Inorganica Chimica Acta, 63 (1982) 249–256

Synthesis and Crystal Structure of 1:2 Molecular Complex between N,N'-(1,3-Trimethylene)bis(2-oxy-1-naphthaldimine)copper(II) and 7,7',8,8'-Tetracyanoquinodimethane

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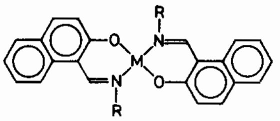
Received March 29, 1982

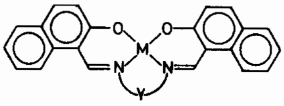
The tetradentate Schiff base nickel(II) and copper(II) complexes with the condensation products of 2-hydroxy-1-naphthaldehyde and diamines such as trimethylenediamine and 1,2-diaminopropane were examined to determine whether the complex can form the molecular complex with TCNQ. The title compound was subjected to a single-crystal X-ray diffraction study. The crystals are monoclinic, space group C2/c, $a = 37.343(8)$, $b = 7.717(1)$, $c = 13.888(2)$ Å, $\beta = 96.26(1)^\circ$, *and* $Z = 4$. *The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method to give an* R *factor of 6.9%. The crystal structure showed that the π-electron donors (naphthalene moieties of the complex) and acceptors (TCNQ) stack alternately, where the naphthalene ring overlaps just on one of the two neighbouring TCNQ molecules and partly on the other and the coordination geometry around the copper ion is pseudo-tetrahedron with the dihedral angle of 26.5° between the CuNO planes.*

Introduction

In a previous paper one of the authors reported the synthesis and crystal structure of a 1:2 molecular complex of bis-(N-alkyl-2-oxy-1-naphthylideneaminato)copper(II) (I) and TCNQ, and elucidated that the donor-acceptor interaction is an important factor in determining the coordination geometry of the metal complex. The copper ion of the molecular complex assumed a square planar coordination geometry with a markedly stepped chair-like shape due to a compromise of the steric effect of the alkyl group and the donor-acceptor interaction operating between naphthalene rings and TCNQ molecule, while the coordination geometry of the parent complex is a pseudo-tetrahedron [1].



M(2,1-R)$_2$ (I)



M(2,1-Y) (II)

Fig. 1. Structures of M(2,1-R)$_2$ (I) and M(2,1-Y) (II).

In this work, we have prepared the tetradentate Schiff base nickel(II) and copper(II) complexes with the condensation products of 2-hydroxy-1-naphthaldehyde and several diamines such as ethylenediamine(en), 1,2-diaminopropane(pn), trimethylenediamine(tn) and *o*-phenylenediamine(ϕ) (hereafter abbreviated as M(2,1-Y), M = Ni^{2+}, Cu^{2+}, Y = en, pn, tn, ϕ), and examined whether the complexes can form the molecular complex with TCNQ. Since the orientation of two naphthalene moieties of the tetradentate complex with *cis*-geometry (II) is apparently different from that of the bis-bidentate complex with *trans*-geometry (I), it is of interest to compare the overlapping mode of the bis-bidentate complex (I) and TCNQ with that of the tetradentate complex (II) and TCNQ. The coordination geometries of the parent complexes were investigated through their electronic spectra, and the molecular complex was subjected to the single-crystal X-ray diffraction method in order to confirm the overlapping mode. In addition, the donor-acceptor interaction was studied by the infrared spectra of the component molecules and the molecular complexes.

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0020-1693/82/0000-0000/$02.75

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Experimental

Physical Measurements

Visible and ultraviolet spectra were recorded with a Hitachi recording spectrometer 323, while infrared spectra were recorded as KBr disk with a JASCO A-702. Elemental analyses were performed by Mr. Miyazaki at the Technical Service Center of Kumamoto University.

Preparations

The tetradentate Schiff base ligands $H_2(2,1\text{-}Y)$ were prepared by refluxing 0.05 mol of 2-hydroxy-1-naphthaldehyde and 0.025 mol of the diamines (ethylenediamine(en), 1,2-propanediamine(pn), trimethylenediamine(tn), *o*-phenylenediamine(ϕ)) in 30 ml of ethanol for 30 min and cooling the reaction mixture, according to the method described in the literature [2], and were identified by elemental analyses and melting points. The general method of the preparation for the nickel(II) and copper(II) complexes was used according to the literature [3]. To a warm solution of 0.01 mol of the Schiff base ligand and 0.02 mol of NaOH in 200 ml of methanol was added 100 ml of methanol containing 0.01 mol of nickel(II) acetate tetrahydrate or copper(II) acetate monohydrate. The solution was refluxed for 30 min, during which time the complex precipitated. The complexes were identified by elemental analyses and melting points. The complexes prepared were M(2,1-Y) where M = Ni^{2+}, Cu^{2+}, A = en, tn, pn, ϕ.

