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The Preparation and Structure of the Copper(II) Chloride Complex of 5,5′-Carbonylbis[1,3-dimethyl-3,4,5,6-tetrahydro-1,3,5-triazin-2(1*H*)-one]

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Synopsis. A new 1,3-dimethylurea-formaldehyde condensate like a crown compound with two rings, 5,5′-carbonylbis[1,3-dimethyl-3,4,5,6-tetrahydro-1,3,5-triazin-2(1*H*)-one], was prepared. The molecular structure of the complex with the condensate and copper(II) chloride (1 : 1) was determined by means of X-ray analysis. The copper(II) ion was coordinated intermolecularly between two oxygen atoms (O(2) and O(2)′ in the adjacent molecule).

The previous papers[1,2] reported that the addition of 1,3-dimethylurea-formaldehyde condensates, such as 1,3,5,7-tetramethyltetrahydro-1,3,5,7-tetrazocine-2,6-(1*H*,3*H*)-dione and bis(1,3-dimethylureido)methane, changed the absorption spectrum of a solution of the metal salts of phenol into that of free phenol. An apparent specific interaction between these condensates and the metal ions was suggested.

A new 1,3-dimethylurea-formaldehyde condensate like a crown compound with two rings, 5,5′-carbonylbis[1,3-dimethyl-3,4,5,6-tetrahydro-1,3,5-triazin-2(1*H*)-one] (CDTTO), was prepared, and the molecular structure of the complex with CDTTO and copper(II) chloride (1 : 1) was determined by means of X-ray analysis in order to elucidate the coordination between the CDTTO and copper(II) chloride.

Experimental

Preparation of a Complex with 5,5′-Carbonylbis[1,3-dimethyl-3,4,5,6-tetrahydro-1,3,5-triazin-2(1*H*)-one] and Copper(II) Chloride. One mole of 1,3-bis(methoxymethyl)-urea, two moles of 1-methoxymethyl-1,3-dimethylurea, and a small amount of *p*-toluenesulfonic acid as an acid catalyst were dissolved in DMF. The solution was then heated at 110 °C in an oil bath for 30 min. After the DMF has distilled away, the crystals deposited (CDTTO) were recrystallized from EtOH (Yield, 76%). Elemental analysis: Found, C, 46.45; H, 7.11; N, 29.47%; Calcd for $C_{11}H_{20}N_6O_3$, C, 46.47; H, 7.09; N, 29.56%. ^{1}H NMR (DMSO-d_6): δ=4.58 (8H, s, $-C\underline{H}_2-$), 2.74 (12H, s, $-C\underline{H}_3$): ^{13}C NMR (DMSO-d_6): δ=160.43 ($O{=}\underline{C}\langle$), 150.79 ($O{=}\underline{C}\langle$), 61.74 ($-\underline{C}H_2-$), 31.98 ($-\underline{C}H_3$). MS (FD): m/z=284 ($\underline{M}^+$).

Equimolecular quantities of CDTTO and copper(II) chloride were dissolved in distilled water, after which the solution was stirred for 30 min at room tempersture. After the evaporation of the solvent, the deposited crystals were recrystallized from EtOH. The copper content in the complex with CDTTO and copper(II) chloride was determined by atomic absorption analysis. CDTTO : Cu=1.01 : 1.

X-Ray Analysis. A brown, transparent crystal with dimensions of ca. 0.2×0.2×0.2 mm^3 was mounted on a Rigaku AFC-6S automated diffractometer. The systematic absences of (h00) reflections for h odd and (0k0) for k odd led to the space group of $P2_12_12$. The intensity data were measured by means of the ω-2θ scan mode (scan speed 4° min^{-1} in ω) up to 2θ of 60° by using graphite-monochromated Mo $K\alpha$ radiation (λ=0.7107 Å). Lorentz and polarization corrections were made, but no correction for absorption. Among the 1495 reflections measured, 1351 reflections with $|F_o|>3\sigma(|F_o|)$ were used for the structure determination.

