Crystal Structures and Single-crystal Electron Spin Resonance Spectra of π–π Type Molecular Complexes of Bis(1-methyliminomethyl-2-naphtholato)copper(II) †

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The donor–acceptor molecular complexes of bis(1-methyliminomethyl-2-naphtholato)copper(II) [CuL_2] with 7,7,8,8-tetracyanoquinodimethane (tcnq), tetrachloro-1,4-benzoquinone (tcbq) and 1,3,5-trinitrobenzene (tnb), as well as the parent complex have been subjected to single-crystal X-ray diffraction analysis. The molecular complexes [CuL_2]·2tcnq and [CuL_2]·2tnb crystallize in the triclinic space group $P\bar{1}$ and [CuL_2]·2tcbq crystallizes in the monoclinic space group $P2_1/n$, the copper atoms of all complexes being positioned at an inversion centre. The molecular complexes showed a typical π–π type structure consisting of alternately stacked π-electron donor (naphthalene moiety of copper complex) and π-electron acceptor (tcnq, tcbq and tnb) along the *c* axis (needle axis). The ESR spectrum for a copper(II) doped sample of diamagnetic [NiL_2]·2tnb showed simple copper quartet lines due to $I = \frac{3}{2}$. The X-ray analyses indicated that the donor–acceptor interaction operating along the *c* axis gives a one-dimensional structure consisting of alternately stacked donor and acceptor molecules, but no distinct two-dimensional interaction.

Besides the molecular design of discrete metal complexes, design of the crystal lattice has attracted much attention.[1] The donor–acceptor interaction is known to be one of the important factors in determining the molecular orientation and packing in crystals.[2] We have been interested in the crystal structures of donor–acceptor charge-transfer complexes.[3] Previously[3] we have determined the crystal structure of a 1:2 molecular complex of bis(1-isopropyliminomethyl-2-naphtholato)copper-(II) and 7,7,8,8-tetracyanoquinodimethane (tcnq) as well as that of the parent complex, the co-ordination geometry of the latter being intermediate between square planar and tetrahedral and that of the molecular complex being square planar. This result demonstrated that the donor–acceptor interaction operating between the naphthalene moiety and the tcnq molecule can affect the co-ordination geometry. In this study, in order to examine how the donor–acceptor interaction can control the orientation and packing of the metal complex in the crystal lattice, three molecular complexes of bis(1-methyliminomethyl-2-naphtholato)copper(II) [CuL_2] with the π-electron acceptors tcnq, tetrachloro-1,4-benzoquinone (tcbq) and 1,3,5-trinitrobenzene (tnb) have been prepared and their crystal structures and ESR spectra studied.

Experimental

Synthesis.—[CuL_2]. The complex was prepared by mixing bis(1-formyl-2-naphtholato)copper(II) and excess of methylamine in methanol and recrystallized from a mixture of dichloromethane and methanol.[3,4] IR: ν(C=N, C=C) 1620, 1610 cm^{-1} (Found: C, 66.55; H, 4.65; N, 6.50. Calc. for $C_{24}H_{20}CuN_2O_2$: C, 66.75; H, 4.65; N, 6.50%).

[CuL_2]·2tcnq. An acetone solution (50 cm^3) of tcnq (204 mg, 1 mmol) was added to a dichloromethane solution (50 cm^3) of [CuL_2] (216 mg, 0.5 mmol) on a water-bath (*ca.* 50 °C). After stirring for a few minutes, black needle microcrystals appeared slowly. The solution was allowed to stand for several hours. The crystals were then filtered off, dried in air and recrystallized from dichloromethane (*ca.* 70% yield). IR: ν(C≡N) 2270 cm^{-1} (Found: C, 68.60; H, 3.40; N, 16.65. Calc. for $C_{48}H_{28}CuN_{10}O_2$: C, 68.60; H, 3.35; N, 16.65%).

[CuL_2]·2tcbq. The method employed was practically the same as that for the tcnq adduct, except for the use of tetrachloro-1,4-benzoquinone instead of tcnq. Black needle crystals were obtained (*ca.* 70% yield). IR (characteristic bands for tcbq): 1690, 1560, 1115 and 710 cm^{-1} (Found: C, 46.90; H, 2.20; N, 3.05. Calc. for $C_{36}H_{20}Cl_8CuN_2O_6$: C, 46.80; H, 2.20; N, 3.05%).

