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Synthesis and Spectroscopy of Coordination Compounds of a Versatile Bridging Ligand. Molecular Structures of the Dinuclear Compounds $[Co_2(bdnol)(NCS)_3]$, $[Zn_2(bdnol)Cl(NCS)_2]$, and $[Cu_2(bdnol)(NO_3)_3]$ and of the Polymeric Copper(I) Compound $[Cu_2(Hbdnol)(NCS)_2]$

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The synthesis and characterization are described of transition metal coordination compounds with the novel pentadentate ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithia-5-nonanol (Hbdnol). Most of the compounds are of the general formula $[M_2(bdnol)X_3]\cdot n(solvent)$ with M = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Cd^{2+} and $X^- = Cl^-$, Br^-, NO_3^-, and NCS^-. Additionally, a polymeric copper(I) compound of the formula $[Cu_2(Hbdnol)(NCS)_2]$ and an unusual trinuclear nickel compound of the formula $[Ni_3(bdnol)Cl_5(EtOH)]\cdot 3EtOH$ are described. Hbdnol acts as a pentadentate ligand in all compounds; the alcohol group is generally dehydronated and bridging between the metal ions, except in the case of the copper(I) compound, where the alcohol group is noncoordinating. Single crystals of $[Co_2(bdnol)(NCS)_3]\cdot MeCN$ (**A**), $[Zn_2(bdnol)Cl(NCS)_2]\cdot {}^1/_2MeCN$ (**B**), $[Cu_2(bdnol)(NO_3)_3]$ (**C**), and $[Cu_2(Hbdnol)(NCS)_2]$ (**D**) were used for X-ray structure determinations. $[Co_2(bdnol)(NCS)_3]\cdot MeCN$: orthorhombic, space group *Pnma*, $a = 17.7487(7)$ Å, $b = 20.095(2)$ Å, $c = 8.569(2)$ Å, $Z = 4$, and $T = 150$ K; $R_F = 0.060$, $wR2 = 0.108$ for 3606 reflections. $[Zn_2(bdnol)Cl(NCS)_2]\cdot {}^1/_2MeCN$: monoclinic, space group $P2_1$, $a = 8.7369(7)$ Å, $b = 16.416(1)$ Å, $c = 11.222(1)$ Å, $\beta = 108.84(1)°$, $Z = 2$, and $T = 293$ K; $R_F = 0.051$, $R_w = 0.062$ for 2983 reflections. $[Cu_2(bdnol)(NO_3)_3]$: triclinic, space group *P*-1, $a = 8.012(4)$ Å, $b = 12.430(6)$ Å, $c = 13.702(16)$ Å, $\alpha = 95.61(7)°$, $\beta = 102.34(5)°$, $\gamma = 97.46(5)°$, $Z = 2$, and $T = 293$K; $R_F = 0.042$, $R_w = 0.041$ for 3805 reflections. $[Cu_2(Hbdnol)(NCS)_2]$: triclinic space group *P*-1, $a = 9.241(4)$ Å, $b = 10.32(2)$ Å, $c = 15.27(1)$ Å, $\alpha = 103.1(1)°$, $\beta = 98.92(8)°$, $\gamma = 113.85(5)°$, $Z = 2$, and $T = 293$ K; $R_F = 0.050$, $R_w = 0.052$ for 2999 reflections. The compounds were further characterized by IR, ligand field spectroscopy, EPR, and magnetic susceptibility measurements. The dinuclear compound $[Ni_2(bdnol)Cl_3]$ shows a ferromagnetic intramolecular interaction J and an antiferromagnetic ordering between adjacent dimers with interaction j. Using a model taking into account the zero-field splitting effect (D), the experimental data are shown to fit well with the calculated values $J = 9.0$ K, $zj = -1.29$ K, $D = -0.22$ K (1 K = 0.6951 cm^{-1}), and $g = 2.25$. The behavior of the trinuclear $[Ni_3(bdnol)Cl_5(EtOH)]$ hints toward ferromagnetic interactions with a transition to a long-range antiferromagnetic order below 5.5 K. The properties of the latter suggest the presence of 1d or 2d arrangements of the magnetic moments. The dinuclear copper(II) compounds are strongly antiferromagnetically coupled: they are EPR silent at room temperature.

Introduction

In the last decade, the biological significance of nickel has been recognized.[2,3] Nickel appears to be an important metal in a number of enzymes, notably in hydrogenases and in urease. EPR measurements and EXAFS data suggest that the nickel-containing hydrogenases share a common nickel active site, and this site was believed to be of distorted octahedral or square-pyramidal geometry, in which the nickel ion is surrounded by sulfur, oxygen, and/or nitrogen donor atoms. Only after completion of the study described below, did a crystal structure determination on the NiFe-hydrogenase from *Desulfovibrio gigas* at 2.85 Å resolution become available.[4] This structure shows the presence of two metal ions in the active site, in close proximity, bridged by two cysteine sulfurs. The one metal is believed to be nickel in a severely distorted geometry formed by four sulfur ligands, while the other metal is considered to be iron in a five-coordination, consisting of two sulfurs and three water molecules. Some controversy still exists about the oxidation states of the nickel ion in the catalytic cycle,[2,3] which is now more complicated by the presence of another (presumably iron) metal ion. EXAFS measurements of the nickel site in urease have suggested that a dinuclear site with at least some histidine ligands is present.[3]

The ligand 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithia-5-nonanol (Hbdnol), a pentadentate ligand with two azole nitrogens, two thioether sulfurs, and an alcohol function has been

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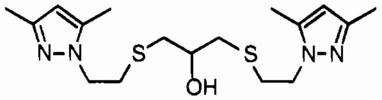

Hbdnol

Figure 1. Schematic drawing of the ligand Hbdnol.

designed and successfully synthesized. A schematic drawing of the ligand Hbdnol is shown in Figure 1. The ligand was designed to form mononuclear, square-planar, or five-coordinated nickel compounds, so that at least one open site for substrate coordination would remain available. However, reaction of Hbdnol with nickel chloride yields a green trinuclear compound and a red dinuclear compound.[5]

This paper describes the synthesis and characterization of coordination compounds of the ligand Hbdnol with the transition metals cobalt, nickel, copper, zinc, and various anions, as well as a cadmium chloride complex. Four new X-ray structures, all with some unusual features, are described. Some structural data of the nickel chloride compounds have been communicated.[5]

Experimental Section

General Information. All starting materials were commercially available and used as purchased. The compounds *N*-(2-hydroxyethyl)-3,5-dimethylpyrazole and *N*-[2-(*p*-toluenesulfonyl)ethyl]-3,5-dimethylpyrazole were prepared according to published procedures.[6]

***N*-(2-Mercaptoethyl)-3,5-dimethylpyrazole.** *N*-[2-(*p*-Toluenesulfonyl)ethyl]-3,5-dimethylpyrazole (0.14 mol) and tetramethylthiourea (0.14 mol) were suspended together in distilled water (200 mL). This suspension was refluxed for 3 h; during this period the suspended materials dissolved. At this point the solution was yellow. Sodium hydroxide (0.3 mol) dissolved in distilled water (40 mL) was added. The reaction mixture was then further refluxed for 2 h, whereupon the solution had become orange. The workup was carried out as follows: The aqueous solution was extracted with dichloromethane (5 × 40 mL) in order to remove tetramethylurea, unreacted starting materials, and any neutral side products. The aqueous layer was then acidified to approximately pH 5.5 with concentrated hydrochloric acid. The acidified solution was then extracted with dichloromethane (3 × 40 mL). The yellow solution was subsequently dried over anhydrous magnesium sulfate. The solvent was removed using a rotary evaporator, leaving an orange oil. The overall yield was found to fluctuate between 40 and 60%. The oil still contained small amounts of tetramethylurea. The synthesis and workup procedure are performed in air, but the resultant thiol can best be stored under a nitrogen atmosphere. In air, the thiol is resistant to oxidation for several weeks, but disulfide slowly crystallizes out of the oil. Characterization was performed by ^{1}H and ^{13}C NMR and IR. The ^{1}H NMR spectrum (solvent $CDCl_3$, internal standard TMS) showed the following signals for the thiol: 1.37 (t, 1H, S*H*), 2.20 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.89 (q, 2H, CH_2SH), 4.08 (t, 2H, pz-CH_2), 5.78 ppm (s, 1H, pz-*H*); the disulfide is characterized by peaks at 3.05 (t, 2H, CH_2SS) and 4.21 ppm (t, 2H, pzCH_2). ^{13}C NMR ($CDCl_3$): 10.6 and 13.0 (pz-CH_3), 24.3 (CH_2CH_2-SH), 50.5 (pz-CH_2CH_2), 104.3 (pz-*C*H), 138.7 and 147.2 (pz-CCH_3), (disulfide: 37.34 ppm (CH_2CH_2SS)), and 46.48 ppm (pz-CH_2CH_2). IR (neat): 2920 (s), 2860 (m), 2540 (w, br), 1557 (vs), 1460 (s), 1425 (s), 1310 (s), 1272 (m), 1240 (m), 1160 (w), 1120 (m), 1035 (m), 1020 (m), 980 (w), 780 (s, br), 680 (m), 670 (m), 640 (w), 620 (w), 570 (w, br), 480 (w) cm^{-1}.