The attempts to prepare the molecular complex of M(2,1-Y) with TCNQ were carried out under the conditions described below. For the complexes M(2,1-Y) with M = Ni^{2+}, Cu^{2+}, A = ϕ, en, no attempt was made owing to the insolubility in chloroform. A solution of 1 mmol of Cu(2,1-tn) in 100 ml of chloroform was added to a solution of 2 mmol of TCNQ in 100 ml of acetone. After standing for several weeks, black prismatic crystals precipitated; these were filtered off and dried *in vacuo. Anal.* Calcd. for $CuO_2N_2C_{25}H_{20}\cdot(C_{12}H_4N_4)_2$: C, 69.05; H, 3.31; N, 16.43%. Found: C, 68.87; H, 3.07; N, 16.38%. According to the same reaction conditions, only the molecular complex Cu(2,1-tn)·2TCNQ was obtained with a satisfactory adjustment of elemental analyses. For the compounds $H_2(2,1\text{-tn})$ and Ni(2,1-tn), black colored precipitates (black is the characteristic color for the molecular complex) were obtained, but did not give the satisfactory agreement of the elemental analyses. For the compounds M(2,1-Y) with M = Ni^{2+}, Cu^{2+}, Y = pn), the starting materials were recovered separately.

The complexes $Cu(2,1\text{-}R)_2$ $Ni(2,1\text{-}R)_2$ and their TCNQ adducts were prepared according to the previously described method, for the purpose of the comparison of their infrared spectra with those of Cu(2,1-tn) and Cu(2,1-tn)·2TCNQ. These complexes were identified by the elemental analyses.

X-ray Diffraction

The black prismatic crystals were isolated from the acetone-chloroform solution at room temperature. A crystal was examined with Rigaku Denki AFC-5 four-circle automated diffractometer. The unit cell dimensions and their estimated standard deviations were obtained from a least-squares fit to 15 reflections using Mo Kα monochromatized radiation at room temperature. The crystal data obtained are as follows: black prism, $CuO_2N_2C_{25}H_{20}(N_4C_{12}H_4)_2$, F. W. = 852.2, monoclinic system, space group = *C*2/*c*, a = 37.343(8), b = 7.717(1), c = 13. 888(2) Å, β = 96.26(1)°, V = 3978.3(16) Å^3, Z = 4, D_m = 1.42 (by flotation method in KI aqueous solution), D_x = 1.423 g/cm^3.

The intensity data were collected by the $2\theta-\theta$ scan technique with a scan rate of 12°/min. For weak reflections the peak scan was repeated up to four times depending on the intensities. Three standard reflections were monitored every 100 reflections and their intensities showed a good stability. The reflections with $2\theta < 48°$ were collected. The intensity data were corrected for Lorentz and polarization effects, but not for absorption. 1263 independent reflections with $|F_o| > 3\sigma|F_o|$ were considered as 'observed' and used for the following structure determination.

Structure Determination

The systematic absences observed h + k odd for *hkl* and *l* odd for *h0l*, indicating either the space group *C*2/*c* or *Cc*. Since the Wilson statistics showed the centrosymmetric space group, *C*2/*c* was selected and later confirmed in the course of the structure determination. The structure was solved by the conventional heavy-atom method. The position of the copper atom was obtained from a three-dimensional Patterson synthesis. Successive Fourier and difference Fourier syntheses revealed all the non-hydrogen atoms. Refinement was carried out by the block-diagonal least-squares method. Anisotropic thermal parameters being introduced, the refinement yielded the discrepancy factors $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ = 0.098, $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ = 0.098. Hydrogen atoms were inserted in their calculated positions and included in the refinement to give the final values of 6.9 and 7.0% for R_1 and R_w, respectively. In the least-squares refinement, the function minimized was $\Sigma w(|F_o|-k|F_c|)^2$, and the weight $w = 1/\sigma(|F_o|)^2$ was used. The atomic scattering factors and the anomalous dispersion corrections ($\Delta f'$ and $\Delta f''$) for Cu, O, N, C_{val} and H were taken from the International Tables for X-ray Crystallography Vol. IV [4]. All the calculations were carried out on a FACOM M-200

