

Synthesis and Characterization of the Isoelectronic d^{10} Species $[\text{Cu}\{\text{N}(\text{SiMePh}_2)_2\}_2]^-$ and $\text{Zn}\{\text{N}(\text{SiMePh}_2)_2\}_2$

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The compounds $[\text{Li}(\text{THF})_4][\text{Cu}\{\text{N}(\text{SiMePh}_2)_2\}_2]$ (**1**) and $\text{Zn}\{\text{N}(\text{SiMePh}_2)_2\}_2$ (**2**) have been synthesized and characterized by X-ray crystallography and IR and ^1H NMR spectroscopy. They were prepared by the reaction of 2 equiv of $\text{LiN}(\text{SiMePh}_2)_2$ with CuBr or ZnCl_2 in Et_2O or THF solution. The compounds form part of the series $\text{M}\{\text{N}(\text{SiMePh}_2)_2\}_2$ ($\text{M} = \text{Mn}$ (**3**), Fe (**4**), Co (**5**)) which display N-M-N angles in the range 147.0 (**1**)- 170.7 (**1**)°. In contrast, the N-Cu-N and N-Zn-N moieties have almost perfectly linear angles at the metal of 179.2 (**2**) and 177.5 (**2**)°. The average Cu-N and Zn-N distances are near 1.88 and 1.85 Å. The major conclusion from the structural data is that the angle at the metal is not necessarily determined by the metal size and that secondary interactions between low-lying unfilled metal orbitals and the electron-rich phenyl group(s) play a key role in determining the overall structure. Crystal data with $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069$ Å) at 130 K: **1**, $a = 17.643$ (**4**) Å, $b = 14.433$ (**3**) Å, $c = 26.085$ (**10**) Å, $\beta = 98.79$ (**2**)°, $Z = 4$, space group $P2_1/c$, 6487 ($I > 2\sigma(I)$) data, $R = 0.072$; **2**, $a = 10.917$ (**5**) Å, $b = 15.485$ (**8**) Å, $c = 26.963$ (**14**) Å, $\beta = 90.81$ (**4**)°, $Z = 4$, space group $P2_1/c$, 3894 ($I > 2\sigma(I)$) data, $R = 0.055$.

Introduction

The use of the crowding ligand $-\text{N}(\text{SiMePh}_2)_2$ has permitted the isolation of a number of crystalline two-coordinate complexes of manganese, iron, and cobalt.^{1,2} The metal coordination in these complexes, however, was not linear, and in the case of the species $\text{Co}\{\text{N}(\text{SiMePh}_2)_2\}_2$,³ the deviation from linearity was quite severe, as indicated by the N-Co-N angle of 147.0 (**1**)°. The origin of the bending is not known with certainty although it may be influenced by factors such as metal size, electron configuration, and the availability of electron density at other parts of the ligand. In this paper, the compounds $[\text{Li}(\text{THF})_4][\text{Cu}\{\text{N}(\text{SiMePh}_2)_2\}_2]$ (**1**) and $\text{Zn}\{\text{N}(\text{SiMePh}_2)_2\}_2$ (**2**) have been synthesized and characterized in order to shed further light on this question.

Experimental Section

General Procedures. All reactions were performed by using modified Schlenk techniques under an inert atmosphere of N_2 or a Vacuum Atmospheres HE43-3 drybox. Solvents were freshly distilled under N_2 from Na/K or sodium/potassium benzophenone ketyl and degassed twice immediately before use. $\text{HN}(\text{SiMePh}_2)_2$ was synthesized as previously described.³ Anhydrous CuBr and ZnCl_2 and $n\text{-BuLi}$ (1.6 M in hexane) were purchased from commercial suppliers and used as received. ^1H NMR spectra were recorded in C_6D_6 solution by using a General Electric QE-300 spectrometer. IR spectra (Nujol mull, CsI plates) were recorded in the range $4000\text{--}200$ cm^{-1} with a Perkin-Elmer 1420 spectrometer.

