most reduced (dithiolato) forms of these, MS_4^{2-} and MS_6^{3-}, formally contain dinegative ligands and place the metals in the ordinary oxidation states, M(II) and M(III), respectively. The dithiolato complexes are susceptible to stepwise oxidations which remove electrons from molecular orbitals of predominantly ligand character. For example, in dimethylformamide[3] *vs.* Ag–AgCl

$$Ni(S_2C_2(CH_3)_2)_2^0 \underset{-0.1V}{\rightleftarrows} Ni(S_2C_2(CH_3)_2)_2^- \underset{-1.1V}{\rightleftarrows} Ni(S_2C_2(CH_3)_2)_2^{2-}$$

It is emphasized that $Ni(SacSac)_2$ is properly compared with the dianionic "dithiolate" rather than the neutral "dithiene." Stepwise oxidations of the dithioacetylacetonates are obviously relatively inaccessible, since the present polarographic range extends only to +0.8 V with reference to Ag–AgCl, though their possible occurrence could be further investigated.

Comparison of this work with other polarographic or voltammetric studies carried out in other solvents on the same or other similar compounds is unwise because of possible solvolysis effects. It is believed that acetone is noncoordinating toward the dithioacetylacetone complexes and this may explain for instance why the relatively simple polarographic behavior is observed in this work for planar complexes compared with that of Ouchi, *et al.*,[12] in acetonitrile or dimethylformamide, where solvolysis problems were encountered.

Solvent-Induced Linkage Isomerizations
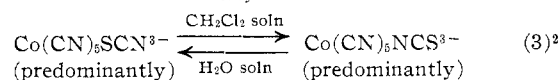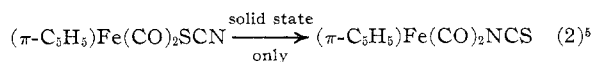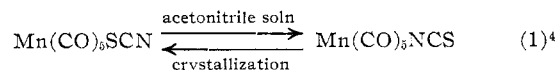
BY JOHN L. BURMEISTER,* ROBERT L. HASSEL, AND ROBERT J. PHELAN

A systematic study of the behavior of complexes of the types ML_2X_2 (M = Pd(II), Pt(II); L = a variety of neutral ligands; X^- = $-SCN^-$, $-NCS^-$, $-SeCN^-$, $-NCO^-$), $Rh(P(C_6H_5)_3)_2(CO)NCX$ (X = O, S, Se), and $Ir(P(C_6H_5)_3)_2(CO)NCS$ in solvents of varying polarity has resulted in the discovery that, in most cases, the bonding mode adopted by the thiocyanate and selenocyanate groups in solution is determined by the nature of the solvent, whereas the bonding mode of the cyanate group is insensitive to solvent effects. The results of infrared and electronic spectral studies of the solutions indicate that, with the exception of the Rh(I) and Ir(I) complexes, all of the thiocyanate and selenocyanate complexes adopt only the S- or Se-bonded mode in solvents which are generally characterized by their relatively high dielectric constants, *e.g.*, DMF and DMSO. In solvents which, in general, have relatively low dielectric constants, *e.g.*, benzene and chloroform, the thiocyanate and selenocyanate complexes (with the exception of $Pd(phen)(SCN)_2$) exhibit either a mixture of X- and N-bonding modes or N-bonding alone (M–SCN–M bridging is also observed when L = triphenylarsine or -stibine). Except for the methanol and ethanol solutions, where the equilibria involved are attained more slowly, the solutions exhibit spectra which do not change with time following their initial preparation. A possible explanation of the solvent effect, in terms of Klopman's treatise on charge-controlled *vs.* frontier orbital-controlled reactions, is presented.

Introduction

The bonding modes of various ambidentate ligands have been shown to be subject to a variety of directive influences,[1,2] among them being the nature of the coordinated metal atom, the electronic or steric requirements of other ligands in the coordination sphere, the physical state of the complex, the mechanism of the reaction used to synthesize the complex, and the nature of the counterion used to isolate ionic complexes. The occurrence of a specific solvent effect has been noted in only a few cases. The solid nitrito complexes [Ni(N,N'-diethylethylenediamine)$_2$(ONO)$_2$] and [Ni-(N,N-dimethylethylenediamine)$_2$(ONO)$_2$] have been found[3] to exist in a nitrito–nitro equilibrium in chloroform solution and three rather disparate examples involving the thiocyanate ion have been reported, *i.e.*

$$Mn(CO)_5SCN \underset{\text{crystallization}}{\overset{\text{acetonitrile soln}}{\rightleftarrows}} Mn(CO)_5NCS \quad (1)^4$$

$$(\pi\text{-}C_5H_5)Fe(CO)_2SCN \underset{\text{only}}{\overset{\text{solid state}}{\longrightarrow}} (\pi\text{-}C_5H_5)Fe(CO)_2NCS \quad (2)^5$$

$$\underset{\text{(predominantly)}}{Co(CN)_5SCN^{3-}} \underset{H_2O \text{ soln}}{\overset{CH_2Cl_2 \text{ soln}}{\rightleftarrows}} \underset{\text{(predominantly)}}{Co(CN)_5NCS^{3-}} \quad (3)^2$$

No rationale was offered for the behavior exhibited in reaction 1; that shown in reaction 2 was attributed to a process which requires an ordered and close arrangement of the molecules, two possible bridged activated complexes being suggested. Reaction 3 will be discussed in the context of the present work. In an effort to ascertain the nature of the role played by the solvent in linkage isomeric systems, we have systematically studied the effects of dissolution of a number of thiocyanate, cyanate, and selenocyanate complexes in a series of solvents of differing polarity. We now wish to present the results of these studies

(1) See J. L. Burmeister and J. C. Lim, *Chem. Commun.*, 1346 (1968), for examples and references.

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

(3) D. M. L. Goodgame and M. A. Hitchman, *Inorg. Chem.*, **5**, 1303 (1966).

(4) M. F. Farona and A. Wojcicki, *ibid.*, **4**, 857 (1965).

(5) T. E. Sloan and A. Wojcicki, *ibid.*, **7**, 1268 (1968).

