Crystal Structure and Magnetic Properties of the Heterobinuclear Complex $[(CH_3CN)LNi(mnt)Cu(mnt)]\cdot CH_3CN$ (L = tetrabenzo[*b,f,j,n*][1,5,9,13]tetra-azacyclohexadecine and mnt = maleonitriledithiolate)†

Zhuang Jin Zhong, Naohide Matsumoto, Hisashi Ōkawa,* and Sigeo Kida
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812, Japan

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The complex $[(CH_3CN)LNi(mnt)Cu(mnt)]\cdot CH_3CN$ (L = tetrabenzo[*b,f,j,n*][1,5,9,13]tetra-azacyclohexadecine and mnt = maleonitriledithiolate) has been synthesized and its crystal structure determined. The complex crystallizes in the orthorhombic system, space group *Pbca* with cell dimensions, a = 16.691(2), b = 32.256(3), c = 14.581(1) Å, and Z = 8. The crystal structure consists of a discrete binuclear NiCu unit with a unique bridging mode. The copper(II) ion is co-ordinated by four sulphur atoms of the two mnt ligands in a distorted planar environment. One mnt ligand is linked through one of its cyano groups to an axial site of the nickel(II) ion completing an octahedral co-ordination formed by L (in equatorial positions) and CH_3CN (in an axial position). Cryomagnetic data (5—300 K) show practically no magnetic interaction between the high-spin nickel(II) and the copper(II) ions.

In a previous paper we reported that the reaction of 5,10,15,20-tetraphenylporphyrinatogold(III) $[Au(tpp)]^+$ and bis(maleonitriledithiolato)metalates(III) $[M(mnt)_2]^-$ (M = Ni, Pt, or Au) formed 1:1 salts $[Au(tpp)][M(mnt)_2]$, which were presumed to be one-dimensional heterometal assemblies from electric conductivity measurements.[1] Of these complexes $[Au(tpp)][Ni(mnt)_2]$ and $[Au(tpp)][Pt(mnt)_2]$ are paramagnetic, but there is essentially no magnetic interaction probably because the diamagnetic $[Au(tpp)]^+$ is unable to mediate spin exchange between paramagnetic $[M(mnt)_2]^-$ ions. Because of considerable interest in the magnetic properties of one-dimensional assemblies comprising dissimilar paramagnetic ions,[2] we have attempted to synthesize such a complex by the use of tetrabenzo[*b,f,j,n*][1,5,9,13]tetra-azacyclohexadecinenickel(II) $[NiL]^{2+}$ as the cationic counterpart and bis(maleonitriledithiolato)cuprate(II) $[Cu(mnt)_2]^{2-}$ as the anionic counterpart. The complex obtained, however, was shown to be a heterobinuclear complex with a unique bridging mode. This paper reports the preparation, crystal structure, and magnetic properties of the complex.

Experimental

The salts $[NBu^n_4]_2[Cu(mnt)_2]$[3] and $[NiL][BF_4]_2$[4] were prepared according to the literature methods.

Preparation of $[(CH_3CN)LNi(mnt)Cu(mnt)]\cdot CH_3CN$.—To a hot acetonitrile solution (20 cm^3) of $[NiL][BF_4]_2$ (16 mg) was added a hot acetonitrile solution (25 cm^3) of $[NBu^n_4]_2[Cu(mnt)_2]$ (21 mg). Black needle crystals of [LNi(mnt)Cu(mnt)] which formed were separated by filtration. The filtrate was allowed to stand for about 2 weeks to give well shaped black plate crystals of $[(CH_3CN)LNi(mnt)Cu(mnt)]\cdot CH_3CN$ (Found: C, 53.70; H, 2.90; Cu, 6.95; N, 15.60; Ni, 6.60. Calc. for $C_{40}H_{26}CuN_{10}NiS_4$: C, 53.55; H, 2.90; Cu, 7.10; N, 15.60; Ni, 6.55%).

