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Synthesis and Crystal Structure of 1:2 Molecular Complexes of Bis(N-alkyl-2-oxy-1-naphthylideneaminato)copper(II) and -nickel(II) with 7,7′,8,8′-Tetracyanoquinodimethane

NAOHIDE MATSUMOTO, YASUOMI NONAKA, SIGEO KIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812, Japan

SHIGEAKI KAWANO and IKUHIKO UEDA

College of General Education, Kyushu University 01, Ropponmatsu, Chuo-ku, Fukuoka 810, Japan

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The 1:2 molecular complexes of bis(N-alkyl-2-oxy-1-naphthylideneaminato)copper(II), and -nickel(II) with 7,7′,8,8′-tetracyanoquinodimethane (TCNQ) have been prepared and characterized, where N-alkyl group = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7. *The crystal structures of bis(N-isopropyl-2-oxy-1-naphthylideneaminato)copper(II) [I] and its 1:2 molecular complex with TCNQ [II] have been determined by the single-crystal X-ray diffraction method and refined by the block-diagonal least-squares method to give R = 3.55 and 3.71% for [I] and [II], respectively. The copper atom of compound [I] has a coordination geometry intermediate between square planar and tetrahedron, where the dihedral angle between CuNO planes is 38.6°. The crystal structure of compound [II] shows a typical* π–π *type molecular complex structure of alternately stacked donor (naphthalene moieties of metal complex) and acceptor (TCNQ) molecules, where the copper atom assumes a square planar coordination geometry with a markedly stepped chair-like shape. ESR measurements have revealed that the* $|A_\parallel|$ *values of the component copper(II) complexes are decreased and the* $g_\parallel$ *values are increased in the order of increasing bulkiness of the alkyl groups. On the other hand, the* $|A_\parallel|$ *and* $g_\parallel$ *values of the molecular complexes are less influenced by the bulkiness of the alkyl groups. The above results were discussed in relation to the coordination geometry around the copper atom.*

Introduction

In this study, we have prepared 1:2 molecular complexes of bis(N-alkyl-2-oxy-1-naphthylideneaminato)copper(II) (abbreviated as $Cu(L\text{-}R)_2$)) with 7,7′8,8′-tetracyanoquinodimethane (TCNQ), where R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7 (Fig. 1).

The coordination geometry around the copper atom of these molecular complexes should depend on both the steric hindrance of the alkyl groups and the π–π type donor–acceptor interactions between the naphthalene moieties of the metal complex (electron donor) and TCNQ (electron acceptor) molecules. It is known that the energy of the π–π type donor–acceptor interactions is of the same order as the square planar $\rightleftharpoons$ tetrahedral enthalpy difference [1, 2]. Therefore, it is of interest to investigate the structure of the molecular complex in which both effects are operating simultaneously.

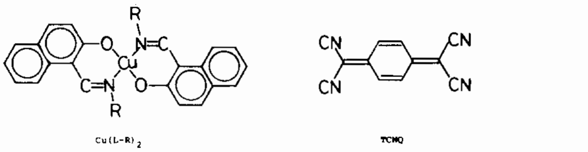

Fig. 1. Bis(N-alkyl-2-oxy-1-naphthylideneaminato)copper(II) and 7,7′,8,8′-tetracyanoquinodimethane are abbreviated as $Cu(L\text{-}R)_2$ and TCNQ, respectively, where R = CH_3, C_2H_5, n-C_3H_7 and iso-C_3H_7.

Thus, in this study, the crystal structures of two compounds, bis(N-isopropyl-2-oxy-1-naphthylideneaminato)copper(II) and its 1:2 molecular complex with TCNQ have been determined from the single crystal X-ray diffraction method, and ESR spectra have been measured for a series of $Cu(L\text{-}R)_2$ and their molecular complexes.

Experimental

Preparation

Bis(N-alkyl-2-oxy-1-naphthylideneaminato)copper(II) and -nickel(II), abbreviated as $Cu(L\text{-}R)_2$ and $Ni(L\text{-}R)_2$, where N-alkyl group = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, t-C_4H_9, were prepared by the method of Chakravorty *et al.* [3], from bis(2-oxy-1-naphthoaldehyde)copper(II) or -nickel(II) and monoamines.

The methods for the preparation of the molecular complexes are practically the same, and are

TABLE I. Elemental Analysis (%).

Molecular Complex	C		H		N	
	Found	Calcd.	Found	Calcd.	Found	Calcd.
Ni(L-me)$_2$·2Chl^a	47.02	(47.06)	2.20	(2.19)	3.01	(3.05)
Ni(L-me)$_2$·2TCNQ	68.97	(69.00)	3.39	(3.38)	16.69	(16.76)
Ni(L-et)$_2$·2TCNQ	69.22	(69.54)	3.62	(3.73)	16.42	(16.22)
Cu(L-me)$_2$·2Chl^a	46.72	(46.81)	2.11	(2.18)	2.98	(3.03)
Cu(L-me)$_2$·2TCNQ	68.38	(68.60)	3.30	(3.36)	16.62	(16.67)
Cu(L-et)$_2$·2TCNQ	69.25	(69.15)	3.67	(3.71)	16.13	(16.13)
Cu(L-npr)$_2$·2TCNQ	69.65	(69.67)	3.94	(4.05)	15.47	(15.62)
Cu(L-ipr)$_2$·2TCNQ	69.55	(69.67)	3.89	(4.05)	15.37	(15.62)

^{a}Chl denotes Chloranil ($C_6O_2Cl_4$).

exemplified by the synthesis of the molecular complex from Cu(L-ipr)$_2$ and TCNQ, *i.e.*, Cu(L-ipr)$_2$·2TCNQ. An acetone solution (50 ml) of TCNQ (204 mg, 1 mmol) was added to a hot chloroform solution (50 ml) of Cu(L-ipr)$_2$ (244 mg, 0.5 mmol). After being left standing for several hours, black, needle-like crystals separated out. They were collected and dried *in vacuo*. They were recrystallized from a mixture of chloroform and acetone. By this method, the 1:2 molecular complexes of Cu(L-R)$_2$ and TCNQ, where R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, were isolated as black, needle-like crystals, and those of nickel complexes, where R = CH_3, C_2H_5, were isolated as black, needle-like crystals. The results of elemental analyses are given in Table I.

Measurements

ESR spectra were measured with a JEOL ESR apparatus model JES-3X-ME using an X-band in chloroform at room temperature and 77 K. DPPH was used as a standard marker.