Crystal Data. $C_{11}H_{20}N_6O_3 \cdot CuCl_2$. F.W.=418.77, orthorhombic, space group $P2_12_12$, a=12.772(2), b=10.850(4), c=6.004(1) Å, V=832.1 Å^3, Z=2, D_c=1.67 g·cm^{-3} μ (Mo $K\alpha$)=16.6 cm^{-1}.

The structure was solved by the direct method (MULTAN78[3]). The positions of the H atoms were determined from a difference Fourier map. The structure was refined anisotropically for non-H atoms and isotropically for H atoms by a block-diagonal least-squares method. The final discrepancy factors were R=0.056 and R_w=0.085 (w=unit wt), and $(\Delta/\sigma)_{max}$ in the final refinement cycle was 0.110 for non-H atoms. The scattering factors were taken from Ref. 4. The calculations were carried out on a HITAC M-680H computer at the Computer Center of The University of Tokyo, using the local version of UNICS III.[5]

Results and Discussion

The final atomic and equivalent isotropic thermal parameters, as defined by Hamilton,[6] are listed in Table 1.[7] The selected bond lengths and bond angles, and also some interatomic distances, are shown in Table 2. A perspective view of the complex along the b-axis, with atomic numbering, is shown in Fig. 1. The carbonyl group of C(1)-O(1) and Cu^{2+} are on the two-fold rotation axis. The four atoms of C(1), O(1), N(1), and N(1)′ lie on the same plane. The least-squares plane formed by the seven atoms of O(2), C(2), C(3), C(4), N(1), N(2), and N(3) intercepts another least-squares plane formed by seven symmetric atoms (O(2)′, C(2)′, C(3)′, C(4)′, N(1)′, N(2)′, and N(3)′) at

Table 1. Final Atomic Parameters (Positional ×10^4) and Equivalent Isotropic Thermal Parameters (B_{eq}×10), with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2
Cu	0	0	2203(3)	23(1)
Cl	290(2)	1902(2)	1035(6)	39(1)
O(1)	5000(0)	0	6048(14)	38(4)
O(2)	1388(4)	−253(6)	3468(11)	29(3)
N(1)	4343(5)	761(7)	2775(13)	13(3)
N(2)	2665(6)	1112(8)	4366(14)	29(3)
N(3)	2823(4)	−150(8)	1200(12)	25(3)
C(1)	5000(0)	0	4028(18)	22(4)
C(2)	3710(7)	1636(8)	3991(19)	28(4)
C(3)	3858(6)	350(10)	678(15)	31(3)
C(4)	2258(6)	235(7)	3007(15)	22(3)
C(5)	2006(8)	1741(11)	5978(19)	39(5)
C(6)	2400(8)	−1030(10)	−402(18)	31(4)

Table 2. Selected Bond Lengths and Bond Angles, with Their Estimated Standard Deviations in Parentheses

Bond		Bond	
length	l/Å	angle	ϕ/°
O(1)-C(1)	1.213(3)	O(1)-C(1)-N(1)	122.6(5)
C(1)-N(1)	1.397(9)	C(1)-N(1)-C(2)	116.9(8)
N(1)-C(2)	1.445(12)	C(1)-N(1)-C(3)	122.3(8)
N(1)-C(3)	1.473(12)	C(2)-N(1)-C(3)	113.3(7)
C(2)-N(2)	1.468(10)	N(1)-C(2)-N(2)	109.4(7)
C(3)-N(3)	1.463(9)	N(1)-C(3)-N(3)	108.0(7)
N(2)-C(4)	1.357(12)	C(2)-N(2)-C(4)	121.9(8)
N(2)-C(5)	1.453(14)	C(2)-N(2)-C(5)	116.5(8)
N(3)-C(4)	1.368(11)	C(4)-N(2)-C(5)	120.5(8)
N(3)-C(6)	1.459(13)	C(3)-N(3)-C(4)	122.2(8)
C(4)-O(2)	1.261(9)	C(3)-N(3)-C(6)	115.8(7)
Cu-Cl	2.211(3)	C(4)-N(3)-C(6)	121.8(7)
Cu-O(2)	1.948(6)	N(2)-C(4)-O(2)	120.0(8)
		N(3)-C(4)-O(2)	120.7(8)
		N(2)-C(4)-N(3)	119.3(7)
		N(1)-C(1)-N(1)′	114.8(8)
		Cl-Cu-Cl′	143.0(1)
		Cl-Cu-O(2)	98.3(2)
		Cl-Cu-O(2)″[a]	95.9(2)
		O(2)-Cu-O(2)″[a]	134.1(3)

