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(15) Abbreviations used for the ligand systems in this article are as follows: bis(salicylaldehyde)ethylenediimine, salen; bis(7-deuteriosalicylaldehyde)ethylenediimine, 7-*d*-salen; bis(5,7-dideuteriosalicylaldehyde)ethylenediimine, 5,7-di-*d*-salen; bis(4-methyoxysalicylaldehyde)ethylenediimine, 4-CH_3O-salen; bis(5-methoxysalicylaldehyde)ethylenediimine, 5-CH_3O-salen; bis(3-ethoxysalicylaldehyde)ethylenediimine, 3-C_2H_5O-salen; bis(4,6-dimethoxysalicylaldehyde)ethylenediimine, 4,6-di-CH_3O-salen; bis(7-methylsalicylaldehyde)ethylenediimine, 7-CH_3-salen; bis(5-halosalicylaldehyde)ethylenediimine, 5-X-salen; bis(5-halo-7-deuteriosalicylaldehyde)ethylenediimine, 5-X,7-*d*-salen; bis(3-nitrosalicylaldehyde)ethylenediimine, 3-NO_2-salen; bis(5-nitrosalicylaldehyde)ethylenediimine, 5-NO-salen. All ligands are coordinated to the cobalt as the dianion.

Selenium-77 Nuclear Magnetic Resonance Studies. 1. Chemical Shifts, Coupling Constants, and Relaxation Times for *Se-dl*-Cystine, *Se-dl*-Methionine, and Several Se-Containing Transition Metal Complexes

W-H. Pan and John P. Fackler, Jr.*

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received April 4, 1978*

Abstract: ^{77}Se NMR spectra of 29 Se-containing compounds are reported. The ^{77}Se chemical shifts reported cover a range of ~1000 ppm. In dialkyldiselenocarbamato metal complexes, the magnetic anisotropy associated with d^8 nickel triad complexes contributes significantly to the ^{77}Se chemical shielding, giving rise to upfield shifts with respect to the anionic ligands and zinc and cadmium complexes. Electronic effects arising from the ligand also significantly contribute to the shielding. Solvent, temperature, and concentration dependence studies have also been carried out on a few of the diselenocarbamate complexes. Both P-Se and Pt-Se coupling constant data and an NMR trans influence argument have been utilized in making peak assignments. Spin-lattice relaxation times (T_1) of a few of the compounds are also reported and they range from 0.46 to 4-5 s in the temperature range −28 to 27 °C. With $Zn(Se_2CNEt_2)_2$ and $Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$, the chemical shift anisotropy appears to be the dominant relaxation mechanism for the ^{77}Se nuclei.

Introduction

The use of Fourier transform ^{77}Se NMR was first reported by Gronowitz et al.[1a] in 1973. Since then, these workers[1b-d] have reported the ^{77}Se chemical shifts of a variety of organoselenium compounds. Recently, Odom and co-workers[2] presented spin-lattice relaxation time measurements on some diaryldiselenides, alkyl selenols, and dimethyl selenide. These studies have demonstrated the relative ease with which ^{77}Se NMR spectra can be obtained despite a number of potential drawbacks, including a low natural abundance of the ^{77}Se isotope (7.58%) and an NMR sensitivity of 6.97×10^{-3} with respect to the proton at constant field. Previously, ^{77}Se NMR studies of a number of inorganic and organic compounds had been carried out using the continuous wave[3,4] and INDOR[5] techniques. The former technique suffers from the shortcomings mentioned above while the latter is useful only when protons are coupled to ^{77}Se. These studies and others published prior to 1972 have been reviewed by Lardon.[6]

Selenium compounds generally show structural properties similar to those of their sulfur analogues. Hence, several years ago we became attracted to the use of ^{77}Se NMR for the study of the intramolecular rearrangements of coordination compounds of the type $Pt(Se_2CNR_2)_2L$ (where L is a phosphine and R an alkyl group). Our interest in ^{77}Se NMR was further stimulated by recent studies which have demonstrated the biological importance of selenium in the enzymes glutathione peroxidase,[7] glycine reductase,[8] and formate dehydrogenase.[9] Selenium also has been implicated as a protective trace element against cancer[10a] and heart disease.[10b] Therefore considerable incentive exists to develop ^{77}Se NMR for the study of molecular structure, particularly in solution with metal-organic species. The first results of these investigations are reported here.

Our experience with dithiocarbamates[21] has provided an excellent background for the study of diselenocarbamate complexes, the compounds we chose to initiate our ^{77}Se NMR studies generally. In this paper, we report some chemical shifts, coupling constants, and spin-lattice relaxation times (T_1) of a number of compounds which are in the main transition metal