X-ray Diffraction

Cu(L-ipr)$_2$

The dark-brown plate crystals were prepared according to the literature [3] and recrystallized from methanol solution at room temperature. The cell parameters and intensities were measured on a Syntex P$\bar{1}$ four-circle automated diffractometer with MoKα radiation monochromated by a graphite plate (λ = 0.71073 Å). The cell parameters were determined by the least-squares procedure using the values of the Bragg angles of 15 reflections. The systematic absences of 0k0 for k = odd and h0l for l = odd indicate that the space group is P2$_1$/c. The density was measured by floatation in aqueous KI solution. Crystal data: $(C_{14}H_{14}NO)_2Cu$, M.W. = 488.08, monoclinic system, P2$_1$/c, Z = 4, a = 12.295(4), b = 18.843(5), c = 10.427(3) Å, β = 85.23(3)°, V = 2407.6 Å^3, D_m = 1.33, D_x = 1.346 g/cm^3. Intensity data were collected by the θ–2θ scan technique with a variable scan rate from 4.0 to 24.0 °/min. Three standard reflections were monitored after every 50 reflections and their intensities showed a good stability. A total of 1947 independent reflections within $2\theta < 40°$ were collected and were used for the structure determination. The Lorentz and polarization corrections were applied to the data, but no corrections for absorption and extinction effects were applied, because of the small crystal size and the low absorption coefficient.

Cu(L-ipr)$_2$·2TCNQ

The black needle-like crystals exhibited a strong dichroism. Weissenberg photographs about the needle (crystallographic c-axis) indicated that the crystals were triclinic. The cell parameters were obtained from the least-squares procedure using the values of the Bragg angles of 15 reflections measured on a Syntex P1 four-circle diffractometer. The density was measured by floatation method in aqueous KI solution. Crystal data: $(C_{12}H_4N_4)_2(C_{14}H_{14}NO)_2Cu$, M.W. = 888.4, triclinic system, Z = 1, a = 11.118(3), b = 14.178(1), c = 7.141(1) Å, α = 92.97(1), β = 101.54(2), γ = 103.88(2)°, D_m = 1.37, D_x = 1.376 g/cm^3, μ(MoKα) = 5.88 cm^{-1}. For the intensity measurements, a crystal of dimensions 0.2 X 0.1 X 0.3 mm was used. Intensity data were collected on a Syntex P$\bar{1}$ automated four-circle diffractometer with MoKα radiation monochromated by a graphite plate, using the θ–2θ scan technique to a limit of 2θ = 42°. The variable scan rate from 4.0 to 24.0 °/min was adopted. Three reflections were monitored after every measurements of 47 reflections. A total of 2264 independent reflections were collected and were used for the structure determination. Corrections were applied to the data for Lorentz and polarization effects. No absorption and extinction corrections were applied, because of the low absorption coefficient (μ = 5.88 cm^{-1}) and the small crystal size.

TABLE II. Fractional Atomic Coordinates and Temperature Factors.

Cu(L-ipr)$_2$

(a) *Non-hydrogen atoms*

All values have been multiplied by 10^4. The anisotropic temperature factors are expressed in the form: $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	1498(1)	816(0)	2252(1)	66(1)	29(0)	69(1)	6(0)	−1(0)	−1(0)
O(1)	1123(3)	799(2)	529(3)	82(3)	45(2)	68(4)	20(2)	−2(3)	−12(2)
O(2)	1441(3)	430(2)	3933(3)	87(3)	35(1)	72(4)	9(2)	18(3)	3(2)
N(1)	397(3)	1554(2)	2700(4)	66(4)	28(2)	65(5)	2(2)	−7(3)	−6(2)
N(2)	2998(3)	477(2)	1841(4)	68(4)	30(2)	75(5)	1(2)	2(3)	5(2)
C(1)	−582(4)	1407(3)	770(4)	59(4)	24(2)	63(5)	0(2)	−4(4)	1(3)
C(2)	217(4)	1001(3)	85(5)	66(5)	29(2)	88(6)	4(2)	−4(4)	2(3)
C(3)	65(5)	790(3)	−1212(5)	95(5)	41(2)	60(6)	2(3)	−6(4)	−6(3)
C(4)	−845(5)	983(3)	−1756(5)	113(6)	32(2)	59(6)	−7(3)	−4(4)	−8(3)
C(5)	−1675(4)	1387(3)	−1122(5)	83(5)	26(2)	61(5)	−9(2)	−7(4)	3(3)
C(6)	−2633(5)	1587(3)	−1714(5)	107(6)	29(2)	76(6)	−8(3)	−28(5)	2(3)
C(7)	−3432(5)	1981(3)	−1107(6)	102(6)	36(2)	113(7)	−4(3)	−41(5)	8(3)
C(8)	−3328(5)	2196(3)	154(6)	77(5)	41(2)	124(8)	12(3)	−6(5)	9(4)
C(9)	−2416(4)	2006(3)	778(5)	75(5)	39(2)	80(6)	0(3)	−11(4)	−4(3)
C(10)	−1558(4)	1606(3)	163(5)	68(4)	22(2)	71(6)	−4(2)	0(4)	1(3)
C(11)	−386(4)	1712(3)	1999(5)	62(4)	25(2)	71(6)	0(2)	5(4)	2(3)
C(12)	438(4)	1999(3)	3892(5)	85(5)	30(2)	93(6)	6(3)	−23(5)	−18(3)
C(13)	−136(6)	1636(3)	5029(6)	134(7)	45(3)	84(7)	16(3)	2(5)	−17(3)
C(14)	1608(6)	2177(4)	4065(7)	116(7)	46(3)	206(11)	−8(4)	−51(7)	−38(5)
C(15)	3165(4)	−155(3)	3862(5)	65(4)	24(2)	75(6)	−2(2)	−11(4)	−2(3)
C(16)	2170(4)	45(3)	4459(5)	86(5)	25(2)	81(6)	1(2)	−11(4)	3(3)
C(17)	1882(5)	−157(3)	5785(5)	91(5)	41(2)	71(6)	5(3)	−3(4)	7(3)
C(18)	2575(5)	−548(3)	6405(5)	121(6)	42(2)	59(6)	−15(3)	−1(5)	7(3)
C(19)	3594(4)	−791(3)	5834(5)	92(5)	28(2)	85(6)	−15(3)	−31(4)	3(3)
C(20)	4325(5)	−1214(3)	6496(6)	123(6)	38(2)	104(7)	−23(3)	−52(5)	21(3)
C(21)	5269(5)	−1452(3)	5922(7)	77(5)	40(3)	206(10)	−5(3)	−59(6)	13(4)
C(22)	5565(5)	−1296(3)	4636(6)	91(6)	44(3)	136(8)	1(3)	−23(5)	11(4)
C(23)	4879(5)	−884(3)	3976(5)	84(5)	37(2)	108(7)	1(3)	−14(5)	12(3)
C(24)	3889(4)	−610(3)	4531(5)	81(5)	25(2)	82(6)	−5(2)	−21(4)	0(3)
C(25)	3522(4)	89(3)	2609(5)	66(4)	27(2)	93(6)	1(2)	−4(4)	0(3)
C(26)	3636(5)	654(3)	587(6)	75(6)	48(3)	124(8)	14(3)	13(5)	25(4)
C(27)	3306(5)	149(4)	−495(6)	102(6)	70(3)	96(7)	28(4)	−2(5)	−13(4)
C(28)	3520(6)	1426(4)	283(7)	109(7)	52(3)	187(10)	−3(4)	5(6)	44(5)

