diamagnetism. Orbital switching from $d_{x^2-y^2}$ to d_{z^2} magnetic orbitals explains the lower magnitude of magnetic coupling in related complexes. However, a comparison of acetate and nitrite complexes, which differ magnetically much more than might be expected on the basis of their isostructural d_{z^2} interactions, reveals a more subtle effect of orbital symmetry complementarity in the HOMOs of bridging ligands. This concept of orbital of complementarity and noncomplementarity should prove to be a general consideration in multibridged magnetically interacting systems and a particular consideration in unsymmetrical dibridged copper(II) dimers where magnetic coupling phenomena are not so well understood.[22,23,41] We note that in the proposed structure for oxyhemocyanin the RO$^-$ and O_2^{2-} bridging ligands do indeed have complementary orbital symmetries. They are the 2p orbital on oxygen and the π_g^* of O_2^{2-}. Their complementary antibonding overlap with the antisymmetric combination of $d_{x^2-y^2}$ orbitals is illustrated in Figure 6e. The diamagnetism of oxyhemocyanin is no longer surprising when viewed in this light.

These magnetic arguments as well as structural ones based on the dimensions of the bridging ligands continue to support the present structural model[39,16] for oxyhemocyanin and the credibility of $[Cu_2(L\text{-}Et)(N_3)]^{2+}$ as a model for methemocyanin.

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Registry No. $[Cu_2(L\text{-}Et)(NO_2)](ClO_4)_2$, 97316-49-9.

Supplementary Material Available: Tables of bond lengths and angles (Tables III and IV), anisotropic temperature factors (Table V), hydrogen coordinates (Table VI), and observed and calculated structure factors (Table VII) and a unit cell packing diagram (Figure 2) (22 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Gorlaeus Laboratories,
State University Leiden, 2300 RA Leiden, The Netherlands

Transition-Metal Coordination Compounds of a Tripodal Tetradentate Pyrazole Derivative. X-ray Structure of the Dimer [Aqua(tris((3,5-dimethylpyrazol-1-yl)methyl)amine)cobalt(II)][fluoro(tris((3,5-dimethylpyrazol-1-yl)methyl)amine)cobalt(II)] Tris(tetrafluoroborate)–1.5-Ethanol

GERTJAN J. VAN DRIEL, WILLEM L. DRIESSEN,* and JAN REEDIJK

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The synthesis and characterization of transition-metal coordination compounds containing the newly synthesized ligand tris((3,5-dimethylpyrazol-1-yl)methyl)amine (abbreviated amtd) are described. The tetrafluoroborate compounds, which are all dimers, have the general formula $M_2(amtd)_2F(BF_4)_3(EtOH)_x(H_2O)_y$ (M = Co, Cu, Zn; x = 0–1.5; y = 1–2), $Ni_2(amtd)_3(BF_4)_4(H_2O)_2$, and $Ni_2(amtd)_2F_2(BF_4)_2(EtOH)_{0.5}$. The fluorides are formed upon tetrafluorobrate decomposition. The nitrate compounds have the general formula $M(amtd)(NO_3)_2$ (M = Co, Ni, Cu, Zn). The chloride and thiocyanate compounds have the general formula $[M(amtd)X]_2(MX_4)(EtOH)_x(H_2O)_y$ (M = Co, Cu, Zn; X = Cl, NCS; x = 0.5–1; y = 0–1.5) and $Ni(amtd)X_2(H_2O)_x$ (X = Cl, NCS; x = 0–1.5). In all compounds amtd acts as a chelating tripodal tetradentate ligand. In the cases of Co, Cu, and Zn also one counterion (F, monodentate NO_3, Cl, or NCS) is coordinated to the metal ion, resulting in five-coordination. Octahedrally based six-coordination is found in all Ni(II) cases, with two counterions (F, Cl, or NCS) or one bidentate nitrate ion bound to the nickel ion. Six nitrogen atoms donated by two ligands in the case of $Ni_2(amtd)_3(BF_4)_4(H_2O)_2$ yield a distorted-octahedral geometry. The ligand field spectra of the nickel compounds are typical for six-coordination. In the case of five-coordination (M = Co, Cu, Zn; anion = BF_4, NO_3, Cl, NCS) the coordination geometry is distorted trigonal bipyramidal. This is deduced from the X-ray structure determination of the cobalt tetrafluorobrate compound, the ligand field spectra of Co(II), the EPR spectrum of a cobalt-doped zinc tetrafluorobrate compound, the EPR spectra of Cu(II), and isomorphism within the group of compounds with the same anion. A crystal of $[Co_2(amtd)_2F(H_2O)(EtOH)](BF_4)_3(EtOH)_{0.5}$ was used in a structure determination: monoclinic, space group $P2_1/n$, a = 29.312 (9) Å, b = 11.822 (7) Å, c = 14.244 (7) Å, β = 103.41 (3)°, Z = 4, and T = −162 °C. The structure was solved by heavy-atom techniques and refined by least-squares methods to a residual R value of 0.055 (R_w = 0.078). The coordination geometry of both cobalt atoms in this dimer is five-coordinated distorted trigonal bipyramidal. A fluoride ion and a water molecule are coordinated respectively to the cobalt ions (Co–F = 1.902 (5) Å, Co–O = 2.032 (6) Å). The Co–Co distance is 6.254 (2) Å. The amtd ligands are coordinated identically to both cobalt ions. The two cobalt to amine nitrogen distances are 2.30 Å, and the six cobalt to pyrazole nitrogen distances are about 2.03 Å. The bridge in this dimer is built up from the coordinated fluoride ion, an ethanol molecule, and the coordinated water molecule, which are linked to one another by hydrogen bonds.

Introduction

The increasing interest in chelating polydentate nitrogen-donor ligands, especially heterocyclic compounds, is based on the occurrence of such systems in nature.[1] Most attention is given to model systems containing imidazoles, benzimidazoles, and pyridines.[2-4] Attention is also paid to pyrazole derivatives,[5,6] because of the similarity of pyrazoles and imidazoles. A large variety of pyrazole derivatives can now be prepared through a novel method for the synthesis of N-substituted pyrazole chelates.[7-9] The

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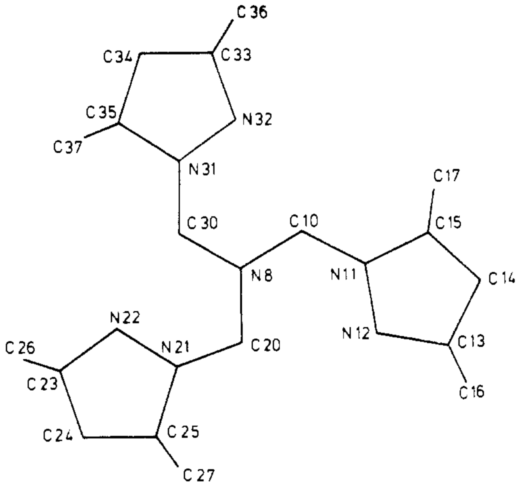

Figure 1. Atomic numbering of the ligand tris((3,5-dimethylpyrazol-1-yl)methyl)amine (abbreviated amtd), adopted for the description of the structure of $[Co_2(amtd)_2F(H_2O)(EtOH)](BF_4)_3(EtOH)_{0.5}$. The second ligand has an analogous numbering.

pyrazole derivative of ammonia, tris((3,5-dimethylpyrazol-1-yl)methyl)amine (abbreviated amtd, see Figure 1), is tripodal in shape and a potential tetradentate ligand. This ligand was selected for a detailed study of its coordination properties. The 3,5-dimethylpyrazole substituent is a strong base and acts as a bulky group. As shown recently, this may result in unusual compounds. For instance, coordination compounds containing fluorides are formed through the decomposition of the BF_4^- anion in the presence of metal ions and substituted pyrazoles.[10,11]

It appears that amtd indeed acts as a tetradentate ligand to a variety of metal ions. To investigate the binding in detail and to prove the chelating nature of amtd, a crystal structure determination of one of the coordination compounds was performed.