TABLE I
INFRARED SPECTRA OF COMPLEXES IN GROUP A AND B SOLVENTS[a]

Complex	ν_{CN}, cm⁻¹ (Nujol mull)	Solvents utilized[c]	ν_{CN}, cm⁻¹ Coordinated (bonded atom)	Ionic
Pd(As(C₆H₅)₃)₂(SCN)₂ ⎫	2119 s, sp ⎱	1, 2	2115 m (S)	2058 s
Pd(As(C₆H₅)₃)₂(NCS)₂[b] ⎭	2089 s, br ⎰	3–7	2120–2113 s, sp (S)	...
		8–16	2170–2152 br (Pd–SCN–Pd), 2125–2113 sp (S), 2095–2082 br (N)	...
Pd(P(C₆H₅)₃)₂(NCS)₂[b]	2093 s, br	8	2087–2075 s, br (N)	...
Pd(Sb(C₆H₅)₃)₂(SCN)₂[b]	2115 s, sp	1, 2	2110–2109 m (S)	2058 s, br
		4, 5	2110–2109 s, sp (S)	...
		8–10, 12, 13	2165–2145 vs, br (Pd–SCN–Pd), 2125–2110 w (S), 2085 vw, sh (N)	...
Pd(P(C₆H₅)₃)₂(SeCN)₂[b]	2127 s, sp	1, 2	2120 m (Se)	2068 s, br
		10, 11	2125 (Se), 2100 (N)	...
Pd(P(C₆H₅)₃)₂(NCO)₂[b]	2215 s, br	2	2230 s, br (N)	2158 s, br
		10	2230 s, br (N)	...
Pt(P(C₆H₅)₃)₂(NCS)₂[b]	2097 s, br	1	2106 m (?)	2058 s, br
		2	2120–2100 sh (?)	2058 s, br
		10	2100 s, br (N)[d]	...
		11	2100 s, br (N)[e]	...
Pt(As(C₆H₅)₃)₂(NCS)₂[b]	2090 s, br	2	2120–2100 sh (?)	2058, br
		11	2150 sh (Pt–SCN–Pt), 2105 br (?)	...
Pt(Sb(C₆H₅)₃)₂(SCN)₂[b]	2120 s, sp	2	2120–2100 sh (?)	2058 s, br
		5	2120 s, sp (S)	...
		11	2165 (Pt–SCN–Pt), 2123 (S), 2103 (N)	...

[a] Solutions *ca.* 10^{-2} *M*. Abbreviations: s, strong; sp, sharp; m, medium; w, weak; sh, shoulder; br, broad. [b] Stable isomer in solid state. [c] Solvents utilized: group A: 1, DMF; 2, DMSO; 3, pyridine; 4, acetone; 5, acetonitrile; 6, benzonitrile; 7, adiponitrile; group B: 8, benzene; 9, carbon tetrachloride; 10, chloroform; 11, dichloromethane; 12, cyclopentanone; 13, cyclohexanone; 14, nitrobenzene; 15, 2-butanone; 16, 3-pentanone. [d] Integrated absorption intensity 11×10^4 M^{-1} cm⁻². [e] Integrated absorption intensity 8.6×10^4 M^{-1} cm⁻².

and a possible explanation for the existence of what has proved to be a very important solvent effect.[6]

Experimental Section

Preparation of Compounds.—The complex palladium(II) thiocyanates,[7] selenocyanates,[8] and cyanate,[9] platinum(II) thiocyanates,[7] rhodium(I)[10] thiocyanate, selenocyanate, and cyanate, and iridium(I)[10] thiocyanate were prepared by methods given in the literature. All gave satisfactory C, H, and N analyses.

Infrared and Visible–Ultraviolet Spectra.—Solution infrared spectral data were obtained using a Perkin-Elmer 421 spectrophotometer and matched 0.1- and 1.0-mm sodium chloride cells. The solutions were prepared at room temperature and then repetitively scanned in the ν_{CN} range (2300–2000 cm⁻¹), using a fourfold wave number scale expansion, to ascertain if any spectral changes were occurring with time. Visible–ultraviolet spectra were measured on a Cary 14 spectrophotometer, using matched 1-cm quartz cells, for those complexes which did not exhibit sufficient solubility to permit the acquisition of solution infrared data, as well as selected examples of the more soluble complexes, for reference purposes.

The solvents utilized were either Spectrograde (DMF, acetone, benzene, carbon tetrachloride, and chloroform) or reagent grade. The solvents DMF, DMSO, acetonitrile, dichloromethane, and ethanol were dried and stored over Linde 4A Molecular Sieves.

For reasons which will become apparent, the solvents utilized in this study may be conveniently divided into three groups: (A) *N,N*-dimethylformamide, dimethyl sulfoxide, pyridine, acetone, acetonitrile, benzonitrile, and adiponitrile; (B) benzene, carbon tetrachloride, chloroform, dichloromethane, cyclopentanone, cyclohexanone, nitrobenzene, 2-butanone, and 3-pentanone; (C) methanol and ethanol. All of the spectra obtained were found to be invariant with time, except for the group C solvents, and, in the case of linkage isomers, independent of the isomer initially dissolved. Because of the large amount of data involved, the individual frequencies for each solution will not be reported. Instead, the general infrared and visible–ultraviolet spectral behavior of each compound investigated in the group A and B solvents has been summarized in Tables I
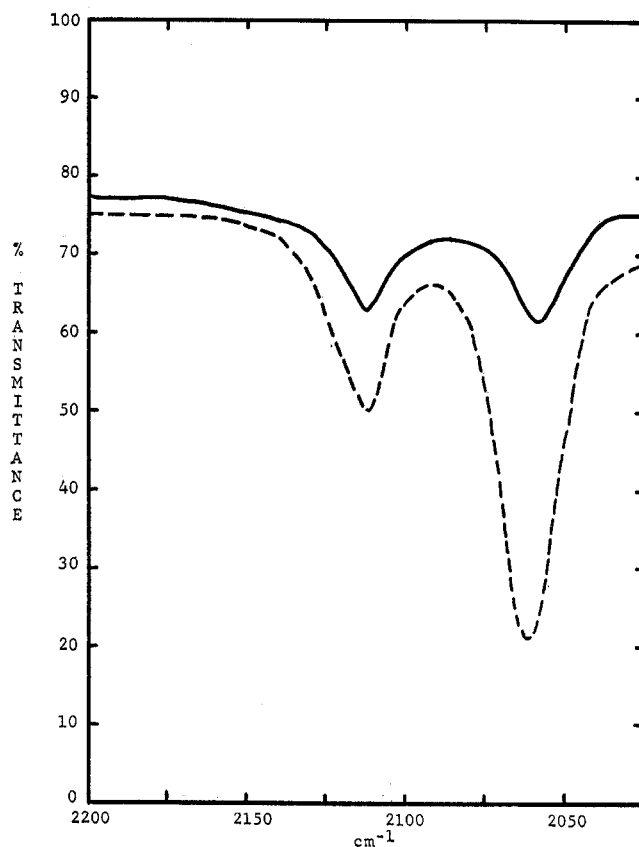
(6) J. L. Burmeister, R. L. Hassel, and R. J. Phelan, *Chem. Commun.*, 679 (1970).

