Crystal and Molecular Structure of a Binuclear Copper(II) Complex with 1,2,3,4-Tetrakis(salicylideneamino)-2,3-dimethylbutane[1)]

Masahiro MIKURIYA,*,† Tatsuo IZUMITANI, Hisashi ŌKAWA, and Sigeo KIDA*,†
Department of Chemistry, Faculty of Science, Kyushu University 33,
Hakozaki, Higashi-ku, Fukuoka 812
(Received April 23, 1986)

Synopsis. The crystal structure of a binuclear copper(II) complex with 1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane (abbreviated as H_4sata), Cu_2(sata), was determined by the single-crystal X-ray diffraction method. The complex molecule has two coordination units formed by a planar 6-5-6 fused chelate ring and takes a nonstacked form.

In recent years there has been a considerable interest in binuclear metal complexes because of their unique properties arising from the two metal ions in close proximity. As a face-to-face binucleating ligand, Ōkawa et al. have prepared 1,2,3,4-tetrakis(salicylideneamino)-2,3-dimethylbutane (abbreviated as H_4sata) which contains two "salpn" moieties (H_2salpn=*N*,*N*′-disalicylidene-1,2-propanediamine) combined at the 2-carbon atom of the diamine chain (Fig. 1).[2)] This ligand forms binuclear complexes M_2(sata) (M=Cu, Ni, Fe, Mn) which take two possible configurations, (i.e., stacking and nonstacking), caused by the rotation about the bridging C–C bond. The electronic and ESR spectra and electrochemical data suggested that the two MN_2O_2 planes are stacked in a face-to-face manner and interact with each other in solution.[3)] The structures of these complexes have not yet been confirmed by X-ray analysis, since we have obtained no crystal suitable for the analysis. In this study, however, another batch of crystals have proved to have better quality, thus we have carried out the X-ray structure analysis of Cu_2(sata).

Experimental

The Cu_2(sata) complex was prepared by the method previously reported.[2)] Crystals suitable for X-ray study were obtained as dark brown plates by crystallization from a dilute ethanol solution after standing one year. Anal. Found: C, 56.03; H, 4.83; N, 7.21%. Calcd for $C_{36}H_{40}Cu_2N_4O_7$=Cu_2(sata)·C_2H_5OH·$2H_2O$: C, 56.31; H, 5.25; N, 7.30%. A crystal with dimensions of 0.11×0.36×0.40 mm^3 was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å) at 24±1 °C.

Crystal Data: $C_{36}H_{40}Cu_2N_4O_7$, F.W.=767.83; triclinic; $P\bar{1}$; a=16.691(1), b=17.106(1), c=15.641(1) Å; α=117.25(1), β=117.95(1), γ=88.83(1)°; D_m=1.50; D_c=1.50 g cm^{-3}; Z=4.

The intensity data were collected by the 2θ-ω scan technique with a scan rate of 3° min^{-1} in ω. A total of 8144 reflections with 2θ<43° were collected. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. 4829 Independent reflections with $|F_o|>3\sigma(|F_o|)$ were considered as "observed" and were used for the structure analysis. The structure was solved by the direct method and refined by the block-diagonal least-squares method. The ethyl groups of ethanol molecules could not be located probably due to the disorder in the solvent molecules. Hydrogen atoms are not included in the calculation. In the least-squares refinement a weighting scheme, $w=(6.81+|F_o|+0.005|F_o|^2)^{-1}$ was employed. The final discrepancy factors were $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0.080$ and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.119$.

The atomic scattering factors and the anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography.[4)] All the calculations were carried out on the FACOM M-200 computer in the Computer Center of Kyushu University by the use of a local version of the UNICS-III programs.[5)] The final positional and thermal parameters are given in Table 1. The anisotropic thermal parameters and the F_o—F_c tables have been deposited as a Document No. 8643 at the Office of the Editor.