TABLE I. Fractional Atomic Parameters of Non-hydrogen Atoms, Atomic Coordinates and Thermal Parameters Have Been Multiplied by 10^4 and 10^3, Respectively.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	BEQV
Cu	0(0)	1630(2)	2500(0)	32(1)	21(1)	52(1)	0(0)	−6(1)	0(0)	2.8
C13	0(0)	6043(19)	2500(0)	16(10)	25(10)	133(18)	0(0)	−13(13)	0(0)	4.7
O1	377(2)	−83(8)	2394(5)	42(6)	20(4)	38(5)	−3(4)	12(5)	11(4)	2.6
N1	296(2)	3394(11)	1968(6)	32(6)	21(5)	39(6)	7(5)	11(5)	−3(5)	2.4
C1	842(3)	1702(14)	1916(7)	38(8)	31(6)	16(7)	−7(6)	6(6)	−4(6)	2.2
C2	699(3)	128(14)	2179(8)	19(7)	35(7)	59(9)	−9(5)	−11(8)	−12(7)	3.1
C3	917(3)	−1430(14)	2201(8)	28(8)	34(7)	44(8)	2(6)	3(7)	−4(6)	2.8
C4	1258(3)	−1301(14)	2049(8)	34(8)	40(8)	46(8)	9(6)	0(8)	3(7)	3.2
C5	1432(3)	308(15)	1832(8)	36(9)	61(9)	36(8)	15(7)	−14(8)	−12(7)	3.6
C6	1796(3)	414(17)	1725(9)	43(10)	75(10)	48(9)	7(7)	−10(9)	0(8)	4.5
C7	1949(3)	1891(19)	1519(10)	50(11)	96(12)	73(11)	−13(9)	−17(10)	−7(10)	5.9
C8	1746(3)	3397(18)	1457(9)	43(9)	68(10)	74(10)	−13(8)	−2(9)	−9(9)	4.9
C9	1393(3)	3380(17)	1567(9)	48(10)	59(9)	60(9)	−1(8)	−12(9)	13(8)	4.5
C10	1216(3)	1822(14)	1789(7)	37(8)	39(7)	32(8)	−10(6)	−8(7)	3(6)	2.9
C11	616(3)	3231(14)	1775(7)	18(7)	34(7)	39(7)	−5(6)	13(7)	6(6)	2.3
C12	100(3)	4995(14)	1638(9)	45(10)	27(7)	67(10)	−4(6)	−2(9)	10(7)	3.7
N2	190(3)	1755(14)	4880(7)	71(9)	52(7)	63(8)	−11(7)	6(8)	7(7)	4.9
N3	717(3)	−3316(13)	4508(7)	68(9)	41(6)	57(7)	−5(6)	−5(7)	0(6)	4.4
N4	2611(3)	1830(15)	3737(8)	49(9)	76(9)	107(10)	14(7)	11(9)	−4(8)	6.1
N5	2035(3)	6755(15)	3802(9)	63(9)	55(8)	144(11)	−4(7)	33(10)	6(9)	6.8
C14	434(3)	927(14)	4774(8)	48(9)	34(7)	42(9)	−4(6)	1(8)	−3(6)	3.3
C15	746(3)	21(13)	4624(8)	45(9)	30(7)	44(8)	−3(6)	−11(8)	−3(7)	3.2
C16	730(3)	−1840(14)	4546(8)	59(10)	33(7)	43(8)	−2(7)	−22(8)	4(7)	3.7
C17	1068(3)	816(13)	4504(7)	35(9)	38(7)	10(7)	−6(6)	13(7)	−1(5)	2.2
C18	1078(3)	2690(15)	4482(8)	57(10)	37(8)	47(9)	8(6)	−11(9)	−11(6)	3.8
C19	1387(3)	3535(14)	4294(9)	54(9)	27(7)	72(10)	1(6)	−18(9)	2(7)	4.2
C20	1710(3)	2587(14)	4140(8)	28(9)	42(7)	31(8)	7(6)	−2(7)	−5(6)	2.7
C21	1699(3)	713(14)	4214(8)	30(9)	49(8)	39(9)	5(6)	10(8)	8(6)	3.1
C22	1397(3)	−109(14)	4365(9)	51(9)	27(7)	60(9)	18(6)	−12(8)	1(7)	3.7
C23	2010(3)	3436(15)	3957(8)	30(8)	45(8)	61(9)	2(6)	−2(8)	−6(7)	3.6
C24	2026(3)	5283(16)	3882(10)	36(9)	49(9)	97(11)	−4(7)	9(10)	0(8)	4.8
C25	2337(4)	2554(16)	3847(9)	67(11)	57(9)	40(9)	−22(7)	0(9)	−1(7)	4.3

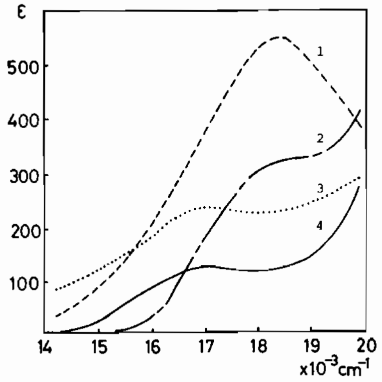

Fig. 2. Electronic absorption spectra of Cu(2,1-pn) (1), Ni(2,1-pn) (2), Cu(2,1-tn) (3) and Ni(2,1-tn) (4) in chloroform.

computer at the Computer Center of Kyushu University by use of a local version of the UNICS II program system [5].