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Table I. Analytical Results

compd	color	mp (bp), °C	calcd C	calcd H	calcd N	calcd Se	found C	found H	found N	found Se
selenophene	colorless	110-111	36.67	3.08		60.26	37.0	3.3		59.5
$Zn(Se_2CNEt_2)_2$	light yellow	152-154	21.86	3.64	5.10	57.50	21.9	3.8	5.2	57.8
$Zn(Se_2CN\text{-}i\text{-}Bu_2)_2$	off-white	137-139	32.67	5.49	4.23		32.7	5.7	4.1	
$Cd(Se_2CN\text{-}n\text{-}Bu_2)_2$	light yellow	129-130	30.50	5.13	3.95		30.7	5.3	4.0	
$Ni(Se_2CN\text{-}i\text{-}Bu_2)_2$	olive green	170-173	33.00	5.50	4.28	48.22	32.7	5.5	4.2	48.5
$Ni(Se_2CNEt_2)PEt_3Cl$	dark red	93-95	29.08	5.55	3.08		29.2	5.7	3.0	
$Pd(Se_2CNEt_2)_2$	red	290 dec	20.35	3.38			20.5	3.6		
$Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$	red	199-202	30.76	5.17			31.0	5.3		
$Pd(Se_2CNEt_2)PPh_3Cl$	red orange	199-201	42.75	3.90			43.1	4.1		
$Pd(Se_2CN\text{-}i\text{-}Bu_2)PPh_3Cl$	red orange	228-230	46.18	4.74			46.0	4.8		
$Pt(Se_2CNEt_2)_2$	yellow	300 dec	17.68	2.94	4.12		17.5	3.1	4.1	
$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2$	yellow	216-218	27.32	4.58	3.40	39.91	27.4	4.7	3.6	39.8
$Pt(Se_2CNEt_2)PPh_3Cl$	yellow	205-208	37.59	3.43			37.6	3.3		
$Pt(Se_2CN\text{-}i\text{-}Bu_2)PPh_3Cl$	yellow	237-240	41.00	4.21	1.77		40.8	4.2	1.8	
$Pt(Se_2CNEt_2)PPh_3CH_3$	yellow	167-169	40.34	3.95		22.10	40.3	4.1		21.9
$[Pt(Se_2CN\text{-}i\text{-}Bu_2)(PPh_3)_2]Cl$	white	224 dec	51.31	4.60	1.33		51.3	5.8	1.1	
cis-$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2Br_2$	red orange	233-236	22.73	3.81			22.9	3.8		
cis-$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2I_2$	dark red	178-182	20.67	3.47			20.8	3.6		

diselenocarbamate complexes. We have also included early results of studies of the solvent, temperature, and concentration dependence of the chemical shifts with a few of these complexes.

Experimental Section

Preparation of Compounds. All solvents were reagent grade and were used without further purification unless otherwise stated. Benzyl selenocyanate was prepared according to Gronowitz et al.[1c] using KSeCN (98% pure, Apache Chemicals) and benzyl chloride. Trimethylselenonium iodide was prepared by mixing stoichiometric amounts of dimethyl selenide (Strem Chemicals) and methyl iodide and subjecting the resulting white solid (after 24 h at room temperature) to house vacuum (~5-7 Torr) to remove any excess reagents. The compounds $MCl_2(PR_3)_2$ (M = Ni, Pd, Pt)[11a,b] and *cis*-$Pt(CH_3)_2(PPh_3)_2$[12] were prepared according to literature methods. Carbon diselenide, $(NR_2H_2)Se_2CNR_2$ (R = ethyl or isobutyl), and $K(Se_2CN\text{-}i\text{-}Bu_2)$ were prepared according to Rosenbaum et al.[13] K_2PdCl_4 and K_2PtCl_4 were prepared from the respective metals, the former following the method of Kauffman and Tsai[14] for Na_2PdCl_4 and the latter according to Brauer.[15] Selenophene was prepared following the method of Umezawa et al.[16] *p*-Methylphenylselenocyanate and *trans*-$Pd(CH_3SeCH_3)_2Cl_2$ are generous gifts from Professor J. D. McCullough. *Se-dl*-Cystine and *Se-dl*-methionine were purchased from Vega-Fox Biochemicals. Bis(*N,N*-diethyldiselenocarbamato)-nickel(II) was purchased from Strem Chemicals. All chemical analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

The preparations of complexes of the type $M(Se_2CNR_2)_2$ have been reported previously.[19,20] In the present study, a complex of this type generally was prepared by adding an ethanol suspension or solution (depending on the alkyl group) of $(NR_2H_2)Se_2CNR_2$ to a stirred aqueous solution of the appropriate metal halide (except for Cd(acetate)$_2$) using stoichiometric quantities. The resulting precipitate was filtered and washed with water, dried, and recrystallized from chloroform and petroleum ether. Some of the complexes (R = ethyl) have been prepared by a metathetical reaction between $Zn(Se_2CNEt_2)_2$ (in acetone) and the metal halide (in water). In such cases, the reaction mixture was heated to about 60 °C. Workup was the same as above.

Complexes of the type $M(Y_2CNR_2)PR_3X$ (Y = S; X = halide) have been previously prepared.[21,22a] To date the selenium analogues (Y = Se) have not been reported.[22b] The general method of preparation involves mixing stoichiometric amounts of $M(PR_3)_2Cl_2$ and $M(Se_2CNR'_2)_2$ stirred in an appropriate solvent. For the nickel complex, acetone was used as the solvent and the mixture was heated (ca. 50 °C) and stirred for about 20 min. The resulting deep red solution was reduced in volume on the rotoevaporator and *n*-heptane, ~50 v/v, was added. Storing in the freezer (−22 °C) yielded deep red crystals. When M is Pd(II) purified benzene (refluxed over sodium benzophenone) was the solvent. Under nitrogen, the mixture was stirred and heated at reflux for about 3 h. The resulting clear solution gave orange-red crystals upon cooling. Addition of *n*-heptane and refrigerating yielded more crystals. The latter were usually recrystallized from $CHCl_3$/*n*-heptane. The Pt(II) complex was prepared in the same manner except that about 12-24 h of refluxing was required. When *cis*-$Pt(CH_3)_2(PPh_3)_2$ was used and refluxing extended to 24-48 h, $Pt(Se_2CNR_2)CH_3PPh_3$ was obtained.

cis-$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2X_2$ (X = I, Br) was prepared according to the method used to prepare the dithio analogue as reported by Willemse et al.[17] Chemical analyses and some physical properties of the complexes are listed in Table I.