(7) J. L. Burmeister and F. Basolo, *Inorg. Chem.*, **3**, 1587 (1964).

(8) J. L. Burmeister and H. J. Gysling, *Inorg. Chim. Acta*, **1**, 100 (1967).

(9) A. H. Norbury and A. I. P. Sinha, *J. Chem. Soc. A*, 1598 (1968).

(10) Supplied by Mr. N. J. DeStefano; N. J. DeStefano and J. L. Burmeister, *Inorg. Chem.*, **10**, 998 (1971).

Figure 1.—Infrared spectra of 9.3×10^{-2} *M* DMF solutions of Pd(As(C₆H₅)₃)₂(NCS)₂: ———, complex alone; ------, with 10^{-1} *M* added KSCN.

and II. Characteristic infrared and visible–ultraviolet spectra of the Pd(As(C₆H₅)₃)₂(SCN/NCS)₂ complexes in representative group A and B solvents are shown in Figures 1–4.

Effects of Added Potassium Thiocyanate.—The addition of KSCN to the DMF and DMSO solutions of the [Pd(As(C₆H₅)₃)₂-(SCN/NCS)₂] complexes resulted in an enhancement of the

TABLE II
VISIBLE–ULTRAVIOLET SPECTRA OF COMPLEXES IN GROUP A AND B SOLVENTS[a]

Complex	Solvents utilized	Absorption max, nm
Pd(As(C$_6$H$_5$)$_3$)$_2$(SCN)$_2$ Pd(As(C$_6$H$_5$)$_3$)$_2$(NCS)$_2$[b]	DMSO	305
	Acetonitrile	292
	C$_6$H$_6$, CCl$_4$, HCCl$_3$, H$_2$CCl$_2$	350–353
Pd(P(C$_6$H$_5$)$_3$)$_2$(NCS)$_2$[b]	DMSO	310
	Acetonitrile	294
	C$_6$H$_6$, CCl$_4$, HCCl$_3$	284–312, 340–359
Pd(Sb(C$_6$H$_5$)$_3$)$_2$(SCN)$_2$[b]	C$_6$H$_6$, CCl$_4$, HCCl$_3$	365–367, 450–460 w, br
Pd(phen)(SCN)$_2$[b]	DMF, DMSO, CH$_3$CN, acetone	260–270
	CCl$_4$, HCCl$_3$	260–270
Pd(bipy)(SCN)$_2$ Pd(bipy)(NCS)$_2$[b]	DMF, DMSO, CH$_3$CN, acetone	310
	CCl$_4$, HCCl$_3$	270, 360
Pd(P(C$_6$H$_5$)$_3$)$_2$(SeCN)$_2$[b]	DMF, DMSO, CH$_3$CN	280–290
	C$_6$H$_6$, HCCl$_3$, H$_2$CCl$_2$	280–290, 330–340
Pd(phen)(SeCN)$_2$[b]	DMF, DMSO, CH$_3$CN	270
	HCCl$_3$, H$_2$CCl$_2$	270, 350
Pd(bipy)(SeCN)$_2$[b]	DMF, DMSO, CH$_3$CN	310
	HCCl$_3$, H$_2$CCl$_2$	270, 360
Pd(P(C$_6$H$_5$)$_3$)$_2$(NCO)$_2$[b]	DMF, DMSO	325
	HCCl$_3$, H$_2$CCl$_2$	325
trans-M(P(C$_6$H$_5$)$_3$)$_2$(CO)NCX		
M = Rh(I), X = O	DMF	270–280 sh, 369
	HCCl$_3$	275, 369
M = Rh(I), X = S	DMF	290, 371
	HCCl$_3$	290, 370
M = Rh(I), X = Se	DMF	290–300 sh, 369
	HCCl$_3$	299, 374
M = Ir(I), X = S	DMF	298, 345, 393, 440
	HCCl$_3$	297, 345, 395, 440

[a] Solutions *ca.* 10^{-5} *M*. Abbreviations: phen, 1,10-phenanthroline; bipy, 2,2'-bipyridine. [b] Stable isomer in solid state.
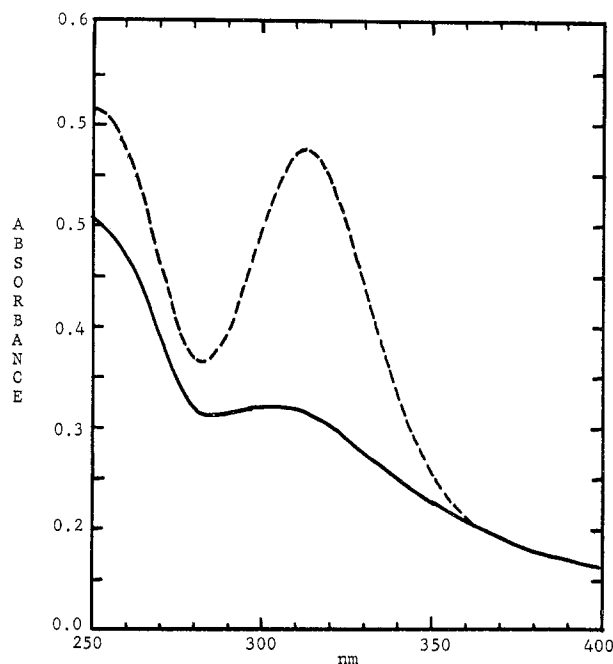
Figure 2.—Visible–ultraviolet spectra of 2.3×10^{-5} *M* DMSO solutions of Pd(As(C$_6$H$_5$)$_3$)$_2$(NCS)$_2$: ———, complex alone; ------, with 10^{-4} *M* added KSCN.

intensity of both the S-bonded and ionic ν_{CN} bands, as shown in Figure 1 for the DMF solution. The ultraviolet absorption maximum of the DMSO solution was observed (Figure 2) to increase in intensity and shift slightly to 312 nm following the KSCN addition. Comparable behavior was also exhibited by the DMSO solution of Pd(P(C$_6$H$_5$)$_3$)$_2$(NCS)$_2$. The ultraviolet absorption maxima of the free thiocyanate ion are found at considerably lower wavelengths.

