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Nucleophilic Attack on Dichloromethane. Synthesis and Structure of *mer*-[Cu(2-(Aminomethyl)Pyridine)₃]²⁺

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NUCLEOPHILIC ATTACK ON DICHLOROMETHANE. SYNTHESIS AND STRUCTURE OF *mer*-[Cu(2-(AMINOMETHYL)PYRIDINE)₃]²⁺

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Solutions of copper(II) β -diketone complexes in CH₂Cl₂ or CHCl₃ react with 2-(aminomethyl)pyridine (AMP) to produce Cu(AMP)₃²⁺, which precipitates as its chloride salt. *mer*-[Cu(AMP)₃]Cl₂·CH₂Cl₂ is monoclinic, space group *P*2₁/*c*; *a* = 11.072(1), *b* = 22.306(3), *c* = 11.388(2) Å; β = 117.39(2)^o; *Z* = 4; *R* = 0.076; *R*_w = 0.068 for 375 parameters and 3477 reflections with *I* > 1 σ (*I*). The *mer*-Cu(AMP)₃²⁺ ion has a tetragonally distorted octahedral geometry; distances from Cu to two *trans*-oriented pyridine N atoms are elongated (2.420(5) and 2.437(5) Å), while the third is normal (2.060(4) Å). Distances from Cu to the equatorial NH₂ N atoms range from 2.012(5) to 2.048(5) Å. The chloride ion in this compound is produced by nucleophilic attack of AMP on the CH₂Cl₂ solvent.

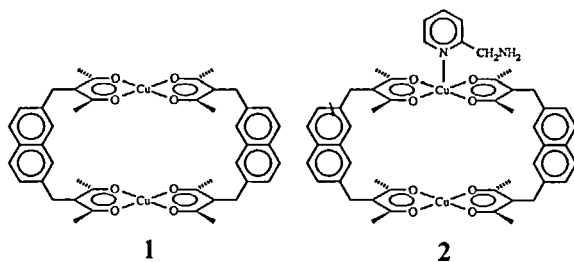
Keywords: Copper(II), ligand substitution, 2-(aminomethyl)pyridine, X-ray structure

INTRODUCTION

Copper(II) forms stable complexes with a large variety of chelating diamines. With most such ligands, however, the thermodynamically favoured product is the square-planar species Cu(NN)₂²⁺ (NN = diamine), and binding constants for the third ligand are much smaller. Only a few Cu(NN)₃²⁺ complexes have been crystallized: Cu(phen)₃²⁺,¹ Cu(bpy)₃²⁺,² and Cu(en)₃²⁺^{3†} (other Cu^{II}N₆ complexes with non-macrocyclic ligands, such as Cu(imidazole)₆²⁺⁴ and Cu(trpy)₂²⁺,⁵ have also been structurally characterized).

We have recently studied the capacity of the cofacial binuclear complex Cu₂(NBA)₂ (**1**) for intra- and extramolecular coordination of Lewis bases.^{6,7,8} We discovered that, although the initial product of the reaction of Cu₂(NBA)₂ with 2-(aminomethyl)pyridine (AMP) in CHCl₃ or CH₂Cl₂ is probably a simple adduct (such as that shown in **2**), the solutions slowly deposit a bright blue crystalline precipitate.⁸ We now report that the precipitate contains *mer*-Cu(AMP)₃²⁺, and that this reaction occurs with simpler copper β -diketone complexes as well. The procedure represents an unusual and high-yield non-aqueous synthetic approach to Cu^{II}N₆ complexes, which are difficult to obtain by traditional methods. The reaction in CH₂Cl₂, for example, is likely to proceed *via* nucleophilic attack on the solvent by the excess of amine present, followed by acid hydrolysis of the copper β -diketone complex.

* Ligand abbreviations: AMP = 2-(aminomethyl)pyridine; phen = 1,10-phenanthroline; bpy = 2,2'-bipyridine; en = ethylenediamine; trpy = 2,2':6',2''-terpyridine.



EXPERIMENTAL

Materials and Procedures

2-(Aminomethyl)pyridine (AMP) was used as received from the Aldrich Chemical Co. $\text{Cu}_2(\text{NBA})_2 \cdot 2\text{CHCl}_3$ was prepared by the literature procedure;⁶ $\text{Cu}(\text{acac})_2$ was prepared by an analogous method. Solvents were of the highest grade commercially available and were used as received.

