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Transition metal compounds of a chelating imidazole-thioether-amine ligand. Crystal and molecular structures of (4-(5-methyl-4-imidazolyl)-1-amino-3-thiabutane)di(chloro)copper(II), bis(4-(5-methyl-4-imidazolyl)-1-amino-3-thiabutane)copper(II) dichloride dihydrate, and bis(4-(5-methyl-4-imidazolyl)-1-amino-3-thiabutane)cobalt(III) tris(tetrafluoroborate)

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Abstract

The synthesis and characterization of a series of monomeric transition metal coordination compounds with the ligand 4-(5-methyl-4-imidazolyl)-1-amino-3-thiabutane (abbreviated memia) are described, *viz.* $[M(memia)Cl_2](H_2O)_n$, with M = Co, Ni, Cu; $[M(memia)_2]X_2(H_2O)_n$, with M = Ni, Cu and X = Cl, NO_3, BF_4; and $[Co(memia)_2]X_3$ with X = NO_3, BF_4. Single crystals of $[Cu(memia)Cl_2]$ (**A**), $[Cu(memia)_2]Cl_2(H_2O)_2$ (**B**) and $[Co(memia)_2](BF_4)_3$ (**C**) were used in structure determinations. **A** crystallizes in the monoclinic space group $P2_1/n$ ($Z = 4$) and **B** and **C** crystallize in the monoclinic space group $P2_1/c$ ($Z = 2$ and 4, respectively). The cell dimensions for compound **A** are $a = 7.025(2)$, $b = 8.486(2)$, $c = 19.484(6)$ Å, $\beta = 98.07(3)°$, $V = 1150$ Å^3, $D_x = 1.76$ g cm^{-3}. The cell dimensions for compound **B** are $a = 7.742(1)$, $b = 14.845(4)$, $c = 9.936(2)$ Å, $\beta = 104.80(2)°$, $V = 1104$ Å^3, $D_x = 1.53$ g cm^{-3}. The cell dimensions for **C** are $a = 19.841(4)$, $b = 9.166(5)$, $c = 14.813(3)$ Å, $\beta = 99.71(2)°$, $V = 2656$ Å^3, $D_x = 1.65$ g cm^{-3}. The structures were solved by heavy-atom techniques and refined by least-squares methods to residual R_w values of 0.043 (**A**), 0.048 (**B**)and 0.079 (**C**). The coordination geometry of the copper(II) ion in **A** is intermediate between square pyramidal and trigonal bipyramidal. The copper(II) ion is surrounded by an imidazole nitrogen (Cu–N = 1.96 Å), an amine nitrogen (Cu–N = 1.99 Å) and a thioether sulfur (Cu–S = 2.43 Å) from the ligand and by two chloride anions (Cu–Cl(1) = 2.55, Cu–Cl(2) = 2.28 Å). The coordination geometry of the metal ions in the bis(ligand) complexes **B** and **C** is distorted octahedral. The metal ions are coordinated by two imidazole nitrogens, two amine nitrogens and two thioether sulfurs. For compound **B** the imidazole nitrogens and the amine nitrogens are in the equatorial plane at 2.02 and 2.03 Å, respectively, and the thioether sulfurs are at the axial positions at rather large distances, e.g. 2.77 Å. For compound **C** the equatorial positions are also occupied by two imidazole nitrogens at 1.91 Å and two amine nitrogens at 1.99 Å. The thioether sulfur atoms are situated at the axial positions at 2.25 Å.

Introduction

Thioether-imidazole ligands are being used for the synthesis of model compounds for the redox-active sites in blue-copper proteins [1]. Recently, some copper(II) compounds of the ligand 5-methyl-4-(ethylthiomethyl)imidazole were found to be active catalysts for the oxidative coupling of phenols [2].

To investigate the possible applications of a heterogenized thioether-imidazole ligand, the amine-thioether-imidazole ligand 4-(5-methyl-4-imidazolyl)-1-amino-3-thiabutane (memia) (Fig. 1) was immobilized onto the organic polymer poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) by reaction of the primary amine with the epoxy group of the polymer [3]. The ion exchange properties of the resulting resin were tested [3].

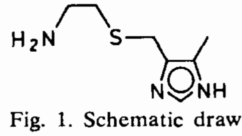

Fig. 1. Schematic drawing of the ligand memia.

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For complexes in the polymer phase relatively little information can be obtained about the way the metal ions are bound to the ligand. Therefore a number of coordination compounds was prepared in the homogeneous phase. In this paper copper(II), cobalt(II) and nickel(II) complexes with the ligand memia itself are presented. Crystal structure determinations were performed of one cobalt(III) and two copper(II) compounds. The complexes were characterized by ligand field and EPR spectroscopy.

