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MOLECULAR AND CRYSTAL STRUCTURE OF 3,7-DI(2-PROPENYL)-1,5-DIPHENYL-3,7-DIAZABICYCLO[3.3.1]-NONAN-9-ONE COMPLEXED WITH COPPER(II) CHLORIDE*

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We have investigated the molecular and crystal structure of 3,7-di(2-propenyl)-1,5-diphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one complexed with copper(II) chloride. We have shown for the first time that the reason for the distortion of the coordination polyhedron of the metal is the interaction of the substituents at the nitrogen atoms with the halogen atoms.

Derivatives of 3,7-diazabicyclo[3.3.1]nonane (bispidines), structural analogs of the natural alkaloids in the lupine series, display various types of physiological activity, which is explained by the ability of these compounds to form stable complexes with many metals [2-7]. The coordination characteristics of such complexes involve the fact that the ligand forms a stable diazametallocyclic structure of the adamantane type with the metal ion [8, 9]. In this case, we may expect that complexes formed with metal ions of different sizes will have substantially different stability constants; this is supported by the data in [10, 11].

In this paper, we have investigated the spectral and structural characteristics of complex compound I, obtained according to the modified technique in [10] using anhydrous copper(II) chloride and 3,7-di(2-propenyl)-1,5-diphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one [12]. Compound I, recrystallized from ethanol, is a bright green crystalline material with melting point 162-164°C (with decomposition). In the IR spectrum of compound I, the absorption band of the carbonyl group appears at 1750 cm^{-1} and, compared with the original bispidone, is shifted 25 cm^{-1} toward the short-wavelength region. This shift is observed for all the complex compounds of bispidones with copper ions that we studied, and can serve as a test for their formation [13].

The crystals of compound I are monoclinic: at −80°C, $a = 15.496(3)$, $b = 20.334(4)$, $c = 15.334(5)$ Å, $\beta = 90.34(2)°$, $V = 4832(4)$ Å^3, $Z = 8$, $d_{calc} = 1.39$ g/cm^3, space group $P2_1/c$. The cell parameters and the intensities of 3671 reflections with $I > 3\sigma$ (I) were measured on a Syntex $P2_1$ automatic diffractometer (λMoKa, $2\theta/\theta$ scanning, $\theta < 26°$). The structure was deciphered by the Patterson method. The hydrogen atoms were located from an electron density difference synthesis. The structure was refined in the anisotropic approximation (isotropic for the hydrogen atoms) down to $R = 0.038$, $R_w = 0.038$. The coordinates for the atoms of the two crystallographically independent basis molecules A and B are presented in Table 1. The bond lengths and bond angles are given in Tables 2 and 3.

A perspective view of one of the basis molecules of complex I with the numbering scheme for the atoms is shown in Fig. 1. The average value of the bond lengths in the bicyclic skeleton of the molecule is: for C_{sp3}—C_{sp3}, 1.542(7) Å; for C_{sp3}—C_{sp3}, 1.534(8) Å; and for C_{sp3}—N, 1.486(7) Å. These match their statistical mean values in [14] within experimental accuracy. The average value of the Cu—N and Cu—Cl bond lengths is 2.011(4) Å and 2.225(4) Å, which are shorter than the statistical mean values in [15] by 0.04 Å and 0.02 Å respectively.

In Fig. 2, we show a projection of one of the basis molecules onto the $C_{(2)}C_{(4)}C_{(6)}C_{(8)}$ plane. The coordination environment of the copper atom is a distorted tetrahedron. The angles between the N—Cu—N and Cl—Cu—Cl planes are equal