$\text{mer-}[\text{Cu}(\text{AMP})_3]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$

$\text{Cu}(\text{acac})_2$ (0.019 g; 0.073 mmol) was dissolved in 5 cm³ of CH_2Cl_2 and the resulting blue-grey solution treated with 1.0 g (9.2 mmol) AMP. There was no immediate reaction, but bright blue crystals grew in the solution over a period of 12–24 h. These were collected, washed with a small amount of CH_2Cl_2 , air-dried briefly and stored in a desiccator or glove-box to prevent reaction with atmospheric moisture. Yield 0.030–0.038 g (75–95%). *Anal.*: Calcd. for $\text{CuC}_{19}\text{H}_{26}\text{N}_6\text{Cl}_4$: C, 41.96; H, 4.82; N, 15.45%. Found: C, 41.47; H, 5.12; N, 15.47%. The blue solid rapidly turns violet on exposure to moist air, probably indicating conversion to $\text{Cu}(\text{AMP})_2^{2+}$.

Crystals of $\text{mer-}[\text{Cu}(\text{AMP})_3]\text{Cl}_2 \cdot \text{CH}_2\text{Cl}_2$ suitable for X-ray analysis were prepared by the above method, and mounted in glass capillaries (along with some of the mother liquor) to limit solvent loss and reaction with H_2O . The capillaries were then flame-sealed.

Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer fitted with $\text{CuK}\alpha$ source and graphite monochromator, using the θ – 2θ scan method and variable scan rates. Final unit cell constants were determined from the orientations of twenty-five centred high-angle reflections. No significant change was noted in the intensities of three standard reflections during data collection. Additional crystallographic data are summarized in Table I.

The structure was solved by direct methods, using the Enraf-Nonius VAXSDP series of programs. Repeated cycles of full-matrix least-squares refinement and difference Fourier syntheses located the remaining atoms. All non-hydrogen atoms were refined anisotropically, except $\text{Cl1s}'$ of the disordered solvent, which was assigned a fixed isotropic displacement parameter. All H atoms were located and their positional and isotropic displacement parameters refined, except those in the CH_2Cl_2 molecule, which were placed at calculated positions with fixed displacement parameters. The model chosen for the solvent disorder has two orientations, of 80% (Cl1s , Cl1s) and 20% ($\text{Cl1s}'$, $\text{Cl1s}'$) population, with one common Cl atom (Cl2s).

TABLE I
Data collection and refinement parameters for *mer*-[Cu(AMP)₃]Cl₂·CH₂Cl₂.^a

chem. formula	CuC ₁₉ H ₂₆ N ₆ Cl ₄	transmission coeff	0.8244–0.9917
fw	543.81	θ range/°	2–75
colour	blue	octants collcd	<i>h, k, ±l</i>
habit	parallelepiped	reflins. measd	4959
<i>a</i> /Å	11.072(1)	reflins. obsd	3477, <i>I</i> > 1σ(<i>I</i>)
<i>b</i> /Å	22.306(3)	<i>R</i> _{INT} ^b	0.025
<i>c</i> /Å	11.388(2)	parameters	375
β/°	117.39(2)	<i>P</i> ^c	0.02
<i>V</i> /Å ³	2497.0	<i>R</i> (<i>F</i> _o) ^d	0.076
<i>Z</i>	4	<i>R</i> _w (<i>F</i> _o) ^e	0.068
space group	<i>P</i> 2 ₁ / <i>c</i> , No. 14	GOF ^f	1.875
temp/°C	21	max. shift/esd	0.19
λ/Å	1.54184 (Cu Kα)	max. residual/e Å ⁻³	0.54
ρ _{obsd} , ρ _{calcd} /g cm ⁻³	1.48(2); 1.446	min. residual/e Å ⁻³	-0.72
cryst. dimen./mm	0.20 × 0.23 × 0.38	extinction param. ^g	3.2(5) × 10 ⁻⁷
μ(Cu Kα)/cm ⁻¹	54.05		

^a In Tables I–IV, estimated standard deviations in the least significant digits of the values are given in parentheses. ^b Agreement factor on *I* for equivalent observed reflections. ^c Instability factor in non-Poisson weighting scheme: $w = 4F_o^2/(\sigma^2(I) + (P \cdot F_o^2)^2)$. ^d $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^e $R_w = \sqrt{(\Sigma w(|F_o| - |F_c|)^2)/\Sigma w F_o^2}$. ^f $GOF = \sqrt{[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]}$. ^g The correction factor $(1 + gI_c)^{-1}$ was applied to *F_c*.

