mentation. The diffractometer used in this work was purchased through an equipment grant from the National Science Foundation to Wayne State University.

Registry No. [Cu([14]aneNS$_3$)]$^{2+}$, 87464-55-9; [Cu([14]aneN$_2$S$_2$)]$^{2+}$, 87464-56-0; [Cu([14]aneNSSN)]$^{2+}$, 87464-57-1; [Cu([14]aneNS$_4$)]$^{2+}$, 116197-98-9; [Cu([15]aneN$_2$S$_3$)]$^{2+}$, 137195-80-3; [Cu([14]aneNS$_3$)]$^{+}$, 87464-71-9; [Cu([14]aneN$_2$S$_2$)]$^{+}$, 87464-72-0; [Cu([14]aneNSSN)]$^{+}$, 87464-73-1; [Cu([14]aneNS$_4$)]$^{+}$, 137167-80-7; [Cu([15]aneN$_2$S$_3$)]$^{+}$, 137167-81-8; [Cu([14]aneS$_4$)]$^{2+}$, 57673-86-6; [Cu([14]aneS$_4$)]$^{+}$, 93645-98-8; [Cu([14]aneN$_3$S)]$^{2+}$, 87464-58-2; [Cu([14]aneN$_3$S)]$^{+}$, 87464-77-5; [Cu([14]aneN$_4$)]$^{2+}$, 52304-87-7; [Cu([14]aneN$_4$)]$^{+}$, 88279-82-7; [Cu([15]aneS$_5$)]$^{2+}$, 60165-93-7; [Cu([15]aneS$_5$)]$^{+}$, 137167-82-9; [Cu([14]aneNS$_3$)]ClO$_4$, 137167-83-0; C, 7440-44-0; ClO$_4^-$, 14797-73-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen parameters, least-squares planes, and torsion angles for [Cu^{I}([14]aneNS$_3$)]ClO$_4$ and cyclic voltammetric data for all five copper–polyamino polythiaether complexes studied (23 pages); a listing of calculated and observed structure factors for [Cu^{I}([14]aneNS$_3$)]ClO$_4$ (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of Isostructural Transition-Metal (Copper, Nickel, Cobalt, and Iron) Compounds with 7,7′,8,8′-Tetracyanoquinodimethanide(1−) in an Unusual Monodentate Coordination Mode. Crystal Structure of Bis(3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole)bis(7,7′,8,8′-tetracyanoquinodimethanido)copper(II)

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The synthesis and properties of compounds M(abpt)$_2$(TCNQ)$_2$, with M = Cu, Ni, Co, and Fe, abpt = 3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole, and TCNQ = 7,7′,8,8′-tetracyanoquinodimethane, are described. The complexes exhibit very similar spectroscopical and electrical properties. The four compounds appear to be isostructural according to their IR spectra and X-ray powder diffraction data. The crystal structure of CuC$_{48}$H$_{28}$N$_{20}$ has been solved. It crystallizes in the triclinic space group, $P\bar{1}$ with a = 9.194 (1) Å, b = 9.761 (2) Å, c = 12.235 (2) Å, α = 68.29 (1)°, β = 86.72 (1)°, γ = 81.80 (1)°, V = 1009.7 (3) Å^3, and Z = 1. Heavy-atom techniques were used, and the structure was refined by least-squares methods to a residual R value of 0.052 for 1957 reflections. The copper(II) atom is elongated octahedrally, surrounded by four nitrogens of two symmetry-related abpt ligands (Cu–N = 1.987(5) and 2.046(5) Å) and by two axial, monodentately coordinating TCNQ$^-$ anions (Cu–N = 2.442 (5) Å). The intermolecular TCNQ units form eclipsed dimers, with their mean planes at a close distance of 3.22 Å. At room temperature, all four compounds behave virtually as insulators ($\sigma_{300\,\mathrm{K}}$ = 10^{-7}–10^{-10} S cm^{-1}).

Introduction

The 3,(4),5-substituted 1,2,4-triazoles have been extensively investigated in our laboratories during the last decade.[2-5] They were studied mainly in combination with various transition-metal salts, because of their tendency to form coordination compounds exhibiting interesting magnetic properties. This kind of ligands can also be used for synthesizing coordination compounds with typically low-dimensional properties, such as electrical conductivity, since the starting materials can be described as *quasi*-square-planar compounds.

In recent years, a number of attempts have been made to obtain so-called molecular metals using more or less square-planar transition-metal chelates that possess one or more paramagnetic centers, in combination with the radical anion TCNQ$^-$, with TCNQ$^-$ = 7,7′,8,8′-tetracyanoquinodimethanide(1−). The copper(II) chelates are of special interest as a donor, because by varying the nature of the ligand the Cu(II)/Cu(I) redox potential of the chelates can be optimized.[6] Therefore, these compounds have the capacity to provide a new type of synthetic metal. Potentially, in these compounds magnetic electrons and conducting electrons can coexist. Examples are the highly conducting compounds of the kind Cu(phen)$_2$(TCNQ)$_2$ or Cu(bpy)$_2$(TCNQ)$_2$, with phen = 1,10-phenanthroline and bpy = 2,2′-bipyridine.[7,8] On the other hand, a *semi*conductive or insulating behavior was found in compounds of the formula Cu$_2$(PPA)(TCNQ)$_3$ or Cu$_2$(PPA)(TCNQ)$_4$[9] and Cu$_2$(L)(TCNQ)$_2$,[10] where PPA = 3,6-bis(2-pyridyl)pyridazine and LH$_2$ is the tetra Schiff base macrocycle resulting from the 2/2 condensation of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol.