[CuL_2]·2tnb. This adduct was prepared similarly, except for the use of 1,3,5-trinitrobenzene instead of tcnq. Red needles were obtained (*ca.* 70% yield). IR (characteristic bands for tnb): 3110, 1540, 1340 and 715 cm^{-1} (Found: C, 50.45; H, 3.05; N, 13.05. Calc. for $C_{36}H_{26}CuN_8O_{14}$: C, 50.40; H, 3.05; N, 13.05%).

Samples for ESR measurements. Approximately 10% copper(II) ion was doped in the corresponding nickel(II) complex [NiL_2] and single needle crystals of the molecular adduct with tnb were obtained according to the method for [CuL_2]·2tnb. Suitable crystals of the doped compound [$Ni(Cu)L_2$]·2tcbq could not be obtained, thus a crystal of the non-doped compound was used.

Physical Measurements.—Elemental analyses of C, H and N were obtained at the Elemental Analysis Service Center of Kyushu University. Infrared spectra were recorded on a JASCO IR-810 spectrophotometer on KBr discs, X-band ESR spectra of single crystals on a JES-FE3X ESR spectrometer at room temperature. The resonance from a polycrystalline diphenylpicrylhydrazyl (dpph) sample was used as a *g* marker. The crystal of the complex was rotated about the axis perpendicular to the needle axis (crystallographic *c* axis) and the angular variation of the ESR spectrum was measured. When the direction of the internal magnetic tensor orientation coincided with the needle axis, the angle θ was taken as zero.

X-Ray Diffraction Study.—Single needle crystals suitable for X-ray diffraction study of the three 1:2 molecular complexes were obtained by slow evaporation of their solutions in a mixture of dichloromethane and acetone. All the reflection data were measured on a Rigaku Denki AFC-5 automated

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

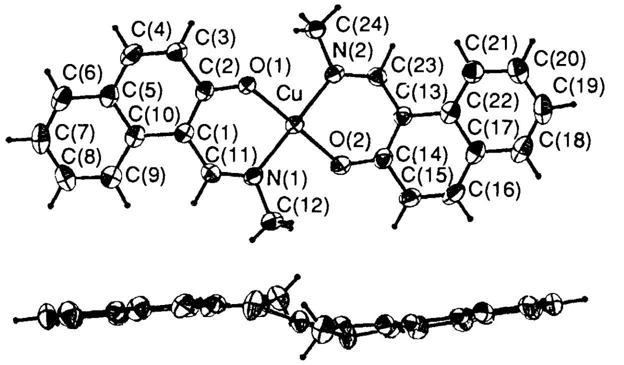

Fig. 1 An ORTEP[9] view of $[CuL_2]$ with the atom numbering scheme (thermal ellipsoids at the 50% probability level)

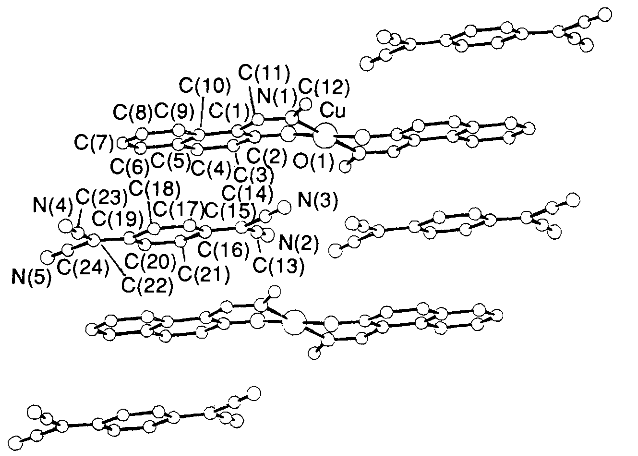

Fig. 2 Molecular packing of $[CuL_2]$·2tcnq along the *c* axis with the atom numbering scheme

