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A Selenium-77 and Cadmium-113 NMR Spectroscopic Study of Phenylselenolate Complexes of Cadmium

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The reduced-temperature slow-exchange ^{77}Se and ^{113}Cd NMR spectra of the complexes $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ have been measured. At 213 K, the ^{113}Cd chemical shifts change linearly from ca. *541 ppm (n = 0) to* ca. *590 ppm (n = 4) relative to external 0.1* M *$Cd(ClO_4)_2(aq)$ at ambient probe temperature. Also $^1J(^{113}Cd–^{77}Se)$ changes linearly from 126 ± 3 Hz to 46 ± 4 Hz and the ^{77}Se complexation shifts (= δ_{Se}(complex) – δ_{Se}(free)) decrease monotonically from* ca. *–22 ppm to* ca. *–30 ppm as n is increased from 0 to 3.*

In the ternary mixtures $Cd^{2+}–PhS^-–PhSe^-$, the selenolate binds preferentially, the ratio of the overall formation constants $K([Cd(SePh)_4]^{2-})/K([Cd(SPh)_4]^{2-})$ being of the order $10^3–10^4$; the significance of this finding to the well-known antagonism of selenium compounds towards cadmium intoxication is discussed.

Introduction

In recent work from this laboratory [1] the ^{113}Cd NMR spectra of a wide range of simple thiolatocadmates were reported. These 'fingerprint' data were intended to ease the interpretation of the metal NMR spectra of more-complicated biologically-important cadmium complexes.

To complement our earlier study, we have now measured ^{113}Cd and ^{77}Se NMR spectra of several cadmium complexes with a representative selenolate, $PhSe^-$. The cadmium–selenolate linkage, which has been scarcely studied previously, might be involved in the cadmium–selenium complex(es) which are formed by simultaneous administration of selenium and cadmium to rats *in vivo*** [2] and which may provide the basis for the remarkable, well-established (*e.g.* Refs. 3–5), protective effect of certain selenium compounds against cadmium intoxication. At the same time, the Cd–Se bond is an ideal candidate for scrutiny by NMR: both ^{77}Se (7.6% natural abundance, μ = 0.5325 nuclear magnetons) and ^{113}Cd (12.3% natural abundance, μ = 0.6195 nuclear magnetons) have spin I = ½, and their resonances are readily accessible with modern instrumentation.

Experimental

Phenylthiol (Aldrich Chemical Company) and phenylselenol (Alfa Products) showed no significant impurity by ^{13}C NMR and were used as received. Cadmium-113 oxide (96.3 atom % ^{113}Cd), from Oak Ridge National Laboratory, was converted to the nitrate for use in the NMR study.

All solvents were deaerated with high-purity nitrogen or argon, and all manipulations were performed in a glove bag under high-purity nitrogen or argon, or using a Teflon–glass vacuum line. The NMR samples, which contained $[Cd^{2+}]$:([PhSeH] + [PhSH]):$[OH^-]$ or $[OMe^-]$ in the approximate range 0.05:0.6:1.2 *M*, were prepared in sealed 10 mm od NMR tubes as described previously for $Cd^{2+}–RS^-–R'S^-$ mixtures [1].

Initial ^{77}Se and ^{113}Cd NMR samples were measured, in the manner reported earlier for ^{113}Cd NMR [1], using an XL-100-12 Spectrometer System operating at 19.12 and 22.34 MHz for ^{77}Se and ^{113}Cd, respectively. Typically, acceptable ^{77}Se spectra of samples without ^{113}Cd enrichment required several thousand transients using a pulse angle of 45°, 12.5 kHz spectral window, 1 s acquisition time and 4.3 s cycle time. ^{113}Cd NMR spectra without clearly resolved ^{77}Se satellites (except in solutions containing $[^{113}Cd(SePh)_4]^{2-}$ only) were obtained in several thousand transients using a pulse angle of 21°, 10 kHz spectral window, 1 s acquisition time and 3.6 s cycle time. To obtain readily identifiable ^{77}Se satellites in the ^{113}Cd NMR spectra, and ^{113}Cd-coupled ^{77}Se NMR, selected samples were later run

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**A complex containing Cd:Se = 1:1 is formed in rat plasma following administration of cadmium and selenite *in vivo* or when cadmium, selenite, plasma and erythrocytes are incubated *in vitro* [2].

