state of germanium by the ring is analogous to the results obtained with lead.[7] Germanium(II) is apparently stabilized by the ring system and oxidation to germanium(IV) only occurs after the ring system is destroyed. A further example of this stabilization may be noted in the reaction between phenylgermane and metal-free phthalocyanine. This remarkably facile reaction removes two hydrogens from the metal-free phthalocyanine structure and three hydrogens and a phenyl group from the germanium in the process of coordinating the germanium with the phthalocyanine unit.

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Synthesis and Properties of Bis(*N*,*N*-dialkylthioselenocarbamato)nickel, -palladium, and -platinum: M[SSeCNR$_2$]$_2$ (M = Ni(II), Pd(II), Pt(II); R = CH$_3$, C$_2$H$_5$)

BY TOSHIO TANAKA* AND NOBUO SONODA

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One of the authors has recently reported the synthesis and infrared and pmr spectra of some *N*,*N*-dimethylthioselenocarbamato complexes of tin(IV), (CH$_3$)$_2$SnCl[SSeCN(CH$_3$)$_2$] and (CH$_3$)$_2$Sn[SSeCN(CH$_3$)$_2$]$_2$, in which the Sn–Se bond is more ionic than the Sn–S bond.[1] Finding this new anionic chelate ligand has prompted us to prepare transition metal complexes in order to learn their properties and especially to compare the abilities of sulfur and selenium atoms to coordinate to transition metals. This paper reports the preparation and spectroscopic studies of bis(*N*,*N*-dialkylthioselenocarbamato)nickel(II), -palladium(II), and -platinum(II).

Experimental Section

Preparation of Dimethylchloro(*N*,*N*-dialkylthioselenocarbamato)tin(IV).—Dimethylchloro(*N*,*N*-dimethylthioselenocarbamato)tin(IV), (CH$_3$)$_2$SnCl(dmtsc) (dmtsc = SSeCN(CH$_3$)$_2$), was prepared as described elsewhere.[1] The *N*,*N*-diethylthioselenocarbamato derivative, (CH$_3$)$_2$SnCl(detsc) (detsc = SSeCN(C$_2$H$_5$)$_2$), was similarly obtained by the reaction of dimethyltin selenide[2] with *N*,*N*-diethylthiocarbamoyl chloride[3] in benzene, giving colorless crystals, mp 86–88°.

Preparation of Bis(*N*,*N*-dialkylthioselenocarbamato)nickel(II), -palladium(II), and -platinum(II).—To an ethanol solution of NiCl$_2$·6H$_2$O (3.0 g, 12.6 mmol) was added a small excess of (CH$_3$)$_2$SnCl(detsc) (9.6 g, 25.3 mmol) in ethanol; this was followed by stirring for 30 min. A precipitate formed which was recrystallized from dichloromethane to give dark green crystals of Ni(detsc)$_2$ (5.1 g, 11 mmol), mp 239–240°. *Anal.* Calcd for C$_{10}$H$_{20}$N$_2$S$_2$Se$_2$Ni: C, 26.73; H, 4.50; N, 6.24; mol wt 449. Found: C, 27.00; H. 4.73; N, 6.38; mol wt 436 (by a Mechrolab vapor pressure osmometer).

The Pd(detsc)$_2$ complex was similarly prepared by the reaction of Na$_2$PdCl$_4$·3H$_2$O (0.50 g, 1.44 mmol) with (CH$_3$)$_2$SnCl(detsc) (1.10 g, 2.90 mmol) in ethanol. Recrystallization from dichloromethane gave orange-red crystals (0.48 g, 0.97 mmol), mp 259–260°. *Anal.* Calcd for C$_{10}$H$_{20}$N$_2$S$_2$Se$_2$Pd: C, 24.18; H, 4.07; N, 5.64; mol wt 497. Found: C, 23.67; H, 4.22; N, 5.48; mol wt 533 (by a Mechrolab vapor pressure osmometer).

To synthesize Pt(detsc)$_2$, an aqueous solution of K$_2$PtCl$_4$ (0.30 g, 0.72 mmol) was mixed with (CH$_3$)$_2$SnCl(detsc) (0.55 g, 1.45 mmol) in ethanol, followed by stirring for 3 hr. A precipitate appeared which was recrystallized from dichloromethane to yield orange crystals (0.18 g, 0.43 mmol), mp 264–265°. *Anal.* Calcd for C$_{10}$H$_{20}$N$_2$S$_2$Se$_2$Pt: C, 20.50; H, 3.45; N, 4.79; mol wt 585. Found: C, 20.62; H, 3.45; N, 4.74; mol wt 572 (by a Mechrolab vapor pressure osmometer).