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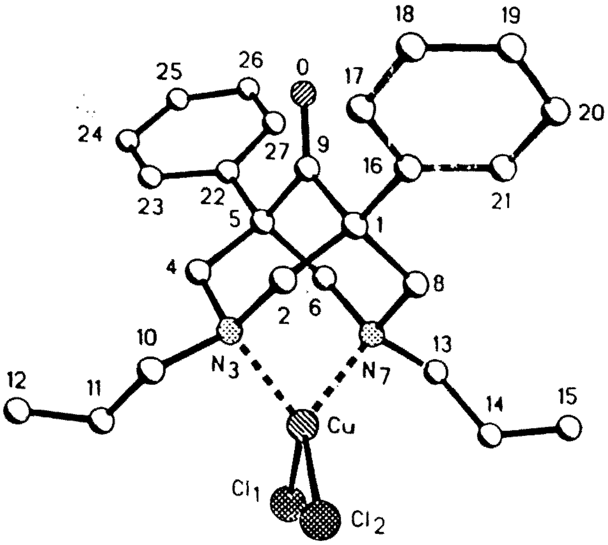

Fig. 1. Perspective view of one of the basis molecules of I.

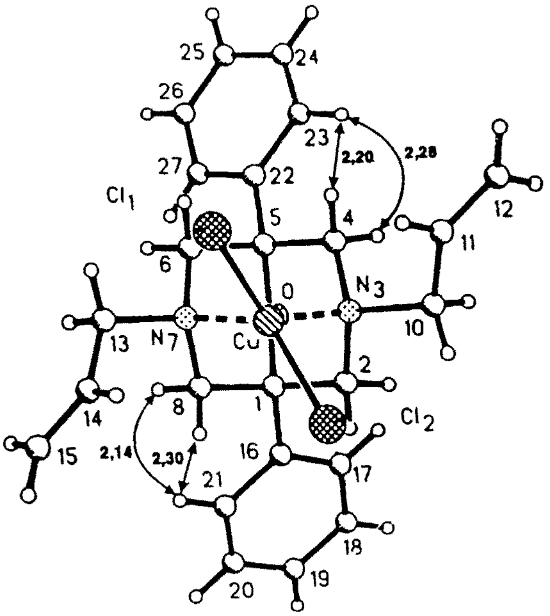

Fig. 2. Projection of one of the basis molecules of I onto the $C_{(2)}C_{(4)}C_{(6)}C_{(8)}$ plane (the distances from the hydrogen atoms of the skeleton to the nearest hydrogen atoms of the phenyl groups are indicated).

to 62.7° and 62.6° in molecules A and B, which suggests large distortion of the coordination polyhedron of the metal compared with the 3,7-dimethyl analog, where this value is 82.0° [9]. If we consider the undistorted structure, the distance between the halogen atoms and the 11-H and 14-H atoms should be significantly less than the sum of the van der Waals radii. Consequently, this effect may be explained by interaction between the chlorine atoms and the substituents on the nitrogen atoms. Obviously, introduction of one more alkyl group to each of the $C_{(10)}$ and $C_{(13)}$ atoms considerably hinders formation of such complexes. In fact, we could detect the copper chloride complex of 3,7-diisopropyl-1,5-diphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one only in solution (by cyclic voltammetry) [13].

TABLE 1. Coordinates of Nonhydrogen Atoms ($\times 10^4$) of Crvstallographically Independent Molecules A and B