1,9-Bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithia-5-nonanol. *N*-(2-Mercaptoethyl)-3,5-dimethylpyrazole (0.07 mol) and 1,3-dichloropropan-2-ol (0.035 mol) were dissolved in thf (50 mL). To this mixture was added a solution of sodium hydroxide (0.07 mol) in water (50 mL), resulting in a two-layer system. The mixture was refluxed for 4.5 h, after which time the reaction mixture had become homogeneous. The reaction mixture was evaporated partly in order to remove the thf and so to facilitate extraction with dichloromethane. Extraction of the aqueous solution with dichloromethane (3 × 40 mL), followed by drying with $MgSO_4$ and evaporation, resulted in a yellow oil. All attempts to crystallize this oil have failed. Over a period of time the oil becomes dark brown, which does not affect the NMR spectra or the formation of coordination compounds. Depending on the purity of the starting thiol, small amounts of tetramethylurea were present in the product. Yield 11.7 g (95%). The ^{1}H NMR spectrum (solvent $CDCl_3$, internal standard TMS) showed the following signals: 2.21 (s, 6H, CH_3), 2.30 (s, 6H, CH_3), 2.56 (dd, 4H, SCH_2CHOH), 3.02 (t, 4H, CH_2CH_2S), 3.76 (m, 1H, C*H*OH), 4.18 (t, 4H, pz-CH_2CH_2), 4.8 (br, OH), 5.82 ppm (s, 2H, pz-H). ^{13}C NMR ($CDCl_3$): 10.3 (CH_3), 12.7 (CH_3), 31.9 (SCH_2CHOH), 37.3 (CH_2CH_2S), 47.7 (pz-CH_2CH_2), 69.4 (*C*HOH), 104.3 (pz-*C*H), 138.4 and 146.6 ppm (pz-CCH_3). IR (neat): 2920 (m), 1555 (vs), 1462 (s), 1425 (s), 1390 (s), 1310 (m), 1280 (w), 1230 (w), 1190 (m), 1180 (s), 1070 (w), 1030 (m, br), 980 (w), 910 (w, br), 780 (m, br), 665 (m) cm^{-1}.

Synthesis of the Coordination Compounds. (a) [M_2(bdnol)X_3] (General Procedure). The coordination compounds were prepared by dissolving the appropriate (hydrated) metal salt (2 mmol) in 40 mL of warm acetonitrile and adding this solution to a solution of the ligand Hbdnol (1 mmol) in 5 mL of acetonitrile. After filtration of the hot reaction mixture, the complex crystallized on cooling. For the preparation of the thiocyanate compounds, a solution of the metal perchlorate (2 mmol) in 40 mL of acetonitrile was added to the solution of the ligand (1 mmol), followed by a solution of ammonium thiocyanate (NH_4NCS, 3 mmol) in 2 mL of water. In some cases, the addition of a few drops of triethylamine stimulated the crystallization of the coordination compounds. Yields were in general 30–40%. IR of [Co_2(bdnol)Cl_3] as an example of the class-I halides (Table 4): 2960 (w), 2920 (w), 2860 (w), 1557 (vs), 1500 (w), 1472 (s), 1440 (sh), 1422 (s), 1395 (m), 1382 (m), 1360 (m), 1320 (m), 1280 (sh), 1267 (m), 1220 (w), 1155 (w), 1130 (m), 1090 (s), 1055 (m), 1030 (m), 1002 (m), 902 (w), 853 (m), 812, 800, 780 (w, br), 710 (w), 645 (m, sh), 630 (s), 500 (w), 450 (w, br), 350 (w), 294 (s, br) cm^{-1}.

(b) [Ni_3(bdnol)(EtOH)Cl_5]·3EtOH. Nickel chloride (3 mmol) dissolved in 5 mL of triethyl orthoformate, and 5 mL of warm absolute ethanol was added to a solution of the ligand Hbdnol in 5 mL of warm absolute ethanol. The reaction mixture was filtered and the green microcrystalline material crystallized on cooling. Yield ca. 33%. IR: 2970 (m), 2920 (m), 1625 (w, br), 1555 (s), 1495 (w), 1470 (s), 1445 (s), 1418 (s), 1399 (s), 1345 (w), 1312 (s), 1280 (s), 1250 (w), 1182 (w), 1167 (m), 1120 (m), 1090 (w), 1052 (s), 1035 (vs), 990 (w), 880 (m), 795 (s), 760 (w), 718 (w), 670 (w), 620 (w), 590 (m), 553 (m), 500 (w), 440 (m), 430 (m), 383 (m), 350 (w) cm^{-1}.

(c) [Cu_2(Hbdnol)(NCS)$_2$]. This copper(I) compound has been synthesized in aerobic conditions. Copper(II) perchlorate (2 mmol) was dissolved in 30 mL of warm acetonitrile. This solution was added to a warm solution of the ligand Hbdnol (1 mmol) in 5 mL of acetonitrile, followed by a solution of ammonium thiocyanate (2 mmol) in 4 mL of water and a small amount of ascorbic acid to reduce the copper. The dark green solution becomes colorless, and a small amount of a white solid (CuNCS) is formed. The solution is filtered and after several days colorless crystalline material is formed. Yield ca. 40%. IR: 3440 (br), 2925 (m), 2875 (w), 2100 (vs), 1558 (s), 1495 (w), 1470 (s), 1440 (s), 1425 (s), 1395 (s), 1370 (w), 1340 (w), 1315 (m), 1280 (m), 1235 (w), 1157 (w), 1125 (w), 1090 (w), 1050 (s), 1020 (w), 995 (w), 910 (w), 890 (w), 808 (s), 770 (m), 670 (w), 620 (w), 550 (w), 500 (w), 460 (w), 435 (w), 390 (w) cm^{-1}.

Analyses. Metal analyses were carried out complexometrically with Na_2H_2edta as the complexing agent.[7] Halogen analyses were performed by potentiometric titrations with silver nitrate.[7] C, H, N, S analyses were performed by the Microanalytical Laboratory of the University College in Dublin, Ireland, the Microanalytical Laboratory Pascher in Remagen, Germany, or the Microanalytical department of Groningen University, Groningen The Netherlands.

Spectroscopic Measurements. Infrared spectra in the 4000–200 cm^{-1} range of the samples, pelleted in KBr, were recorded on a Perkin-

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Table 1. Crystallographic Data for $[Co_2(bdnol)(NCS)_3]$ (**A**), $[Zn_2(bdnol)Cl(NCS)_2]$ (**B**), $[Cu_2(bdnol)(NO_3)_3]$ (**C**), and $[Cu_2(Hbdnol)(NCS)_2]$ (**D**)

	A	**B**	**C**	**D**
chem formula	$C_{20}H_{27}Co_2N_7OS_5 \cdot C_2H_3N$	$C_{19}H_{27}ClN_6OS_4Zn_2 \cdot {}^1/_2C_2H_3N$	$C_{17}H_{27}Cu_2N_7O_{10}S_2$	$C_{19}H_{28}Cu_2N_6OS_4$
formula wt	700.7	670.4	680.7	611.8
a (Å)	17.7487(7)	8.7369(7)	8.012(4)	9.241(4)
b (Å)	20.095(2)	16.416(1)	12.430(6)	10.32(2)
c (Å)	8.569(2)	11.2220(7)	13.70(2)	15.27(1)
α (deg)	90	90	95.61(7)	103.1(1)
β (deg)	90	108.84(1)	102.34(5)	98.92(8)
γ (deg)	90	90	97.46(5)	113.85(5)
V (Å^3)	3056.2(8)	1523.3(2)	1310(2)	1247(3)
Z	4	2	2	2
T (K)	150	293	293	293
space group	*Pnma*	$P2_1$	P-1	P-1
ρ_{calcd} (g cm^{-3})	1.52	1.45	1.72	1.62
μ (cm^{-1})	14.4	55.0	18.4	20.4
radiation (λ (Å))	Mo Kα (0.710 69)	Cu Kα (1.541 84)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
S	0.94	3.307	1.71	1.83
R_F[a]	0.060	0.051	0.042	0.050
R_w[b]		0.062	0.041	0.052
$wR2$[c]	0.108			

[a] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. [c] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Elmer 580 spectrophotometer. Ligand field spectra of the solids (300–2000 nm, diffuse reflectance) were taken on a Perkin-Elmer 330 spectrophotometer equipped with a data station. Electron paramagnetic resonance (EPR) spectra of the powdered copper(II) compounds were taken with a JEOL JES-RE2X spectrometer equipped with an Esprit 330 data system at X-band frequencies. ^1H and ^{13}C NMR spectra were recorded on a JNM-FX 200 spectrometer. Magnetic susceptibility and magnetization data were recorded from powder samples by using a SQUID magnetometer (Métronique) in the range 1.6–300 K, 0–8 T.

Crystal Structure Determination of A. A blue, plate-shaped crystal of $[Co_2(bdnol)(NCS)_3] \cdot MeCN$ (**A**) suitable for X-ray structure determination was mounted on a Lindemann glass capillary and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Accurate unit cell parameters and an orientation matrix were determined by least-squares refinement of the setting angles of 25 well-centered reflections (SET4) in the range 9.9° $< \theta <$ 15.6°. Reduced cell calculations did not indicate higher lattice symmetry.[8] Crystal data and details on data collection are collected in Table 1.