A few compounds with this ligand have been described recently by Mani et al.,[6] as model compounds for cobalt-substituted carbonic anhydrase.

Experimental Section

Starting Materials. The synthesis of the ligand tris((3,5-dimethylpyrazol-1-yl)methyl)amine was performed by a modification of the method reported by Driessen.[7] Equivalent amounts of *N*-(hydroxymethyl)-3,5-dimethylpyrazole (0.45 mol) and of ammonium acetate (0.15 mol) were stirred for 24 h at room temperature in 100 mL of acetonitrile. The organic solvent was removed with use of a vacuum rotary evaporator, rendering a colorless oil, which, after treating with 20 mL of water and cooling to 4 °C, yielded a white crystalline product. The compound was characterized by infrared and NMR spectra. The ^1H NMR spectrum (solvent MeOH-d_4, internal reference $SiMe_4$) showed the following signals: singlets at 1.77 ppm (9 H) and at 2.15 ppm (9 H), representing the pyrazole methyl groups, and singlets at 4.92 ppm (6 H) and 5.78 ppm (3 H), representing respectively the methylene bridges and the pyrazole hydrogens.

This method gives much higher yields than that reported by Mani.[6]

Except for the metal thiocyanates, all other chemicals were commercially available, were of sufficient purity, and were used without further treatment.

Syntheses. The coordination compounds were prepared by dissolving the appropriate hydrated metal salt (5 mmol) in 25 mL of absolute ethanol and adding this solution to a solution of the ligand amtd (5, 7.5, or 10 mmol of amtd, depending on the metal:ligand ratio) in 25 mL of absolute ethanol. The crystal used for the X-ray structural determination was grown from a warm solution (ca. 60 °C). For the preparation of the coordination compounds with the thiocyanate anion, with the exception of $Co(NCS)_2$, which was commercially available, a different procedure was followed: $Cu(SCN)_2$ was synthesized as published[12] from 5 mmol of $Cu(NO_3)_2$ and 10 mmol of NH_4SCN. The resulting black powder was added to a solution of 5 mmol of the ligand in 50 mL of methanol. The zinc and nickel thiocyanate compounds with amtd were prepared by adding a solution of 2.5 mmol of the metal nitrate and 5 mmol of ammonium thiocyanate in 25 mL of ethanol to a solution of 2.5 mmol of the ligand in 12.5 mL of ethanol. When the mixture was allowed to stand at room temperature, in some cases only after evaporation of part of the solvent on a rotary evaporator, solid compounds formed, which were collected by filtration.

Analyses. Metal analyses were carried out complexometrically with EDTA as the complexing agent.[15] C, H, N, F, B, O, and S analyses were performed either by Dr. F. Pascher, Bonn, FRG, or by the Canadian Microanalytical Service Ltd., Vancouver, Canada.

Spectroscopic Measurements. Infrared spectra in the 4000–300-cm^{-1} range of the samples mulled in Nujol between KRS-5 disks or pelleted in KBr, and far-infrared spectra in the 400–200-cm^{-1} range of the samples mulled in Nujol between polyethylene disks with a polyethylene pellet as reference, were recorded on a Perkin-Elmer spectrophotometer, equipped with a PE data station. Solid-state electronic spectra (28 000–5000 cm^{-1}) were recorded on a Beckman DK-2A spectrophotometer fitted with a reflectance attachment, with MgO as a reference, and on a Perkin-Elmer 330 spectrophotometer, equipped with a PE data station.

Electron spin resonance spectra of the powdered copper compounds were obtained with Varian spectrometers at X-band and A-band frequencies at room temperature and at 77 K (liquid nitrogen). EPR spectra of frozen solutions of the copper compounds in $MeOH/Me_2SO$ were taken at 77 K. EPR spectra of the cobalt compounds and the cobalt-doped zinc compounds were taken at X-band frequencies at 15 K (liquid-helium cooling).

The conductivity of 10^{-3} M solutions in nitromethane ($\kappa = 5.4 \times 10^{-6}$ cm^{-1} Ω^{-1}) was measured at 20 °C on a Seybold type LTB conductometer (cell constant 1.09). Proton nuclear magnetic resonance spectra were recorded on a JEOL PS-100 instrument employing a frequency of 99.5 MHz, with Me_4Si as internal standard. X-ray powder diagrams of the compounds were obtained with a Guinier type camera using Cu Kα radiation. The samples were protected from atmospheric vapor by adhesive tape.

Magnetic susceptibility measurements down to 3 K were carried out on solid polycrystalline samples, with a parallel field vibrating-sample magnetometer (PAR Model 150A).

Crystal Data: $Co_2C_{39}H_{65}N_{14}B_3F_{13}O_{2.5}$, M_r = 1167.31, monoclinic, a = 29.312 (9) Å, b = 11.822 (7) Å, c = 14.224 (7) Å, β = 103.41 (3)°, V = 5199.9 Å^3 by least-squares refinement on diffractometer angles for 24 reflections, λ(Mo Kα) = 0.71073 Å, T = 111 K, space group $P2_1/n$ (alternate setting of $P2_1/c$[14]), Z = 4, D_{exptl} = 1.48 g cm^{-3}, purple, baculiform crystal with dimensions 0.55 × 0.30 × 0.17 mm, μ(Mo Kα) = 7.25 cm^{-1}, $F(000)$ = 2415.

Data Collection and Processing. The data collection was carried out on a four-circle Enraf-Nonius CAD4 diffractometer, with a liquid-nitrogen cooling device at −162 °C. Initial measurements at ambient temperatures indicated that cooling was needed to increase the number of significant reflections. The equipment operated in the ω/θ mode, and graphite-monochromatized Mo Kα radiation was used; 5700 reflections were measured ($2.0° < \theta < 21.0°$ $0 < h < 29$, $0 < k < 12$, $-14 < l < 14$), of which 5564 were unique (merging R = 0.080, based on 91 reflections, no absorption correction was applied, because the effect was only 2% in I_{obsd}), giving 3627 reflections with $I > 2\sigma(I)$. Intensities were corrected for Lorentz and polarization effects.

The scanning rate was adjusted to the required precision of $\sigma(I)/I$ = 0.01, with a maximum scan time of 120 s/reflection. The instrument and crystal stability were checked every 5400 s of radiation time by measuring three reference reflections: no significant changes in the intensities were observed.

