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CRYSTAL STRUCTURE OF THE COPPER COMPLEX OF THE SCHIFF BASE FROM 1-(*N,N*-DIMETHYLAMINOMETHYL)-2-FORMYLCYMANTRENE AND (*S*)-ALANYL-(*S*)-ALANINE

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Summary

The mechanism of stereoselective syntheses of amino acids via glycine Schiff base/metal complexes is discussed on the basis of data from the X-ray structure determination of $(OC)_3Mn[\eta^5\text{-}C_5H_3(CH_2NMe_2)(CHNCHMeC(O)N\text{—}CHMeCOO)Cu]$. The absolute configuration of the latter complex is *S* (the Mn and Cu atoms are *trans* with respect to the Cp plane).

Introduction

Synthesis of racemic amino acids by *C*-alkylation of glycine in metal complexes of its Schiff bases is a well-established procedure [1]. Recently, we reported on the asymmetric synthesis of threonine by hydroxyethylation of the *N*-terminal glycine fragment in the mixed Cu^{II} complex of (*S*)- and (*R*)-1-(*N,N*-dimethylaminomethyl)-2-formylcymantrene (AFCMT) * with GlyGly according to Scheme 1 [3]. The enantiomeric excess of threonine formed according to this Scheme is 92 to 98%.

For a better understanding of the origin of such a considerable enantioselective effect in this reaction, it was necessary to carry out an X-ray structural study of at least one copper complex of chiral AFCMT with a dipeptide.

In the present paper we report on the results of the X-ray study of the Cu^{II} complex of 1-(*N,N*-dimethylaminomethyl)-2-formylcymantrene Schiff base with (*S*)-alanyl-(*S*)-alanine[(*S*)-AFCMT-((*S*)-Ala-(*S*)-Ala)Cu^{II}] and suggest some

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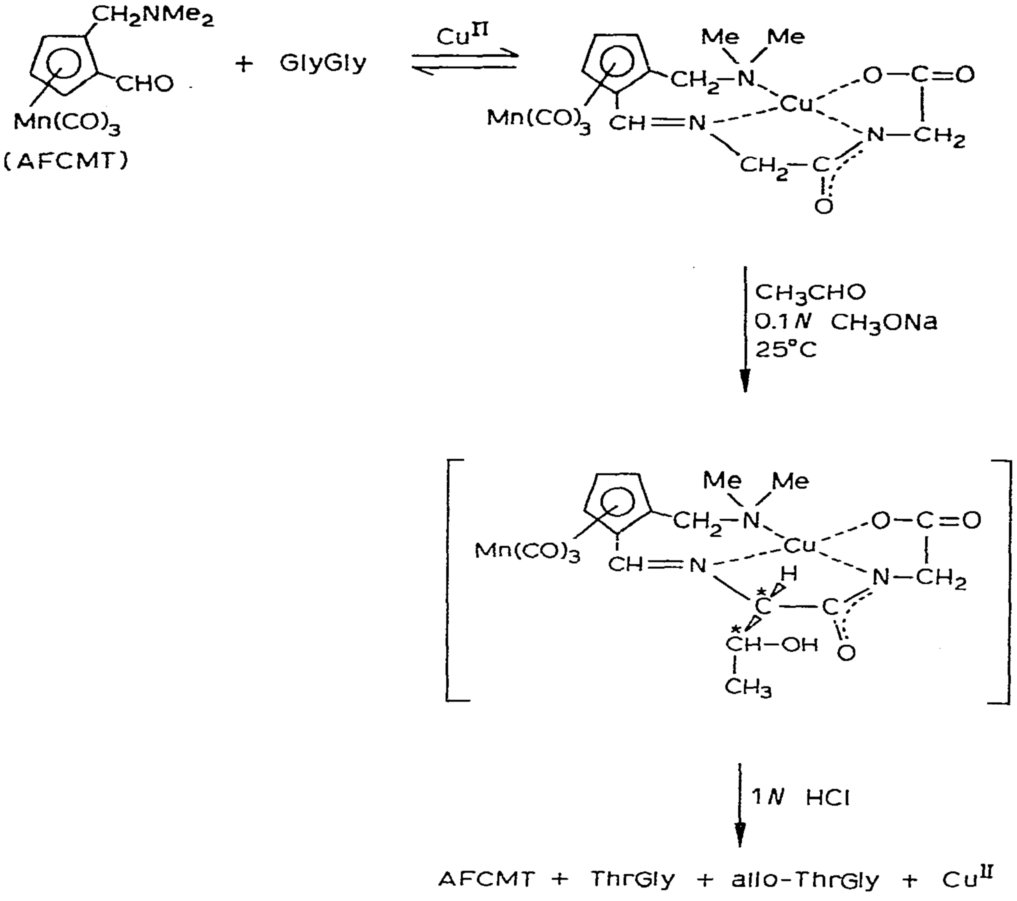
* Here and below the notation of the absolute configuration of AFCMT is given in accordance with ref. 2.



ideas concerning the origin of the strong enantioselective effects in the series of similar Cu^{II} complexes of (*S*)- and (*R*)-AFCMT with dipeptides.