(b) *Hydrogen atoms*

The hydrogen atoms are labelled in terms of the atoms to which they are attached. The coordinate values have been multiplied by 10^3.

Atom	x/a	y/b	z/c	B(A^2)	Atom	x/a	y/b	x/c	B(A^2)
H(3)	73(5)	60(3)	−172(6)	9.3(18)	H(17)	110(4)	−1(3)	627(5)	5.8(13)
H(4)	−83(3)	84(2)	−258(4)	4.6(11)	H(18)	241(3)	−65(2)	719(4)	3.3(10)
H(6)	−262(4)	146(2)	−258(4)	4.9(12)	H(20)	411(3)	−130(2)	733(4)	4.3(11)
H(7)	−420(5)	210(3)	−156(6)	9.2(18)	H(21)	578(4)	−171(3)	632(5)	5.8(13)
H(8)	−395(4)	245(3)	59(4)	5.5(12)	H(22)	634(5)	−151(3)	410(6)	8.7(17)
H(9)	−240(3)	215(2)	160(4)	3.8(10)	H(23)	516(4)	−78(3)	306(5)	6.0(13)
H(11)	−93(4)	202(2)	232(4)	4.9(12)	H(25)	431(4)	−4(2)	227(4)	4.4(11)
H(12)	8(4)	251(3)	369(4)	7.0(15)	H(26)	442(3)	61(2)	72(4)	4.8(11)
H(13A)	24(4)	114(3)	514(5)	7.0(15)	H(27A)	365(6)	23(4)	−7(7)	14.1(23)
H(13B)	−85(4)	162(3)	499(5)	7.4(15)	H(27B)	242(5)	25(3)	−64(5)	8.5(16)
H(13C)	−11(4)	191(3)	588(5)	7.7(16)	H(27C)	357(4)	−28(3)	−28(3)	8.7(16)
H(14A)	160(4)	246(3)	465(5)	5.9(12)	H(28A)	276(4)	148(3)	7(5)	7.6(14)

(continued overleaf)

TABLE II. *(continued)*

Atom	x/a	y/b	z/c	B(A^2)	Atom	x/a	y/b	x/c	B(A^2)
H(14B)	208(5)	176(3)	432(6)	9.1(18)	H(28B)	362(5)	181(3)	99(5)	8.1(16)
H(14C)	203(5)	245(3)	318(6)	9.8(18)	H(28C)	398(5)	153(3)	−53(6)	10.0(17)

Cu(L-ipr)$_2$•2TCNQ

(a) *Non-hydrogen atoms*

All values have been multiplied by 10^4. The anisotropic temperature factors are expressed in the form: $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$

Atom	x/a	y/b	z/c	B$_{11}$	B$_{22}$	B$_{33}$	B$_{12}$	B$_{13}$	B$_{23}$
Cu	0	0	0	58(0)	37(0)	225(1)	17(0)	35(0)	7(0)
O	−1668(2)	162(1)	−695(3)	57(2)	37(1)	359(7)	11(1)	14(3)	−4(2)
N(1)	670(2)	1407(1)	−317(4)	56(2)	44(1)	212(7)	18(1)	42(3)	10(2)
C(1)	−2045(3)	946(2)	−398(4)	60(3)	41(2)	197(8)	19(2)	21(4)	17(3)
C(2)	−3362(3)	812(2)	−414(5)	53(3)	47(2)	224(9)	10(2)	18(4)	20(3)
C(3)	−3822(2)	1579(2)	−47(5)	43(3)	53(2)	224(9)	15(2)	38(4)	25(3)
C(4)	−3057(2)	2541(2)	330(4)	56(3)	46(2)	151(7)	17(2)	25(4)	16(3)
C(5)	−3544(3)	3342(2)	736(4)	65(3)	57(2)	184(8)	29(2)	38(4)	20(3)
C(6)	−2806(3)	4273(2)	1108(5)	96(4)	48(2)	197(9)	34(2)	48(4)	7(3)
C(7)	−1532(3)	4448(2)	1061(5)	88(3)	40(2)	200(9)	19(2)	40(4)	18(3)
C(8)	−1026(3)	3690(2)	657(4)	63(3)	41(2)	188(8)	14(2)	35(4)	8(3)
C(9)	−1754(2)	2716(2)	280(4)	60(3)	41(2)	135(7)	20(2)	20(3)	17(3)
C(10)	−1254(2)	1894(2)	−94(4)	47(3)	36(1)	159(7)	10(2)	18(3)	9(3)
C(11)	43(3)	2060(2)	−224(4)	60(3)	42(2)	190(8)	14(2)	36(4)	13(3)
C(12)	2033(3)	1787(2)	−391(5)	70(3)	45(2)	294(10)	20(2)	69(5)	16(3)
C(13)	2795(3)	2110(3)	1622(6)	62(3)	73(3)	373(13)	7(2)	31(5)	2(4)
C(14)	2240(4)	2540(3)	−1772(7)	99(4)	87(3)	489(16)	29(3)	138(7)	89(6)
N(2)	−5250(3)	4440(2)	7009(5)	122(4)	102(3)	346(10)	66(2)	90(5)	68(4)
N(3)	−1579(3)	6009(2)	6001(5)	106(4)	62(2)	424(12)	19(2)	0(5)	12(4)
N(4)	−3584(3)	−759(2)	4107(5)	102(3)	63(2)	382(11)	12(2)	36(5)	1(4)
N(5)	218(3)	860(2)	3779(5)	125(4)	84(2)	374(11)	59(2)	114(5)	75(4)
C(15)	−4321(3)	4405(2)	6626(5)	99(4)	60(2)	217(9)	40(2)	40(5)	32(3)
C(16)	−3137(3)	4375(2)	6186(4)	79(3)	59(2)	158(8)	26(2)	21(4)	16(3)
C(17)	−2284(3)	5294(2)	6111(5)	83(4)	62(2)	228(9)	35(2)	10(5)	7(3)
C(18)	−2845(3)	3510(2)	5791(4)	66(3)	50(2)	134(7)	20(2)	20(4)	8(3)
C(19)	−3740(3)	2588(2)	5686(4)	69(3)	57(2)	177(8)	18(2)	43(4)	18(3)
C(20)	−3456(3)	1749(2)	5247(4)	64(3)	52(2)	187(8)	8(2)	34(4)	12(3)
C(21)	−1613(3)	3506(2)	5462(4)	67(3)	47(2)	178(8)	14(2)	23(4)	11(3)
C(22)	−1327(3)	2671(2)	5064(4)	54(3)	54(2)	175(8)	14(2)	41(4)	13(3)
C(23)	−2227(3)	1748(2)	4924(4)	69(3)	50(2)	147(7)	16(2)	31(4)	9(3)
C(24)	−1936(3)	889(2)	4474(4)	68(3)	52(2)	174(8)	16(2)	34(4)	13(3)
C(25)	−734(3)	876(2)	4103(5)	102(4)	47(2)	219(9)	28(2)	47(5)	23(3)
C(26)	−2836(3)	−34(2)	4293(5)	83(4)	58(2)	223(9)	27(2)	28(4)	9(3)