The M(dmtsc)$_2$ complexes (M = Ni(II), Pd(II), and Pt(II)) were similarly prepared by the reaction of the nickel(II), palladium(II), or platinum(II) salts described above with (CH$_3$)$_2$SnCl(dmtsc) at the mole ratio of about 1:2. The precipitates obtained were collected, washed repeatedly with dichloromethane, and dried. *Anal.* Calcd for Ni(dmtsc)$_2$, yellowish green crystals, mp >210° dec, C$_6$H$_{12}$N$_2$S$_2$Se$_2$Ni: C, 18.34; H, 3.08; N, 7.13. Found: C, 18.55; H, 3.14; N, 7.18. Calcd for Pd(dmtsc)$_2$, orange yellow crystals, mp >250° dec, C$_6$H$_{12}$N$_2$S$_2$Se$_2$Pd: C, 16.35; H, 2.75; N, 6.36. Found: C, 16.31; H, 2.86; N, 6.12. Calcd for Pt(dmtsc)$_2$, yellow crystals, mp >265° dec, C$_6$H$_{12}$N$_2$S$_2$Se$_2$Pt: C, 13.61; H, 2.29; N, 5.29. Found: C, 13.67; H, 2.34; N, 5.17.

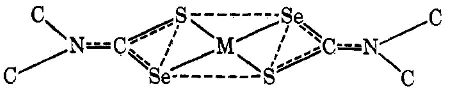
Physical Measurements.—Magnetic susceptibility was determined by the Gouy method. Infrared spectra were recorded on a Hitachi-Perkin 225 spectrophotometer, and electronic spectra were measured on a Hitachi 124 spectrophotometer with 1-cm cells at room temperature. Proton magnetic resonance spectra were measured on a Japan Electron Optics 3H-60 spectrometer at 60 MHz at ambient temperature probe (*ca.* 20°). The spectrometer was carefully calibrated by the audioside-band technique, and the chemial shifts were measured against tetramethylsilane as an internal standard.

Toxicity.—Many selenium compounds are highly toxic; they cause eczema and inflammation on contact with the skin.[4] Accordingly, the present complexes were synthesized in a well-ventilated draft chamber and the handling of the compounds was carried out by using a pair of rubber gloves throughout experiments.

Results and Discussion

The detsc complexes are soluble in polar organic solvents but less soluble in nonpolar solvents. On the other hand, the dmtsc complexes are only slightly soluble even in polar organic solvents and water. All the complexes are stable to air when in the solid state, and the detsc complexes are not particularly sensitive to oxygen or humidity when in solution.

Magnetic susceptibility measurement indicates that Ni(detsc)$_2$ is diamagnetic ($\chi_{\text{mol}} = -1.15 \times 10^{-6}$ cgs emu). The corresponding palladium(II) and platinum(II) complexes are also believed to be diamagnetic, since the pmr spectra are consistent with the diamagnetism of the both compounds, as described below. In the infrared spectra, these complexes exhibit a strong ν(C$\overset{\cdots}{-}$N) band above 1500 cm^{-1} (Table I), suggesting a partial double-bond character of the C–N bond. In view of these results, the bis(thioselenocarbamato)metal(II) complexes may be assumed to have almost planar structure



like bis(*N*,*N*-diethyldithiocarbamato)nickel(II), Ni-

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TABLE I

PROTON CHEMICAL SHIFTS[a] AND $\mathrm{C \stackrel{...}{-} N}$ STRETCHING FREQUENCIES[b] OF $\mathrm{M(dedtc)_2}$, $\mathrm{M(detsc)_2}$, AND $\mathrm{M(dedsc)_2}$ (M = Ni(II), Pd(II), Pt(II))

Complex	$\nu(\mathrm{C \stackrel{...}{-} N})$,[c] $\mathrm{cm^{-1}}$	$\tau(\mathrm{N{-}CH_2})$,[d] ppm Trans to Se	$\tau(\mathrm{N{-}CH_2})$,[d] ppm Trans to S	$\tau(\mathrm{C{-}CH_3})$,[d] ppm Trans to Se	$\tau(\mathrm{C{-}CH_3})$,[d] ppm Trans to S
$\mathrm{Ni(dedtc)_2}$	1507	. . .	6.40 q	. . .	8.77 t
$\mathrm{Ni(detsc)_2}$	1520	6.35 q	6.39 q	8.74 t	8.77 t
$\mathrm{Ni(dedsc)_2}$	1511	6.36 q	. . .	8.74 t	. . .
$\mathrm{Pd(dedtc)_2}$	1503	. . .	6.30 q	. . .	8.73 t
$\mathrm{Pd(detsc)_2}$	1515	6.23 q	6.28 q	8.68 t	8.71 t
$\mathrm{Pd(dedsc)_2}$	1506	6.24 q	. . .	8.68 t	. . .
$\mathrm{Pt(dedtc)_2}$	1513	. . .	6.45 q	. . .	8.72 t
$\mathrm{Pt(detsc)_2}$	1525	6.40 q	6.46 q	8.68 t	8.71 t
$\mathrm{Pt(dedsc)_2}$	1519	6.42 q	. . .	8.67 t	. . .