Physical Measurements. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are reported uncorrected. ^{77}Se NMR spectra were obtained on a Varian XL-100-15 NMR spectrometer equipped with Fourier transform capability and operated at 19.08 MHz in the Gyro observe mode. Field-frequency internal lock was effected by using deuterated solvents (Norell). When nondeuterated solvents were used, a ^{19}F external lock was employed. All the chemical shifts were referenced to a 2 M solution of selenophene in $CHCl_3$. The latter, sealed under vacuum, in a 5-mm NMR tube, was inserted coaxially in a 12-mm tube. For upfield shifts greater than 300 ppm, a 15% solution of carbon diselenide in CH_2Cl_2 or a 1 M solution of dimethyl selenide in $CHCl_3$ was used as the external reference. These shifts were then referenced to 2 M selenophene by the following empirical relationships: $\delta = \delta_{CSe_2} - 317.6$; $\delta = \delta_{DMSe} - 317.6 - 299.8$ (DMSe = CH_3SeCH_3).

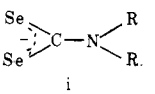
The spin-lattice relaxation time (T_1) measurements were carried out by using 180°, τ, 90° pulse sequences with a delay time of 5-10T_1 between each pulse sequence.[18] The 90° pulse width was obtained according to the directions given by a Varian Analytical Instrument publication. Using 1 M $Zn(Se_2CNEt_2)_2$ in $CDCl_3$, the intensities of peaks obtained using pulse widths corresponding to spin flip angles near 360° were plotted against the pulse width. The resulting straight line was extrapolated to zero intensity. This gave the 360° pulse width. One-fourth of this then gave the 90° pulse width. In a typical case, intensities (arbitrary units) of −3.0, −1.9, −1.4, and −2.5 were obtained with pulse widths of 200, 210, 215, and 205 μs, respectively. These data extrapolated to a zero intensity at 229 μs, giving a 90° pulse width of 57 μs.

Low temperatures (below 0 °C) were measured by inserting a SGA Scientific Inc. JM-7600 thermometer in a tube containing an appropriate solvent in the NMR probe. High temperatures were measured with a Fisher Scientific thermometer. Samples for spin-lattice relaxation time measurements were prepared in the following manner. $CDCl_3$ (Norell) and spectrograde $CHCl_3$ were refluxed over P_4O_{10} for 6 h and then distilled. Prior to use, they were freeze-thaw purged (at least three times) with purified nitrogen gas. Crystals of the complex were first dried under vacuum in a 12-mm NMR tube modified for sealing. Solvent was then vapor transferred into the tube. Before sealing under vacuum, the solution was freeze-thaw purged twice with purified nitrogen.

Table II. Chemical Shifts and Coupling Constants for ^{77}Se in Se-Containing Compounds

compd[a]	solvent	δ,[b] ppm	J_{Se-X}, Hz	concn, M	T, °C
$Cd(Se_2CN\text{-}n\text{-}Bu_2)_2$	$CDCl_3$	99.4		0.15	29
$Zn(Se_2CN\text{-}i\text{-}Bu_2)_2$	$CDCl_3$	51.4		0.15	29
$Zn(Se_2CNEt_2)_2$	$CDCl_3$	30.7		0.12	29
cis-$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2I_2$	$CDCl_3$	8.7	X = Pt, 173.6	0.12	32
selenophene	$CHCl_3$	0.0	X = H, 9.6; 47.6	2.0	*f*
$NEt_2H_2(Se_2CNEt_2)$	$CDCl_3$	−1.2 (broad)		0.15	32
$NEt_2H_2(Se_2CNEt_2)$	$CDCl_3$	−6.5			~−5
cis-$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2Br_2$	$CDCl_3$	−29.4	X = Pt, 224.6	0.12	29
$K(Se_2CN\text{-}i\text{-}Bu_2)$	D_2O	−35			30
cis-$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2Br_2$	$CDCl_3$	−39.8	X = Pt, 249.6	0.12	29
cis-$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2I_2$	$CDCl_3$	−86.4	X = Pt, 216.1	0.12	32
$Ni(Se_2CNEt_2)PEt_3Cl$	$CDCl_3$	−170 (broad)	trans[c]	~0.2	30
$Pt(Se_2CNEt_2)PPh_3CH_3$	$CDCl_3$	−198.3	X = Pt, 47.5; X = P, 7.8	0.15	33
$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2$	$CDCl_3$	−201.2	X = Pt, 111.7	0.15	30
$Ni(Se_2CN\text{-}i\text{-}Bu_2)$	$CDCl_3$	−216.4		0.15	30
$Pt(Se_2CNEt_2)PPh_3CH_3$	$CDCl_3$	−218.1	X = P, 111.9; X = H, 8.0	0.15	33
$Pt(Se_2CN\text{-}i\text{-}Bu_2)PPh_3Cl$	$CDCl_3$	−224.0	trans[c] X = Pt, 115.7, X = P, 100.0	0.10	32
$Pt(Se_2CN\text{-}i\text{-}Bu_2)PPh_3Cl$	$CDCl_3$	−231.1	cis[c] X = Pt, 288.8; X = P, 10.0	0.10	32
$Ni(Se_2CNEt_2)_2$	$CDCl_3$	−231.1		saturated <0.09	32
$[Pt(Se_2CN\text{-}i\text{-}Bu_2)(PPh_3)_2]Cl$	$CDCl_3$	−233.3	X = Pt 2nd X = P order	0.15	32
$Pd(Se_2CN\text{-}i\text{-}Bu_2)PPh_3Cl$	$CDCl_3$	−237.4	trans[c] X = P, 103.9	0.19	32
$Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$	$CDCl_3$	−238.6		0.16	30
$Pt(Se_2CNEt_2)PPh_3Cl$	$CDCl_3$	−238.7	trans[c] X = Pt, 115.2 X = P, 100.5	0.24	32
$Pt(Se_2CNEt_2)PPh_3Cl$	$CDCl_3$	−242.7	cis[c] X = Pt, 291.4 X = P, 10.0	0.24	32
$Pd(Se_2CNEt_2)_2$	$CDCl_3$	−251.9		saturated	29
$Pd(Se_2CN\text{-}i\text{-}Bu_2)PPh_3Cl$	$CDCl_3$	−254.5	cis[c] X = P, 0	~0.01 0.19	32
$Ni(Se_2CNEt_2)PEt_3Cl$	$CDCl_3$	−274 (broad)	cis[c]	~0.2	30
p-$CH_3C_6H_4SeCN$	$CDCl_3$	−302.5		1	29
CSe_2	CH_2Cl_2	−317.6		~15% (w/v)	29
Se-dl-cystine	2.5 mL D_2O + 15 drops concd HCl	−322.7[d] −325.6	X = H, 17.4	0.27	30
$C_6H_5CH_2SeCN$	$CDCl_3$	−328.7	X = H, 14.9		30
$[(CH_3)_3Se]I$	D_2O	−361.5	X = H, 8.8		30
trans-$Pd(CH_3SeCH_3)_2Cl_2$	$CDCl_3$	−473.1	X = H, 9.2		30
Se-dl-methionine	2.5 mL D_2O + 5 drops 38% DCl	−541.8[e]		0.47	28
CH_3SeCH_3	$CHCl_3$	−617.4	X = H, 10.5	1.0	30
KSeCN	abs ethanol	−938.6		~0.5	30

