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Tetracyanoquinodimethane Salts of Transition-Metal Complexes. Crystal and Molecular Structures and Magnetic Properties of Tris(1,10-phenanthroline)zinc(II) Bis(tetracyanoquinodimethanide) and Tris(1,10-phenanthroline)copper(II) Bis(tetracyanoquinodimethanide)

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The compounds tris(1,10-phenanthroline)zinc(II) bis(tetracyanoquinodimethanide), Zn(phen)$_3$(TCNQ)$_2$ (**1**), and tris(1,10-phenanthroline)copper(II) bis(tetracyanoquinodimethanide), Cu(phen)$_3$(TCNQ)$_2$ (**2**), were synthesized and their crystal structures solved at room temperature. They crystallize in the triclinic system, space group $P\bar{1}$. The lattice constants for Zn(phen)$_3$(TCNQ)$_2$ are $a = 2197.2$ (5) pm, $b = 1116.4$ (3) pm, $c = 1016.5$ (3) pm, $\alpha = 86.03$ (4)°, $\beta = 84.81$ (6)°, and $\gamma = 83.36$ (3)°, and those for Cu(phen)$_3$(TCNQ)$_2$ are $a = 2194.5$ (5) pm, $b = 1110.6$ (3) pm, $c = 1018.6$ (3) pm, $\alpha = 86.50$ (5)°, $\beta = 84.41$ (6)°, and $\gamma = 83.21$ (4)°. Least-squares refinement of the structures leads to conventional R factors of 0.060 and 0.064 for **1** and **2**, respectively. The asymmetric units of **1** and **2** are formed by [M(phen)$_3$]$^{2+}$ cations (M = Zn, Cu) and two crystallographically independent TCNQ$^-$ anions, called A and B, respectively, not directly bound to the metals and rather different from each other. The A anions form dimeric units with a ring-to-external-bond (R-B) overlap, while the B molecules arrange themselves to form rather unusual discrete dimers, with an external-bond-to-external-bond overlap (B-B mode). The temperature dependences of the magnetic susceptibilities for **1** and **2** indicate that a magnetic coupling occurs, and the χ_M values suggest that one of the two crystallographically independent dimers seen in the crystal structures is essentially diamagnetic also at room temperature.

Introduction

A number of TCNQ$^-$ salts have shown highly anisotropic physical properties, in particular quasi-one-dimensional metallic behavior or magnetic properties.[1-4] An active area of research has recently been the synthesis of new solids with anisotropic electrical and magnetic properties. The interest in this field is both practical and theoretical. New compounds exhibiting unusual physical properties can in principle be used to construct new devices for industrial applications as well as to modify and test physical theories that describe the electronic structure and behavior of solids.

TCNQ-containing solids are perhaps the most extensively studied systems; they range from simple salts containing TCNQ$^-$ anions and positive counterions to charge-transfer complexes in which an amount of charge has been transferred from the anion to an acceptor molecule.[3,4,6,7] The best thoroughly known compound of the latter type is perhaps the low-temperature superconductor (TTF)(TCNQ) (TTF = tetrathiafulvalene).[1,2] A few TCNQ salts showed peculiar physical phenomena, such as mobile triplet excitations (excitons), due to inequivalent π interactions between the organic radicals, which cause the radicals to stack one over the other, forming a chain of dinuclear moieties.[6-8]

In recent years some papers appeared reporting the synthesis and the physical properties of TCNQ$^-$ salts with counterions as complex as a niobium trinuclear cluster[9] or decamethylferrocenium[10-12] in which the peculiar arrangement of the TCNQ$^-$ ions were found as a consequence of some interactions with the cations. In particular, for the decamethylferrocenium compound three different phases, paramagnetic, metamagnetic, and conductive, were observed.

Table I. Crystallographic Data for Zn(phen)$_3$(TCNQ)$_2$ and Cu(phen)$_3$(TCNQ)$_2$

	Zn(phen)$_3$(TCNQ)$_2\cdot$ 0.5CH$_3$OH	Cu(phen)$_3$(TCNQ)$_2\cdot$ 0.5CH$_3$OH
formula	$C_{60}H_{32}N_{14}Zn\cdot C_{0.5}H_2O_{0.5}$	$C_{60}H_{32}N_{14}Cu\cdot C_{0.5}H_2O_{0.5}$
a, Å	21.972 (5)	21.945 (5)
b, Å	11.164 (3)	11.106 (3)
c, Å	10.165 (3)	10.186 (3)
α, deg	86.03 (4)	86.50 (5)
β, deg	84.81 (6)	84.41 (6)
γ, deg	83.36 (3)	83.21 (4)
V, Å^3	2462.2	2450.4
Z	2	2
space group	$P\bar{1}$	$P\bar{1}$
dens, g cm^{-3}	1.352	1.356
μ, cm^{-1}	5.63	4.99
transmission coeff	0.78-0.96	
$R(F_o)$	0.060	0.064
$R_w(F_o)$	0.061	0.062

We have planned to investigate the possibility of obtaining solids with new properties by forming salts of TCNQ$^-$ with mono- and polynuclear transition-metal complexes. The variety of structures observed in these complexes can, in principle, modulate the π interaction between the organic radicals, giving rise to solids exhibiting new physico-chemical properties.

As a first attempt, we succeeded in synthesizing salts of general formulas M(phen)$_3$(TCNQ)$_2$, where M is a bipositive first-row transition-metal ion and phen is the ligand 1,10-phenanthroline, and we wish to report here the crystal and molecular structures of the compounds tris(1,10-phenanthroline)zinc(II) bis(tetracyanoquinodimethanide) and tris(1,10-phenanthroline)copper(II) bis(tetracyanoquinodimethanide), together with their bulk magnetic properties.

Experimental Section

Synthesis of the Complexes. The complexes M(phen)$_3$(ClO$_4$)$_2$, with M = Zn and Cu, were prepared as previously described.[13] The reactions were carried out under a nitrogen atmosphere.

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Table II. Atomic Positional Parameters (×10^4) for the Non-Hydrogen Atoms of Zn(phen)$_3$(TCNQ)$_2$