The potentially dinucleating ligand 3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole (hereafter abbreviated as abpt, Figure 1) was selected to investigate the conducting, magnetic, and spectroscopic properties of the coordination compounds after combination with the TCNQ$^-$ anion. The results of this study are described below.

Experimental Section

Starting Materials. The ligand abpt was prepared according to the method of Geldard and Lions.[11] The elemental analyses, melting point, and NMR and infrared spectroscopy agreed with the literature data.[11] TCNQ was obtained from Janssen Chemicals. LiTCNQ was prepared by adding a boiling solution of 0.03 mol of LiI in 20 mL of acetonitrile to a boiling solution of 0.01 mol of TCNQ in 200 mL of acetonitrile.

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(1) (a) Leiden University. (b) Rijksuniversiteit Utrecht.

(2) Keij, F. S.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1984**, 2093.

(3) Prins, R. Forthcoming Ph.D. Thesis, Leiden University, and references therein.

(4) Prins, R.; Birker, P. J. M. W. L.; Haasnoot, J. G.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 4128.

(5) Faulmann, C.; van Koningsbruggen, P. J.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *Acta Crystallogr., C* **1990**, *C46*, 2357.

(6) Lacroix, P.; Kahn, O.; Valade, L.; Cassoux, P.; Thompson, L. K. *Synth. Met.* **1990**, *39*, 81.

(7) Inoue, M. B.; Inoue, M. *Chem. Phys. Lett.* **1981**, *80*, 585.

(8) Seto, T.; Inoue, M. B.; Inoue, M.; Nakamura, D. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1903.

(9) Wang, W.; Jeng, J. *Synth. Met.* **1988**, *27*, B205.

(10) Lacroix, P.; Kahn, O.; Gleizes, A.; Valade, L.; Cassoux, P. *Nouv. J. Chim.* **1984**, *8*, 643.

(11) Geldard, J. F.; Lions, F. *J. Org. Chem.* **1965**, *30*, 318.

0020-1669/92/1331-0198$03.00/0

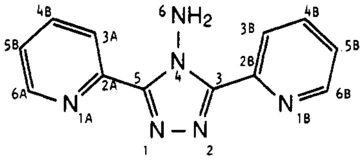

Figure 1. Numbering scheme of abpt.

Table I. Crystal and Refinement Data for $Cu(abpt)_2(TCNQ)_2$

chem formula	$CuC_{48}H_{28}N_{20}$	T, K	100
fw	948.43	λ, Å	0.71073
a, Å	9.194 (1)	space group	$P\bar{1}$
b, Å	9.761 (2)	Z	1
c, Å	12.235 (2)	D_x, g cm^{-3}	1.560
α, deg	68.29 (1)	μ, cm^{-1}	6.0
β, deg	86.72 (1)	R^a	0.052
γ, deg	81.80 (1)	$R_w{}^b$	0.037
V, Å^3	1009.7 (3)		

$^a R = \sum(|F_o| - |F_c|)/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $w = 1/\sigma^2(F)$.

Dark purple microcrystals precipitated.[12] $Cu(TCNQ)_2$ was prepared in the following way: to a filtered solution of 11 mmol of LiTCNQ in 200 mL of water was added a solution of an excess of $Cu(SO_4)(H_2O)_5$ in water. The green solid was collected and analyzed.[13]

Synthesis of the Complexes. $M(abpt)_2(TCNQ)_2$ was synthesized in bulk quantity by dissolving 10 mmol of $M(abpt)_2(NO_3)_2$ (or $M(abpt)_2(PF_6)_2$ in the case of M = Fe) in 40 mL of a mixture of deoxygenated acetonitrile and methanol (2:1) and subsequently adding 20 mmol of LiTCNQ, also in a deoxygenated 2:1 acetonitrile/methanol solution. When this mixture was allowed to stand at room temperature and under nitrogen atmosphere, small, black shiny crystals were formed. They were collected by filtration, washed with cold ethanol, and analyzed after drying under vacuum.

Single crystals of $Cu(abpt)_2(TCNQ)_2$, large enough for X-ray data collection, were made by slow interdiffusion of a solution of $Cu(TCNQ)_2$ in acetonitrile/methanol into abpt dissolved in methanol. An H-shaped tube equipped with a fine-porosity frit was used. Black, cubic crystals with a metallic luster appeared after about 5 days.

From the literature, it is known that in $Cu(TCNQ)_2$ the copper atoms are in the Cu(I) state rather than in the Cu(II) state.[14,15] This means that in theory the single crystals of $Cu(abpt)_2(TCNQ)_2$ could contain copper centers in a different oxidation state than the ones in the corresponding microcrystalline material. To check if these different methods of preparation yielded the same compound, the infrared spectra as well as the X-ray powder diagrams of both compounds were compared to each other. They proved to be identical. Apparently, during the reaction of $Cu(TCNQ)_2$ with the abpt ligand a complete charge transfer has taken place between the metal and the TCNQ ligands:

$$Cu^+(TCNQ^-)(TCNQ^0) + 2abpt \rightarrow Cu^{2+}(abpt)_2(TCNQ^-)_2$$

This gives the same net result as the reaction between $Cu(abpt)_2(NO_3)_2$ and LiTCNQ.

