Monomeric, Coloured Germanium(II) and Tin(II) Di-t-Butylamides, and the Crystal and Molecular Structure of $\mathrm{Ge(\overline{NCMe_2[CH_2]_3C}Me_2)_2}$

By MICHAEL F. LAPPERT* and MARTIN J. SLADE
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

and JERRY L. ATWOOD* and MICHAEL J. ZAWOROTKO
(*Department of Chemistry, The University of Alabama, University, Alabama* 35486)

Summary The orange (Ge^{II}) or maroon (Sn^{II}) bivalent group 4 metal di-t-butylamides were obtained from $LiNBu^t_2$ and $GeCl_2$·dioxan or $SnCl_2$ in tetrahydrofuran, and are low melting diamagnetic, volatile, monomeric (cryoscopy in C_6H_{12}), labile compounds (readily yielding $\cdot NBu^t_2$); *X*-ray analysis of the title compound to $R = 0{\cdot}091$ shows that this related Ge^{II} amide is a monomer in the crystal with a long Ge–N bond of $1{\cdot}88_5$ Å and an NGeN angle of 111·4(5)°.

WE report (a) the first well defined metal di-t-butylamides, $M(NBu^t_2)_2$ (M = Ge or Sn),[1] (b) their characterisation (see Table) as coloured, volatile, monomeric (in C_6H_{12}), diamagnetic, thermally and photochemically labile compounds, and (c) the *X*-ray and molecular structure of a closely related amide bis(2,2,6,6-tetramethylpiperidinato)germanium[2] (see Figure), the first group 4 metal(II) compound established to be a discrete two-co-ordinate monomer in the crystal at ambient temperature.[3]

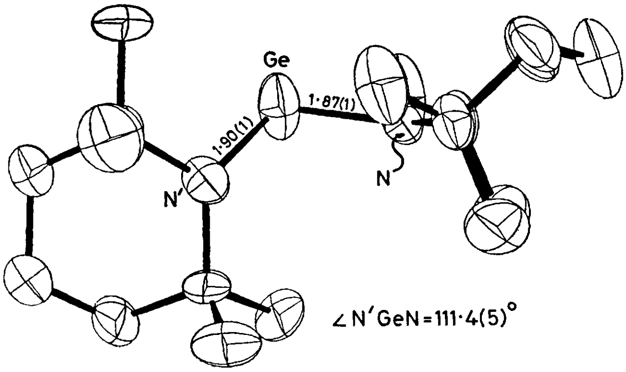

FIGURE. Molecular structure of $\mathrm{Ge(\overline{NCMe[CH_2]_3C}Me_2)_2}$, showing important bond lengths and the NGeN angle.

Di-t-butylamine has only recently become readily accessible, from 2-methyl-2-nitropropane.[4] It is a highly hindered base (*e.g.*, it cannot be acetylated[4] although it may be formylated[5]) and thus may become of interest in synthesis, either as the free amine or a metal derivative, being an efficient proton acceptor but otherwise a poor nucleophile. *In situ* preparations of $LiNBu^t_2$ (from $HNBu^t_2$ and LiPh in OEt_2) or $NaNBu^t_2$ (from $HNBu^t_2$ and NaH in OEt_2) have been mentioned, but neither reagent was reactive towards methyl iodide.[5] It is interesting therefore that the Ge^{II} and Sn^{II} amides are now obtained in good yield from the reaction in diethyl ether of $LiNBu^t_2$ with $GeCl_2$·dioxan and $SnCl_2$, respectively. The compound $Sn(NBu^t_2)_2$ decomposed readily either thermally or in light affording tin and $\cdot NBu^t_2$. The latter was detected by e.s.r. spectroscopy, g_{av} 2·0046, $a(^{14}N) = 1{\cdot}50$ mT and was also conveniently generated by photolysis of $Ge(NBu^t_2)_2$ in n-C_6H_{14} at 25 °C in the cavity of an e.s.r. spectrometer. The amides are thermally less stable than the analogous $\mathrm{M(\overline{NCMe_2[CH_2]_3C}Me_2)_2}$.[2]

The electronic properties (first ionisation potentials and electronic spectra) of the di-t-butylamides are closely similar to those of $\mathrm{M(\overline{NCMe_2[CH_2]_3C}Me_2)_2}$, rather than $M[N(SiMe_3)(CMe_3)]_2$ or $M[N(SiMe_3)_2]_2$ (see Table).[2] In particular we note the much lower first i.p. of the amides bearing only β-carbon substituents and this may be related to the degree of s-character of the metal-centred lone pair. A direct structural comparison is not yet possible; however the NGeN angle in $\mathrm{Ge(\overline{NCMe_2[CH_2]_3C}Me_2)_2}$ (see Figure) is 111·4(5)°, whereas the NSnN angle in (gaseous) $Sn[N(SiMe_3)_2]_2$ is 96·0°.[2] The difference may largely be steric in origin although $SiN(d \leftarrow p)\pi$-bonding may also be a contributing cause for the higher first i.p.s of the silylamides.

The crystal structure of the title compound was solved from 1659 independent observed reflections and refined to $R = 0{\cdot}091$; *crystal data*: $C_{18}H_{36}GeN_2$, triclinic, space group $P\bar{1}$, $M = 353{\cdot}1$, $a = 7{\cdot}559(5)$, $b = 10{\cdot}716(7)$, $c = 13{\cdot}001(9)$ Å, $\alpha = 77{\cdot}03(5)$, $\beta = 71{\cdot}75(5)$, $\gamma = 80{\cdot}08(5)$°, $U = 968{\cdot}6$ Å^3, $D_c = 1{\cdot}21$ g cm^{-3}, $Z = 2$, and $\mu(\text{Mo-}K_\alpha) = 16{\cdot}7$ cm^{-1}. A view of the molecule, with significant parameters, is shown in the Figure. The most interesting feature is the NGeN angle of 111·4(5)° which is significantly

TABLE. Metal di-t-butylamides, $M(NBu_2)_2$.

M	Yield (%)	Appearance	M.p. (t/°C)	M[a]	λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})[b]	1st i.p. /eV[c]	ν_{as} (MN_2)/ cm^{-1}[d]	^1H N.m.r. τ[e]	^{13}C N.m.r. (shift in p.p.m. rel. to $SiMe_4$)[e,f]
Ge	60	Orange oil	−2 to 0	377 (329)	445 (420)	6·78	412	8·28	36·31, 58·87
Sn	63	Maroon solid	44—47	413 (375)		6·74	405	8·26	36·58, 58·79

[a] Cryoscopically in cyclohexane, with calc. values for monomer in parentheses. [b] In C_6H_{12}; the Ge compound also has a band at 227 nm (ε 7000) and a shoulder at 310 nm; the Sn compound decomposed too readily for satisfactory spectrum to be recorded (an asymmetric band at 225 nm with ε 56,000 extended into the visible region). [c] Obtained by Dr. R. J. Suffolk by He(I) spectroscopy. [d] Nujol mull. [e] In C_6D_6. [f] The lower figure is due to CH_3.

greater than the OGeO angle in $Ge(OAr)_2$ [92·0(4)°];[5] we attribute this to more serious steric inter-ligand repulsion in the amide. There appear to be only two previous structural studies of germanium amides: in $N(GeH_3)_3$ the Ge–N bond length is 1·836 Å[6] and in $(Cl_2GeNMe)_3$ it is *ca.* 1·79 Å.[7] The Ge–N distance now found in the Ge^{II} amide (1·885 Å) is thus unexpectedly long, as the Ge^{2+} radius will certainly be significantly greater than that of Ge^{4+}, again consistent with a substantial steric effect.†

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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