The final positional parameters with their estimated standard deviations are given in Table I. Lists of structure factors have been listed as supplementary data.

Results and Discussion

Visible and ultraviolet spectra for the parent complexes M(2,1-Y) (M = Ni^{2+}, Cu^{2+}, Y = pn, tn) were obtained on 10^{-3}–10^{-4} *M* solution in chloroform, as seen in Fig. 2. For the complexes with Y = en and ϕ the spectra could not be obtained owing to their insolubility in chloroform. As shown in Fig. 2, the complexes exhibit a remarkable decrease in ligand field strength as the number of methylene groups is increased from 2(pn) to 3(tn). Such a spectral feature had been also observed for the related complexes and interpreted as being indicative of an increasing distortion from planarity toward

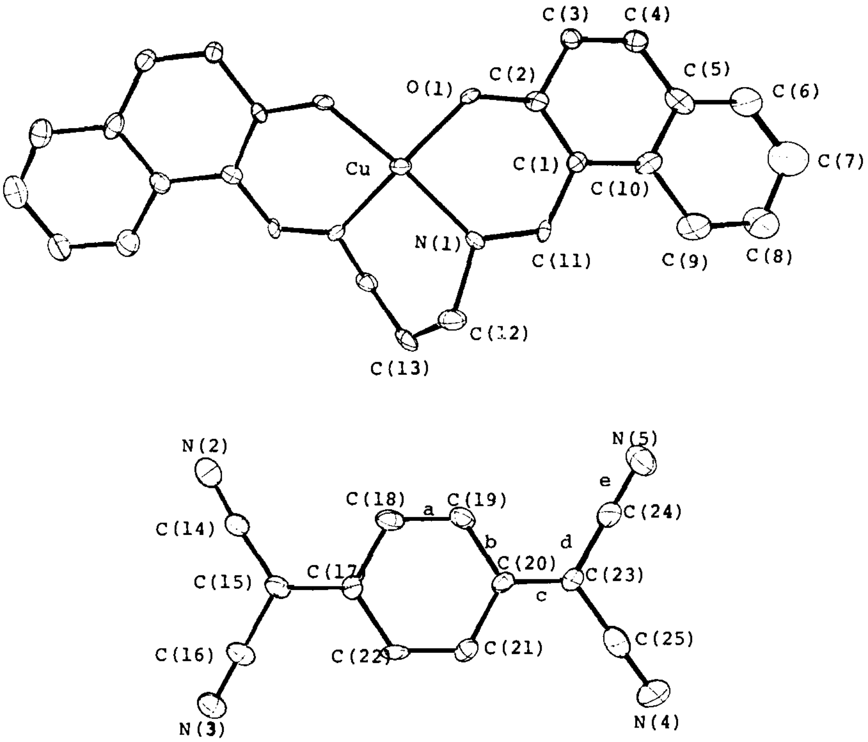

Fig. 3. ORTEP plot of Cu(2,1-tn)•2TCNQ and atom numbering scheme.