Physical Measurements and Analyses. Infrared spectra were recorded on a Perkin-Elmer Model 580B IR spectrophotometer in the region 4000–180 cm^{-1} as KBr pellets. Ligand field spectra were taken on a Perkin-Elmer 330 UV-vis-near-IR spectrophotometer using MgO as a reference in the diffuse reflectance technique. EPR spectra of the powdered samples were recorded at room temperature and at liquid-nitrogen temperature on a Varian E3 (9.5 GHz) spectrometer. NMR spectra were taken on a Jeol PS-100 (100 MHz) spectrometer using TMS (tetramethylsilane) as an internal reference. Magnetic susceptibility measurements between 300 and 500 K were performed by means of an automated Faraday balance.[16] $HgCo(NCS)_4$ was used as a calibrant.[17] The conductivity measurements were carried out at the Kamerlingh Onnes Laboratory, Leiden, The Netherlands. Electrical conductivities of the powdered compounds were measured with the aid of the compressed pellet technique. The pellets were pressed in a die, and their resistance was measured directly using a Keithly multimeter.[18] Elemental analyses were performed by the Microanalytical Laboratory, University College, Dublin, Ireland.

Table II. Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) for the Non-Hydrogen Atoms of $Cu(abpt)_2(TCNQ)_2$

atom	x/a	y/b	z/c	U_{eq}
Cu	1	0	0	0.0169 (4)
N(1)	0.9210 (5)	0.1952 (5)	0.0105 (4)	0.016 (2)
N(2)	0.8144 (5)	0.2465 (5)	0.0716 (4)	0.016 (2)
N(4)	0.8901 (5)	0.4349 (5)	−0.0753 (4)	0.015 (2)
N(6)	0.9054 (6)	0.5784 (6)	−0.1573 (5)	0.024 (2)
N(1a)	1.1192 (5)	0.1351 (5)	−0.1321 (4)	0.015 (2)
N(1b)	0.6807 (5)	0.6398 (5)	−0.0071 (4)	0.018 (2)
N(1T)	1.1907 (5)	−0.0372 (5)	0.1429 (4)	0.021 (2)
N(2T)	1.5168 (6)	0.0927 (6)	0.3212 (5)	0.030 (2)
N(3T)	0.5082 (6)	0.3023 (6)	0.4818 (4)	0.028 (2)
N(4T)	0.8190 (5)	0.4141 (6)	0.6771 (4)	0.024 (2)
C(3)	0.7955 (6)	0.3937 (6)	0.0190 (5)	0.015 (2)
C(5)	0.9666 (6)	0.3091 (6)	−0.0774 (5)	0.014 (2)
C(1T)	1.1311 (6)	0.1167 (6)	0.3607 (5)	0.017 (2)
C(2a)	1.0821 (6)	0.2825 (6)	−0.1556 (5)	0.014 (2)
C(2b)	0.6877 (6)	0.4928 (6)	0.0564 (5)	0.014 (2)
C(2T)	0.9831 (6)	0.1032 (6)	0.3428 (5)	0.016 (2)
C(3a)	1.1497 (6)	0.3902 (7)	−0.2417 (5)	0.016 (2)
C(3b)	0.5936 (7)	0.4340 (7)	0.1495 (5)	0.018 (2)
C(3T)	0.8693 (6)	0.1567 (7)	0.3994 (5)	0.019 (2)
C(4a)	1.2611 (6)	0.3428 (7)	−0.3073 (5)	0.018 (2)
C(4b)	0.4894 (7)	0.5290 (7)	0.1790 (6)	0.023 (2)
C(4T)	0.8955 (6)	0.2287 (6)	0.4759 (5)	0.015 (2)
C(5a)	1.2979 (7)	0.1937 (7)	−0.2839 (6)	0.020 (2)
C(5b)	0.4781 (7)	0.6799 (7)	0.1153 (6)	0.022 (2)
C(5T)	1.0422 (6)	0.2454 (6)	0.4930 (5)	0.017 (2)
C(6a)	1.2260 (7)	0.0918 (7)	−0.1963 (5)	0.018 (2)
C(6b)	0.5768 (7)	0.7305 (7)	0.0248 (6)	0.021 (2)
C(6T)	1.1563 (7)	0.1902 (6)	0.4373 (5)	0.019 (2)
C(7T)	1.2462 (6)	0.0641 (6)	0.2990 (5)	0.018 (2)
C(8T)	0.7778 (6)	0.2864 (6)	0.5342 (5)	0.020 (2)
C(9T)	1.2177 (6)	0.0055 (6)	0.2121 (5)	0.017 (2)
C(10T)	1.3964 (7)	0.0801 (6)	0.3108 (5)	0.018 (2)
C(11T)	0.6292 (7)	0.2902 (6)	0.5071 (5)	0.020 (2)
C(12T)	0.8025 (6)	0.3566 (7)	0.6131 (5)	0.016 (2)

$^a U_{eq} = {}^1/_3\sum_{ij}U_{ij}a_i{}^*a_j{}^*a_ia_j$.

