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Short Communication

Selenium-77 NMR of C_3Se_5–metal complexes ($C_3Se_5^{2-}$ = 1,3-diselenole-2-selone-4,5-diselenolate)

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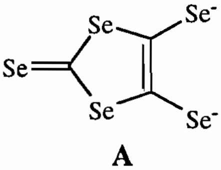
Abstract

^{77}Se NMR spectra of $Na_2C_3Se_5$ and $[M(C_3Se_5)_2]^{n-}$ complexes ($C_3Se_5^{2-}$ = 1,3-diselenole-2-selone-4,5-diselenolate; $n = 1$, M = Au(III); $n = 2$, M = Zn(II), Cd(II), Ni(II), Pd(II) and Pt(II)) as well as those of $Na_2C_3Se_5$ and $C_3Se_5[C(O)Ph]_2$ were measured. Chemical shifts of the ^{77}Se nuclei directly bound with the metal ions are greatly affected by them; Se nuclei of the Ni(II), Pd(II), Pt(II) and Au(III) complexes are more deshielded than those of the Na(I), Zn(II) and Cd(II) complexes. ^{77}Se–^{77}Se and ^{77}Se–^{195}Pt spin–spin coupling constants were also measured and discussed.

Introduction

Metal complexes with the selenium-rich ligand ($C_3Se_5^{2-}$; A) [1–3] attract much attention from the standpoint of their electrical conductivities in connection with the highly electrically conducting $C_3S_5^{2-}$–metal complexes [1–4]. To clarify the electronic properties of the metal complexes with this ligand, ^{77}Se NMR may be useful. In particular, chemical shifts of ^{77}Se nuclei bound with metal ions may reflect the metal–selenium bonding properties. Although ^{77}Se NMR studies have been reported for many organic selenium compounds [5], data for metal complexes with selenium-donor ligands are limited [6–11].



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We report ^{77}Se NMR spectra of several C_3Se_5–metal complexes together with that of the organic compound with the C_3Se_5 skeleton and discuss the electronic properties of the ligand and ligand–metal bonds.

Experimental

Preparation of C_3Se_5–metal complexes

$Na_2C_3Se_5$ was obtained by dissolution of $C_3Se_5[C(O)Ph]_2$ [12, 13] and sodium metal in methanol, followed by removal of the solvent under reduced pressure. Without any further purification of the residual solid it was dissolved in dimethyl sulfoxide-d_6 for the ^{77}Se NMR measurement. $[PPh_4]_2[Zn(C_3Se_5)_2]$ [13], $[NBu^n_4]_2[Ni(C_3Se_5)_2]$ [2] and $[NBu^n_4][Au(C_3Se_5)_2]$ [3] were prepared according to the previous methods. $[NBu^n_4]_2[Cd(C_3Se_5)_2]$, $[NBu^n_4]_2[Pd(C_3Se_5)_2]$ and $[NBu^n_4]_2[Pt(C_3Se_5)_2]$ were prepared by reactions of $Na_2C_3Se_5$ with $CdCl_2$, Na_2PdCl_4 in methanol, and $K_2PtCl_4 \cdot 2H_2O$ in a mixture of methanol–water (1:1), respectively, as described for $[NBu^n_4]_2[Ni(C_3Se_5)_2]$ [2].

Measurement of ^{77}Se NMR spectra

The spectra were recorded on a JEOL JNM-GSX-450 spectrometer (Instrumental Analysis Center, Faculty of Engineering, Osaka University) at 76.10 MHz in chloroform-d_1 or dimethyl sulfoxide-d_6. The chemical shifts were referenced to external dimethyl selenide in chloroform-d_1. The probe temperature was held at 30±0.5 °C for all measurements. The conditions for the measurement were as follows: pulse 45°, relaxation delay 2 s, digital resolution 0.6 Hz, 600–30000 scans accumulated.

Results and discussion

All the compounds exhibit three ^{77}Se NMR signals, which are clearly assigned based on the results of $C_3Se_5[C(O)Ph]_2$ [14, 15] and of five-membered selenium heterocycles with the C=Se group [16]. Chemical shifts of the present metal complexes are given in Table 1, together with the reported data. ^{77}Se NMR chemical shifts are greatly affected by the metal ions; the variation widths are 671 ppm for Se(1) (directly bound with the metal ions), 68 ppm for Se(2), and 196 ppm for Se(3). In particular, the large variation observed for the Se(1) nuclei seems to reflect the electronic properties of the selenium–metal bonding. The magnitude of the ^{77}Se chemical shift is considered to be predominantly affected

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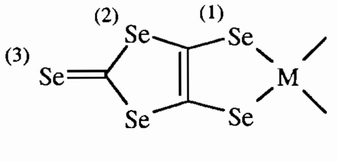
TABLE 1. ^{77}Se chemical shifts[a] (ppm) for the C_3Se_5–metal complexes[b] and $C_3Se_5[C(O)Ph]_2$[c]