[a] Measured in *ca.* 3 wt % chloroform solution. [b] Measured in Nujol mulls. [c] $\mathrm{Ni[dmtsc]_2}$, 1540 $\mathrm{cm^{-1}}$; $\mathrm{Pd[dmtsc]_2}$, 1543 $\mathrm{cm^{-1}}$; $\mathrm{Pt[dmtsc]_2}$, 1550 $\mathrm{cm^{-1}}$. [d] Key: q, quartet; t, triplet.

$\mathrm{(dedtc)_2}$ (dedtc = $\mathrm{S_2CN(C_2H_5)_2}$),[5] and bis(*N*,*N*-diethyldiselenocarbamato)nickel(II), $\mathrm{Ni(dedsc)_2}$ (dedsc = $\mathrm{Se_2CN(C_2H_5)_2}$),[6] which were studied by X-ray crystallographic analyses, although it is not obvious in the present complexes whether the coordination positions of the sulfur and selenium atoms are cis or trans on the square plane around the central metal(II).

The planarity of the thioselenocarbamato ligand is also indicated by the pmr spectra; the $\mathrm{Ni(detsc)_2}$ complex in chloroform exhibits doublets of quartets and triplets for the $\mathrm{N{-}CH_2}$ and $\mathrm{C{-}CH_3}$ proton signals, as is shown in Figure 1. Similar spectra are observed for $\mathrm{Pd(detsc)_2}$ and $\mathrm{Pt(detsc)_2}$ (Table I). The slight splitting of these signals may be due to the existence of two kinds of $\mathrm{N{-}C_2H_5}$ protons located in magnetically different environments; the one is trans with respect to the sulfur atom in a given planar thioselenocarbamate and the other is trans with respect to the selenium atom on the same ligand. These signals can be assigned by comparison of the pmr spectra of the detsc complexes with those of $\mathrm{M(dedtc)_2}$[7] and $\mathrm{M(dedsc)_2}$[8,9] (M = Ni(II), Pd(II), and Pt(II)). As is listed in Table I, the $\mathrm{N{-}CH_2}$ and $\mathrm{C{-}CH_3}$ proton signals of the dedtc complexes occur at slightly higher magnetic fields than do those of the dedsc complexes, and their chemical shifts are all close to those observed in the detsc complexes. A similar splitting of N-alkyl proton signals was previously reported in the pmr spectrum of $\mathrm{(CH_3)_2SnCl(dmtsc)}$, in which the lower field signal in dichloromethane has been assigned as the $\mathrm{N{-}CH_3}$ protons trans to the selenium atom on the basis of benzene-induced solvent shifts of the $\mathrm{N{-}CH_3}$ proton signals.[1] Further, it may be noted that the $\mathrm{N{-}CH_3}$ proton signal of dimethylchloro(*N*,*N*-dimethyldithiocarbamato)tin(IV), $\mathrm{(CH_3)_2SnCl(dmdtc)}$ (dmdtc = $\mathrm{S_2CN(CH_3)_2}$),[10] occurs at rather higher magnetic field than that of the corresponding diselenocarbamato complex, $\mathrm{(CH_3)_2SnCl(dmdsc)}$ (dmdsc = $\mathrm{Se_2CN(CH_3)_2}$),[11] although the difference in chemical shifts is very small, as is shown in Table II. In view of the analogy between the proton chemical shifts of these tin(IV) complexes and those of the nickel(II), palladium(II), and platinum(II) complexes, the quartet and the triplet at the lower magnetic field of the detsc complexes may tentatively be assigned to the $\mathrm{N{-}CH_2}$ and $\mathrm{C{-}CH_3}$ protons trans to the selenium atom in a given ligand, while those in the higher field may be assigned to the $\mathrm{N{-}CH_2}$ and $\mathrm{C{-}CH_3}$ protons trans to the sulfur.