Effects of Added Triphenylarsine, -stibine, and -phosphine.— Of the three ν_{CN} bands exhibited by the group B solutions of the Pd(As(C$_6$H$_5$)$_3$)$_2$(SCN/NCS)$_2$ complexes, the highest frequency band, which is characteristic[11] of bridging thiocyanate groups,

i.e., Pd–SCN–Pd, is the most intense. The intensities of the middle-frequency band, assigned to S-bonded thiocyanates, and the lowest frequency band, assigned to N-bonded thiocyanates, are generally comparable. However, since the molar extinction coefficients of the ν_{CN} bands of S-bonded thiocyanates have been found[12] to be 2–8 times smaller than those of the ν_{CN} bands of N-bonded thiocyanates, it is clear that, initially, the number of N-bonded thiocyanates present in the solutions is the smallest of the three bond types represented. When triphenylarsine was added stepwise to the solutions, the bridging peak was observed to diminish in intensity, concurrent with the marked growth of the N-bonded peak, as is shown in Figure 3 for the benzene solution. It was not possible to determine from the spectra whether or not the number of S-bonded thiocyanates changes in the process because of the large degree of overlap between the S-bonded peak and the growing, much more intense, broad N-bonded peak. However, the data clearly indicate that, under conditions where bridging is minimized, the N-bonded mode is a major component in all of the group B solutions.

The visible–ultraviolet spectra of *ca.* 2.5×10^{-5} *M* benzene, carbon tetrachloride, chloroform, and dichloromethane solutions of the isomers exhibited only a single intense band at 350–353 nm. The stepwise addition of triphenylarsine, which does not exhibit any absorption maxima above 260 nm, resulted in the eventual disappearance of this band, concurrent with the appearance of two new bands at 320–323 and 378–388 nm, the former being the more intense of the two, as is shown in Figure 4 for the carbon tetrachloride solution.

The behavior of the Pd(Sb(C$_6$H$_5$)$_3$)$_2$(SCN)$_2$ complex in the group B solvents studied was quite similar. In the infrared spectra, the addition of triphenylstibine results in a marked diminution in intensity of the bridging (highest frequency) band, little change in the S-bonded (middle) band, and a very large growth in the N-bonded (lowest frequency) band. In the visible–ultraviolet spectra, an intense peak is observed at 365–367 nm, along with a broad, weak absorption maximum at 450–460 nm. The addition of triphenylstibine results in a diminution in intensity of the former band, a growth in intensity of the latter band, and the formation of a new band at 320–350 nm. The group B solutions of the corresponding platinum(II) triphenylarsine and -stibine thiocyanate complexes exhibited analogous behavior following the addition of the free L ligand.

No bridging was observed in any of the group B solutions of the triphenylphosphine complexes. The addition of free triphenyl-

(11) J. Chatt and L. A. Duncanson, *Nature (London)*, **178**, 997 (1956).

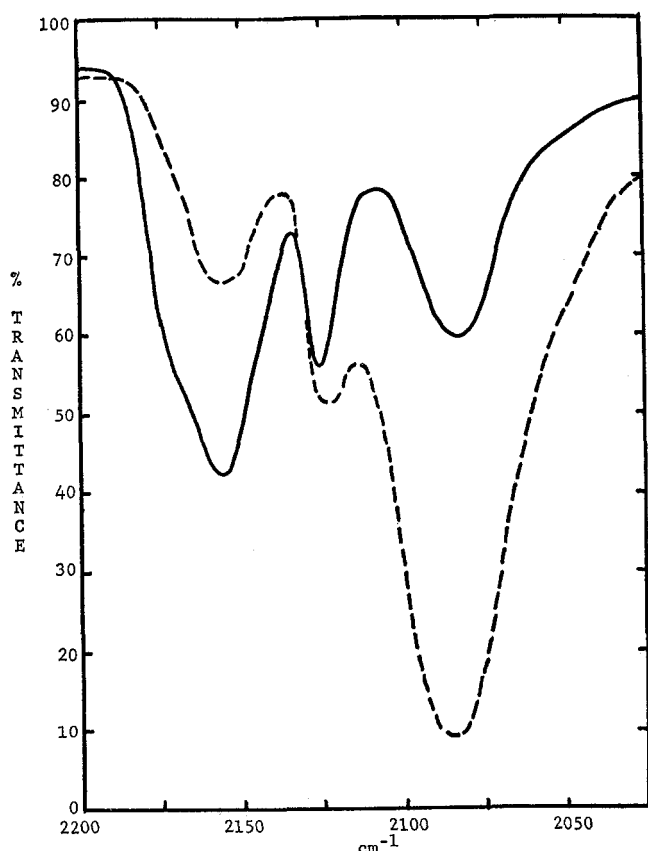(12) C. Pecile, *Inorg. Chem.*, **5**, 210 (1966).

Figure 3.—Infrared spectra of 9.6×10^{-3} M benzene solutions of $Pd(As(C_6H_5)_3)_2(SCN)_2$: ———, complex alone; -----, with 5.8×10^{-2} M added triphenylarsine.

phosphine to the solutions of $Pd(P(C_6H_5)_3)_2(SeCN)_2$ results[13] in the formation of $(C_6H_5)_3P{=}Se$ (ν_{PSe} 560 cm^{-1}) and $Pd(CN)_4{}^{2-}$ (ν_{CN} 2135 cm^{-1}). The N isomer is attacked first, its peak disappearing before that of the Se isomer starts to diminish in intensity.