TABLE I. The ^{77}Se and ^{113}Cd NMR Spectral Parameters of the Complexes $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ at 213 K in CH_3OH-CD_3OD[a]

n in $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$	$\Delta\delta_{Se}$[b] (ppm)	$\Delta\delta_{Cd}$[c] (ppm)	$^1J(^{113}Cd-^{77}Se)$[d] (Hz)
0	0	0	126
1	−2.4	12.9	99
2	−5.2	25.4	72
3	−8.3	37 4	46[e]
4	–	49.0	–

[a] $CH_3OH:CD_3OD$ = 4·1. [b] $\Delta\delta_{Se} = \delta_{Se}(\text{complex}) - \delta_{Se}([Cd(SePh)_4]^{2-})$. In a solution where $[^{113}Cd]\cdot[PhSe^-]\ [PhS^-] \approx 0.035:0.11:0.32$ *M*, $\delta_{Se}([Cd(SePh)_4]^{2-})$ and $\delta_{Se}(PhSe^-(\text{free}))$ are −9.9 and 12.1 ppm, respectively, at 213 K in CH_3OH-CD_3OD. A 0.6 *M* solution of $PhSe^-$ in CH_3OH has δ_{Se} = 12.5 and 35.9 ppm at 213 K and 306 K, respectively. [c] $\Delta\delta_{Cd} = \delta_{Cd}(\text{complex}) - \delta_{Cd}([Cd(SePh)_4]^{2-})$. A 0.035 *M* solution of $[^{113}Cd(SePh)_4]^{2-}$ in $CH_3OH:CD_3OD$ at 213 K has $\delta_{Cd} \approx 541$ ppm. [d] Observed in both 76 31 MHz ^{77}Se and 88 74 MHz ^{113}Cd NMR spectra except where noted Estimated error ± 3 Hz except where noted. [e] Estimated error ± 4 Hz; observed in ^{77}Se NMR spectrum only.

on a Bruker WH-400 NMR spectrometer operating at 76.31 MHz and 88.74 MHz for ^{77}Se and ^{113}Cd, respectively. At these higher frequencies $1-2 \times 10^3$ transients were required with operating parameters similar to those used on the XL-100. Cadmium-113 chemical shifts were measured relative to external aqueous 4 *M* $Cd(NO_3)_2$ at ambient probe temperature as primary reference and converted to aqueous 0.1 *M* $Cd(ClO_4)_2$ as reference using $\delta_{0.1\,M\ Cd(ClO_4)_2} = \delta_{4\,M\ Cd(NO_3)_2} - 65$ ppm [6]. Selenium-77 chemical shifts were referred to external neat Me_2Se at ambient probe temperature. All shifts are reported with increasing shift corresponding to increasing frequency. Because the absolute ^{77}Se and ^{113}Cd chemical shifts of the various complexes studied varied somewhat with solution composition, whereas the relative shifts did not, relative shifts have been given in Table I.

Results and Discussion

When an aqueous solution of $PhSe^-$ is added to aqueous cadmium nitrate, precipitation occurs up to *ca.* L/M = 2, by comparison with the system $Cd^{2+}-PhS^-$ [7], the solid is most probably $Cd(SePh)_2$. Addition of further $PhSe^-$ causes dissolution of the precipitate