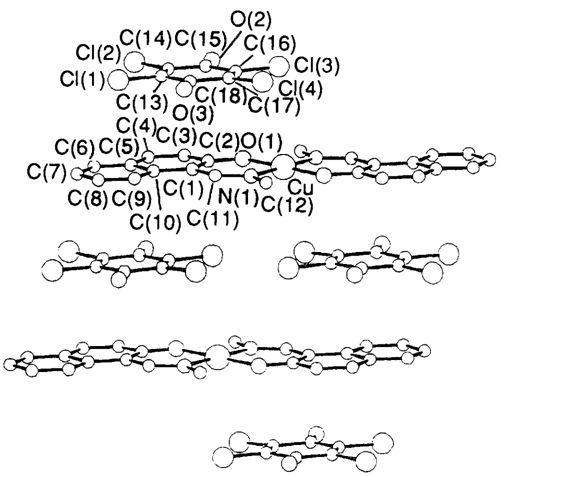

Fig. 3 Molecular packing of $[CuL_2]$·2tcbq along the *c* axis with the atom numbering scheme

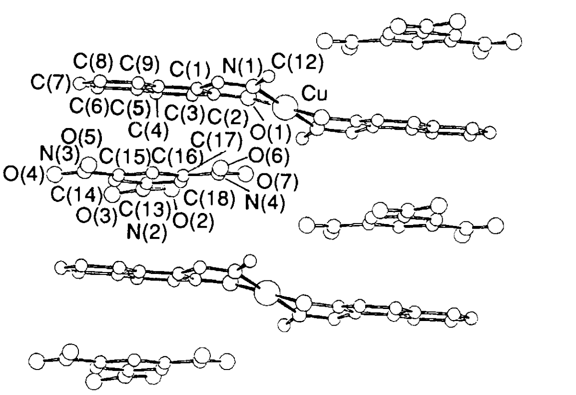

Fig. 4 Molecular packing of $[CuL_2]$·2tnb along the *c* axis with the atom numbering scheme

four-circle diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 710 69 Å) at room temperature. The standard reflections were monitored every 100 reflections and showed no systematic decrease in intensities for all the complexes. The reflection data were corrected for Lorentz-polarization effects but not for absorption. Unit-cell parameters were determined from 25 reflections with $20 < 2\theta < 30°$. The data collection and crystal parameters are listed in Table 2. It was confirmed that the needle axes of the three 1 : 2 complexes correspond to the *c* axis.

The structures were solved by direct methods using the MULTAN 78 program[5] and were successively determined by Fourier and Fourier-difference syntheses. The hydrogen atoms were located on the Fourier-difference maps. In the final least-squares calculation, block-diagonal refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms was carried out, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. Final Fourier-difference syntheses for all the complexes were featureless, with no peaks larger than 0.52 e Å^{-3}. Neutral atomic scattering factors for non-hydrogen atoms were taken from ref. 6 and those of hydrogen atoms from Stewart *et al.*[7] All computations were performed on a FACOM VP-100 computer at the Computer Center of Kyushu University using the UNICS III program system.[8] The final atomic coordinates for $[CuL_2]$, $[CuL_2]$·2tcnq, $[CuL_2]$·2tcbq and $[CuL_2]$·2tnb are given in Table 3, selected bond distances and angles with their estimated standard deviations in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Synthesis and Properties.—The 1 : 2 molecular complexes of $[CuL_2]$ with π-electron-acceptor molecules tcnq, tcbq and tnb can easily be obtained as well grown needle crystals by mixing dichloromethane solutions of $[CuL_2]$ and acetone solutions of the acceptor molecules. Infrared spectra of the molecular adducts showed characteristic bands due to the acceptors, as noted in Experimental section. When the molecular complexes are dissolved in dichloromethane the electronic spectra of the solutions are consistent with the superimposed spectra of $[CuL_2]$ and the acceptor, indicating that charge-transfer interactions are absent in solution.