Group C Behavior.—Intermediate behavior was exhibited by the methanol and ethanol solutions of $Pd(As(C_6H_5)_3)_2(SCN)_2$. Solubility considerations precluded the measurement of their infrared spectra. Unlike the foregoing, the visible–ultraviolet spectra of these solutions were not found to be invariant with time. Initially, each solution exhibited only a single, intense, asymmetric band (at 311 and 332 nm, respectively). The intensity of the band increased with time and experienced a slight red shift (to 334 and 344 nm, respectively). At this point, the addition of triphenylarsine resulted in spectral behavior analogous to that exhibited by the group B solutions—disappearance of the initial band concurrent with the growth of two new bands (325 and 405, 320 and 389 nm, respectively).

Discussion

Group A Solvents.—Based on the frequencies of the ν_{CN} bands in their infrared spectra, it is apparent that the complexes $Pd(As(C_6H_5)_3)_2(SCN)_2$, $Pd(P-(C_6H_5)_3)_2(SeCN)_2$, and $M(Sb(C_6H_5)_3)_2(SCN)_2$ [M = Pd(II), Pt(II)] retain their bonding modes in the group A solvents studied, the arsine–thiocyanate complex doing so in spite of the fact that its N-bonded isomer is the more stable form in the solid state. Since only one high-energy (260–310 nm) charge-transfer band is observed in the group A visible–ultraviolet spectra of the arsine–thiocyanate and phosphine–selenocyanate complexes as well as in the spectra of the PdL-(XCN)$_2$ (L = bipy, phen; X = S, Se) complexes, it can be concluded that the latter complexes are also

(13) P. Nicpon and D. W. Meek, *Inorg. Chem.*, **5**, 1297 (1966).
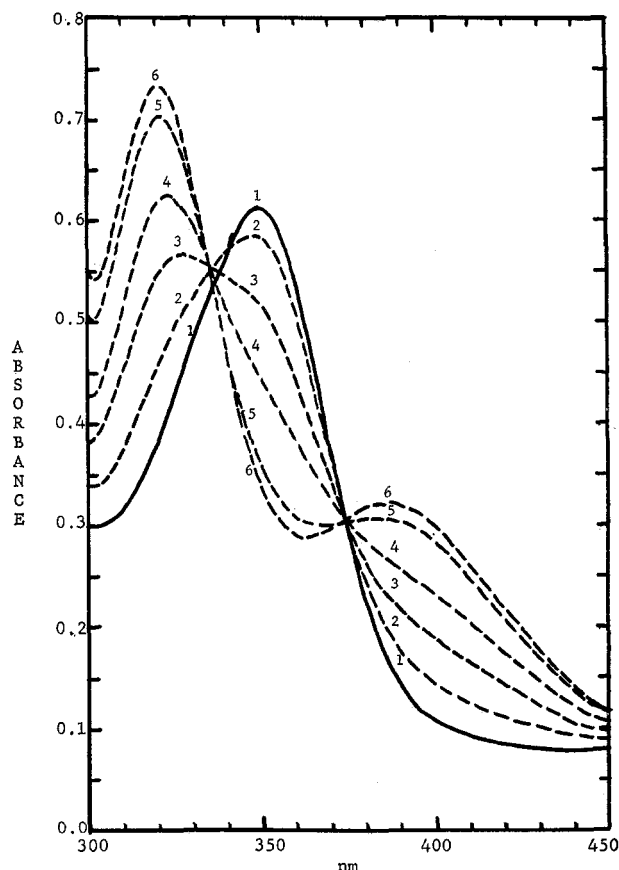

Figure 4.—Visible–ultraviolet spectra of 3.1×10^{-5} M carbon tetrachloride solutions of $Pd(As(C_6H_5)_3)_2(SCN)_2$: 1 (———), complex alone; 2–6 (– – – –), with successively larger amounts $(3.5–5.0 \times 10^{-4}$ $M)$ of added triphenylarsine.

only S or Se bonded in the group A solvents studied. Of greater significance is the observation that the complexes $Pd(As(C_6H_5)_3)_2(NCS)_2$, $Pd(P(C_6H_5)_3)_2(NCS)_2$, and $Pd(bipy)(NCS)_2$, which are stable N-bonded species in the solid state, undergo complete isomerizations to their S-bonded isomers in the group A solvents studied. Only the palladium(II) cyanate, the Rh-$(P(C_6H_5)_3)_2(CO)NCX$ (X = O, S, Se) complexes, and $Ir(P(C_6H_5)_3)_2(CO)NCS$ were found to retain their N-bonded modes in these solvents (the interpretation of the infrared data for the platinum(II)–phosphine and –arsine complexes is ambiguous). Clearly, however, the preponderant driving force in the group A solutions is toward S and Se bonding.

As is indicated by the presence of the ionic ν_{CN} bands in their infrared spectra, dissolution of the complexes in either DMF or DMSO invariably results in the partial ionization of the coordinated pseudohalide groups. Knowing the molar extinction coefficients of the free ions, their concentrations and the per cent ionization of the complexes could be calculated. Representative data, which provide a number of interesting comparisons, are shown in Table III. Ionization in DMSO is more extensive, as would be expected on the basis of its having a soft coordination site available (the sulfur atom). The labile palladium(II) complex was found to ionize to a greater degree than its relatively substitution-inert platinum(II) counterpart; ionization of the bulkier stibine complex is greater than that of the arsine; and ionization of the cyanate is less than that of the thiocyanates.
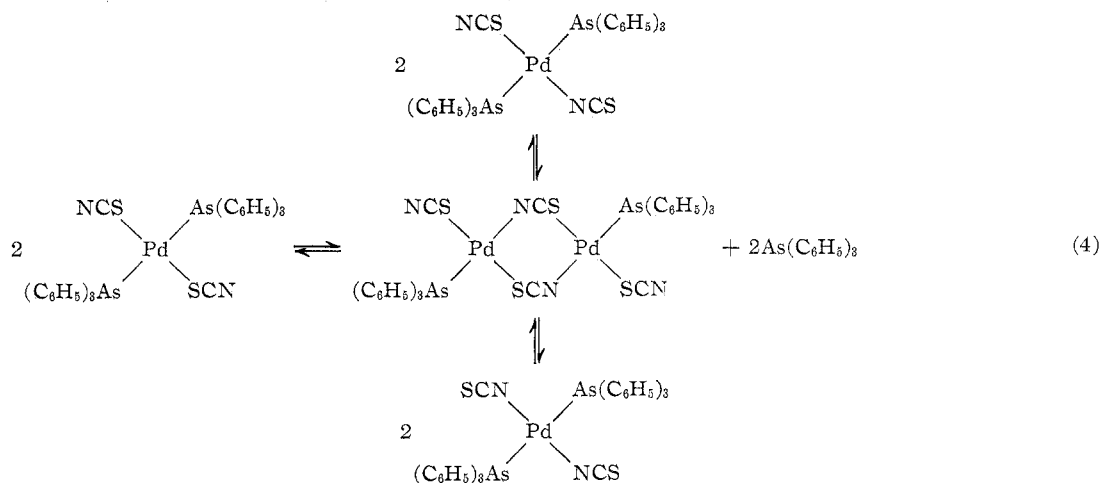
TABLE III
PER CENT IONIZATION IN DMF AND DMSO SOLUTIONS[a]