[a] *n*-Bu = *n*-butyl; *i*-Bu = isobutyl; Et = ethyl; Se_2CNR_2 = i. [b] Negative sign indicates upfield of the reference, 2 M selenophene. Chemical



i

shifts are reproducible to within ±0.6 ppm. Half-height line widths are less than 0.7 Hz unless otherwise stated. [c] I.e., trans to P and cis to P. [d] Half-height line width ~5 Hz. [e] Half-height line width ~30 Hz. [f] See ref 34.

Results and Discussion

The ^{77}Se NMR data for a variety of selenium-containing compounds are listed in Table II. The chemical shifts also are presented in graphic form in Figure 1. Data already available in the literature[6] have established the chemical shift range to be ~1800 ppm. With the compounds studied here (involving mostly divalent selenium), the high-field half of this range is covered. The selenium chemical shifts of compounds with selenium in oxidation states of 4 or 6 generally are found[6] at lower fields. For the symmetrical diselenocarbamates such as $Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$, with four equivalent selenium nuclei and with a concentration of ~0.15 M, spectra with signal to noise ratios (S/N) of better than 10:1 can be attained in less than 90 min. At the same concentration, with only one selenium nucleus per molecule, times between ~4 and 6 h are required to obtain a comparable S/N. Coupling to protons, ^{195}Pt (nuclear spin, I = ½, 33% natural abundance) or ^{31}P also attenuates peak intensities. With compounds in which Se is coupled to other nuclei, longer accumulation times are required.

Chemical Shifts. In Table II we have included the ^{77}Se chemical shifts of organic and metal-organic compounds in order to illustrate the nature of the sensitivity of the ^{77}Se chemical shift to changing chemical environment. According to Saika and Slichter,[30] the observed chemical shielding can be expressed as a function of three parameters:

$$\sigma_{obsd} = \sigma_d + \sigma_p + \sigma' \quad (1)$$

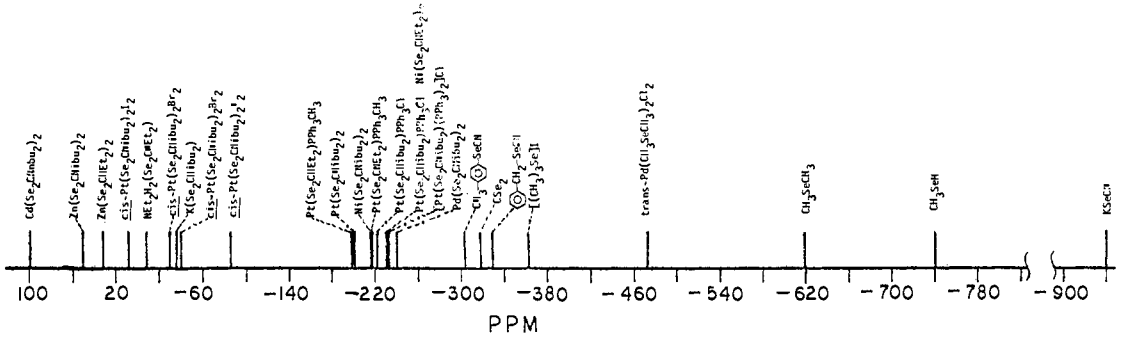
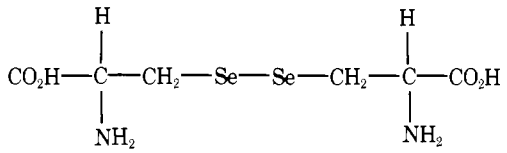


Figure 1. ^{77}Se chemical shift scale in Se-containing compounds. Shifts are referenced to 2 M selenophene as external standard. Negative shifts indicate upfield shifts.

In eq 1, σ_d is the local diamagnetic term, σ_p the paramagnetic term, and σ' the term arising from electronic effects on neighboring atoms. As Lardon[6] suggested, the large chemical shift range indicates that the paramagnetic shielding term (σ_p) is dominant. Illustrative of this is the substantial shift (>600 ppm) downfield upon going from KSeCN to benzyl- and *p*-methylphenylselenocyanate.

In view of the biological significance of selenium (vide supra), development of the use of ^{77}Se NMR to study biochemical systems is an obvious goal. Accordingly, we have obtained the spectra of *Se-dl*-cystine (**1**) and *Se-dl*-methionine (**2**).



