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Synthesis and Spectroscopic Studies on Transition-metal Nitrates and Thiocyanates of a Chelating Imidazole-thioether Ligand. The Crystal Structures of Diaquabis[5-methyl-4-(ethyl-mercaptomethyl)imidazole]nickel(II) Dinitrate, Diaquabis[5-methyl-4-(ethyl-mercaptomethyl)imidazole] copper(II) Dinitrate and Bis[5-methyl-4-(ethyl-mercaptomethyl)imidazole]bis(thiocyanato-*N*)cobalt(II)

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Abstract

The synthesis and characterization of some monomeric transition-metal coordination compounds with the novel bidentate ligand 5-methyl-4-(ethyl-mercaptomethyl)imidazole (abbreviated memi) are described, viz. $[M(memi)_2(H_2O)_2](NO_3)_2$ and $M(memi)_2(NCS)_2$ with M = Co, Ni, Cu. Single crystals of $[Ni(memi)_2(H_2O)_2](NO_3)_2$ (**A**), $[Cu(memi)_2(H_2O)_2](NO_3)_2$ (**B**) and $Co(memi)_2(NCS)_2$ (**C**) were used in structure determinations. The three compounds all crystallize in the monoclinic space group $P2_1/n$ with $Z = 2$. The cell dimensions for compound **A** are $a = 10.402(2)$, $b = 13.589(4)$, $c = 8.476(3)$ Å, $\beta = 108.35(2)°$, $V = 1137.21$ Å^3 and $D_x = 1.551$ g cm^{-3}. The cell dimensions of compound **B** are $a = 10.451(3)$, $b = 13.430(5)$, $c = 8.757(4)$ Å, $\beta = 109.24(3)°$, $V = 1160.35$ Å^3 and $D_x = 1.53$ g cm^{-3}. The cell dimensions for compound **C** are $a = 12.147(7)$, $b = 9.096(4)$, $c = 10.363(4)$ Å, $\beta = 102.14(4)°$, $V = 1119.27$ Å^3, and $D_x = 1.447$ g cm^{-3}. The structures were solved by heavy-atom techniques and refined by least-squares methods to residual R_w values of 0.032 (**A**), 0.033 (**B**) and 0.046 (**C**). The coordination geometry of the metal ion in all compounds is distorted octahedral. In compounds **A** and **B** the metal ion is lying on a centre of symmetry and is surrounded by two thioether sulfur atoms, two imidazole nitrogen atoms and two oxygen atoms from water molecules. In contrast to the nickel ion in structure **A** the copper ion in compound **B** has a significantly elongated octahedral geometry in the direction of the oxygen molecules. The compound with the much stronger coordinating anion, NCS (compound **C**) resembles the structures of **A** and **B** in having the same coordination geometry with the thiocyanate anions coordinating instead of the water molecules.

Introduction

The fascinating properties of the blue copper proteins initiated the preparation of model systems to mimic the environment of the copper ion in those proteins [1]. For this purpose chelating ligands containing both sulfur- and nitrogen-donor atoms, mimicking the histidine nitrogens and cysteine thiolate or methionine thioether sulfurs, were developed. These ligands were subsequently used in the synthesis of coordination compounds with copper [2]. Recently, a new, facile route to obtain imidazole-thioether containing ligands has been developed [3]. The coordinating behaviour of the ligands 1,6-bis(5-methyl-4-imidazolyl)-2,5-dithiahexane (bidhx) and 1,7-bis(5-methyl-4-imidazolyl)-2,6-dithiaheptane (bidhp) towards the transition metals cobalt, nickel, copper, and zinc were studied in detail [4, 5]. In addition to copper, divalent cobalt, nickel and zinc were also used to obtain coordination compounds to use their spectroscopic properties in elucidating the coordination behaviour of the ligands.

To investigate whether the $-(CH_2)_n-$ bridge between the two thioether sulfurs in these ligands is essential for their coordination mode, the bridge was 'broken' by synthesizing the new ligand, 5-methyl-4-(ethyl-mercaptomethyl)imidazole (abbreviated memi). The coordination compounds of this ligand with the divalent transition-metal ions of cobalt, nickel and copper with the nitrate and thiocyanate anions are described in the present contribution. To obtain accurate data on the coordination geometry, X-ray structure determinations of a few representative compounds, viz. $[Ni(memi)_2(H_2O)_2](NO_3)_2$, $[Cu(memi)_2(H_2O)_2](NO_3)_2$ and $[Co(memi)_2(NCS)_2]$ were performed.

Experimental

Starting Materials

The synthesis of the ligand 5-methyl-4-(ethyl-mercaptomethyl)imidazole (abbreviated memi) was

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performed from ethanethiol and 5-methyl-4-hydroxymethylimidazole hydrochloride by a method described before [3]. All chemicals were commercially available, were of sufficient purity, and were used without further treatment.