Atom	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Cu	9298,1(4)	8183,2(3)	553,7(4)	4324,3(4)	8131,5(3)	312,2(4)
$Cl_{(1)}$	9225(1)	7775,5(8)	1895(1)	4340(1)	7493,2(8)	-880,1(9)
$Cl_{(2)}$	8211(1)	8899,5(8)	487(1)	3174(1)	8761,5(8)	130(1)
O	11370(3)	7715(2)	-2036(2)	6436(3)	7906(2)	2956(3)
$N_{(3)}$	9221(3)	7791(2)	-656(3)	4240(3)	7888(2)	1587(3)
$N_{(7)}$	10580(3)	8263(2)	390(3)	5596(3)	8251(2)	490(3)
$C_{(1)}$	10458(4)	8478(3)	-1243(3)	5751(4)	7410(3)	1685(3)
$C_{(2)}$	9486(3)	8313(3)	-1285(3)	4781(3)	7292(3)	1754(3)
$C_{(4)}$	9773(3)	7193(3)	-739(3)	4517(3)	8453(3)	2139(3)
$C_{(5)}$	10738(3)	7327(3)	-692(3)	5497(4)	8595(3)	2081(3)
$C_{(6)}$	11002(3)	7630(3)	205(3)	5771(4)	8776(3)	1143(3)
$C_{(8)}$	10741(4)	8731(3)	-337(3)	6018(4)	7636(3)	765(3)
$C_{(9)}$	10940(4)	7833(3)	-1409(3)	5968(4)	7967(3)	2328(3)
$C_{(10)}$	8304(4)	7589(3)	-854(3)	3326(3)	7718(3)	1809(4)
$C_{(11)}$	8002(4)	7090(3)	-218(4)	2983(4)	7178(3)	1255(4)
$C_{(12)}$	7645(4)	6521(4)	-430(4)	2567(4)	6656(3)	1535(4)
$C_{(13)}$	11006(4)	8532(3)	1202(3)	6006(4)	8461(3)	-367(4)
$C_{(14)}$	10628(4)	9166(3)	1513(4)	5566(4)	9057(3)	-737(4)
$C_{(15)}$	11056(5)	9718(3)	1545(4)	5974(6)	9620(4)	-806(5)
$C_{(16)}$	10663(3)	8984(3)	-1960(3)	6266(4)	6778(3)	1875(3)
$C_{(17)}$	10407(4)	8865(3)	-2812(3)	5855(4)	6167(3)	1899(4)
$C_{(18)}$	10585(4)	9314(3)	-3474(4)	6337(5)	5592(3)	2045(4)
$C_{(19)}$	11038(4)	9881(3)	-3290(4)	7219(5)	5636(4)	2184(4)
$C_{(20)}$	11295(4)	10008(3)	-2451(4)	7625(5)	6237(3)	2159(4)
$C_{(21)}$	11119(4)	9566(3)	-1791(4)	7158(4)	6804(3)	2006(3)
$C_{(22)}$	11269(4)	6695(3)	-788(3)	5714(4)	9161(3)	2710(4)
$C_{(23)}$	10893(4)	6071(3)	-807(4)	5538(4)	9083(3)	3593(4)
$C_{(24)}$	11402(4)	5512(3)	-792(4)	5729(4)	9585(3)	4180(4)
$C_{(25)}$	12291(4)	5565(3)	-778(4)	6079(5)	10169(4)	3894(5)
$C_{(26)}$	12673(4)	6179(3)	-812(4)	6249(5)	10249(4)	3024(5)
$C_{(27)}$	12168(4)	6737(3)	-827(3)	6063(4)	9750(3)	2438(4)

TABLE 2. Bond Lengths (Å)

