figurations and ascribe variations in isomer shift to bonding changes in the t_{2g} orbitals and variations in d^2sp^3 hybrid populations owing to σ bonding. This procedure is consistent with experience in low-spin Fe(II) complexes.[13]

Changes in the iridium–ligand wave function will mainly depend on the surrounding neighbor ligands. When π acceptors are present, back-donation from the metal to the ligand may occur. Likewise, when σ donors are present, a ligand donation to the metal is a possibility. In both cases the effect is to increase the net s-electron density at the iridium nucleus: in the former process because of shielding and in the latter by direct s donation into d^2sp^3 type orbitals. Perhaps the best example of such a situation involves metal cyanide ligands.[14] The $K_3[Ir^{III}Cl_6]$ complex fits in nicely with the trends of Wagner, *et al.*,[10,11] but these authors note that $K_3[Ir^{III}(CN)_6]$ shows rather different behavior, owing to the π-acceptor nature of the cyanides. For $K_3[IrCl_6]$ the shift is -0.17 cm/sec and for $K_3[Ir(CN)_6]$ it is $+0.082$ cm/sec. The difference is 0.25 cm/sec and for two such acceptor adducts an approximate shift of $+0.08$ cm/sec is implied.

There are no cyano adducts among the compounds reported here, but it is empirically observed that the H^- ligand acts as a σ donor and produces shifts in $3d^6$ low-spin Fe(II) compounds that are at least as large as those due to CN^-.[13] This implies an approximate range of 0.1 cm/sec for the effects of ligand donor or acceptor properties in Vaska adducts. The data in Figure 1 are in agreement with this estimate. The loss of an electron density on going from Cl-VA–H_2 to Cl-VA–Cl_2 therefore becomes explicable in terms of the fact that the H^- ligand represents a much stronger σ donor than Cl^-. The intermediate adducts are also consistent with their relative powers as σ donors.[13,15]

The implication of σ donation for variations in the carbonyl stretch frequencies is less direct. The data show a decrease in ν_{CO} as the s-electron density increases. This suggests that increased shielding of t_{2g} electrons by s electrons can allow an expansion of the former into carbonyl π^* orbitals. This would result in decreased stretching frequencies.

The complication of σ and π effects is further illustrated by the Cl-VA–O_2 compound. Here a relatively small isomer shift is observed, though a substantial decrease in ν_{CO} occurs (both shifts relative to Cl-Vask–Cl_2). Finally we note that the two planar systems Cl-VA and Br-VA, formally $t_{2g}^6e_g^2$ configurations, do not show substantially decreased s-electron densities relative to Cl-VA–Cl_2. It seems likely that the presence of the 5d electrons in axial orbitals produces a relatively weak screening of the bonding s-type electrons which reside primarily in planar orbitals.

Acknowledgment.—It is a pleasure to acknowledge useful conversations with A. P. Ginsberg, R. L. Martin, and G. K. Wertheim.

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The Synthesis of Phthalocyaninogermanium(II)[1]

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Previous work with phthalocyaninogermanium complexes has included germanium(IV) compounds,[2-5] but the germanium(II) compound has not been described in the literature. Both phthalocyaninotin(IV) and phthalocyaninotin(II) compounds have been known for some time, and phthalocyaninolead(II) is the only lead phthalocyanine known.[6,7] This report concerns the synthesis and characterization of phthalocyaninogermanium(II).

An analytical method developed by Elvidge[8] was used to confirm the oxidation state of germanium. In this method a metal phthalocyanine consumes 2 equiv of oxidizing agent/mol if the central metal is not also oxidized. Additional oxidizing agent is needed if the central metal is in a low oxidation state and can be oxidized to a higher state.

Experimental Section

Reduction of Dichloro(phthalocyanino)germanium(IV)(PcGe-Cl₂)[9] with Sodium Borohydride.—A mixture of 0.80 g of PcGeCl₂ (0.0012 mol) and 0.14 g of sodium borohydride (0.0037 mol) was stirred at reflux (164–166°) in a mixture of 20 ml of benzyl alcohol and 10 ml of anisole for 1 hr. The mixture was filtered hot (medium-fritted glass Büchner), and the filtrate was allowed to stand for 2 days at room temperature. The cooled filtrate was again filtered (medium-fritted glass Büchner), and the solid residue was successively washed with water, dilute hydrochloric acid, water, and acetone. The oven-dried (110°) product weighed 0.55 g for a 78% yield of PcGe based on PcGeCl₂.

Purification was effected by heating a 490-mg sample in a vacuum sublimator at 450° for 30 min, under a pressure of 1–2 μ. The collecting finger of the sublimator was maintained at 357° by boiling mercury. A yield of 164 mg of β-PcGe crystals was obtained. The crystals were blue-green by transmitted light and had a reddish reflex. *Anal.* Calcd for $C_{32}H_{16}N_8Ge$: C, 65.69; H, 2.76; Ge, 12.41. Found: C, 65.86; H, 2.91; Ge, 12.63.[10]

Reduction of PcGeCl₂ with Sodium Borodeuteride.—Reaction of PcGeCl₂ with NaBD₄ in dry quinoline followed by sublimation gave a compound with an infrared spectrum identical with that of β-PcGe.