Compound	Se(1)	Se(2)	Se(3)
$Na_2C_3Se_5$	95.2	1068.1	1135.6
$[PPh_4]_2[Zn(C_3Se_5)_2]$[d]	104.7	1066.9	1134.2
	(94.8	1124.1	1056.6)[e]
$[NBu^n_4]_2[Cd(C_3Se_5)_2]$	57.6	1060.9	1148.3
$[NBu^n_4]_2[Ni(C_3Se_5)_2]$	409.2	1119.1	1160.6
$[NBu^n_4]_2[Pd(C_3Se_5)_2]$	454.9	1129.3	1185.1
	(445.6	1119.2	1174.8)[e]
$[NBu^n_4]_2[Pt(C_3Se_5)_2]$	420.0	1115.9	1226.5
	(409.4	1105.4	1215.7)[e]
$[NBu^n_4][Au(C_3Se_5)_2]$	729.0	1120.9	1330.1
	(718.2	1110.6	1317.2)[e]
$C_3Se_5[C(O)Ph]_2$	665.7	1118.6	1252.6
	(621.3	1074.1	1209.0)[f]

[a]External reference, dimethyl selenide in chloroform-d_1. [b]Measured in dimethyl sulfoxide-d_6. [c]Measured in chloroform-d_1. [d]Ref. 13. [e]Measured in dimethyl sulfoxide-d_6; external reference, dimethyl selenide [11]. [f]Measured in chloroform-d_1; external reference, dimethyl selenide [14, 15].



by the deshielding paramagnetic term arising from electronic circulation on the observed nucleus [5]. Since this paramagnetic term depends on the mean inverse cube of the radius of 4p orbitals ($\langle r^{-3}\rangle$4p) of the Se atom [17], an increase in the electron-withdrawing ability of groups attached to the Se atom decreases r, thereby increasing $\langle r^{-3}\rangle$ and the deshielding effect. The Se nuclei are more deshielded in d^8 Ni(II), Pd(II) and Pt(II) complexes compared with those of d^{10} Zn(II) and Cd(II) complexes as well as those of the Na(I) salt. This is consistent with the stabilized selenium–metal bonds for the former complexes, as pointed out previously [2]. In the Au(III) complex the deshielding effect is also considered to be important. The Se(1) signal of this complex occurs at an appreciably lower field than those of the above-described d^8-metal complexes and the chemical shift is rather close to that of the Se atom covalently bound with the benzoyl group in $C_3Se_5[C(O)Ph]_2$. This deshielding seems to result from the more oxidized state of the selenium donor atoms which is caused by the higher oxidation state of the Au(III) ion. The same tendency was observed for bis(diselenocarbamato)Ni(II)/-Ni(IV) and -Pt(II)/-Pt(IV) complexes [6] and (diselenolato)Ni(II)/-Ni(IV) complexes [9]. This tendency observed for the Se(1) nuclei depending on the metal ions is also roughly the same for Se(2) and Se(3), although the effects are rather small (see Table 1).

For the diselenocarbamato– and 1,1-diselenolato–metal complexes, the signals of the Se atoms bound directly with Na(I), Cd(II) and Zn(II) ions occur at higher fields than the corresponding signals of the Ni(II), Pd(II) and Pt(II) complexes [6, 9]. These findings are in great contrast to the present results. Since the ^{77}Se NMR data for selenium–donor metal complexes are limited, it is difficult to explain this inverse tendency. Any neighboring effect on the Se nuclei may be important for these 1,1-disubstituted selenium-donor complexes.

Figure 1 shows the ^{77}Se NMR spectra of $C_3Se_5[C(O)Ph]_2$ in chloroform-d_1 and $[NBu^n_4]_2[Pt(C_3Se_5)_2]$ in dimethyl sulfoxide-d_6. The signals of the former compound are accompanied by satellites due to the ^{77}Se–^{77}Se spin–spin couplings. Both the Se(1) and Se(2) signals exhibit the Se–Se coupling satellites with the splitting of 20 Hz. For this splitting there are two possibilities of the $^3J[^{77}Se(1)–^{77}Se(2)]$ transannular and $^2J[^{77}Se(1)–^{77}Se(2)]$ geminal couplings. The coupling schemes for this compound can be reasonably compared with those of tetraselenafulvalene derivatives, where the $^3J(^{77}Se–^{77}Se)$ transannular couplings (19–23 Hz) are clearly smaller than the $^2J(^{77}Se–^{77}Se)$ endocyclic (geminal) couplings (68–75 Hz) [18]. Thus, in the present compound the Se(1)–Se(2) coupling is ascribed to the $^2J[^{77}Se(1)–^{77}Se(2)]$ geminal coupling. Furthermore, both