Data were collected in $\omega/2\theta$ scan mode with scan angle $\Delta\omega = 0.57 + 0.35 \tan \theta°$. Intensity data of 4704 reflections were measured, of which 3606 were independent ($R_{int} = 0.025$). Data were corrected for Lp effects and for 2% linear decay of the three periodically measured reference reflections during 16 h of X-ray exposure time. An empirical absorption/extinction correction was applied (DIFABS,[9] correction range 0.92–1.15). The structure was solved by automated Patterson methods and subsequent difference Fourier techniques (DIRDIF-92[10]). Refinement on F^2 was carried out using full-matrix least-squares techniques (SHELXL-93[11]); no observance criterion was applied during refinement. Hydrogen atoms were included in the refinement on calculated positions riding on their carrier atoms. The methyl hydrogen atoms were refined as a rigid group, allowing for rotation around the C–C bond. All nonhydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in the refinement with a fixed isotropic thermal parameter related to the value of the equivalent isotropic thermal parameter of their carrier atoms by a factor of 1.5 for the methyl hydrogen atoms and 1.2 for the other hydrogen atoms. Convergence was reached at $wR2 = 0.087$, $w^{-1} = \sigma^2(F^2) + (0.0383P)^2$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$, $R1 = 0.060$ for $1992F_o > 4\sigma(F_o)$, $S = 0.94$ for 187 parameters. No residual density was found outside −0.74 and 0.72 eÅ^{-3}. Positional parameters are listed in Table 2a; selected bond distances and angles are given in Table 3a. Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[12] Geometrical calculations and illustrations were performed with PLATON.[13] All calculations were performed on a DEC5000 cluster.

Data Collection and Structure Refinement for B–D. The reflection intensities of $[Zn_2(bdnol)Cl(NCS)_2] \cdot {}^1/_2MeCN$ (**B**), $[Cu_2(bdnol)(NO_3)_3]$ (**C**), and $[Cu_2(Hbdnol)(NCS)_2]$ (**D**) were measured and collected on a four-circle Enraf-Nonius CAD-4 diffractometer with monochromatized Cu Kα radiation (λ = 1.541 78 Å) (**B**) or Mo Kα radiation (λ = 0.710 73 Å) (**C** and **D**). For all four structures, a selection of the crystal data and additional particulars of the data collection and refinement are presented in Table 1; full details are given in the supporting information. Intensities were corrected for Lorentz and polarization effects. The positions of the heavy metals in **B–D** were obtained from Patterson maps. The other nonhydrogen atoms of **B** were located using the program AUTOFOUR,[14] and of **C** and **D** were found in Fourier maps. Refinement of **B–D** was accomplished using XTAL.[15] Absorption correction was applied in all cases. Transmission factors were estimated using the program DIFABS.[9] The structures were refined by full-matrix least-squares fitting. Refinement was continued until all shifts were smaller than one-third of the parameters involved. Scattering factors were taken from ref 12. Hydrogen atoms were located from difference Fourier maps or in some cases, were placed at calculated positions. The nonhydrogen atoms were refined anisotropically. The positions and thermal motions of the hydrogens have not been refined. The function minimized was $\sum w(||F_o| - |F_c||)^2$ with $w = 1/\sigma^2(F)$. The fractional coordinates of the nonhydrogen atoms of **B–D** are listed, respectively, in Table 2b–d. Selected bond distances and selected bond angles are given in Table 3b–d. The estimated standard deviations in the distances and angles were calculated from the full correlation matrix. Lists of the atomic coordinates of the hydrogen atoms, of the nonhydrogen anisotropic thermal parameters and of the bond distances and angles are available as supporting information.

Results

Description of the Structures: (a) Structures of $[Co_2(bdnol)(NCS)_3] \cdot MeCN$ (A) and $[Zn_2(bdnol)Cl(NCS)_2] \cdot {}^1/_2MeCN$ (B).

PLUTON[16] projections of the complexes **A** and **B** are given in Figures 2 and 3, respectively.

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Table 2. Final Coordinates and Equivalent Isotropic Thermal Parameters (Å^2) of Non-Hydrogen Atoms

atom	*x*	*y*	*z*	*U*(eq)^a	atom	*x*	*y*	*z*	*U*(eq)^a
(a) [Co_2(bdnol)$(NCS)_3$]·MeCN (**A**)									
Co(1)	0.21956(3)	0.17195(3)	0.99081(8)	0.0219(2)	C(12)	0.3950(2)	0.1076(2)	0.9240(5)	0.0247(14)
S(13)	0.33465(7)	0.11273(6)	1.09248(14)	0.0224(3)	C(14)	0.3683(3)	0.1875(2)	1.1868(5)	0.0223(16)
S(43)	0.03420(7)	0.06603(6)	1.29466(15)	0.0332(4)	C(15)	0.3555(3)	$^1/_4$	1.0901(7)	0.0200(19)
S(53)	−0.01657(10)	$^1/_4$	0.9536(3)	0.0504(9)	C(23)	0.1772(3)	0.0933(2)	0.6946(6)	0.0303(17)
O(20)	0.2810(2)	$^1/_4$	1.0304(5)	0.0210(14)	C(24)	0.2124(3)	0.0616(2)	0.5716(5)	0.0343(19)
N(21)	0.2970(2)	0.1096(2)	0.7176(4)	0.0237(12)	C(25)	0.2877(3)	0.0724(2)	0.5863(5)	0.0317(16)
N(22)	0.2288(2)	0.1235(2)	0.7844(4)	0.0227(12)	C(26)	0.0954(3)	0.0958(2)	0.7359(6)	0.0413(19)
N(41)	0.1533(2)	0.1278(2)	1.1405(5)	0.0327(14)	C(27)	0.3532(3)	0.0504(2)	0.4898(6)	0.0447(19)
N(51)	0.1400(3)	$^1/_4$	0.9282(7)	0.0293(19)	C(42)	0.1034(3)	0.1027(2)	1.2056(5)	0.0253(17)
C(11)	0.3654(2)	0.1404(2)	0.7758(5)	0.0250(16)	C(52)	0.0750(4)	$^1/_4$	0.9386(9)	0.032(3)
(b) [Zn_2(bdnol)Cl$(NCS)_2$]·$^1/_2$MeCN (**B**)									
Zn(1)	0.84790(10)	0.521(2)	0.74180(10)	0.0391(3)	C(16)	1.1130(10)	0.328(2)	0.9677(8)	0.046(3)
Zn(2)	0.9726(2)	0.492(2)	1.04230(10)	0.0435(4)	C(18)	0.9100(10)	0.291(2)	1.1079(8)	0.047(3)
Cl(3)	0.8293(4)	0.606(2)	0.9117(2)	0.0584(8)	C(19)	0.7560(10)	0.339(2)	1.0577(9)	0.050(3)
S(13)	0.8792(3)	0.395(2)	0.6008(2)	0.0414(6)	C(23)	0.5170(10)	0.585(2)	0.5682(9)	0.055(3)
S(17)	1.0924(3)	0.344(2)	1.1190(2)	0.0490(6)	C(24)	0.3750(10)	0.556(2)	0.4990(10)	0.065(4)
S(43)	1.0765(4)	0.720(2)	0.5602(3)	0.0713(12)	C(25)	0.3760(10)	0.474(2)	0.5187(8)	0.054(4)
S(63)	1.3831(4)	0.680(2)	1.1981(3)	0.0674(10)	C(26)	0.581(2)	0.669(2)	0.5780(10)	0.079(5)
O(20)	0.9441(7)	0.443(2)	0.8772(5)	0.0378(19)	C(27)	0.240(2)	0.408(2)	0.4640(10)	0.090(5)
N(21)	0.5176(9)	0.455(2)	0.5979(7)	0.042(2)	C(33)	0.7730(10)	0.525(2)	1.2178(9)	0.061(3)
N(22)	0.6112(9)	0.524(2)	0.6313(6)	0.046(3)	C(34)	0.6660(10)	0.483(2)	1.2639(9)	0.067(4)
N(31)	0.7378(9)	0.404(2)	1.1365(6)	0.043(2)	C(35)	0.6420(10)	0.405(2)	1.2078(8)	0.053(3)
N(32)	0.8190(10)	0.476(2)	1.1400(6)	0.048(3)	C(36)	0.839(2)	0.610(2)	1.2410(10)	0.091(5)
N(41)	0.9790(10)	0.591(2)	0.6722(8)	0.061(3)	C(37)	0.538(2)	0.337(2)	1.2170(10)	0.082(5)
N(61)	1.1720(10)	0.555(2)	1.1317(9)	0.066(3)	C(42)	1.0180(10)	0.646(2)	0.6237(8)	0.049(3)
C(11)	0.5830(10)	0.378(2)	0.6501(9)	0.045(3)	C(62)	1.2590(10)	0.607(2)	1.1615(8)	0.045(3)
C(12)	0.7000(10)	0.339(2)	0.5863(9)	0.051(3)	N(2)	0.573(2)	−0.059(2)	0.1260(10)	0.046(3)
C(14)	1.0230(10)	0.351(2)	0.7378(8)	0.043(3)	C(1)	0.585(2)	0.002(2)	0.1250(10)	0.026(3)
C(15)	0.9830(10)	0.361(2)	0.8582(8)	0.038(3)	C(3)	0.599(2)	0.088(2)	0.123(2)	0.043(4)
(c) [Cu_2(bdnol)$(NO_3)_3$] (**C**)									
Cu(1)	0.99909(7)	0.30598(4)	0.13398(4)	0.0305(2)	N(50)	1.2430(5)	0.2565(3)	0.0401(3)	0.0437(16)
Cu(2)	0.98009(7)	0.27430(4)	0.36859(4)	0.0287(2)	N(60)	1.1687(5)	0.1109(3)	0.3450(3)	0.0390(14)
S(13)	0.7949(2)	0.46016(9)	0.11314(9)	0.0400(4)	C(11)	0.7568(6)	0.3447(4)	−0.0794(3)	0.0417(17)
S(17)	0.7159(2)	0.30820(10)	0.40340(9)	0.0351(4)	C(12)	0.6707(6)	0.4169(4)	−0.0155(3)	0.0406(17)
O(20)	0.8655(4)	0.2628(2)	0.2290(2)	0.0295(12)	C(14)	0.6687(6)	0.3940(4)	0.1922(4)	0.0418(17)
O(41)	1.1889(4)	0.4131(3)	0.2301(3)	0.0534(12)	C(15)	0.6882(6)	0.2762(4)	0.2032(3)	0.0330(14)
O(42)	1.0679(5)	0.4600(3)	0.3532(3)	0.0551(14)	C(16)	0.5984(6)	0.2333(4)	0.2819(3)	0.0408(17)
O(43)	1.2496(5)	0.5770(3)	0.3084(3)	0.0670(16)	C(18)	0.6778(6)	0.2161(4)	0.4941(3)	0.0411(17)
O(51)	1.1499(4)	0.3337(3)	0.0369(3)	0.0486(12)	C(19)	0.8229(6)	0.1523(4)	0.5269(3)	0.0379(17)
O(52)	1.2347(5)	0.1958(3)	0.1055(3)	0.0571(12)	C(23)	0.7926(6)	0.0923(3)	0.0192(3)	0.0349(16)
O(53)	1.3321(5)	0.2471(3)	−0.0217(3)	0.0778(17)	C(24)	0.6672(6)	0.0541(4)	−0.0690(4)	0.0426(17)
O(61)	1.1836(4)	0.2126(2)	0.3331(2)	0.0378(12)	C(25)	0.6369(6)	0.1427(4)	−0.1178(4)	0.0429(17)
O(62)	1.2913(5)	0.0616(3)	0.3425(3)	0.0640(14)	C(26)	0.8697(7)	0.0304(4)	0.0984(4)	0.0472(19)
O(63)	1.0293(4)	0.0650(3)	0.3577(3)	0.0482(12)	C(27)	0.5151(7)	0.1501(5)	−0.2143(4)	0.066(2)
N(21)	0.7399(5)	0.2312(3)	−0.0605(3)	0.0346(12)	C(33)	1.2194(6)	0.3337(4)	0.5739(3)	0.0372(17)
N(22)	0.8368(5)	0.2004(3)	0.0235(3)	0.0336(12)	C(34)	1.2171(6)	0.3191(4)	0.6735(4)	0.0449(17)
N(31)	0.9852(5)	0.2239(3)	0.5720(3)	0.0339(12)	C(35)	1.0673(6)	0.2491(4)	0.6699(3)	0.0394(17)
N(32)	1.0782(5)	0.2744(3)	0.5121(3)	0.0336(12)	C(36)	1.3518(7)	0.4009(4)	0.5348(4)	0.0523(19)
N(40)	1.1685(5)	0.4853(3)	0.2980(3)	0.0429(14)	C(37)	0.9951(8)	0.2071(4)	0.7527(4)	0.0560(19)
(d) [Cu_2(Hbdnol)$(NCS)_2$] (**D**)									
Cu(1)	0.79468(9)	0.98867(8)	0.32330(5)	0.0466(3)	C(15)	0.6797(8)	0.4794(7)	0.2715(6)	0.068(3)
Cu(2)	1.14320(9)	0.47099(9)	0.16898(6)	0.0511(3)	C(16)	0.8328(7)	0.4634(7)	0.2624(4)	0.053(2)
S(13)	0.8530(2)	0.7928(2)	0.34420(10)	0.0521(5)	C(18)	0.7494(7)	0.3083(9)	0.0711(5)	0.074(3)
S(17)	0.8922(2)	0.4851(2)	0.15740(10)	0.0523(6)	C(19)	0.7931(7)	0.1813(7)	0.0708(4)	0.058(2)
S(43)	1.2392(2)	0.4181(2)	0.30610(10)	0.0499(6)	C(23)	0.7532(7)	1.1798(7)	0.4946(5)	0.053(3)
S(53)	1.5941(2)	0.9161(2)	0.18320(10)	0.0449(5)	C(24)	0.7347(7)	1.1804(8)	0.5826(4)	0.057(3)
O(20A)	0.5550(9)	0.3631(8)	0.2186(5)	0.061(2)	C(25)	0.7029(7)	1.0434(8)	0.5869(4)	0.053(3)
O(20B)	0.6050(10)	0.4290(10)	0.3315(7)	0.049(3)	C(26)	0.7910(10)	1.3016(8)	0.4519(6)	0.086(3)
N(21)	0.7030(6)	0.9640(6)	0.5028(3)	0.0509(17)	C(27)	0.6814(9)	0.9825(9)	0.6651(5)	0.076(3)
N(22)	0.7331(6)	1.0476(6)	0.4445(3)	0.0472(17)	C(33)	1.1455(7)	0.2664(7)	−0.0104(4)	0.0423(19)
N(31)	0.9131(5)	0.1817(5)	0.0193(3)	0.0460(17)	C(34)	1.0397(8)	0.1342(7)	−0.0809(4)	0.055(3)
N(32)	1.0690(5)	0.2958(5)	0.0521(3)	0.0441(17)	C(35)	0.8941(7)	0.0815(7)	−0.0610(4)	0.046(2)
N(41)	0.9857(6)	0.1553(6)	0.3104(3)	0.0486(17)	C(36)	1.3223(7)	0.3694(7)	0.0032(4)	0.054(3)
N(51)	1.3220(6)	0.6615(6)	0.1798(3)	0.0498(17)	C(37)	0.7356(8)	−0.0574(7)	−0.1102(5)	0.060(2)
C(11)	0.6649(9)	0.8068(8)	0.4701(5)	0.066(3)	C(42)	1.0909(7)	0.2627(7)	0.3077(4)	0.0420(19)
C(12)	0.8097(9)	0.7796(7)	0.4535(5)	0.068(3)	C(52)	1.4349(7)	0.7669(7)	0.1825(4)	0.0400(19)
C(14)	0.6827(7)	0.6236(7)	0.2630(4)	0.051(2)					