Structure Analysis and Refinement. The structure was solved by direct methods (yielding first the Co atoms), followed by normal heavy-atom procedures and refined by full-matrix least-squares calculations. The refinement was considered to be complete when the changes in the parameters were smaller than one-third of the standard deviation. Scattering factors were taken from ref 14. The three BF_4^- anions are partly disordered. The nonbridging ethanol is oriented with the center of the C–C bond on a twofold axis. Hydrogen atoms were located from difference-Fourier maps, except H(673), which was calculated. The hydrogen to parent-atom distances were constrained to 0.95 Å. The thermal parameters of the hydrogen atoms were kept fixed (6.6 Å^2), and those of the non-hydrogen atoms were refined anisotropically. The function

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Table I. Fractional Coordinates (Co(1) and Co(2), $\times 10^5$; Others, $\times 10^4$) of the Non-Hydrogen Atoms in $Co_2(amtd)_2F(BF_4)_3(EtOH)_{1.5}(H_2O)$

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
Co(1)	66763 (4)	21575 (9)	6205 (8)	C(43)	7377 (3)	−998 (7)	411 (6)
Co(2)	84311 (4)	−5373 (10)	4327 (8)	C(44)	7015 (3)	−1594 (7)	−164 (7)
F(3)	8419 (2)	287 (4)	1538 (3)	C(45)	7177 (3)	−1911 (7)	−949 (7)
O(4)	7316 (2)	2807 (5)	1153 (4)	C(46)	7385 (3)	−466 (8)	1355 (7)
O(5)	8100 (2)	1975 (5)	2036 (4)	C(47)	6941 (4)	−2547 (8)	−1799 (7)
C(6)	8417 (4)	2500 (9)	2812 (8)	C(50)	8746 (3)	−1140 (8)	−1400 (7)
C(7)	8901 (4)	2061 (8)	3068 (7)	N(51)	8742 (3)	−18 (6)	−1314 (5)
N(8)	5957 (2)	1454 (6)	−4 (5)	N(52)	8700 (3)	412 (6)	−452 (5)
C(10)	5693 (3)	2238 (7)	−666 (6)	C(53)	8830 (3)	1397 (8)	−473 (7)
N(11)	5825 (2)	3263 (6)	−281 (5)	C(54)	8963 (3)	1603 (8)	−1357 (7)
N(12)	6279 (3)	3436 (6)	204 (5)	C(55)	8904 (3)	695 (8)	−1855 (6)
C(13)	6305 (3)	4479 (7)	363 (6)	C(56)	8821 (4)	2154 (8)	319 (7)
C(14)	5873 (3)	4932 (8)	−12 (6)	C(57)	9006 (4)	434 (9)	−2820 (7)
C(15)	5575 (3))	4155 (8)	−438 (6)	C(60)	8536 (4)	−2628 (7)	−540 (7)
C(16)	6743 (4)	4978 (7)	894 (7)	N(61)	8887 (3)	−2551 (6)	350 (5)
C(17)	5080 (3)	4195 (8)	−989 (6)	N(62)	8860 (3)	−1722 (6)	955 (5)
C(20)	5746 (3)	1215 (7)	806 (6)	C(63)	9214 (4)	−1885 (8)	1736 (7)
N(21)	6120 (3)	903 (5)	1614 (5)	C(64)	9450 (4)	−2799 (8)	1636 (7)
N(22)	6530 (2)	1473 (5)	1813 (5)	C(65)	9239 (3)	−3206 (7)	743 (7)
C(23)	6762 (3)	1183 (7)	2690 (6)	C(66)	9297 (4)	−1112 (8)	2538 (7)
C(24)	6499 (3)	442 (7)	3061 (6)	C(67)	9321 (4)	−4219 (8)	260 (7)
C(25)	6086 (3)	297 (7)	2364 (6)	B(70)	437 (4)	6909 (9)	4296 (8)
C(26)	7220 (3)	1613 (8)	3174 (6)	F(71)	183 (2)	7811 (4)	4256 (4)
C(27)	5670 (4)	−370 (8)	2356 (7)	F(72)	270 (2)	6313 (4)	3471 (4)
C(30)	6034 (3)	492 (7)	−508 (6)	F(73)	907 (2)	7133 (5)	4410 (4)
N(31)	6417 (3)	711 (6)	−991 (5)	F(74)	375 (2)	6321 (5)	5095 (4)
N(32)	6799 (2)	1249 (6)	−480 (5)	B(80)	2351 (5)	5334 (11)	792 (10)
C(33)	7112 (3)	1210 (7)	−1038 (6)	F(81)	2059 (3)	5831 (6)	1287 (6)
C(34)	6932 (3)	631 (7)	−1860 (6)	F(82)	2297 (2)	4302 (5)	718 (5)
C(35)	6489 (3)	314 (7)	−1818 (6)	F(83)	2293 (2)	5779 (4)	−114 (4)
C(36)	7583 (3)	1707 (8)	−737 (7)	F(84)	2802 (3)	5565 (7)	1322 (5)
C(37)	6132 (3)	−357 (8)	−2478 (6)	B(90)	245 (6)	2929 (13)	1720 (10)
N(9)	8409 (3)	−1585 (6)	−909 (5)	F(91)	−13 (3)	2575 (8)	2304 (5)
C(40)	7927 (3)	−1520 (8)	−1494 (6)	F(92)	121 (3)	2512 (6)	803 (4)
N(41)	7614 (3)	−1528 (6)	−822 (5)	F(93)	118 (3)	4023 (7)	1569 (7)
N(42)	7742 (3)	−952 (6)	4 (5)	F(94)	719 (2)	2959 (5)	2035 (4)
				C(96)	70 (4)	194 (11)	9576 (9)
				O(97)	−110 (6)	−372 (12)	8790 (11)

[a] Estimated standard deviations in the least significant digits are given in parentheses.

minimized was $\sum w(||F_o| - |F_c||)^2$ with $w = 1/\sigma^2(F)$. At the final stage the conventional discrepancy index $R_F = \sum(||F_o| - |F_c||)/\sum|F_o|$ had been reduced to 0.055 and the weighted factor $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ to 0.078. The fractional coordinates of the non-hydrogen atoms are listed in Table I. Selected bond distances and bond angles of the non-hydrogen atoms are given in Table II. Lists of the atomic coordinates of the hydrogen atoms, of the non-hydrogen anisotropic thermal parameters, of the bond distances and bond angles, and of the observed and calculated structure factors are available as supplementary material.[15]

Results and Discussion

General Considerations. X-ray types, infrared types, melting points, conductance data, and proposed chromophores of the transition-metal compounds with amtd are listed in Table III. The analytical data, which are available as supplementary material,[15] already gave information about the possible structures of the compounds. From their infrared spectra and their X-ray powder photographs it is obvious that the compounds described in this work show a large structural variety. Isomorphism is only found for the cobalt and zinc tetrafluoroborate compounds, for the cobalt, copper, and zinc nitrate compounds, and for the cobalt and zinc thiocyanate compounds (see Table III). In all cases the nickel ion has a deviating geometry. The nickel ion apparently tends to obtain a six-coordinate surrounding, while for the other metal ions, obviously, a five-coordinate surrounding seems appropriate.

In Tables IV–VI are listed ligand field absorption bands, EPR results, infrared spectral data of the metal amtd nitrate compounds, and ligand field parameters of the nickel amtd compounds. Assignment of some of the metal-nitrogen stretching vibrations (see below) is based on earlier work.[16] The details of the spectral data will be discussed after the description of the crystal structure.

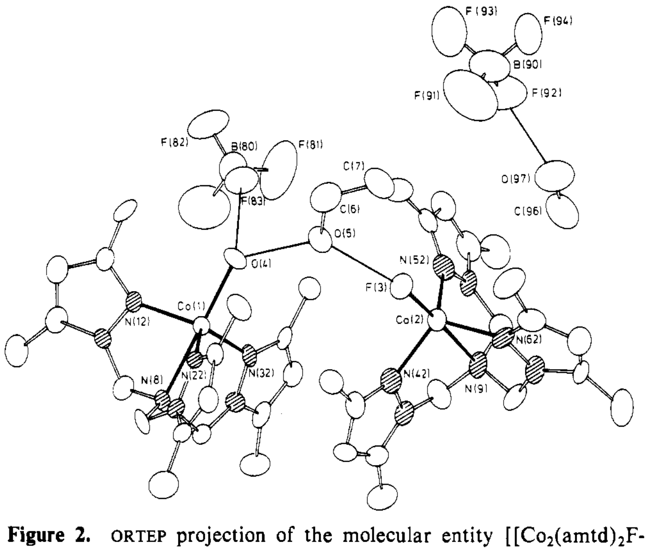

Figure 2. ORTEP projection of the molecular entity $[[Co_2(amtd)_2F(H_2O)(EtOH)](BF_4)_2(EtOH)_{0.5}]^{2+}$. The hydrogen atoms are omitted.