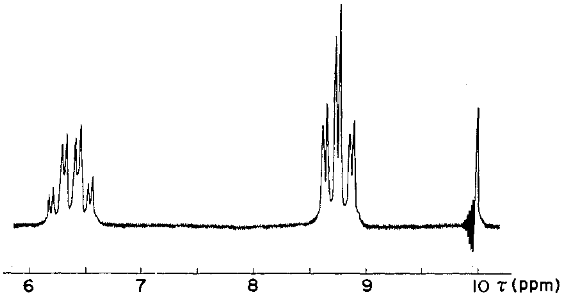

Figure 1.—The pmr spectrum of $\mathrm{Ni[SSeCN(C_2H_5)_2]_2}$ in chloroform.

TABLE II

THE $\mathrm{N{-}CH_3}$ PROTON CHEMICAL SHIFTS (τ) OF $\mathrm{(CH_3)_2SnCl(dmdtc)}$, $\mathrm{(CH_3)_2SnCl(dmtsc)}$, AND $\mathrm{(CH_3)_2SnCl(dmdsc)}$ IN CHLOROFORM (PPM)

Complex[a]	Trans to Se	Trans to S
$\mathrm{(CH_3)_2SnCl(dmdtc)}$	. . .	6.59[b]
$\mathrm{(CH_3)_2SnCl(dmtsc)}$	6.57	6.63
$\mathrm{(CH_3)_2SnCl(dmdsc)}$	6.58	. . .

[a] The pmr spectra of these complexes in chloroform or dichloromethane have already been reported,[1,10,11] but in order to compare the $\mathrm{N{-}CH_3}$ proton chemical shifts precisely the redetermination has been carried out in the same solvent. [b] Previously reported value in chloroform is 6.65 ppm.[10]

The electronic absorption spectra of $\mathrm{M(detsc)_2}$ (M = Ni(II), Pd(II), and Pt(II)) complexes and band maxima are shown in Figure 2 and Table III, respectively.

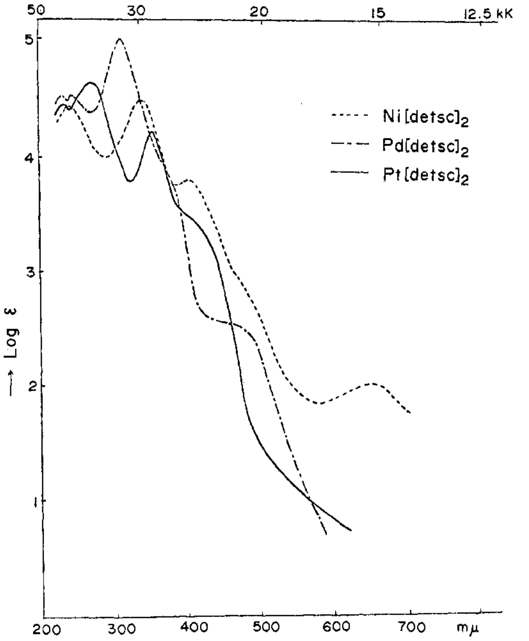

Figure 2.—Electronic spectra of $\mathrm{M[SSeCN(C_2H_5)_2]_2}$ (M = Ni(II), Pd(II), and Pt(II)) in dichloromethane.

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TABLE III

ELECTRONIC SPECTRA OF M(detsc)$_2$ (M = Ni(II), Pd(II), Pt(II)) IN DICHLOROMETHANE[a]

Complex	d–d band	CT band	Ligand band
Ni(detsc)$_2$	15.4 (1.99)	24.8 (3.78)	29.4 (4.43), 40.8 (4.42)
Pd(detsc)$_2$	21.3 (2.52)	27.0 (3.93)	31.9 (4.99), 40.0 (4.44), 42.9 (4.47)
Pt(detsc)$_2$	24.4 (3.40)	27.6 (4.16)	36.6 (4.60), 43.1 (4.39)

[a] Band maxima in kK; log ϵ values given in parentheses.

It is noted that the spectra of Ni(detsc)$_2$ and Pd(detsc)$_2$ resemble those[9] of the corresponding dedsc complexes, but the position of each band maximum of the detsc complexes somewhat shifts to the blue region compared with the maxima of the dedsc complexes.

The lowest frequency bands (ν_1) may be due to a spin-allowed d-d transition, in view of their ϵ values. Since M(detsc)$_2$ are formulated as square-planar d^8 complexes, the ν_1 band is assigned to a singlet–singlet transition from d_{xy} to $d_{x^2-y^2}$. The ν_1 of Ni(detsc)$_2$ occurs at 15.4 kK, which is higher in frequency than that of Ni(dedsc)$_2$ (14.8 kK[9]), while lower than that of Ni(dedtc)$_2$ (15.8 kK[9]). A similar trend is observed in the palladium complexes: 20.6,[9] 21.3, and 22.6[9] kK for the dedsc, detsc, and dedtc complexes, respectively. The ligand field strength of detsc is therefore intermediate between dedsc and dedtc.