Synthesis of the ligand

Equivalent amounts of 5-methyl-4-hydroxymethylimidazole hydrochloride (0.1 mol) and of ethanethiol (0.1 mol) were refluxed at 40 °C for 4 h in 100 ml of acetic acid. The acid solvent was removed with a vacuum rotary evaporator, rendering an off-white precipitate. This product was recrystallized by dissolving the crude product in 15 ml of ethanol. Upon addition of 10 ml acetone the pure white product precipitated. This intermediate product, the hydrochloride salt of memi, was characterized by infrared and NMR spectroscopy; melting point (m.p.) = 178–180 °C.

The free ligand was obtained as a white crystalline product by treating the solution of memi hydrochloride salt in 15 ml water with an equivalent amount of 25% ammonia and cooling the reaction mixture to 4 °C (m.p. = 110–112 °C). The compound was characterized by infrared and NMR spectroscopy. The ^1H NMR spectrum (solvent $CD_3OD/CDCl_3$, internal reference $SiMe_4$) showed the following signals: 1.21 ppm (t, 3H) and 2.43 ppm (q, 2H) of the ethyl group, 2.20 ppm (s, 3H) methyl group, 3.62 ppm (s, 2H) methylene, 7.41 ppm (s, 1H) imidazole-2H. This method gives good yields of the ligand memi (73%).

Synthesis of the coordination compounds

The nitrate coordination compounds were prepared by dissolving the appropriate hydrated metal nitrate (1 mmol) in 15 ml of ethanol and adding a solution of the ligand memi (2 mmol) in 15 ml of ethanol to this solution. For the preparation of the coordination compounds with the thiocyanate anion the following procedure was followed. A solution of the corresponding hydrated metal nitrate (1 mmol) in 10 ml of ethanol was added to a solution of the ligand memi (2 mmol) and NH_4SCN (2 mmol) in 20 ml of ethanol.

When the mixture was allowed to stand at room temperature solid compounds formed, which were collected by filtration. In some cases, evaporation of part of the solvent was necessary to induce crystallization.

Analyses

Metal analyses were carried out complexometrically with Na_2H_2edta as the complexing agent [6].

Spectroscopic Measurements

Infrared spectra in the 4000–180 cm^{-1} range of the samples pelleted in KBr 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 Perkin-Elmer 330 spectrophotometer fitted with a reflectance attachment, with MgO as a reference and equipped with a PE data station.

Electron paramagnetic resonance spectra of the crystalline copper compounds were obtained with a Varian E-3 spectrophotometer at X-band frequencies at room temperature. Proton nuclear magnetic resonance spectra were recorded on a JEOL PS-100 instrument employing a frequency of 99.5 MHz.

X-ray powder diagrams of the compounds were obtained with a Guinier type camera using Cu Kα radiation.

Crystal Data

Crystal and refinement data of $[Ni(memi)_2(H_2O)_2](NO_3)_2$ (**A**), $[Cu(memi)_2(H_2O)_2](NO_3)_2$ (**B**) and $Co(memi)_2(NCS)_2$ (**C**) are collected in Table 1.

Data Collection and Processing

The data collection of the crystals was carried out on a four-circle Enraf-Nonius CAD4 diffractometer. The equipment operated in the ω/θ mode, and graphite-monochromatized Mo Kα radiation was used. The cell dimensions were determined from the setting angles of 24 reflections. For all crystals the intensities were corrected for Lorentz and polarization effects. Absorption correction was not applied as the variations in transmission coefficients and the values of μ were not too high.

The scanning rate was adjusted to the required precision of $\sigma(I)/I = 0.01$, with a maximum scan time of 60 s/reflection. The instrument and crystal stability were checked every 5400 s of radiation time by three reference reflections: no significant changes in the intensities were observed.

Structure Analyses and Refinement

The structures were solved by normal heavy-atom procedures and refined by full-matrix least-squares calculations. The calculations were performed on the Leiden University Mainframe Computer (Amdahl 5860). The position of the metal ion in all three structures was determined by symmetry considerations. The positions of the other non-hydrogen atoms were located using the program AUTOFOUR [7]. 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 the literature [8]. Hydrogen atoms were located from difference-Fourier maps, except H(163) in the structure of compound A, which was calculated. The thermal parameters of the hydrogen atoms were coupled to each other and refined isotropically (final values 6.93 Å^2 for **A**, 6.76 Å^2 for **B** and 6.05 Å^2 for **C**. The thermal parameters of the

TABLE 1. Crystal and refinement data of the compounds $[Ni(memi)_2(H_2O)_2](NO_3)_2$ (**A**), $[Cu(memi)_2(H_2O)_2](NO_3)_2$ (**B**) and $Co(memi)_2(NCS)_2$ (**C**)