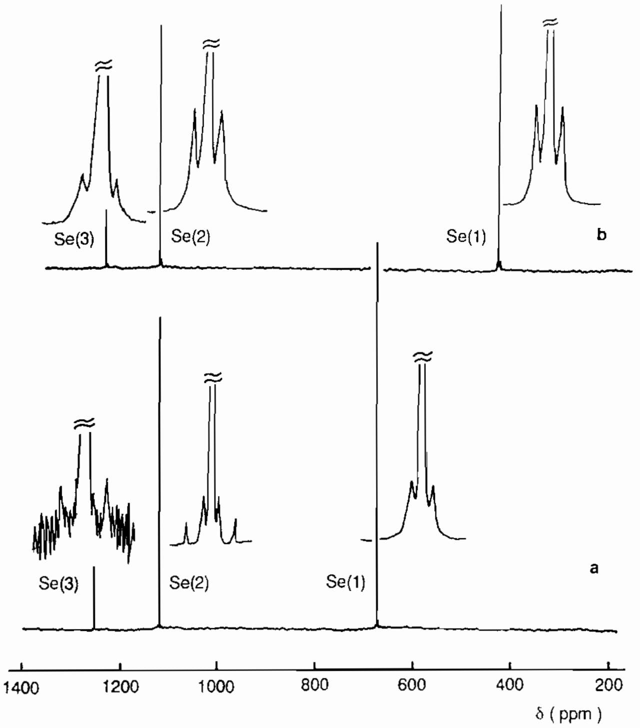


Fig. 1. ^{77}Se NMR spectra of $C_3Se_5[C(O)Ph]_2$ in chloroform-d_1 (a) and $[NBu^n_4]_2[Pt(C_3Se_5)_2]$ in dimethyl sulfoxide-d_6 at 30 °C (b); external reference, dimethyl selenide in chloroform-d_1.

the Se(2) and Se(3) signals have the satellites due to the ${}^{2}J[{}^{77}\mathrm{Se}(2)\text{–}{}^{77}\mathrm{Se}(3)]$ coupling (100 Hz). This magnitude is close to that of the corresponding coupling in the $[\mathrm{Zn}(C_3Se_5)_2]^{2-}$ (96 Hz) [13] and $[\mathrm{Pt}(C_3Se_5)_2]^{2-}$ complexes (95 Hz) described below. The somewhat large Se(2)–Se(3) coupling constant compared with the Se(1)–Se(2) one reflects the electron delocalization in the CSe_3 moiety of the $C_3Se_5{}^{2-}$ ligand, as pointed out for the molecular structure of $[\mathrm{PPh_4}]_2[\mathrm{Zn}(C_3Se_5)_2]$ [13].

The signals of the $[\mathrm{Pt}(C_3Se_5)_2]^{2-}$ complex show satellites due to the ${}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}$ coupling. The ${}^{77}\mathrm{Se}\text{–}{}^{77}\mathrm{Se}$ and ${}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}$ coupling constants are summarized in Table 2. The ${}^{1}J({}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se})$ direct couplings in square-planar Pt(II) complexes are sensitive to the ligand atom *trans* to the Se atom. The present complex has a rather small coupling constant compared with those of (diselenocarbamato)Pt(II) complexes (112–291 Hz) [6], dihalogeno(diselenoether)Pt(II) complexes (170–600 Hz) [7, 19] and bis(tributylphosphine)(C_3Se_5)Pt(II) (330 Hz) [20]. The ${}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}(2)$ coupling is somewhat larger than the ${}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}(1)$ coupling. This is unusual, in contrast to the rather smaller ${}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}(2)$ coupling (93 Hz) compared with the ${}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}(1)$ coupling of bis(tributylphosphine)(C_3Se_5)Pt(II) [20]. Satellites observed for the Se(3) signal are due to the ${}^{77}\mathrm{Se}(2)\text{–}{}^{77}\mathrm{Se}(3)$ coupling. The ${}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}(3)$ coupling seems to be too small to be noticed at satellites of the Se(3) signal.

TABLE 2. ${}^{77}\mathrm{Se}\text{–}{}^{77}\mathrm{Se}$ and ${}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}$ coupling constants (Hz) for the C_3Se_5–metal complexes

Compound	${}^{2}J[{}^{77}\mathrm{Se}(1)\text{–}{}^{77}\mathrm{Se}(2)]$	${}^{2}J[{}^{77}\mathrm{Se}(2)\text{–}{}^{77}\mathrm{Se}(3)]$
$C_3Se_5[C(O)Ph]_2$	20	100
$[\mathrm{PPh_4}]_2[\mathrm{Zn}(C_3Se_5)_2]$[a]	[b]	96
$[\mathrm{NBu^n{}_4}]_2[\mathrm{Pt}(C_3Se_5)_2]$	[b]	95
	${}^{1}J[{}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}(1)]$	${}^{3}J[{}^{195}\mathrm{Pt}\text{–}{}^{77}\mathrm{Se}(2)]$
	68 (67)[c]	75 (74)[c]

[a] Ref. 13. [b] <12 Hz. Not resolved. [c] Ref. 11.

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