Results and Discussion

The crystal contains two crystallographically independent binuclear molecules; they are represented as A and B. There are no significant differences in bond lengths and angles between A and B. The molecular structure of A is shown in Fig. 2, the "en-chelated structure" (Fig. 1) which was supposed from the electronic spectrum[2)] has been confirmed. The molecule consists of two "Cu(salpn)" moieties linked by the C(8)–C(8)′ bond. All the coordination geometries are nearly square planar, four donor atoms around a copper atom being coplanar with the deviations within ±0.14 Å. Each "Cu(salpn)" moiety does not form a rigorous plane, and may be described as "umbrella-shape."[6)] The five-membered chelate rings (Cu–N(1)–C(8)–C(9)–N(2), Cu′–N(1)′–C(8)′–C(9)′–N(2)′) assume a gauche conformation similar to that observed in the Cu(salpn)[7)] and Cu(salen)[8)] complexes (H_2salen=*N*,*N*′-disalicylidene-1,2-ethanediamine). Bond lengths and angles of the "Cu(salpn)"

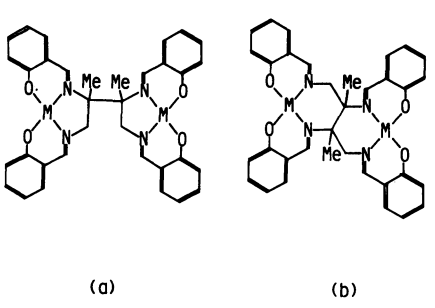

Fig. 1. Possible structures of Cu_2(sata): (a) en-chelated and (b) tn-chelated structures.

† Present address: Coordination Chemistry Laboratories, Institute for Molecular Science, Okazaki National Research Institutes, Okazaki 444.