The ligand memia has been used before [4, 5] as a starting compound for the synthesis of Schiff base ligands, which were used as model systems for blue-copper proteins.

Experimental

Starting materials

The starting materials 4-methyl-5-imidazolemethanol hydrochloride (Janssen Chimica), 2-aminoethanethiol hydrochloride (Janssen Chimica) and the metal salts were commercially available and were used without purification. The synthesis, the ^{1}H NMR spectrum and the ^{13}C NMR spectrum of memia have been described elsewhere [3].

Synthesis of the complexes

The coordination compounds were prepared by dissolving the appropriate metal salts $MX_2(H_2O)_n$ (1 mmol), where M = Cu, Ni, Co and X = Cl, NO_3, BF_4, in warm ethanol (*c.* 25 ml) and adding the solutions to solutions of memia (0.5–3 mmol) in warm ethanol (*c.* 25 ml). In some cases triethyl orthoformate was added to the metal salt solution for dehydration. The resulting solutions were filtered to remove any impurity. Subsequent cooling of the solutions often resulted in the crystallization of the complexes. In some cases, however, evaporation of part of the solvent was necessary before crystallization. The crystals were filtered and washed with ethanol. It was found that the use of 1:1 (M:memia) ratios during the syntheses often resulted in mixtures of 1:1 and 1:2 complexes. Therefore different starting ratios were employed: a 2:1 ratio resulted in pure 1:1 complexes, while a 1:3 ratio yielded pure 1:2 compounds. Addition of purple ethanolic solutions of $Co(H_2O)_6(NO_3)_2$ and $Co(H_2O)_6(BF_4)_2$ to solutions of memia immediately resulted in a colour change to orange, suggesting oxidation of Co(II) to Co(III). Attempts to synthesize Co(II) coordination compounds with these metal salts in a dinitrogen atmosphere were unsuccessful: under these conditions also only Co(III) complexes were obtained.

Analyses

Metal analyses were carried out complexometrically with EDTA as the complexing agent [6] after destruction of the samples with nitric acid. $[Co(memia)_2(NO_3)_3$ and $[Co(memia)_2](BF_4)_3$ were destructed using sulfuric acid and nitric acid. Chloride contents were determined by potentiometric titrations with $AgNO_3$ [7]. Other elements (C, H, N) were analysed at the Microanalytical Laboratory of University College (Dublin) and at the Mikroanalytisches Labor Pascher, Remagen (F.R.G.).

Spectroscopic measurements

Infrared spectra of the compounds pressed in KBr pellets were recorded in the 4000–180 cm^{-1} range on a Perkin-Elmer spectrophotometer, equipped with a PE data station. Solid-state electronic spectra (28 000–5000 cm^{-1}), using the diffuse reflectance method with MgO as reference, were recorded on a Perkin-Elmer 330 spectrophotometer, equipped with a PE data station. Electron paramagnetic resonance spectra of the powdered copper(II) complexes were recorded on a Varian spectrometer at X-band frequency at room temperature. X-ray powder diagrams of the powdered coordination compounds were obtained with a Guinier type camera using Cu Kα radiation.

Data collection and structure refinement

The data collection for the compounds was carried out at room temperature on four-circle Enraf-Nonius CAD4 diffractometers with graphite-monochromatized Mo Kα radiation (λ(Mo Kα) = 0.71073 Å). Crystal data and additional details of the data collection and refinement for all three structures are presented in Table 1. 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 scantime 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 intensities were observed. For compound **C** empirical absorption correction was applied using the program DIFABS [8]. The positions of the heavy atoms were calculated from the Patterson map. The remaining atoms were found from subsequent Fourier maps. The structures were 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. 9. The non-hydrogens of structures **A** and **B** were refined anisotropically. The

TABLE 1. Crystal and refinement data of the compounds [Cu(memia)Cl_2] (**A**), [Cu(memia)$_2$]$Cl_2(H_2O)_2$ (**B**) and [Co(memia)$_2$]$(BF_4)_3$ (**C**)