Physical Measurements.—Elemental analyses were obtained at the Elemental Analysis Service Centre of Kyushu University. Magnetic susceptibilities were measured in the temperature range 5—100 K by the use of a HOXAN HSM 2000 SQUID magnetometer and in the range 80—300 K by the use of a Faraday balance designed in our laboratory. The apparatus was calibrated with $[Ni(en)_3][S_2O_3]$ (en = ethylenediamine)[5] and correction for diamagnetism of the component atoms was made by the use of Pascal's constants.[6]

X-*Ray Structural Determination.*—Reflection data were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite monochromated Mo-K_α radiation at 20 ± 1 °C. The cell dimensions were determined by 25 high-angle reflections in the range of $20 < 2\theta < 30°$. Three standard reflections were monitored every 100 reflections and their intensities showed no decay. The diffraction data were corrected for Lorentz and polarization effects but not for absorption. Crystal data and details of the data collection and reduction are as follows: $C_{40}H_{26}CuN_{10}NiS_4$, M = 897.21, crystal size 0.4 × 0.4 × 0.3 mm, orthorhombic, space group *Pbca*, a = 16.691(2), b = 32.256(3), c = 14.581(1) Å, U = 7 850.2 Å^3, Z = 8, D_c = 1.518 g cm^{-3}, D_m = 1.51 g cm^{-3}, μ(Mo-K_α) = 5.61 cm^{-1}, scan mode θ—2θ, scan range 2.5—45°, scan width $(1.2 + 0.35\tan\theta)°$, octant measured $+h$, $+k$, $+l$, number of observed reflections $[|F_o| > 2.5\sigma(|F_o|)]$ 3 761, R = 0.0526, R' = 0.0657.

The structure was solved by the direct method and refined by the block-diagonal least-squares method, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and $w = 1$ was adopted. Hydrogen atoms were inserted in their calculated positions and included in the structure-factor calculation but not refined. Atomic scattering factors were taken from ref. 7. All the calculations were carried out on a FACOM M 780 computer at the Computer Centre of Kyushu University using a local version of the UNICS III and ORTEP programs.[8] The final positional parameters of the non-hydrogen atom are given in Table 1.

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

Results and Discussion

The crystal structure consists of a discrete binuclear unit $[(CH_3CN)LNi(mnt)Cu(mnt)]$ and a CH_3CN molecule as crystal solvate. The molecular structure of the binuclear unit is shown in Figures 1 and 2, together with the atom labelling scheme. Selected bond distances and angles with their estimated standard deviations in parentheses are given in Table 2. The copper(II) ion is co-ordinated by four sulphur atoms of the two

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† *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Positional parameters (× 10^4) of non-hydrogen atoms for $[(CH_3CN)LNi(mnt)Cu(mnt)]\cdot CH_3CN$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	2 316(1)	3 752(0)	808(1)	C(24)	4 967(6)	2 954(3)	−116(7)
N(1)	2 788(4)	3 538(2)	2 002(5)	C(25)	4 983(5)	2 773(3)	728(7)
N(2)	1 196(4)	3 626(2)	1 267(5)	C(26)	4 490(6)	2 910(3)	1 407(7)
N(3)	1 859(5)	4 078(2)	−261(5)	C(27)	3 961(5)	3 231(3)	1 256(6)
N(4)	3 426(4)	3 770(2)	224(5)	C(28)	3 438(5)	3 326(3)	2 044(6)
C(1)	2 404(5)	3 633(2)	2 854(5)	Cu	3 091(1)	6 018(0)	2 041(1)
C(2)	2 835(6)	3 702(3)	3 636(6)	S(1)	4 211(2)	5 625(1)	1 853(2)
C(3)	2 433(7)	3 788(3)	4 465(6)	S(2)	2 298(2)	5 484(1)	1 688(2)
C(4)	1 619(7)	3 813(3)	4 506(6)	S(3)	2 038(2)	6 365(1)	2 638(2)
C(5)	1 196(6)	3 761(3)	3 708(6)	S(4)	3 831(2)	6 597(1)	1 984(2)
C(6)	1 569(5)	3 682(2)	2 865(5)	N(5)	4 744(6)	4 534(3)	1 386(9)
C(7)	1 007(6)	3 623(2)	2 107(6)	N(6)	2 443(5)	4 349(2)	1 433(5)
C(8)	590(5)	3 519(3)	611(6)	N(7)	1 473(7)	7 441(3)	3 244(7)
C(9)	25(6)	3 229(3)	818(6)	N(8)	3 694(7)	7 704(3)	2 431(8)
C(10)	−580(6)	3 134(3)	203(7)	C(29)	4 304(6)	4 804(3)	1 506(8)
C(11)	−619(7)	3 329(3)	−643(7)	C(30)	3 797(6)	5 149(3)	1 644(6)
C(12)	−38(7)	3 608(3)	−863(7)	C(31)	2 991(5)	5 089(2)	1 601(6)
C(13)	591(5)	3 703(3)	−264(6)	C(32)	2 674(6)	4 680(3)	1 505(6)
C(14)	1 186(5)	4 004(3)	−616(6)	C(33)	1 869(6)	7 186(3)	2 986(6)
C(15)	2 306(6)	4 417(3)	−609(5)	C(34)	2 423(6)	6 867(3)	2 660(6)
C(16)	1 937(6)	4 782(3)	−853(7)	C(35)	3 166(6)	6 960(2)	2 388(6)
C(17)	2 376(7)	5 127(3)	−1 134(7)	C(36)	3 454(7)	7 376(3)	2 430(7)
C(18)	3 194(7)	5 111(3)	−1 168(7)	NA	2 229(5)	3 126(2)	230(5)
C(19)	3 569(6)	4 749(3)	−909(7)	CA(1)	2 201(5)	2 779(3)	119(6)
C(20)	3 138(5)	4 401(2)	−608(6)	CA(2)	2 190(7)	2 332(3)	−15(8)
C(21)	3 652(6)	4 053(3)	−311(6)	NS(1)	−483(9)	4 387(5)	1 003(16)
C(22)	3 964(5)	3 429(3)	393(6)	CS(1)	−21(9)	4 634(5)	1 189(12)
C(23)	4 470(5)	3 282(3)	−298(6)	CS(2)	510(8)	4 916(6)	1 462(11)