X-ray Data Collection and Refinement. Crystal data are presented in Table I. X-ray data were collected [Zr-filtered Mo Kα radiation (λ = 0.71073 Å): Θ_{max} = 24.2°; Δω = 1.33 + 0.35 tan Θ°; ω/2Θ-scan; 3257 reflections; h = −10 to +10, k = −10 to +11, l = 0–14] on an Enraf-Nonius CAD4-F diffractometer at 100 K for a block shaped crystal (0.15 × 0.15 × 0.23 mm^3) glued on top of a glass fiber. Unit-cell dimensions were derived from the SET4 setting angles of 25 reflections in the range 11 < 2Θ < 29°. Two reference reflections showed no decay during 56 h of X-ray exposure. Data were corrected for Lorentz and polarization. Absorption correction was not necessary as judged from a 360° ψ-scan for the close to axial (006) reflection. The structure was solved by Patterson and Fourier methods and refined on F by full-matrix least-squares methods on a micro-VAX II with SHELX76.[19a] Hydrogen atoms were located from a difference Fourier map and their positions refined with one common isotropic thermal parameter. Convergence was reached at R = 0.052 for 1957 observed reflections with $I > 2.5\sigma(I)$ [S = 1.31; $(\Delta/\sigma)_{max}$ = 0.03; −0.58 < Δρ < 0.53 e Å^{-3}; 356 parameters]. Final positional parameters are listed in Table II. Scattering factors were taken from ref 19b and corrected for anomalous dispersion.[19c] The calculation of geometrical data and the preparation of the illustrations were done either with ORTEP or with the programs PLATON and PLUTON of the EUCLID package.[19d]

Results and Discussion

Spectroscopic Results. The infrared spectra of the four $M(abpt)_2(TCNQ)_2$ (M = Fe, Co, Ni, Cu) compounds are very

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(12) Bozio, R.; Girlando, A.; Pecile, C. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1237.

(13) Groeneveld, L. R. Thesis, Leiden University, 1988.

(14) Sano, M.; Ohta, T.; Akamatu, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2204.

(15) Ikemoto, I.; Thomas, J. M.; Kuroda, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2237.

(16) Arbouw, J. W. Thesis, Leiden University, 1974.

(17) O'Conner, C. J.; Sinn, E.; Cukauskas, E. J.; Deaver, B. S., Jr. *Inorg. Chim. Acta* **1979**, *32*, 29.

(18) Kramer, G. J. Thesis, Leiden University, 1988.

(19) (a) Sheldrick, G. M. SHELX76. Crystal Structure Analysis Package. University of Cambridge, Cambridge, England, 1976. (b) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. A* **1968**, *A24*, 321. (c) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891. (d) Spek, A. L. The Euclid Package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, U.K., 1982; p 528.

much the same, with regard to both peak positions and intensities. Also the X-ray powder diagrams are very similar.

In the infrared spectra, the ν_{CN} stretching vibration of the nitrile groups is split into a very strong peak around 2180 cm^{-1} and a strong peak at approximately 2150 cm^{-1}, its exact position depending on the nature of the metal atom. This splitting can only be explained by assuming that the nitrile groups are inequivalent, e.g. when a certain number of the CN groups of the TCNQ anions are coordinating to the metal centers. Coordination to M^{2+} obviously results in a decrease of the force constant of the C–N bond (although the actual bond length becomes shorter!), which is reflected in a lowering of is stretching frequency.

Extensive infrared spectroscopy studies of TCNQ salts have demonstrated that IR spectra provide significant information on charge occupation and intermolecular interactions.[20,21] As pointed out by Lunelli et al.,[22] it is possible to determine whether TCNQ^{2-}, TCNQ$^-$, TCNQ$^{\delta-}$ ($0 < \delta < 1$), or TCNQ^0 (or a combination of these possibilities) is present in a certain compound by examining its infrared spectrum in the region 800–880 cm^{-1}. Thus, the absorptions in the spectrum of $M(abpt)_2(TCNQ)_2$ at 829 cm^{-1} are a clear indication that solely TCNQ$^-$ is present. Therefore, the exact composition of these compounds can be described as $M^{2+}(abpt)_2(TCNQ^-)_2$. The Cu(II) chelate is definitely not partially reduced to the corresponding Cu(I) chelate by the TCNQ$^-$ ion, as is known for other cases.[23]

Ligand-field spectra in the solid state have been measured to obtain more insight into the possible electronic distributions and the intermolecular interactions found for TCNQ compounds. However, the broad, intense bands made it impossible to assign or even detect the d–d bands of the transition metals. For TCNQ, Iida[24] showed that in general three types of transitions can exist in the visible and near-infrared region. Theoretically, the lowest energy transition, found around 6000 cm^{-1}, can be ascribed to an electron transition from the anionic to the neutral species, and it is denoted as CT_2.[25] An electron transition found in the region 9000–12000 cm^{-1}, resulting from a charge transfer between the TCNQ$^-$ ions, is called CT_1. The LE_1 excited level, which means the lowest locally excited level of the TCNQ anion, is found between 16 000 and 18 000 cm^{-1}.[26] Maxima in this region have been found for several dimerized TCNQ compounds.[27] Finally, the second excited level of the TCNQ anions, called LE_2, gives rise to maxima between 25 000 and 30 000 cm^{-1}.[26] The four diffuse reflectance spectra of the $M(abpt)_2(TCNQ)_2$ compounds are closely related (see Table IV). From infrared data it was already concluded that only TCNQ$^-$ is present. This means that a CT_2 transition at approximately 6000 cm^{-1} should not be present in their ligand-field spectra, which is indeed the case, as seen from Table IV.

Because of the observed similarity between the X-ray powder diffractogram patterns of the four $M(abpt)_2(TCNQ)_2$ compounds, it was concluded that they have a molecular structure almost identical to that of $Cu(abpt)_2(TCNQ)_2$, which is described below.

Description of the Crystal Structure of $Cu(abpt)_2(TCNQ)_2$. The triclinic unit cell contains one centrosymmetrically related Cu(abpt)$_2$ unit and a pair of centrosymmetrically related TCNQ anions. A view of the $Cu(abpt)_2(TCNQ)_2$ unit together with the atom-labeling scheme is presented in Figure 2. Relevant bond lengths and angles are summarized in Table III.