atom^a	x/a	y/b	z/c	atom^a	x/a	y/b	z/c
Zn	2541 (1)	2090 (1)	3524 (1)	C(25)	2190 (3)	1194 (5)	6473 (6)
N(1)	7325 (3)	1367 (6)	11706 (8)	C(26)	1884 (3)	1278 (6)	7733 (6)
N(2)	5721 (3)	3928 (6)	12882 (6)	C(27)	1455 (3)	2235 (6)	7976 (7)
N(3)	3709 (3)	1125 (5)	7444 (6)	C(28)	1322 (3)	3117 (6)	6952 (6)
N(4)	5292 (3)	−1397 (6)	6269 (6)	C(29)	1647 (3)	2974 (5)	5730 (6)
N(5)	9660 (3)	−2283 (6)	5871 (8)	C(30)	848 (3)	4116 (7)	7123 (8)
N(6)	10269 (4)	−1949 (7)	1696 (10)	C(31)	732 (3)	4933 (7)	6098 (7)
N(7)	8108 (4)	4464 (7)	689 (8)	C(32)	1063 (3)	4812 (6)	4853 (6)
N(8)	7393 (4)	4298 (6)	4885 (8)	C(33)	1526 (3)	3837 (5)	4643 (6)
N(9)	2085 (2)	2019 (4)	5491 (4)	C(34)	954 (3)	5634 (7)	3767 (7)
N(10)	1856 (2)	3672 (4)	3485 (5)	C(35)	1288 (3)	5466 (7)	2601 (8)
N(11)	3275 (2)	3038 (4)	3998 (4)	C(36)	1746 (3)	4481 (6)	2456 (7)
N(12)	2964 (2)	2713 (4)	1561 (4)	C(37)	3445 (3)	3161 (5)	5187 (6)
N(13)	2005 (2)	971 (5)	2554 (5)	C(38)	3907 (3)	3853 (5)	5423 (6)
N(14)	3038 (2)	291 (4)	3798 (4)	C(39)	4188 (3)	4474 (5)	4395 (6)
C(1)	5850 (3)	1705 (5)	10563 (5)	C(40)	4015 (3)	4381 (5)	3113 (6)
C(2)	5234 (3)	2186 (5)	10363 (6)	C(41)	3561 (3)	3636 (5)	2949 (5)
C(3)	4908 (3)	1740 (5)	9460 (5)	C(42)	4279 (3)	5038 (5)	1963 (6)
C(4)	5174 (3)	769 (5)	8676 (5)	C(43)	4094 (3)	4928 (6)	771 (7)
C(5)	5782 (3)	285 (5)	8871 (6)	C(44)	3641 (3)	4150 (5)	567 (6)
C(6)	6112 (3)	742 (5)	9771 (6)	C(45)	3382 (2)	3495 (5)	1665 (5)
C(7)	6200 (3)	2183 (5)	11467 (6)	C(46)	3431 (3)	3994 (6)	−662 (7)
C(8)	6817 (4)	1736 (6)	11611 (7)	C(47)	3021 (3)	3212 (6)	−768 (7)
C(9)	5937 (3)	3140 (6)	12274 (7)	C(48)	2804 (3)	2565 (6)	362 (6)
C(10)	4826 (3)	301 (5)	7764 (5)	C(49)	1500 (3)	1300 (7)	1974 (7)
C(11)	4221 (3)	766 (5)	7581 (6)	C(50)	1234 (4)	481 (7)	1216 (8)
C(12)	5085 (3)	−632 (6)	6945 (6)	C(51)	1510 (4)	−638 (7)	1102 (8)
C(13)	9291 (3)	127 (6)	3553 (8)	C(52)	2035 (3)	−1041 (6)	1722 (7)
C(14)	9292 (3)	792 (6)	2311 (7)	C(53)	2278 (3)	−198 (5)	2461 (6)
C(15)	8922 (3)	1841 (6)	2157 (7)	C(54)	2347 (4)	−2241 (7)	1713 (8)
C(16)	8529 (3)	2317 (5)	3195 (7)	C(55)	2822 (4)	−2596 (7)	2395 (8)
C(17)	8540 (3)	1681 (5)	4455 (7)	C(56)	3077 (3)	−1767 (6)	3173 (6)
C(18)	8919 (3)	627 (6)	4613 (7)	C(57)	2802 (3)	−556 (5)	3146 (6)
C(19)	9661 (3)	−1006 (6)	3690 (9)	C(58)	3565 (3)	−2079 (7)	3927 (7)
C(20)	9661 (3)	−1706 (7)	4904 (10)	C(59)	3796 (3)	−1236 (6)	4582 (7)
C(21)	9999 (4)	−1526 (7)	2595 (11)	C(60)	3519 (3)	−33 (5)	4481 (6)
C(22)	8118 (3)	3401 (6)	3000 (7)	O*	305 (9)	3252 (19)	837 (19)
C(23)	8108 (4)	3998 (7)	1739 (9)	C*	192 (16)	4225 (31)	563 (33)
C(24)	7720 (4)	3895 (7)	4042 (9)				

^{a}Atoms marked with an asterisk belong to solvate methanol molecules.

Li(TCNQ) (0.2 mmol in 30 mL of CH_3OH) was added at room temperature to M(phen)$_3$(ClO$_4$)$_2$ (0.1 mmol in 20 mL of CH_3CN). After 2 h well-shaped dark brown crystals of composition M(phen)$_3$(TCNQ)$_2$ precipitated. They were filtered out, washed with methanol and, then, with petroleum ether, and dried in a current of nitrogen.

Elemental analysis well agrees with the above formulation.

X-ray Structure Determination. Single-crystal diffraction data for Zn(phen)$_3$(TCNQ)$_2$ (**1**) and Cu(phen)$_3$(TCNQ)$_2$ (**2**) were collected at room temperature on a Philips PW1100 automated diffractometer using Mo Kα radiation (λ = 70.170 pm). Details on crystal data are reported in Table I. Lattice constants were obtained by a least-squares fit of 21 reflections in the range $10° \leq \theta \leq 20°$ for both **1** and **2**. Stationary background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections measured every 90 min did not show any systematic variation.

All the examined crystals of **2** showed a net decrease of the intensities of the reflections measured at $2\theta \geq 40°$. The R factor for merging equivalent measurements was R = 0.023 and R = 0.036 for **1** and **2** respectively. Data were processed by using a p value of 0.03 in the calculations of $\sigma(I)$'s.[15] Corrections for the Lorentz and polarization effects[16a] as well as for absorption were applied.[16b] Due to the laminar shape of the crystals of **2** the absorption correction was applied by using the empirical (DIFABS) procedure.[16c] Patterson and Fourier techniques were used to solve the structure in the centrosymmetric $P\bar{1}$ space group. The computer programs used in the crystallographic calculations are listed in ref 16. All the calculations have been performed on a IBM 80/111 Personal System 2 computer.

A total of 4383 reflections for **1** and 2253 for **2** having $F_o > 6\sigma(F_o)$ were retained during the refinement. The minimized function was $\sum w[|F_o| - |F_c|]^2$ with weights $w = 1/\sigma^2(F_o)$. The scattering factors for neutral atoms were taken from ref 17, and anomalous dispersion terms for the metal atoms were included in F_c.[18] All the atoms in **1**, except the hydrogen and carbon atoms of the phenanthroline rings, were assigned anisotropic thermal parameters. In **2** only copper and nitrogen atoms bound to the copper were assigned anisotropic thermal parameters. All the other atoms were refined isotropically. Hydrogen atoms were introduced in calculated positions (C–H = 108 pm), and their contributions were included in F_c. During the last cycles of refinement two peaks more than 1 e Å^{-3} were found in the Fourier map. They were assigned to a solvate CH_3OH molecule. Since, however, the thermal factors were high, a site-occupation factor of 0.5 was assigned to the C and O atoms. This led to final thermal factors of 0.183 (7) and 0.20 (1) for O* and C* of **1** and 0.15 (1) and 0.22 (3) for O* and C* of **2**, indicative of some disorder in the solvent molecule.