Reduction of PcGeCl₂ with Anhydrous Stannous Chloride.—A mixture of 3.0 g of PcGeCl₂ (0.0046 mol) and 3.0 g of SnCl₂ (0.016 mol) in 100 ml of dry quinoline was refluxed under nitrogen for 4 hr. The resulting mixture was allowed to cool and then filtered (medium-fritted glass Büchner) and washed with benzene, methanol, and ether. After air-drying, the product weighed 0.93 g. A second batch of product weighing 0.40 g for

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(9) Pc = $C_{32}H_{16}N_8$, the phthalocyanino ligand.

(10) Galbraith Laboratories, Inc., Knoxville, Tenn.

an overall yield of 50% was obtained by evaporation of half of the quinoline followed by filtration of the cooled mixture. The product was identified as β-PcGe by the infrared spectrum. (This preparation is similar to that reported for PcSn.[6,7])

Reaction of PcGeCl₂ with Phenylgermane.—A mixture of 1.0 ml of phenylgermane (0.0079 mol) and 0.45 g of PcGeCl₂ (0.00070 mol) was stirred for 2.5 hr at reflux in 50 ml of quinoline. The reaction mixture was cooled to 160° and filtered (medium-fritted glass Büchner). A few purple crystals were collected on the filter. These crystals were identified as β-phthalocyaninogermanium(II) by infrared spectrum (identical with those of the analyzed crystals reported in the earlier section). The dark olive green filtrate from this reaction was allowed to stand at room temperature for 2 days and was again filtered. A yield of 0.32 g (78% based on PcGeCl₂) of blue-green crystals was obtained. The product was identified by infrared as α-phthalocyaninogermanium(II), slightly contaminated with metal-free phthalocyanine.

Reaction of Phenylgermane with Metal-Free Phthalocyanine. —A mixture of 2.0 ml of phenylgermane (0.016 mol) and 1.4 g of metal-free phthalocyanine (0.0028 mol) was stirred for 3 hr at reflux in 50 ml of quinoline. The reaction mixture was cooled to 150° and filtered (medium-fritted glass Büchner). A yield of 0.42 g of purple crystals was identified by infrared spectrum as β-phthalocyaninogermanium(II). The dark olive green filtrate was allowed to stand at room temperature for 1 day and was again filtered. A yield of 0.62 g of blue-green crystals was obtained for an overall yield of 63% based on PcH₂. The product was identified by infrared spectrum as α-phthalocyaninogermanium(II), slightly contaminated with metal-free phthalocyanine.

Determination of Oxidation State of Germanium.—The method according to Elvidge[8] was followed except that *o*-phenanthroline was used as the indicator rather than barium diphenylaminesulfonate. The PcGe oxidation used 3.1 equiv/mol (theoretical value 4.0).

Results

Spectral Studies.—The ultraviolet–visible spectrum of PcGe is interesting in that the most intense absorption band occurs in the visible region at 4450 Å with an intense shoulder at 4150 Å (see Table I). The intense absorption band at 6550 Å (in pyridine) with a shoulder at 6020 Å is the typical absorption band that gives the intense blue color to all phthalocyanines.[11] The additional intense bands at 4450 and 4150 Å give a green cast to the solutions of PcGe.

TABLE I

VISIBLE AND ULTRAVIOLET ABSORPTIONS
[λ_{max}, Å (LOG ϵ)] OF PHTHALOCYANINOGERMANIUM(II)

Chloroform solvent	Pyridine solvent
	6550 (4.83)
6600	
	6020 (4.21)
6050	
	4450 (5.07)
4450	
	4150 (5.63)
4150	
	3300 (~4.1)
3260	
2930 (~4.2)	

Chemical Studies.—Phthalocyaninogermanium(II) is a very different chemical species from phthalocyaninotin(II). Kroenke and Kenney[7] oxidized PcSn with bromine and iodine to obtain the dibromo- and the diiodo(phthalocyanino)tin(IV) compounds. The PcGe did not give the germanium(IV) compounds in a similar reaction, even with a large excess of bromine or iodine. Except for some decomposition of the complex, the PcGe was recovered unchanged from a naphthalene

(11) A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, **7**, 67 (1965).

solution of bromine or iodine. Thirty per cent hydrogen peroxide also did not oxide the PcGe to a Ge(IV) compound.

Kroenke and Kenney[7] also found that PcSn does not exhibit the typical phthalocyanine polymorphism. The PcGe does exhibit this polymorphism, with the β modification giving the additional infrared absorption bands at 860 and 887 cm^{-1} (see Table II). The β modification was obtained in vacuum sublimation when the collecting finger was maintained at 367.9° with boiling mercury, but the α modification was obtained when the sublimate was collected by air cooling.

