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Selenium-77 Nuclear Magnetic Resonance Studies. 3.* Chemical Shifts of Ionic, N- and Se-Coordinated Selenocyanate

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A considerable variety of instrumental techniques have been employed [1, 2] as diagnostic probes of the bonding modes adopted by the ambidentate pseudohalide ions NCO^-, NCS^- and $NCSe^-$ in coordination complexes. Although, historically, infrared spectroscopy has been the most widely used of these techniques [3], nuclear quadrupole [4] and nuclear magnetic [5–11] resonance spectroscopy have recently been developed as more sensitive, unequivocal indicators of bond type. The NMR techniques employed have ranged from indirect methods, wherein nuclei external to the pseudohalides are probed, *e.g.*, ^1H [5], ^1H with lanthanide-induced shift [6], $^1H\{^{195}Pt\}$INDOR [7], ^{31}P [8], and ^{195}Pt [9], to direct utilization of NMR active nuclei in the pseudohalides themselves, *e.g.* ^{14}N [10], ^{15}N [9] and ^{13}C [11]. In the latter category, only the Group VI atoms of the pseudohalides have not heretofore been utilized. In this context, the long-term interest in one of our laboratories [1] in the coordination chemistry of ambidentate ligands has happily come into coincidence with a major interest [12, 13] in the other laboratory concerning ^{77}Se NMR spectroscopy. The first result is this preliminary report concerning the efficacy of using ^{77}Se NMR spectroscopy as a means of identifying the bonding mode of the coordinated $NCSe^-$ ion.

Experimental Section

The ^{77}Se NMR spectra were obtained at 30 °C 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 lock was effected by employing an ^{19}F external lock.

$Zn(t\text{-}bupy)_2(NCSe)_2$ [14] (t-bupy = t-butylpyridine)

This complex (0.2 g) was not very soluble in DMSO (2.5 mL). Heating, however, induced complete dissolution. However, upon cooling the complex crystallized out. Addition of ~0.7 mL $CDCl_3$ led to complete dissolution of the crystals. This solution was filtered into a 12 mm NMR tube (a very small amount of greyish precipitate (possibly elemental Se) formed).

$Cd(t\text{-}bupy)_2(NCSe)_2$ [14]

Based on the above experience, 2.5 mL $CDCl_3$ was used to dissolve 0.33 g of the complex. The clear solution gradually turned cloudy (within 20 min). Addition of ~1 mL DMSO resulted in complete dissolution to give a colorless solution. There was no sign of decomposition.

$K_2[Hg(SeCN)_4]$ [15]

The complex (0.1–0.3 g) was dissolved in ~2.5 mL D_2O. A clear yellow solution formed, which soon became cloudy (within 5 min). A small amount of $NaHCO_3$ was added to the suspension. The latter was then filtered into a 12 mm NMR tube (the solution was found to decompose with time, depositing a shiny grey material (possibly elemental Se) on the walls of the tube and, in one week, the solution had turned very pale yellow).

KSeCN, 98% pure, was obtained from Apache Chemicals.

Results and Discussion

Selenocyanate complexes formed by the Group IIB triad proved to be ideal for our purpose, since the selenocyanate's bonding mode changes from N-bonded (with Zn(II) and Cd(II)) to Se-bonded (with Hg(II)) as one descends through the group [1, 2]. The ^{77}Se chemical shifts obtained for these complexes and KSeCN, as well as those exhibited by two organoselenocyanates reported earlier [12] are shown in Table I.

Two ^{77}Se peaks (labeled A and B) were obtained for the Group IIB triad complexes. Peak A arises from the coordinated $SeCN^-$ in the complex originally dissolved. Peak B represents a minor constituent (the intensity of B was always less than 10% of the intensity of A) whose identity is still somewhat in doubt.

Peak B clearly does not arise from dissociated $SeCN^-$ (compare values in Table I). When $Cd(t\text{-}bupy)_2(NCSe)_2$ was dissolved (1:1) in a solution containing KSeCN (third entry in Table I), only a single peak was observed. The position of this peak (–282

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*Parts 1 and 2: see references 12 and 13.