	A	B	C
Formula	$NiC_{14}H_{28}N_6O_8S_2$	$CuC_{14}H_{28}N_6O_8S_2$	$CoC_{16}H_{24}N_6S_4$
Formula weight	531.24	536.08	487.581
a (Å)	10.402(2)	10.451(3)	12.147(7)
b (Å)	13.589(4)	13.430(5)	9.096(4)
c (Å)	8.476(3)	8.757(4)	10.363(4)
α (°)	90	90	90
β (°)	108.35(2)	109.24(3)	102.14(4)
γ (°)	90	90	90
V (Å^3)	1137.21	1160.35	1119.27
F(000)	557.12	559.07	507.48
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	2	2	2
D_x (g/cm^3)	1.55	1.53	1.45
μ (cm^{-1})	10.82	11.62	11.36
Transmission coefficients (min., max.)	97, 102	95, 105	93, 105
Crystal dimensions (mm)	0.13 × 0.15 × 0.45	0.23 × 0.25 × 0.30	0.23 × 0.25 × 0.25
Reference reflections	510; $1\bar{7}0$; $45\bar{1}$	$24\bar{4}$; $13\bar{4}$; $2\bar{3}3$	$6\bar{2}\bar{2}$; $\bar{3}43$; $51\bar{4}$
h Values	−14 to 14	−14 to 14	−17 to 17
k Values	0 to 19	0 to 18	0 to 12
l Values	0 to 11	−12 to 12	0 to 14
Scan range θ	2.0 to 30.0	2.0 to 30.0	2.0 to 30.0
No. measured reflections	3647	3720	3623
No. unique reflections	3441	3514	3453
No. used in refinement[a]	1672	1668	2130
R_f[b]	0.0303	0.0306	0.0386
R_w[c]	0.0316	0.0325	0.0457
Max., min Δ_ρ excursions in final difference Fourier (e/Å^3)	0.26–0.28	0.32–0.22	1.08–0.89

[a] $I > 2\sigma(I)$. [b] $R_f = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

non-hydrogen atoms were refined anisotropically. The function minimized was $\Sigma w(||F_o| - |F_c||)^2$ with $1/\sigma^2(F)$. The final conventional discrepancy index R_f and the weighted factor R_w are given in Table 1. The fractional coordinates of the non-hydrogen atoms of structure **A**, **B** and **C** are listed in Table 2. Selected bond distances, selected bond angles and hydrogen bond distances of the three structures are given in Table 3. See also 'Supplementary Material'.

Results and Discussion

General Considerations

Colours, X-ray and infrared types, and metal content of the coordination compounds with the ligand memi are listed in Table 4; ligand field absorption bands and EPR data are listed in Table 5. From the infrared spectra and the X-ray powder diagrams it is obvious that the cobalt and nickel compounds are isomorphous. The details of the spectral data will be discussed after the description of the crystal structures.

The nickel and copper nitrates showed different X-ray and IR patterns (see Table 4), but the structure of compound **A**, $[Ni(memi)_2(H_2O)_2](NO_3)_2$, resembles the structure of compound **B**, $[Cu(memi)_2(H_2O)_2](NO_3)_2$, very much. Because of this resemblance, these structures are discussed together. The structure of compound **C**, $Co(memi)_2(NCS)_2$, resembles the structures of compounds **A** and **B** by having the same kind of coordination geometry, but with the thiocyanate anion coordinating instead of a water molecule.

The X-ray Structures of $[M(memi)_2(H_2O)_2](NO_3)_2$ (A and B)

The asymmetric unit consists of one half of a molecule of $[M(memi)_2(H_2O)_2]^{2+}$ and a nitrate ion. The metal ion lies on a centre of symmetry and is surrounded by two nitrogens, two sulfurs and two oxygens in a distorted octahedral geometry. An ORTEP [9] projection of the molecule $[M(memi)_2(H_2O)_2](NO_3)_2$ is given in Fig. 1. Although the X-ray diagrams and IR spectra of compounds **A** and **B** are different, the two molecular structures appear to be almost the same. The two structures are so much

TABLE 2. Fractional coordinates (×10^5 for Ni(01), Cu(01), Co(01); others ×10^4) and isotropic thermal parameters (×10^3 for Ni(01), Cu(01), Co(01); others ×10^2 Å^2) of the non-hydrogen atoms in [Ni(memi)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**A**), [Cu(memi)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**B**), and in [Co(memi)$_2$(NCS)$_2$] (C)[a]