^{a} *U*(eq), one-third of the trace of the orthogonalized *U*.

The hydrogen atoms and the solvent molecules are omitted for clarity. Coordination bond distances and angles are given in Table 3a,b. In both compounds, the metal ion is in a five-coordinated geometry. The dinuclear structure is quite symmetrical, with a mirror plane running through C15, O20 and the bridging anion. In the zinc compound, this mirror plane is

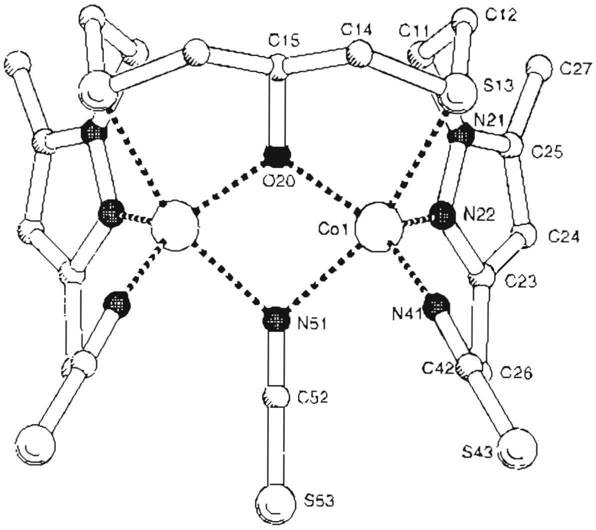

Figure 2. PLUTON projection and atomic labeling of [Co$_2$(bdnol)(NCS)$_3$] (**A**). For clarity the hydrogen atoms and the solvent molecule are omitted.

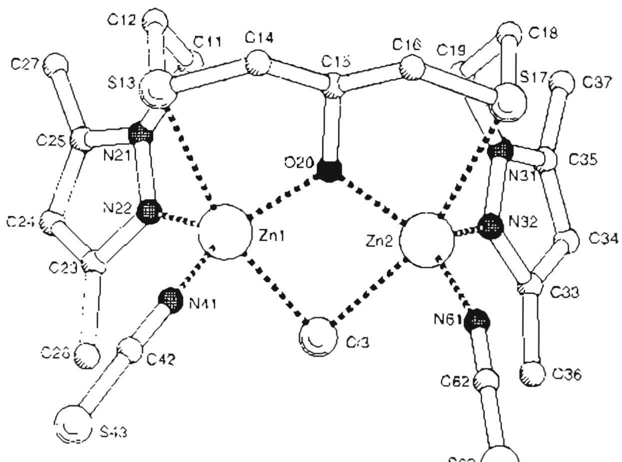

Figure 3. PLUTON projection and atomic labeling of [Zn$_2$(bdnol)Cl(NCS)$_2$] (**B**). For clarity the hydrogen atoms and the solvent molecule are omitted.

noncrystallographic; in the cobalt compound a crystallographic mirror plane is present. The structures resemble that of the nickel chloride compound [Ni$_2$(bdnol)Cl$_3$], which was published earlier.[5] The geometry of the metal ions can best be described as a trigonal bipyramid, in which the thioether sulfur and the bridging anion are in the apical positions. The trigonal plane is then formed by the pyrazole nitrogen, the bridging alcohol, and the terminal anion. The distortions from the ideal trigonal bipyramid are slightly different for each compound as is reflected in the bond angles. The cobalt to nitrogen distance is considerably shorter for the terminal thiocyanate (1.95 Å) than for the bridging thiocyanate (2.18 Å), which is not unusual,[17,18] but the bond angle Co−N−Co (92.2°) is rather small in comparison with those found in other structures.[17,18] The zinc to bdnol bond distances are all slightly longer than those in the cobalt compound, in agreement with the difference in atomic radii. The zinc to sulfur distance (2.67 Å) is much longer than the cobalt to sulfur bond (2.52 Å), but it still can be regarded as a bonding distance. Differences in the geometry will also be caused partly by the difference in the bridging anion. Apart from the described coordination compound, the crystals of both structures also contain acetonitrile in the crystal lattice.