The final values of the discrepancy indices defined by $R = \sum[|F_o| - |F_c|]/\sum|F_o|$ and $R_w = [\sum_w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ were R = 0.060 and R_w = 0.061 for **1** and R = 0.064 and R_w = 0.062 for **2**. In the final least-squares cycles, shift/error ratios as high as 0.1 and 0.6 were found for the solvent molecules of **1** and **2**, respectively, all the other values being smaller than 0.06.

The final atomic positional parameters for the non-hydrogen atoms of **1** and **2** are listed in Tables II, III, respectively. Complete crystallographic data and data collection details for **1** and **2** (Table SI), thermal parameters and positional parameters of the hydrogen atoms for **1** (Ta-

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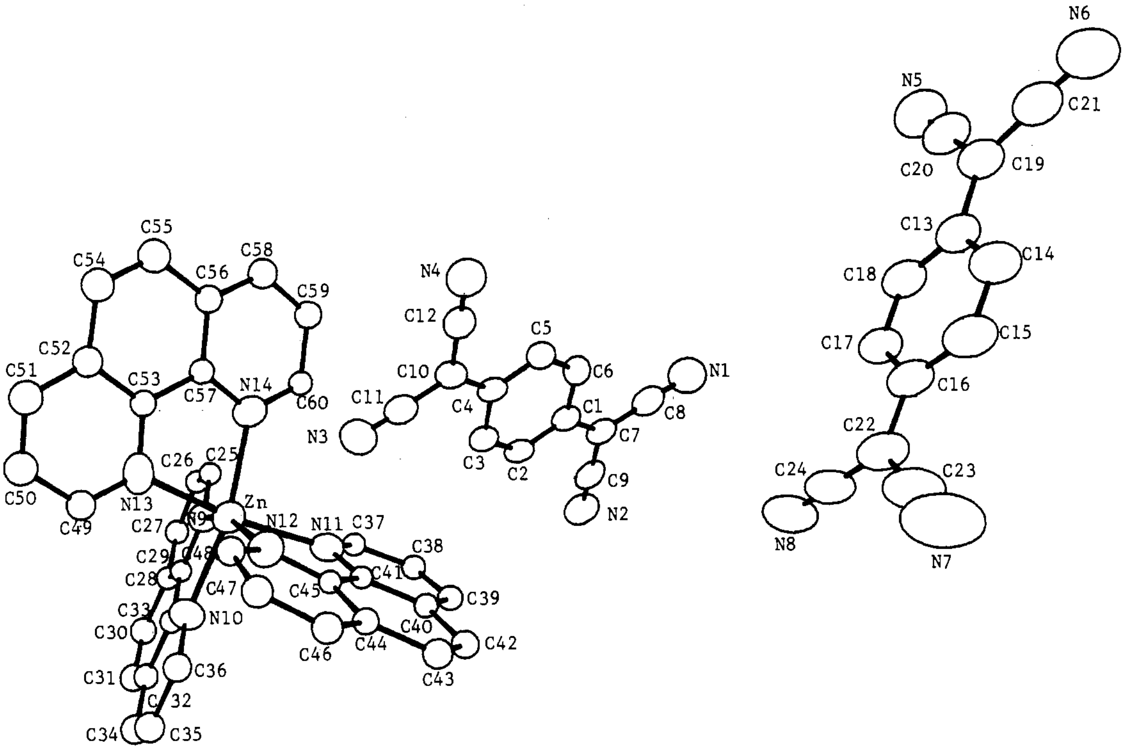

Figure 1. ORTEP view of the asymmetric unit of $Zn(phen)_3(TCNQ)_2$.

bles SII and SIII) and for **2** (Tables SIV and SV), and a listing of the observed and calculated structure factors for **1** and **2** (Tables SVI and SVII) are available as supplementary material.[19]

Magnetic Measurements. The temperature dependences of the magnetic susceptibilities of **1** and **2** were measured on polycrystalline samples in the temperature range 4.2–300 K. The measurements were performed by using an automated DSM5 susceptometer equipped with an Oxford Instruments CF1200S continuous-flow cryostat. $CoHg(NCS)_4$ was used as a calibrant of the magnetic field and of the temperature by using the data in ref 20.

Description of the Structures

The asymmetric units of **1** and **2** are formed by $[M(phen)_3]^{2+}$ cations (M = Zn, Cu) and two TCNQ⁻ anions not directly bound to the metals. The ORTEP view of the asymmetric unit of **1** is shown in Figure 1. Analogous numbering of the atoms was used for **2**. Selected bond distances and angles within the cations and the anions are collected in Table IV for **1** and in Table V for **2**. The complexes are almost isomorphous.

The six-coordinate cations show in both cases two bond angles equal within experimental error, namely N(10)–M–N(13) and N(11)–M–N(14). For M = Zn, these angles are 94.9 (2) and 95.3 (2)°, and for M = Cu, they are 95.2 (4) and 94.7 (3)°. The coordination polyhedron around M can thus be described with an approximate C_2 symmetry, the C_2 axis being the bisector of the N(10)–M–N(13) and N(11)–M–N(14) angles. The largest deviation from C_2 symmetry is given by the M–N(12) bond lengths (222.5 (4) pm for **1** and 227 (1) pm for **2**), which are also the largest bonds observed. The coordination around the zinc atom is more regular as compared to that observed around the copper.

The phenanthroline ligands are quasi-planar, the largest deviation from planarity being 0.1 Å. The angles between the least-squares phenanthroline planes are [phen(N(9)–N(10))]–[phen(N(11)–N(12))] = 91.84 (7)°, [phen(N(9)–N(10))]–[phen(N(13)–N(14))] = 108.47 (8)°, and [phen(N(11)–N(12))]–[phen(N(13)–N(14))] = 73.67 (8)° for **1** and [phen(N(9)–N(10))]–[phen(N(11)–N(12))] = 92.1 (1)°, [phen(N(9)–N(10))]–[phen(N(13)–N(14))] = 107.7 (2)°, and [phen(N(11)–N(12))]–[phen(N(13)–N(14))] = 72.9 (2)° for **2**.

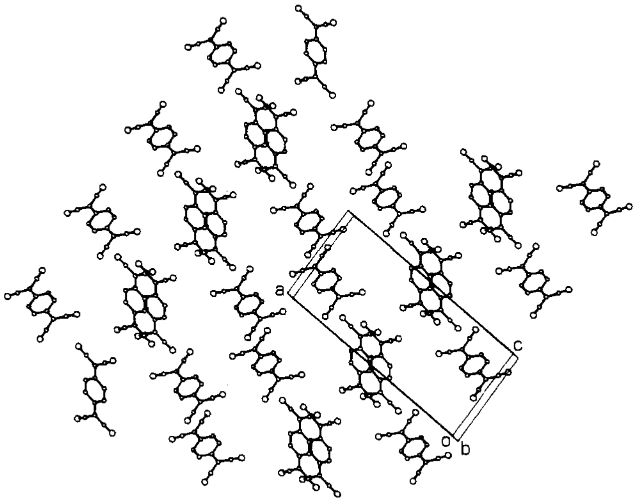

Figure 2. View of the unit cell for $Zn(phen)_3(TCNQ)_2$, showing the arrangement of the TCNQ⁻ anions, including far-neighbor molecules translated along the *a* and *c* crystallographic axes. The $[Zn(phen)_3]^{2+}$ cations are omitted for the sake of simplicity.