(b) *Hydrogen atoms*

The hydrogen atoms are labelled in terms of the atoms to which they are attached. The coordinate values have been multiplied by 10^3.

Atom	x/a	y/b	z/c	B(A^2)	Atom	x/a	y/b	z/c	B(A^2)
H(2)	−391(2)	11(2)	−71(4)	4.0(7)	H(13B)	268(3)	275(2)	213(5)	7.4(10)
H(3)	−467(2)	146(2)	−4(4)	3.3(6)	H(13C)	266(3)	158(2)	248(5)	7.0(10)
H(5)	−441(2)	318(2)	80(4)	3.2(6)	H(14A)	219(3)	318(2)	−115(5)	7.0(10)
H(6)	−312(2)	479(2)	149(4)	4.3(7)	H(14B)	310(3)	269(2)	−184(5)	6.7(10)
H(7)	−99(2)	512(2)	123(4)	3.6(7)	H(14C)	175(4)	240(3)	−304(6)	9.8(13)
H(8)	−15(2)	385(2)	72(4)	3.4(6)	H(19)	−456(3)	256(2)	595(4)	5.0(8)
H(11)	54(2)	277(2)	−20(4)	4.3(7)	H(20)	−408(2)	115(2)	520(4)	3.7(7)
H(12)	222(2)	124(2)	−87(4)	3.9(7)	H(21)	−104(2)	413(2)	550(4)	3.5(7)
H(13A)	366(3)	230(2)	161(5)	6.5(9)	H(22)	51(2)	269(2)	477(4)	3.3(6)