Table 3. Selected Bond Distances (Å) and Angles (deg)

(a) [Co$_2$(bdnol)(NCS)$_3$] (**A**)			
Co(1)−Co(1)′^{a}	3.1368(11)	Co(1)−N(22)	2.026(4)
Co(1)−S(13)	2.5195(15)	Co(1)−N(41)	1.953(4)
Co(1)−O(20)	1.940(2)	Co(1)−N(51)	2.178(4)
S(13)−Co(1)−O(20)	82.28(9)	O(20)−Co(1)−N(51)	79.94(14)
S(13)−Co(1)−N(22)	90.53(11)	N(22)−Co(1)−N(41)	113.82(16)
S(13)−Co(1)−N(41)	92.67(12)	N(22)−Co(1)−N(51)	100.58(18)
S(13)−Co(1)−N(51)	162.02(11)	N(41)−Co(1)−N(51)	95.65(18)
O(20)−Co(1)−N(22)	119.72(17)	Co(1)−O(20)−Co(1)′^{a}	107.88(17)
O(20)−Co(1)−N(41)	126.21(18)	Co(1)−N(51)−Co(1)′^{a}	92.2(2)
(b) [Zn$_2$(bdnol)Cl(NCS)$_2$] (**B**)			
Zn(1)−Zn(2)	3.227(7)		
Zn(1)−Cl(3)	2.41(3)	Zn(2)−Cl(3)	2.46(4)
Zn(1)−S(13)	2.67(4)	Zn(2)−S(17)	2.68(4)
Zn(1)−O(20)	1.96(3)	Zn(2)−O(20)	1.96(2)
Zn(1)−N(22)	2.040(8)	Zn(2)−N(32)	2.006(10)
Zn(1)−N(41)	1.95(3)	Zn(2)−N(61)	2.00(3)
Cl(3)−Zn(1)−S(13)	164.3(13)	Cl(3)−Zn(2)−S(17)	162.7(9)
Cl(3)−Zn(1)−O(20)	83.5(9)	Cl(3)−Zn(2)−O(20)	82.2(10)
Cl(3)−Zn(1)−N(22)	98.8(9)	Cl(3)−Zn(2)−N(32)	97.1(10)
Cl(3)−Zn(1)−N(41)	100.0(15)	Cl(3)−Zn(2)−N(61)	95.7(15)
S(13)−Zn(1)−O(20)	81.5(13)	S(17)−Zn(2)−O(20)	81.3(13)
S(13)−Zn(1)−N(22)	86.3(10)	S(17)−Zn(2)−N(32)	88.1(13)
S(13)−Zn(1)−N(41)	91.9(9)	S(17)−Zn(2)−N(61)	97.0(10)
O(20)−Zn(1)−N(22)	125.8(14)	O(20)−Zn(2)−N(32)	124.0(12)
O(20)−Zn(1)−N(41)	122.3(6)	O(20)−Zn(2)−N(61)	120.8(5)
N(22)−Zn(1)−N(41)	110.7(11)	N(32)−Zn(2)−N(61)	115.0(8)
Zn(1)−Cl(3)−Zn(2)	83.1(11)	Zn(1)−O(20)−Zn(2)	110.9(18)
(c) [Cu$_2$(bdnol)(NO$_3$)$_3$] (**C**)			
Cu(1)−Cu(2)	3.308(5)		
Cu(1)−S(13)	2.674(4)	Cu(2)−S(17)	2.347(4)
Cu(1)−O(20)	1.926(4)	Cu(2)−O(20)	1.919(4)
Cu(1)−O(41)	2.024(5)	Cu(2)−O(42)	2.367(5)
Cu(1)−O(51)	2.004(5)	Cu(2)−O(61)	2.018(4)
Cu(1)−O(52)	2.544(6)	Cu(2)−O(63)	2.676(5)
Cu(1)−N(22)	2.008(5)	Cu(2)−N(32)	1.955(5)
S(13)−Cu(1)−O(20)	82.93(11)	S(17)−Cu(2)−O(20)	86.23(12)
S(13)−Cu(1)−O(41)	90.68(13)	S(17)−Cu(2)−O(42)	92.96(13)
S(13)−Cu(1)−O(51)	104.00(13)	S(17)−Cu(2)−O(61)	168.16(11)
S(13)−Cu(1)−O(52)	158.91(12)	S(17)−Cu(2)−O(63)	115.65(10)
S(13)−Cu(1)−N(22)	92.91(14)	S(17)−Cu(2)−N(32)	90.50(14)
O(20)−Cu(1)−O(41)	98.25(15)	O(20)−Cu(2)−O(42)	85.07(14)
O(20)−Cu(1)−O(51)	172.96(15)	O(20)−Cu(2)−O(61)	91.45(14)
O(20)−Cu(1)−O(52)	118.15(14)	O(20)−Cu(2)−O(63)	94.04(12)
O(20)−Cu(1)−N(22)	90.65(16)	O(20)−Cu(2)−N(32)	174.17(16)
O(41)−Cu(1)−O(51)	83.07(17)	O(42)−Cu(2)−O(61)	98.41(14)
O(41)−Cu(1)−O(52)	86.66(15)	O(42)−Cu(2)−O(63)	151.35(13)
O(41)−Cu(1)−N(22)	170.75(17)	O(42)−Cu(2)−N(32)	99.93(16)
O(51)−Cu(1)−O(52)	54.91(15)	O(61)−Cu(2)−O(63)	52.82(12)
O(51)−Cu(1)−N(22)	87.79(17)	O(61)−Cu(2)−N(32)	90.77(16)
O(52)−Cu(1)−N(22)	86.93(16)	O(63)−Cu(2)−N(32)	83.02(14)
Cu(1)−O(20)−Cu(2)	118.75(15)		
(d) [Cu$_2$(Hbdnol)(NCS)$_2$] (**D**)^b			
Cu(1)−Cu(2)	7.42(1)		
Cu(1)−Cu(2)^c	5.95(1)	Cu(1)−Cu(1)^d	6.00(1)
Cu(1)−Cu(2)^a	5.85(1)	Cu(2)−Cu(2)^e	5.70(1)
Cu(1)−S(13)	2.366(5)	Cu(2)−S(17)	2.364(5)
Cu(1)−N(22)	2.053(6)	Cu(2)−S(43)^b	2.409(5)
Cu(1)−S(53)^a	2.344(5)	Cu(2)−N(32)	2.020(6)
Cu(1)−N(41)	1.980(7)	Cu(2)−N(51)	1.940(7)
S(13)−Cu(1−N(22)	100.3(2)	S(17)−Cu(2)−S(43)^b	114.76(12)
S(13)−Cu(1)−S(53)^a	113.09(12)	S(17)−Cu(2)−N(32)	98.27(18)
S(13)−Cu(1)−N(41)	112.7(2)	S(17)−Cu(2)−N(51)	111.1(2)
S(53)^a−Cu(1)−N(22)	116.2(2)	S(43)^b−Cu(2)−N(32)	111.16(18)
N(22)−Cu(1)−N(41)	112.9(2)	S(43)^b−Cu(2)−N(51)	103.28(18)
S(53)^a−Cu(1)−N(41)	102.26(18)	N(32)−Cu(2)−N(51)	118.9(2)

^{a} At x, $^1/_2 - y$, z. ^{b} $a = x + 1, y, z$; $b = x, y + 1, z$; $c = x, y - 1, z$; $d = -x, -y, 1 - z$; $e = -x, 1 - y, 2 - z$.

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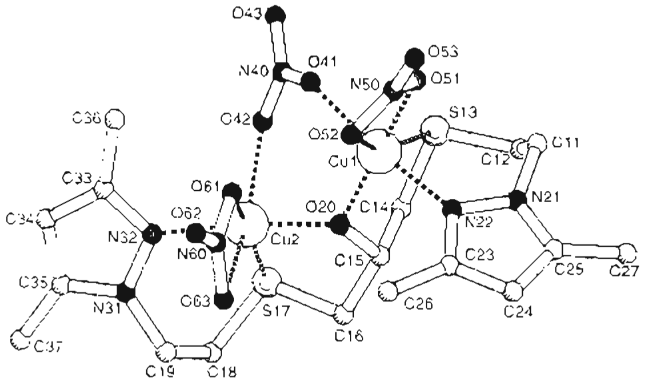

Figure 4. PLUTON projection and atomic labeling of [Cu_2(bdnol)(NO_3)$_3$] (C). For clarity the hydrogen atoms are omitted.