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Electron Paramagnetic Resonance Spectrum of Binuclear Copper *n*-Butyrate Monohydrate[1a]

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Since the definitive work of Bleaney and Bowers on the anomalous magnetic properties of copper acetate monohydrate,[2] numerous dimeric copper compounds have been synthesized and largely characterized by magnetic susceptibility and optical spectroscopy.[3] Measurements of zero-field splitting parameters by electron paramagnetic resonance (epr) spectroscopy[4] have often been hampered by inability to grow suitable single crystals. Recently, the epr spectra of randomly oriented triplet-state molecules in powdered samples of copper alkanoates[5–7] and frozen solutions of copper and vanadyl dimers have been successfully analyzed.[8,9]

From a single-crystal study at 24 GHz, the epr parameters of copper butyrate monohydrate, $Cu_2(C_4H_7O_2)_4 \cdot 2H_2O$, have been reported to be $D = 0.35$ cm^{-1}, $g_z = 2.40$, and $g_\perp = 2.04$–2.10.[10] The perpendicular parameters were not well characterized; apparently the spectrum is complicated by the presence of seven independent magnetic units in the crystal having nearly identical parameters. We report here significantly different parameters (an average of the seven units) from a spectral analysis of powdered copper butyrate monohydrate at 77°K. Our values are $|D| = 0.333 \pm 0.005$ cm^{-1}, $|E| = 0.011 \pm 0.003$ cm^{-1}, $g_z = 2.342 \pm 0.005$, and $g_\perp\,[= (g_x + g_y)/2] = 2.063 \pm 0.008$.[11] This study provides conclusive evidence for a rhombic component in the crystalline field.

Results and Discussion

Spectra were collected by standard procedures on a Varian V-4502 spectrometer operating at X band. The marked temperature dependence of the spectrum is shown in Figure 1. From the reported singlet–triplet separation ($-J$) of 339 cm^{-1} [12] we estimate that 37% of the dimers are in the paramagnetic triplet state at 298°K compared to 0.5% at 77°K. The sharp lines around 3300 G are due to a monomer impurity of about 0.01%; monomer lines have been observed for several other binuclear systems. The splitting around 4500 G (H_{x2} and H_{y2}) arises from a rhombic distortion in the crystalline field of the Cu^{2+} ion.

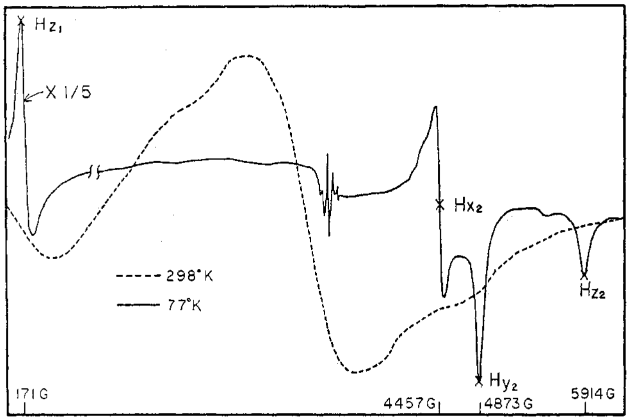

Figure 1.—First-derivative X-band epr spectrum of powdered copper butyrate monohydrate at 298 and 77°K. Both spectra have comparable signal levels. × 1/5 denotes a signal level one-fifth as large as that used in the rest of the spectrum. Principal resonance fields are indicated by ×. H_0 = 3342.2 G.

These spectra are governed by the usual $S = 1$ spin Hamiltonian[2]

$$\mathcal{H} = \beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + D(S_z^2 - {}^2/_3) + E(S_x^2 - S_y^2) \qquad (1)$$

where D and E are the zero-field splitting parameters. Here we have omitted the metal hyperfine terms since they only serve to broaden the principal resonance features. Assuming that the principal axes of the D and g tensors coincide, a full-matrix calculation of the energy levels[13] gives six principal resonance fields ($\Delta M_s = \pm 1$)

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(1) (a) Supported in part by the National Science Foundation under Grant GP-11387. (b) National Institutes of Health Postdoctoral Fellow, 1969–1970. Present address: Department of Chemistry, Lawrence University, Appleton, Wis. 54911.

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