An aqueous solution containing $[^{113}Cd^{2+}]\ [PhSe^-]:[(\text{excess})\ OH^-] = 0.05:0.6:0.6$ *M* gives, at 306 K, a ^{113}Cd resonance having δ_{Cd} = 538 ppm but no observable ^{77}Se satellites, and a single, broad ($w_{1/2} \approx 120$ Hz) 19.1 MHz ^{77}Se resonance with $\delta_{Se} \approx 24.8$ ppm shielded by 9.4 ppm from the comparatively sharp ($w_{1/2}$ = 5 Hz) resonance of a 0.6 *M* solution of $PhSe^-$. The last result shows that free–bound ligand exchange is fast on the NMR timescale at 306 K in this system. In a corresponding solution in methanol at reduced temperature, ligand exchange is slow on the NMR timescale: at 213 K, the cadmium resonance at δ_{Cd} = 541 ppm is flanked by a pair of ^{77}Se satellites with intensity *ca.* 25% of the total intensity and a one-bond $^{113}Cd-^{77}Se$ coupling of 126 Hz, while the ^{77}Se resonance of the complex is a doublet of 126 Hz separation, deshielded by 23.5 ppm from the signal due to the excess ligand which has δ_{Se} = 12.3 ppm. The satellite intensity in the ^{113}Cd spectrum is close to the 23.9% population of $CdSe_3\,^{77}Se$ expected for a statistical distribution of zero-spin selenium and selenium-77 in natural abundance [8], suggesting that the species formed from Cd^{2+} and excess $PhSe^-$ is $[Cd(SePh)_4]^{2-}$.

The formation of $[Cd(SePh)_4]^{2-}$ is confirmed by an examination of the low-temperature slow-exchange ^{113}Cd and ^{77}Se NMR spectra of ternary mixtures of $^{113}Cd^{2+}$, $PhSe^-$ and PhS^-; NMR spectral details are given in the Table. In the ^{113}Cd spectra, a total of *five* equally spaced signals are observed as the $PhSe^-/PhS^-$ ratio is varied.* This series of resonances is just that expected for the five complexes $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ (n = 0–4), which presumably contain tetrahedrally coordinated cadmium. The most shielded resonance is identified by its ^{113}Cd chemical shift as that of $[Cd(SePh)_4]^{2-}$ and the least shielded is similarly attributable to $[Cd(SPh)_4]^{2-}$ [1]. The signals from the mixed species are readily assigned on the basis of their order of appearance as the $PhSe^-/PhS^-$ ratio is changed, the linear variation of the incremental shifts, $\Delta\delta_{Cd}$, and the intensity and separation of the ^{77}Se satellite doublets. The satellite intensity about the signal from $[Cd(SPh)(SePh)_3]^{2-}$ is *ca.* 20% of the total, close to the 19.5% population of the $CdSSe_2\,^{77}Se$ kernel expected statistically, while that about the signal from $[Cd(SPh)_2(SePh)_2]^{2-}$ is 16% or less (overlap with the centre band is signifi-

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*Signals from all five species may be observed in the same solution when $^{113}Cd^{2+}\ PhS^-.PhSe^- \simeq 1.9:3$, with $[^{113}Cd] \simeq 0.05$ *M* cant), close to the expected 14.0%. The ^{77}Se satellites of $[Cd(SPh)_3(SePh)]^{2-}$ were obscured by the centre band of the cadmium resonance. However, all the one-bond ^{113}Cd–^{77}Se couplings can be obtained from the slow-exchange ^{77}Se NMR spectrum which consists of a free ligand resonance together with a series of doublets for the various $PhSe^-$ complexes. The doublets from $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ ($n = 0-2$) have the separations expected from the ^{77}Se satellite splittings in the ^{113}Cd NMR spectra and the separation of the doublet from $[Cd(SPh)_3(SePh)]^{2-}$ is that expected from the *ca.* 27 Hz decrease in magnitude associated with replacement of one selenium by sulfur.