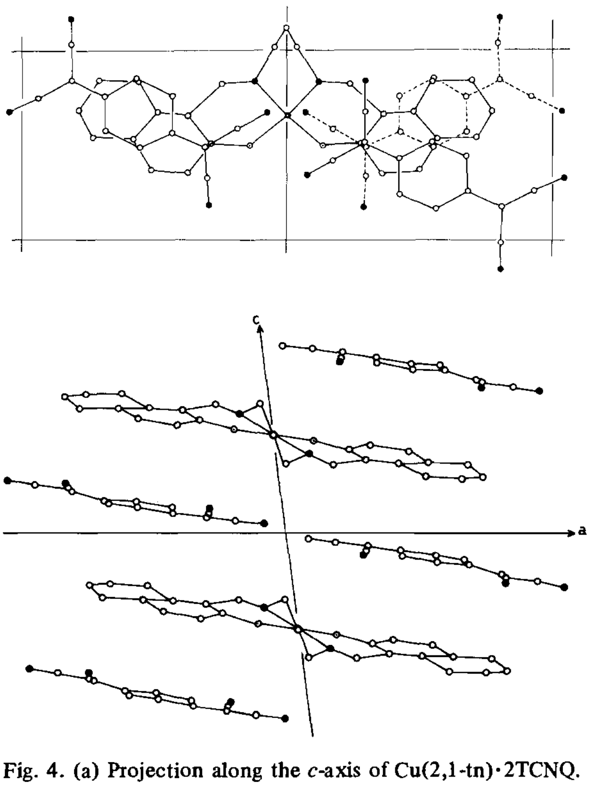

Fig. 4. (a) Projection along the *c*-axis of Cu(2,1-tn)•2TCNQ. (b). Projection along the *b*-axis of Cu(2,1-tn)•2TCNQ.

tetrahedral geometry [6]. Therefore, it can be considered that the complex M(2,1-tn) assumes a larger distortion towards tetrahedron than does the complex M(2,1-pn).

The complexes M(2,1-tn) (M = Ni^{2+}, Cu^{2+}, Y = pn, tn) were examined to see whether they can form the molecular complex with TCNQ. Among the attempts only the complex Cu(2,1-tn) formed the 1:2 molecular complex with TCNQ, indicating that the complex (II) with some degree of tetrahedral distortion is likely to form the molecular complex with TCNQ. On the other hand, the complex (I) with bulky substituted groups, which had been confirmed to have tetrahedral distortion based on the X-ray analysis of $Cu(2,1\text{-iso-Pr})_2$ and the ESR spectra, was not likely to form the molecular complex with TCNQ [1].

A perspective drawing of Cu(2,1-Y)•2TCNQ with the atom numbering scheme is shown in Fig. 3. Figures 4(a) and 4(b) show the crystal structure projected along the *b* and *c* axes, respectively, showing how the molecules overlap in such a way that TCNQ molecule lies on the naphthalene rings of the copper complex. The bond distances, angles and intermolecular distances less than 3.5 Å are given in Table II. Some selected least-squares planes with the deviations of atoms from these planes are given in Table III.

TABLE II. Interatomic Bond Distances, Angles and Intermolecular Bond Distances less than 3.5 Å.

Bond Distances			
Copper(II) Complex			
Cu–O(1)	1.948(7)	C(3)–C(4)	1.31(1)
Cu–N(1)	1.948(8)	C(4)–C(5)	1.44(1)
O(1)–C(2)	1.27(1)	C(5)–C(6)	1.38(1)
N(1)–C(11)	1.26(1)	C(5)–C(10)	1.41(1)
N(1)–C(12)	1.48(1)	C(6)–C(7)	1.32(1)
C(1)–C(2)	1.39(1)	C(7)–C(8)	1.38(2)
C(1)–C(10)	1.42(1)	C(8)–C(9)	1.34(1)
C(1)–C(11)	1.45(1)	C(9)–C(10)	1.42(1)
C(2)–C(4)	1.45(1)	C(12)–C(13)	1.52(1)
TCNQ			
N(2)–C(14)	1.13(1)	C(17)–C(22)	1.45(1)
N(3)–C(16)	1.14(1)	C(18)–C(19)	1.37(1)
N(4)–C(25)	1.19(1)	C(19)–C(20)	1.44(1)
N(5)–C(24)	1.14(1)	C(20)–C(21)	1.45(1)
C(14)–C(15)	1.39(1)	C(20)–C(23)	1.34(1)
C(15)–C(16)	1.44(1)	C(21)–C(22)	1.33(1)
C(15)–C(17)	1.37(1)	C(23)–C(24)	1.43(1)
C(17)–C(18)	1.44(1)	C(23)–C(25)	1.42(1)
Bond Angles			
Copper(II) Complex			
O(1)–Cu–N(1)	90.0(3)	C(3)–C(4)–C(5)	124(1)
O(1)–Cu–O(1)*	94.5(3)	C(4)–C(5)–C(6)	122(1)
N(1)–Cu–N(1)*	91.3(3)	C(4)–C(5)–C(10)	116(1)
Cu–O(1)–C(2)	129.4(7)	C(6)–C(5)–C(10)	120(1)
Cu–N(1)–C(11)	126.9(7)	C(5)–C(6)–C(7)	121(1)
Cu–N(1)–C(12)	114.7(6)	C(6)–C(7)–C(8)	119(1)
C(11)–N(1)–C(12)	117.7(8)	C(7)–C(8)–C(9)	121(1)
C(2)–C(1)–C(10)	119.9(9)	C(8)–C(9)–C(10)	121(1)
C(2)–C(1)–C(11)	120.5(9)	C(1)–C(10)–C(5)	120.1(9)
C(10–C(1)–C(11)	119.5(9)	C(1)–C(10)–C(9)	124(1)
O(1)–C(2)–C(1)	124(1)	C(5)–C(10)–C(9)	115(1)
O(1)–C(2)–C(3)	115.4(9)	N(1)–C(11)–C(1)	127.1(9)
C(1)–C(2)–C(3)	119(1)	N(1)–C(12)–C(13)	110.7(9)
C(2)–C(3)–C(4)	119(1)	C(12)–C(13)–C(12)*	115(1)
TCNQ			
N(2)–C(14)–C(15)	176(1)	C(19)–C(20)–C(21)	118(1)
C(14)–C(15)–C(16)	119(1)	C(19)–C(20)–C(23)	120(1)
C(14)–C(15)–C(17)	123(1)	C(21)–C(20)–C(23)	122(1)
C(16)–C(15)–C(17)	118(1)	C(20)–C(21)–C(22)	121(1)
N(3)–C(16)–C(15)	178(1)	C(17)–C(22)–C(21)	122(1)
C(15)–C(17)–C(18)	118(1)	C(20)–C(23)–C(24)	123(1)
C(15)–C(17)–C(22)	124(1)	C(20)–C(23)–C(25)	122(1)
C(18)–C(17)–C(22)	118(1)	C(24)–C(23)–C(25)	115(1)
C(17)–C(18)–C(19)	120(1)	N(5)–C(24)–C(23)	179(1)
C(18)–C(19)–C(20)	121(1)	N(4)–C(25)–C(23)	179(1)
Intermolecular Interation			
C(14)–O(1)	3.38	N(3)–C(11)*	3.21
C(15)–O(1)	3.25	C(15)–C(1)*	3.43