l	A	Б	*l*	A	Б
$Cu—Cl_{(1)}$	2,221(2)	2,242(2)	$C_{(5)}—C_{(22)}$	1,534(8)	1,536(8)
$Cu—Cl_{(2)}$	2,228(2)	2,212(2)	$C_{(10)}—C_{(11)}$	1,483(8)	1,484(8)
$Cu—N_{(3)}$	2,022(4)	2,021(4)	$C_{(11)}—C_{(12)}$	1,322(9)	1,316(8)
$Cu—N_{(7)}$	2,010(4)	2,003(4)	$C_{(13)}—C_{(14)}$	1,495(8)	1,500(9)
$O—C_{(9)}$	1,197(7)	1,209(7)	$C_{(14)}—C_{(15)}$	1,304(9)	1,31(1)
$N_{(3)}—C_{(2)}$	1,494(7)	1,495(7)	$C_{(16)}—C_{(17)}$	1,385(7)	1,398(8)
$N_{(3)}—C_{(4)}$	1,491(7)	1,489(7)	$C_{(16)}—C_{(21)}$	1,402(8)	1,396(8)
$N_{(3)}—C_{(10)}$	1,509(7)	1,499(7)	$C_{(17)}—C_{(18)}$	1,394(8)	1,403(9)
$N_{(7)}—C_{(6)}$	1,472(7)	1,487(7)	$C_{(18)}—C_{(19)}$	1,378(9)	1,38(1)
$N_{(7)}—C_{(8)}$	1,489(6)	1,471(7)	$C_{(19)}—C_{(20)}$	1,369(9)	1,38(1)
$N_{(7)}—C_{(13)}$	1,509(7)	1,524(7)	$C_{(20)}—C_{(21)}$	1,383(9)	1,380(9)
$C_{(1)}—C_{(2)}$	1,544(8)	1,527(7)	$C_{(22)}—C_{(23)}$	1,396(8)	1,393(8)
$C_{(1)}—C_{(8)}$	1,542(7)	1,543(7)	$C_{(22)}—C_{(27)}$	1,398(8)	1,380(8)
$C_{(1)}—C_{(9)}$	1,532(8)	1,536(7)	$C_{(23)}—C_{(24)}$	1,384(9)	1,392(9)
$C_{(1)}—C_{(16)}$	1,540(7)	1,539(8)	$C_{(24)}—C_{(25)}$	1,38(1)	1,38(1)
$C_{(4)}—C_{(5)}$	1,521(8)	1,550(8)	$C_{(25)}—C_{(26)}$	1,383(9)	1,37(1)
$C_{(5)}—C_{(6)}$	1,560(7)	1,546(7)	$C_{(26)}—C_{(27)}$	1,379(9)	1,38(1)
$C_{(5)}—C_{(9)}$	1,539(7)	1,519(8)			

TABLE 3. Bond Angles (degrees)