The shielding sequence $\delta_{Cd}(CdS_4) > \delta_{Cd}(CdSe_4)$ found here has also been observed for the resonances of $[Cd(SPR_3)_4^{2+}]$ and $[Cd(SePR_3)_4^{2+}]$ [9], and solid CdS and CdSe (in which the cadmium is tetrahedrally coordinated) [10], and a similar relationship holds for the ^{119}Sn chemical shifts of $Sn(SPh)_4$ and $Sn(SePh)_4$ (and other $Sn(SR)_4$–$Sn(SeR)_4$ pairs) [11]. The shift difference $\delta_{Cd}([Cd(SPh)_4]^{2-}) - \delta_{Cd}([Cd(SePh)_4]^{2-})$, 49 ppm, is similar in magnitude to $\delta_{Cd}([Cd(SPR_3)_4]^{2+}) - \delta_{Cd}([Cd(SePR_3)_4]^{2+})$ (45 ppm and 68 ppm for R = Ph and C_6H_{11}, respectively), but significantly smaller than either $\delta_{Cd}(CdS) - \delta_{Cd}(CdSe)$ (142 ppm) or $\delta_{Sn}(Sn(SPh)_4) - \delta_{Sn}(Sn(SePh)_4)$ (175 ppm). The change of cadmium chemical shift on substituting selenolate for thiolate in $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ (*i.e.* 13 ppm per substitution) is sufficiently small compared with the range of shifts established for mononuclear thiolatocadmates (*ca.* 250 ppm [1]), and the ^{77}Se complexation shifts small enough compared with changes due to solution composition, that, in general, δ_{Cd} and δ_{Se} alone will be insufficient to distinguish a complex, with mixed thiolate–selenolate ligands, from a 'pure' thiolate complex together with free selenolate; for definitive evidence of a Cd–Se bond the ^{77}Se satellites in the ^{113}Cd spectrum and ^{113}Cd satellites in the ^{77}Se spectrum had better be observed. As $^1J(^{113}Cd-^{77}Se)$ may be quite small, as in $[Cd(SPh)_3SePh]^{2-}$, enrichment in both ^{113}Cd and ^{77}Se seems desirable to both ease measurements and prevent ambiguity.

The linear dependence of the ^{113}Cd resonances of $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ on the substituents about the cadmium is not unexpected, as near-linear dependences have been found for $[Cd(SP(C_6H_{11})_3)_n(SeP(C_6H_{11})_3)_{4-n}]^{2+}$ [9] and $Sn(SMe)_n(SeMe)_{4-n}$ [11] also. More surprising is the marked change in $^1J(^{113}Cd-^{77}Se)$ across the series $[Cd(SPh)_n(SePh)_{4-n}]^{2-}$ (see Table), though here too a first order substituent effect is evident. It would be of interest to measure one-bond M–^{77}Se couplings for a wider range of $[Cd(SR)_n(SeR)_{4-n}]^{2-}$ and for their tin analogues.

It was readily apparent in measuring the NMR spectra of the ternary systems Cd^{2+}–$PhSe^-$–PhS^- that the selenolate is a strong competitor for coordination to cadmium. For instance, the average stoichiostoichiometry of the complexes approximated $[Cd(SPh)_{2.4}(SePh)_{1.6}]^{2-}$ and $[Cd(SPh)_{1.6}(SePh)_{2.4}]^{2-}$ in solutions of composition $[Cd^{2+}]:[PhS^-]:[PhSe^-]$ = 0.05:0.50:0.10 *M* and 0.05:0.40:0.20 *M*, respectively. At the same time, the distribution of mixed species at any $(PhS^-/PhSe^-)$ bound ratio is close to statistical; for example, the ^{113}Cd NMR spectra of each of the aforementioned solutions provided evidence for four complexes in equilibrium, the major species at any $(PhS^-/PhSe^-)_{bound}$ ratio is close to and 1 and 2, respectively. From the ^{113}Cd NMR signal intensities in solutions of known composition it was possible to estimate that the ratio of the overall formation constants, $K([Cd(SePh)_4]^{2-})/K(Cd(SPh)_4]^{2-})$ is of order 10^3–10^4. Thus cadmium, like mercury [12], binds preferentially at selenolate donor sites, and it is tempting to speculate that the ready formation of the Cd–Se bond may be involved in the antagonism of selenium compounds towards cadmium toxicity *in vivo*.

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