Experimental

Crystals of the studied complex $(CO)_3Mn[\eta^5\text{-}C_6H_3(CH_2NMe_2)(CHNCHMeC(O)N{-}CHMeCOO)Cu]$ (I) are monoclinic. At 20°C $a = 9.712(2)$, $b = 22.286(4)$, $c = 9.5017(7)$ Å, $\beta = 94.44(2)^\circ$, $V = 2050.3(9)$ Å^3, $d_{meas} = 1.54$, $d_{calc} = 1.55$ g/cm^{-3}, $Z = 4$, space group $P2_1$, two molecules in the asymmetric unit.

Unit cell parameters and intensities of reflections were measured with a Hilger and Watts four-circle automatic diffractometer (λ Cu-K_α, graphite monochromator, $2^\circ \leqslant 2\theta \leqslant 130^\circ$, $\theta/2\theta$-scan, 1760 independent reflections with $|F|^2 \geqslant 3\sigma$). The structure was solved by the heavy atom method and refined by the least-square method in full-matrix anisotropic approximation. Hydrogen atoms were included in refinement with fixed positional parameters (from the difference synthesis) and temperature parameters (assumed $B_{iso} = 5.0$ Å^2). All calculations were carried out with a Eclipse S/200 minicomputer, using EXTL-programs modified by us. The final discrepancy factors are $R = 0.0743$, $R_G =$

0.0774. Complex I has the absolute configuration (*S*)-AFCMT((*S*)-Ala-(*S*)-Ala)-Cu^{II}, as determined by the Hamilton test [4], taking into account anomalous corrections for Cu and Mn atoms (for the inverted structure R = 0.0880, R_G = 0.0910).

TABLE 1

FINAL ATOMIC PARAMETERS (X 10^3, FOR Cu AND Mn X 10^4)

Atoms	Molecule A			Molecule B		
	x	*y*	*z*	*x*	*y*	*z*
Cu	3978(2)	0	8688(2)	3045(2)	1452(1)	13642(2)
Mn	6572(3)	—801(1)	4440(3)	614(3)	2293(1)	8999(3)
O(1)	407(1)	36(1)	1060(1)	296(1)	109(1)	1555(1)
O(2)	283(1)	49(0)	1245(1)	420(1)	94(1)	1758(1)
O(3)	—10(1)	—27(1)	807(1)	712(1)	170(1)	1353(1)
O(4)	454(2)	—140(1)	241(2)	—155(2)	291(1)	717(2)
O(5)	893(2)	—116(1)	296(2)	285(1)	264(1)	724(2)
O(6)	685(2)	—191(1)	603(2)	112(2)	336(1)	1073(2)
N(1)	216(1)	—15(1)	900(1)	487(1)	156(1)	1423(1)
N(2)	327(1)	—35(1)	677(1)	369(1)	175(1)	1177(1)
N(3)	602(1)	—17(1)	886(1)	100(1)	160(1)	1349(1)
C(1)	292(1)	32(1)	1124(2)	410(2)	113(1)	1632(2)
C(2)	172(1)	3(1)	1046(1)	535(1)	141(1)	1569(2)
C(3)	122(2)	—55(1)	1125(2)	587(2)	196(1)	1664(2)
C(4)	118(1)	—29(1)	806(2)	587(1)	167(1)	1335(2)
C(5)	180(1)	—45(1)	665(2)	521(2)	184(1)	1187(2)
C(6)	154(2)	—116(1)	652(3)	547(2)	251(1)	1157(2)
C(7)	381(2)	—28(1)	553(2)	311(2)	166(1)	1051(2)
C(8)	524(1)	—17(1)	535(2)	171(2)	161(1)	1012(2)
C(9)	568(2)	7(1)	404(1)	116(2)	139(1)	871(1)
C(10)	717(2)	15(1)	419(2)	—24(2)	140(1)	863(2)
C(11)	760(1)	—9(1)	561(2)	—66(2)	162(1)	997(2)
C(12)	644(1)	—27(1)	626(2)	56(1)	176(1)	1085(2)
C(13)	653(2)	—55(1)	770(2)	55(2)	204(1)	1233(2)
C(14)	627(2)	—57(2)	1020(2)	61(2)	194(1)	1482(2)
C(15)	690(2)	40(1)	901(2)	14(2)	104(1)	1338(2)
C(16)	535(2)	—117(1)	318(2)	—69(2)	269(1)	793(2)
C(17)	795(2)	—103(1)	351(2)	196(2)	251(1)	789(2)
C(18)	673(2)	—148(1)	543(2)	90(2)	287(1)	1000(2)
H(2)	92	33	1039	618	113	1568
H(31)	209	—72	1142	484	213	1664
H(32)	87	—44	1234	667	221	1634
H(33)	42	—75	1072	608	182	1778
H(5)	140	—20	583	563	156	1122
H(61)	225	—140	714	481	263	1079
H(62)	154	—129	552	538	283	1241
H(63)	59	—125	686	644	255	1130
H(7)	315	—30	466	375	162	969
H(9)	505	17	316	172	124	793
H(10)	777	33	350	—91	130	780
H(11)	856	—11	603	—162	167	1026
H(131)	752	—67	797	—41	220	1245
H(132)	597	—94	756	118	240	1237
H(141)	583	—101	1001	—53	206	1466
H(142)	719	—42	1031	92	233	1482
H(143)	590	—60	1117	93	167	1565
H(151)	652	68	998	—75	117	1336
H(152)	772	31	893	31	83	1250
H(153)	679	71	820	34	75	1416