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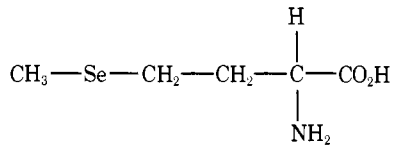


2

The reduced form of **1**, *Se-l*-cysteine, has been implicated in the selenoenzymes glycine reductase[8] and glutathione peroxidase.[23] The ^{77}Se NMR spectrum of **1** shows two triplets of equal intensity. One triplet is from *Se-dd*-cystine and *Se-ll*-cystine and the other from *Se-dl*-cystine and *Se-ld*-cystine, the triplet resulting from a two-bond coupling to the methylene protons. The peaks are relatively broad, having a half-height width of about 5 Hz. Coupling to the other methylene protons three bonds away could not be resolved. Such coupling is observed in $CH_3SeSeCH_3$, where $^3J_{Se-H}$ = 2.3 Hz.[3,24] Three-bond coupling to the methine proton also was not evident. In $CH_3CH_2SeCH_2CH_3$ and $CH_3CH_2SeSeCH_2CH_3$, such coupling is observed, $^3J_{Se-H}$ = 10.8 and 9.6 Hz, respectively.[3] In **2**, the spectrum shows one single broad peak with a half-height width of ~30 Hz, the broadness arising from an unresolved multiplet.

The ^{77}Se chemical shifts of the diselenocarbamates studied here cover a range of 353 ppm. The chemical shift is seen to be sensitive to the particular metal ion, its oxidation state, other ligands on the metal, and the alkyl groups on the nitrogen. The trend in chemical shifts seen in Figure 1 for the nickel triad complexes leads us to believe that shielding arising from neighboring atom electronic effects (σ') contributes significantly to the chemical shielding (σ_{obsd}). The upfield shifts in the planar d^8 nickel triad complexes relative to the filled d shell cadmium and zinc complexes and the free ligand (NEt_2H_2)-Se_2CNEt_2 are consistent with the anisotropic magnetic behavior of the d^8 complexes with Se nuclei in the molecular plane. Downfield shifts relative to the planar species are observed for the selenium nuclei in the more nearly isotropic six-coordinate platinum(IV) complexes.

The large ^{77}Se shielding arising from neighboring magnetic anisotropy can be explained by an argument similar to the one put forth by Buckingham and Stephens[25] to account for the large shielding of protons in planar platinum hydrides. In the hydrides the paramagnetic shielding (σ') which causes the proton shift was found to vary with the platinum to hydride distance (r), and the energy difference between the ground and first excited states (ΔE) of the metal:[25]

$$\sigma' \propto 1/(r^3 \Delta E) \qquad (2)$$

It might be argued that the long platinum-selenium distances in the present complexes (~1.5 times longer[29] than the platinum-hydride distances considered by Buckingham and Stephens) have the effect of reducing σ' by about a factor of ~3.4 compared with the effect on the proton. Thus the magnetic anisotropy of the metal would have little or no influence on the ^{77}Se chemical shift. The effect of large r, however, is attenuated by the small ΔE values, where ΔE is 2.37 μm^{-1} for $Pt(Se_2CNEt_2)_2$, for example,[27] as compared with the 4.0 μm^{-1} estimated[25] for the hydrides. Moreover, as indicated by Buckingham et al. in their study of the platinum hydrides, distortions from an orthogonal arrangement of ligands around the metal atom may contribute to σ'. Available crystal structure data[29,39] clearly show that such distortions are common among the complexes studied here. To what extent the large ^{77}Se shifts observed for the nickel triad complexes are due to the magnetic anisotropy centered at the metal is uncertain since other factors such as electronic effects arising from the ligand itself and solvent-solute interactions also contribute to the shielding of the ^{77}Se.

In a qualitative sense, the data for the diselenocarbamates generally are consistent with the explanation given above for the shielding experienced by selenium coordinated to d^8 metal ions. In planar complexes of the type $M(Se_2CNR_2)PR'_3Cl$, the selenium trans to P always appears downfield of the selenium cis to P. The M-Se bond trans to P is expected[28] to be longer than the one cis to P owing to the large trans influence of the phosphine. Replacing the Cl^- by a $-CH_3$ group causes the selenium trans to P to appear upfield of the ^{77}Se cis to P. Since the methyl group has a larger[28] trans influence than triphenylphosphine, the M-Se bond trans to the methyl group is expected to be longer than the one cis to it.[29]

The electronic spectra of the bis(diselenocarbamato) complexes of the nickel triad have been reported by Jensen et al.[27] The lowest energy transitions decrease in energy in the order Pt > Pd > Ni. The metal-selenium distance (r) is believed to decrease in the same sequence. The ^{77}Se chemical shielding, however, follows a different sequence, Pd > Ni > Pt (decreased shielding), the positions of Pd and Ni in the sequence being

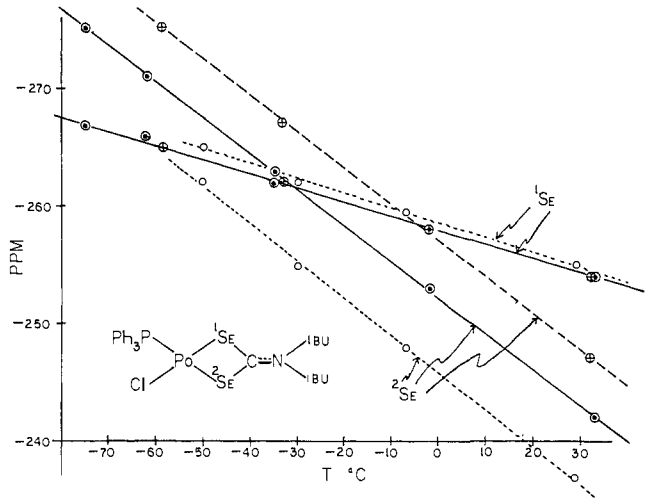


Figure 2. Temperature and solvent dependence of ^{77}Se chemical shifts of Pd(Se_2CN-*i*-Bu_2)PPh_3Cl (0.15 M solutions). Negative shifts indicate upfield from 2 M selenophene external reference. (- - -) in CD_2Cl_2; (—) in ~50/50 (v/v) $CDCl_3/CD_2Cl_2$; (- - -) in $CDCl_3$. Average slopes of the two sets of lines are 0.13 and 0.32 ppm/°C.