(b) Structure of [Cu_2(bdnol)(NO_3)$_3$] (C). A projection of the structure of C is given in Figure 4. Relevant bond distances and angles are given in Table 3c. As in the structures of A and B, the alcohol group of the ligand bdnol is dehydronated and bridging the two copper ions. Due to the didentate binding of the terminal nitrate groups, the resulting geometry of the copper ions is distorted octahedral. There is no mirror plane in the dinuclear molecule, and the geometry of the two copper ions is significantly different from each other. The ligand is folded in a facial way around Cu(1), but in a meridional fashion around Cu(2). The geometry of Cu(1) is elongated octahedral, with the thioether sulfur (S(13)) and one of the oxygens of the terminal nitrate (O(52)) in the axial positions. The plane is formed by the alkoxide oxygen, the pyrazole nitrogens, and the two remaining nitrate oxygens. The coordination geometry of Cu(2) is also elongated octahedral, but the octahedron is formed in a different way. Now the axis is formed by the oxygen of the bridging nitrate and one of the oxygens of the terminal nitrate. This second oxygen may be regarded as semi-coordinating (distance Cu(2)−O(63) = 2.68 Å). The equatorial plane is formed by the three donors of the ligand bdnol and an oxygen of the terminal nitrate. The two different binding modes of the ligand result in quite different bond distances for the thioether sulfurs, being 2.67 and 2.35 Å for S(13) and S(17), respectively. Such differences have been observed before for thioether−copper bonds.[19]

Structure of [Cu_2(Hbdnol)(NCS)$_2$] (D). A projection of the asymmetric unit with the atomic labeling is given in Figure 5a. Relevant bond distances and angles are given in Table 3d. Notably, unlike the other structures described, the alcohol group of the ligand is not dehydronated and does not bridge the two metal ions; in fact it does not bind to copper at all. However, the ligand as a whole is still able to bind two metal ions. Each copper(I) ion is coordinated to a thioether sulfur and a pyrazole nitrogen from the ligand and a nitrogen of a thiocyanate group. The distorted tetrahedral configuration of the copper ions is completed by a thiocyanate sulfur from a neighboring molecule. An impression of the two-dimensional network which is the result of the bridging thiocyanate groups is given in Figure 5b. As the copper ions are not bridged by the alcohol group of the ligand, the copper to copper distance within the dinuclear molecule is quite large, 7.42 Å. Shorter copper to copper contacts are obtained through the thiocyanate bridges, resulting in distances of 5.95 and 5.85 Å; in fact, even shorter copper to copper distances are observed between the layers (5.7 Å). The noncoordinating alcohol group of the ligand is disordered and is found in two different locations of approximately equal occupation factors.

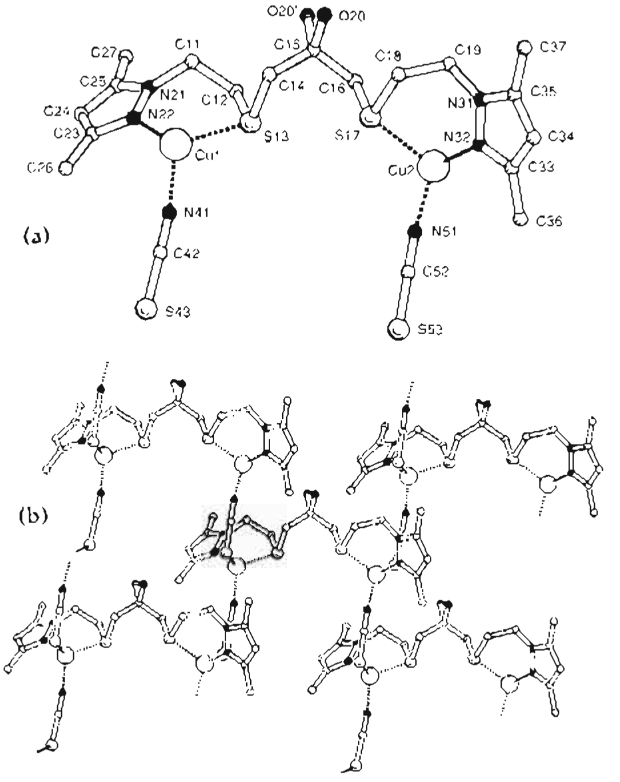

Figure 5. (a) PLUTON projection and atomic labeling of [Cu_2(Hbdnol)(NCS)$_2$] (D). For clarity the hydrogen atoms are omitted. (b) PLUTON projection of a part of the two-dimensional structure formed by [Cu_2(Hbdnol)(NCS)$_2$].

Spectroscopy and Analyses. The composition and spectroscopic data (Ligand field data, infrared and X-ray type) of the coordination compounds obtained with Hbdnol are given in Table 4. Full analysis data are available as supporting information.

Most of the compounds were analyzed as [M_2(bdnol)(anion)$_3$]·solvent, a fact that was surprising at first, since in most cases the addition of a base was not required to obtain the material.

The crystal structures of the dinuclear and the trinuclear nickel chloride compounds have been described earlier.[5] The structure of the dinuclear [Ni_2(bdnol)Cl_3] is comparable to the structures of A and B; the structure of the trinuclear compound [Ni_3(bdnol)Cl_5(EtOH)] is redrawn in Figure 6. The ligand field spectra of these unusual nickel compounds are given in Figure 6. From the unusual color and the ligand field spectrum of the red high-spin nickel chloride compound, a five-coordinate geometry was already expected. The octahedral geometry of the metal ions in the green trinuclear nickel chloride compound was not immediately apparent from the irregular ligand field spectrum, as displayed in Figure 7. The temperature dependence of the magnetic susceptibility of the nickel(II) compounds are plotted in Figure 8 as $\chi_M T$ versus T. The dinuclear compound, [Ni_2(bdnol)Cl_3], exhibits an increase of the $\chi_M T$ product from 2.61 K·cm^3/mol at 260.0 K to 2.88 K·cm^3/mol at 40 K. A rounded maximum is observed at ca. 40 K with a decrease of $\chi_M T$ at lower temperature. For the trimer compound, [Ni_3(bdnol)Cl_5(EtOH)], a large increase of the $\chi_M T$ product is observed from 4.61 K·cm^3/mol at 280.0 K to 12.99 K·cm^3/mol at 5.5 K. A sharp decrease of $\chi_M T$ down to zero occurs below 5.5 K.

The dinuclear halide and thiocyanate compounds all are very similar, as is indicated by the observed X-ray and IR similarities. The cobalt and zinc halide complexes are isomorphous but differ

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Table 4. Summary of the Compounds Obtained with Hbdnol and Their Spectroscopic Data

compound	IR[a]	X-ray[a,b]	LF bands[c] (color)
$[Co_2(bdnol)Cl_3]\cdot MeCN$	I	A	16.6, 11.2, 5.5 (blue)
$[Co_2(bdnol)Br_3]\cdot MeCN$	I	A	17.0, 10.9, 5.5 (blue)
$[Co_2(bdnol)(NCS)_3]\cdot MeCN$	II	B	16.7, 12.2, 5.6 (blue-purple)
$[Co_2(bdnol)(NO_3)_3]\cdot 2MeCN$	III	C	18.3, 7.9 (red-purple)
$[Ni_2(bdnol)Cl_3]\cdot MeCN$	I	D	20.9, 18.6, 11.7, 10.4, 7.5 (red)
$[Ni_3(bdnol)Cl_5(EtOH)]\cdot 3EtOH$	–	–	23.8, 21.7, 13.2, 9.1 (light green)
$[Ni_2(bdnol)Br_3]\cdot 1^1/_2MeCN$	I	E	20.5, 18.3, 11.4, 10.2, 7.5 (red)
$[Ni_2(bdnol)(NO_3)_3]\cdot 2MeCN$	III	C	23.6, 13.7, 8.3 (light green)
$[Cu_2(bdnol)Cl_3]$	–	–	13.5 (very broad) (dark green)
$[Cu_2(bdnol)Cl_3(H_2O)_2]$	–	–	12.9 (very broad) (yellow green)
$[Cu_2(Hbdnol)(NCS)_2]$	–	–	(white)
$[Cu_2(bdnol)(NO_3)_3]$	–	–	14.9, 10.7 (dark green)
$[Zn_2(bdnol)Cl_3]\cdot MeCN$	I′	A	(white)
$[Zn_2(bdnol)Br_3]\cdot MeCN$	I′	A	(white)
$[Zn_2(bdnol)(NCS)_3]$	II′	B	(white)
$[Zn_2(bdnol)Cl(NCS)_2]\cdot {}^1/_2MeCN$	I′	–	(white)
$[Zn_2(bdnol)(NO_3)_3]$	III′	–	(white)
$[Cd_2(bdnol)Cl_3]\cdot MeCN$	I″	–	(white)

[a] The same capital or Roman numeral when identical, primed when very similar; – if no similarities with any of the other compounds is observed. [b] Guinier photographs of crystalline material ("powder patterns"). [c] d-d transitions in 10^3 cm^{-1} (diffuse reflectance).

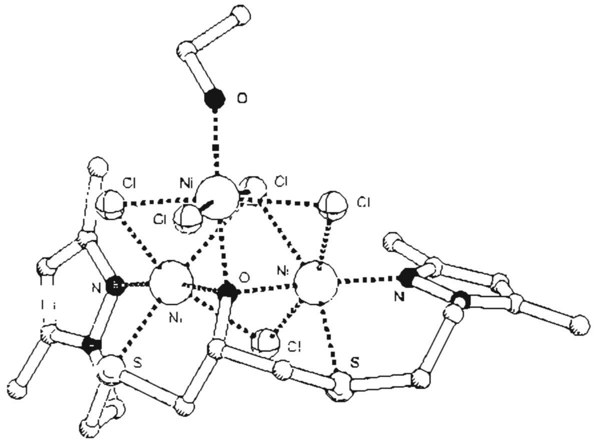

Figure 6. Projection of the trinuclear compound $[Ni_3(bdnol)Cl_5(EtOH)]$.

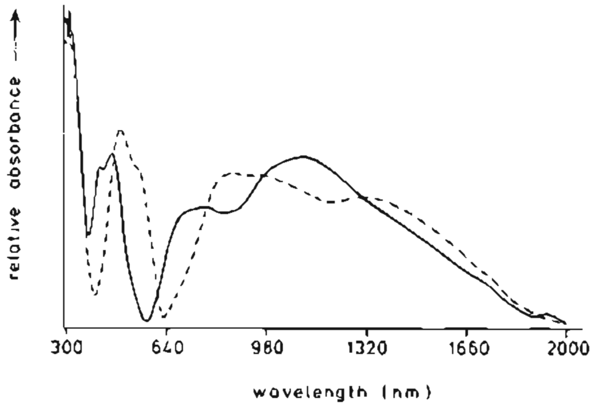

Figure 7. Ligand field spectra (diffuse reflectance) of the red dinuclear compound $[Ni_2(bdnol)Cl_3]$ (dashed line) and the green trinuclear compound $[Ni_3(bdnol)Cl_5(EtOH)]$ (solid line).