RESULTS AND DISCUSSION

Synthesis of *mer*-[Cu(AMP)₃]Cl₂·CH₂Cl₂

The nature of the product obtained on reaction of copper(II) with chelating diamines (NN) depends to some extent on the steric bulk of NN. The large flat ligands bpy and phen make formation of square-planar Cu(NN)₂²⁺ very difficult; as a result, coordination of a third ligand is relatively favourable. Thus, Cu(bpy)₃²⁺ and Cu(phen)₃²⁺ are sufficiently stable to be studied in aqueous solution. With less bulky ligands, such as en and AMP, Cu(NN)₂²⁺ is the most stable complex and Cu(NN)₃²⁺ can be prepared only in nonaqueous solution or in the presence of large amounts of excess ligand. Equilibria between Cu²⁺ and AMP in aqueous solution were studied by Utsuno and Sone, who estimated that the binding constant at room temperature for the third AMP ligand was *ca* 2–3 M⁻¹.⁹

Solutions of the cofacial binuclear complex Cu₂(NBA)₂ (1) in CH₂Cl₂ or CHCl₃ bind diamines such as dabco (1,4-diazabicyclo[2.2.2]octane)⁶ and pyrazine⁸ internally. With monodentate amines such as pyridine, however, only an extramolecular adduct 2 is possible. The initial product with Cu₂(NBA)₂ and AMP is probably of type 2, since the two N atoms in AMP are not properly oriented for intramolecular coordination. However, these solutions slowly deposit a light blue crystalline solid. This material is water-soluble and is therefore unlikely to be a simple Cu₂(NBA)₂·AMP adduct. Furthermore, the same product is obtained when simpler complexes such as Cu(acac)₂ react with AMP. This procedure has afforded a convenient, high-yield synthesis of *mer*-Cu(AMP)₃²⁺ for the first time.

Structure of mer-[Cu(AMP)₃]Cl₂·CH₂Cl₂

The structure consists of *mer*-Cu(AMP)₃²⁺ cations with no crystallographically imposed symmetry, chloride anions, and disordered CH₂Cl₂ molecules. The overall geometry of the cation is similar to those of other *mer*-M(AMP)₃²⁺ complexes; see, for example, a discussion of the Zn and Fe complexes by Mikami-Kido and Saito¹⁰ (although most M(AMP)₃ complexes appear to be produced as the *mer* isomer, the *fac* isomers of the iron(II)¹¹ and nickel(II)¹² complexes have been crystallized).

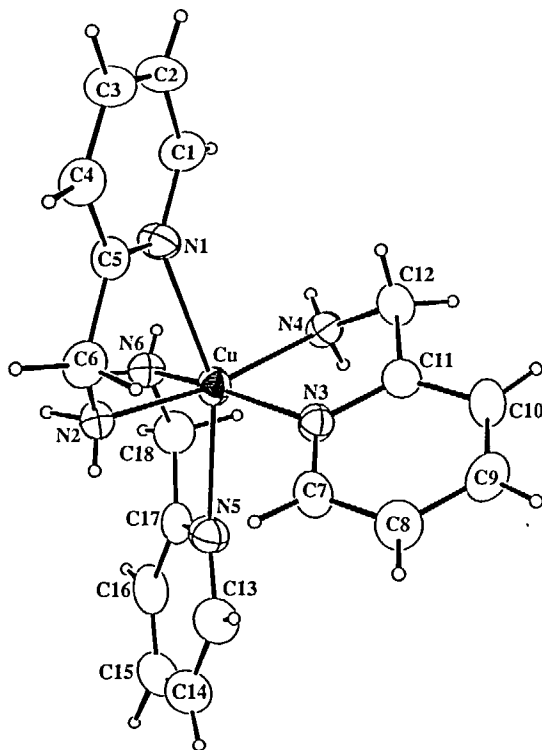


FIGURE 1. ORTEP¹³ drawing for *mer*-[Cu(AMP)₃]²⁺, with ellipsoids drawn at the 33% probability level.