Table 1. Fractional Positional Parameters ($\times 10^4$) and Thermal parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
Cu(A)	432(1)	561(1)	−528(1)	5.3	C(11A)′	5212(10)	−1221(9)	748(13)	5.3
Cu(A)′	3610(1)	−863(1)	−1187(1)	4.9	C(12A)′	5928(11)	−1327(12)	1629(15)	6.9
Cu(B)	1391(1)	5863(1)	1064(1)	5.0	C(13A)′	6369(13)	−2027(13)	1418(17)	8.2
Cu(B)′	4566(1)	4436(1)	3475(1)	5.2	C(14A)′	6062(13)	−2668(12)	267(19)	8.5
O(1A)	−566(8)	225(9)	−1972(10)	8.5	C(15A)′	5360(12)	−2587(11)	−624(16)	7.2
O(2A)	−37(7)	1566(7)	23(10)	6.9	C(16A)′	4943(10)	−1826(10)	−376(13)	5.9
O(1A)′	3152(8)	−1324(8)	−2726(8)	8.0	C(17A)′	2629(10)	1350(8)	318(11)	5.1
O(2A)′	4314(7)	−1744(7)	−1248(8)	6.3	C(1B)	2448(11)	6057(10)	160(14)	6.6
O(1B)	1851(9)	6331(8)	461(11)	8.2	C(2B)	2745(14)	6519(14)	−268(18)	8.8
O(2B)	680(7)	6728(6)	1184(9)	6.3	C(3B)	3374(15)	6308(14)	−551(18)	9.0
O(1B)′	5565(7)	4784(9)	3364(10)	8.3	C(4B)	3852(14)	5636(14)	−437(18)	9.0
O(2B)′	5041(7)	3438(7)	3498(9)	7.1	C(5B)	3615(13)	5220(13)	6(16)	8.2
N(1A)	1062(8)	−328(7)	−1051(9)	5.5	C(6B)	2933(10)	5408(9)	305(12)	5.5
N(2A)	1371(7)	793(7)	950(9)	4.5	C(7B)	2779(9)	4933(9)	791(10)	5.3
N(1A)′	2764(7)	−81(7)	−1109(9)	4.5	C(8B)	2206(9)	4607(8)	1791(9)	4.2
N(2A)′	4153(7)	−282(7)	410(8)	4.6	C(9B)	1227(9)	4521(9)	1615(11)	5.0
N(1B)	2238(7)	5079(7)	1213(8)	4.7	C(10B)	196(9)	5493(9)	1786(10)	4.9
N(2B)	829(7)	5260(7)	1521(9)	5.1	C(11B)	−217(10)	6215(9)	1761(11)	5.6
N(1B)′	3922(7)	5338(7)	3215(8)	5.1	C(12B)	−930(12)	6346(13)	2029(13)	7.4
N(2B)′	3623(7)	4211(8)	3785(8)	5.1	C(13B)	−1347(13)	7068(15)	2093(15)	9.0
C(1A)	−687(14)	−434(13)	−2891(16)	9.2	C(14B)	−1034(14)	7691(13)	1870(13)	8.8
C(2A)	−1568(18)	−596(19)	−3898(17)	14.0	C(15B)	−374(12)	7576(12)	1577(13)	7.5
C(3A)	−1701(22)	−1261(24)	−4922(21)	19.7	C(16B)	67(10)	6855(10)	1526(11)	6.1
C(4A)	−1136(26)	−1857(22)	−5035(20)	19.7	C(17B)	2383(10)	3654(8)	1340(10)	5.2
C(5A)	−272(20)	−1822(18)	−4104(17)	14.5	C(1B)′	5714(13)	5458(14)	3238(15)	9.7
C(6A)	−98(14)	−1017(14)	−3005(14)	9.5	C(2B)′	6559(18)	5593(19)	3260(21)	14.4
C(7A)	760(12)	−971(11)	−2054(13)	7.8	C(3B)′	6696(21)	6318(21)	3109(24)	16.2
C(8A)	2022(10)	−257(9)	−112(12)	5.6	C(4B)′	6114(22)	6879(21)	2897(25)	16.1
C(9A)	1946(11)	146(10)	945(13)	6.1	C(5B)′	5264(19)	6807(15)	2977(18)	12.3
C(10A)	1468(10)	1396(10)	1885(13)	5.9	C(6B)′	5073(14)	6061(12)	3125(14)	8.6
C(11A)	924(11)	2084(10)	1973(13)	6.4	C(7B)′	4232(11)	5986(11)	3168(12)	7.7
C(12A)	1161(13)	2750(13)	3105(18)	9.2	C(8B)′	2967(10)	5274(9)	3111(11)	5.1
C(13A)	644(19)	3389(14)	3251(22)	12.2	C(9B)′	3059(10)	4866(10)	3855(12)	5.9
C(14A)	−24(17)	3443(11)	2332(24)	11.9	C(10B)′	3532(10)	3586(11)	3998(11)	5.9
C(15A)	−245(12)	2837(10)	1275(18)	8.2	C(11B)′	4071(11)	2910(11)	3975(13)	6.7
C(16A)	211(11)	2150(10)	1067(15)	6.5	C(12B)′	3822(13)	2275(13)	4213(14)	9.0
C(17A)	2240(11)	−1201(10)	−357(15)	7.0	C(13B)′	4320(19)	1591(16)	4190(19)	12.6
C(1A)′	2537(11)	−1053(10)	−3357(12)	6.4	C(14B)′	4986(18)	1542(13)	3905(15)	12.3
C(2A)′	2316(14)	−1515(13)	−4497(13)	8.8	C(15B)′	5258(14)	2165(12)	3662(13)	9.4
C(3A)′	1614(17)	−1307(14)	−5241(16)	10.1	C(16B)′	4766(11)	2859(9)	3693(10)	6.1
C(4A)′	1197(14)	−621(13)	−4900(15)	8.7	C(17B)′	2764(11)	6188(9)	3614(13)	6.9
C(5A)′	1402(11)	−192(11)	−3800(12)	6.9	O(SA1)	1911(13)	−1435(16)	2013(20)	17.1
C(6A)′	2063(11)	−408(9)	−3030(12)	5.6	O(SA2)	1574(19)	−3222(23)	−3148(29)	23.7
C(7A)′	2231(10)	65(9)	−1912(12)	5.5	O(SA3)	1141(23)	−3806(19)	−5258(21)	23.1
C(8A)′	2784(9)	393(8)	−25(10)	4.3	O(SB1)	6897(12)	3571(14)	3464(16)	15.8
C(9A)′	3786(9)	497(9)	884(11)	5.2	O(SB2)	3452(20)	−1682(26)	3533(22)	26.1
C(10A)′	4805(10)	−477(9)	1108(13)	5.3	O(SB3)	3879(22)	−1160(18)	2446(25)	22.3

moieties fall in the range of the values reported for a series of Cu(salen)-type complexes.[6-8]

It was pointed out that the ligand was diastereomeric (dl and meso) with respect to the 2- and 3-carbon atoms of the 2,3-dimethyl-1,2,3,4-butanetetramine moiety, and its configuration was inferred as the dl-form from the configurational study for the related complexes.[9] The present structural data have confirmed that the configuration of the tetramine moiety is the dl-form.