Complex	Solvent	% ionization
$Pd(As(C_6H_5)_3)_2(SCN)_2$	DMF	37
$Pd(As(C_6H_5)_3)_2(SCN)_2$	DMSO	50
$Pd(P(C_6H_5)_3)_2(NCO)_2$	DMSO	45
$Pd(Sb(C_6H_5)_3)_2(SCN)_2$	DMSO	86
$Pt(Sb(C_6H_5)_3)_2(SCN)_2$	DMSO	72

[a] Molar extinction coefficients (M^{-1} cm^{-1}): SCN$^-$, 1.47×10^3 in DMF, 1.55×10^3 in DMSO (ν_{CN} at 2058 cm^{-1}); OCN$^-$, 1.03×10^3 in DMSO (ν_{CN} at 2158 cm^{-1}).

Group B Solvents.—The behavior of $Pd(As(C_6H_5)_3)_2(SCN)_2$ and its N-bonded isomer in the group B solvents may be rationalized in terms of the equilibria in eq 4. The formation and cleavage of the dinuclear-

of the palladium(II) was in the form of a dinuclear complex prior to the addition of excess free triphenylarsine.

Based on their analogous infrared spectral behavior, the $Pt(As(C_6H_5)_3)_2(NCS)_2$ and $M(Sb(C_6H_5)_3)_2(SCN)_2$ [M = Pd(II), Pt(II)] complexes are probably involved in comparable equilibria when dissolved in the group B solvents studied. It should be noted, however, that the stibines exist as stable S-bonded species in the solid state, and the N-bonded species existing in solution are therefore promoted by the solvent. Likewise, $Pd(P(C_6H_5)_3)_2(SeCN)_2$ also undergoes partial isomerization in the group B solvents studied. This is especially significant in view of the fact that the selenocyanate has heretofore been observed to bond only

$$2 \quad \begin{array}{c} NCS \\ \\ (C_6H_5)_3As \end{array} Pd \begin{array}{c} As(C_6H_5)_3 \\ \\ NCS \end{array}$$

$$2 \quad \begin{array}{c} NCS \\ \\ (C_6H_5)_3As \end{array} Pd \begin{array}{c} As(C_6H_5)_3 \\ \\ SCN \end{array} \rightleftharpoons \begin{array}{c} NCS \quad NCS \\ \\ (C_6H_5)_3As \quad SCN \quad SCN \end{array} Pd \quad Pd \begin{array}{c} As(C_6H_5)_3 \\ \\ \end{array} + 2As(C_6H_5)_3 \quad (4)$$

$$2 \quad \begin{array}{c} SCN \\ \\ (C_6H_5)_3As \end{array} Pd \begin{array}{c} As(C_6H_5)_3 \\ \\ NCS \end{array}$$

bridged complex provides a facile pathway for the interconversion of the linkage isomers. The data do not permit an assessment of whether or not the mixed bonding mode mononuclear complex ever exists in an appreciable concentration. Although other isomeric dinuclear species are undoubtedly involved in the equilibria, the one shown is the predominant form present prior to the addition of triphenylarsine insofar as the bonding mode of its terminal thiocyanates is concerned for, as previously mentioned, N bonding is minimized when bridging is maximized. This would also be anticipated in view of the fact that only one π-electron-withdrawing triphenylarsine is coordinated to each palladium(II).[7] Jennings and Wojcicki[14] have also noted the tendency of complexes of the type $Rh(AsR_3)_2(CO)NCS$ to form dinuclear thiocyanate-bridged species in solution. In addition to the dinuclear complex shown in reaction 4, the presence of some

$$\begin{array}{c} (C_6H_5)_3As \quad SCN \quad NCS \\ \\ Pd \quad Pd \\ \\ SCN \quad NCS \quad As(C_6H_5)_3 \end{array}$$
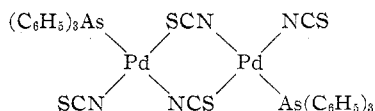
would be necessary, if all three mononuclear species are to be generated solely by cleavage. Knowing the molar extinction coefficient of free triphenylarsine for its absorption maximum at 248 nm (14.8×10^3 M^{-1} cm^{-1}), its concentration in the group B solutions of $Pd(As(C_6H_5)_3)_2(SCN)_2$ could be determined. Calculations for the chloroform solution showed that 49.5% of the total triphenylarsine was noncoordinated; *i.e.*, 99%

(14) M. A. Jennings and A. Wojcicki, *Inorg. Chem.*, **6**, 1854 (1967).

via its Se atom in sterically unhindered palladium(II) complexes.[8] Since two charge-transfer bands appear in the visible–ultraviolet spectra of all of the solutions known to contain N-bonded thiocyanates or selenocyanates, it may be concluded that the bipyridine- and phenanthroline–selenocyanate complexes, but not the phenanthroline–thiocyanate complex, also undergo at least partial isomerization to the N-bonded form in the group B solvents studied. The remaining complexes, all of which are stable as the N-bonded isomer in the solid state, exhibited only N bonding in these solvents (no bridging was observed for the phosphines due to the stronger Pd–P and Pt–P bonds). Clearly, a driving force toward N bonding exists in the group B solvents.