For both **1** and **2** the two crystallographically independent TCNQ⁻ anions, called A and B, respectively, are rather different from each other. In **1** and A anion is almost planar. The carbon atoms of the aromatic ring do not deviate significantly from planarity, the largest deviation of the other atoms of A from this least-squares plane being 9.7 (7) pm for C(8). The carbon atoms of the aromatic ring of the B anion show the largest deviations from planarity, with C(13), C(16), and C(18) being at 2.1 (7), 1.5 (7), and −1.6 (7) pm from the least-squares plane. The other atoms of B also deviate from this plane, the largest deviations being found for N(6) (32.2 (9) pm) and N(5) (21.4 (8) pm). The dihedral angle between the least-squares planes of the A and B aromatic rings is 116.5 (2)°.

In **2** the B ring results more planar than the B ring of **1**. The other atoms, however, still deviate from this plane, the largest deviations being observed for N(6) (37 (1) pm) and N(5) (22 (1) pm). The A anion of **2** is very similar to the A anion described for **1**.

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(19) See paragraph at end of paper regarding supplementary material.

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Table III. Positional Parameters (×10⁴) for the Non-Hydrogen Atoms of $Cu(phen)_3(TCNQ)_2$

atom[a]	*x/a*	*y/b*	*z/c*	atom[a]	*x/a*	*y/b*	*z/c*
Cu	2542 (1)	2057 (1)	3563 (2)	C(25)	2189 (6)	1136 (11)	6586 (14)
N(1)	7317 (6)	1417 (10)	11616 (13)	C(26)	1870 (6)	1232 (10)	7835 (15)
N(2)	5717 (5)	3932 (10)	12889 (12)	C(27)	1449 (6)	2216 (11)	8074 (15)
N(3)	3702 (5)	1099 (8)	7466 (12)	C(28)	1318 (5)	3093 (10)	7063 (14)
N(4)	5290 (5)	−1401 (10)	255 (12)	C(29)	1649 (5)	2924 (10)	5810 (14)
N(5)	9679 (5)	−2262 (10)	5798 (14)	C(30)	862 (6)	4101 (11)	7192 (15)
N(6)	10281 (6)	−2017 (12)	1598 (16)	C(31)	744 (6)	4899 (11)	6183 (15)
N(7)	8120 (6)	4428 (12)	636 (17)	C(32)	1083 (6)	4770 (10)	4917 (15)
N(8)	7405 (6)	4269 (11)	4807 (15)	C(33)	1536 (5)	3792 (10)	4756 (14)
N(9)	2093 (4)	1948 (8)	5574 (10)	C(34)	975 (7)	5583 (12)	3863 (16)
N10)	1886 (4)	3619 (8)	3564 (12)	C(35)	1302 (6)	5412 (12)	2664 (16)
N(11)	3233 (4)	3013 (7)	3988 (11)	C(36)	1771 (6)	4415 (11)	2555 (16)
N(12)	2968 (4)	2674 (8)	1548 (11)	C(37)	3410 (5)	3111 (10)	5181 (15)
N(13)	2015 (4)	990 (8)	2664 (11)	C(38)	3860 (5)	3803 (9)	5465 (13)
N(14)	3055 (4)	326 (7)	3849 (10)	C(39)	4160 (5)	4412 (9)	4443 (14)
C(1)	5846 (5)	1726 (9)	10540 (12)	C(40)	3977 (5)	4369 (9)	3145 (13)
C(2)	5225 (5)	2190 (9)	10361 (12)	C(41)	3535 (5)	3604 (9)	2962 (13)
C(3)	4900 (5)	1750 (9)	9473 (12)	C(42)	4264 (5)	5009 (9)	2024 (13)
C(4)	5169 (5)	773 (9)	8667 (12)	C(43)	4067 (5)	4932 (10)	842 (14)
C(5)	5778 (5)	290 (9)	8857 (12)	C(44)	3631 (5)	4149 (9)	590 (13)
C(6)	6106 (5)	768 (9)	9743 (12)	C(45)	3360 (5)	3479 (9)	1661 (13)
C(7)	6194 (5)	2205 (10)	11446 (13)	C(46)	3417 (6)	4029 (10)	−630 (15)
C(8)	6803 (6)	1793 (11)	11570 (15)	C(47)	3011 (6)	3258 (10)	−765 (15)
C(9)	5943 (6)	3156 (11)	12253 (14)	C(48)	2808 (6)	2559 (11)	313 (16)
C(10)	4820 (5)	296 (9)	7774 (12)	C(49)	1512 (6)	1334 (12)	2083 (15)
C(11)	4216 (6)	761 (10)	7588 (13)	C(50)	1228 (7)	542 (12)	1373 (16)
C(12)	5080 (5)	−630 (10)	6941 (14)	C(51)	1505 (7)	−597 (12)	1218 (16)
C(13)	9316 (5)	100 (10)	3474 (14)	C(52)	2032 (6)	−1032 (11)	1812 (15)
C(14)	9313 (5)	751 (10)	2236 (14)	C(53)	2284 (5)	−168 (10)	2538 (13)
C(15)	8943 (6)	1800 (10)	2064 (15)	C(54)	2342 (6)	−2239 (12)	1812 (15)
C(16)	8545 (5)	2303 (10)	3123 (13)	C(55)	2814 (6)	−2589 (12)	2496 (15)
C(17)	8552 (5)	1681 (10)	4378 (14)	C(56)	3092 (6)	−1754 (10)	3243 (14)
C(18)	8945 (5)	615 (10)	4538 (14)	C(57)	2803 (5)	−538 (10)	3216 (13)
C(19)	9686 (6)	−1055 (12)	3621 (16)	C(58)	3566 (6)	−2071 (11)	4002 (14)
C(20)	9688 (6)	−1723 (12)	4811 (15)	C(59)	3796 (6)	−1197 (11)	4625 (14)
C(21)	10034 (7)	−1597 (13)	2524 (18)	C(60)	3532 (6)	−3 (10)	4518 (13)
C(22)	8143 (6)	3381 (11)	2908 (15)	O*	291 (14)	3187 (28)	928 (31)
C(23)	8127 (7)	3968 (14)	1679 (20)	C*	363 (28)	4005 (55)	820 (61)
C(24)	7725 (7)	3888 (12)	3927 (17)				

[a] Atoms marked with an asterisk belong to solvate methanol molecules.

No intermolecular contact between A and B less than 400 pm has been computed for both the compounds. The $[M(phen)_3]^{2+}$ ions show intermolecular contacts with the A and B anions; in particular, N(3)–C(37) = 315.9 (8) pm and N(3)–C(60) = 343.6 (8) pm for **1** and N(3)–C(37) = 318 (2) pm and N(3)–C(60) = 338 (2) pm for **2**.

