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X-ray Crystal Structure of a Late-Transition-Metal Dialkylamide, [$(CuNEt_2)_4$]

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The first complete X-ray crystal structure of a copper amide is described. Reaction of $LiNEt_2$ with CuBr gives colorless crystals of [$(CuNEt_2)_4$], which are thermally stable and hydrocarbon soluble. An X-ray crystal structure determination at ca. 140 K shows that the compound consists of discrete tetramers involving an almost perfect square plane of two-coordinate copper atoms bridged by diethylamido groups. The crystals are tetragonal with a = 16.012 (6) Å and c = 8.473 (4) Å, space group $I4_1/a$, and Z = 4. The Cu–Cu distance is 2.664 (2) Å, and the average Cu–N bond length is 1.904 (3) Å. The N–Cu–N angle is 175.4 (1)°, and the Cu–Cu–Cu angle is 89.9 (1)°. The crystals may be handled briefly in air, but hydrocarbon solutions are quite air-sensitive.

Introduction

Despite the large number of publications that have appeared on transition-metal amides no structural characterizations of homoleptic dialkylamides have been reported for elements later than chromium.[1] Derivatives of the $-N(SiMe_3)_2$[2] ligand have proven to be the only exception to this "rule". This unique group has been used to stabilize low coordination numbers[3] throughout the transition metals and lanthanides. More recently Saegusa and co-workers have reported the synthesis of a number of copper dialkylamides via amine exchange with mesitylcopper.[4,5] In this paper we describe a shorter synthesis and the first X-ray crystal structure of a thermally stable late-transition-metal dialkylamide, $(CuNEt_2)_4$. The X-ray crystal structure shows that it is tetrameric with the metals linked through nitrogen bridges. The structure appears to be similar to that claimed for $[CuN(SiMe_3)_2]_4$, but the details for this compound have not been reported.[6]

Experimental Section

All manipulations were carried out under a purified nitrogen atmosphere in Schlenk apparatus. Ether and *n*-hexane were purified by distillation under nitrogen from Na/K/benzophenone ketyl and degassed several times. Diethylamine was distilled from Na/K alloy; copper(I) bromide (Aldrich) was used as received.

[Tetrakis(diethylamido)tetracopper(I)]. A solution formed by the addition of 11.8 mL of a 1.7 M solution of *n*-butyllithium in *n*-hexane to diethylamine (2.05 mL, 0.02 mol) in ether (10 mL) was added dropwise to a well stirred slurry of copper(I) bromide (2.81 g, 0.02 mol) in ether (20 mL) at −10 °C. The solution was protected from excessive light exposure by carrying out the reaction in a Schlenk tube wrapped in aluminum foil. During the addition the solution turned brown (but not intensely so). Stirring was continued for 4 h at −10 °C, and the solution was filtered rapidly through Celite. Reduction of the volume in vacuo to ca. 25 mL and cooling to −20 °C overnight afforded the product as large colorless crystals: mp 134–35 °C dec; yield 1.9 g, 70%. The product was dissolved in a minimum volume of cold ca. 10 °C *n*-hexane. Cooling to −20 °C gave the pure, solid product. At 0 °C the crystals show only a little decomposition (slight darkening) after several weeks. They may be handled briefly in the air, but solutions in *n*-hexane or ether undergo a rapid color change to blue or green even after brief exposure to air.

Table I. Atom Coordinates (×10^4) and Thermal Parameters (Å^2 × 10^{-3})

atom	x	y	z	u^a
Cu	4641 (1)	6381 (1)	1170 (1)	24 (1)
N	3554 (2)	6743 (2)	1783 (3)	23 (1)
C(1)	3359 (2)	6543 (2)	3442 (4)	28 (1)
C(2)	3969 (2)	6906 (3)	4615 (4)	33 (1)
C(3)	2859 (2)	6420 (2)	803 (4)	28 (1)
C(4)	2909 (2)	6681 (2)	−915 (4)	32 (1)

[a] Equivalent isotropic u defined as one-third of the trace of the orthogonalized u_{ij} tensor.