Crystal Structure of the Parent Complex $[CuL_2]$.—The molecular structure of $[CuL_2]$ with the atom numbering scheme is shown in Fig. 1. The complex crystallizes in the monoclinic space group $P2_1/a$ and one molecule in the asymmetric unit. The copper atom has a slightly distorted square-planar co-ordination geometry, where the distortion parameter from square planar to tetrahedral defined by the dihedral angle between Cu–N(1)–O(1) and Cu–N(2)–O(2) is 9.0°. The lower edge-on view in Fig. 1 shows that the molecule has a stepped structure.

Crystal Structures of the 1 : 2 *Adducts.*—The molecular packing diagrams along the *c* axis with the atom numbering schemes for $[CuL_2]$·2tcnq, $[CuL_2]$·2tcbq and $[CuL_2]$·2tnb are shown in Figs. 2, 3 and 4, respectively. Each asymmetric unit of the three molecular complexes is half of the molecular adduct and the copper atom is positioned at the inversion centre. The tcnq and tnb adducts crystallize in the triclinic space group $P\bar{1}$, while the tcbq adduct crystallizes in the

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations

	$[CuL_2]$	$[CuL_2]\cdot 2tcnq$	$[CuL_2]\cdot 2tcbq$	$[CuL_2]\cdot 2tnb$
(*a*) CuL_2 part				
Cu–O(1)	1.898(3)	1.901(2)	1.897(7)	1.898(7)
Cu–N(1)	1.980(3)	1.981(3)	1.990(7)	1.976(7)
O(1)–C(2)	1.296(5)	1.292(4)	1.297(11)	1.298(11)
N(1)–C(11)	1.291(5)	1.286(4)	1.320(11)	1.301(11)
N(1)–C(12)	1.464(4)	1.465(5)	1.452(13)	1.461(15)
C(1)–C(2)	1.394(4)	1.410(4)	1.405(12)	1.412(12)
C(2)–C(3)	1.434(5)	1.427(5)	1.423(13)	1.405(13)
C(3)–C(4)	1.340(6)	1.350(5)	1.340(13)	1.339(13)
C(4)–C(5)	1.417(5)	1.422(5)	1.435(13)	1.429(13)
C(5)–C(6)	1.406(6)	1.412(5)	1.379(13)	1.418(13)
C(5)–C(10)	1.419(5)	1.419(5)	1.420(12)	1.422(12)
C(6)–C(7)	1.351(5)	1.365(5)	1.350(14)	1.360(14)
C(7)–C(8)	1.383(6)	1.397(5)	1.391(14)	1.395(14)
C(9)–C(10)	1.412(5)	1.419(5)	1.427(13)	1.419(12)
C(1)–C(11)	1.436(5)	1.437(4)	1.427(12)	1.424(12)
O(1)–Cu–N(1)	89.7(1)	89.5(1)	90.3(3)	90.3(3)
Cu–O(1)–C(2)	127.8(2)	128.9(2)	131.6(6)	129.2(6)
Cu–N(1)–C(11)	120.1(2)	124.8(2)	124.9(6)	132.22(6)

(*b*) π-Acceptor part

tcnq							
N(2)–C(13)	1.124(5)	N(3)–C(15)	1.135(5)	C(16)–C(21)	1.441(5)	C(17)–C(18)	1.342(5)
N(4)–C(23)	1.128(5)	N(5)–C(24)	1.125(5)	C(20)–C(21)	1.338(5)	C(18)–C(19)	1.442(5)
C(13)–C(14)	1.444(5)	C(14)–C(15)	1.434(5)	C(19)–C(20)	1.442(5)	C(19)–C(22)	1.373(5)
C(14)–C(16)	1.370(5)	C(16)–C(17)	1.442(5)	C(22)–C(23)	1.431(5)	C(22)–C(24)	1.440(5)
tcbq							
Cl(1)–C(13)	1.723(10)	Cl(2)–C(14)	1.708(10)	C(13)–C(14)	1.326(13)	C(14)–C(15)	1.454(13)
Cl(3)–C(16)	1.703(9)	Cl(4)–C(17)	1.705(10)	C(15)–C(16)	1.498(13)	C(16)–C(17)	1.321(13)
O(2)–C(15)	1.199(12)	O(3)–C(18)	1.194(12)	C(17)–C(18)	1.509(13)	C(13)–C(18)	1.445(13)
tnb							
N(2)–O(2)	1.209(11)	N(2)–O(3)	1.208(11)	N(4)–C(17)	1.446(12)	C(13)–C(14)	1.379(13)
N(3)–O(4)	1.210(11)	N(3)–O(5)	1.217(11)	C(14)–C(15)	1.358(13)	C(15)–C(16)	1.363(13)
N(4)–O(6)	1.231(12)	N(4)–O(7)	1.226(11)	C(16)–C(17)	1.371(13)	C(17)–C(18)	1.398(13)
N(2)–C(13)	1.489(12)	N(3)–C(15)	1.478(12)	C(13)–C(18)	1.337(13)		