Description of the Structure of $[Co_2(amtd)_2F(H_2O)(EtOH)](BF_4)_3(EtOH)_{0.5}$. The structure of the cationic species is dimeric. The two cobalt ions have different surroundings (see Figure 2). Co(1) is surrounded by four nitrogens and one oxygen, and Co(2) is surrounded by four nitrogens and one fluoride. Definite proof for the identity of the fluoride ion bound to Co(2) and for the identity of the oxygen atom bound to Co(1) was obtained from the refinement results. Moreover, hydrogen atoms were located near the oxygen atom, while no significant electron density was found near the fluoride ion at hydrogen atom bonding distances. In both cases the coordination geometry can be described as

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Table II. Selected Bond Lengths (Å) and Bond Angles (deg) of $Co_2(amtd)_2F(BF_4)_3(EtOH)_{1.5}(H_2O)$

Co(1)–O(4)	2.031 (6)	Co(2)–F(3)	1.902 (5)
Co(1)–N(8)	2.276 (7)	Co(2)–N(9)	2.322 (7)
Co(1)–N(12)	2.019 (7)	Co(2)–N(42)	2.041 (8)
Co(1)–N(22)	2.043 (7)	Co(2)–N(52)	2.037 (8)
Co(1)–N(32)	2.049 (7)	Co(2)–N(62)	2.002 (8)
N(8)–C(10)	1.469 (11)	N(9)–C(40)	1.467 (11)
N(8)–C(20)	1.461 (11)	N(9)–C(50)	1.451 (12)
N(8)–C(30)	1.470 (11)	N(9)–C(60)	1.454 (12)
C(10)–N(11)	1.441 (12)	C(40)–N(41)	1.471 (12)
C(20)–N(21)	1.447 (11)	C(50)–N(51)	1.444 (12)
C(30)–N(31)	1.472 (11)	C(60)–N(61)	1.438 (12)
O(5)–C(6)	1.435 (12)	C(96)–O(97)	1.335 (19)
C(6)–C(7)	1.491 (15)		

O(4)–Co(1)–N(8)	178.7 (2)	F(3)–Co(2)–N(9)	177.0 (3)
O(4)–Co(1)–N(12)	101.3 (3)	F(3)–Co(2)–N(42)	100.6 (3)
O(4)–Co(1)–N(22)	102.7 (3)	F(3)–Co(2)–N(52)	105.3 (3)
O(4)–Co(1)–N(32)	101.9 (3)	F(3)–Co(2)–N(62)	104.2 (3)
N(8)–Co(1)–N(12)	77.8 (3))	N(9)–Co(2)–N(42)	76.5 (3)
N(8)–Co(1)–N(22)	78.5 (3)	N(9)–Co(2)–N(52)	77.2 (3)
N(8)–Co(1)–N(32)	77.7 (3)	N(9)–Co(2)–N(62)	76.2 (3)
N(12)–Co(1)–N(22)	112.0 (3)	N(42)–Co(2)–N(52)	118.0 (3)
N(12)–Co(1)–N(32)	115.4 (3)	N(42)–Co(2)–N(62)	114.0 (3)
N(22)–Co(1)–N(32)	119.9 (3))	N(52)–Co(2)–N(62)	112.5 (3)
Co(1)–N(8)–C(10)	106.4 (5)	Co(2)–N(9)–C(40)	105.8 (5)
Co(1)–N(8)–C(20)	107.3 (5)	Co(2)–N(9)–C(50)	106.0 (6)
Co(1)–N(8)–C(30)	106.9 (5)	Co(2)–N(9)–C(60)	106.3 (5)
Co(1)–N(12)–N(11)	116.4 (6)	Co(2)–N(42)–N(41)	117.0 (6)
Co(1)N(12)–C(13)	138.2 (6)	Co(2)–N(42)–C(43)	136.2 (6)
Co(1)–N(22)–N(21)	113.5 (5)	Co(2)–N(52)–N(51)	116.0 (6)
Co(1)–N(22)–C(23)	137.7 (6)	Co(2)–N(52)–C(53)	137.7 (7)
Co(1)–N(32)–N(31)	115.1 (5)	Co(2)–N(62)–N(61)	118.3 (5)
Co(1)–N(32)–C(33)	137.4 (6)	Co(2)–N(62)–C(63)	136.1 (7)
O(5)–C(6)–C(7)	114.9 (9)		

distorted trigonal bipyramidal. Analogous coordination geometries have been encountered for cobalt compounds with related ligands.[3a,6,17] The coordination of Co(1) appears to be almost identical with that found in the very recently published X-ray structure[6c] of $[Co(amtd)(H_2O)](ClO_4)_2$. The ligand amtd utilizes all its N-donor sites for coordination, thereby acting as a tripodal tetradentate ligand. The cobalt–nitrogen distances (see Table II) can be regarded as normal for this class of compounds.[5,8,9,18] The cobalt to amine nitrogen distance is somewhat larger than the cobalt pyrazole nitrogen distances. The corresponding coordination angles around Co(1) and Co(2) are very similar: the angles between the amine nitrogen, the cobalt atom, and the respective pyrazole nitrogens vary from 75 to 80° (see Table II), thus deviating significantly from the ideal coordination angle of 90°. This too small coordination angle is due to the limited dimensions of the ligand. Opening up the bite of the ligand thereby enlarging the three five-membered rings formed by the ligand and the central cobalt ion would impose a severe strain on the ligand. Coordination angles that are smaller than ideal have also been encountered with coordination compounds of other *N*-methylpyrazole-substituted amines[8,9] and for tripodal benzimidazole chelates.[3c] The tertiary amine nitrogen to cobalt to fluoride/oxygen angle is close to 180° (see Table II). The actual symmetry of both cobalt environments is C_{3v}.