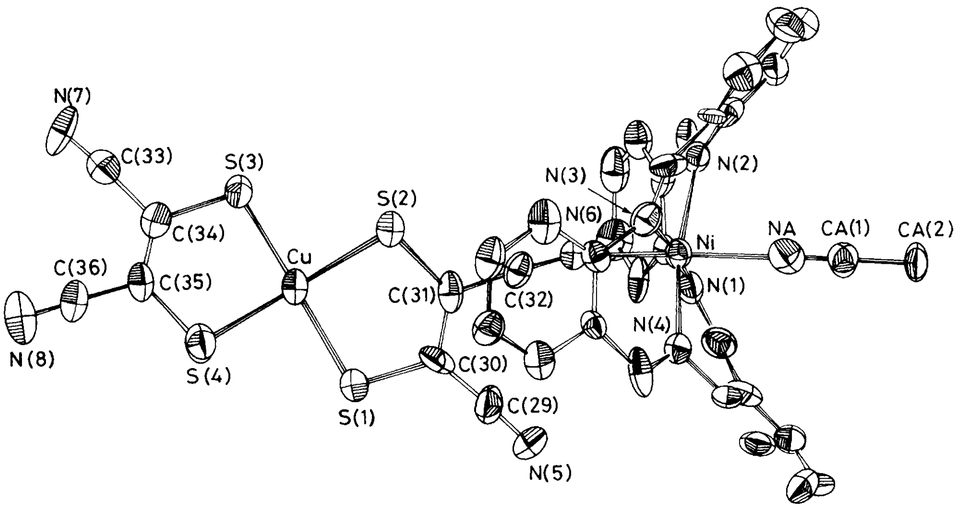

Figure 1. ORTEP projection on the copper co-ordination plane and atomic labelling of $[(CH_3CN)LNi(mnt)Cu(mnt)]$

mnt ligands, one of which is linked with one of the cyano nitrogen atoms N(6) to an axial site of the nickel(II) ion, so completing an octahedral co-ordination with L and CH_3CN.

As seen in Figure 1, the molecule L is saddle-shaped, and the four nitrogen atoms deviate considerably from the least-squares plane defined by the nitrogens [N(1) +0.200, N(2) −0.199, N(3) +0.198, N(4) −0.199 Å]. A similar saddle-shaped distortion occurs in $[NiL][BF_4]_2$ and $[NiL(I)(H_2O)]I$.[9] In the present complex the equatorial Ni–N bond distances fall in the range 2.026(7)—2.040(7) Å and the axial Ni–N(6) and Ni–NA distances are 2.141(7) and 2.193(7) Å, respectively. Practically no deviation from the equatorial plane was observed for the nickel atom. Thus, the co-ordination geometry of the nickel can be described as an octahedron slightly elongated along the nitrile co-ordination bond.