Table 2 Crystallographic parameters and details of the analyses*

	$[CuL_2]$	$[CuL_2]\cdot 2tcnq$	$[CuL_2]\cdot 2tcbq$	$[CuL_2]\cdot 2tnb$
Formula	$C_{24}H_{20}CuN_2O_2$	$C_{48}H_{28}CuN_{10}O_2$	$C_{36}H_{20}Cl_8CuN_2O_6$	$C_{36}H_{26}CuN_8O_{14}$
M	432.91	840.36	923.73	858.19
Crystal symmetry	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
a/Å	12.584(3)	7.858(2)	7.772(2)	7.828(1)
b/Å	14.746(3)	17.777(5)	31.944(9)	17.231(3)
c/Å	10.504(2)	7.029(2)	7.366(2)	6.803(1)
α/°	90	93.24(2)	90	97.47(2)
β/°	104.84(2)	102.15(2)	105.08(2)	100.71(2)
γ/°	90	91.26(2)	90	95.32(2)
U/Å^3	1884.1(7)	957.1(4)	1765.6(7)	887.5(3)
Z	4	1	2	1
D_c/g cm^{-3}	1.523	1.458	1.737	1.606
$F(000)$	892	431	926	439
Crystal size/mm	0.3 × 0.3 × 0.3	0.2 × 0.2 × 0.3	0.1 × 0.2 × 0.2	0.1 × 0.2 × 0.2
μ/cm^{-1}	11.83	6.248	12.81	6.963
No. independent reflections $[\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)]$	2354	3019	2103	2041
R	0.0406	0.0504	0.0558	0.0867
R'	0.0296	0.0330	0.0762	0.0733

* Details in common: scan method θ–2θ; scan range 2.5–52°; scan width 1.0 + 0.35 tan θ; scan speed 2° min^{-1}; weighting scheme $1/\sigma^2(F_o)$.

monoclinic space group $P2_1/n$. The three molecular complexes showed a typical π–π type structure which consists of alternately stacked π-electron donor (naphthalene moiety of copper complex) and π-electron acceptor along the c axis. The needle axis of all the molecular complexes coincides with the c axis. As the copper atoms are positioned at an inversion centre, the CuN_2O_2 co-ordination geometry is perfectly square planar. The dihedral angles between the co-ordination plane (CuNO) and the naphthalene ring [C(1)–C(10)] are 21.0, 3.1 and 23.4° for $[CuL_2]\cdot 2tcnq$, $[CuL_2]\cdot 2tcbq$ and $[CuL_2]\cdot 2tnb$, respectively. As shown in the Figures, the donor parts of the tcnq and tnb adducts have a stepped structure, while that of the tcbq