(continued overleaf)

TABLE II. *(continued)*

C(16)–O(1)	3.41	C(16)–C(1)*	3.27
C(15)–C(2)	3.38	C(16)–C(10)*	3.42
C(17)–C(2)	3.41	C(16)–C(11)*	3.34
C(16)–C(3)	3.41	C(17)–C(5)*	3.47
C(22)–C(3)	3.47	C(22)–C(5)*	3.41
C(22)–C(4)	3.33	C(22)–C(6)*	3.45
C(21)–C(5)	3.36	N(2)–N(2)**	3.09
C(25)–C(7)	3.43	*(x, –y, z + ½)	
C(24)–C(8)	3.50	**(–x, –y, –z + 1)	
N(2)–Cu	3.30		
C(14)–Cu	3.43		

TBLE III. Equations of Least-Squares Planes, and, in Brackets, Distances of Atoms from the Plane.

Plane (1): Cu, O(1), N(1)
$0.3080x + 0.2297y + 0.8841z = 3.3584$

Plane (2): Cu, O(1)*, N(1)* (*–x, y, ½ – z)
$0.3080x - 0.2297y + 0.8841z = 2.7807$

Plane (3): Cu, N(1), N(1)* (*–x, y, ½ – z)
$0.5264x + 0.0000y + 0.7877z = 2.7349$
[C(13) 0.000, C(12) –0.746, C(12) *0.746]

Plane (4): C(1)–C(10)
$0.1313x + 0.1614y + 0.9579z = 3.2036$
[C(1) –0.029, C(2) 0.054, C(3) –0.003, C(4) – 0.022, C(5) –0.025, C(6) 0.023, C(7) 0.005, C(8) 0.014, C(9) 0.014, C(10) –0.014]

Plane (5): C(1)–C(10) (symmetry operation –x, y, ½ – z)
$0.1313x - 0.1614 + 0.9579z = 3.4498$

Plane (6): N(2)–N(5), C(14)–C(25)
$0.1698x + 0.0170y + 0.9609z = 6.6200$
[N(2) 0.036, N(3) –0.192, N(4) 0.047, N(5) –0.166, C(14) 0.038, C(15) 0.023, C(16) –0.114, C(17) 0.078, C(18) 0.080, C(19) 0.036, C(20) 0.023, C(21) 0.090, C(22) 0.090, C(23) –0.018, C(24) –0.084, C(25) 0.030]

Plane (7): N(2)–N(5), C(14)–C(25) (symmetry operation x, –y, z – ½)
$0.1698x - 0.0170y + 0.9609z = -0.0525$

Dihedral Angle between Least-squares Planes

(1)–(2)	26.5
(4)–(5)	18.5
(4)–(6)	8.5
(4)–(7)	10.4

As shown in Fig. 3 and Table IV, the coordination environment of the copper atom is an intermediate between square planar and tetrahedron (distorted tetrahedron), where the dihedral angle between the CuNO planes is 26.5°. This coordination geometry is attributable to the skew conformation of the saturated six-membered chelate ring, where C(12), C(12)* (–x, y, –z + ½) and C(13) atoms are positioned at –0.75, 0.75 and 0.00 Å from the plane of Cu, N(1) and N(1)* (–x, y, –z + ½). It should be noted that the copper atom in $Cu(2,1\text{-iso-Pr})_2 \cdot 2TCNQ$ takes a square planar coordination geometry

TABLE IV. Molecular Parameters of Selected TCNQ Systems (Å).