TABLE 2

PARAMETERS OF ANISOTROPIC TEMPERATURE FACTORS IN THE FORM $T = \exp[-1/4(B_{11}h^2a^{*2} + ... + 2B_{23}klb^*c^*)]$

Atom	Molecule A						Molecule B					
	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1,56(7)	3.3(1)	2,28(9)	0,08(9)	0,32(6)	−0,60(9)	1,89(8)	3,2(1)	2,48(9)	−0,20(9)	0,26(7)	0,37(9)
Mn	2,8(1)	2,4(1)	2,1(1)	0,17(9)	0,47(8)	−0,14(9)	3,4(1)	2,3(1)	2,6(1)	−0,2(1)	0,03(9)	0,2(1)
O(1)	1,9(4)	4,0(6)	2,7(5)	0,2(4)	0,0(4)	−0,6(4)	1,7(4)	3,4(5)	3,9(6)	0,0(4)	0,0(4)	0,6(5)
O(2)	3,7(5)	2,4(5)	1,2(4)	0,2(4)	0,4(4)	−0,9(4)	4,1(6)	4,3(6)	1,2(4)	−0,3(5)	−0,4(4)	0,9(4)
O(3)	1,8(4)	8,6(9)	2,6(6)	0,0(5)	−0,5(4)	−2,0(6)	1,7(4)	5,0(7)	5,1(7)	0,7(5)	0,8(4)	0,5(5)
O(4)	6,6(9)	5,6(8)	5,3(8)	−1,9(7)	−2,6(7)	0,0(7)	7,7(9)	5,4(8)	9(1)	2,6(8)	−4,1(8)	0,4(8)
O(5)	5,6(8)	5,2(8)	10(1)	−0,8(7)	4,9(8)	−0,9(8)	5,1(7)	4,3(7)	7,0(9)	0,6(6)	3,0(6)	1,5(6)
O(6)	14(1)	2,6(6)	5,8(9)	2,1(8)	1,5(9)	1,2(6)	14(1)	2,7(6)	5,1(8)	−1,6(8)	−0,3(9)	−0,4(6)
N(1)	2,6(6)	3,5(7)	3,8(7)	−0,2(5)	−1,9(5)	0,8(6)	4,5(7)	2,7(6)	2,9(6)	0,0(6)	2,3(5)	0,1(5)
N(2)	2,6(6)	2,1(6)	2,2(6)	0,5(5)	1,0(4)	−0,2(5)	2,1(5)	2,9(6)	2,5(6)	0,0(5)	−0,4(5)	0,6(5)
N(3)	4,3(6)	4,2(6)	0,2(6)	0,5(6)	0,0(6)	0,0(6)	2,9(6)	4,4(7)	1,4(5)	1,0(6)	−0,3(4)	−1,0(5)
C(1)	1,7(6)	1,2(6)	3,1(8)	0,5(5)	−0,2(5)	0,0(6)	1,7(6)	2,8(8)	4,8(9)	0,8(6)	0,1(6)	−1,0(7)
C(2)	2,0(6)	3,1(7)	1,8(6)	−0,3(6)	0,4(5)	0,4(6)	2,1(6)	3,6(8)	2,3(7)	−1,2(6)	−0,3(5)	1,5(7)
C(3)	6(1)	5(1)	3,5(9)	−3,2(9)	1,0(8)	0,7(8)	4,3(9)	5(1)	3,8(9)	−1,7(8)	0,2(8)	−0,4(8)
C(4)	1,8(6)	4,3(8)	1,5(7)	−0,4(6)	0,2(5)	0,3(6)	1,0(5)	3,6(8)	3,6(8)	0,4(6)	−0,2(5)	−0,8(7)
C(5)	1,6(6)	4,4(9)	2,6(8)	0,5(6)	0,7(5)	−1,0(7)	3,3(8)	3,7(9)	3,3(9)	−0,6(7)	1,1(7)	−0,2(7)
C(6)	4,0(9)	8(1)	10(1)	−4(1)	3(1)	−5(1)	4,7(9)	4,1(9)	8(1)	−1,7(8)	0,6(9)	3,1(9)
C(7)	3,7(8)	2,8(8)	3,5(9)	1,5(7)	−1,1(7)	0,1(7)	4,1(8)	1,2(6)	4,2(9)	0,3(6)	0,7(7)	1,0(6)
C(8)	2,0(6)	1,3(6)	2,4(7)	−0,1(5)	−0,2(5)	−0,3(5)	2,9(6)	1,8(7)	1,9(7)	−0,2(5)	0,7(5)	−0,4(5)
C(9)	4,4(8)	2,9(8)	1,3(6)	1,0(7)	−0,5(5)	−0,3(6)	3,4(7)	2,8(8)	1,6(7)	−0,4(7)	0,3(5)	0,2(6)
C(10)	5,1(9)	2,0(7)	3,5(9)	0,9(7)	0,5(7)	−0,1(6)	5,7(9)	2,5(8)	3,5(9)	0,1(8)	−0,4(7)	−1,7(7)
C(11)	1,8(6)	2,3(7)	3,4(7)	0,0(5)	0,0(5)	0,6(6)	2,2(7)	3,9(9)	4,8(9)	0,3(7)	0,7(7)	0,7(8)
C(12)	2,2(6)	1,3(6)	3,9(8)	−0,2(5)	0,5(6)	0,3(6)	1,8(6)	2,5(7)	2,6(7)	−0,3(5)	−0,3(5)	0,0(6)
C(13)	2,8(7)	2,4(7)	1,8(7)	1,4(6)	0,0(5)	−1,1(6)	4,3(9)	3,6(8)	2,0(7)	−0,7(7)	0,8(6)	−0,2(7)
C(14)	6(1)	8(1)	2,1(8)	2(1)	0,7(8)	2,4(9)	5,2(9)	5,1(9)	1,6(7)	1,8(8)	0,5(7)	−0,3(7)
C(15)	4,0(9)	3,7(9)	5(1)	−0,9(7)	0,5(8)	−0,9(8)	3,5(7)	2,5(7)	3,0(8)	−1,0(6)	0,5(6)	−0,1(6)
C(16)	4,3(9)	3,6(9)	5(1)	0,3(8)	0,1(8)	1,6(8)	2,9(8)	3,6(9)	7(1)	−0,5(7)	−1,8(8)	−0,7(9)
C(17)	2,9(8)	2,3(8)	7(1)	−0,4(7)	2,3(8)	0,3(8)	4,3(9)	1,8(8)	8(1)	0,5(7)	1,2(9)	−0,4(8)
C(18)	6(1)	4,1(9)	1,1(7)	1,1(8)	1,3(7)	−1,3(6)	9(1)	2,2(8)	2,2(8)	−0,9(9)	−1,9(8)	0,7(6)