$[\text{Li}(\text{THF})_4][\text{Cu}\{\text{N}(\text{SiMePh}_2)_2\}_2]$ (1**).** $\text{HN}(\text{SiMePh}_2)_2$ (1.64 g, 4 mmol) in Et_2O (20 mL) and THF (5 mL) was treated with $n\text{-BuLi}$ (2.5 mL of a 1.6 M solution in hexane) with cooling in an ice bath. This solution was stirred for 1 h and was then added to a suspension of CuBr (0.287 g, 2 mmol) in Et_2O (10 mL). The reaction afforded an almost colorless solution with a small amount of an off-white precipitate. After 1 h of stirring, the volume was reduced to ~ 25 mL and the solution was filtered. Further reduction in volume to ~ 10 mL and the addition of pentane to incipient crystallization afforded the product **1** as colorless crystals: yield 1.4 g, 59%; mp $128\text{--}130$ °C. ^1H NMR (δ): 7.28 (m, Ph), 7.12 (m, Ph), 3.45 (m, THF), 1.4 (m, THF), 0.4 (s, Me). IR: Cu-N (asym str), 405 cm^{-1} .

$\text{Zn}\{\text{N}(\text{SiMePh}_2)_2\}_2$ (2**).** ZnCl_2 (1.14 g, 8.5 mmol) in Et_2O (30 mL) was treated dropwise with a solution formed from the addition of $n\text{-BuLi}$ (10.6 mL of a 1.6 M solution in hexane) to $\text{HN}(\text{SiMePh}_2)_2$ (6.96 g, 17 mmol) in Et_2O (30 mL) and THF (10 mL) with cooling in an ice bath. This gave a colorless solution, together with a white precipitate, which was stirred for a further 2 h. The volatile materials were removed under reduced pressure, and the residue was extracted with warm (50 °C) toluene (35 mL). Filtration, followed by reduction of the solution volume to ca. 20 mL and addition of pentane (~ 30 mL), gave, upon cooling in a -20 °C freezer, the product **2** as colorless needles: yield (not optimized) 4.3 g, 57%; mp $119\text{--}121$ °C. ^1H NMR (δ): 7.3 (m, Ph), 7.11 (m, Ph), 0.4 (s, Me). IR: Zn-N (asym str), 435 cm^{-1} .

Table I. Selected Crystallographic Data for Compounds **1** and **2**

	$[\text{Li}(\text{THF})_4][\text{Cu}\{\text{N}(\text{SiMePh}_2)_2\}_2]$ (1)	$\text{Zn}\{\text{N}(\text{SiMePh}_2)_2\}_2$ (2)
formula	$\text{C}_{68}\text{H}_{84}\text{N}_2\text{O}_4\text{Si}_4\text{CuLi}$	$\text{C}_{52}\text{H}_{52}\text{N}_2\text{Si}_4\text{Zn}$
fw	1176.26	882.7
a , Å	17.643 (4)	10.917 (5)
b , Å	14.433 (3)	15.485 (8)
c , Å	26.085 (10)	26.963 (14)
β , deg	98.79 (2)	90.81 (4)
V , Å ³	6564 (3)	4557 (4)
Z	4	4
space group	$P2_1/c$	$P2_1/c$
T , K	130	130
λ , Å	0.71069	0.71069
$d(\text{calcd})$, g/cm^3	1.19	1.286
$\mu(\text{Mo K}\alpha)$, cm^{-1}	4.48	6.90
range of transm factors	0.72-0.85	0.93-0.95
R	0.072	0.055
R_w	0.068	0.038

X-ray Crystallographic Studies. X-ray data for **1** and **2** were collected at 130 K with either a Syntex $P2_1$ (**1**) or a Siemens R3m/v (**2**) diffractometer equipped with locally modified low-temperature devices. Calculations for **1** were carried out on a Data General Eclipse computer and those for **2** on a Microvax 3200 computer using the SHELXTL program systems. In all cases, scattering factors were from common sources,⁴ and an absorption correction was applied by using the method described in ref 5.