The *mer*-Cu(AMP)₃²⁺ cation (see ORTEP¹³ drawing in Figure 1) is approximately octahedral, but it shows a "z-out" tetragonal distortion, with the heterocyclic atoms N1 and N5 representing the z axis. These elongations, which are attributable to the Jahn-Teller effect, are similar to those in the structures of [Cu(en)₃]Cl₂·0.75en,³ Cu(phen)₃²⁺,¹ and Cu(bpy)₃²⁺.² The long Cu-N1 and Cu-N5 distances are associated with relatively small chelate-ring N-Cu-N angles (N1-Cu-N2, 73.0(2)°; N5-Cu-N6, 75.2(2)°); the corresponding angle in the equatorial plane, N3-Cu-N4, is 80.5(2)°. The latter value is similar to that found (average value 81.6(2)°) in the low-spin form of Fe(AMP)₃²⁺,¹⁰ whose M-N distances (average values 2.002(4) and 2.024(4) Å) are close to those in the equatorial plane of Cu(AMP)₃²⁺. The chelate rings in the present structure are non-planar (torsion angles: N1-C5-C6-N2, -16.9(7)°; N3-C11-C12-N4, -30.6(7)°; N5-C17-C18-N6, -39.9(7)°).

TABLE II
Atomic coordinates for *mer*-[Cu(AMP)₃]Cl₂·CH₂Cl₂.

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B_{eq}/Å²^a</i>
Cu	0.53818(8)	0.12977(4)	0.81650(8)	3.36(2)
Cl1	0.5979(1)	-0.07301(6)	0.9123(1)	3.72(3)
Cl2	0.7646(1)	0.23932(7)	0.6221(2)	4.36(4)
N1	0.3589(4)	0.1961(2)	0.8019(4)	3.7(1)
N2	0.5919(4)	0.2147(2)	0.7904(4)	3.8(1)
N3	0.4539(4)	0.1052(2)	0.6204(4)	3.2(1)
N4	0.4408(4)	0.0547(2)	0.8230(4)	3.2(1)
N5	0.7654(4)	0.0950(2)	0.8665(5)	4.2(1)
N6	0.6436(4)	0.1302(2)	1.0184(4)	3.9(1)
C1	0.2517(6)	0.1878(3)	0.8259(6)	4.3(2)
C2	0.1436(6)	0.2249(3)	0.7833(6)	4.8(2)
C3	0.1414(6)	0.2744(3)	0.7087(7)	5.2(2)
C4	0.2507(6)	0.2845(3)	0.6856(6)	4.6(2)
C5	0.3574(5)	0.2437(2)	0.7331(6)	3.7(1)
C6	0.4762(6)	0.2524(3)	0.7028(6)	4.6(2)
C7	0.4905(6)	0.1229(3)	0.5293(6)	4.0(2)
C8	0.4400(6)	0.0968(3)	0.4068(6)	4.8(2)
C9	0.3480(6)	0.0517(3)	0.3762(6)	4.6(2)
Cl0	0.3080(6)	0.0335(3)	0.4656(6)	4.3(2)
Cl1	0.3628(5)	0.0608(3)	0.5888(5)	3.5(1)
Cl2	0.3254(6)	0.0440(3)	0.6956(6)	3.9(1)
Cl3	0.8339(6)	0.0947(3)	0.7947(7)	5.4(2)
Cl4	0.9748(7)	0.0867(3)	0.8560(7)	6.6(2)
Cl5	1.0424(6)	0.0777(3)	0.9850(8)	6.4(2)
Cl6	0.9729(6)	0.0784(3)	1.0585(7)	5.6(2)
Cl7	0.8353(5)	0.0863(2)	0.9959(6)	3.9(2)
Cl8	0.7519(6)	0.0847(3)	1.0693(6)	4.7(2)
Cl1s ^b	-0.0990(7)	0.1712(3)	0.4311(7)	4.0(2)
Cl1s ^{c,d}	-0.045(3)	0.076(1)	0.496(3)	4.3(7)
Cl1s ^b	-0.2433(3)	0.1244(1)	0.3846(3)	7.92(8)
Cl1s ^{c,e}	-0.158(1)	0.1032(6)	0.453(1)	8.0
Cl2s	0.0491(2)	0.1387(1)	0.4510(3)	11.53(9)

^a The isotropic equivalent displacement parameter B_{eq} is defined as $\frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ac \cos \beta_{13})$. ^b Occupancy 0.80. ^c Occupancy 0.20. ^d Refined isotropically. ^e Modelled with fixed isotropic displacement parameter.