TABLE 3

BOND DISTANCES (Å) IN MOLECULES A AND B

Bond	A	B	Average	Bond	A	B	Average
Cu—O(1)	1.99(1)	1.99(1)	1.99(1)	C(4)—O(3)	1.24(2)	1.21(2)	1.23(2)
Cu—N(1)	1.84(1)	1.84(1)	1.84(1)	C(4)—C(5)	1.55(2)	1.54(2)	1.55(2)
Cu—N(2)	2.05(1)	2.05(1)	2.05(1)	C(5)—N(2)	1.45(2)	1.49(2)	1.47(2)
Cu—N(3)	2.01(1)	2.01(1)	2.01(1)	C(5)—C(6)	1.59(3)	1.54(3)	1.57(3)
Cu—O(2) [a]	2.37(1)	2.42(1)	2.40(2)	N(2)—C(7)	1.34(2)	1.30(2)	1.32(2)
Mn—C(8)	2.13(1)	2.10(2)	2.12(2)	C(7)—C(8)	1.43(2)	1.40(2)	1.42(2)
Mn—C(9)	2.14(2)	2.11(2)	2.13(2)	C(8)—C(12)	1.41(2)	1.40(2)	1.41(2)
Mn—C(10)	2.21(2)	2.16(2)	2.19(2)	C(12)—C(13)	1.50(2)	1.54(2)	1.52(2)
Mn—C(11)	2.14(2)	2.19(2)	2.17(2)	C(13)—N(3)	1.51(2)	1.52(2)	1.52(2)
Mn—C(12)	2.11(2)	2.12(2)	2.12(2)	N(3)—C(14)	1.56(2)	1.55(2)	1.56(2)
Mn—C(16)	1.82(2)	1.79(2)	1.81(2)	N(3)—C(15)	1.52(2)	1.49(2)	1.51(2)
Mn—C(17)	1.74(2)	1.81(2)	1.78(2)	C(8)—C(9)	1.46(2)	1.48(2)	1.47(2)
Mn—C(18)	1.78(2)	1.79(2)	1.79(2)	C(9)—C(10)	1.45(3)	1.36(2)	1.41(2)
O(1)—C(1)	1.31(2)	1.27(2)	1.29(2)	C(10)—C(11)	1.48(2)	1.44(3)	1.46(2)
O(2)—C(1)	1.23(2)	1.23(2)	1.23(2)	C(11)—C(12)	1.38(2)	1.43(2)	1.41(2)
C(1)—C(2)	1.47(2)	1.52(2)	1.50(2)	C(16)—O(4)	1.15(2)	1.17(3)	1.16(3)
C(2)—N(1)	1.54(2)	1.47(2)	1.51(2)	C(17)—O(5)	1.16(2)	1.14(2)	1.15(2)
C(2)—C(3)	1.59(3)	1.59(3)	1.59(3)	C(18)—O(6)	1.12(2)	1.13(2)	1.13(2)
N(1)—C(4)	1.30(2)	1.35(3)	1.33(2)				