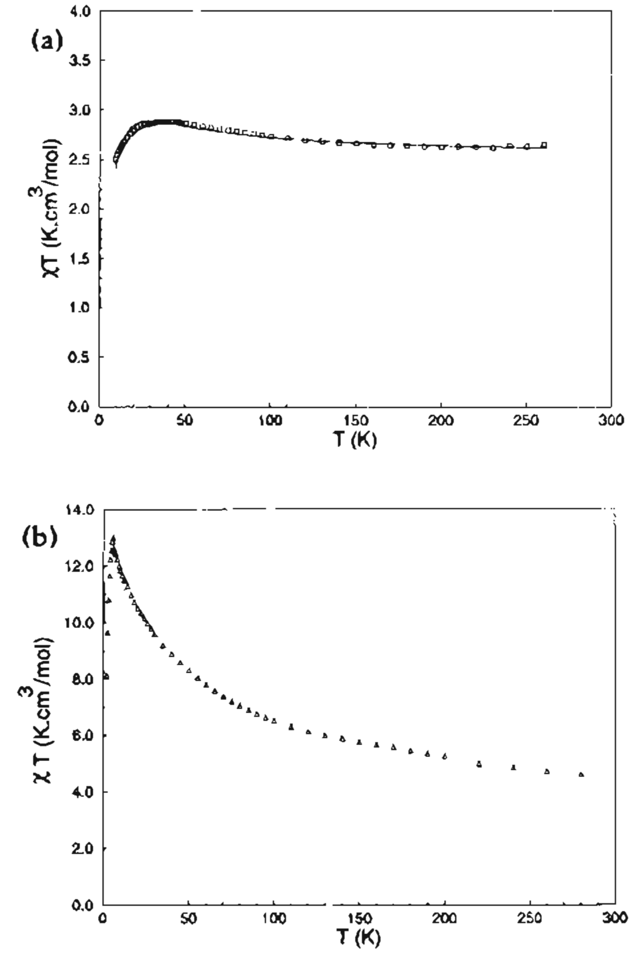

Figure 8. (a) Temperature dependence of the $\chi_M T$ product for $[Ni_2(bdnol)Cl_3]$. The solid line corresponds to the best fit of the experimental data (see text). (b) Temperature dependence of the $\chi_M T$ product for $[Ni_3(bdnol)Cl_5(EtOH)]$.

from the nickel halide compounds. However, similar structures are expected on the basis of the IR spectra, which closely resemble each other. Even the thiocyanate compounds have IR spectra very similar to those of the halide compounds, indicating a similar way of folding for the bdnol ligand. The ligand field spectra of the cobalt chloride, bromide, and thiocyanate compounds are all representative for a five-coordinate geometry, and this geometry is proved by the crystal structure of the cobalt thiocyanate compound. The copper chloride compounds are different from the other metal halides. Two different forms were obtained, one of the same formula as the others and resulting in five-coordinate copper, and one containing two additional water molecules probably bound to the copper ions, resulting in octahedral geometry. The ligand field spectra of these copper halides are dominated by charge-transfer transitions, and therefore, no definite conclusions concerning the geometry of the copper ions can be drawn. The nitrate complexes all belong to a different group, with octahedral geometry of the metal ions. This is clearly shown by the crystal structure for the copper compound and, additionally, by the ligand field spectra of the cobalt and nickel compounds.

EPR spectroscopy showed that the dinuclear copper(II) compounds are diamagnetic at room temperature: only a very weak signal of a paramagnetic impurity was observed. A magnetic susceptibility measurement of $[Cu_2(bdnol)(NO_3)_3]$ showed that it remains diamagnetic up to its melting point (150 °C), indicative of a $-2J$ value higher than 1000 cm^{-1}. Some attempts to study the redox chemistry of the copper complexes have been undertaken. The spontaneous reduction observed in the synthesis of the copper complexes suggests that copper(I) is stabilized by this ligand, which should be reflected in high redox potentials for the Cu(II)/Cu(I) couple. Cyclovoltammetry, however, proved difficult. The cyclovoltammograms obtained for the dinuclear copper(II) chloride compounds show that upon dissolution of the complex already part of the copper(II) ions is reduced. This was deduced from the fact that no potential with zero current can be found, indicating that at all potentials both Cu(I) and Cu(II) ions are present in solution. Mixed-valence Cu(I)/Cu(II) dinuclear complexes have not been obtained.

Discussion

Syntheses. The synthesis of the ligand Hbdnol was first attempted via the reaction of *N*-(2-(*p*-toluenesulfonyl)ethyl)-3,5-dimethylpyrazole with 1,3-dimercapto-2-propanol according to a literature procedure.[6] However, the dithiol is not commercially available and must be prepared from 1,3-dichloro-2-propanol and sodium trithiocarbonate.[20] Difficulties were encountered in obtaining the pure dithiol, and an alternative route to the ligand was developed. The synthesis of *N*-(2-mercaptoethyl)-3,5-dimethylpyrazole proceeded without problems, in a reasonable yield. The reaction of this thiol with 1,3-dichloro-2-propanol was at first carried out in absolute ethanol with sodium ethoxide according to literature procedures,[21] but the reaction in a water/thf mixture with sodium hydroxide appeared to proceed more smoothly and in almost quantitative yields. This new reaction path to pyrazole−thioether ligands opens the road to the development of new chelating ligands.

The synthesis of the coordination compounds is rather straightforward. The initial aim in using this particular ligand was to obtain mononuclear, square-planar compounds in which one of the axial sites would be protected for coordination by steric hindrance of the (intended to be noncoordinating) alcohol group. Instead, a range of dinuclear compounds has been isolated. It was rather a surprise that, even without the addition of a base, the alcohol group is dehydronated and dinuclear compounds are formed. Spontaneous dehydronation has been observed before with similar ligands, but usually a base is added in order to obtain dinuclear complexes, while without the addition of a base a mononuclear compound can be isolated.[22] Recently, a crystal structure of such a mononuclear compound with a similar alcohol- and pyrazole-containing ligand has been obtained.[23]

The dinuclear cobalt, nickel, zinc, and cadmium halides were obtained as fluffy material, which crystallized as very long and thin needles. Attempts to obtain better crystals from ethanol surprisingly yielded a different compound for nickel chloride, the unprecedented trinuclear compound $[Ni_3(bdnol)Cl_5(EtOH)]$ (Figure 6).[5]

Another unexpected compound is the mixed-anion zinc complex, $[Zn_2(bdnol)Cl(NCS)_2]$: the crystal structure of this compound was determined because of the differences in the thiocyanate region in the IR spectra which could not be explained. The bridging chloride found in the structure explained the absence of an absorption for a bridging thiocyanate, but now the synthesis of the compound had to be reexamined. It was deemed most likely that a small impurity of sodium chloride (from the ligand synthesis performed in ethanol with sodium ethoxide) had helped the crystallization of the zinc complex. The $[Zn_2(bdnol)(NCS)_3]$ compound proved difficult to crystallize; however, it was finally prepared from a very concentrated solution. In contrast, when 1 equiv of ammonium chloride is added together with the ammonium thiocyanate, the zinc mixed-anion complex is readily reproduced. A dinuclear nickel thiocyanate compound could not be isolated, probably because of the high solubility of the complex in the solvents used, as is the case for the zinc thiocyanate compound.

Furthermore, use of the acetate ion, which is known for its bridging properties, surprisingly did not result in coordination compounds with the ligand Hbdnol.

Copper(I) compounds are stabilized by the ligand Hbdnol, as is demonstrated by the synthesis of $[Cu_2(Hbdnol)(NCS)_2]$. Initially, this compound was synthesized from copper(II) without the addition of a reducing agent such as ascorbic acid; a copper(II) thiocyanate complex could not be obtained, and the solution slowly bleached, indicating reduction of the copper ions. The addition of ascorbic acid speeds up the reduction. The copper(I)-containing solution is very stable: even when the solution is standing in air for weeks, the copper(I) ions are not oxidized. Similar observations, but less pronounced, have been made with the copper halides. Copper(II) bromide yields mixtures of copper(I) and copper(II) complexes: starting from copper(II), the solution slowly bleaches, but a mixture of copper(I) and copper(II) compounds eventually precipitate. The copper(I) chloride solution, however, is not stable and slowly oxidizes back to the copper(II)-containing solution. Two different modifications of a copper(II) chloride coordination compound were isolated. Attempts to obtain the copper(I) chloride or copper(I) bromide compound in anaerobic conditions were not undertaken. With other pyrazole-containing ligands it has been observed that copper(I) compounds are stabilized and can even be prepared from copper(II) in aerobic conditions.[24] The nature of the reducing equivalents can only be guessed. The spontaneous reduction of copper(II) to copper(I) usually is found with thiocyanate or bromide salts, suggesting that these anions play a role in the reduction of the copper ions. Studies to unravel the stoichiometry in these spontaneous reductions have not yet been undertaken.

Structures. The structures described in this paper all show some unusual features, each of which has been reported for only a few cases or has not been reported before.

Only a limited number of structures with N-bridging thiocyanate have been published. That the cobalt and zinc thiocyanate complexes had to contain such a bridging group was expected from the elemental analyses and the similarities with the halide compounds. Furthermore, both compounds showed two distinct bands in the thiocyanate region (2100−1900 cm^{-1}) of the IR spectra (see below). No zinc compounds with

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N-bridging thiocyanates have been reported so far, but the IR similarities are conclusive for the case described in this paper.