Table 3 Atomic coordinates (× 10⁴)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
[CuL_2]							
Cu	177(0)	1078(0)	4538(0)	C(11)	2510(3)	1057(2)	4657(3)
O(1)	428(2)	1557(2)	2963(2)	C(12)	2213(3)	1013(3)	6763(3)
O(2)	−121(2)	625(2)	6129(2)	C(13)	−1914(3)	1257(2)	5907(3)
N(1)	1784(2)	1045(2)	5330(2)	C(14)	−921(3)	879(2)	6641(3)
N(2)	−1409(2)	1317(2)	3819(3)	C(15)	−762(3)	731(3)	8016(3)
C(1)	2306(3)	1157(2)	3255(3)	C(16)	−1553(3)	956(3)	8618(3)
C(2)	1280(3)	1438(2)	2502(3)	C(17)	−2579(3)	1312(2)	7919(3)
C(3)	1134(3)	1628(3)	1129(3)	C(18)	−3418(3)	1520(3)	8557(4)
C(4)	1958(3)	1494(3)	556(3)	C(19)	−4397(3)	1855(3)	7885(4)
C(5)	3011(3)	1187(2)	1264(3)	C(20)	−4605(3)	1996(2)	6543(4)
C(6)	3869(3)	1048(3)	651(4)	C(21)	−3820(3)	1808(2)	5884(3)
C(7)	4867(3)	750(3)	1336(4)	C(22)	−2777(3)	1468(2)	6553(3)
C(8)	5054(3)	565(3)	2666(4)	C(23)	−2106(3)	1401(2)	4523(3)
C(9)	4245(3)	683(3)	3299(4)	C(24)	−1833(3)	1471(3)	2404(3)
C(10)	3195(3)	1007(2)	2631(3)				
[CuL_2]·2tcnq							
Cu	0	0	0	N(3)	−1774(4)	341(2)	3827(4)
O	952(3)	1002(1)	502(3)	N(4)	−6818(4)	4192(2)	6203(5)
N(1)	−2327(3)	406(1)	−977(4)	N(5)	−1963(4)	5336(2)	8950(5)
C(1)	−1629(4)	1693(2)	403(4)	C(13)	1783(4)	1496(2)	6062(5)
C(2)	190(4)	1615(2)	864(4)	C(14)	−94(4)	1518(2)	5629(4)
C(3)	1281(4)	2245(2)	1760(5)	C(15)	−1031(4)	860(2)	4630(5)
C(4)	613(4)	2907(2)	2225(4)	C(16)	−929(4)	2151(2)	6082(4)
C(5)	−1216(4)	3006(2)	1802(4)	C(17)	−2802(4)	2176(2)	5594(4)
C(6)	−1896(4)	3704(2)	2279(5)	C(18)	−3618(4)	2804(2)	5982(5)
C(7)	−3650(5)	3804(2)	1867(5)	C(19)	−2652(4)	3474(2)	6906(4)
C(8)	−4793(4)	3210(2)	987(5)	C(20)	−779(4)	3447(2)	7419(5)
C(9)	−4170(4)	2527(2)	513(5)	C(21)	28(4)	2821(2)	7017(5)
C(10)	−2357(4)	2399(2)	897(4)	C(22)	−3507(4)	4116(2)	7253(5)
C(11)	−2758(4)	1085(2)	−612(4)	C(23)	−5362(5)	4154(2)	6693(5)
C(12)	−3725(5)	−100(2)	−2096(5)	C(24)	−2610(4)	4795(2)	8207(5)
N(2)	3247(4)	1502(2)	6369(4)				
[CuL_2]·2tcbq							
Cu	0	0	0	C(6)	−1712(12)	2033(3)	2638(12)
Cl(1)	274(4)	2150(1)	−1356(4)	C(7)	−226(13)	2231(3)	3625(13)
Cl(2)	−3725(4)	1925(1)	−3462(4)	C(8)	1400(13)	2023(3)	3965(13)
Cl(3)	−1618(3)	394(1)	−5066(4)	C(9)	1513(12)	1631(3)	3342(13)
Cl(4)	2377(3)	630(1)	−3095(4)	C(10)	−16(11)	1407(3)	2303(11)
O(1)	−1712(8)	431(2)	−160(9)	C(11)	1656(11)	767(3)	1923(11)
O(2)	−4027(8)	1077(2)	−4880(10)	C(12)	3750(12)	239(3)	1939(15)
O(3)	2630(9)	1456(2)	−1410(10)	C(13)	−341(12)	1670(3)	−2390(12)
N	1909(9)	379(2)	1430(10)	C(14)	−2017(12)	1576(2)	−3253(12)
C(1)	10(11)	988(2)	1589(11)	C(15)	−2517(11)	1170(3)	−4119(12)
C(2)	−1589(11)	803(3)	566(11)	C(16)	−1029(11)	864(2)	−3996(11)
C(3)	−3202(11)	1035(3)	283(13)	C(17)	642(12)	961(3)	−3154(12)
C(4)	−3241(12)	1425(3)	941(13)	C(18)	1125(12)	1382(3)	−2240(12)
C(5)	−1648(11)	1631(3)	1981(11)				
[CuL_2]·2tnb							
Cu	0	0	0	O(2)	−3631(8)	2330(4)	−4922(11)
O(1)	−1418(7)	822(3)	343(10)	O(3)	−2959(9)	3564(4)	−4974(12)
N(1)	2077(8)	695(4)	1591(11)	O(4)	2993(9)	4728(4)	−2715(11)
C(1)	780(10)	1924(5)	1345(12)	O(5)	5009(8)	3999(4)	−1869(10)
C(2)	−973(10)	1578(5)	678(13)	O(6)	3611(9)	1194(4)	−2540(12)
C(3)	−2319(10)	2063(5)	418(13)	O(7)	923(10)	689(4)	−3401(11)
C(4)	−1988(11)	2848(5)	653(13)	N(2)	−2601(9)	2916(5)	−4689(11)
C(5)	−237(11)	3236(5)	1228(12)	N(3)	3498(9)	4096(4)	−2513(11)
C(6)	111(12)	4066(5)	1453(14)	N(4)	2048(10)	1258(5)	−3101(11)
C(7)	1787(13)	4422(5)	2004(15)	C(13)	−717(10)	2824(5)	−4034(12)
C(8)	3181(11)	3976(5)	2360(13)	C(14)	481(11)	3491(5)	−3593(13)
C(9)	2879(11)	3175(5)	2145(12)	C(15)	2191(11)	3390(5)	−2995(12)
C(10)	1161(10)	2769(5)	1957(11)	C(16)	2746(10)	2671(5)	−2830(12)
C(11)	2155(10)	1458(5)	1889(12)	C(17)	1501(11)	2028(5)	−3266(12)
C(12)	3668(13)	386(6)	2416(19)	C(18)	−273(11)	2099(5)	−3917(12)