X-ray-quality crystals of the title compounds were removed from the Schlenk tube under a stream of N_2 and immediately covered with hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber on a mounting pin, and immediately placed in the low-temperature N_2 stream. Some details of the data collection and refinement are provided in Table I. Further details are provided in the supplementary material. The structures were solved by direct methods and subsequently refined by blocked-cascade (**1**) or blocked-diagonal (**2**) least-squares refinement. The H atoms were included by use of a riding model with C-H distances of 0.96 Å and isotropic thermal parameters equal to 1.2 times that of the bonded carbon (**1**) or equated to 0.04 Å² (**2**). All non-hydrogen atoms were refined anisotropically. Fractional coordinates for important atoms in **1** and **2** are given in Table II.

Structural Descriptions

$[\text{Li}(\text{THF})_4][\text{Cu}\{\text{N}(\text{SiMePh}_2)_2\}_2]$ (1**).** The structure of **1** is composed of well-separated cations and anions as illustrated in Figure 1. In the cation, the Li^+ ion is surrounded, in a fairly regular manner, by four THF donors with an average Li-O bond length near 1.92 Å. In the anion, the copper is bound to two $-\text{N}\{\text{SiMePh}_2\}_2$ ligands and has almost perfectly linear coordination

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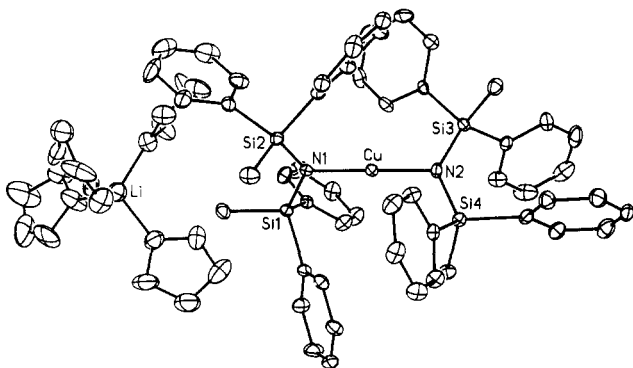
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Table II. Selected Atomic Coordinates and Isotropic Thermal Parameters ($\text{\AA}^2 \times 10^3$) for **1** and **2**

	x	y	z	U^a
Compound 1				
Cu	2262 (1)	7860 (1)	3698 (1)	22 (1)
N(1)	2063 (3)	6860 (3)	3872 (2)	25 (2)
N(2)	3260 (3)	8860 (3)	3535 (2)	26 (2)
Si(1)	2077 (1)	6800 (1)	4517 (1)	23 (1)
Si(2)	1487 (1)	6318 (1)	3393 (1)	25 (1)
Si(3)	4062 (1)	8649 (1)	3273 (1)	24 (1)
Si(4)	2840 (1)	9878 (1)	3645 (1)	25 (1)
Li	2041 (8)	2914 (11)	5897 (6)	66 (6)
O(1)	1126 (3)	2882 (3)	5389 (2)	59 (2)
O(2)	2873 (3)	2679 (4)	5522 (2)	59 (2)
O(3)	2137 (3)	4123 (4)	6213 (2)	73 (3)
O(4)	1946 (4)	1986 (5)	6401 (2)	97 (3)
Compound 2				
Zn	2378 (1)	2062 (1)	1416 (1)	26 (1)
N(1)	1792 (6)	1916 (3)	2051 (2)	23 (2)
N(2)	2942 (5)	2258 (3)	781 (2)	23 (2)
Si(1)	2412 (2)	1033 (1)	2347 (1)	26 (1)
Si(2)	780 (2)	2697 (1)	2266 (1)	26 (1)
Si(3)	2315 (2)	1639 (1)	313 (1)	27 (1)
Si(4)	3986 (2)	3093 (1)	719 (1)	28 (1)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