Group C Solvents.—The occurrence of the induction period leading to the formation of the dinuclear-bridged species in methanol and ethanol may be attributed to the necessity of breaking hydrogen bonds of the type Pd–SCN---HO–R. Pecile[12] has previously noted the existence of such interactions in solutions of thiocyanates in hydroxylic solvents.

Explanation of Solvent Effect.—As is indicated by the data given in Table IV, the group A solvents may be differentiated from those in group B in that the former generally exhibit larger dipole moments, dielectric constants, and internal pressures. There are exceptions in each case, the most glaring being pyridine in group A and nitrobenzene in group B. It should be noted, however, that pyridine is a good coordinating solvent, despite its relatively low polarity and dielectric constant, and nitrobenzene is a poor coordinating sol-

TABLE IV
PHYSICAL DATA FOR SOLVENTS

Solvent	Dipole moment,[a] D	Dielectric constant[a,b]	Internal pressure,[c,d] cal cm^{-3}
DMF	3.82	26.6 (25°)[e]	117
DMSO	3.96	46.0 (25°)[j]	140
Pyridine	2.19	12.3 (25°)	101
Acetone	2.88	20.7 (25°)	90.6
Acetonitrile	3.92	37.5[f]	139
Benzonitrile	4.18	25.2 (25°)[f]	97.5
Adiponitrile	?	?	112
Benzene	0	2.28	81.5
Carbon tetrachloride	0	2.24	74.4
Chloroform	1.01	4.81	84.7
Dichloromethane	1.60	9.08	98.5
Cyclopentanone	?	16.3 (−51°)[g]	96.7
Cyclohexanone	2.75[h]	18.3	94.5
Nitrobenzene	4.22	35.7	102
2-Butanone	?	18.5	80.9
3-Pentanone	?	17.0	73.6
Methanol	1.70	33.6 (25°)	68.1[i]
Ethanol	1.69	24.3 (25°)	69.5[i]

[a] R. C. Weast, Ed., "Handbook of Chemistry and Physics," 50th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1969, pp E-61 to E-71. [b] Measured at 20°, unless indicated otherwise. [c] Suggested by R. G. Pearson, private communication. [d] Calculated by equation given by S. C. Srivastava, *Indian J. Phys.*, **33**, 503 (1959); equation derived from relationships given by J. H. Hildebrand, "Solubility of Non-electrolytes," Reinhold, New York, N. Y., 1936, pp 103–105, and substantiated by data given therein. [e] C. Marsden, "Solvents Guide," 2nd ed, Interscience, New York, N. Y., 1963, p 216. [f] N. A. Lange, Ed., "Handbook of Chemistry," 10th ed, McGraw-Hill, New York, N. Y., 1967, p 1234. [g] D. E. Gray, Ed., "American Institute of Physics Handbook," 2nd ed, McGraw-Hill, New York, N. Y., 1963, p 5-125. [h] A. Weissberger and E. Proskauer, "Organic Solvents," The Clarendon Press, Oxford, England, 1935, p 41. [i] I. A. Wiehe and E. B. Bagley, *AIChE J.*, **13**, 836 (1967). [j] I. M. Kolthoff and E. B. Sandell, "Quantitative Chemical Analysis," 4th ed, Macmillan, London, 1969, p 96.

vent, its relatively high dipole moment and dielectric constant notwithstanding, indicating the importance of specific interactions which are not reflected in the physical parameters chosen.

Nonetheless, it would appear that the recent treatise by Klopman,[15] concerning chemical reactivity and the concept of charge- and frontier-controlled reactions, is quite germane to the question at hand. One of the predictions resulting from Klopman's equations is that solvents with high dielectric constants tend to enhance frontier orbital-controlled (largely covalent) interactions whereas those with low dielectric constants favor charge-controlled (largely ionic) reactions. In the present case, this implies that the former solvent type, group A, should promote Pd–SCN bonding, whereas the latter, group B, should promote Pd–NCS bonding—precisely the general bonding pattern observed. It should be noted that the solvent-induced isomerization of Co-(CN)$_5$SCN^{3-} observed by Gutterman and Gray[2] is in the same direction (the Co(CN)$_5$SeCN^{3-} complex also behaves[16] in an analogous manner). Indeed, these examples represent the first experimental verification of this prediction. That there are a few exceptions to the general trend is to be anticipated, for, as Klopman pointed out,[15] other factors like those associated with the Coulomb interaction are varying at the same time. The most surprising result involves the striking difference in behavior found for Pd(As(C$_6$H$_5$)$_3$)$_2$(SCN)$_2$

in acetone and 2-butanone. Here, the addition of a single methylene group in the solvent molecule results in a switch from group A to group B behavior, the latter type of behavior being even more pronounced in 3-pentanone.

In retrospect, it is perhaps not too surprising that solvents should be able to influence the bonding mode adopted in solutions of linkage isomeric systems for which the energy difference is sufficiently small to permit the isolation of both isomers in the solid state.[6] However, the results of this study indicate that the importance of the solvent effect is much greater than initially expected, complete reversals in bonding modes having been accomplished in the case of thiocyanate and selenocyanate complexes for which linkage isomerism had not previously been observed. The failure to effect a change in the bonding mode of the cyanate ion in the palladium(II) and rhodium(I) complexes is not surprising in view of the fact that O bonding has only been observed in the complexes of a few very hard, highly charged metal ions.[17,18] The apparent inertness toward isomerization of the rhodium(I) and iridium(I) isothiocyanate and isoselenocyanate complexes in DMF may be attributed[10,19] to the strong π withdrawal by the trans CO group. The Pd(phen)-(SCN)$_2$ complex is the only complex studied which gave no evidence of N bonding in group B solvents, an anomaly which is not understood. Its behavior becomes all the more puzzling when compared with that of the bipy complex, especially in view of their similar structure and basicity (pK_a: bipy,[20] 4.37; phen,[21] 4.96).