adduct is nearly planar. In the former cases each one-dimensional chain consisting of alternately stacked [CuL_2] and π-acceptor is related to the neighbouring chains by the symmetry operation $(x + 1, y, z)$ or $(x, y + 1, z)$ indicating that the chains are arrayed in the same orientation and same phase in the crystal. On the other hand, in the case of [CuL_2]·2tcbq, each one-dimensional chain is related to the neighbouring chains by the symmetry operation $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$.

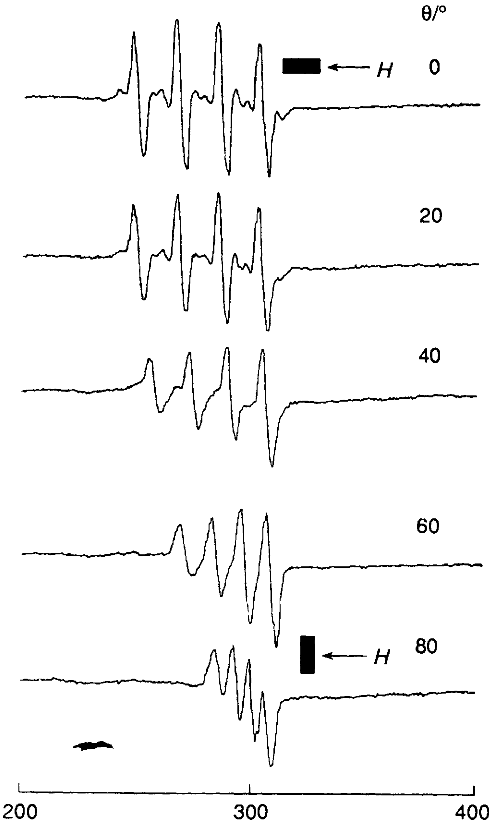

Fig. 5 Angular variation of the ESR spectrum for copper(II)-doped $[NiL_2]$·2tnb where the crystal was rotated about the axis perpendicular to the *c* axis (needle axis)

It is well known that the extent of charge-transfer interaction in tcnq complexes can be estimated from the bond distances, three types of bond being important {*b*, C(16)–C(17); *c*, C(14)–C(16); *d*, C(14)–C(15) according to the atom numbering scheme for $[CuL_2]$·2tcnq}. The molecular parameters $b - c$ and $c - d$ are, respectively, typically 0.070 and −0.063 Å for $tcnq^0$ and 0.012 and −0.006 Å for $tcnq^-$.[10] These parameters for the present complex are 0.069 and −0.065 Å, respectively, similar to the values of $tcnq^0$.