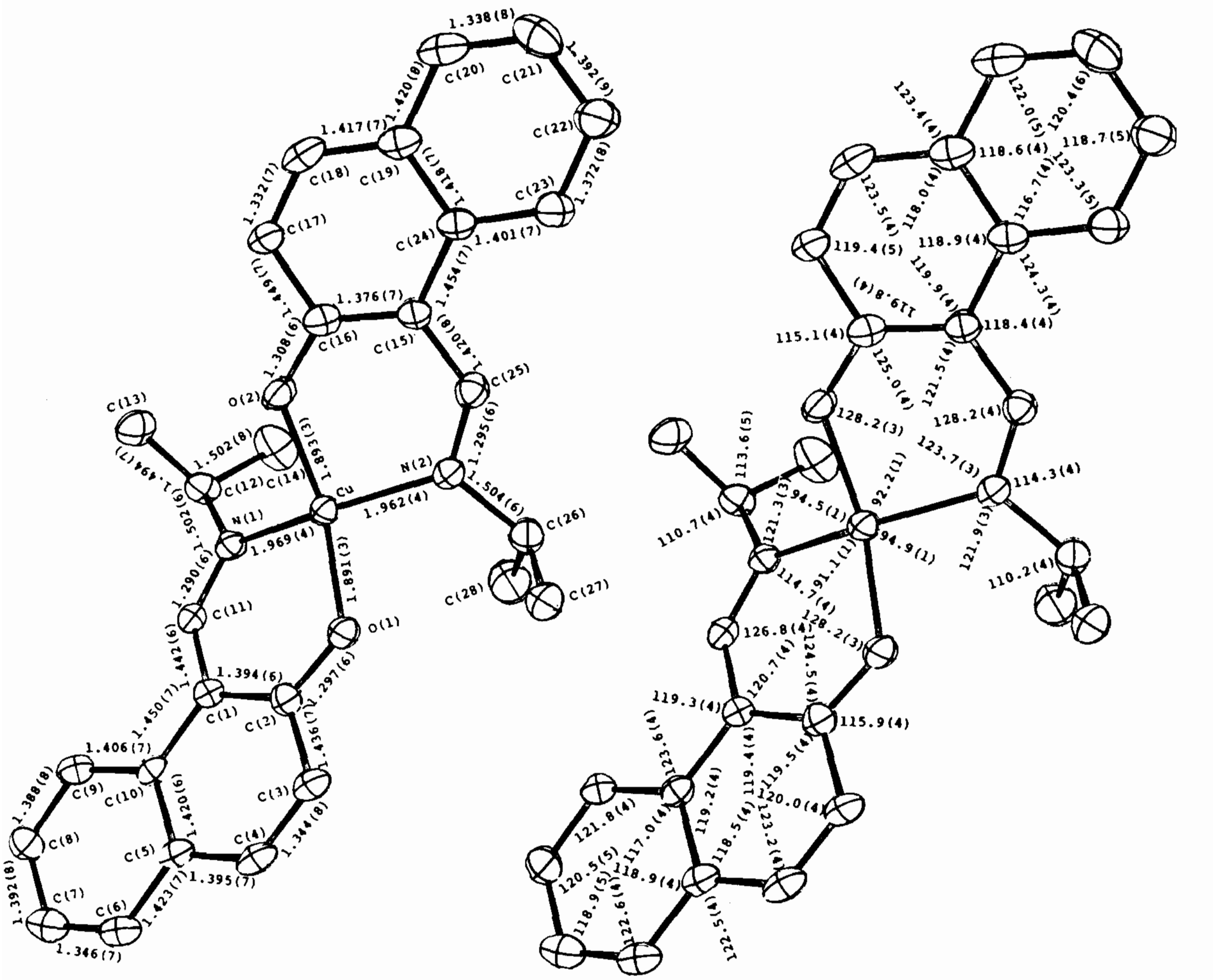

Fig. 2. Atom numbering scheme, bond lengths (Å) and bond angles (°) of Cu(L-ipr)$_2$ with estimated standard deviations in parentheses. The thermal ellipsoids are drawn at 25% probability level [6].

Solution and Refinement

The structures were solved by the heavy atom method, and refined by the block-diagonal least-squares method. In the least-squares procedure, the function minimized was $\Sigma w(|F_o| - k|F_c|)^2$ and the equal weight was adopted for all the reflections. The atomic scattering factors were taken from International Tables for X-Ray Crystallography [4]. All the calculations were carried out on a FACOM M-190 computer in the Computer Center of Kyushu University with UNICS II program system [5]. The drawings were made by use of ORTEP program [6]. The final positional and thermal parameters with their estimated standard deviations are given in Table II. A list of observed and calculated structure factors is available from the Editor.

Cu(L-ipr)$_2$

The coordinates of the copper atom were obtained from a three dimensional Patterson synthesis. Successive Fourier and difference Fourier syntheses revealed all the non-hydrogen atoms. Refinement with isotropic thermal parameters was carried out by the block-diagonal least-squares method and the discrepancy indices $R_1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were 10.02 and 13.94%, respectively. The block-diagonal least-squares refinement with anisotropic thermal parameters yielded R_1 = 7.20 and R_2 = 12.36%, respectively. At this stage, a difference Fourier synthesis was calculated and revealed all the hydrogen atoms. Further refinement including the hydrogen atoms yielded the final values of 3.55 and 3.78% for R_1 and R_2, respectively. The final shifts in the atomic parameters are less than one-tenth of their estimated standard deviations. A final difference Fourier synthesis showed no important features, the peaks being varied in the range of ±0.17 eÅ^{-3} except one peak of 0.32 eÅ^{-3}.

Cu(L-ipr)$_2$·2TCNQ

The space group $P\bar{1}$ was selected and confirmed later in the course of the structure determination.

TABLE III. Least-squares Planes and Dihedral Angles of Cu(L-ipr)$_2$.

(a) *Equations of several least-squares planes with the form AX + BY + CZ = D*

Plane	Atoms	A	B	C	D
(I)	CuO(1)N(1)	0.6646	0.7077	−0.2396	1.8813
(II)	CuO(2)N(2)	0.3836	0.8583	0.3407	2.8982
(III)	C(1) C(10)	0.4276	0.8377	−0.3395	1.6653
(IV)	C(15) C(24)	0.4807	0.8240	0.2997	2.9406
(V)	CuO(1)N(1)C(1)C(2)C(11)	0.5191	0.7788	−0.3520	1.5785
(VI)	CuO(2)N(2)C(15)C(19)C(25)	0.4151	0.8328	0.3661	3.0165

(b) *Atom distances (Å) from least-squares planes*

(I)	O(2) −0.882, N(2) 0.851, C(12) 0.397, C(13) −0.772, C(14) 1.558
(II)	O(1) −0.871, N(1) 0.848, C(26) 0.100, C(27) −1.290, C(28) 1.176
(III)	Cu −0.300, O(1) 0.018, N(1) 0.144, C(11) 0.202
(IV)	Cu 0.006, O(2) −0.032, N(2) 0.221, C(25) 0.198
(V)	Cu −0.147, O(1) 0.140, N(1) 0.090, C(1) −0.131, C(2) 0.002, C(11) 0.046
(VI)	Cu −0.033, O(2) 0.031, N(2) 0.028, C(15) −0.037, C(19) 0.005, C(25) 0.005

(c) *Dihedral angles (deg) between planes*

(I)–(II)	38.6	(III)–(IV)	37.4	(V)–(VI)	42.6

Fourier synthesis based on the copper atom revealed all the non-hydrogen atoms. The block-diagonal least-squares refinement with isotropic thermal parameters was carried out and the discrepancy indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ were 10.00 and 10.05%, respectively. Anisotropic thermal parameters were introduced and five-additional cycles brought the R_1 and R_2 values down to 6.00 and 6.05%, respectively. A difference Fourier synthesis calculated at this stage gave the peaks which correspond to all the hydrogen atoms. Introduction of these hydrogen atoms and refinement for all the atoms gave the final R_1 and R_2 values of 3.71 and 3.88%, respectively. Shifts of the positional and thermal parameters of non-hydrogen atoms in the last cycle were less than one-tenth of their estimated standard deviations. A final difference Fourier synthesis showed no significant features in the undulations, which varied from −0.2 to +0.2 eÅ^{-3}.

Results and Dicussion

Structure of Cu(L-ipr)$_2$

A perspective drawing of the molecule with the atom numbering scheme, the bond distances and angles is shown in Fig. 2. Some least-squares planes with the deviations of atoms from the planes are given in Table III.

As shown in Fig.3, the coordination environment of the copper atom is intermediate between square planar and tetrahedron (distorted tetrahedron), where the dihedral angle between CuNO planes is 38.6°. The single crystal X-ray diffraction method has been applied to a number of bis(N-substituted-salicylideneaminato)copper(II) and verified that the coordination environment of the copper atom is a distorted tetrahedron and the degree of distortion depends on the steric effects of the alkyl groups [7]. The dihedral angles between CuNO planes have been reported to be 0° (11.4, 7.4°), 35.6°, 59.7° and 53.6° for bis(N-alkylsalicylideneaminato)copper(II) with alkyl group = CH_3, C_2H_5 (α-form), C_2H_5 (β-form), iso-C_3H_7, and t-C_4H_9, respectively [7]. Therefore, the dihedral angle (38.6°) of the present complex is smaller than that of the corresponding bis(N-isopropyl-salicylideneaminato)copper(II) (59.7°).