Atom	x/a	y/b	z/c	B_{iso}
A				
Ni(01)	100000	0	100000	2610(13)
O(30)	10060(2)	717(1)	7809(2)	349(5)
C(07)	11839(3)	2740(2)	10293(5)	661(13)
C(08)	10421(3)	2543(2)	10290(4)	399(9)
S(09)	10462(1)	1533(1)	11702(1)	313(2)
C(10)	8792(2)	1582(2)	11929(4)	340(8)
N(11)	5881(2)	660(2)	8642(3)	387(7)
C(12)	6910(3)	153(2)	8408(4)	364(8)
N(13)	8061(2)	422(2)	9527(3)	289(5)
C(14)	7731(2)	1129(2)	10503(3)	288(7)
C(15)	6380(3)	1283(2)	9975(4)	328(7)
C(16)	5499(3)	1930(2)	10610(4)	484(10)
N(20)	12562(2)	458(2)	16051(3)	316(6)
O(21)	11437(2)	177(2)	15208(3)	543(7)
O(22)	13570(2)	286(2)	15626(3)	654(9)
O(23)	12711(2)	898(2)	17375(3)	524(7)
B				
Cu(01)	100000	0	100000	3113(14)
C(07)	11850(3)	2682(3)	10293(5)	630(12)
C(08)	10452(3)	2494(2)	10347(4)	449(9)
S(09)	10518(1)	1478(1)	11734(1)	347(2)
C(10)	8862(2)	1517(2)	11975(3)	373(8)
N(11)	5965(2)	662(2)	8630(3)	394(7)
C(12)	6997(3)	170(2)	8403(4)	375(8)
N(13)	8138(2)	411(2)	9548(3)	313(6)
C(14)	7803(3)	1093(2)	10531(3)	313(7)
C(15)	6448(3)	1256(2)	9973(4)	359(8)
C(16)	5550(3)	1892(2)	10582(4)	522(10)
N(20)	12673(3)	475(2)	16071(4)	426(8)
O(21)	11513(2)	222(2)	15262(3)	597(8)
O(22)	13640(2)	253(2)	15643(3)	697(9)
O(23)	12872(2)	958(2)	17338(3)	597(8)
O(30)	10013(2)	854(1)	7546(2)	449(6)
C				
Co(01)	100000	0	100000	1976(11)
C(07)	11712(3)	4854(4)	11224(4)	418(9)
C(08)	11197(3)	3559(3)	10451(3)	308(8)
S(09)	11187(1)	1924(1)	11456(1)	242(2)
C(10)	10084(2)	2356(3)	12340(3)	286(7)
N(11)	7137(2)	2277(3)	10666(3)	287(6)
C(12)	7618(2)	1256(3)	10032(3)	260(7)
N(13)	8706(2)	1187(2)	10513(2)	214(5)
C(14)	8933(2)	2211(3)	11520(3)	233(6)
C(15)	7957(2)	2906(3)	11618(3)	278(7)
C(16)	7724(3)	4086(4)	12519(4)	491(12)
N(20)	10179(2)	−1231(3)	11767(2)	280(6)
C(21)	10346(2)	−1843(4)	12750(3)	290(7)
S(22)	10590(1)	−2746(2)	14152(1)	653(4)

[a] The estimated standard deviations are given in parentheses.

TABLE 3. Geometry of [Ni(memi)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**A**), [Cu(memi)$_2$(H$_2$O)$_2$](NO$_3$)$_2$ (**B**) and [Co(memi)$_2$(NCS)$_2$] (C), selected bond distances (Å), selected bond angles (°) and hydrogen bond distances (Å)[a]

A	
Ni(01)–O(30)	2.116(2)
Ni(01)–S(09)	2.4929(7)
Ni(01)–N(13)	2.012(2)
C(07)–C(08)	1.499(4)
C(08)–S(09)	1.813(3)
S(09)–C(10)	1.808(2)
C(10)–C(14)	1.490(4)
N(11)–C(12)	1.340(3)
N(11)–C(15)	1.376(4)
C(12)–N(13)	1.324(3)
N(13)–C(14)	1.379(3)
C(14)–C(15)	1.351(3)
C(15)–C(16)	1.488(4)
O(30)–Ni(01)–S(09)	94.01(5)
O(30)–Ni(01)–N(13)	89.91(8)
O(30)–Ni(01)–S(09)′	85.99(5)
O(30)–Ni(01)–N(13)′	90.09(8)
S(09)–Ni(01)–N(13)	82.84(6)
S(09)–Ni(01)–O(30)′	85.99(5)
S(09)–Ni(01)–N(13)′	97.16(6)
O(30)–O(21)′	2.816(2)
H(31)–O(21)′	1.997(3)
O(30)–O(21)″	3.072(3)
H(32)–O(21)″	2.350(3)
O(30)–O(23)″	2.905(2)
H(32)–O(23)″	1.961(3)
N(11)–O(22)‴	2.950(3)
H(11)–O(22)‴	2.166(3)
N(11)–O(23)‴	3.147(3)
H(11)–O(23)‴	2.297(3)
B	
Cu(01)–S(09)	2.4487(7)
Cu(01)–N(13)	1.934(2)
Cu(01)–O(30)	2.440(2)
C(07)–C(08)	1.500(4)
C(08)–S(09)	1.812(3)
S(09)–C(10)	1.812(3)
C(10)–C(14)	1.493(4)
N(11)–C(12)	1.334(3)
N(11)–C(15)	1.373(4)
C(12)–N(13)	1.320(3)
N(13)–C(14)	1.378(3)
C(14)–C(15)	1.355(3)
C(15)–C(16)	1.491(4)
S(09)–Cu(01)–N(13)	84.11(7)
S(09)–Cu(01)–O(30)	95.79(5)
S(09)–Cu(01)–N(13)′	95.89(7)
S(09)–Cu(01)–O(30)′	84.21(5)
N(13)–Cu(01)–O(30)	89.04(8)
N(13)–Cu(01)–O(30)′	90.96(8)