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TABLE I. Summary of ^{77}Se NMR Results.

Compound	Solvent(s)^a	δ(ppm)^b from external 1 *M* CH_3SeCH_3 (in $CHCl_3$)	
		Peak A	Peak B
$Zn(t\text{-}bupy)_2(NCSe)_2$	0.7 mL $CDCl_3$/2.5 mL DMSO	−318	−465
$Cd(t\text{-}bupy)_2(NCSe)_2$	2.5 mL $CDCl_3$/1 mL DMSO	−305	−466
$Cd(t\text{-}bupy)_2(NCSe)_2$	1:1 with KSeCN in 0.5 mL $CDCl_3$/2.5 mL DMSO	−282	−467
KSeCN	0.5 mL $CDCl_3$/2.5 mL DMSO	−273	–
$K_2[Hg(SeCN)_4]$	2.5 mL D_2O	−191	−471
$C_6H_5CH_2SeCN$	$CDCl_3$	289^c	–
$p\text{-}CH_3C_6H_4SeCN$	$CDCl_3$	315^c	–

^{a}Sample concentrations were *ca.* 0.1–0.2 *M*. For mode of sample preparation, see Experimental Section. ^{b}Negative shifts are upfield of the CH_3SeCH_3 reference. ^{c}Taken from reference [12], initially measured relative to external 2 *M* selenophene in $CHCl_3$; converted to CH_3SeCH_3 reference by means of the empirical relationship $\delta_{CH_3SeCH_3} \approx \delta_{\text{selenophene}} + 317.6 + 299.8$.

ppm), being approximately the average of the chemical shifts of the Cd complex and KSeCN obtained separately, indicates that there is rapid exchange between coordinated and uncoordinated $SeCN^-$. Peak B, however, remained unchanged. Peak B cannot be due to H_2Se, since H_2Se resonates [17] at −226 ppm. A remaining, untested possibility is NCSe– SeCN. If B is a coordination isomer, it does not rapidly exchange with $SeCN^-$ or the initial complex dissolved.

The foregoing discussion concerning this relatively minor point should not obscure the more salient observation that ^{77}Se NMR spectroscopy appears to have lived up to our expectations as an effective selenocyanate bonding mode probe. Although more data are needed to confirm this generality, it appears that the ^{77}Se chemical shifts vary in an ideal manner for diagnostic purposes, shielding increasing in the order:

$$\text{Ar-SeCN} \leqslant \text{R-SeCN} \ll \text{M-SeCN} < \text{SeCN}^- < \text{M-NCSe}$$

Although the chemical shifts of the Se-bound compounds were not determined in the same solvent as that used for $SeCN^-$ and the N-bound compounds, the solvent-induced differences would be expected [12] to be considerably smaller than those observed between $NCSe^-$ and the Hg or organic compounds. This order is the reverse of the order of shielding observed [14] for selenocyanate ^{13}C chemical shifts, as well as the reverse of the order predicted for ^{77}Se chemical shifts on the basis of calculated π-electron atomic charges [16].

It should be noted that the ^{77}Se chemical shift difference between $Zn(t\text{-}bupy)_2(NCSe)_2$ and $Cd(t\text{-}bupy)_2(NCSe)_2$ in DMSO is only ~13 ppm while the difference between the Zn and Cd diselenocarbamates is [12] about 60 ppm. In the diselenocarbamates the Se is bonded directly to the metal and hence is more sensitive to the differences between zinc and cadmium. It is of interest that the total chemical shift range exhibited for various species containing -SeCN is over 600 ppm. In accord with a suggestion by Lardon [17], this large chemical shift range indicates that the paramagnetic shielding term (σ_p) is dominant among the three terms [18] which determine the magnitude of the observed chemical shielding: $\sigma_{\text{observed}} = \sigma_{\text{local diamagnetic}} + \sigma_{\text{paramagnetic}} + \sigma_{\text{neighboring atom}}$.

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