Although the X-ray structure of compound **B** has no bridging thiocyanate, it also has its unusual feature: the thioether to zinc distances are rather long (2.67 and 2.68 Å), but they must be regarded as bonding. In the compounds described in this paper, an elongation of the metal to sulfur bond in going from nickel to cobalt to zinc (2.46, 2.52, 2.67 Å) was observed, in agreement with previous observations with other thioether-containing ligands.[25-27] So far, only very few crystal structures of zinc compounds with coordinating thioether sulfurs have been reported. In our group, several structures in which the thioether group does not participate in coordination to the zinc ion have been reported.[6,28] In our laboratory, only one other structure with thioether sulfurs coordinating to zinc was found, but the X-ray data were too poor for the structure to be published.[25,29] Some structures with coordinating thioethers from a macrocycle were reported,[30] but when the constraints within the macrocyclic ring are released, the thioethers move away from the zinc ion.[31] Another example is bis(methionine)zinc, where only the amine and carboxylate groups are coordinated to the zinc ion.[32] However, some examples where the thioether group is coordinated although not constrained by the ligand have also been reported,[33,34] although the bond distances in these compounds are very long (2.63–2.8 Å). One example of a zinc compound with only thioether donor atoms was recently given by bis(1,4,7-trithiacyclononane)zinc^{2+}.[35] In this compound the zinc ion is octahedrally coordinated by six thioether donors at a comparatively short distance (2.49 Å), in view of the other zinc structures.

Several structures have been reported with bridging nitrate groups, but the present structure is quite surprising, as an analogous acetate compound could not be obtained. Acetate bridges are encountered more often than nitrate bridges.

Going from the "smaller" bridging anion to the largest one (thiocyanate–chloride–nitrate), the bond angle around the alkoxide oxygen (M–O(20)–M) increases from 107 to 118°, accompanied by an increase in the metal to metal distance from 3.14 to 3.31 Å. If there is no second bridging group present, the bond angle increases up to 140° with an accompanying metal to metal distance of 4.13 Å.[36]

In the unique polymeric copper(I) thiocyanate compound, the alcohol group is not bridging the copper ions within the ligand, resulting in an *intra* copper to copper distance of 7.4 Å. Shorter *inter* copper to copper distances (5.85 and 5.95 Å) are obtained through the end-to-end bridging thiocyanate groups, and even shorter copper to copper contacts are observed between the layers (5.7 Å). To our knowledge, polymeric copper(I) structures in which the copper ion is coordinated to a chelating ligand and bridged by thiocyanate ions have not been reported before. Some mixed-valence copper(II)–copper(I) compounds have been reported,[37,38] in which the ligand is coordinated to the copper(II) ions and a polymeric structure is formed by thiocyanate bridges to copper(I). Also, some structures in which discrete cations exist alongside polymeric $[Cu_2(NCS)_3]^-$ anions have been reported.[39,40]

Spectroscopy. In the infrared spectra, the dinuclear halide and thiocyanate compounds show a lot of similarities, indicating similar folding of the ligand bdnol in these compounds. The thiocyanate region of $[Co_2(bdnol)(NCS)_3]$ and $[Zn_2(bdnol)(NCS)_3]$ show quite unusual features: the cobalt thiocyanate compound **A** shows a broad band for νCN at 2080 cm^{-1} originating from the terminal N-bonded thiocyanate and a sharp band for νCN at 1993 cm^{-1} due to the bridging thiocyanate; for the analogous zinc compound these bands appear at 2085 and 2010 cm^{-1}, respectively. In the zinc mixed-anion compound $[Zn_2(bdnol)Cl(NCS)_2]$, only the terminal νCN at 2080 cm^{-1} is observed. The polymeric copper(I) thiocyanate compound, representing an end-to-end N, S bridging mode of the thiocyanate, shows a rather sharp νCN at 2100 cm^{-1}.

Although the color of the cobalt chloride and bromide complexes (bright blue) might suggest tetrahedral Co(II) with the thioether sulfurs noncoordinating, the ligand field spectra of these compounds clearly indicate that the geometry of the cobalt ions is five-coordinate. The ligand field data of the cobalt halide compounds are close to those found for the blue-purple cobalt thiocyanate complex, and the five-coordinate geometry of the cobalt ion is confirmed by the X-ray determination of **A**. The ligand field spectrum of the cobalt nitrate compound can be interpreted with an octahedral geometry, although the values of the transitions (Table 4) are indicative of very weak donating groups.

Of the nickel compounds, only $[Ni_2(bdnol)(NO_3)_3]$ shows a straighforward ligand field spectrum, indicating a "normal" octahedral geometry of the nickel ions. The spectra of the red dinuclear nickel halides and the green trinuclear nickel compound are shown in Figure 7. The red nickel compounds appeared to be high spin, so that a square-planar coordination could be ruled out. From the ligand field maxima, a five-coordination was considered to be the most likely geometry[41] for the nickel ions in these dinuclear complexes, as was confirmed by the X-ray structure determination.[5] The ligand field spectrum of the trinuclear compound $[Ni_3(bdnol)Cl_5(EtOH)]$ (Figure 7) did not give any clue for what the geometry of the nickel ions might be: the structure determination of the unique compound showed the presence of three independent nickel ions in octahedral geometry, giving insight into the irregular patterns of the electronic spectrum.

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The ligand field spectra of the copper(II) complexes all show very broad bands, out of which no definite conclusions regarding the geometry of the copper ions can be drawn. The X-ray determination of the compound $[Cu_2(bdnol)(NO_3)_3]$ shows that the copper ions are in an elongated octahedral environment. From similarities of the various compounds and the elemental analyses it is safe to suggest that the coordination environments of the copper ions in $[Cu_2(bdnol)Cl_3]$ and $[Cu_2(bdnol)Cl_3(H_2O)_2]$ are five-coordinate and octahedral, respectively.

All three copper(II) compounds are diamagnetic at room temperature: the EPR spectra only show a very weak signal of traces of monomeric impurities. A magnetic susceptibility measurement of $[Cu_2(bdnol)(NO_3)_3]$ showed that this compound remains diamagnetic up to its melting point (decomposition) at 150 °C, indicating a strong antiferromagnetic interaction between the two copper ions ($-2J > 1000$ cm^{-1}).

Magnetic Susceptibility Measurements of the Nickel Chloride Compounds. The temperature dependence of the magnetic susceptibility of the nickel(II) compounds differs from that of the copper(II) system. Thus, the dimer compound, $[Ni_2(bdnol)Cl_3]$, exhibits the typical signature of ferromagnetic interaction between nickel(II) ions, as deduced from the increase of the $\chi_M T$ product upon cooling from room temperature to 40 K. At lower temperature, the drop of $\chi_M T$ may be related to antiferromagnetic interdimer interactions and/or the influence of a zero-field splitting, stabilizing $s_z = 0$ with respect to $s_z = \pm 1$. Assuming that both effects may be responsible for the observed behavior, a fit of the experimental data was made by using the Ginsberg expression[42] deduced from the spin Hamiltonian:

$$H = -2JS_1S_2 - D(S_{1z}^2 + S_{2z}^2) - g\mu_B H(S_{1z} + S_{2z}) - 2zjS_z\langle S\rangle$$

in which J and j refer to the intra- and interdimer interactions, respectively, and D is the anisotropy parameter.

Clearly, this system is at first overparametrized, so that a unique set of parameters is illusive. In fact, it appears that g and J refine more efficiently at high temperature (above 50 K), while the low temperature behavior is mainly due to the influence of D and j. Then, we obtain reliable values of the parameters ($J = 9.0$ K, $j = -1.29$ K, $D = -0.22$ K, and $g = 2.25$; 1 K = 0.6951 cm^{-1}) giving a satisfying agreement between theory and experiment, as shown in Figure 8a. This result clearly confirms the ferromagnetic character of the intradimer interaction and the antiferromagnetic ordering between adjacent dimers.

In the case of the trinuclear compound, $[Ni_3(bdnol)Cl_5(EtOH)]$, the behavior somewhat differs since $\chi_M T$ increases up to 13 K·cm^3/mol (Figure 8b). This value is much larger than the expected value for isolated ferromagnetic units ($\chi_M T$ should not exceed 6 K·cm^3/mol at low temperature). Such behavior shows that the dimensionality of the basic unit is likely 1d or 2d and not 0d as expected. At low temperature, a transition to a long-range antiferromagnetic order occurs at $T = 5.5$ K, giving a drop of $\chi_M T$ to zero.

Conclusion

This paper describes a new, versatile ligand, which was designed originally to form mononuclear four- or five-coordinate nickel compounds as model systems for hydrogenases. A variety of dinuclear complexes, including a dinuclear Cu(I) compound, has been obtained, as well as a unique trinuclear nickel compound, in which the dehydronated alcohol group of the ligand is bridging between all three nickel ions.

The ligand Hbdnol, originally aimed for metal complexes mimicking hydrogenase, in fact has turned out to be a very powerful dinucleating ligand, which yields complexes that may be mimics for several enzymes with two metal ions in the active site, such as tyrosinase and urease. The enzyme urease contains two nickel ions in each protein subunit, and it is believed that the nickel ions are in close proximity.[2,3] EXAFS measurements of the nickel site in urease have suggested that a dinuclear site with at least some histidine ligands is present.[3] Recently, the design and synthesis of model systems for urease have gained in interest[43,44] and some of the ligands used in these model studies resemble the ligand bdnol, as they contain a bridging alcohol or phenol group.[43]

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Supporting Information Available: Table of elemental analyses of the compounds, crystallographic data, bond distances, bond angles, hydrogen coordinates, and anisotropic temperature factors and ORTEP projections of the structures (32 pages). Ordering information is given on any current masthead page.

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