The bridge from Co(1) to Co(2), which makes this compound a dimer, is an unusual one. Going from Co(1) to Co(2) consecutively a molecule of water, a molecule of ethanol, and a fluoride ion are encountered, which are linked to one another by hydrogen bonds. The link between the molecule of water and the molecule of ethanol is made by a hydrogen bridge (H(042)) from O(4) to O(5), with distances O(4)–O(5) = 2.581 (8) Å, O(4)–H(042) = 0.841 (6) Å, and H(042)–O(5) = 1.798 (6) Å. The second hydrogen atom of the water molecule bridges to one of the tetrafluoroborates. The bridge between the cobalt atoms is closed by a hydrogen bridge from the hydrogen of ethanol (H(05)) to the fluoride anion, with distances O(5)–F(3) = 2.523 (8) Å, O(5)–H(05) = 1.140 (6) Å, and H(05)–F(3) = 1.398 (5) Å (see Figure 2). The distance between Co(1) and Co(2) is 6.254 (2) Å. The amtd molecule coordinated to Co(1), amtd (1), is not independently oriented from the molecule coordinated to Co(2), amtd(2). One of the pyrazole rings of amtd(1) is parallel to one of the pyrazole rings of amtd(2) (the angle between the planes of these two rings is very small, viz. 1.6 (4)°). The distance between the centers of gravity of both rings is 3.49 Å, indicating that stacking occurs between these rings. All pyrazole rings are planar (distances to the least-squares planes are less than 0.02 Å). The cobalt ions lie in the plane of each pyrazole ring. Furthermore, the structure contains three BF_4^- groups and half a molecule of ethanol. This ethanol molecule has a site occupancy of 0.5, with the center of the C–C bond on a twofold axis. This ethanol molecule is hydrogen bridged (H(97)) to a fluoride (F(92)) of one of the tetrafluoroborate anions, with distances O(97)–F(92) = 2.81 (2) Å, O(97)–H(97) = 1.29 (2) Å, and H(97)–F(92) = 1.654 (8) Å. The molecule of water, bound to Co(1) and part of the Co(1) to Co(2) bridge, is also hydrogen bonded to a fluoride (F(83)) of another tetrafluoroborate anion, with distances O(4)–F(83) = 2.751 (8) Å, O(4)–H(041) = 1.000 (6) Å, and H(041)–F(83) = 1.852 (5) Å. The third tetrafluoroborate anion, containing B(70), is disordered. The two tetrafluoroborate anions that are hydrogen bridged show some disorder in the fluoride atoms that are not hydrogen bonded. The hydrogen bridge apparently imposes some ordering stabilization. The additional packing of the coordination units in the crystal lattice proceeds via normal van der Waals contacts.

Compounds with an extended water to ethanol to fluoride bridge have not been reported earlier, to the best of our knowledge. Reported coordination compounds containing fluoride ions, mostly obtained after tetrafluorobrate decomposition, are monomers, containing one or two fluoride ions, dimers or chains, with MF_2M bridging units, or cubane type M_4F_4 tetramers.[19,20]

The Tetrafluoroborate Compounds. The stoichiometry of the cobalt compound was established from elemental analyses[15] and confirmed by the X-ray structure determination. A conductivity value of 276 Ω^{-1} mol^{-1} cm^2 (see Table III) agrees with a 2:3 electrolyte for this compound,[21] which means that the dimer decomposes into two cationic species in nitromethane. The ligand field spectrum is typical for high-spin five-coordinate Co(II) in a distorted-trigonal-bipyramidal environment[22] and is thus consistent with the X-ray structure description given above. The ligand field maxima are very similar to those found[6c] recently for $[Co(amtd)(H_2O)](ClO_4)_2$. In the far-infrared spectrum absorptions observed at 440 and at 354 cm^{-1} are assigned respectively to Co–O and Co–F vibrations.[23,24] The near-infrared spectrum shows a pattern containing three weak frequencies at approximately 3580, 3440, and 3135 cm^{-1}, which are assigned to the water molecule and the hydrogen-bridging system in the compound.[24] Magnetic susceptibility measurements show that a very weak exchange between the cobalt ions may exist as deduced from the Θ value obtained between 4 and 80 K of approximately −2 K. A μ_{eff} value of 4.18 μ_B per cobalt ion at 285 K is in agreement with a value reported before[25] for a trigonal-bipyramidal compound. The zinc compound has the same stoichiometry as the cobalt compound (see Table III), identical infrared spectra, except for the far-infrared region, and identical X-ray powder patterns. The Zn–O and Zn–F stretching vibrations are observed at 440 and 353 cm^{-1}, respectively.[24]

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Table III. Ismorphism, Colors, Melting Points, Conductance Data, and Chromophores of the Complexes with amtd

	isomorphism[a]					
compd	X-ray type	IR type	color	mp, °C	conductance[b]	proposed chromophore
$Co_2(amtd)_2F(BF_4)_3(EtOH)_{1.5}(H_2O)$	A	I	dark purple	217–221	276	(CoN_4F, CoN_4O)
$Ni_2(amtd)_3(BF_4)_4(H_2O)_2$	B	II	lilac	>220	349	NiN_6
$Ni_2(amtd)_2F_2(BF_4)_2(EtOH)_{0.5}$	C	III	light blue	>220	177	NiN_4F_2
$Cu_2(amtd)_2F(BF_4)_3(H_2O)_2$	D	IV	dark green	188–190	253	(CuN_4F, CuN_4O)
$Zn_2(amtd)_2F(BF_4)_3(EtOH)_{1.5}(H_2O)$	A	I	white	196–198	ni[c]	(ZnN_4F, ZnN_4O)
$Co(amtd)(NO_3)_2$	E	V	red-purple	>220	80.1	CoN_4O
$Ni(amtd)(NO_3)_2$	F	VI	blue	>220	70.6	NiN_4O_2
$Cu(amtd)(NO_3)_2$	E	V′	green	168	ni	CuN_4O
$Zn(amtd)(NO_3)_2$	E	V	white	183–186	ni	ZnN_4O
$Co_3(amtd)_2Cl_6(EtOH)_{0.5}(H_2O)$	G	VII	dark blue	177–178	125	$(CoN_4Cl, CoCl_4)$
$Ni(amtd)Cl_2(H_2O)_{1.5}$	H	VIII	green	>220	55.5[d]	NiN_4Cl_2
$Cu_3(amtd)_2Cl_6(EtOH)$	I	IX	light green	176–177	74.1	$(CuN_4Cl, CuCl_4)$
$Zn_3(amtd)_2Cl_6$	J	X	white	141–144	73.1	$(ZnN_4Cl, ZnCl_4)$
$Co_3(amtd)_2(NCS)_6$	K	XI	blue-purple	>220	171	$(CoN_4\mathit{N}CS, Co(\mathit{N}CS)_4)$
$Ni(amtd)(NCS)_2$	L	XII	blue	>220	5.0	$NiN_4(\mathit{N}CS)_2$
$Cu_3(amtd)_2(NCS)_6(H_2O)_{1.5}$	M	XIII	green	142–144	102	$(CuN_4\mathit{N}CS, Cu(\mathit{N}CS)_4)$
$Zn_3(amtd)_2(NCS)_6$	K	XI	white	179–182	ni	$(ZnN_4\mathit{N}CS, Zn(\mathit{N}CS)_4)$

[a] Similar letters indicate identical or almost identical X-ray types; similar Roman numerals indicate identical or almost identical infrared spectra. [b] Values are given in Ω^{-1} mol^{-1} cm^2 for 10^{-3} M solutions in nitromethane (given per formula unit as tabulated). [c] Not investigated because of isomorphism with another compound in the table. [d] 10^{-3} M solution in dimethylformamide because of insolubility in nitromethane.