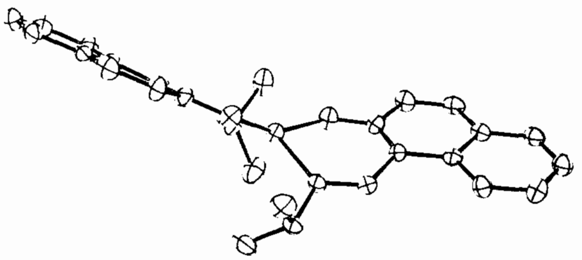

Fig. 3. An edge-on view of Cu(L-ipr)$_2$ projected to the napthalene plane. The dihedral angle between CuNO planes is 38.6°. The thermal ellipsoids are drawn at 25% probability level [6].

Structure of Cu(L-ipr)$_2$•2TCNQ

A perspective drawing of Cu(L-ipr)$_2$•2TCNQ with the atom numbering scheme, the bond distances and angles is shown in Fig. 4. Figures 5(a) and 5(b) show the crystal structure projected along the *a* and *c*-axis.

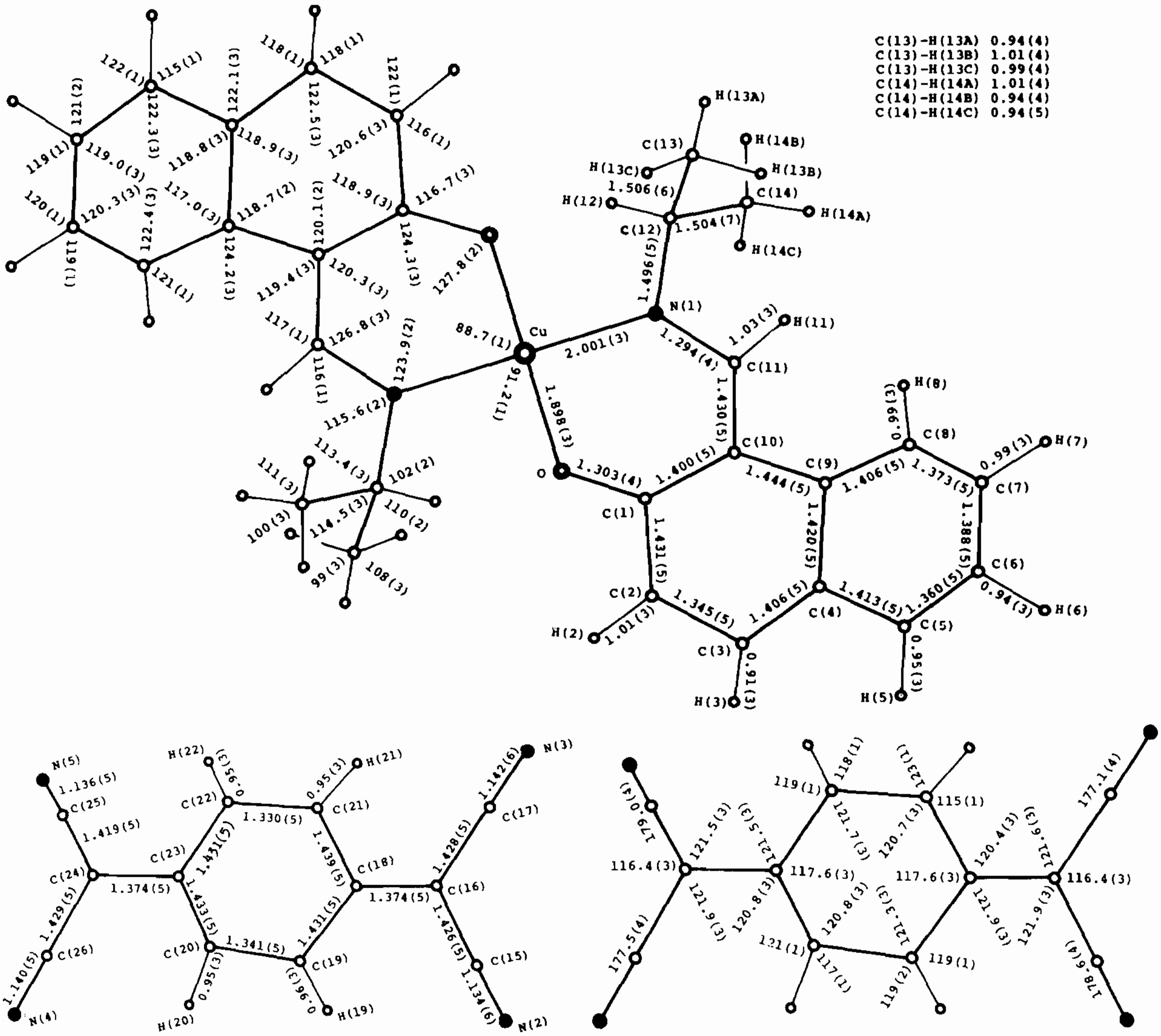

Fig. 4. Atom numbering scheme, bond lengths (Å) and bond angles (°) of Cu(L-ipr)$_2$·2TCNQ with their estimated standard deviations in parentheses.

respectively, showing how the molecules overlap in such a way that TCNQ molecule lies over or under the naphthalene rings of the copper(II) complex. Some least-squares planes with the deviations of atoms from these planes are given in Table IV. Donor–acceptor intermolecular distances less than 3.5 Å are given in Table V.

As shown in Fig. 5(a) and 5(b), the crystal structure shows a typical π–π type molecular complex structure [8] of alternately stacked Cu(L-ipr)$_2$ and TCNQ molecules, held by electron donor–acceptor interactions. Direct evidence for the π–π type donor–acceptor interactions between the TCNQ and the copper component molecule is provided by interatomic distances which are considerably shorter than the sum of the expected van der Waals distance of aromatic systems, as tabulated in Table V.