**Figure 1.** Thermal ellipsoidal drawing of **1**. Hydrogen atoms are omitted for clarity.

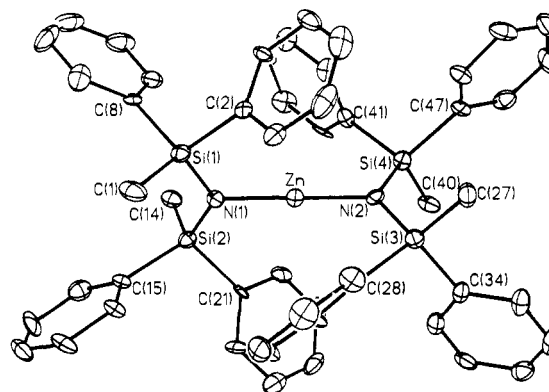
with a $\text{N}(1)\text{--Cu--N}(2)$ angle of $179.2(2)^\circ$. The average Cu--N bond length is near 1.88 \AA . In the silylamide groups the average N--Si distance is 1.685 \AA and the Si--N--Si angle averages 129.7° . Within each ligand there is noticeable asymmetry in the Cu--N--Si angles, which have an average difference of 7.7° . The angle between the planes containing the --NSi_2 moieties is 74.2° .

$\text{Zn}\{\text{N}(\text{SiMePh}_2)_2\}_2$ (**2**). The structure of **2** is illustrated in Figure 2. It can be seen that the zinc is coordinated in an almost linear fashion ($\text{N}(1)\text{--Zn--N}(2) = 177.5(2)^\circ$) by the two amide groups. The Zn--N distances are $1.849(3)$ and $1.850(3) \text{ \AA}$. Within the amide ligands the Si--N--Si angles average 128.6° , and although there is some evidence for asymmetry in the N--Si bonds (average $\text{N--Si} = 1.73 \text{ \AA}$ but $\text{N}(1)\text{--Si}(1)$ and $\text{N}(2)\text{--Si}(3)$ are marginally shorter than $\text{N}(1)\text{--Si}(2)$ and $\text{N}(2)\text{--Si}(4)$), there is little asymmetry in the Zn--N--Si angles, which span the range $112.9(3)\text{--}116.9(3)^\circ$. The angle between the --NSi_2 moieties of the amide ligands is 75.8° .

Discussion

Compounds **1** and **2** form part of a more extensive series of monomeric two-coordinate metal amide derivatives.⁶ Important structural data for **1** and **2** and the related Mn (**3**), Fe (**4**), and Co (**5**) species are listed in Table III. Attempts to crystallize the corresponding Ni(II) (d^8) derivative have not yet been successful, although a dark yellow brown oil which gave an approximately correct C, H, and N analysis for $\text{Ni}\{\text{N}(\text{SiMePh}_2)_2\}_2$ was obtained by the reaction of NiI_2 with $\text{LiN}(\text{SiMePh}_2)_2$ in Et_2O .

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**Figure 2.** Thermal ellipsoidal drawing of **2**. Hydrogen atoms are omitted for clarity.

The syntheses of **1** and **2**, however, were straightforward and gave crystalline products with little difficulty.

The most notable feature in the structures of **1** and **2** is the two-coordination of the metals. Only minor deviations from strict linearity are observed. In this respect they provide a sharp contrast to their Mn, Fe, and Co analogues, which show significant bending (up to 33° from linearity) and fairly close $\text{M}\cdots\text{C}$ contacts. The shorter M--N bond lengths in **1** and **2** reflect the trend toward progressively smaller metal radii upon proceeding across the series Mn–Zn. No structures for an ion of the type $[\text{Cu}(\text{NR}_2)_2]^-$ have been reported previously,⁷ although the structures of several neutral copper amides of formula $[\text{CuNR}_2]_4^{8,9}$ have been published. In these tetrameric compounds the Cu--N bond length is generally near 1.91 \AA . This distance is a little longer than the average Cu--N bond length of 1.88 \AA observed in **1**. The small difference in the Cu--N values is somewhat surprising, but it may be due to the negatively charged nature of the anion, which increases interelectronic repulsion and may lengthen the Cu--N bond. Another contributing factor to the bond lengthening might be the large size of the ligands (but see discussion on **2**). All the Cu--N bonds, whether they are bridging, as in the tetramers, or terminal, as in **1**, are considerably shorter than the value predicted¹⁰ ($\sim 2.0 \text{ \AA}$) on the basis of covalent radii. Much of the shortening can be attributed to the low coordination number of copper. Indeed, shorter than predicted metal–ligand bond distances are a general characteristic for low-coordination complexes, since estimates of bond lengths are generally based on structural parameters of substances that involve atoms with the common coordination number of 4–6.