Table III. Relevant Bond Lengths (Å) and Angles (deg) for $Cu(abpt)_2(TCNQ)_2$

Cu–N(1)	1.987 (5)	C(1T)–C(7T)	1.412 (8)
Cu–N(1a)	2.046 (5)	C(1T)–C(2T)	1.422 (8)
Cu–N(1T)	2.442 (5)	C(1T)–C(6T)	1.420 (9)
N(2)–C(3)	1.329 (8)	C(2a)–C(3a)	1.376 (8)
N(1)–N(2)	1.350 (7)	C(2b)–C(3b)	1.386 (8)
N(1)–C(5)	1.329 (8)	C(2T)–C(3T)	1.370 (8)
N(2)–C(3)	1.329 (8)	C(3b)–C(4b)	1.365 (10)
N(4)–C(3)	1.375 (7)	C(3T)–C(4T)	1.410 (9)
N(4)–C(5)	1.333 (8)	C(4a)–C(5a)	1.370 (10)
N(4)–N(6)	1.410 (8)	C(4b)–C(5b)	1.380 (10)
N(1a)–C(2a)	1.354 (8)	C(4T)–C(5T)	1.418 (8)
N(1a)–C(6a)	1.341 (8)	C(4T)–C(8T)	1.425 (8)
N(1b)–C(2b)	1.350 (8)	C(5a)–C(6a)	1.376 (9)
N(1b)–C(6b)	1.349 (9)	C(5b)–C(6b)	1.379 (9)
N(1T)–C(9T)	1.126 (8)	C(5T)–C(6T)	1.373 (9)
N(2T)–C(10T)	1.150 (9)	C(7T)–C(9T)	1.432 (8)
N(3T)–C(11T)	1.150 (9)	C(7T)–C(10T)	1.433 (9)
N(4T)–C(12T)	1.146 (8)	C(8T)–C(11T)	1.416 (9)
C(3)–C(2b)	1.459 (8)	C(8T)–C(12T)	1.418 (9)
C(5)–C(2a)	1.449 (8)	C(3a)–C(4a)	1.397 (9)
N(1)–Cu–N(1a)	80.5 (2)	C(5)–C(2a)–C(3a)	125.7 (6)
N(1)–Cu–N(1T)	90.8 (2)	N(1a)–C(2a)–C(3a)	123.2 (5)
N(1)–Cu–N(1)′	180	C(3)–C(2b)–N(1b)	116.9 (5)
N(1)–Cu–N(1a)′	99.5 (2)	C(3)–C(2b)–C(3b)	119.9 (6)
N(1)–Cu–N(1T)′	89.2 (2)	N(1b)–C(2b)–C(3b)	123.1 (6)
N(1a)–Cu–N(1T)	91.1 (2)	C(1T)–C(2T)–C(3T)	121.0 (6)
N(1a)–Cu–N(1a)′	180	C(2a)–C(3a)–C(4a)	117.4 (6)
N(1a)–Cu–N(1T)′	88.9 (2)	C(2b)–C(3b)–C(4b)	118.6 (6)
N(1T)–Cu–N(1T)′	180	C(2T)–C(3T)–C(4T)	120.9 (5)
Cu–N(1)–N(2)	136.8 (4)	C(3a)–C(4a)–C(5a)	119.4 (6)
Cu–N(1)–C(5)	112.7 (4)	C(3b)–C(4b)–C(5b)	119.9 (6)
N(2)–N(1)–C(5)	109.4 (5)	C(3T)–C(4T)–C(5T)	118.8 (5)
N(1)–N(2)–C(3)	106.3 (5)	C(3T)–C(4T)–C(8T)	121.4 (5)
C(3)–N(4)–C(5)	106.1 (5)	C(5T)–C(4T)–C(8T)	119.9 (5)
C(3)–N(4)–N(6)	128.9 (5)	C(4a)–C(5a)–C(6a)	120.2 (6)
C(5)–N(4)–N(6)	125.0 (5)	C(4b)–C(5b)–C(6b)	118.2 (6)
Cu–N(1a)–C(2a)	114.8 (4)	C(4T)–C(5T)–C(6T)	120.3 (6)
Cu–N(1a)–C(6a)	126.6 (4)	N(1a)–C(6a)–C(5a)	121.3 (6)
C(2a)–N(1a)–C(6a)	118.6 (5)	N(1b)–C(6b)–C(5b)	123.4 (6)
C(2b)–N(1b)–C(6b)	116.7 (5)	C(1T)–C(6T)–C(5T)	121.3 (6)
Cu–N(1T)–C(9T)	140.5 (5)	C(9T)–C(7T)–C(1T)	121.6 (5)
N(2)–C(3)–N(4)	109.4 (5)	C(9T)–C(7T)–C(10T)	116.1 (5)
N(2)–C(3)–C(2b)	124.0 (5)	C(1T)–C(7T)–C(10T)	122.0 (5)
N(4)–C(3)–C(2b)	126.5 (5)	C(4T)–C(8T)–C(11T)	121.4 (5)
N(1)–C(5)–N(4)	108.8 (5)	C(4T)–C(8T)–C(12T)	122.0 (5)
N(1)–C(5)–C(2a)	119.9 (5)	C(11T)–C(8T)–C(12T)	116.2 (5)
N(4)–C(5)–C(2a)	131.3 (5)	N(1T)–C(9T)–C(7T)	177.5 (6)
C(7T)–C(1T)–C(2T)	120.0 (5)	C(7T)–C(10T)–N(2T)	179.5 (6)
C(7T)–C(1T)–C(6T)	122.3 (5)	C(8T)–C(11T)–N(3T)	175.9 (7)
C(2T)–C(1T)–C(6T)	117.7 (5)	C(8T)–C(12T)–N(4T)	178.4 (6)
C(5)–C(2a)–N(1a)	111.2 (5)		

Table IV. Diffuse Reflectance Ligand Field Maxima of $M(abpt)_2(TCNQ)_2$ ($\times 10^3$ cm^{-1})[a]

M	CT_1	CT_2	LE_1	LE_2
Cu	11.7	...	17.5	28.5
Co	12.9	...	17.5	27.8
Ni	12.8	...	17.5	28.5
Fe	12.4	...	17.5	28.5

[a] No d–d transitions could be detected, due to the high intensity of the CT bands.