ω	A	B	ω	A	B
$Cl_{(1)}CuCl_{(2)}$	104,1(1)	104,2(1)	$C_{(4)}C_{(5)}C_{(22)}$	111,9(4)	108,4(4)
$Cl_{(1)}CuN_{(3)}$	134,4(1)	130,4(1)	$C_{(6)}C_{(5)}C_{(22)}$	106,1(4)	110,2(4)
$Cl_{(2)}CuN_{(3)}$	100,1(1)	102,0(1)	$C_{(9)}C_{(5)}C_{(22)}$	112,3(4)	111,7(4)
$Cl_{(1)}CuN_{(7)}$	101,7(1)	99,6(1)	$N_{(7)}C_{(6)}C_{(5)}$	113,6(4)	113,9(4)
$Cl_{(2)}CuN_{(7)}$	133,5(1)	137,6(1)	$N_{(7)}C_{(8)}C_{(1)}$	114,4(4)	113,2(4)
$N_{(3)}CuN_{(7)}$	88,3(2)	88,1(2)	$OC_{(9)}C_{(1)}$	125,4(5)	124,3(5)
$CuN_{(3)}C_{(2)}$	107,3(3)	108,9(3)	$OC_{(9)}C_{(5)}$	123,8(5)	124,7(5)
$CuN_{(3)}C_{(4)}$	111,7(3)	109,9(3)	$C_{(1)}C_{(9)}C_{(5)}$	110,6(4)	110,9(4)
$C_{(2)}N_{(3)}C_{(4)}$	111,4(4)	111,7(4)	$N_{(3)}C_{(10)}C_{(11)}$	110,7(4)	112,1(4)
$CuN_{(3)}C_{(10)}$	110,0(3)	110,1(3)	$C_{(10)}C_{(11)}C_{(12)}$	124,7(5)	125,7(5)
$C_{(2)}N_{(3)}C_{(10)}$	109,0(4)	107,6(4)	$N_{(7)}C_{(13)}C_{(14)}$	113,9(4)	111,2(5)
$C_{(4)}N_{(3)}C_{(10)}$	107,5(4)	108,6(4)	$C_{(13)}C_{(14)}C_{(15)}$	123,6(6)	121,1(6)
$CuN_{(7)}C_{(6)}$	113,2(3)	110,7(3)	$C_{(1)}C_{(16)}C_{(17)}$	119,8(5)	120,8(5)
$CuN_{(7)}C_{(8)}$	108,4(3)	111,8(3)	$C_{(1)}C_{(16)}C_{(21)}$	122,5(5)	120,5(5)
$C_{(6)}N_{(7)}C_{(8)}$	109,7(4)	109,8(4)	$C_{(17)}C_{(16)}C_{(21)}$	117,6(5)	118,7(5)
$CuN_{(7)}C_{(13)}$	110,8(3)	109,3(3)	$C_{(16)}C_{(17)}C_{(18)}$	121,0(6)	120,2(6)
$C_{(6)}N_{(7)}C_{(13)}$	106,5(4)	107,7(4)	$C_{(17)}C_{(18)}C_{(19)}$	120,2(6)	119,7(6)
$C_{(8)}N_{(7)}C_{(13)}$	108,1(4)	107,4(4)	$C_{(18)}C_{(19)}C_{(20)}$	119,7(6)	120,2(7)
$C_{(2)}C_{(1)}C_{(8)}$	112,5(4)	112,3(4)	$C_{(19)}C_{(20)}C_{(21)}$	120,5(6)	120,5(6)
$C_{(2)}C_{(1)}C_{(9)}$	106,5(4)	106,4(4)	$C_{(16)}C_{(21)}C_{(20)}$	121,0(5)	120,7(6)
$C_{(8)}C_{(1)}C_{(9)}$	107,4(4)	108,0(4)	$C_{(5)}C_{(22)}C_{(23)}$	122,7(5)	118,7(5)
$C_{(2)}C_{(1)}C_{(16)}$	108,7(4)	111,4(4)	$C_{(5)}C_{(22)}C_{(27)}$	119,2(5)	123,0(5)
$C_{(8)}C_{(1)}C_{(16)}$	111,2(4)	106,3(4)	$C_{(23)}C_{(22)}C_{(27)}$	118,0(5)	118,2(5)
$C_{(9)}C_{(1)}C_{(16)}$	110,6(4)	112,5(4)	$C_{(22)}C_{(23)}C_{(24)}$	120,6(6)	120,1(6)
$N_{(3)}C_{(2)}C_{(1)}$	113,5(4)	114,3(4)	$C_{(23)}C_{(24)}C_{(25)}$	120,3(6)	120,7(6)
$N_{(3)}C_{(4)}C_{(5)}$	114,4(4)	113,0(4)	$C_{(24)}C_{(25)}C_{(26)}$	119,8(6)	119,3(7)
$C_{(4)}C_{(5)}C_{(6)}$	111,5(4)	111,9(4)	$C_{(25)}C_{(26)}C_{(27)}$	120,0(6)	120,3(7)
$C_{(4)}C_{(5)}C_{(9)}$	106,9(4)	107,4(4)	$C_{(22)}C_{(27)}C_{(26)}$	121,0(5)	121,4(6)
$C_{(6)}C_{(5)}C_{(9)}$	108,3(4)	107,3(4)			

The indicated interactions may be decreased by flattening the "wings" of the bicyclic skeleton, but the presence of phenyl groups in the 1 and 5 positions prevents this. The orientation of the phenyl rings relative to the bicyclic skeleton of the molecule is rigidly fixed by H-H interactions. The distances from the 21-H and 23-H atoms to the nearest hydrogen atoms of the skeleton of the molecule are indicated in Fig. 2. According to the data in [16], the length of the "normal" nonvalence H-H contact is equal to 2.31 Å; i.e., the phenyl hydrogen atoms 21-H and 23-H are clamped between the hydrogen atoms at $C_{(4)}$ and $C_{(8)}$.

Thus our investigation shows that the structure of complexes of 3,7-dialkyl-1,5-diphenyl-3,7-diazabicyclo[3.3.1]nonan-9-ones is substantially affected by the degree of branching of the substituent on the nitrogen atom. Consequently, variation of the alkyl substituents should affect the selectivity of formation and the stability of complexes with different metals. Further investigations in this direction will help us clarify the mechanism of the physiological action of 3,7-diazabicyclo[3.3.1]nonanes.

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