(continued)

TABLE 3. *(continued)*

B	
O(30)–O(21)'	2.845(3)
H(31)–O(21)'	2.093(3)
O(30)–O(21)''	3.040(3)
H(32)–O(21)''	2.384(3)
O(30)–O(23)''	3.055(3)
H(32)–O(23)''	2.169(3)
N(11)–O(22)'''	2.976(3)
H(11)–O(22)'''	2.258(4)
N(11)–O(23)'''	3.078(3)
H(11)–O(23)'''	2.167(3)
C	
Co(01)–S(09)	2.5504(7)
Co(01)–N(13)	2.066(2)
Co(01)–N(20)	2.118(2)
C(07)–C(08)	1.486(4)
C(08)–S(09)	1.817(3)
S(09)–C(10)	1.817(3)
C(10)–C(14)	1.481(4)
N(11)–C(12)	1.340(2)
N(11)–C(15)	1.371(3)
C(12)–N(13)	1.312(3)
N(13)–C(14)	1.383(3)
C(14)–C(15)	1.366(3)
C(15)–C(16)	1.489(5)
N(20)–C(21)	1.141(3)
C(21)–S(22)	1.641(3)
S(09)–Co(01)–N(13)	81.67(2)
S(09)–Co(01)–N(20)	84.78(2)
S(09)–Co(01)–N(13)'	98.33(2)
S(09)–Co(01)–N(20)'	95.22(2)
N(13)–Co(01)–N(20)	89.97(9)
N(13)–Co(01)–N(20)'	90.03(9)
S(22)–H(11)''	2.378(4)
S(22)–N(11)''	3.357(2)

[a] The estimated standard deviations are given in parentheses. Symmetry positions for **A** and **B**: ' $2 - x$, $-y$, $2 - z$; '' $x, y, z - 1$; ''' $x - 1$, y, $z - 1$. Symmetry positions for C: $2 - x$, $-y, 2 - z$; '' $1.5 - x, y - 0.5, 2.5 - z$.

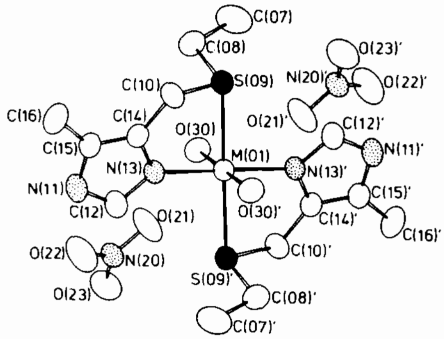

Fig. 1. ORTEP projection and atomic labelling of the compounds $[M(memi)_2(H_2O)_2](NO_3)_2$ (**A**) and (**B**). The primed atoms are at the positions $2 - x$, $-y$, $2 - z$. For clarity the hydrogen atoms are omitted.

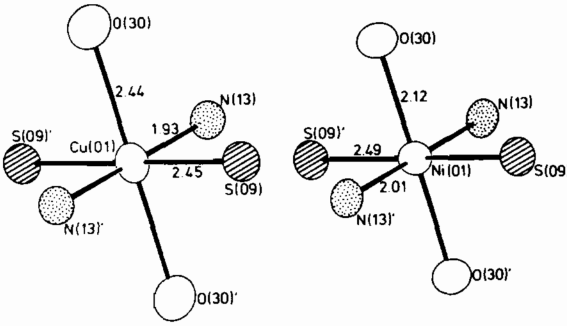

Fig. 2. ORTEP projection of the coordination geometries around the nickel and copper ions in $[M(memi)_2(H_2O)_2](NO_3)_2$ (**A**) and (**B**), with the coordination distances (Å).

alike, that projections of both structures can in fact hardly be distinguished from each other (Fig. 1). The ligands are coordinated in a *trans* position. The coordination angles around the metal do not deviate significantly from octahedral. The difference in geometry around the two metal ions as shown in Fig. 2, however, is remarkable. The Ni–N and Cu–N distances are comparable (2.012(2) and 1.934(2) Å, respectively) as are the Ni–S and Cu–S distances (2.4929(7) and 2.4487(7) Å). The metal to oxygen

TABLE 4. Colours, X-ray type, IR type, and metal content of the thiocyanate and nitrate compounds of the ligand memi

Compound	Colour	X-ray type	IR type	M (%) exp.(calc.)
$[Co(memi)_2(H_2O)_2](NO_3)_2$	pink	A	I	10.9(11.1)
$[Ni(memi)_2(H_2O)_2](NO_3)_2$	blue	A	I	10.9(11.1)
$[Cu(memi)_2(H_2O)_2](NO_3)_2$	dark green	A'	II	11.9(11.9)
$Co(memi)_2(NCS)_2$	pink	B	III	12.1(12.1)
$Ni(memi)_2(NCS)_2$	purple	B	III	11.7(12.0)
$Cu(memi)_2(NCS)_2$	brown	C	IV	12.9(12.9)