In the $[Cu(mnt)_2]^{2-}$ anion the four Cu–S bond distances show a moderate spread lying in the range 2.232(2)—2.274(2) Å whereas in $[M(mnt)_2]^{n-}$ complexes so far characterized differences in the M–S bond distances are less than 0.02 Å.[10] Since the highest occupied molecular orbital of $[M(mnt)_2]^{n-}$ is antibonding with respect to the metal–sulphur bonding,[10] the short Cu–S(2) distance may be ascribed to the reduced electron density on S(2), effected by co-ordination of the nearest cyano group [C(32)N(6)] to the nickel ion. Another noticeable geometrical feature is the relative deviation from coplanarity of the mnt ligands. Whereas the mnt ligand unco-ordinated to the nickel is essentially coplanar (deviation from the least-squares plane is less than 0.03 Å), the mnt ligand functioning as the bridge to the nickel is fairly distorted from coplanarity. The largest deviation is seen at S(2) which is 0.14 Å out of the best plane

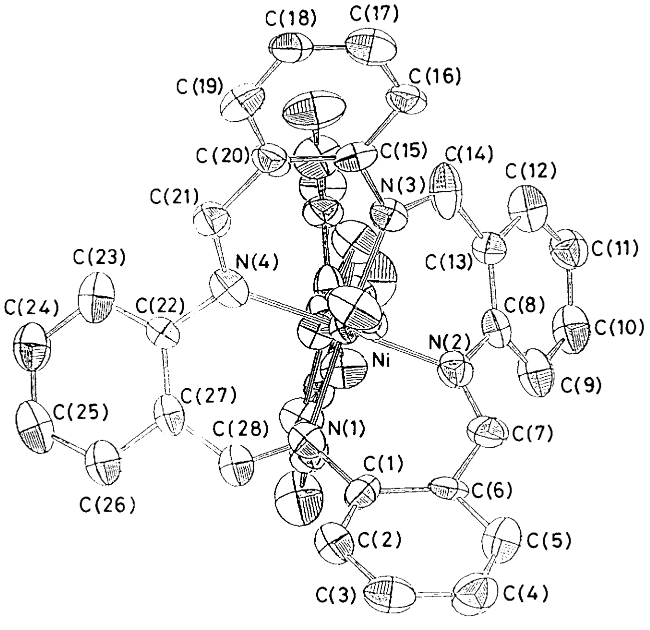

Figure 2. ORTEP projection on the nickel co-ordination plane and atomic labelling of [(CH$_3$CN)LNi(mnt)Cu(mnt)]

Table 2. Selected bond distances (Å) and angles (°)

Ni–N(1)	2.031(7)	Ni–N(2)	2.026(7)
Ni–N(3)	2.027(7)	Ni–N(4)	2.040(7)
Ni–N(6)	2.141(7)	Ni–NA	2.193(7)
Cu–S(1)	2.274(2)	Cu–S(2)	2.232(2)
Cu–S(3)	2.258(2)	Cu–S(4)	2.240(2)
S(1)–C(30)	1.711(9)	S(2)–C(31)	1.725(8)
S(3)–C(34)	1.744(8)	S(4)–C(35)	1.717(9)
N(5)–C(29)	1.154(14)	C(29)–C(30)	1.412(13)
C(29)–C(30)	1.412(13)	C(30)–C(31)	1.361(13)
N(6)–C(32)	1.139(10)	C(31)–C(32)	1.427(11)
N(7)–C(33)	1.119(13)	C(33)–C(34)	1.462(12)
C(34)–C(35)	1.336(14)	N(8)–C(36)	1.131(13)
C(35)–C(36)	1.426(12)	NA–CA(1)	1.133(11)
CA(1)–CA(2)	1.454(12)		