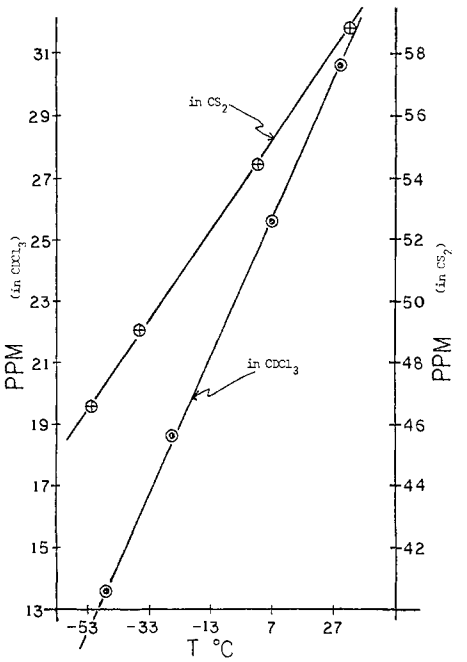


Figure 3. Temperature dependence of ^{77}Se chemical shifts in $Zn(Se_2CNEt_2)_2$ (0.11 M solutions) in CS_2 and $CDCl_3$. Shifts are downfield of 2 M selenophene as external reference.

inverted from what is to be expected if eq 2 were followed. In dithiocarbamate complexes, it has been suggested[31-33] that the NR_2 group has the capability of shifting electron density toward the sulfur atoms. A similar mesomeric effect in the diselenocarbamate complexes could also contribute to the shielding at the selenium, thus producing the above variance with expected shifts for the nickel triad complexes. Changing the R groups (Table III) does influence the mesomeric effect and hence the chemical shielding. (Besides the mesomeric effect, the R groups also affect the steric environment about the selenium atoms and hence would influence the solvent interactions at these sites. This is discussed below.)

Solvent and Temperature Effects. The ^{77}Se chemical shifts in some of the complexes reported here have been found to be solvent and temperature dependent.[34] Lowering the temperature from the ambient temperature of the probe (ca. 30 °C) results in upfield shifts. Figure 2 gives the ^{77}Se chemical shifts in Pd(Se_2CN-*i*-Bu_2)PPh_3Cl as a function of temperature in $CDCl_3$, CD_2Cl_2, and in a ~50/50 mixture of the two solvents. The selenium atom trans to the phosphine is seen to be more temperature sensitive than the Se atom cis to P. Moreover, the chemical shift of the latter Se is practically independent of the solvent used, while shifts for the former vary substantially with solvent changes. This solvent dependence is consistent with the presence of a strong specific interaction at this particular Se atom. Solvent ($CHCl_3$) interaction with the sulfur atoms in dithiocarbamate complexes is known to occur.[35] Also, ultraviolet and visible spectroscopic studies of derivatives of diselenocarbamic acids[36] have shown that the solvent dependence of the electronic spectra of these compounds arises from a hydrogen bonding between the selenium and the solvent. Since the selenium cis to the phosphine interacts little, if at all, with the solvent, steric hindrance produced by the bulky triphenylphosphine and the isobutyl group on the diselenocarbamate is suggested.

The upfield shift with decreasing temperature observed with the Se compounds reported here also has been observed for the ^{59}Co NMR chemical shifts in tris(acetylacetonato)cobalt(III) and potassium hexacyanocobaltate(III).[37] Freeman et al.[37] suggested that the temperature dependence arises from a change in the crystal field due to thermal motions of the ligands. Earlier, Ramsey[38] had suggested that a change in population distribution between the ground state and low-energy excited states is responsible for the temperature dependence of the ^{59}Co shifts. However, as Griffith and Orgel have pointed out,[26] the energy separation between the ground and excited states is large (~13 000 cm^{-1}). Hence the latter is not populated significantly at ordinary temperatures so that changes in population distribution between ground and excited states cannot be an important contribution to the chemical shielding. Thermal motion involving solvent-solute interactions may be sufficiently temperature sensitive to produce the results obtained for ^{77}Se. The large chemical shift differences observed with $CDCl_3$ and CD_2Cl_2, two rather similar solvents, appear to support the premise that the solvent-solute interactions play an important role in determining the temperature dependence of the observed chemical shifts.

Table III. ^{77}Se Chemical Shift Dependence on Alkyl Groups in Diselenocarbamate Complexes

compd	alkyl group: isobutyl[a]	alkyl group: ethyl[a]	Δδ, ppm
$Zn(Se_2CNR_2)_2$	51.4	30.7	20.7
$Ni(Se_2CNR_2)_2$	−216.4	−213.1	14.7
$Pt(Se_2CNR_2)PPh_3Cl$	−224.0	−238.7	14.7
	−231.1	−242.7	11.7
$Pd(Se_2CNR_2)_2$	−238.6	−251.9	13.3
$Pd(Se_2CNR_2)PPh_3Cl$	−237.4	−251.5	14.1
	−254.5	−265.7	11.2

[a] Chemical shift in parts per million from 2 M selenophene at 32 °C in $CDCl_3$.