[a] For molecule A atom O(2)* = O(2B) (*x*, *y*, *z* — 1); for molecule B atom O(2)* = O(2A) (*x*, *y*, *z*).

Atomic coordinates and temperature factors are given in Tables 1 and 2, bond lengths and angles are given in Tables 3 and 4, respectively. Geometrical parameters of some planar molecular fragments are presented in Table 5, and some important torsional angles can be found in Table 6.

Results and discussion

The molecular structure of I with bond lengths and angles averaged over two crystallographically independent molecules A and B is shown in Fig. 1. In the crystal, molecules A and B are linked with each other through additional coordination of the Cu atom by the carboxylic O(2) atom in A (Cu(B)...O(2A) 2.37(1) Å). On the other hand, the O(2) atom in B also coordinates to the Cu atom, but in the molecule derived from A by the translation (O(2B)...Cu(A)-(x, y, $1 + z$) 2.42(1) Å). Thus, in the crystal, due to the intermolecular interaction Cu...O(2), infinite ...A...B...A...B... chains are formed along the z axis, and Cu atoms in molecules A and B acquire a distorted tetragonal pyramidal coordination with three N atoms and one O atom of the tetradentate ligand at the pyramidal base and the O(2) atom of the neighbouring molecule in an axial position.

The atoms O(1), N(1), N(2), N(3) at the base of the pyramid are essentially non-coplanar: the dihedral angle CuO(1)N(1)/CuN(2)N(3) (planes 1 and 2 in Table 5) is equal to 23° *. The lengths of 1.99(1) Å for the Cu—O(1) bond and of 2.01(1) and 2.05(1) Å for two Cu—N bonds are usual for copper complexes

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* Here and below, average values of structurally equivalent parameters in molecules A and B are given.

TABLE 4

BOND ANGLES (°) IN MOLECULES A AND B

Angle	A	B	Average	Angle	A	B	Average
O(2)*CuO(1) [a]	92.8(4)	93.7(4)	93.1(4)	N(1)C(4)C(5)	110(1)	110(1)	110(1)
O(2)*CuN(1)	110.9(5)	107.7(5)	109.3(5)	C(4)C(5)N(2)	110(1)	112(1)	111(1)
O(2)*CuN(2)	88.8(4)	84.6(4)	86.7(4)	C(5)N(2)Cu	113(1)	111(1)	112(1)
O(2)*CuN(3)	94.3(5)	93.4(4)	93.9(4)	C(2)N(1)C(4)	116(1)	116(1)	116(1)
O(1)CuN(1)	84.2(5)	83.1(5)	83.7(5)	N(1)C(4)O(3)	132(2)	133(2)	133(1)
O(1)CuN(2)	163.0(5)	164.1(5)	163.6(5)	C(5)C(4)O(3)	118(1)	117(1)	118(1)
O(1)CuN(3)	91.6(5)	91.3(5)	91.5(5)	C(4)C(5)C(6)	104(1)	110(1)	107(1)
N(1)CuN(2)	79.4(5)	82.4(6)	80.9(5)	N(2)C(5)C(6)	108(1)	107(1)	108(1)
N(1)CuN(3)	154.6(6)	158.4(4)	156.5(4)	CuN(2)C(7)	128(1)	128(1)	128(1)
N(2)CuN(3)	105.1(5)	104.6(5)	104.8(5)	C(5)N(2)C(7)	114(1)	116(1)	115(1)
C(16)MnC(17)	91(1)	93(1)	92(1)	N(2)C(7)C(8)	125(1)	127(2)	126(1)
C(16)MnC(18)	89(1)	88(1)	89(1)	C(7)C(8)C(12)	132(1)	130(1)	131(1)
C(17)MnC(18)	89(1)	90(1)	90(1)	C(8)C(12)C(13)	127(1)	128(1)	128(1)
CuO(1)C(1)	114(1)	113(1)	114(1)	C(13)N(3)Cu	115(1)	113(1)	114(1)
O(1)C(1)C(2)	118(1)	119(1)	119(1)	C(7)C(8)C(9)	121(1)	123(1)	122(1)
C(1)C(2)N(1)	107(1)	105(1)	106(1)	C(13)C(12)C(11)	122(1)	124(1)	123(1)
C(2)N(1)Cu	116(1)	119(1)	118(1)	C(13)N(3)C(14)	103(1)	101(1)	102(1)
C(1)O(2)Cu** [b]	135(1)	136(1)	136(1)	C(13)N(3)C(15)	109(1)	111(1)	110(1)
O(1)C(1)O(2)	122(1)	121(1)	122(1)	CuN(3)C(14)	105(1)	109(1)	107(1)
C(2)C(1)O(2)	120(1)	120(1)	120(1)	CuN(3)C(15)	113(1)	115(1)	114(1)
C(1)C(2)C(3)	112(1)	109(1)	111(1)	C(14)N(3)C(15)	111(1)	107(1)	109(1)
N(1)C(2)C(3)	109(1)	115(1)	112(1)	Av. CCC(Cp)	109(2)	109(2)	109(2)
CuN(1)C(4)	126(1)	124(1)	125(1)	Av. MnCO	177(2)	176(3)	177(3)