Table IV. Ligand Field Absorption Bands and X-Band EPR Spectral Data (at Room Temperature Unless Indicated Otherwise)[k]

$Co_2(amtd)_2F(BF_4)_3(EtOH)_{1.5}(H_2O)$	6200,[a] 13 000, 17 200, 20 600
$Ni_2(amtd)_3(BF_4)_4(H_2O)_2$	11 000, 12 600 (sh), 16 700 (sh), 18 200, 21 300,[b] 28 400
$Ni_2(amtd)_2F_2(BF_4)_2(EtOH)_{0.5}$	9700, 13 000,[b] 16 000, 20 800,[b] 26 300
$Cu_2(amtd)_2F(BF_4)_3(H_2O)_2$	15 700
	$g_\parallel = 2.26$,[c] $g_\perp = 2.07$
$Zn_2(amtd)_2F(BF_4)_3(EtOH)_{1.5}H_2O$ (doped with Co^{2+})	$g_\parallel(a) = 2.15$, $g_\parallel(b) = 2.21$, $g_\perp = 4.25$[d]
$Co(amtd)(NO_3)_2$	7900, 11 600 (sh), 15 000, 19 60 (21 700 (sh))
	$g_z = 6.16$, $g_x = 2.80$, $g_y = 1.86$[e]
$Ni(amtd)(NO_3)_2$	10 200, 12 500,[b] 17 500, 20 800,[b] 27 300
$Cu(amtd)(NO_3)_2$	11 800
	$g_\parallel = 2.31$,[f,g] $g_\perp = 2.11$ (br)
$Zn(amtd)(NO_3)_2$ (doped with Cu^{2+})	$g_1 = 2.29$,[h,i] $g_2 = 2.12$, $g_3 = 2.04$
$Co_3(amtd)_2Cl_6(EtOH)_{0.5}H_2O$	5800,[a] 11 700, 14 500, 15 000, 15 900, 16 700, 19 500
$Ni(amtd)Cl_2(H_2O)_{1.5}$	9100, 12 700 (sh),[b] 15 100, 21 200 (sh),[b] 25 100
$Cu_3(amtd)_2Cl_6(EtOH)$	5500, 9000, 15 500, 24 700[j]
	$g_\parallel = 2.23$, $g_\perp = 2.11$[h]
$Co_3(amtd)_2(NCS)_6$	7100,[a] 13 100, 15 900, 17 000, 19 600 (sh)
$Ni(amtd)(NCS)_2$	10 400, 13 100,[b] 16 900, 26 900
$Cu_3(amtd)_2(NCS)_6(H_2O)_{1.5}$	13 500
	$g_{max} = 2.13$

[a] Broad asymmetric band. [b] Very weak, assigned to spin-forbidden transitions. [c] $A_\parallel = 164 \times 10^{-4}$ cm^{-1} (hyperfine splittings). [d] Liquid-helium temperature; $A_\parallel = 47 \times 10^{-4}$ cm^{-1} (hyperfine splittings). [e] Liquid-helium temperature. [f] $A_\parallel = 150\ (10) \times 10^{-4}$ cm^{-1}. [g] (hyperfine) splittings only observed at liquid-nitrogen temperature. [h] Liquid-nitrogen temperature. [i] $A_\parallel = 145\ (10) \times 10^{-4}$ cm^{-1}. [j] Charge-transfer band. [k] Legend: sh = shoulder; br = broad.

Table V. Infrared Spectral Data of the Metal amtd Nitrate Compounds[b]

	coordinated nitrate				ionic nitrate	
compd	ν_3	$\nu_1 + \nu_4$	Δ	NO_3 dent.	ν_3[a]	$\nu_1 + \nu_4$
$Co(amtd)(NO_3)_2$	1280, 1490	1710, 1743	33	mono	1350	1743
$Ni(amtd)(NO_3)_2$	1272, 1504	1709, 1763	54	bi	1355	1743
$Cu(amtd)(NO_3)_2$	1287, 1492	1709, 1742	31	mono	1355	1742
$Zn(amtd)(NO_3)_2$	1290, 1488	1714, 1743	29	mono	1350	1743

[a] Very strong, broad. [b] All values are given in cm^{-1}.

Table VI. Ligand-Field Parameters Calculated from Ligand Field Absorption Spectra of the Nickel amtd Complexes

compd	Dq[a]	B[a]	Dq/B	chromophore
$Ni_2(amtd)_3(BF_4)_4(H_2O)_2$	1100	865	1.27	NiN_6
$Ni(amtd)(NCS)_2$	1040	820	1.27	$NiN_4(\mathit{N}CS)_2$
$Ni(amtd)(NO_3)_2$	1020	880	1.16	NiN_4O_2
$Ni_2(amtd)_2F_2(BF_4)_2(EtOH)_{0.5}$	970	865	1.12	NiN_4F_2
$Ni(amtd)Cl_2(H_2O)_{1.5}$	910	845	1.08	NiN_4Cl_2

[a] Values are given in cm^{-1}.

EPR measurements of a cobalt-doped zinc tetrafluoroborate compound rendered an axial spectrum (see Table IV), indicative of a trigonal-bipyramidal coordination geometry,[26] which is consistent with the X-ray structure determination of the cobalt tetrafluoroborate compound (see above). The observed EPR spectrum resembles the spectrum of $[CoBr(Me_6tren)]Br$, a complex of a tripod ligand, with $g_\parallel = 2.27$ and $g_\perp = 4.30$, reported by Benelli and Gatteschi.[26] The observed $g_\parallel$ and $g_\perp$ values of the EPR spectrum of the cobalt-doped zinc amtd tetrafluoroborate compound are in agreement with these values. Hyperfine splitting due to coupling with the cobalt nuclear spins ($I = {}^7/_2$) resulted in a splitting pattern consisting of 10 lines. This partial overlap of two series of eight lines confirms the presence of two slightly different cobalt species.

Two different nickel amtd tetrafluoroborate compounds are isolated, with stoichiometries $Ni_2(amtd)_3(BF_4)_4(H_2O)_2$ and

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$Ni_2F_2(amtd)_2(BF_4)_2(EtOH)_{0.5}$ (see Table III).[15] The ligand field spectrum of the first compound is typical of six-coordinated octahedral nickel ions.[27] Comparison of the *Dq* and *B* values (see Table VI) of this compound with those of $Ni(amtd)(NCS)_2$ points to a NiN_6 chromophore. According to conductivity measurements, this compound is a 1:4 electrolyte,[21] suggesting a dimeric cation, in which at least one ligand is shared by two nickel ions.

The ligand field spectrum of the other nickel compound is also typical for six-coordinated octahedral nickel ions.[27] Calculated *Dq* and *B* values (see Table VI) are comparable with those for $Ni(amtd)Cl_2(H_2O)_{1.5}$, which makes a NiN_4F_2 chromophore highly probable for this compound. For this compound a conductivity value of 177 Ω^{-1} mol^{-1} cm^2 has been established, suggesting a dimer and a 1:2 electrolyte. The absorption at 360 cm^{-1} observed in the far-infrared spectrum[15] agrees with a Ni–F stretching vibration in a Ni_2F_2 bridging unit.[20] From the elemental analyses[15] of the copper amtd tetrafluoroborate compound a stoichiometry of $Cu_2F(amtd)_2(BF_4)_3(H_2O)_2$ is established. A conductivity value of 253 Ω^{-1} mol^{-1} cm^2 is not in contradiction with a 2:3 electrolyte.[21] Thus even in nitromethane the dimer breaks down to monomeric cations, as in the case of the cobalt compound (see above).

In the EPR spectrum (see Table IV), a half-field signal is observed with a *g* value of 4.11. The $g_\parallel$ and $g_\perp$ values of this compound (2.26 and 2.07) show no sign of zero-field splitting, suggesting that a coupling between copper ions—if present—must be very small. In addition, magnetic susceptibility measurements down to 3 K indicate no significant interaction ($\Theta = 0.0 \pm 0.2$ K). The band in the far-infrared spectrum at 452 cm^{-1} could arise from a Cu–F stretching vibration.[28] From the EPR results, the magnetic data, and the observation of space-filling models, a direct Cu–F–Cu bridge is highly improbable. The similarity of the pattern of the near-infrared spectrum of this compound (with absorptions at approximately 3565, 3440, and 3135 cm^{-1}) with that of the cobalt tetrafluoroborate compound suggests a dimer structure with one or two water molecules in a bridge between the fluoride ion coordinated to one copper ion and a water molecule coordinated to the second copper ion. The three pyrazole nitrogens of the amtd ligand are coordinated inequivalently to the copper ions as is clear from the splitting of the absorption at 1556 cm^{-1}, which is characteristic of the heterocyclic pyrazole ring system,[29] into two bands at 1552 cm^{-1} and at 1576 cm^{-1}. The band at 15 700 cm^{-1} in the ligand field spectrum is consistent with an electronic transition in a distorted-trigonal-bipyramidal five-coordinated species. In the proposed coordination geometry for the copper tetrafluoroborate compound the axial atoms (fluoride or water and amine nitrogen) are relatively weaker donors than the equatorial atoms (the pyrazole nitrogens). The axial EPR spectrum is consistent with this configuration when a $d_{x^2-y^2}$ ground state is assumed.