TABLE 5. Ligand field absorption bands (cm^{-1} × 10^3)[a] and EPR spectral data of the thiocyanate and nitrate compounds with the ligand memi

$[Co(memi)_2(H_2O)_2](NO_3)_2$	8.1, 11.1, 17.7, 20.5
$[Ni(memi)_2(H_2O)_2](NO_3)_2$	8.4(sh), 10.5, 15.2(sh), 17.2, 27.1
$[Cu(memi)_2(H_2O)_2](NO_3)_2$	11.6, 16.7; g_{iso} = 2.10
$[Co(memi)_2(NCS)_2]$	9.5, 14.7, 19.5, 24.4
$[Ni(memi)_2(NCS)_2]$	9.9, 15.2, 18.3, 27.8
$[Cu(memi)_2(NCS)_2]$	11.1, 16.9; g_1 = 2.19, g_2 = 2.10, g_3 = 2.03

[a] sh = shoulder.

distances, however, are quite different, the Ni–O distance is relatively short (2.116(2) Å), whereas the Cu–O distance is long (2.440(2) Å). The thermal ellipsoid of the nickel ion is perfectly spherical, indicating an 'ideal' octahedron. The thermal ellipsoid of the copper ion, however, is egg-shaped, indicating an elongated octahedral geometry, apparently due to the Jahn–Teller effect.

The imidazole rings are planar, with deviations from the least-squares planes of less than 0.003 Å. The nitrate ions are planar, with deviations of the least-squares plane of less than 0.01 Å. The hydrogen of the imidazole nitrogen is bridged to an oxygen of the nitrate. The hydrogens of the water molecule, coordinated to the metal ion, are also bridged to oxygens of the nitrate. The hydrogen bridges form an extended two-dimensional network of the compound.

The Structure of $Co(memi)_2(NCS)_2$ *(C)*

The asymmetric unit consists of one half of a molecule of $Co(memi)_2(NCS)_2$. The metal ion lies on a centre of symmetry and is surrounded by two nitrogens and two sulfurs from the ligands and two nitrogens from the thiocyanate anions. An ORTEP [9] projection of the molecule $Co(memi)_2(NCS)_2$ is given in Fig. 3. The ligands are coordinated in a *trans* position just as in the structures described above. The coordination geometry is therefore distorted octahedral. The coordination distances (Co–N(13) = 2.066(2), Co–N(20) = 2.118(2), Co–S = 2.5504(7) Å) are rather normal for cobalt. The coordination angles are close to octahedral. The largest deviation from the octahedral coordination angle is observed for the N(13)–Co–S(09) angle, viz. 81.67(2)°, which is due to the limited ligand bite [10]. The imidazole rings are planar with deviations from the least-square plane of less than 0.005 Å. The thiocyanate ion is almost linear, with deviations from the least-squares line of about 0.008 Å. The only hydrogen bridge is from the imidazole nitrogen to the sulfur of the thiocyanate of a next molecule. The highest peak in the final difference Fourier map is 1.08 e/Å^3, which is near the shlightly disordered thiocyanate sulfur. No attempts were undertaken to solve this disorder.

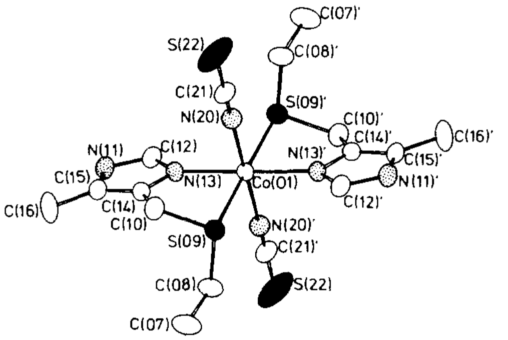

Fig. 3. ORTEP projection and atomic labelling of the compound $[Co(memi)_2(NCS)_2]$. The primed atoms are at the positions 2 – *x*, –*y*, 2 – *z*. For clarity the hydrogen atoms are omitted.

Spectroscopic Results

Nitrate compounds

The complexes have an $N_2S_2O_2$ chromophore around the metal ion with the oxygens originating from the water molecules. The X-ray powder pattern of the nickel and copper compounds are only slightly different, which can be explained with the crystal structures (*vide supra*). The IR spectra, however, are significantly different. In the IR spectra a sharp H–O–H bending vibration is observed at 1665 (**A**) and 1645 (**B**) cm^{-1} in agreement with a coordinated water molecule [11]. This large difference in frequency of the water bending vibration correlates with the bond distances of 2.116(2) (**A**) and 2.440(2) (**B**) Å. The other water absorptions in the IR spectra are shifted likewise, causing the main differences in the spectra: 3420 (**A**), 3500 (**B**) (OH stretching), 1665 (**A**), 1645 (**B**) (HOH bending), 740 (**A**) and 630 (**B**) (H_2O rocking) cm^{-1}. The nitrate stretching vibration at 1760 cm^{-1} is split, indicating C_{2v} symmetry for the nitrates [12], which must originate from the hydrogen bridges, as can be concluded from the X-ray structures.