The diselenocarbamate of zinc(II), $Zn(Se_2CNEt_2)_2$, also displays a chemical shift which is both solvent and temperature dependent. This behavior can be seen in Figure 3 for the solvents CS_2 and $CDCl_3$. The larger slope for the $CDCl_3$ solution suggests that a larger solvent-solute interaction occurs in this solvent. The crystal structure of the zinc complex, as reported by Bonamico et al.,[38] shows the complex to be dimerized. Hence we considered the possibility that the temperature dependence of the ^{77}Se chemical shift arises from a monomer ⇌ dimer equilibrium taking place in solution:

$$[Zn(Se_2CNEt_2)_2]_2 \rightleftharpoons 2Zn(Se_2CNEt_2)_2 \qquad (3)$$

If this equilibrium is important in these solvents, the ^{77}Se resonance must be concentration dependent. Varying the

Table IV. Concentration and Temperature Dependencies of ^{77}Se NMR Data for $Zn(Se_2CNEt_2)_2$ and $Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$[a]

compd		data[b]					
$Zn(Se_2CNEt_2)_2$	concn, M	0.01	0.028	0.14	0.23	0.46	0.92
	δ, ppm[c]	−32.0	−32.1	−31.9	−31.8	−31.7	−31.5
			32 °C	−2 °C		−23 °C	
$Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$	δ (0.29 M)		−238.2	−244.9		−249.5	
	δ (0.12 M)		−238.3			−249.6	

[a] Solvent in $CDCl_3$. [b] Shifts from 2 M selenophene. [c] Temperature 32 °C.

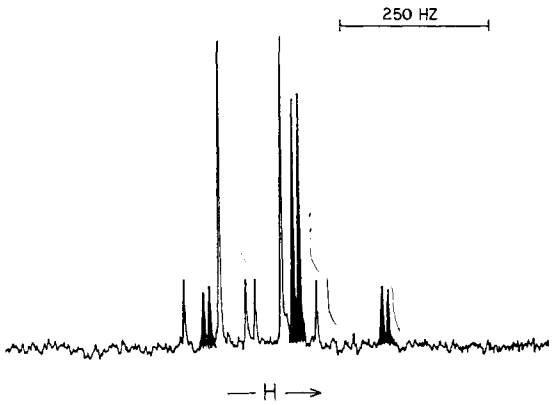


Figure 4. ^{77}Se NMR spectrum of 0.24 M solution of $Pt(Se_2CNEt_2)PPh_3Cl$ in $CDCl_3$ obtained at 19.08 MHz and 32 °C probe temperature. For this spectrum, 14 134 transients were accumulated in the span of 9.4 h using ca. 40° pulse width and a spectrum width of 2.5 kHz. Peak assignments are described in the text.

concentration by two orders of magnitude (Table IV) resulted in a negligible change in the chemical shift. Furthermore, if the complex were dimeric in solution, four nonequivalent ^{77}Se resonances would be expected. Only one peak is observed within the concentration range studied (0.01–0.92 M). The complex $Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$ also shows a similar temperature dependence with no noticeable concentration dependence (Table IV).

Changing the R group from isobutyl to ethyl invariably shifts the ^{77}Se resonance upfield (Table III). The effect of the R groups on the electronic mesomeric shift has been discussed. The R groups also affect the ^{77}Se resonance by influencing the solvent–solute interaction. The bulky diisobutyl complex is more sterically hindered than the ethyl derivative (as seen with space-filling models). Hence the solvent–solute interaction at the ^{77}Se is reduced. The effect of the R group on the solvent interaction at the selenium in the complex $Pd(Se_2CN\text{-}i\text{-}Bu_2)PPh_3Cl$ has been discussed above.

Coupling Constants. There are two nonequivalent selenium atoms in the complexes $M(Se_2CNR_2)PR'_3X$ (X = Cl or CH_3). The assignment of the peaks in these planar complexes can be based on trans influences and the theoretical expression[28] given for coupling between two nuclei covalently bonded to each other:

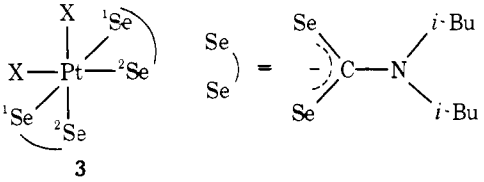
$$J_{ab} \propto \gamma_a\gamma_b\alpha_a^2\alpha_b^2|\psi_{a(ns)}(0)|^2|\psi_{b(ns)}(0)|^2({}^3\Delta E)^{-1} \quad (4)$$

where γ_a is the gyromagnetic ratio of nucleus a, α_a^2 is the s electron contribution by a to the a–b bond, $|\psi_{a(ns)}(0)|^2$ is the ns valence electron density at the nucleus, and ${}^3\Delta E$ is a mean singlet–triplet excitation energy. According to the NMR trans influence argument, a ligand with a large trans influence concentrates metal (M) s character into its metal–ligand bond. This results in a reduction of metal s character in the bond trans to the ligand, producing a smaller α_M^2 in this bond. On the other hand, when the ligand has a weak trans influence, α_M^2 in the trans bond would be relatively larger. The other factors in eq 4 are common for both cis and trans M–Se bonds.

The spectrum of $Pt(Se_2CNEt_2)PPh_3Cl$ is shown in Figure 4. The downfield set of peaks (unshaded) shows a central doublet arising from phosphorus–selenium coupling ($^2J_{P\text{-}Se}$ = 100.5 Hz) and two smaller doublets flanking the central doublet arising from selenium coupled to both phosphorus and ^{195}Pt ($I = \frac{1}{2}$, natural abundance 33.6%). The separation of these two doublets is $^1J_{Pt\text{-}Se}$ = 115.2 Hz. The upfield set of peaks (shaded) shows the corresponding coupling constants $^2J_{P\text{-}Se}$ = 10.0 and $^1J_{Pt\text{-}Se}$ = 291.4 Hz. The smaller $^1J_{Pt\text{-}Se}$ means a smaller α_{Pt}^2 and hence should correspond to Pt–Se bond trans to the phosphine. The upfield set of peaks then is for the selenium cis to the phosphine. (We are assuming here that α_{Se}^2 and $|\psi_{Se(4s)}(0)|^2$ for the two selenium atoms do not differ by much.) The observation that the trans $^2J_{P\text{-}Se}$ is larger than the cis $^2J_{P\text{-}Se}$ is not unusual. For a variety of second- and third-row transition metals, $^2J_{P\text{-}P}$ are much smaller for cis complexes than for the trans isomers.[40] In the palladium and nickel complexes, we have assigned the downfield doublet (with a larger $^2J_{P\text{-}Se}$) to the Se trans to the phosphine and the upfield doublet (singlet for palladium) to Se cis to the phosphine. Note that the cis $^2J_{P\text{-}Se}$ is ~0 (less than 0.5 Hz) in the palladium complex.