[a] For molecule A atom O(2)* = O(2B) $(x, y, z-1)$; for molecule B atom O(2)* = O(2A) (x, y, z). [b] For molecule A atom Cu** = Cu(B) (x, y, z); for molecule B atom Cu** = Cu(A) $(x, y, 1+z)$.

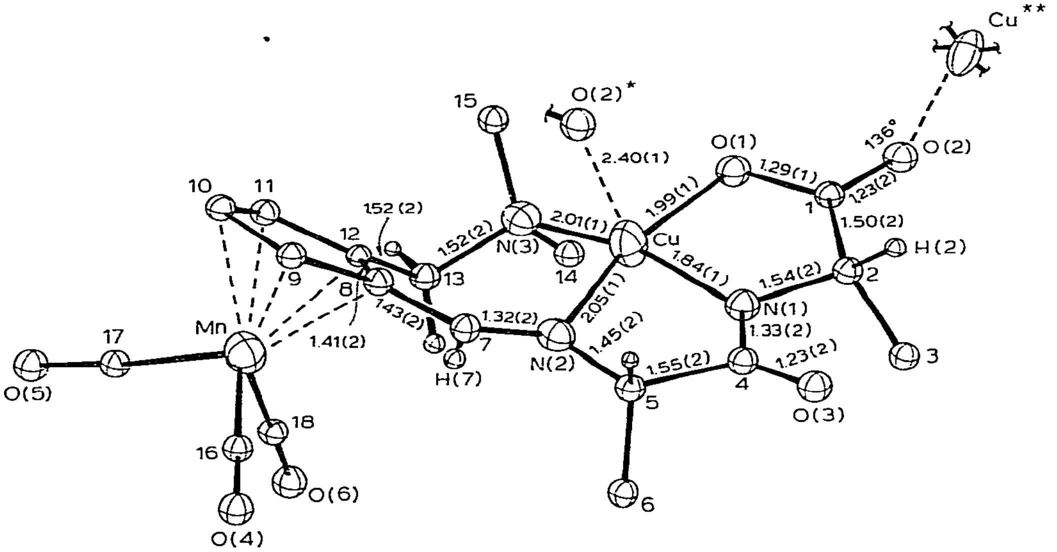

Fig. 1. A perspective view of the molecule A with bond lengths averaged over both independent molecules A and B. The atoms O(2)* and Cu** belong to the neighbouring molecules (see text).

of amino acids and peptides [5,6]. However, due to conjugation in the peptide fragment N(1)C(4)O(3) the Cu—N(1) bond is an essentially covalent σ one, and its length of 1.84(1) Å is considerably shorter than the lengths of donor-acceptor bonds Cu—N(2) and Cu—N(3) of 2.05 and 2.01 Å respectively.