Single-crystal ESR Studies.—The angular variation of ESR spectra was measured at room temperature, with the crystal rotated about the axis perpendicular to the needle axis (*c* axis). When the magnetic field coincides with the *c* axis the angle θ is taken to be zero. The angular dependence of the ESR spectra of the doped sample $[Ni(Cu)L_2]$·2tnb is shown in Fig. 5. The spectrum shows simple copper quartet lines due to $I = \frac{3}{2}$ in all directions, indicating only one copper site in the crystal. This result is consistent with the crystal structure of $[CuL_2]$·2tnb (the complex crystallizes in the triclinic space group $P\bar{1}$ and one-dimensional chains are arrayed in the same orientation). The variation of g^2 with angle θ was fitted to the theoretical curve (1) and the fitting parameters $g_{\perp} = 20.043$, $g_{\parallel} = 2.200$ and $\alpha = -7.7°$ obtained.[11]

$$g^2 = g_{\parallel}{}^2\cos^2(\theta - \alpha) + g_{\perp}{}^2\sin^2(\theta - \alpha) \quad (1)$$

A doped sample of $[CuL_2]$·2tcbq suitable for single-crystal ESR measurements could not be obtained. Thus, the spectra of the non-doped sample were measured (Fig. 6). They were much more complicated probably due to the presence of two copper sites.

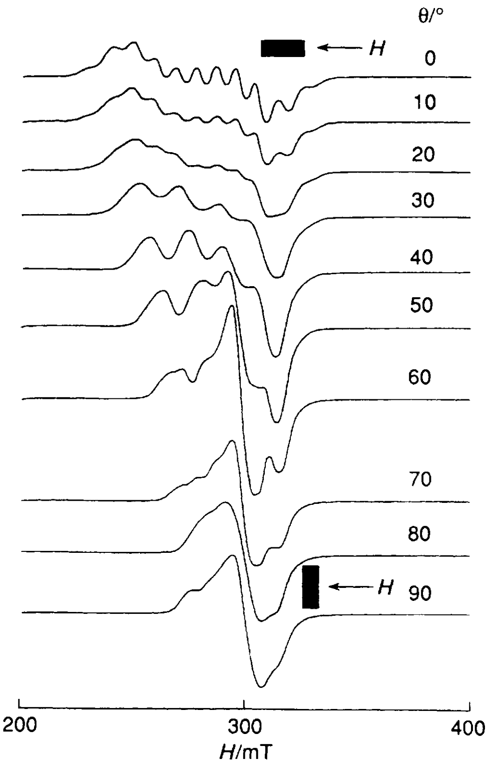

Fig. 6 Angular variation of the ESR spectrum for $[CuL_2]$·2tcbq, where the crystal was rotated as in Fig. 5

Conclusion

The complex $[CuL_2]$ containing a π-electron-donor moiety reacts with the π-electron-acceptor molecules tcnq, tcbq and tnb to give donor–acceptor molecular complexes as needle crystals. The electron-donor moiety of $[CuL_2]$ and the acceptor molecule stack alternately along the *c* axis and a one-dimensional chain structure is formed. In the cases of tcnq and tnb, each one-dimensional chain consisting of alternately stacked $[CuL_2]$ and π-acceptor is related to the neighbouring chains by the symmetry operations $(x + 1, y, z)$ or $(x, y + 1, z)$, indicating that the neighbouring chains are arrayed in the same orientation in the crystal. On the other hand, in the case of $[CuL_2]$·2tcbq, each one-dimensional chain is related to the neighbouring chains by the symmetry operation $(\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$. Since it is expected that the π–π type donor–acceptor interaction operates only along the *c* axis (needle axis), there is no distinct two-dimensional interaction in the crystal.

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