As can be seen in Figure 3, the crystal lattice of $Cu(abpt)_2(TCNQ)_2$ is not formed by segregated stacks of Cu(abpt)$_2$ and TCNQ entities, in contrast to, for instance, $Cu_2(L)(TCNQ)_2$, the only other known structure of a Cu(II) compound with coordinating anionic TCNQ groups.[10] The copper atom, which is lying at a center of inversion, is in a square-planar coordination of four nitrogen atoms of the two abpt ligands. The Cu–N distances of 1.987 (5) and 2.046 (5) Å are unequal and similar to those found in other Cu(II) compounds with 3,(4),5-substituted 1,2,4-triazoles.[4] Two nitrogens N(1T) of two axially coordinating TCNQ molecules at a distance of 2.442 (5) Å complete the elongated octahedral geometry around the copper atom. This Cu–N(1T) distance should be compared to the Cu–N(2t) bond length of 2.378 (5) Å in $Cu_2(L)(TCNQ)_2$.[10] The angle Cu–N(1T)–C(9T) is 140.5 (5)°, which is remarkably small.

The TCNQ units are definitely nonplanar. The planes through the bonding and nonbonding dicyanomethylene groups make an

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(20) Tanner, D. B.; Jacobsen, C. S. *Mol. Cryst. Liq. Cryst.* **1982**, *85*, 137 and references therein.

(21) Inoue, M.; Inoue, M. B. *J. Chem. Soc., Faraday Trans.* **1985**, *81*, 539.

(22) Lunelli, B.; Pecile, C. *J. Chem. Phys.* **1970**, *52*, 2375.

(23) Inoue, M.; Inoue, M. B. *Inorg. Chem.* **1986**, *25*, 37.

(24) Iida, Y. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 673.

(25) Tanaka, J.; Tanaka, M.; Kawai, T.; Takabe, T.; Maki, O. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2358.

(26) Shirotani, I.; Sakai, N. *J. Solid State Chem.* **1976**, *18*, 17.

(27) Oohashi, Y.; Sakata, T. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3330.