The isoelectronic zinc species **2** possesses a structure very similar to that of the copper-centered anion. Its unit cell dimensions indicate that it is isomorphous with the corresponding Mn, Fe, and Co derivatives **3–5**.^{1,2} The average Zn--N bond (1.85 \AA) is marginally shorter than the Cu--N distance in **1**. This is to be expected owing to the slightly smaller size of Zn. Apparently, no X-ray crystal structures of homoleptic Zn amides have been published^{10,11} although a crystal structure of $(\text{MeZnNPh}_2)_2$ showed that it was dimeric with --NPh_2 bridges and Zn--N bonds about 2.07 \AA long.¹² The structure of **1** may be compared with the vapor-phase structure of $\text{Zn}\{\text{N}(\text{SiMe}_3)_2\}_2$ that was determined by electron diffraction.¹³ The Zn--N bond in this molecule, which

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Table III. Important Structural Data for [Cu{N(SiMePh₂)₂}]⁻, Zn{N(SiMePh₂)₂}₂, and their Mn, Fe, and Co Analogues

	3	4	5	1	2
M	Mn	Fe	Co	Cu	Zn
M-N(1)	1.989 (3)	1.916 (2)	1.898 (3)	1.885 (5)	1.850 (3)
M-N(2)	1.988 (3)	1.918 (2)	1.904 (3)	1.874 (5)	1.849 (5)
N-Si(1)	1.719 (3)	1.722 (2)	1.718 (4)	1.681 (5)	1.717 (5)
N-Si(2)	1.706 (3)	1.713 (2)	1.725 (4)	1.679 (5)	1.743 (6)
N-Si(3)	1.708 (3)	1.715 (2)	1.710 (3)	1.691 (5)	1.719 (5)
N-Si(4)	1.716 (3)	1.717 (2)	1.716 (3)	1.689 (5)	1.733 (6)
M...C	2.774 (5) for C(7)	2.695 (4) for C(14)	2.584 (7) for C(7) 2.588 (7) for C(27)	3.291 (5) for C(21)	2.961 (5) for C(2)
N-M-N	170.7 (1)	169.0 (1)	147.0 (1)	179.2 (2)	177.5 (2)
Si-N(1)-Si	127.7 (2)	131.8 (1)	125.5 (2)	129.4 (3)	130.2 (3)
Si-N(2)-Si	131.8 (2)	127.1 (2)	126.7 (2)	129.9 (3)	126.9 (3)
M-N-Si(1)	107.5 (1)	121.9 (1)	103.4 (2)(av)	111.0 (2)	116.9 (3)
M-N-Si(2)	120.6 (1)	106.1 (1)	130.5 (2)(av)	118.4 (2)	112.9 (3)
M-N-Si(3)	116.7 (1)	117.8 (1)		119.2 (3)	116.9 (3)
M-N-Si(4)	115.4 (1)	115.0 (1)		110.8 (3)	116.2 (3)

has a length of 1.824 (14) Å, is marginally shorter than (but within three standard deviations of) the distance in **1**. Good agreement between other structural parameters is also apparent. For example, the N-Si bond (1.728 (7) Å) and the Si-N-Si angle (130.4 (20)°) in Zn{N(SiMe₃)₂}₂ are almost identical to the values observed in **1**.