Table II. Interatomic Distances (Å) and Angles (deg)

Cu-Cu(A)	2.664 (2)	N-C(3)	1.481 (4)
Cu-N	1.907 (3)	C(1)-C(2)	1.511 (5)
Cu-N(A)	1.901 (3)	C(3)-C(4)	1.516 (5)
N-C(1)	1.475 (4)		
N-Cu-N(A)	175.4 (1)	Cu(A)-N-C(3)	114.9 (2)
Cu-N-Cu(A)	88.8 (1)	C(1)-N-C(3)	107.4 (2)
Cu-N-C(1)	112.8 (2)	N-C(1)-C(2)	114.0 (3)
Cu-N-C(3)	115.3 (2)	N-C(3)-C(4)	113.7 (3)
Cu(A)-N-C(1)	117.0 (2)	Cu(A)-Cu-Cu(B)	89.9 (1)

Data Collection and Reduction. X-ray data were collected with a Syntex $P2_1$ diffractometer equipped with a locally modified Syntex LT-1 cooling device. Good quality crystals were obtained by the procedure given above. During manipulation the crystals were protected from air by a layer of hydrocarbon oil. A specimen of cross section 0.4–0.5 mm (~0.1 mm³) was cut from a larger crystal, attached to a mounting fiber, and placed in the cold stream of the low-temperature device. The high-speed data collection technique employed has been described elsewhere.[7a]

Crystal data for [$(CuNEt_2)_4$], $C_{16}H_{40}Cu_4N_4$: mol wt 542.72, colorless blocks, tetragonal, a = 16.012 (6) Å, c = 8.473 (4) Å, λ (Mo K$\bar{\alpha}$) = 0.71069 Å, T = 140 K, space group $I4_1/a$ (No. 88), Z = 4, required symmetry of tetramers $\bar{4}$, d_{exptl} = 1.66 Mg m^{-3}, μ = 39 cm^{-1} (Mo Kα). Data collection: Mo K$\bar{\alpha}$ radiation, graphite monochromator, 1° ω scan; scan speed 58.6° min^{-1}, 0.5-s stationary backgrounds at ω offsets ±1°, $2\theta_{\max}$ = 55°, 1248 unique reflections scanned, 1033 reflections with $F_o > 6\sigma(F_o)$. Standard Lorentz and polarization corrections were applied. An empirical absorption correction was applied.[7b]

Solution and Refinement of the Structure. The structure was solved by a direct methods program in the Nicolet SHELXTL system, light atoms were located by difference Fourier methods, and all parameters were refined by the SHELXTL least-squares program, C, Cu, and N with anisotropic temperature factors, H with isotropic factors. Least-squares weights were $1/(\sigma^2(F_o) + (0.02F)^2)$. Final R indices

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(7) (a) Hope, H.; Nichols, B. G. *Acta* Crystallogr., *Sect. B: Struct. Crystallogr. Cryst. Chem.* **1981**,*B37*, 158–161. (b) An absorption tensor is computed from ΔF values with a program prepared by H. Hope and B. Moezzi.

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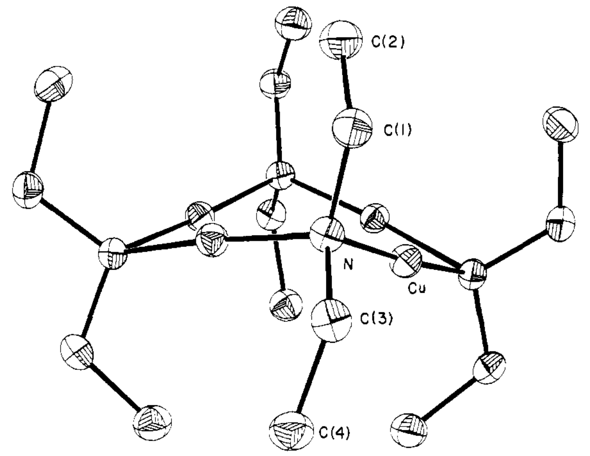

Figure 1. Computer-generated representative diagram of [$(CuNEt_2)_4$].

(for 1033 "observed" reflections) are $R = 3.17\%$, $R_w = 3.54\%$. A final difference map showed no residues of significance.

Positional and thermal parameters and distances and angles are presented in Tables I and II. Anisotropic thermal parameters, H parameters, and tables of observed and calculated structure factors are given as supplementary material.

Results and Discussion

The structure is the first reported for a late-transition-element dialkylamide. As already mentioned, later transition element amides have been generally confined to the $-N(SiMe_3)_2$ ligand. There does not seem to be an adequate explanation for the scarcity of compounds in the later metals. Some authors have pointed to the fact that π bonding via donation of the nitrogen lone pair of electrons to the metal d orbitals is less likely in the later elements since the number of d electrons is greater. Another possible reason is that while steric factors prevent decomposition of the silylamides, the less bulky alkylamide ligands such as $-NMe_2$, $-NEt_2$, and $-NPh_2$ permit decomposition by mechanisms that involve either association or a β-decomposition pathway.