TABLE II
PROMINENT INFRARED BANDS FOR PcGe (CM^{-1})

Common to Both α and β Forms

430	565	700	1065	1295
508	585	745	1095	1338
522	630	800	1110	1416
555	670	930	1170	1615

Present Only in the β Form
860   887

Phthalocyaninogermanium(II) is also a very light-sensitive compound. A pyridine solution (*ca.* 10 mg/l.) of PcGe, purged and stored under nitrogen, decomposed in 5 hr when placed next to a fluorescent light. Decomposition did not occur after 1 week in two other pyridine solutions, one purged and stored under nitrogen in the dark and one purged and stored under oxygen in the dark.

The preparation of PcGe by the reduction of PcGeCl₂ with sodium borohydride required very careful attention. A large excess of sodium borohydride led to complete decomposition of the ring system. Similar reactions between metal-free phthalocyanine and sodium borohydride produce little or no decomposition.

Discussion

The elemental analysis cannot differentiate between the possible compounds PcGe and PcGeH₂. However, the preparation from tin(II) chloride, the preparation from sodium borodeuteride, the oxidation by dichromate, and infrared absorption data did provide this differentiation.

Oxidation of PcGe should theoretically take 4 equiv of oxidizing agent/mol.[8] The compound PcGeH₂ should take 6 equiv/mol. Elvidge's data[8] reveal that PcSnCl₂ took 2 equiv/mol and PcSn took 3.4 equiv/ mol. It is interesting that our results with germanium are very similar to those obtained with tin. PcGeCl₂ gives excellent agreement with the PcSnCl₂ data, *i.e.*, 2 equiv/mol, and for PcGe data are similar to the PcSn data, *i.e.*, 3.4 equiv/mol for PcSn and 3.1 equiv/mol for PcGe. The fact that the compound (same infrared spectrum) was prepared from anhydrous stannous chloride and from sodium borohydride also indicates PcGe rather tha PcGeH₂. Additional evidence that the compound is PcGe rather than PcGeH₂ is inferred from the infrared spectrum. One could reasonably expect to find an absorption band (Ge–H stretch) near 2114 cm^{-1} for PcGeH₂. There is no absorption band in this region for either α- or β-PcGe. These data therefore support the conclusion that the compound is phthalocyaninogermanium(II).

It is interesting that the stabilization of the 2+

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.

Acknowledgment.—The authors are indebted to Dr. Malcolm E. Kenney for helpful discussions and to Mr. Gary E. Donica for repeating some of our experiments.

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Synthesis and Properties of Bis(*N*,*N*-dialkylthioselenocarbamato)nickel, -palladium, and -platinum: M[SSeCNR₂]₂ (M = Ni(II), Pd(II), Pt(II); R = CH₃, C₂H₅)

By Toshio Tanaka* and Nobuo Sonoda

One of the authors has recently reported the synthesis and infrared and pmr spectra of some N,N-dimethyl-thioselenocarbamato 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-di-alkylthioselenocarbamato)nickel(II), -palladium(II), and -platinum(II).

Experimental Section

Preparation of Dimethylchloro(*N*,*N*-dialkylthioselenocarba-mato)tin(IV).—Dimethylchloro (N, N-dimethylthioselenocarba-mato)tin(IV), $(CH_3)_2$SnCl(dmtsc) (dmtsc = $SSeCN(CH_3)_2$), was prepared as described elsewhere.[1] The N,N-diethylthio-selenocarbamato derivative, $(CH_3)_2$SnCl(detsc) (detsc = SSeCN-$(C_2H_5)_2$), 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 NiCl₂·6H₂O (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 C₁₀H₂₀N₂S₂Se₂Ni: C, 26.73; H, 4.50; N, 6.24; mol wt 449,

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Found: C, 27.00; H, 4.73; N, 6.38; mol wt 436 (by a Mechro-lab vapor pressure osmometer).

The Pd(detsc)₂ complex was similarly prepared by the reaction of Na₂PdCl₄·3H₂O (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 C₁₀H₂₀N₂S₂Se₂Pd: 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 K₂PtCl₄ (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 C₁₀H₂₀N₂S₂Se₂Pt: 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, C₆H₁₂N₂S₂Se₂Ni: 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, C₆H₁₂N₂S₂-Se₂Pd: 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, C₆H₁₂N₂S₂Se₂Pt: 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 audio-side-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 ($\chi_{mol} = -1.15 \times 10^{-6}$ 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 $\nu(C \doteq N)$ 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
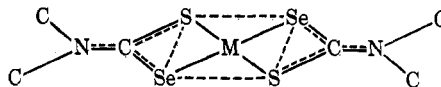
like bis(*N*,*N*-diethyldithiocarbamato)nickel(II), Ni-

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