N(1)–Ni–N(2)	90.3(2)	N(2)–Ni–N(3)	90.6(3)
N(3)–Ni–N(4)	90.3(3)	N(1)–Ni–N(4)	90.8(2)
N(6)–Ni–N(1)	84.4(3)	N(6)–Ni–N(2)	97.5(2)
N(6)–Ni–N(3)	84.1(3)	N(6)–Ni–N(4)	93.5(3)
NA–Ni–N(1)	92.4(3)	NA–Ni–N(2)	83.1(3)
NA–Ni–N(3)	99.0(3)	NA–Ni–N(4)	85.7(3)
Ni–N(6)–C(32)	156.2(9)	Ni–NA–CA(1)	165.5(7)
Ni–N(1)–C(1)	119.9(5)	Ni–N(1)–C(28)	123.6(6)
S(1)–Cu–S(2)	91.7(1)	S(2)–Cu–S(3)	90.5(1)
S(3)–Cu–S(4)	91.7(1)	S(1)–Cu–S(4)	90.3(1)
Cu–S(1)–C(30)	100.8(3)	Cu–S(2)–C(31)	100.9(3)
Cu–S(3)–C(34)	100.3(3)	Cu–S(4)–C(35)	101.5(3)
S(1)–C(30)–C(29)	119.3(7)	S(1)–C(30)–C(31)	122.4(6)
C(29)–C(30)–C(31)	118.1(8)	N(5)–C(29)–C(30)	177.1(11)
S(2)–C(31)–C(32)	116.2(6)	S(2)–C(31)–C(30)	123.5(1)
C(30)–C(31)–C(32)	120.2(7)	N(6)–C(32)–C(31)	178.0(9)
S(3)–C(34)–C(33)	115.2(7)	S(3)–C(34)–C(35)	123.0(6)
C(33)–C(34)–C(35)	121.6(7)	N(7)–C(33)–C(34)	177.0(10)
S(4)–C(35)–C(36)	116.0(7)	S(4)–C(35)–C(34)	123.2(6)
C(34)–C(35)–C(36)	120.7(8)	N(8)–C(36)–C(35)	177.4(12)
NA–CA(1)–CA(2)	178.2(9)		

defined by the mnt ligand and the copper atom. Thus, the dihedral angle between the two chelate rings [defined by CuS(1)S(2) and CuS(3)S(4), respectively] is 18.9°, indicating that the environment of the copper ion is fairly distorted from square planar to tetrahedral. The [Cu(mnt)$_2$]$^{2-}$ mean plane is nearly perpendicular to the basal mean plane of the [NiL]$^{2+}$ with a dihedral angle of 73.7°.

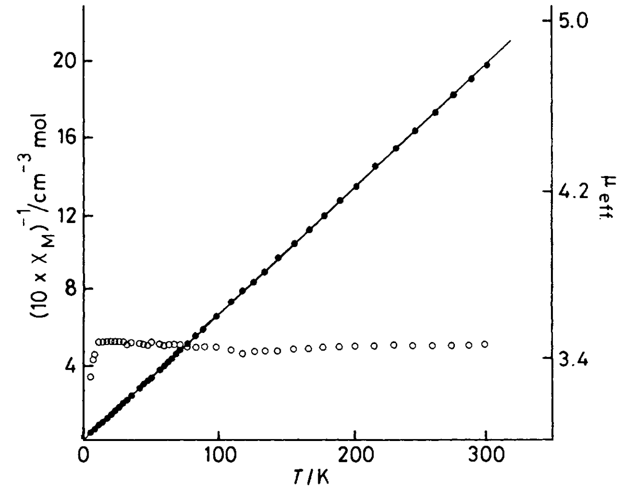

Figure 3. Temperature dependence of the reciprocal magnetic susceptibility (χ_M)$^{-1}$ per molecule (●) and the effective magnetic moment per molecule (○)

It is known that [M(mnt)$_2$]$^{n-}$ often form column[11] or multinuclear structures[12] by co-ordinative interaction through sulphur atoms. In this context the bridging mode (–CN→Ni) found for the present complex is of particular interest. It seems that the sulphur co-ordination of [Cu(mnt)$_2$]$^{2-}$ to the [NiL]$^{2+}$ is sterically hindered, since the nickel is incorporated into the saddle-shaped ligand L.

Magnetic susceptibility values for the complex were determined in the temperature range 5—300 K and are plotted in Figure 3, in the terms of $1/\chi_M$ *vs.* T and $\mu_{eff.}$ *vs.* T, where χ_M is the magnetic susceptibility per molecule, $\mu_{eff.}$ the effective magnetic moment per molecule, and T the temperature. The magnetic susceptibility obeys the Curie law, and the effective magnetic moment is almost constant in the temperature range 10—300 K with a value of *ca.* 3.4, close to the spin-only value (3.32) expected for a non-coupled ($S_1 = \frac{1}{2}$, $S_2 = 1$) binuclear system. Thus, there is practically no magnetic interaction between the copper(II) and nickel(II) ions through the mnt bridge.

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