Due to the tetradentate character of the ligand, two five-membered metallocycles and one seven-membered metallocycle are present in the complex studied. The five-membered metallocycles (planes 4 and 7 in Table 5) are almost planar, and the dihedral angle between their planes is 8°. Along the C(8)—C(12) bond the seven-membered metallocycle is condensed with the cyclopentadienyl ring η^5-coordinated by the metal atom of the $Mn(CO)_3$ fragment. This fragment and the Cu atom are situated over the opposite sides of the plane of the Cp ligand * (the distances between the Mn and Cu atoms and the Cp plane are 1.77 and —1.62 Å, respectively), and the presence of two different substituents at C(8) and C(12) of the Cp ligand causes chirality of the doubly substituted cymantrenyl system, whose configuration, according to ref. 2, is *S*. The involvement of two tetrahedral atoms N(3) and C(13) into the seven-membered cycle leads to its considerable non-planarity. The ring has a boat conformation with the base formed by Cu, N(3), C(8) and C(12). Atoms N(2), C(7), and C(13) are displaced from the boat base plane by —0.75, —0.41 and —0.74 Å, respectively (Table 5).

The N(1) atom has a slightly distorted planar trigonal configuration (the sum of bond angles is 358°). On the contrary, at the N(2) atom this planarity is more distorted (the sum of bond angles is 355°), and the fragment C(4)C(5)-N(2)C(7) is distinctly non-planar (with a torsional angle of —158°). This leads

(Continued on p. 421)

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* Other mutual ("*cis*") orientation of the Mn and Cu atoms in relation to the Cp plane is sterically forbidden [3] due to very short non-bonded distances Mn...C(15) (Me-group at N(3); see Fig. 1).

TABLE 5

LEAST-SQUARES PLANES (WITH THE DEVIATIONS (Å) OF ATOMS) IN MOLECULES A AND B GIVEN BY EQUATION $Ax + By + Cz - D = 0$, WHERE x, y AND z ARE FRACTIONAL UNIT-CELL COORDINATES

Atoms	Plane 1		Plane 2		Plane 3		Plane 4		Plane 5		Plane 6	
	A	B	A	B	A	B	A	B	A	B	A	B
Cu	0.00	0.00	0.00	0.00	0.17 [a]	0.12 [a]	0.00	0.00	−0.10 [a]	−0.07 [a]	0.42 [a]	0.27 [a]
Mn												
O(1)	0.00	0.00			0.16	0.15	0.02	0.02	0.00	0.00		
O(2)									0.00	0.00		
O(3)											0.01	−0.01
N(1)	0.00	0.00			−0.30	−0.28	0.03	0.05	−0.03 [a]	0.03 [a]	0.01	−0.01
N(2)			0.00	0.00	0.19	0.19					0.20 [a]	0.12 [a]
N(3)			0.00	0.00	−0.17	−0.17						
C(1)							−0.02	−0.03	0.01	−0.01		
C(2)							−0.02	−0.03	0.00	0.00	−0.01 [a]	−0.01 [a]
C(4)							0.33 [a]	0.39 [a]			−0.02	0.02
C(5)											0.01	−0.01
C(6)												
C(7)												
C(8)												
C(9)												
C(10)												
C(11)												
C(12)												
C(13)												
H(7)												
A	−0.233	0.244	0.201	−0.119	0.029	0.023	−0.248	0.268	−0.268	0.292	0.004	0.055
B	0.886	−0.898	0.876	−0.910	0.912	−0.923	0.887	−0.898	0.897	−0.901	0.957	−0.966
C	−0.400	−0.366	−0.438	−0.397	−0.409	−0.384	−0.391	−0.349	−0.353	−0.320	−0.291	−0.254
D	−4.048	−7.956	−2.955	−8.306	−3.452	−8.016	−4.015	−6.894	−3.669	−6.041	−2.803	−6.578

TABLE 5 (*continued*)

Atoms	Plane 7		Plane 8		Plane 9		Plane 10		Plane 11		Plane 12	
	A	B	A	B	A	B	A	B	A	B	A	B
Cu	0.00	0.00	−0.77 [a]	−0.80 [a]	−1.72 [a]	−1.50 [a]	0.00	0.00			0.00	0.00
Mn					1.77 [a]	1.76 [a]						
O(1)												
O(2)												
O(3)	0.33 [a]	0.18 [a]										
N(1)	−0.09	−0.09										
N(2)	−0.04	−0.03	0.00	0.00			−0.82 [a]	−0.68 [a]			−0.07	−0.09
N(3)							0.01	0.05	0.00	0.00		
C(1)												
C(2)	−0.06 [a]	−0.07 [a]										
C(4)	0.07	0.08										
C(5)	0.03	0.01	0.00	0.00								
C(6)	−1.34 [a]	−1.28 [a]										
C(7)	0.38 [a]	0.40 [a]	0.00	0.00			−0.50 [a]	−0.31 [a]			0.17	0.18
C(8)					−0.01	−0.01	0.01	0.07			−0.05	−0.06
C(9)					0.02	0.00						
C(10)					−0.02	0.01						
C(11)					0.01	−0.02						
C(12)					0.00	0.01	−0.02	−0.10	0.00	0.00		
C(13)							−0.69 [a]	−0.78 [a]	0.00	0.00		
H(7)			0.00	0.00								
A	−0.176	0.169	0.163	−0.118	0.125	0.038	0.191	−0.182	−0.909	0.956	−0.335	0.305
B	0.930	−0.949	−0.985	0.985	−0.921	0.932	0.981	−0.981	−0.371	0.290	0.908	−0.936
C	−0.324	−0.268	−0.050	−0.125	−0.370	−0.362	−0.034	−0.668	−0.187	−0.045	−0.253	−0.176
D	−3.232	−6.196	0.890	2.137	−0.923	−0.082	0.334	−4.401	−6.157	0.436	−3.158	−4.764

[a] Atoms are not included in calculations of mean least-squares planes.