TABLE III
Bond distances/Å for *mer*-[Cu(AMP)₃]Cl₂·CH₂Cl₂.^a

Cu-N1	2.420(5)	N5-C13	1.35(1)	C10-C11	1.387(8)
Cu-N2	2.048(5)	N5-C17	1.326(7)	C11-C12	1.50(1)
Cu-N3	2.060(4)	N6-C18	1.470(8)	C13-C14	1.397(9)
Cu-N4	2.012(5)	C1-C2	1.349(8)	C14-C15	1.32(1)
Cu-N5	2.437(5)	C2-C3	1.39(1)	C15-C16	1.37(1)
Cu-N6	2.044(4)	C3-C4	1.37(1)	C16-C17	1.365(8)
N1-C1	1.348(9)	C4-C5	1.388(8)	C17-C18	1.50(1)
N1-C5	1.315(8)	C5-C6	1.52(1)	C1s-C11s	1.775(8)
N2-C6	1.473(7)	C7-C8	1.372(8)	Cl1s'-Cl1s'	1.27(3)
N3-C7	1.335(9)	C8-C9	1.358(9)	Cl1s-Cl2s	1.710(8)
N3-C11	1.339(7)	C9-C10	1.35(1)	Cl1s'-Cl2s	1.94(3)
N4-C12	1.445(6)				

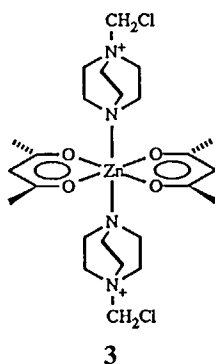
The chloride ions in *mer*-[Cu(AMP)₃]Cl₂·CH₂Cl₂ are positioned between adjacent Cu(AMP)₃²⁺ ions, with the closest approaches to the NH₂ protons. Cl1 lies between H1N6 and H1N4 on one cation (2.72 and 2.56 Å respectively) and H2N4 on another cation (2.40 Å); Cl2 lies between H2N6 and H2N2 on one cation (2.24 and 2.68 Å respectively) and H1N2 on another (2.63 Å). Thus, all of the amino protons are relatively close to the anions. The only other significant non-bonded contact in the structure is between Cl2s and Cl1 (3.54 Å).

Mechanism of Formation

The reaction of Cu(acac)₂ with AMP to produce *mer*-Cu(AMP)₃²⁺ appears to occur only in chlorinated hydrocarbon solvents; solutions of Cu(acac)₂ in CH₃CN or benzene, for example, do not react with AMP. This reaction is similar to that of a copper(II) Schiff base complex with ethylenediamine in the presence of CH₂Cl₂ and CHCl₃ to produce Cu(en)₂Cl₂·2H₂O;¹⁴ however, our work is the first to demonstrate the formation of a Cu(NN)₃²⁺ species by this method.

The oxidizing ability of CHCl₃ has been well demonstrated, for example, in photochemical oxidations of metal carbonyls.¹⁵ In a more closely related reaction, a nickel(II) Schiff base complex was shown to react with AMP in refluxing CHCl₃ to produce Ni(AMP)₂Cl₂·2H₂O.¹⁶ These processes are likely to occur by initial oxidation of AMP by CHCl₃. The resulting amine radical cation (AMP⁺) would be a strong enough acid to protonate coordinated acac⁻ in Cu(acac)₂, especially with the added driving force of the chelating AMP ligand. Oxidative dehydrogenation of AMP has been reported previously in the presence of iron¹⁷ and cobalt¹⁸ complexes.