The LF spectra of the nickel and cobalt compounds are complicated: for cobalt the first band (usually about 10 × 10^3 cm^{-1}) is split in two bands at 8.1 and 11.1 × 10^3 cm^{-1}, and the other bands are also split. The Vis–NIR spectrum of the nickel compound $[Ni(memi)_2(H_2O)_2](NO_3)_2$ indicates a distorted octahedral ligand field, whereas the crystal structure shows an almost ideal octahedral coordination geometry around the Ni(II) ion. This seeming contradiction is caused by the large difference in donor strengths of the coordinated atoms lowering the ligand field to a D_{2h} symmetry.

The EPR spectrum of the hydrated copper compound is isotropic, but the signal is very broad, and a faint indication of an axial *g* value can be detected at a value of approximately 2.28. The LF spectrum of this copper compound is dominated by a large charge transfer band at 24×10^3 cm^{-1}.

Thiocyanate compounds

The cobalt and nickel complexes have an N_4S_2 chromophore around the metal ion, as can be deduced from the X-ray isomorphism. The LF spectra of these compounds are less complicated than those of the nitrate compounds, apparently because the ligand field strength of the thiocyanate ion is not much different from the imidazole donor strength, and a symmetry higher than in the nitrate compounds results. The copper compound has the formula $Cu(memi)_2(NCS)_2$, as determined from metal analysis. Although this copper compound is not isomorphous with the cobalt thiocyanate, the most likely structure is also a distorted octahedral surrounding of copper [13–15]. The LF spectrum of this copper compound shows a broad signal consisting of a large charge transfer band at *c.* 28 000 cm^{-1}, a shoulder at 16.9×10^3 and a less intense band at 11.1×10^3 cm^{-1}. The EPR spectrum is rhombic, and very sharp, probably caused by exchange narrowing.

Comparison with Related Structures

The molecular structures of the described compounds are of great interest in view of the structures of compounds with similar ligands, published earlier by our laboratory and other groups. The structures of our compounds resemble the structures of the compounds $Cu(L)_2(ClO_4)_2$, with L = 4(5)-propylmercaptomethylimidazole or L = 2-propylmercaptomethylpyridine, described by Aoi *et al.* [16, 17], which is not surprising as the ligands are very much like our ligand memi. Both ligands also coordinate in the *trans* position, but the fifth and sixth coordination positions in their compounds are occupied by oxygen atoms of the perchlorate anions instead of the water molecules in our case. It is remarkable, that the perchlorate ion, which is usually non-coordinating, participates in the coordination of the copper ion, whereas in our compounds the nitrate ion, with its better coordinating properties, is not coordinated to the metal ion.

The most important difference between the bidentate NS ligand memi and the tetradentate N_2S_2 thioether-imidazole ligands is of course the 'missing link' between the two thioether sulfurs. In the N_2S_2 ligands the sulfurs are forced into a *cis*-position. In all structures with the ligand memi, the sulfurs coordinate *trans*, yielding less-distorted octahedral geometries. The coordination distances in the compounds $[Ni(bhdhx)(H_2O)_2](NO_3)_2$ [18] and $[Cu(bhdhx)(NO_3)_2]$ [19] (with bhdhx = 1,6-bis(4-imidazolyl)-2,5-dithiahexane) are comparable to those in the memi nitrate compounds.

In $[Cu(bhdhx)(NO_3)_2]$ the nitrate ions coordinate, in contrast to the nickel compound $[Ni(bhdhx)(H_2O)_2](NO_3)_2$. The presence of the water molecules in some of the nitrate compounds must be due to a more favourable crystal packing with hydrogen bridges.

In $Co(bidhp)(NCS)_2$ [5] and $Ni(bidhx)(NCS)_2$ [4], the coordination distances are in good agreement with those in the cobalt thiocyanate structure $[Co(memi)_2(NCS)_2]$, the largest differences being caused by the bridge between the two sulfur atoms in bidhx and bidhp.

With the ligand bidhx, an oxygen containing cobalt(III) dimer was formed spontaneously from the cobalt(II) solution [20]. With the ligand memi this did not occur, not even after flushing the cobalt(II) nitrate–memi solution with oxygen for 2 h. Obviously, the formation of the oxygen-bridged cobalt dimer is stabilized by the link between the sulfur atoms in bidhx.

Another interesting feature of the ligand bidhx, is the spontaneous partial reduction of a copper thiocyanate solution, yielding the mixed-valence compound $Cu_2(bidhx)(NCS)_3$ [21].