A view of the arrangement of the $TCNQ^-$ anions in **1**, including far-neighbor molecules translated along the *a* and *c* crystallographic axes, is shown in Figure 2. The A anions are arranged in an alternating linear-chain mode with shortest and largest interplanar distance of 309 (6) and 333 (5) pm for **1** and 309 (9) and 333 (9) pm for **2**, respectively. The two A molecules form dimeric units with a ring-to-external-bond (R–B) overlap. The shortest interplanar distance is smaller than that usually observed in $TCNQ^-$ alkali-metal salts in which the R–B overlap occurs,[4] ranging from 322 to 343 pm, and compares well with the interplanar distance observed in the isolated dimeric $(TCNQ)_2^{2-}$ unit found in the compound $[Nb_3(\mu\text{-}Cl)_6(C_6Me_6)_3](TCNQ)_2$ (310 pm).[10] The largest distance is in the usual range.

The arrangement of the B anions is rather unusual. In Figure 3, the arrangement of the B $TCNQ^-$ anions in **1** is shown in a view parallel to the aromatic ring planes, and in Figure 4, a view perpendicular to these plane is given. This arrangement can be described as an isolated dimeric unit, drawn in Figure 4, with an interplanar distance of 333 (6) pm for **1** and 330 (9) pm for **2**. The two molecules are related by the symmetry operations (2 − *x*, −*y*, 1 − *z*), and the main interaction seems to occur between the external bonds, namely C–N bonds, of a molecule and the ring of the other one. At 843 (5) pm for **1** and 821 (6) pm for **2** (distance between the center of the aromatic ring) there is a molecule related by the symmetry operation (2 − *x*, −*y*, 1 − *z*) that lies in a plane running 10 (3) pm for **1** and 5 (4) pm for **2** from the original one (see Figure 4).

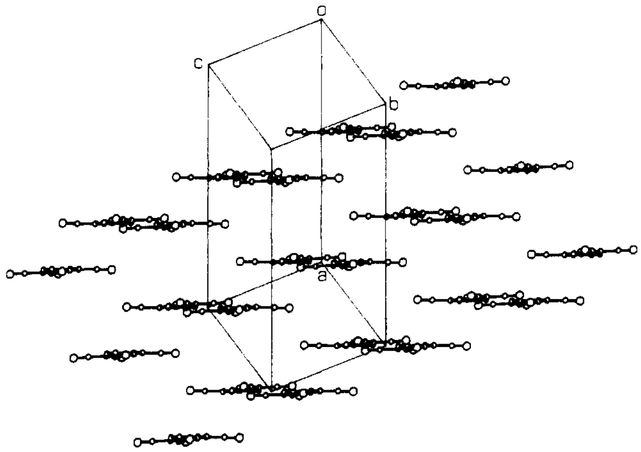

Figure 3. Arrangement of the $TCNQ^-$ ions of the type B (see text) for $Zn(phen)_3(TCNQ)_2$ in a view parallel to the aromatic ring planes. Molecules translated along the crystallographic *b* axis are also shown. An analogous arrangement is observed for $Cu(phen)_3(TCNQ)_2$.

In $TCNQ^-$ species a correlation has been suggested[21,22] between the exocyclic carbon bond distances and the formal charge on the anions. In the present compounds these distance are in the usual range for −1-charged radical species.

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(21) Goldstein, P.; Seff, K.; Trueblood, K. N. *Acta Crystallogr., Sect. B* **1968**, *24*, 778.

(22) Goldberg, S. Z.; Eisenberg, R.; Miller, J. S.; Epstein, A. J. *J. Am. Chem. Soc.* **1976**, *98*, 5173.

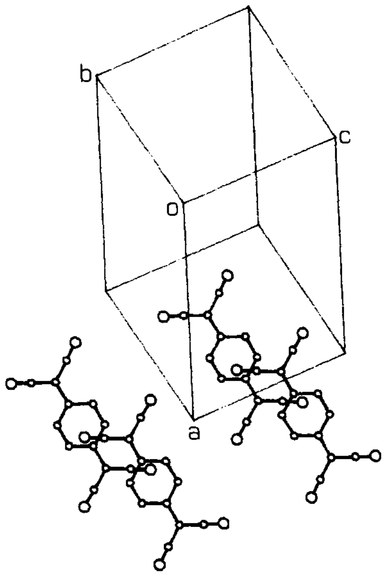

Figure 4. Arrangement of the two nearest TCNQ$^-$ ions of type B (see text) for Zn(phen)$_3$(TCNQ)$_2$ in a view perpendicular to the aromatic ring planes. The two molecules translated along the crystallographic *c* axis are also shown. An analogous arrangement is observed for Cu(phen)$_3$(TCNQ)$_2$.

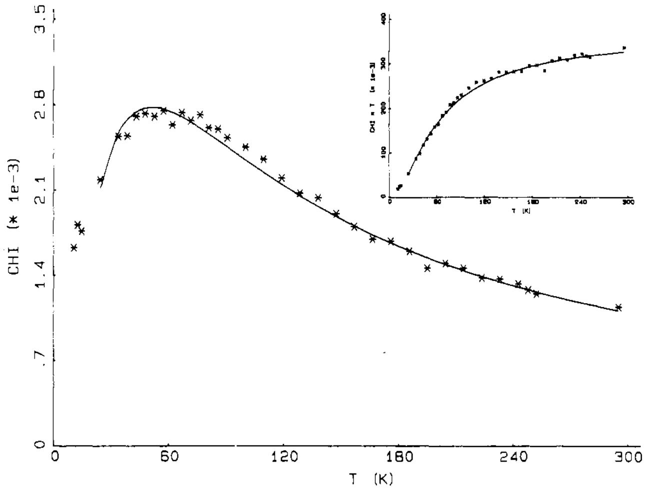

Figure 5. Temperature dependence of the magnetic susceptibilities for Zn(phen)$_3$(TCNQ)$_2$ in the forms χ_M vs T and $\chi_M T$ vs T. The solid lines are computed as described in the text.

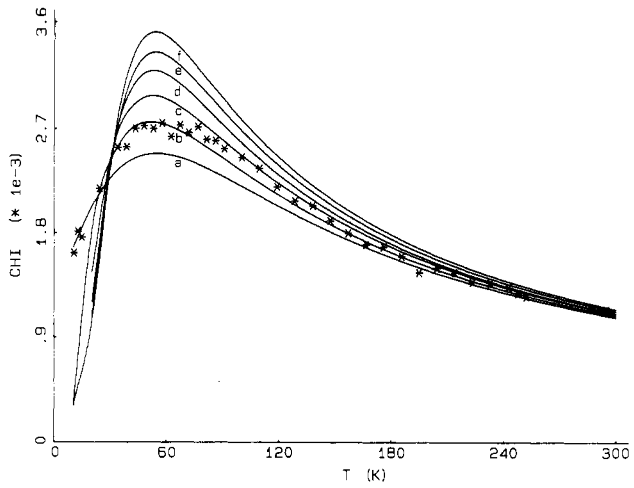

Figure 6. χ_M vs T computed curves[23] with $g = 2.00$, $J = 60$ cm^{-1}, and variable α (see text): (a) $\alpha = 1$; (b) $\alpha = 0.8$; (c) $\alpha = 0.6$; (d) $\alpha = 0.4$; (e) $\alpha = 0.2$; (f) $\alpha = 0$. The stars represent the experimental points obtained for Zn(phen)$_3$(TCNQ)$_2$.