In CH₂Cl₂, nucleophilic substitution is a more likely mechanism for the reaction than free-radical oxidation. Although CH₂Cl₂ is considered a relatively inert solvent, it is known to react with butylamine, releasing Cl⁻ and butyl(chloromethyl)ammonium ion.¹⁹ The corresponding ion in our system, (chloromethyl)(2-pyridylmethyl)ammonium ion, would probably also be sufficiently acidic in the presence of excess AMP to protonate coordinated acac⁻. In a related reaction, we have shown that dabco reacts with CH₂Cl₂ by isolating the resulting quaternary ammonium ion N(CH₂CH₂)₃NCH₂Cl⁺ as its six-coordinate adduct 3 with Zn(acac)₂.²⁰



Our proposal of free-radical reaction in CHCl₃ and nucleophilic displacement in CH₂Cl₂ is supported by two previous comparisons. First, the C–Cl bond energy in CHCl₃ is *ca* 15 kJ mol⁻¹ weaker than that in CH₂Cl₂; this favours radical formation

in CHCl_3 .²¹ Second, experimental and theoretical studies of the gas-phase activation barriers for Cl^- exchange give substantially smaller barriers with CH_2Cl_2 than with CHCl_3 ;²² thus, nucleophilic substitution should be significantly faster with CH_2Cl_2 .

TABLE IV
Bond angles/ $^\circ$ for *mer*-[Cu(AMP)₃]Cl₂·CH₂Cl₂.

N1-Cu-N2	73.0(2)	Cu-N2-C6	114.0(3)	C7-C8-C9	118.8(7)
N1-Cu-N3	98.1(2)	Cu-N3-C7	128.0(3)	C8-C9-C10	119.9(6)
N1-Cu-N4	94.3(2)	Cu-N3-C11	113.4(4)	C9-C10-C11	119.3(6)
N1-Cu-N5	159.5(2)	C7-N3-C11	118.1(5)	N3-C11-C10	121.4(6)
N1-Cu-N6	95.8(2)	Cu-N4-C12	110.0(4)	N3-C11-C12	114.9(4)
N2-Cu-N3	96.1(2)	Cu-N5-C13	132.0(3)	C10-C11-C12	123.7(6)
N2-Cu-N4	166.4(2)	Cu-N5-C17	108.5(4)	N4-C12-C11	109.1(5)
N2-Cu-N5	89.5(2)	C13-N5-C17	118.1(5)	N5-C13-C14	120.6(6)
N2-Cu-N6	96.1(2)	Cu-N6-C18	112.4(4)	C13-C14-C15	120.4(8)
N3-Cu-N4	80.5(2)	N1-C1-C2	124.1(6)	C14-C15-C16	119.1(6)
N3-Cu-N5	94.2(2)	C1-C2-C3	118.2(7)	C15-C16-C17	119.2(6)
N3-Cu-N6	163.8(2)	C2-C3-C4	118.7(6)	N5-C17-C16	122.6(7)
N4-Cu-N5	103.9(2)	C3-C4-C5	119.1(6)	N5-C17-C18	115.3(5)
N4-Cu-N6	90.0(2)	N1-C5-C4	122.5(6)	C16-C17-C18	122.0(6)
N5-Cu-N6	75.2(2)	N1-C5-C6	117.6(5)	N6-C18-C17	111.2(5)
Cu-N1-C1	132.3(4)	C4-C5-C6	119.9(6)	Cl1s-C1s-Cl2s	117.8(4)
Cu-N1-C5	108.7(4)	N2-C6-C5	110.4(5)	Cl1s'-C1s'-Cl2s	97(2)
C1-N1-C5	117.4(5)	N3-C7-C8	122.5(6)		

SUMMARY

The six-coordinate copper(II) complex $\text{Cu}(\text{AMP})_3^{2+}$, which is difficult to prepare by direct reaction in aqueous solution, is readily obtained by reaction of copper β -diketone complexes with AMP in chlorinated hydrocarbon solvents. This type of reaction may be useful in nonaqueous routes to other water-sensitive chelate complexes. In addition, the proposed mechanism for its formation serves as a warning that solvents such as CH_2Cl_2 can be attacked even by mild nucleophiles such as organic amines.

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SUPPLEMENTARY MATERIAL

Tables of anisotropic displacement parameters, hydrogen-atom parameters, and bond distances and angles involving hydrogen atoms (5 pages), and tables of observed and calculated structure factors (9 pages) are available from the authors.

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