A review of copper to thioether distances has been given by Hathaway in his latest copper review [22] and also by Cooper [23]. A brief summary of observed copper to thioether coordination distances is included in Table 6. The largest Cu–S coordination distances observed so far, occurs in the compound $Cu(etmb)Cl_2$ [13]. The shortest distances occur in the compound $Cu(S_4N_2C_{17}H_{24})$ [24]. In the latter compound the coordinating sulfurs are thiolate sulfurs, which are forced close to the copper ion by steric constraints of the ligand. A disulfide bond is apparently not formed due to the rigid conformation of the ligand. The metal to sulfur coordination distances observed in the crystal structures of the memi complexes (Table 3) lie within the range of those of the summarized compounds. The Cu–S coordination distance observed in **B** approaches the distances observed with the other bidentate ligands [16, 17].

Conclusions

The present study has made clear that the new ligand 5-methyl-4-(ethylmercaptomethyl)imidazole is an interesting chelating agent. The ligand coordinates bidentately through the thioether sulfur and the imidazole nitrogen. All compounds described here

TABLE 6. Some copper thioether coordination distances[a]

Compound		Chromophore	Cu–S (Å)	Reference
$Cu(bidhp)Cl_2$	(1)	$N_2S_2Cl_2$	2.970(1); 2.886(1)	25
$Cu(S_4N_2C_{17}H_{24})$	(2)	N_2S_2	2.2225(11)	24
$Cu(Pr^nSCH_2Im)_2(ClO_4)_2$	(3)	$N_2S_2O_2$	2.397(2)	17
$Cu(Pr^nSCH_2Py)_2(ClO_4)_2$	(4)	$N_2S_2O_2$	2.366(1)	16
$[Cu(9\text{-ane-}N_2S)_2]^{2+}$	(5)	N_4S_2	2.707(1)	26
$[Cu(CM)_2]^{2+}$	(6a)	N_4S_2	2.419(1)	15
$[Cu(CM)_2]^{2+}$	(6b)	N_4S_2	2.790(2)	14
$[Cu(1,4,7\text{-TTCN})_2]^{2+}$	(7)	S_6	2.419(3); 2.426(3) 2.459(3)	27
$[Cu(etmb)_2Cl_2]$	(8)	$N_2S_2Cl_2$	3.001(2)	13

[a] Abbreviations used in this Table: **1**, bidhp = 1,7-bis(5-methyl-4-imidazolyl)-2,6-dithiaheptane; **2**, $S_4N_2C_{17}H_{24}$ = N,N′-trimethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate; **3**, Pr^nSCH_2Im = 4-(n-propylmercaptomethyl)imidazole; **4**, Pr^nSCH_2Py = 2-(n-propylmercaptomethyl)pyridine; **5**, 9-ane-N_2S = 1-thia-4,7-diazacyclononane; **6**, CM = cimetidine = *N*-cyano-*N*′-methyl-(2-{[5-methyl-4-imidazolylmethyl]thio}ethyl)guadinine; **7**, 1,4,7-TTCN = 1,4,7-trithiacyclononane; **8**, etmb = 2-(ethylthiomethyl)-benzimidazole.

contain metal ions which are six-coordinated with two memi ligands and two anions or solvent molecules with like donor atoms in *trans* positions. The coordination mode and the spectroscopic properties of the coordination compounds change dramatically when these two NS-donor ligands are coupled together to form one N_2S_2-donor ligand. For instance, the elongated octahedral geometry in the copper memi compounds is due to the *trans* position of the two sulfur atoms of the two memi ligands, while in the coordination compounds of imidazole-thioether ligands derived from certain dithiols (bidhx, bidhp and bhdhx) the sulfur atoms are forced in the *cis* position and compressed octahedral geometries (indicated by inversed axial EPR spectra) are observed.

Remarkable is the large Jahn–Teller distortion observed in the compound $[Cu(memi)_2(H_2O)_2](NO_3)_2$ (**B**). The Jahn–Teller theory accounts for distortion in complexes with six equivalent ligands. One could expect that with three different types of donor atoms degenerate electronic states are absent, and consequently would make a Jahn–Teller distortion unnecessary. However, according to Hathaway and Billing [28] this approach of the problem overlooks the fact that a copper(II) ion can 'feel' a regular octahedral field if the distances of the inequivalent ligands are so arranged that higher positions in the spectrochemical series are exactly counterbalanced by longer bonds. In such a case the effective electronic symmetry is regular and will require a distortion to remove the degeneracy. This seems indeed the case in our compound **B**, where the water molecule is farther away from the metal ion than in the nickel compound **A**. Also, the larger thermal factor of copper in this direction indicates the presence of a Jahn–Teller effect in this compound.

Supplementary Material

Lists of the atomic coordinates of the hydrogen atoms, of the non-hydrogen anisotropic thermal parameters, of bond distances and bond angles, and of the observed and calculated structure factors are available from the authors upon request.

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