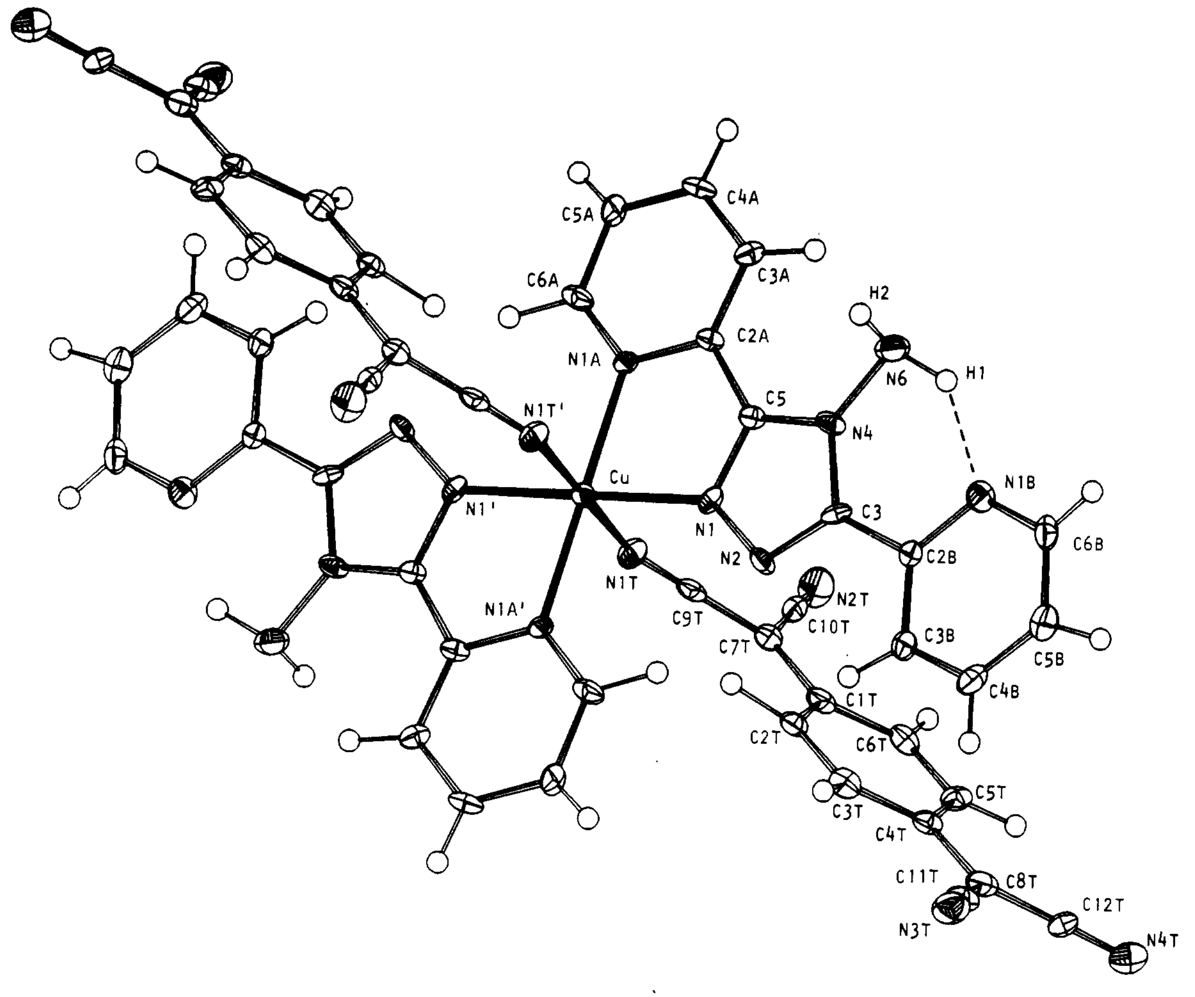

Figure 2. Thermal motion ellipsoid plot (50% probability level) of Cu(abpt)$_2$(TCNQ)$_2$ with the atomic labeling scheme.

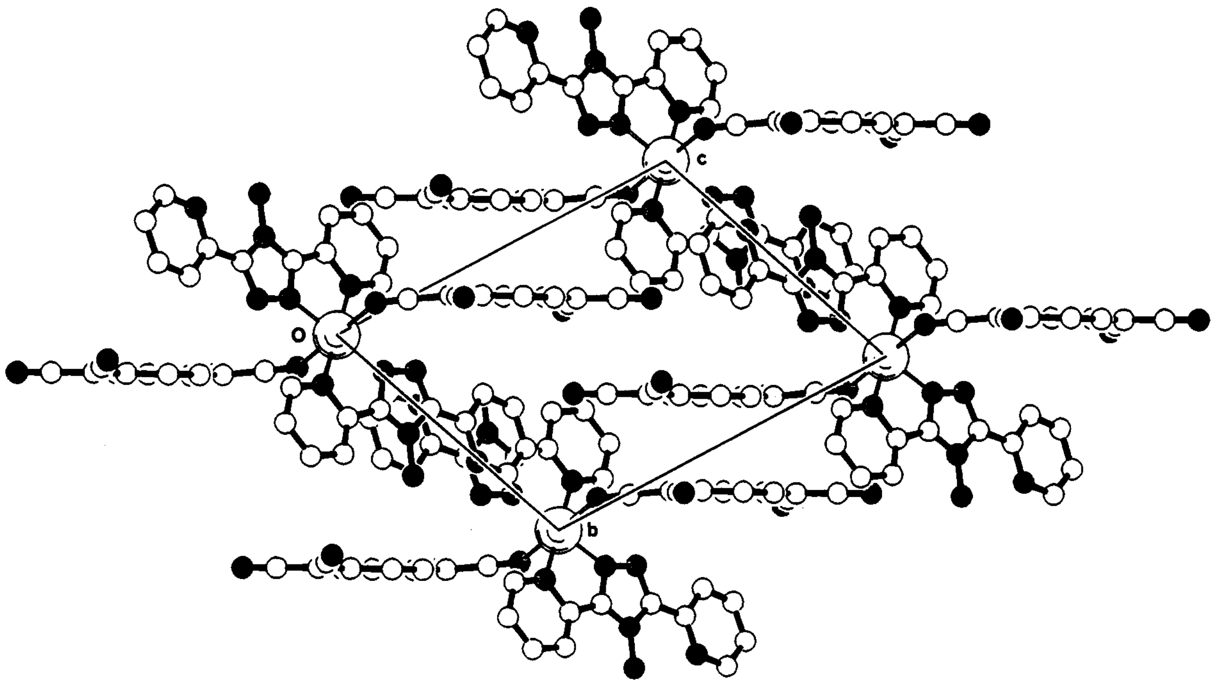

Figure 3. Crystal packing of Cu(abpt)$_2$(TCNQ)$_2$. Black spheres represent nitrogen atoms. Hydrogen atoms are omitted for clarity.

unusually large angle of respectively 8.10 (4)° and 9.40 (4)° with the quinoid ring. As pointed out by Flandrois and Chasseau,[28] an angle between the quinoid plane and the plane through the dicyanomethylene groups larger than 2° corresponds with a C=C bond between them longer than 1.410 Å. Table III proves this to be clearly the case. Three of four C(CN) groups are nonlinear, with C(8T)-C(11T)-N(3T) = 175.9 (7)° having the largest deviation from linearity (Table III). The C-N distances in the nitrile groups are quite different from those found in Cu$_2$(L)-

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[28] Flandrois, S.; Chasseau, D. *Acta Crystallogr., B* 1977, *B33*, 2744.

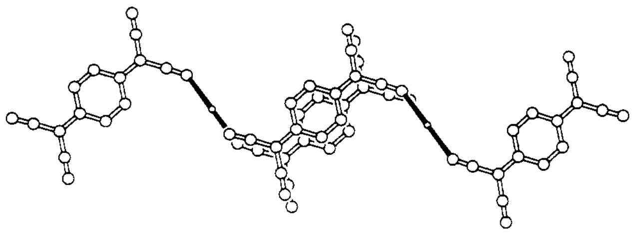

Figure 4. Eclipsed-dimer stacking mode of TCNQ units. The abpt ligands and the hydrogen atoms are omitted for clarity.