The spectrum of $Pt(Se_2CNEt_2)PPh_3CH_3$ shows a downfield triplet of doublets and an upfield doublet of quartets. The downfield set of peaks has been assigned to the selenium cis to the phosphine. This is consistent with the small $^2J_{P\text{-}Se}$ of 7.8 and $^1J_{Pt\text{-}Se}$ of 47.5 Hz. The small $^1J_{Pt\text{-}Se}$ is due to the fact that the selenium is trans to $-CH_3$, a ligand which is higher than $P(C_6H_5)_3$ in the trans influence series. The upfield quartets are separated by $^2J_{P\text{-}Se}$ = 111.9 Hz, the quartet arising from coupling to the methyl protons (coupling to ^{77}Se is also seen in the ^1H NMR). Owing to the poor S/N (ca. 5) and attenuation of the peak intensities due to coupling to $-CH_3$ protons, the ^{195}Pt satellites were not observed.[43]

In assigning the peaks in the spectra of the complexes *cis*-$Pt(Se_2CN\text{-}i\text{-}Bu_2)_2X_2$ (X = I, Br) (**3**), the trans influence



3

argument again has been utilized. In **3**, varying X would affect $^1J_{Pt\text{-}^2Se}$ more than $^1J_{Pt\text{-}^1Se}$ since ^2Se is trans to X. If we look at the upfield peaks of the iodide and bromide, we see that the difference in $^1J_{Pt\text{-}^1Se}$ is 33.5 Hz while the downfield peaks show a difference of 51.0 Hz. Therefore, we assign ^1Se to the upfield peaks and ^2Se to the downfield peaks. The cis influence,[40] though not as strong as the trans influence, might also affect $^1J_{Pt\text{-}Se}$. Thus this might account for the substantial change in $^1J_{Pt\text{-}^1Se}$ (33.5 Hz), ^1Se being cis to two X's. (However, we cannot argue against the possibility that the ^2Se is the upfield peak in the diiodo complex but the downfield one in the dibromo complex, with a similar inversion for ^1Se.)

Spin–Lattice Relaxation Times (T_1). To date we have carried out T_1 measurements on only a few complexes. Results of these measurements are shown in Table V. The T_1's obtained are generally quite short. These T_1's are to be compared with those

Table V. Spin-Lattice Relaxation Times for the ^{77}Se NMR of Some Selected Diselenocarbamates

compd	conditions	T_1, s[a]	T, °C
$Zn(Se_2CNEt_2)_2$	1.0 M in $CDCl_3$	2.0	−20
		2.8	−3
		3.9	+15
		4.4	+24
$Zn(Se_2CNEt_2)_2$	0.53 M in $CHCl_3$	2.1	−20
		3.0	−4
		4.5	+27
$(NEt_2H_2)Se_2CNEt_2$	0.87 M in $CDCl_3$	1.9	−27
		2.7	−8
$Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$	0.42 M in $CHCl_3$	0.46	−28
		0.83	−5
		1.4	+27

[a] Estimated error, <10%. Some measurements were repeated and were found to be reproducible to within ±0.1 s.

of dialkyl (and diaryl) mono- and diselenides,[2] which are generally substantially longer. The alkylselenols,[2] RSeH, however, have more comparable T_1's.

The T_1's of organoselenium compounds were found to decrease with increasing temperature,[2] implicating spin rotation as the dominant relaxation mechanism. However, the T_1 of phenylselenol has been found[41] to increase with increasing temperature. Since proton decoupling leads to a negligible NOE and selenium-proton coupling is maintained, it has been suggested[41] that the chemical shift anisotropy is the dominant relaxation mechanism in phenylselenol.

In the present study, the variable temperature behavior of the T_1 of $Zn(Se_2CNEt_2)_2$ and $Pd(Se_2CN\text{-}i\text{-}Bu_2)_2$ shows[42] that spin rotation is not a dominant relaxation mechanism. The absence of any spin-$\frac{1}{2}$ nuclei with large magnetic moments close to the selenium precludes a dipole-dipole relaxation mechanism. Since we have seen that solvent-solute interactions take place (see above), we also considered a scalar coupling relaxation possibly caused by the interaction between the selenium nuclei and deuterium when $CDCl_3$ is used as solvent. The maximum possible value of $1/T_1$ is given by the equation[42]

$$1/T_1 = (4\pi^2 S(S+1)J^2)/3|\omega_I - \omega_S| \qquad (5)$$

where S is the deuterium spin, J is the selenium-deuterium coupling constant, and ω is the Larmor frequency of the nuclei involved. Since $|\omega_{Se} - \omega_D|$ is of the order of 10^7 Hz, and upon changing the solvent from $CDCl_3$ to $CHCl_3$ there is no significant effect on T_1, we conclude that this mechanism is not important. In the absence of any other acceptable mechanism, chemical shift anisotropy appears to cause the relaxation. Conclusive proof of the dominance of this mechanism involves obtaining T_1's at different magnetic fields, a study which unfortunately is not possible with our instrumentation.

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(43) Owing to a technical problem with our instrument, it is not possible to decouple protons while observing ^{77}Se.