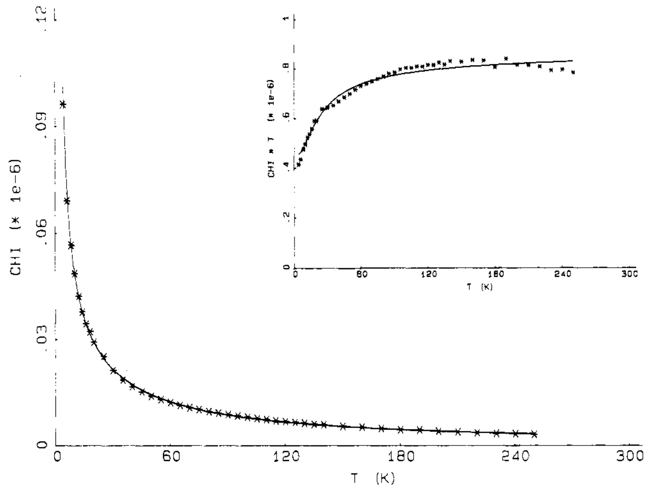

Figure 7. Temperature dependence of the magnetic susceptibilities for Cu(phen)$_3$(TCNQ)$_2$ in the forms χ_M vs T and $\chi_M T$ vs T. The solid lines are computed as described in the text.

Magnetic Properties

The temperature dependence of the magnetic susceptibility for **1** is reported in Figure 5. The molar magnetic susceptibility of the Zn(II) compound shows a maximum at about 60 K, indicating that a magnetic coupling occurs. The actual value of the magnetic moment at 290 K is 1.64 μ_B, well below the expected value for two noninteracting $S = {}^1/_2$ spins. This result is independent of the method of synthesis, and both freshly prepared and 2-month-aged samples gave the same results. This excludes any oxidation of the paramagnetic TCNQ$^-$ ions to diamagnetic TCNQ(0) species. The only way to rationalize this behavior is to consider that one of the two crystallographically independent dimers seen in the crystal structure is essentially diamagnetic also at room temperature. Following this suggestion we computed the χ_M versus T curve using the Heisenberg antiferromagnetic linear-chain model with the equation derived by Hatfield et al.:[23]

$$\chi_M = [Ng^2\mu_B^2(A + Bx + Cx^2)]/[kT(1 + Dx + Ex^2 + Fx^3)] \qquad (1)$$

with $A = 0.25$, $B = -0.13695 + 0.26387\alpha$, $C = 0.017025 - 0.12668\alpha + 0.49113 - 1.1977\alpha^3 + 0.87257\alpha^4$, $D = 0.070509 + 1.3042\alpha$, $E = -0.0035767 - 0.40837\alpha + 3.4862\alpha^2 - 0.73888\alpha^3$, $F = 0.36184 - 0.065528\alpha + 6.65875\alpha^2 - 29.945\alpha^3 + 15.425\alpha^4$, and $x = |J|/kT$.

The computed curves with $g = 2.00$ and $J = 60$ cm^{-1} and variable α are compared to the experimental curve in Figure 6. $\alpha = 0$ corresponded to an isolated dimeric unit while $\alpha = 1$ described a linear regular chain. It is apparent that the curve with $\alpha = 0.8$ can reproduce the experimental data. The best fit χ_M vs. T curve was obtained by a Simplex minimization routine of the function

$$S = \sum_i(\chi_{M_i}{}^c - \chi_{M_i}{}^o)^2 \qquad (2)$$

with a fixed g value of 2.00. The best fit parameters are $J = 60$ (2) cm^{-1} and $\alpha = 0.8$ (1). The calculated curve is shown in Figure 5 as a continuous line.

The experimental χ_M versus T curve for the Cu(II) compounds is shown in Figure 7. The solid line represent the best fit curve obtained by considering the experimental data as a sum of a Heisenberg alternating linear chain and a Curie contribution due to the copper(II) ions. In the fitting procedure we fixed the g value for the chain to 2.00, varying g_{Cu}, J, and α. The best fit parameters, obtained by using the same procedure as for the zinc(II) compound, are $g_{Cu} = 2.221$ (5), $J = 29$ (1) cm^{-1}, and $\alpha = 0.6$ (1).

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[23] Hall, J. W.; Marsh, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1981**, *20*, 1033.

Table IV. Selected Bond Distances (pm) and Angles (deg) for $Zn(phen)_3(TCNQ)_2$

	Bond Distances		
	$[Zn(phen)_3]^{2+}$ Cation		
Zn–N(9)	215.4 (4)	Zn–N10)	218.5 (5)
Zn–N(11)	213.5 (5)	Zn–N(12)	222.5 (4)
Zn–N(13)	215.4 (6)	Zn–N(14)	218.5 (4)
	TCNQ$^-$ (A Type) Anion		
C(8)–N(1)	115 (1)	C(9)–N(2)	114.3 (9)
C(11)–N(3)	117 (1)	C(12)–N(4)	116.0 (9)
C(2)–C(1)	142.4 (8)	C(6)–C(1)	142.4 (8)
C(7)–C(1)	141.8 (9)	C(3)–C(2)	136.7 (9)
C(4)–C(3)	142.9 (8)	C(5)–C(4)	140.7 (8)
C(10)–C(4)	141.6 (9)	C(6)–C(5)	137.6 (9)
C(8)–C(7)	141 (1)	C(9)–C(7)	142.9 (9)
C(11)–C(10)	139.4 (9)	C(12)–C(10)	141.3 (8)
	TCNQ$^-$ (B Type) Anion		
C(20)–N(5)	114 (1)	C(21)–N(6)	114 (1)
C(23)–N(7)	115 (1)	C(24)–N(8)	115 (1)
C(14)–C(13)	142 (1)	C(18)–C(13)	140 (1)
C(19)–C(13)	142.9 (9)	C(15)–C(14)	135.5 (9)
C(16)–C(15)	139.6 (9)	C(17)–C(16)	142.1 (9)
C(22)–C(16)	143.7 (9)	C(18)–C(17)	136.9 (9)
C(20)–C(19)	141 (1)	C(21)–C(19)	140 (1)
C(23)–C(22)	140 (1)	C(24)–C(22)	141 (1)
	Angles		
	$[Zn(phen)_3]^{2+}$ Cation		
N(10)–Zn–N(9)	76.8 (2)	N(11)–Zn–N(9)	96.0 (2)
N(11)–Zn–N(10)	95.5 (2)	N(12)–Zn–N(9)	164.1 (2)
N(12)–Zn–N(10)	90.0 (2)	N(12)–Zn–N(11)	76.1 (2)
N(13)–Zn–N(9)	100.3 (2)	N(13)–Zn–N(10)	94.9 (2)
N(13)–Zn–N(11)	162.3 (2)	N(13)–Zn–N(12)	89.6 (2)
N(14)–Zn–N(9)	93.2 (2)	N(14)–Zn–N(10)	166.0 (2)
N(14)–Zn–N(11)	95.3 (2)	N(14)–Zn–N(12)	101.2 (2)
N(14)–Zn–N(13)	77.1 (2)		
	TCNQ$^-$ (A Type) Anion		
C(6)–C(1)–C(2)	116.9 (6)	C(7)–C(1)–C(2)	122.2 (5)
C(7)–C(1)–C(6)	120.9 (5)	C(3)–C(2)–C(1)	121.6 (5)
C(4)–C(3)–C(2)	121.1 (5)	C(5)–C(4)–C(3)	117.7 (5)
C(10)–C(4)–C(3)	120.4 (5)	C(10)–C(4)–C(5)	121.9 (5)
C(6)–C(5)–C(4)	121.2 (5)	C(5)–C(6)–C(1)	121.6 (5)
C(8)–C(7)–C(11)	121.7 (6)	C(9)–C(7)–C(1)	121.1 (6)
C(9)–C(7)–C(8)	117.2 (6)	C(7)–C(8)–N(1)	178.8 (8)
C(7)–C(9)–N(2)	177.6 (7)	C(11)–C(10)–C(4)	122.2 (5)
C(12)–C(10)–C(4)	121.5 (5)	C(12)–C(10)–C(11)	116.3 (6)
C(10)–C(11)–N(3)	178.1 (7)	C(10)–C(12)–N(4)	179.4 (7)
	TCNQ$^-$ (B Type) Anion		
C(18)–C(13)–C(14)	117.6 (6)	C(19)–C(13)–C(14)	120.1 (7)
C(19)–C(13)–C(18)	122.3 (7)	C(15)–C(14)–C(13)	120.5 (6)
C(16)–C(15)–C(14)	122.2 (6)	C(17)–C(16)–C(15)	117.7 (6)
C(22)–C(16)–C(15)	121.5 (6)	C(22)–C(16)–C(17)	120.8 (6)
C(18)–C(17)–C(16)	120.0 (6)	C(17)–C(18)–C(13)	121.9 (6)
C(20)–C(19)–C(13)	121.7 (7)	C(21)–C(19)–C(13)	121.2 (8)
C(21)–C(19)–C(20)	116.8 (7)	C(19)–C(20)–N(5)	179.0 (9)
C(19)–C(21)–N(6)	179 (1)	C(23)–C(22)–C(16)	119.6 (6)
C(24)–C(22)–C(16)	122.1 (6)	C(24)–C(22)–C(23)	118.3 (6)
C(22)–C(24)–N(8)	179.7 (5)	C(22)–C(23)–N(7)	178.3 (8)