Table V. EPR and Electrical Data for M(abpt)$_2$(TCNQ)$_2$

M	EPR at 300 K	$\sigma_{300\,K}$, S cm^{-1}
Cu	$g_\perp = 2.06$ $g_\parallel = 2.20$ $A_\parallel = 175$ G	7×10^{-7}
Co	...	3×10^{-10}
Ni	...	4×10^{-10}
Fe	...	5×10^{-10}

(TCNQ)$_2$; the origin for that is as yet unclear.

Figure 3 illustrates the molecular packing in Cu(abpt)$_2$(TCNQ)$_2$. Since the TCNQ units are centrosymmetrically related, their mean planes are all parallel. The TCNQ groups of neighboring Cu(abpt)$_2$(TCNQ)$_2$ units along the *c* direction, related through an inversion center (0, 0, $^1/_2$), form dimers in the usually found eclipsed mode[10] (Figure 4). The distance between the mean planes through the anions which make up the lattice dimers is 3.22 Å.

Both amine H atoms are hydrogen bonded to N atoms; one binds intramolecular to a N(16) atom of the corresponding abpt ligand (N(6)–H(1)···H(16)) [N–H = 1.02 (6) Å; H···N = 1.96 (5) Å; N···N = 2.834 (7) Å; N-H···N = 142 (5)°] and the second hydrogen bridges to a nitrogen belonging to a TCNQ of a neighboring Cu(abpt)$_2$(TCNQ)$_2$ molecule (N(6)–H(2)···N(4T) $(x, y, z - 1)$) [N–H = 0.87 (6) Å, H···N = 2.44 (6) Å; N···N = 3.203 (8) Å; N–H···N = 146 (5)°], resulting in infinite hydrogen-bonded chains running in the *c* direction.

Conductivity and Magnetic Results. The powder conductivity of the M(abpt)$_2$(TCNQ)$_2$ compounds was measured on a pressed pellet, using the direct measuring technique. Their room-temperature conductivities are listed in Table V. In accordance to their structure, they all behave virtually as insulators. The EPR signal of Cu(abpt)$_2$(TCNQ)$_2$ exhibits the usual values for $g_\perp$, $g_\parallel$, and $A_\parallel$ normally found for a copper(II) atom in an elongated octahedral N6 chromophore. No radical signal could be found, neither at room temperature or at 77 K, indicating that the TCNQ ions must be diamagnetic in the measured temperature range. This is possible given the short intradimer TCNQ–TCNQ distance. Field-dependent magnetic susceptibility measurements down to 5 K show an interesting behavior, which will be described in a separate paper.

Concluding Remarks

The structure of Cu(abpt)$_2$(TCNQ)$_2$ presents one of the rare examples in which the TCNQ units are monodentately coordinating to the copper(II) centers. A similar case of TCNQ coordinating to Cu(II) atoms was found for Cu$_2$L(TCNQ)$_2$.[10] However, generally this feature is more common for conducting compounds containing TCNQ-like ligands, which possess the general formula M(2,5-Me$_2$DCNQI)$_2$ (where M = Cu or Ag and 2,5-Me$_2$DCNQI = 2,5-dimethyl-*N*,*N*′-dicyanobenzoquinone diimine), but in these cases the metal atoms are not in a 2+ oxidation state.[29,30] Another example of direct metal–TCNQ coordination has been found in the crystal structure of [Cu(pdto)(TCNQ)]$_2$ (with pdto = pyridyl thioether) but again, in this compound the copper ions are Cu(I) rather than Cu(II).[31]

The fact that the Fe, Co, and Ni analogues are isostructural to the copper compound is also quite rare; apparently the expected shorter M–N (axial) bonds for these metals do not change the overall structure.

From its structural and spectral as well as its EPR data, it is clear that the Cu(abpt)$_2^{2+}$ units are not reduced to Cu(abpt)$_2^{+}$ by the TCNQ anions. Since the redox potential of the TCNQ/TCNQ$^-$ system is 0.37 V (vs NHE), and Cu(abpt)$_2^{2+}$ is reduced to Cu(abpt)$_2^{+}$ at 0.44 V, the TCNQ$^-$ ion is theoretically not able to do so.

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Registry No. Fe(abpt)$_2$(TCNQ)$_2$, 137122-14-6; Co(abpt)$_2$(TCNQ)$_2$, 137122-15-7; Ni(abpt)$_2$(TCNQ)$_2$, 137122-16-8; Cu(abpt)$_2$(TCNQ)$_2$, 137122-17-9; Ni(abpt)$_2$(NO$_3$)$_2$, 137122-18-0; Co(abpt)$_2$(NO$_3$)$_2$, 137122-19-1; Cu(abpt)$_2$(NO$_3$)$_2$, 137122-20-4; Fe(abpt)$_2$(PF$_6$)$_2$, 137122-22-6.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen atom positions and isotropic thermal parameters, and complete bond distances and bond angles (3 pages); a listing of the F_o and F_c values (20 pages). Ordering information is given on any current masthead page.

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(29) Aumüller, A.; Erk, P.; Klebe, G.; Hünig, S.; von Schütz, J. U.; Werner, H.-P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 740.

(30) Kato, R.; Kobayashi, H.; Kobayashi, A.; Mori, T.; Inokuchi, H. *Chem. Lett.* **1987**, 1579.

(31) Humphrey, D. G.; Fallon, G. D.; Murray, K. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1356.