a) O(2)″ is the O(2)′ atom in the adjacent molecule.

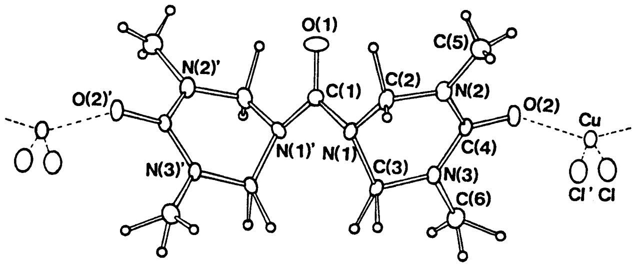

Fig. 1. A view of the molecular structure of the complex with 5,5′-carbonylbis[1,3-dimethyl-3,4,5,6-tetrahydro-1,3,5-triazin-2(1*H*)-one] and copper(II) chloride with the numbering scheme.

the angle of 148°. The Cu^{2+} ion is not located between the two ring structures of 1,3-dimethyl-3,4,5,6-tetrahydro-1,3,5-triazin-2(1*H*)-one in the same molecule; it coordinates intermolecularly to two oxygen atoms (O(2) and O(2)′ in the adjacent molecule).

The observed interatomic distance of Cu-O(2) (1.948 Å) was shorter than that of 2.71—2.75 Å of Cu-O in the complex with 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane and copper(II) chloride.[8] Furthermore, it was shorter than the value of 2.12 Å which was estimated by considering the van der Waals radius of the oxygen atom and the ionic radius of Cu^{2+}. These results suggest a strong interaction between Cu^{2+} and O(2).

The bond lengths for the carbonyl groups of C(1)-O(1) and C(4)-O(2) were 1.213 and 1.216 Å respectively. While C(1)-O(1) has a strong double-bond character, C(4)-O(2) is intermediate between single and double bonds. The resonated structures of $\mathrm{N{-}\underset{\underset{\textstyle O^-}{|}}{C}{=}N^+}$ and $\mathrm{N^+{=}\underset{\underset{\textstyle O^-}{|}}{C}{-}N}$ make a larger contribution to N(2)-C(4)O(2)-N(3) than to N(1)′-C(1)O(1)-N(1), partly because of the effect of the two methyl groups and partly because of the stabilization of the anionic structure of O(2) by the coordination to Cu^{2+}.

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References

1) T. Ebisuno, M. Takimoto, M. Takahashi, and R. Shiba, *Bull. Chem. Soc. Jpn.*, **61**, 2191 (1988).

2) T. Ebisuno, M. Takimoto, M. Takahashi, and R. Shiba, *Bull. Chem. Soc. Jpn.*, **61**, 4441 (1988).

3) P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, MULTAN 78. "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data," Universities of York, England, and Louvain, Belgium (1978).

4) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham (1974), Vol. IV.

5) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku,* **55**, 69 (1979).

6) W. C. Hamilton, *Acta Crystallogr.*, **12**, 609 (1959).

7) The coordinates and isotropic thermal parameters of H atoms, the anisotropic thermal parameters of non-H atoms, and the F_o—F_c tables have been deposited as Document No. 8857 at the Office of the Editor.

8) M. Herceg and R. Weiss, *Acta Crystallogr., Sect. B,* **29**, 542 (1973).