Table V. Selected Bond Distances (pm) and Angles (deg) for $Cu(phen)_3(TCNQ)_2$

	Bond Distances		
	$[Cu(phen)_3]^{2+}$ Cation		
Cu–N(9)	219 (1)	Cu–N(10)	212.0 (9)
Cu–N(11)	204.4 (9)	Cu–N(12)	227 (1)
Cu–N(13e	206 (1)	Cu–N(14)	212.9 (9)
	TCNQ$^-$ (A Type) Anion		
C(8)–N(1)	116 (1)	C(9)–N(2)	115 (1)
C(11–N(3)	116 (1)	C(12)–N(4)	116 (1)
C(2)–C(1)	142 (1)	C(6)–C(1)	141 (1)
C(7)–C(1)	142 (1)	C(3)–C(2)	135 (1)
C(4)–C(3)	144 (1)	C(5)–C(4)	141 (1)
C(10)–C(4)	141 (1)	C(6)–C(5)	137 (1)
C(8)–C(7)	138 (2)	C(9)–C(7)	140 (2)
C(11)–C(10)	139 (1)	C(12)–C(10)	141 (2)
	TCNQ$^-$ (B Type) Anion		
C(20)–N(5)	114 (2)	C(21)–N(6)	114 (2)
C(23)–N(7)	115 (2)	C(24)–N(8)	115 (2)
C(14)–C(13)	141 (2)	C(18)–C(13)	140 (2)
C(19)–C(13)	144 (2)	C(15)–C(14)	135 (1)
C(16)–C(15)	142 (2)	C(17)–C(16)	142 (2)
C(22)–C(16)	142 (1)	C(18)–C(17)	139 (1)
C(20)–C(19)	138 (2)	C(21)–C(19)	141 (2)
C(23)–C(22)	138 (2)	C(24)–C(22)	141 (2)
	Angles		
	$[Cu(phen)_3]^{2+}$ Cation		
N(10)–Cu–N(9)	78.0 (4)	N(11)–Cu–N(9)	96.3 (4)
N(11)–Cu–N(10)	92.9 (3)	N(12)–Cu–N(9)	165.7 (3)
N(12)–Cu–N(10)	90.1 (4)	N(12)–Cu–N(11)	76.1 (4)
N(13)–Cu–N(9)	99.2 (4)	N(13)–Cu–N(10)	95.2 (4)
N(13)–Cu–N(11)	163.7 (4)	N(13)–Cu–N(12)	89.8 (4)
N(14)–Cu–N(9)	91.5 (4)	N(14)–Cu–N(10)	167.7 (4)
N(14)–Cu–N(11e	94.7 (3)	N(14)–Cu–N(12)	101.1 (3)
N(14)–Cu–N(13)	80.0 (4)		
	TCNQ$^-$ (A Type) Anion		
Cn6)–C(1)–C(2)	116 (1)	C(7)–C(1)–C(2)	123 (1)
C(7)–C(1)–C(6)	121 (1)	C(3)–C(2)–C(1)	122 (1)
C(4)–C(3)–C(2)	121 (1e	C(5)–C(4)–C(3)	117 (1)
C(10)–C(4)–C(3)	120 (1)	C(10)–C(4)–C(5)	122 (1)
C(6)–C(5)–C(4)	121 (1)	C(5)–C(6)–C(1)	122 (1)
C(8)–C(7)–C(1)	122 (1)	C(9)–C(7)–C(1)	122 (1)
C(9)–C(7)–C(8)	116 (1)	C(7)–C(8)–N(1)	177 (1)
C(7)–C(9)–N(2)	177 (1)	C(11)–C(10)–C(4)	123 (1)
C(12)–C(10)–C(4)	121 (1)	C(12)–C(10)–C(11)	116 (1)
C(10)–C(11)–N(3)	177 (1)	C(10)–C(12)–N(4)	179 (1)
	TCNQ$^-$ (B Type) Anion		
C(18)–C(13)–C(14)	117 (1)	C(19)–C(13)–C(14)	121 (1)
C(19)–C(13)–C(18)	122 (1)	C(15)–C(14)–C(13)	122 (1)
C(16)–C(15)–C(14)	121 (1)	C(17)–C(16)–C(15)	118 (1)
C(22)–C(16)–C(15)	120 (1)	C(22)–C(16)–C(17)	122 (1)
C(18)–C(17)–C(16)	120 (1)	C(17)–C(18)–C(13)	122 (1)
C(20)–C(19)–C(13)	122 (1)	C(21)–C(19)–C(13)	121 (1)
C(21)–C(19)–C(20)	117 (1)	C(19)–C(20)–N(5)	179 (1)
C(19)–C(21)–N(6)	175 (2)	C(23)–C(22)–C(16)	121 (1)
C(24)–C(22)–C(16)	122 (1)	C(24)–C(22)–C(23)	116 (1)
C(22)–C(23)–N(7)	178 (2)	C(22)–C(24)–N(8)	176 (1)

Discussion

The present compounds show two different arrangements of the TCNQ$^-$ radicals. The A molecules in both **1** and **2** are stacked one over the other to form an alternating linear chain running along the *c* axis. The dinuclear units of the alternating chain are bonded in a R–B mode, which is one of the most widely stacking mode experimentally encountered in TCNQ$^-$ chains.[2-5] The B molecules arrange themselves to form discrete dimers. The bonding mode of the B molecule is rather unusual for $(TCNQ)_2^{2-}$ dinuclear moieties and can be described as an external-bond-to-external-bond overlap (B–B mode). This bonding situation is reasonably intermediate between π- and σ-bonded dimer.[24] In the latter case there is an interaction between the terminal carbon atoms, which are usually formed at ≈160 pm. Also, the largest deviation of the CN groups from the aromatic ring plane as compared to that observed for the A molecules supports this description.