The copper atom must lie on the twofold special position since there is only one formula unit in a unit cell and the space group is P$\bar{1}$. The metal complex is thus required to have a center of symmetry, in which the copper atom is positioned. Therefore, the copper atom has a square planar coordination geometry. As shown in Fig. 5(a), the complex assumes a markedly stepped chair-like shape, where the seat and the rests are formed by the coordination plane (CuN$_2$O$_2$) and two 2-oxy-1-naphthylideneaminato moieties, respectively, the copper atom deviating by 0.72 Å from the least-squares plane of the naphthalene ring. Dihedral angle between the coordination plane (CuN$_2$O$_2$) and the plane of the naphthalene ring is 26.3°. Dihedral angle between the least-squares plane of the TCNQ molecule and that of the naphthalene ring is 9.3°. In addition to

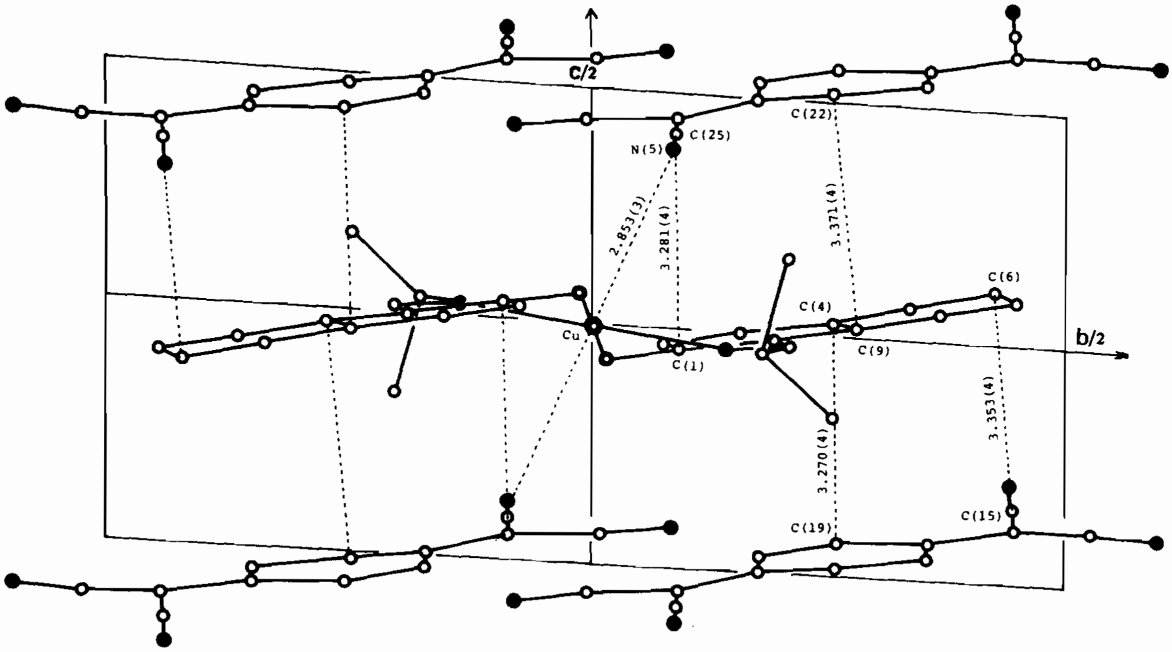

Fig. 5a). Projection along the a-axis of Cu(L-ipr)$_2$·2TCNQ.

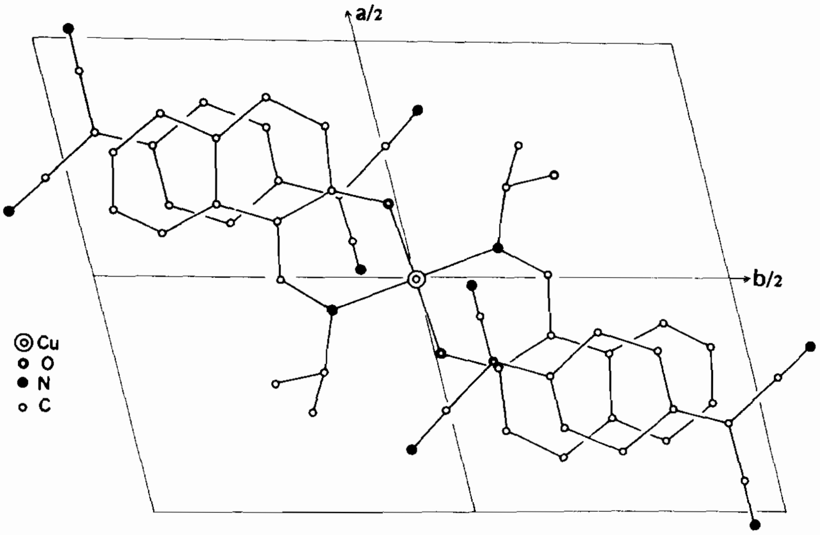

Fig. 5b). Projection along the c-axis of Cu(L-ipr)$_2$·2TCNQ.

the π–π type donor–acceptor interactions, N(4) atoms of TCNQ molecules approach the axial positions of Cu atom, forming a tetragonal bipyramid (Cu–N(4), 2.853(3) Å), as shown in Fig. 5(a).

The above result shows that there is a remarkable difference between the coordination geometries of Cu(L-ipr)$_2$ and Cu(L-ipr)$_2$•2TCNQ. This implies that the donor–acceptor interaction is an important factor in determining the coordination geometry of the metal complex.

The 1:2 complexes of nickel(II) and cobalt(II) with aminotropolonates, N-alkylsalicylideneaminates and β-ketoaminates are known to have a square planar ⇌ tetrahedral configurational equilibrium in solution [1]. Analyses of the temperature dependence of the magnetic moments and the contact shifts in NMR spectra revealed that the enthalpy changes fall in the range of several kcal/mol [1]. On the other hand, the donor–acceptor interaction of the π–π type molecular complexes was estimated from the temperature dependence of the intensity of the electronic spectra [2] (for example, the ΔH values between tetracyanoethane and naphthalene is 3.86 kcal/mol). The results show that the energy of the π–π type donor–acceptor interaction is of the same order as the square planar ⇌ tetrahedral enthalpy difference.

TABLE IV. Distances from Least-squares Planes (A) of Cu(L-ipr)$_2$·2TCNQ (distances for defining atoms asterisked).