Angle between the mean planes: 1/2 = 25° (A), 21° (B); 4/7 = 8° (A), 8° (B); 10/4 = 33° (A), 31° (B); 10/7 = 26° (A), 23° (B); 10/11 = 122° (A), 117° (B); 10/12 = 33° (A), 29° (B).

TABLE 6

SELECTED TORSIONAL ANGLES (°) IN MOLECULES A AND B

Atoms	A	B	Atoms q	A	B	Atoms	A	B
CuO(1)C(1)C(2)	−2	−3	CuN(2)C(7)C(8)	29	34	C(4)C(5)N(2)C(7)	−2	0
O(1)C(1)C(2)N(1)	1	−1	N(2)C(7)C(8)C(12)	19	15	C(5)N(2)C(7)C(8)	180	−176
C(1)C(2)N(1)Cu	2	5	C(7)C(8)C(12)C(13)	4	1	C(5)N(2)C(7)H(7)	0	5
C(2)N(1)CuO(1)	−3	−5	C(8)C(12)C(13)N(3)	−74	−72	C(2)N(1)C(4)O(3)	4	−4
N(1)CuO(1)C(1)	3	5	C(12)C(13)N(3)Cu	67	75	H(2)C(2)N(1)C(4)	−46	−41
CuN(1)C(4)C(5)	14	13	C(13)N(3)CuN(2)	−7	−18	C(3)C(2)N(1)C(4)	73	77
N(1)C(4)C(5)N(2)	−6	−8	N(3)CuN(2)C(7)	−47	−44	H(5)C(5)N(2)C(7)	−36	−39
C(4)C(5)N(2)Cu	−2	0	C(1)C(2)N(1)C(4)	−165	−164	C(6)C(5)N(2)C(7)	90	85
C(5)N(2)CuN(1)	7	5	C(2)N(1)C(4)C(5)	179	−179			
N(2)CuN(1)C(4)	−12	−11	N(1)C(4)C(5)N(2)	−6	−8			

to a difference in steric hindrance between H(5) and C(6) substituents at the tetrahedral C(5) atom and H(7) (at C(7)) and O(3) (at C(4)). Indeed, due to the above-mentioned non-planarity the orientation of the C(5)—H(5) and C(5)—C(6) bonds in relation to the planar fragment H(7)C(7)N(2)C(5) is not equivalent: the corresponding line/plane angles are —35 and 73°. Thus, relative to the H(7)C(7)N(2)C(5) fragment, H(5) is quasi-equatorial and C(6) is sterically less hindred quasi-axial, with intramolecular contacts H(5)...H(7) and H(7)...C(6) of 2.19 and 3.09 Å, respectively. Therefore the real conformation of the tetradentate ligand, when it is coordinated by the copper atom in complex I, leads to stereochemical and energetic non-equivalence of the exocyclic positions of the substituents at C(5). In this situation the *S*-configuration of C(5) in complex I is more favourable than the *R*-configuration, in which the substituents at C(5), viz. H(5) and Me C(6), would exchange places and the H(5)...H(7) and C(6)...H(7) distances would be ~2.8 and ~2.3 Å, respectively. In other words, the non-bonding interaction H(7)...C(6) must be considerably greater for (*S*)-AFCMT-((*R*)-Ala-(*S*)-Ala)Cu^{II} (or (*R*)-AFCMT-((*S*)-Ala-(*S*)-Ala)Cu^{II}), than for (*S*)-AFCMT-((*S*)-Ala-(*S*)-Ala)Cu^{II} (or (*R*)-AFCMT-((*R*)-Ala-(*S*)-Ala)Cu^{II}).

These data allow one to explain why (*S*)-AFCMT (or (*R*)-AFCMT) preferably forms complexes with dipeptides containing an *N*-terminal amino acid of *S*-configuration (resp., *R*-configuration), and also why condensation of (*S*)-AFCMT-(Gly-Gly)Cu^{II} (or (*R*)-AFCMT-(Gly-Gly)Cu^{II}) with CH_3CHO gives excess (*S*)-AFCMT-((*S*)-Thr-Gly)Cu^{II} or (*R*)-AFCMT-((*R*)-Thr-Gly)Cu^{II}) [3].

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