The magnetic properties of **1** have been nicely interpreted within the Heisenberg alternating-chain model:[23] the compound behaves like a rather strong alternating chain of $S = {}^1/_2$ spins ($\alpha = 0.8$ (1)). These results suggest that molecules B should be in the diamagnetic singlet state even at room temperature, indicating the existence of a rather strong interaction between the molecules in the dinuclear unit.

It is apparent at this point that a full magnetic characterization of **1** is needed to confirm these findings. As a matter of fact, preliminary EPR measurements on single crystals showed a typical excitonic behavior with the triplet spectrum, which must be at-

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(24) Hoffmann, S. K.; Corvan, P. J.; Singh, P.; Sethulekshmi, C. N.; Metzger, R. M.; Hatfield, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 4608.

Inorg. Chem. **1989**, *28*, 1969–1975 **1969**

tributed to one dinuclear moiety, appearing at temperature below 20 K. This is one of the lowest temperatures at which EPR spectra of excitonic systems have been observed,[7-9] and a complete single-crystal EPR study of **1** and **2** is being performed and will be reported later.

The magnetic behavior of **2** has been nicely reproduced by considering the magnetism arising from a Heisenberg alternating linear chain plus a Curie paramagnetism from the copper(II) complex. Any interaction between the copper(II) ions and the TCNQ$^-$ ions seems to be too small to be observed with magnetic susceptibility techniques.

Registry No. **1**, 119638-22-1; **2**, 51141-11-8; Zn, 14912-36-8; Cu, 36502-34-8.

Supplementary Material Available: Complete crystallographic data and data collection details for Zn(phen)$_3$(TCNQ)$_2$ and Cu(phen)$_3$(TCNQ)$_2$ (Table SI), thermal parameters for Zn(phen)$_3$(TCNQ)$_2$ (Table SII) and Cu(phen$_3$)(TCNQ)$_2$ (Table SIII), and positional parameters of the hydrogen atoms of Zn(phen)$_3$(TCNQ)$_2$ (Table SIV) and Cu(phen)$_3$(TCNQ)$_2$ (Table SV) (7 pages); listings of the observed and calculated structure factors for Zn(phen)$_3$(TCNQ)$_2$ (Table SVI) and Cu(phen)$_3$(TCNQ)$_2$ (Table SVII) (32 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, University of Florence, Florence, Italy, and Laboratoire de Chimie (UA CNRS 1194), Department de Recherche Fondamentale, Centre d'Etudes Nucleaires de Grenoble, Grenoble, France

Synthesis, X-ray Crystal Structure, and Magnetic Properties of Two Dinuclear Manganese(II) Compounds Containing Nitronyl Nitroxides, Imino Nitroxides, and Their Reduced Derivatives

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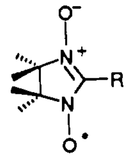
The nitronyl nitroxide 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy 3-oxide (NITPh) is reduced in the reaction with manganese(II) hexafluoroacetylacetonate (Mn(hfac)$_2$) to yield 1-hydroxy-2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole (IMHPh). A solid compound of formula [Mn(hfac)$_2$(IMHPh)]$_2$(NITPh) (I) is obtained, whose crystal structure was determined through X-ray diffraction. I crystallizes in the triclinic $P\bar{1}$ space group: $a = 13.566$ (2) Å, $b = 15.079$ (3) Å, $c = 21.622$ (4) Å, $\alpha = 68.36$ (2)°, $\beta = 77.18$ (2)°, $\gamma = 61.47$ (2)°, $Z = 2$. A similar behavior was observed with the imino nitroxide 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy (IMPh) and Mn(hfac)$_2$·2H$_2$O. In this case a solid compound of formula Mn(hfac)$_2$(IMHPh)(IMPh) (II) is obtained, which crystallizes in the monoclinic space group $P2_1/c$: $a = 13.391$ (2) Å, $b = 22.725$ (3) Å, $c = 14.987$ (2) Å, $\beta = 66.73$ (2)°, $Z = 4$. The crystal structure of I consists of two different centrosymmetric units, of formulas [Mn(hfac)$_2$(IMHPh)(NITPh)]$_2$ and [Mn(hfac)$_2$(IMHPh)]$_2$, respectively. The reduced form of the radical bridges the manganese(II) ions in both units, and in the former, a molecule of radical is hydrogen bonded to its reduced form. The crystal structure of II consists of centrosymmetric units [Mn(hfac)$_2$(IMHPh)(IMPh)]$_2$ with a geometry similar to that of the corresponding unit of I. The magnetic properties of both I and II were studied in the range 5–300 K, showing that the manganese ions are weakly coupled in an antiferromagnetic fashion. The EPR spectra were attributed to the coupled $S = 5$ state.

Introduction

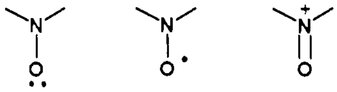
Nitronyl nitroxides, of the general formula



which we abbreviate as NITR, R being phenyl, methyl, ethyl, etc., display a very interesting coordination chemistry with transition-metal ions.[2-4] In fact, it has been found that they can bind in several different ways, with one oxygen atom to one metal ion, yielding discrete mononuclear complexes[5-8] (nuclearity is referred to the metal), with one oxygen to one metal, while the other oxygen interacts weakly with the oxygen of another radical,[9] forming magnetic chains, with the two oxygen atoms to two different metal ions[10,11] (in this case linear chains can be formed, either ferro- or ferrimagnetic, depending on the nature of the metal ion), and with one oxygen atom to two different metal ions, while the second oxygen interacts weakly with the oxygen atom of another radical, thus forming chains of four-spin clusters, which have been called chains of diamonds.[12]

In all these cases the radicals bind to the metal ions, keeping their radical nature; i.e. the spectral and magnetic properties can be best described by considering that the π^* orbital of the nitroxide has a weak overlap with the magnetic orbitals of the metal ions.

Beyond binding to the metal and keeping their radical nature, it is known that nitroxides can undergo redox reactions with transition-metal ions;[13,14] in fact, nitroxyl free radicals are in an oxidation state intermediate between those of the hydroxylamino anion and the nitrosonium cation:



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