Atom	(I)	(II)	(III)	Atom	(II)	(IV)
Cu	0.711	0.665	0.000*	N(2)	3.949	0.086*
O	0.089	0.053*	0.000*	N(3)	2.974	−0.186*
N(1)	0.101	0.066*	0.000*	N(4)	3.550	−0.157*
C(1)	0.034*	0.010*	0.525	N(5)	3.038	0.034*
C(2)	−0.009*	−0.027*	0.820	C(15)	3.740	0.042*
C(3)	−0.014*	−0.021*	1.411	C(16)	3.504	0.013*
C(4)	−0.004*	−0.004*	1.744	C(17)	3.225	−0.084*
C(5)	0.005*	0.017*	2.378	C(18)	3.499	0.034*
C(6)	0.019*	0.037*	2.704	C(19)	3.653	0.006*
C(7)	0.004*	0.017*	2.387	C(20)	3.609	−0.011*
C(8)	−0.015*	−0.014*	1.761	C(21)	3.334	0.083*
C(9)	−0.019*	−0.025*	1.417	C(22)	3.318	0.092*
C(10)	−0.000*	−0.018*	0.794	C(23)	3.447	0.040*
C(11)	−0.067	−0.092*	0.411	C(24)	3.402	0.022*
C(12)	0.010	−0.028	−0.301	C(25)	3.209	0.039*
C(13)	1.344	1.307	0.987	C(26)	3.504	−0.056*
C(14)	−1.160	−1.194	−1.102			
N(5)	–	–	2.807			

Equations of least-squares planes

(I) $-0.00154\,X - 0.21442\,Y + 0.97674\,Z = -0.71157$

(II) $-0.00501\,X - 0.20665\,Y + 0.97840\,Z = -0.66527$

(III) $-0.19321\,X + 0.19787\,Y + 0.96100\,Z = 0.00000$

(IV) $0.15493\,X - 0.17816\,Y + 0.97173\,Z = 2.29300$

X, Y, Z are Cartesian axes lying along $a \times c^*$, b *and* c^*, respectively.

TABLE V. Donor–Acceptor Intermolecular Distances less than 3.5 A of Cu(L-ipr)$_2$·2TCNQ.^{a}

Cu–N(5)	1	2.853(3)	C(4)–C(19)	2	3.270(4)
Cu–C(25)	1	3.455(4)	C(5)–C(15)	2	3.431(5)
O–N(5)	1	3.414(4)	C(6)–C(21)	1	3.475(4)
O–C(25)	1	3.411(4)	C(6)–C(15)	2	3.353(4)
N(1)–N(5)	1	3.180(4)	C(6)–C(16)	2	3.486(4)
C(1)–C(24)	1	3.475(4)	C(7)–C(21)	1	3.498(5)
C(1)–C(25)	1	3.281(4)	C(9)–C(22)	1	3.371(4)
C(2)–C(20)	2	3.436(5)	C(10)–C(23)	2	3.496(4)
C(3)–C(19)	2	3.451(5)	C(11)–N(5)	1	3.408(5)
C(3)–C(20)	2	3.490(5)			

^{a}1: x, y, z; 2: x, y, −1 + z.

Therefore, the difference of the coordination geometries between Cu(L-ipr)$_2$ and Cu(L-ipr)$_2$·2TNCQ can be explained as follows. The coordination geometry of the copper atom of Cu(L-ipr)$_2$ should be determined mainly by the steric hindrance of the isopropyl groups, and as a result of this effect the complex assumes a distorted tetrahedral coordination geometry. On the other hand, the coordination geometry of the molecular complex Cu(L-ipr)$_2$·2TCNQ should be affected by both the steric hindrance of the isopropyl groups and the donor–acceptor interaction operating between the naphthalene moieties and TCNQ. The donor–acceptor interaction requires an arrangement in which the molecular plane of TCNQ is parallel to the plane of the naphthalene ring of the metal complex. The isopropyl groups cause a steric hindrance in achieving the planar arrangement of the whole Cu(L-ipr)$_2$ molecule. As a compromise between these requirements, the molecular complex assumes a square planar coordination with a stepped structure as described above so that parallel stacking of naphthalene rings and TCNQ is achieved.

ESR Spectra

ESR data of Cu(L-R)$_2$ series and these 1:2 molecular complexes with TCNQ are given in Table VI.

ESR spectra of the Cu(L-R)$_2$ series show a typical axial symmetry pattern. The coupling constant $|A_\parallel|$ decreases and the $g_\parallel$ increases with an increase of the bulkiness of the alkyl groups. This tendency has been recognized in structurally well-characterized complexes of copper(II) with N-alkylsalicylideneaminates, bis(pyrazolyl)gallates, and N-substituted-pyrrole-2-carboxaldiminates [9–11]. This tendency has been explained in terms of the increase in tetrahedral distortion from square planar [9–11]. Therefore, on the basis of the above discussion and the crystal structure of Cu(L-ipr)$_2$, the decrease of the $|A_\parallel|$ and the

TABLE VI. ESR Parameters Obtained from Chloroform Solution (g_o and A_o, at room temp.) and Its Glass (at 77 K).

Compound	g_o	$g_{\parallel}$	$g_{\perp}$	A_o	$A_{\parallel}$	$A_{\perp}$
$Cu(L\text{-}me)_2$	2.109	2.183	–	79.5	189.4	–
$Cu(L\text{-}et)_2$	2.110	2.174	2.078	77.6	193.8	19.5
$Cu(L\text{-}npr)_2$	2.112	2.212	2.062	77.0	187.4	21.9
$Cu(L\text{-}ipr)_2$	2.117	2.224	2.064	69.4	160.0	24.1
$Cu(L\text{-}tbu)_2$	2.319	2.252	2.083	53.7	143.8	8.6
$Cu(L\text{-}me)_2 \cdot 2TCNQ$	2.109	2.147	–	78.9	174.0	–
$Cu(L\text{-}et)_2 \cdot 2TCNQ$	2.110	2.188	2.071	76.8	182.5	24.0
$Cu(L\text{-}npr)_2 \cdot 2TCNQ$	2.111	2.207	2.063	75.6	180.8	22.9
$Cu(L\text{-}ipr)_2 \cdot 2TCNQ$	2.118	2.219	2.068	67.6	172.4	15.2

A: $\times 10^{-4} cm^{-1}$

increase of the $g_{\parallel}$ are attributed to the tetrahedral distortion.

On the other hand, the coupling constants $|A_{\parallel}|$ and the $g_{\parallel}$ values of the molecular complexes are less influenced by the alkyl groups compared with those of the $Cu(L\text{-}R)_2$ series, indicating that the coordination geometries of the molecular complexes are similar to each other. Therefore, similar to the case of $Cu(L\text{-}ipr)_2 \cdot 2TCNQ$, it can be assumed that all the molecular complexes of this series are of essentially square planar coordination geometry, because the π–π type donor–acceptor interaction is operating between the naphthalene rings of the metal complex and TCNQ.

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