	$TCNQ^0$	$TCNQ^{-0.59}$	$TCNQ^-$	$TCNQ^a$	$TCNQ^b$
Ref.	12	10	11	1	this work
a	1.344	1.356	1.358	1.336	1.353
b	1.443	1.433	1.422	1.434	1.449
c	1.373	1.402	1.410	1.374	1.360
d	1.436	1.423	1.416	1.426	1.422
e	1.138	1.151	1.155	1.138	1.153
b–c	0.070	0.031	0.012	0.060	0.089
c–d	–0.063	–0.021	–0.006	–0.052	–0.062

^{a}Cu(2,1-iso-Pr)$_2$·2TCNQ. ^{b}Cu(2,1-tn)·2TCNQ.

[1]. The dihedral angle between the two component naphthalene rings is 18.5°, smaller than that of the coordination sphere.

As shown in Fig. 4(a) and 4(b), the crystal structure shows that the π-electron donor (naphthalene ring) and the π-electron acceptor (TCNQ) stack alternately, as is typical for 1:1 neutral, Mulliken type π-molecular complexes [7]. The naphthalene ring overlaps on one of the two neighbouring TCNQ molecules and partly on the other, while the naphthalene ring in Cu(2,1-iso-Pr)$_2$·2TCNQ overlaps on and under the two neighbouring TCNQ molecules [1]. This difference of the overlapping modes might be attributable to the difference of the orientation of the naphthalene rings between Cu(2,1-tn) with *cis*-geometry and Cu(2,1-iso-Pr)$_2$ with *trans*-geometry. The intermolecular distances between the naphthalene moiety and TCNQ (Table II) are in the range reported for the donor-acceptor charge-transfer interaction [8]. The dihedral angles between the least-squares plane of the TCNQ molecule and that of the naphthalene ring for the preferable and partly overlaps are 8.6 and 10.5°, respectively.

There are two formation factors which may be involved in a series of the complexes (I) and (II): (1), the donor-acceptor interaction requires an arrangement in which the TCNQ is parallel to the naphthalene ring and these two molecules stack alternately; (2), the arrangement of the two neighbouring TCNQ which are positioned on the naphthalene moieties of the complex is restricted sterically. For the complex with *trans*-geometry Cu(2,1-R)$_2$ (I), the two requirements were achieved by taking a square planar coordination geometry with the markedly-stepped chair-like shape [1]. For the complex with *cis*-geometry Cu(2,1-tn) (II), the second factor might be more predominant, as suggested by the close contact between N(2) and N(2)* (–x, –y, –z + 1, 3.09 Å) and the consideration of the molecular model. The molecular complex takes a tetrahedral distortion and crystallizes in the overlapping mode described above to overcome the steric restriction.

TABLE V. Selected IR Data for the Parent Complexes and Their TCNQ Adducts (cm^{-1}).

	$C(CN)_2{}^a$	$C–H^b$	$C{\equiv}N^c$
TCNQ	475	860	2230
Cu(2,1-tn)·2TCNQ	470	844	2220
Cu(2,1-Me)$_2$·2TCNQ	468	836	2212
Cu(2,1-Et)$_2$·2TCNQ	468	836	2212
Cu(2,1-n-Pr)$_2$·2TCNQ	468	838	2212
Cu(2,1-iso-Pr)$_2$·2TCNQ	463	844	2212
Cu(2,1-n-Bu)$_2$·2TCNQ	463	836	2212
Ni(2,1-Me)$_2$·2TCNQ	466	836	2212
Ni(2,1-Et)$_2$·2TCNQ	465	836	2212
Ni(TMP)·TCNQ	458	826	2212

^{a}Wagging mode. ^{b}Bending mode. ^{c}Vibration.

	Cu(2,1-tn)	Cu(2,1-tn)·2TCNQ
	743	756

R	Cu(2,1-R)$_2$	Cu(2,1-R)$_2$·2TCNQ
Me	739	756
Et	751	754
n-Pr	744	752
iso-Pr	749	753
n-Bu	742	755

R	Ni(2,1-R)$_2$	Ni(2,1-R)$_2$·2TCNQ
Me	742	755
Et	749	755

Out-of-plane deformation.