In conclusion, there are two possibilities for the structure of this copper dimer, differing only in the bridging unit between both copper ions: either a fluoride to water bridge or an extended fluoride to water to water bridge in analogy with the fluoride to ethanol to water bridge in the cobalt tetrafluoroborate compound (vide supra).

Nitrate Compounds. According to the analyses,[15] all amtd nitrate compounds have the same stoichiometry, $M(amtd)(NO_3)_2$. The cobalt, copper, and zinc compounds are isostructural, because their X-ray powder patterns as well as the infrared spectra of the cobalt and zinc compounds are identical, while the infrared spectrum of the copper compound only shows some slight differences from those of the cobalt and zinc nitrates (see Table III). A conductivity value of 80.1 Ω^{-1} mol^{-1} cm^2 for the cobalt compound (see Table III) is typical for a 1:1 electrolyte,[21] indicating that in the isomorphous cobalt, copper, and zinc amtd nitrate compounds one nitrate is ionic and one is coordinated. This can be concluded also from the occurrence of two distinct nitrate overtone absorptions and their positions in the infrared spectra (see Table V) of the solid nitrate compounds.[30,31] Together with the four nitrogens of the amtd ligand this means an N_4O chromophore around the metal ions (see Table III). The ligand field spectrum of the cobalt nitrate compound (see Table IV) is typical for a five-coordinated configuration,[22] in accordance with the proposed CoN_4O chromophore. A nitrate with a weakly interacting second oxygen cannot be excluded however. The EPR spectrum of the cobalt compound (see Table IV) shows a symmetry lower than C_{3v}.

Analogous chromophores for cobalt are found for the cobalt tetrafluoroborate (see structure description), chloride, and thiocyanate compounds (see below). Our findings disagree with those of Mani and Scapacci,[6] who, although also proposing a distorted pentacoordinated structure for this cobalt compound, claimed amtd to act as a tridentate ligand (the amine nitrogen not coordinated or only semicoordinated to the cobalt ion) and one nitrate group to coordinate bidentately. Other structure determinations in progress in this laboratory indicate that in all cases amtd coordinates as a tetradentate ligand,[32] suggesting a monodentate nitrate in the case of Co, Cu, and Zn in agreement with the infrared spectra. Both the ligand field spectrum and the EPR spectrum of $Cu(amtd)(NO_3)_2$ are consistent with this result[33] (see Table IV). It is obvious that the bound nitrate is monodentately coordinated, or at best with a second oxygen in semicoordination, consistent with the observed infrared overtone absorptions (see Table V). In the far-infrared spectra[15] absorptions at 329 cm^{-1} (Co), at 323 cm^{-1} (Cu), and at 332 cm^{-1} (Zn) are tentatively assigned to M–O or M–N stretching vibrations.[24]

Both the X-ray pattern and the infrared spectrum of the nickel nitrate complex are significantly different from those of the other nitrate compounds (see Table III). The nickel amtd nitrate compound is a 1:1 electrolyte in accordance with a conductivity value of 70.6 Ω^{-1} mol^{-1} cm^2.[21] The occurrence of ionic nitrate is confirmed by an absorption in the infrared spectrum near 1380 cm^{-1}. From the observed nitrate overtone absorptions and the observed ν_3 absorptions in the infrared spectrum (see Table V), it is evident that bidentately coordinated nitrate (the splitting of ν_3 being larger than that for monodentately coordinated nitrate) as well as ionic nitrate are present.[30,31] The ligand field spectrum of the nickel nitrate compound (see Table IV) is characteristic for six-coordinated octahedral nickel ions and consistent with this structure as are the calculated ligand-field parameters for the *cis*-NiN_4O_2 chromophore.[27] In the far-infrared spectrum two absorptions at 310 cm^{-1} and at 290 cm^{-1} are assigned to Ni–O or Ni–N stretching vibrations.[24,34]

Chloride Compounds. Both X-ray powder patterns and infrared spectra of the chloride compounds show that each of these compounds is structurally different from the others, although the cobalt, copper, and zinc compounds have similar stoichiometries.[15]

The nickel compound differs strongly from the other chloride compounds. Its ligand field spectrum is typical for six-coordinated octahedral nickel ions (see Table IV).[27] Calculated *Dq* and *B* values are listed in Table VI. It is plausible to assume a *cis*-NiN_4Cl_2 chromophore, whereby both chlorides are bound to the nickel ion. The broad band at 230 cm^{-1} in the far-infrared spectrum is tentatively assigned to the Ni–Cl stretch.[24] In DMF, however, a conductivity value of 55.5 Ω^{-1} mol^{-1} cm^2 was measured, suggesting a 1:1 electrolyte. The conductivity measurement was carried out in dimethylformamide, because the solubility in nitromethane was insufficient. Apart from its excellent solvent properties, DMF is also a relatively good ligand and apparently capable of replacing part of the bonded chloride ions.[21] The cobalt,

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copper, and zinc chloride compounds are described with the formula $[M(amtd)Cl]_2[MCl_4](solvent)_x$, with $M(amtd)Cl^+$ cations and MCl_4^{2-} anions. This counterion can also be displaced by two tetraphenylborate anions,[35] as has been reported also for cobalt.[6]

The ligand field spectrum of the cobalt chloride complex can be regarded as the superposition of the ligand field spectra of $[Co(amtd)Cl]^+$ and the tetrahedral $CoCl_4^{2-}$ anion. The bands at 14 500, 15 000, 15 900, and 19 500 cm^{-1} agree with those reported for $CoCl_4^{2-}$.[36] Furthermore, the asymmetry of the broad band at 5800 cm^{-1} is due to the combination of an anion absorption and an absorption from $[Co(amtd)Cl]^+$. The bands at 11 700 and 16 700 cm^{-1} belong to the five-coordinate cation. In the far-infrared spectrum of this compound two strong absorptions at 299 and 304 cm^{-1} are assigned as Co–Cl stretching vibrations belonging to each of the two species.[24]

The copper chloride compound is believed to have a similar structure. The ligand field spectrum of the copper compound contains four bands (see Table IV) the bands at 5500 and 9000 cm^{-1} originate from the $CuCl_4^{2-}$ anion,[37] the band at 15 500 cm^{-1} comes from $[Cu(amtd)Cl]^+$. The band at 24 700 cm^{-1} is assigned to a ligand or chloride to copper charge-transfer transition.[37] The observed EPR spectrum of the copper compound is not very informative. Apparently the copper ions are too close together in the crystal lattice.[33] In the far-infrared spectrum four very strong absorptions were observed at 242, 268, 288, and 313 cm^{-1} due to Cu–Cl stretching vibrations; the first three can be assigned to the vibrations of the $CuCl_4^{2-}$ anion.[38] The conductivity value of 73.1 Ω^{-1} mol^{-1} cm^2 of the zinc compound points to a 2:1 electrolyte.[21] In analogy to the cobalt and copper compounds, this compound must be formulated as $[Zn(amtd)Cl]_2^+[ZnCl_4]^{2-}$. In the far-infrared spectrum[15] three Zn–Cl stretching vibrations are observed at 300, 283, and 275 cm^{-1}; the last two can be assigned to the $ZnCl_4^{2-}$ anion.[38]