The close correlation between the crystal and vapor-phase data for the two zinc compounds sheds further light on the differences observed between the M-N distances in the crystal structures^{1,2} of **3-5** and the vapor-phase structures of M{N(SiMe₃)₂}₂ (M = Mn, Fe, Co).¹⁴ In these two sets of compounds, significantly longer (up to 0.07 Å) M-N distances were observed for the crystalline species **3-5**. One explanation for this difference could have involved the greater size of the -N(SiMePh₂)₂ ligand, since the increased steric hindrance could have induced a lengthening of the M-N bonds. The similarity of the Zn-N bond lengths obtained for Zn{N(SiMe₃)₂}₂ and Zn{N(SiMePh₂)₂}₂ (**2**) does not support this explanation. In fact, there is little evidence of severe strain in any of the complexes **1-5**. Thus, the structure of **2** provides further confirmation that the reason for the discrepancy between the solution and solid-state M-N bond lengths in the case of **3-5** and their -N(SiMe₃)₂ analogues is the strong correlation between M-N and Si-C bonds which have very similar distances, especially in the case of the Fe and Co derivatives.^{2,14}

One of the most interesting features of the data in Table III is the variation in the angle at the metal across the series. Clearly, there is no strong correlation between the metal angle and the M-N bond lengths that might have indicated a close connection between the bending and the degree of crowding at the metal. This may be seen most clearly in a comparison of **1** and **5**, which have very similar M-N bond lengths but have N-M-N angles that differ by over 32°. Another notable characteristic of the copper and zinc complexes **1** and **2** is the absence of any secondary interaction between the metals and the ligands. In this respect **1** and **2** are quite distinct from transition-metal species **3-5**, where there are significant M...C approaches. Moreover, these approaches are also accompanied by asymmetry in the M-N-Si angles. It can be seen, in the case of **3** and **4**, that the Mn-N-Si(1) and Fe-N-Si(2) angles are narrower than the other Mn-N-Si and Fe-N-Si angles in the molecules. Significantly, it is a carbon

from the phenyl groups on Si(1) (**3**) and Si(2) (**4**) that interacts, most strongly, with the metal. In **5**, where there are two close Co...C contacts, there is an asymmetry of about 27° in the Co-N-Si angles in both ligands. In sharp contrast to these data, there is very little asymmetry (only ~4°) evident in the Zn-N-Si angles in **2**, where the closest approach involves a Zn...C(2) length of 2.961 Å. All the remaining ipso carbons are over 3 Å distant from the metal. In fact, the Zn...Si distances, which average ~3 Å, are shorter. In view of the smaller size of Zn, it may be concluded that any metal-ligand interaction other than Zn-N is very weak. The corresponding data for the copper species **2** show that there are more substantial differences (~8°) between the Cu-N-Si angles in each ligand. However, no close Cu...C contacts are evident. The shortest such distance is 3.291 Å for Cu...C(21) whereas the Cu...Si contacts span the range 2.931-3.069 Å. As in the case of Zn, it seems safe to conclude that the only significant Cu-ligand interactions in **1** involve the nitrogens. A possible explanation for the greater Cu-N-Si asymmetry in **1** may have a basis in the more ionic nature of the anion of **1**. Thus, the restrictions on the directional requirements of the bonding N orbital may be less severe in the more ionic copper species and the Cu-N-Si angles may be more easily distorted.

In summary, the structural data for **1** and **2** suggest that the bonding observed in **3-5** is probably caused by a tendency of the low-lying empty metal valence orbitals on Mn, Fe, or Co to interact further with electron-rich parts (i.e. the aromatic rings) of the -N(SiMePh₂)₂ ligands. Why this interaction should be strongest in the cobalt complex **5** is not certain. It may be connected to the fact that the d⁷ electron configuration provides the maximized crystal field stabilization in a tetrahedral field.¹⁵ Accordingly, the gain in energy provided by the distorted tetrahedral array of the N(1), N(2), C(7), and C(27) atoms in **5** may induce the anomalously large bending observed at cobalt.

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Supplementary Material Available: Full tables of data collection parameters, atom coordinates, bond distances, bond angles, hydrogen coordinates, and thermal parameters (21 pages); listings of structure factors (68 pages). Ordering information is given on any current masthead page.

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