The molecule is shown in the diagram in Figure 1. It is tetrameric, in agreement with the osmometric results obtained for the related compound $CuN(n\text{-}Bu)_2$.[4,5] The four copper atoms define an almost perfect square as evidenced by the Cu-Cu(A)-Cu angle of 89.9° and Cu-Cu bond distance of 2.664 (3) Å. The four copper atoms are coplanar to within ±0.07 Å. Alternate nitrogen atoms are significantly above and below the Cu_4 plane, and the plane defined by each Cu_2N triad is at an angle of 19.6° to the Cu_4 square. The overall symmetry of the molecule is $\bar{4}$. The two copper-nitrogen distances are almost equivalent at 1.907 (3) and 1.901 (3) Å, which are slightly less than what is predicted (2.00 Å) by the sum of the covalant radii.[8] The copper-copper distances at 2.664 Å are slightly greater than the sum of the covalent radii for copper and very much greater than the sum of the Shannon-Prewitt values for the copper(I) (two-coordinate) ion.[9]

It is of interest to compare the amide structure with those obtained for [$(CuCH_2SiMe_3)_4$][10] and [$(CuO\text{-}t\text{-}Bu)_4$].[11] In both the alkyl and the alkoxo complex the Cu_4C_4 and Cu_4O_4 moieties are very nearly planar. In the alkyl the Cu-Cu and Cu-C distances are 2.418 (2) and 1.98 Å, respectively, while for the alkoxo compound the four copper atoms form a rectangle with Cu-Cu distances varying from 2.646 (2) to 2.771 (3) Å and an average Cu-O distance of 1.85 Å. A comparison of these bond distances and the angles at the bridging heteroatom is given in Table III. This table shows the expected smooth trend in the Cu-X bond distances, with Cu-C > Cu-N > Cu-O. These lengths might lead to the expectation that the Cu-Cu distances should follow the same sequence. However, the trend is in the opposite direction and is reflected in the increasing Cu-X-Cu angle. The X-Cu-X angle also changes, but a comparison here is not fruitful due to the nonplanarity of the Cu amide molecule.

Table III. Selected Bond Distances and Angles of Cu(I) Alkyl, Amide, and Alkoxide Complexes

	[$(CuR)_4$][a]		
	[$(CuCH_2SiMe_3)_4$]	[$(CuNEt_2)_4$]	[$(CuO\text{-}t\text{-}Bu)_4$]
Cu-X,[b] Å	1.98-2.04	1.907 (3)	1.85 (av)
Cu-Cu, Å	2.418 (2)	2.664 (3)	2.71 (av)
Cu-X-Cu, deg	73.6 (3)	88.8 (1)	93.85

[a] R represents alkyl, amide, or alkoxide. [b] X represents the atom bonded to copper.

The aggregation of Cu-X units in these tetrameric molecules can arise from either (i) M-M interaction or (ii) ligand bridging. In this regard there have been a number of publications[12,13] on M-M interactions between d^{10} systems which have indicated that there is a weak attractive force due to σ bonding if the effect of the metal s and p orbitals is taken into account. In this scheme, the empty metal σ^* antibonding orbital is of the proper symmetry to accept lone pair electron density from a nitrogen or oxygen atom.[12] This extra electron density in the case of nitrogen and oxygen would decrease Cu-Cu bonding and increase the Cu-Cu distance. In view of the long Cu-Cu distances in the amido compound, it is probable that the tetrameric unit is held together by donor bonds with little or no d^{10}-d^{10}, Cu-Cu interaction. In the case of the alkyl compound, where there is no available electron-pair donor, a three-center-two-electron bonding scheme has been proposed. The shorter Cu-Cu bond distance indicates some metal-metal bonding is permitted by the lack of available electron density in the σ^* orbital.

The stability of [$(CuNEt_2)_4$] is unique in the later-transition-metal amides. We ascribe this stability to the closed-shell electronic configuration of the copper atom. The stability of the Cu(I)-N bond has already been demonstrated in the use of stable heteroorganocuprates such as Li[Cu(R)X], where $X = NR_2$, OR, or PR_2, in place of less stable homocuprates as synthetic reagents in organic chemistry.[14] No structure of these interesting compounds has been described.

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Registry No. $(CuNEt_2)_4$, 88780-37-4.

Supplementary Material Available: Tables of structure factors, anisotropic thermal parameters, and hydrogen coordinates (9 pages). Ordering information is given on any current masthead page.

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