It is well known that the bond lengths of TCNQ depend on the degree of charge-transfer of TCNQ. Among the numerous methods based on bond length examination, the test of Flandrois and Chasseau appears to be one of the most sensitive [9]. In Fig. 2, the bonds in TCNQ are labelled from 'a' to 'e' in order to use the same nomenclature. In Table IV, the bond lengths of TCNQ with various degree of charge-transfer are compared with those of TCNQ in Cu(2,1-tn)2TCNQ and Cu(2,1-iso-Pr)$_2$·2TCNQ [1, 10–12]. The differences b–c and c–d indicate that the TCNQ molecule in this complex is neutral (or only very weakly charged) even if uncertainties in bond lengths are taken into account. The data also suggests that the TCNQ in Cu(2,1-tn)·2TCNQ is slightly less charged than that in Cu(2,1-isoPr)$_2$·2TCNQ.

The infrared spectrum of Cu(2,1-tn)·2TCNQ is essentially a superposition of the spectra of the individual component molecules, as expected for the weak molecular complex. However, there are slight changes in the frequencies of the some bands as a result of the formation of the molecular complex. Some selected bands of the component and their molecular complexes are given in Table V. Three of the strongest bands in the spectrum of TCNQ are the C–H bending mode (860 cm^{-1}), the C(CN)$_2$ wagging mode (475 cm^{-1}), and the C≡N stretching frequency (2230 cm^{-1}) and these bands decrease to 844, 470 and 2220 cm^{-1}, respectively in Cu(2.1-tn)·2TCNQ, where the shifts are slightly smaller than those of NiTMP·TCNQ (tetramethylporphyrinatonickel(II) TCNQ) [13]. The characteristic band in the naphthalene ring of the component complex Cu(2,1-tn) is the out-of-plane deformation mode (743 cm^{-1}) and its band increases to 756 cm^{-1}. Such tendencies are also observed in the related complexes M(2,1-R)$_2$ and their TCNQ adducts, indicating the donor-acceptor interaction between the naphthalene ring of the complex and TCNQ.

Acknowledgements

We thank Prof. S. Kida at the Faculty of Science, Kyushu University for allowing us to use the diffractometer.

References

1 N. Matsumoto, Y. Nonaka, S. Kida, S. Kawano and I. Ueda, *Inorg. Chim. Acta, 37,* 27 (1979).
2 P. Pfeiffer, W. Christeleit, T. Hesse, H. Pfitzer and H. Thielert, *J. Prakt. Chem., 150,* 261 (1938).
3 A. Chakravorty and R. H. Holm, *Inorg. Chem., 3,* 1010 (1964).
4 'International Tables for X-ray Crystallography', Vol. IV, Kynoch Press, Birmingham (1974).
5 T. Sakurai, H. Iwasaki, Y. Watanabe, K. Kobayashi, Y. Bando and Y. Nakamichi, *Rikagaku Kenkyusho Hokoku (in Japanese), 50,* 75 (1974);
C. K. Johnson, ORTEP, Oak Ridge National Laboratory ORNL 3794 (1965);
S. Kawano, *Rep. Comp. Cent. Kyushu University, 13,* 39 (1980).
6 G. W. Everett Jr. and R. H. Holm, *Inorg. Chem., 7,* 776 (1968) and references therein.
7 S. C. Wallwork, *J. Chem. Soc.,* 494 (1961);
B. Shaanan and U. Shmueli, *Acta Crystallogr., B36,* 2076 (1980);
P. Cassoux and A. Gleizes, *Inorg. Chem., 19,* 665 (1980);
J. J. Mayerle, *Inorg. Chem., 16,* 916 (1977).
8 F. H. Herbstein, *Perspect. Sruct. Chem., 4,* 166 (1971).
9 S. Flandrois and D. Chasseau, *Acta Crystallogr., B33,* 2744 (1977).
10 T. J. Kistenmacher, T. E. Phillips and D. O. Cowan, *Acta Crystallogr., B30,* 763 (1974).
11 M. Konno and Y. Saito, *Acta Crystallogr., B31,* 2007 (1975).
12 R. E. Long, R. A. Sparks and K. N. Truebbood, *Acta Crystallogr., B30,* 932 (1965).
13 L. J. Pace, A. Ulman and J. A. Ibers, *Inorg. Chem., 21,* 199 (1982);
M. Siegmund, *Z. Chem., 15,* 194 (1975).