The Cu_2(sata) molecule in the crystal takes a nonstacked form though the discussions based on the

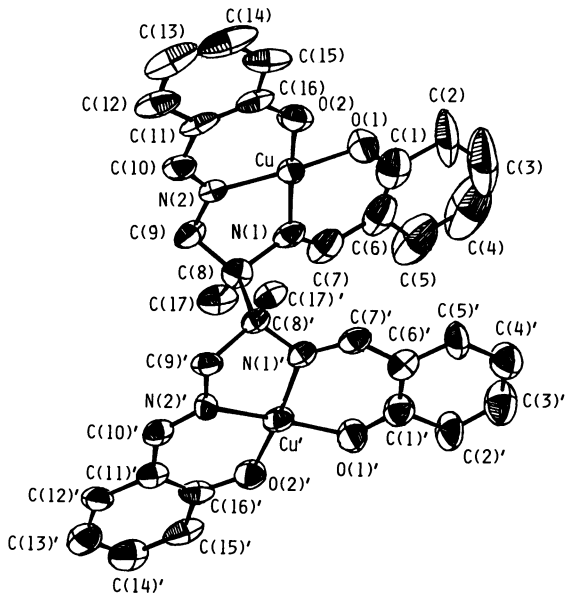

Fig. 2. Molecular structure of the Cu_2(sata) complex with thermal ellipsoids (35% probability level). Distances (l/Å): Cu–O(1) 1.879(12), 1.876(20); Cu–O(2) 1.879(12), 1.876(11); Cu–N(1) 1.921(13), 1.936(12); Cu–N(2) 1.936(11), 1.949(17); Cu′–O(1)′ 1.887(12), 1.888(16); Cu′–O(2)′ 1.888(12), 1.875(13); Cu′–N(1)′ 1.932(12), 1.950(13); Cu′–N(2)′ 1.921(11), 1.944(15). Angles (ϕ/°): O(1)–Cu–O(2) 87.2(5), 88.7(7); O(1)–Cu–N(1) 94.8(5), 95.2(6); N(1)–Cu–N(2) 84.9(5), 84.0(6); O(2)–Cu–N(2) 94.2(5), 93.1(6); O(1)′–Cu′–O(2)′ 88.1(6), 87.7(7); O(1)′–Cu′–N(1)′ 94.7(6), 94.7(6); N(1)′–Cu′–N(2)′ 84.3(5), 84.1(6); O(2)′–Cu′–N(2)′ 93.8(5), 94.6(6). Dihedral angles (τ/°) between the coordination planes, O(1)–N(1)–N(2)–O(2) and O(1)′–N(1)′–N(2)′–O(2)′: 11.2, 10.4 for molecules A and B, respectively.

electronic and ESR spectra and electrochemical properties in solution all pointed a stacked form. The intramolecular copper-copper distance is 6.118(3) Å. There is neither axial coordination nor intermolecular association, the closest atom, N(2), of neighboring molecule being separated from the copper atom by 3.447(14) Å. The present results do not contradict the conclusions derived from the solution studies, since the rotation about the C(8)–C(8)′ bond is feasible in solution so that the two coordination planes stack.

References

1) Binuclear Metal Complexes Part 60 (Part 59: D. Liao, J.-Z. Zhuang, H. Ōkawa, and S. Kida, submitted to *Inorg. Chim. Acta*, for publication.

2) T. Izumitani, H. Ōkawa, and S. Kida, *Chem. Lett.*, **1981**, 483; T. Izumitani, M. Nakamura, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **55**, 2122 (1982).

3) H. Ōkawa, M. Kakimoto, T. Izumitani, M. Nakamura, and S. Kida, *Bull. Chem. Soc. Jpn.*, **56**, 149 (1983); M. Nakamura, H. Ōkawa, and S. Kida, *Inorg. Chim. Acta*, **75**, 9 (1983); M. Nakamura, *Bull. Chem. Soc. Jpn.*, **56**, 2529 (1983); H. Ōkawa, A. Honda, M. Nakamura, and S. Kida, *J. Chem. Soc., Dalton Trans.*, **1985**, 59.

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

5) S. Kawano, *Rep. Comp. Cent. Kyushu Univ.*, **16**, 113 (1983); T. Sakurai and K. Kobayashi, *Rep. Inst. Phys. Chem. Res.*, **55**, 69 (1979); C. K. Johnson, Report No. 3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee (1965).

6) M. Calligaris, G. Nardin, and L. Randccio, *Coord. Chem. Rev.*, **7**, 385 (1972).

7) F. J. Llewellyn and T. N. Waters, *J. Chem Soc.*, **1960**, 2639.

8) D. Hall and T. N. Waters, *J. Chem. Soc.*, **1960**, 2644.

9) H. Ōkawa, M. Kakimoto, T. Izumitani, and S. Kida, *Bull. Chem. Soc. Jpn.*, **55**, 2671 (1982).