Solvent control of the bonding mode can also be obliterated by steric effects, *e.g.*, the N-bonded mode is preferred[22] for Pd(Et$_4$dien)NCX$^+$ (Et$_4$dien = 1,1,7,7-tetraethyldiethylenetriamine; X = S, Se) in DMF solutions. Here, the steric hindrance created by the ethyl groups is the controlling factor, rather than the metal ion or the solvent, both of which tend to favor X bonding. In the solid state, when the tetraphenyl-borate ion is the counterion, crystal-packing considerations are of greater consequence, and the X-bonded mode is favored.

As discussed herein, solvent control of the bonding modes of ambidentate ligands involves a dependence of the *equilibrium position in solution* on the nature of the solvent. It does not include solid-state *vs.* solution comparisons, for Klopman's treatise does not apply to such comparisons. Thus, the S→N-bonded isomerization observed[4] when Mn(CO)$_5$SCN is dissolved in acetonitrile, a class A type solvent, is not the anomaly it would appear to be. Likewise, the recent communication[23] by Norbury, *et al.*, concerning solvent control of the bonding mode of the coordinated thiocyanate ion is quite misleading. They have observed that the complex *trans*-thiocyanatobis(dimethylglyoximato)-pyridinecobalt(III) undergoes an S→N-bonded isomerization in formamide and DMF, class A type sol-

(15) G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968).
(16) J. L. Burmeister and J. B. Melpolder, unpublished results.

(17) R. A. Bailey and S. L. Kozak, *J. Inorg. Nucl. Chem.*, **31**, 689 (1969).
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(20) H. H. Perkampus and H. Köhler, *Z. Elektrochem.*, **64**, 365 (1960).
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(22) J. L. Burmeister, H. J. Gysling, and J. C. Lim, *ibid.*, **91**, 44 (1969).
(23) A. H. Norbury, P. E. Shaw, and A. I. P. Sinha, *Chem. Commun.*, 1080 (1970).

vents, but does not isomerize in the class B type solvents $CHCl_3$, CH_2Cl_2, $ClCH_2CH_2Cl$, CH_3CN, and CH_3NO_2. They cited this as evidence for a solvent effect which is in opposition to that reported earlier by us[6] and discussed in greater detail herein.

We have investigated their system in detail,[24] and find that they have completely misinterpreted their results, insofar as a solvent effect is concerned. While it is true that the S-bonded isomer does not isomerize to an appreciable extent in chloroform solution at room temperature over a period of 1 month, we have found that this is *also* true for the N isomer. However, an S→N-bonded isomerization can be effected in this solvent by refluxing the solution. The difference in behavior of the complex in DMF *vs.* chloroform in this case is therefore due to kinetic effects, not thermodynamic effects, as is the case in our system. The relatively high dielectric constant of DMF lowers the

(24) R. L. Hassel and J. L. Burmeister, *Chem. Commun.*, 568 (1971).

activation energy for the isomerization, which undoubtedly proceeds *via* a dissociative or ion-pair mechanism, by providing for better solvation of the free ion (a relatively large concentration of noncoordinated NCS^- is formed in the DMF solution, but none is observed in the chloroform solution). Comparable behavior is observed in DMSO, which also has a relatively high dielectric constant.

Despite the fact that it is not always of preponderant importance, the synthetic and theoretical ramifications of the solvent effect promise to be greater than any of the ambidentate ligand bonding mode determinants yet discovered.

Spin–Spin Coupling in Magnetically Condensed Complexes. XI. Out-of-Plane Interactions and Triplet Ground State in Tetrakis(N,N-diethyldithiocarbamato)dicopper(II)

BY JUAN F. VILLA AND WILLIAM E. HATFIELD*

The electronic nature of tetrakis(N,N-diethyldithiocarbamato)dicopper(II) is characterized by a best-fit convergence study of the magnetic parameters. It is shown that this compound possesses a triplet ground state 24.0 cm^{-1} below the singlet. There are, also, some additional weak lattice antiferromagnetic interactions observable at low temperatures. The spin coupling mechanism is seen to be of the superexchange σ-orbital type *via* the out-of-plane bonds, with interatomic electron transfer and intraatomic orbital coupling.

Introduction

The compound tetrakis(N,N-diethyldithiocarbamato)dicopper(II), [Cu(edtc)$_2$]$_2$, is composed of dimers[1] where, as shown in Figure 1, the sulfur atoms act as bridges. The copper ions are in a distorted tetragonal-pyramidal environment with four sulfur atoms comprising the basal plane at distances ranging from 2.30 to 2.34 Å and a fifth apical sulfur atom at 2.85 Å. The Cu–Cu distance is 3.54 Å. Some attention has been given to the magnetic properties of this complex[2,3] in the temperature region from 77 to 300°K. However, since it is below 77°K where the magnetic parameters change dramatically with temperature (therefore providing better data to characterize the type of magnetic interaction), we undertook the investigation of the magnetic susceptibility of tetrakis(N,N-diethyldithiocarbamato)dicopper(II) from 4.2 to 56°K. We had recently demonstrated[4] by epr measurements that there was spin–spin coupling in this system and proposed that

it was transmitted through the orbitals of the sulfur atoms. We also gave recently a preliminary account of this work,[5] where it was reported that the spin coupling constant was positive. Now we present the complete data, a best-fit study of the data, comparisons to the previously available magnetic susceptibility and epr data, and a theoretical model for the coupling in this biologically related[6,7] compound.

Experimental Section

[Cu(edtc)$_2$]$_2$ was prepared by mixing water solutions of $CuCl_2$ and sodium N,N-diethyldithiocarbamate (excess of edtc). The dark brown precipitate which formed immediately was filtered, washed repeatedly with water, and dried at 110°. *Anal.* Calcd for Cu(C$_5$H$_{10}$NS$_2$)$_2$: C, 33.33; H, 5.60; N, 7.78. Found: C, 33.39; H, 5.74; N, 7.58.

The magnetic measurements were carried out with a Foner-type[8] vibrating-sample magnetometer from Princeton Applied Research, Inc. We used a sample size of about 0.1 g and a previously calibrated germanium resistor thermometer from Scientific Instruments, Inc. The field was held constant at 10,000 G with a Ventron Instruments Corp. power supply equipped with

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