Thiocyanate Compounds. With the exception of $Ni(amtd)(NCS)_2$, all thiocyanates can be described as the ionic species $[M(amtd)(NCS)]_2[M(NCS)_4]$[15] (M = Co, Cu, Zn). The infrared spectra of these three compounds are all very similar, and the X-ray powder patterns are almost identical (see Table III). The infrared spectra in the C–N stretching region agree with nitrogen coordination in all cases.[39] Bands at 2074 and 2090 cm^{-1} (shoulder) agree with those reported before[40] for $Co(NCS)_4^{2-}$, as do the bands at 2080 and 2095 cm^{-1} (shoulder) for $Zn(NCS)_4^{2-}$. The far-infrared spectra[15] show bands at 320 cm^{-1} (Co), 262 cm^{-1} (Cu), and 317 cm^{-1} (Zn), to be assigned to metal–nitrogen stretching vibrations, and bands at 300 cm^{-1} (Co), 300 cm^{-1} (Cu), and 270 cm^{-1} (Zn), to be assigned to the $M(NCS)_4^{2-}$ anions.[41]

Conductivity data in nitromethane also agree with the ionic structure,[21] although the value of 102 Ω^{-1} mol^{-1} cm^2 in the case of copper suggests some decomposition in solution for this compound. The single g EPR spectrum of the copper compound (see Table IV) is not very informative, indicating exchange narrowing due to copper ions which are too close together in the crystal lattice.[33]

The ligand field maxima (see Table IV) of the cobalt compound with bands at 15 900 and 19 600 cm^{-1} agree with those observed for $[(C_2H_5)_4N]_2^+[Co(NCS)_4]^{2-}$, prepared as a reference compound,[41] whereas the bands at 13 100 and 17 000 cm^{-1} must originate from the trigonal-bipyramidal species, in agreement with the bands observed for the trigonal-bipyramidal cation $Co(amtd)Cl^+$. The band at 7100 cm^{-1} appears to be a superposition of electronic transitions due to the tetrahedral and the five-coordinate species.

The rather large counterions $M(NCS)_4^{2-}$ in the thiocyanate compounds described above can be replaced by two tetraphenylborate anions,[35] as is known for cobalt.[6] The nickel compound is analyzed as $Ni(amtd)(NCS)_2$.[15]

The low molar conductivity of 5.0 Ω^{-1} mol^{-1} cm^2 of this compound reveals that it is a nonelectrolyte[21] and that both anions are thus bonded to the nickel ion. This is consistent with the observed ligand field spectrum (see Table IV), which is typical for six-coordinated octahedral nickel ions.[27] The calculated ligand field parameters are in agreement with a $NiN_4(NCS)_2$ chromophore (see Table VI). The positions of the infrared bands (at approximately 2085 and 2095 cm^{-1}) due to the C–N stretching vibration of NCS^- clearly indicate the presence of cis-N-bonded thiocyanate.[42,43] The band at 292 cm^{-1} in the far-infrared spectrum[15] is tentatively assigned to the Ni–NCS stretching vibration.[42]

Concluding Remarks. The present study has made clear that the new ligand tris((3,5-dimethylpyrazol-1-yl)methyl)amine in all its compounds acts as a tripodal tetradentate ligand, coordinating through the amine nitrogen and the three pyrazole nitrogens.

Five-coordination is observed in the species $[M(amtd)X]^+$ and $M(amtd)(H_2O)^{2+}$ for cobalt, copper, and zinc, while nickel is six-coordinate in all its amtd compounds.

In many coordination compounds of first-row transition-metal halides and thiocyanates the halides or thiocyanate anions either are bonded to the central metal ion (compounds with general formula $[M(ligand)_nX_2]$) or are part of a large counterion as in $[M(ligand)_n](SbCl_6)_2$[44] and $[Ni(Me_2SO)_6](NiCl_4)$.[45] The cobalt, copper, and zinc chlorides and thiocyanates of amtd constitute an intermediate case. In the compounds $[M(amtd)X]_2^+[MX_4]^{2-}$ one X^- ion is bonded in the complex cation, which apparently is forced upon the metal ion by the tripodal tetradentate ligand amtd. This leaves one "loose" X^- ion, which then forms complex anions MX_4^{2-}, resulting in a (low energy) 1:1 lattice with complex ions of comparable size. Another remarkable feature is the occurrence of the fluoride to ethanol to water bridge observed for the cobalt and zinc amtd tetrafluoroborate compounds. Apparently the BF_4^- anion is not large enough to form compounds in analogy to the $M(NCS)_4^{2-}$ and MCl_4^{2-} amtd compounds.

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Registry No. amtd, 85264-49-9; $Co_2(amtd)_2F(BF_4)_3(EtOH)_{1.5}H_2O$, 97570-44-0; $Ni_2(amtd)_3(BF_4)_4$, 97591-86-1; $Ni(amtd)F(BF_4)$, 97570-45-1; $Cu_2(amtd)_2F(BF_4)_3(H_2O)$, 97591-89-4; $Zn_2(amtd)_2F(BF_4)_3(H_2O)$, 97591-92-9; $Co(amtd)(NO_3)_2$, 97570-47-3; $Ni(amtd)(NO_3)_2$, 97570-49-5; $Cu(amtd)(NO_3)_2$, 97570-51-9; $Zn(amtd)(NO_3)_2$, 97570-53-1; $[Co(amtd)Cl]_2[CoCl_4]$, 97570-54-2; $Ni(amtd)_2Cl_2$, 97570-55-3; $[Cu(amtd)Cl]_2[CuCl_4]$, 97570-57-5; $[Zn(amtd)Cl]_2[ZnCl_4]$, 97570-59-7; $[Co(amtd)(NCS)]_2[Co(NCS)_4]$, 97570-60-0; $Ni(amtd)(NCS)_2$, 97570-61-1; $[Cu(amtd)(NCS)]_2[Cu(NCS)_4]$, 97643-59-9; $[Zn(amtd)(NCS)]_2[Zn(NCS)_4]$, 97570-63-3; *N*-(hydroxymethyl)-3,5-dimethylpyrazole, 85264-33-1; ammonium acetate, 631-61-8.

Supplementary Material Available: Listings of fractional coordinates of the hydrogen atoms of $Co_2(amtd)_2F(BF_4)_3(EtOH)_{1.5}(H_2O)$ (I), anisotropic thermal parameters of the non-hydrogen atoms of I, observed and calculated structure factors of I, analytical data of the amtd compounds, bond distances of the non-hydrogen atoms of I, bond angles of the non-hydrogen atoms of I, and far-infrared spectral data of the amtd compounds (22 pages). Ordering information is given on any current masthead page.

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(35) Compounds of composition $[M(amtd)X]^+BPh_4^-$, with M = Co, Cu, Zn and X = Cl^-, NCS^-, were synthesized by adding a solution of 2.5 mmol of metal chloride in 12.5 mL of ethanol to a solution of 2.5 mmol of amtd and 2.5 mmol of sodium tetraphenylborate in 25 mL of ethanol.

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