	A	**B**	**C**
Formula	$CuC_7H_{13}Cl_2N_3S$	$CuC_{14}H_{30}Cl_2N_6O_2S_2$	$C_{14}H_{26}B_3CoF_{12}N_6S_2$
Formula weight	305.71	512.64	661.86
a (Å)	7.025(2)	7.742(1)	19.841(4)
b (Å)	8.486(2)	14.845(4)	9.166(5)
c (Å)	19.484(6)	9.936(2)	14.813(3)
α (°)	90	90	90
β (°)	98.07(3)	104.80(2)	99.71(2)
τ (°)	90	90	90
V (Å^3)	1150	1104	2655.5
T (K)	297	297	293
F (000)	620	534	1336
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
Z	4	2	4
D_x (g/cm^3)	1.76	1.53	1.65
μ (cm^{-1})	24.98	14.30	8.88
Crystal dimensions	0.25×0.30×0.20	0.3×0.2×0.3	0.45×0.25×0.10
Color	green	purple	orange
Habit	parallellepiped	parallellepiped	needle
h-values	0 to 7	−8 to 8	−20 to 20
k-values	0 to 9	0 to 17	0 to 9
l-values	−21 to 21	0 to 11	0 to 15
Scan range θ	1.5–24.0	1.5–24.0	2.0–22.0
Intensity variation	0	0	8.2
No. measured reflections	1855	1727	3663
No. unique reflections	1855	1727	3499
No. used in refinement	1525[a]	1502[a]	3240[b]
No. parameters	179	184	274
R_f[c]	0.035	0.034	0.161
R_w[d]	0.043	0.048	0.079
excursions max., min. (e/Å^3)	0.31, −0.19	0.24, −0.32	0.87, −0.72

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

function minimized was $\Sigma w(||F_o| - |F_c||)^2$ with $w = 1/\sigma^2(F)$. Because of the small size and poor quality of the single crystal of **C**, not many (1538) significant reflections ($I > 2\sigma(I)$) could be collected. Refinement using these reflections only resulted in large standard deviations in the fractional coordinates and isotropic temperature factors. Therefore, all reflections (3240) with $I > \sigma(I)$ were used in the refinement, which resulted in smaller standard deviations and a lower value for R_w (0.079), but a rather high R_f value (0.161). For compound **C** only the Co and S atoms were refined anisotropically. Hydrogen atoms were calculated at 0.95 Å from their parent atom.

The fractional coordinates and the isotropic thermal parameters of the non-hydrogen atoms of **A**, **B** and **C** are listed in Table 2. Selected bond distances, selected bond angles and hydrogen bonding distances are given in Table 3. See also 'Supplementary material'.

Results and discussion

General

A listing of colours and spectroscopic characteristics (ligand field and EPR data) of the complexes with copper(II), nickel(II) and cobalt(II) is presented in Table 4. Elemental analyses (metal, C, H, Cl, N) are satisfactory, see 'Supplementary material'. All compounds within the series exhibit different X-ray powder patterns and different IR spectra. The IR spectra are consistent with the presence of the various anions. A more detailed discussion of these results will be presented after the description of the crystal structures.

Description of the structures of [Cu(memia)Cl$_2$] (A)

A PLUTO [10] drawing of compound **A** is given in Fig. 2, together with the atomic labelling scheme.

TABLE 2. Atomic coordinates and equivalent thermal parameters of the non-hydrogen atoms of [Cu(memia)Cl$_2$] (**A**), [Cu(memia)$_2$Cl$_2$(H$_2$O)$_2$ (**B**) and [Co(memia)$_2$](BF$_4$)$_3$ (**C**)

Atom	x/a	y/b	z/c	B_{eq}[a]
[Cu(memia)Cl$_2$] (**A**)[b]				
Cu	2559(7)	22500(6)	12007(3)	292(3)
Cl(1)	−665(2)	5157(2)	1075(1)	38(1)
Cl(2)	−2009(2)	422(2)	812(1)	41(1)
N(6)	1338(6)	2449(4)	317(2)	30(2)
C(7)	3440(7)	2810(6)	386(3)	36(3)
C(8)	4142(7)	3636(6)	1065(2)	37(3)
S(9)	3574(2)	2334(1)	1755(1)	29(1)
C(10)	2916(7)	3616(6)	2443(2)	35(3)
N(11)	−1164(6)	1999(5)	3182(2)	35(2)
C(12)	−1590(7)	1715(6)	2499(2)	33(3)
N(13)	−212(5)	2251(4)	2168(2)	28(2)
C(14)	1165(7)	2917(5)	2666(2)	27(2)
C(15)	589(7)	2768(5)	3299(2)	29(2)
C(16)	1537(8)	3230(6)	4005(3)	41(3)
[Cu(memia)$_2$]Cl$_2$(H$_2$O)$_2$ (**B**)[c]				
Cu	0	0	0	215(3)
N(6)	208(4)	1289(2)	−634(3)	36(2)
C(7)	2032(5)	1521(2)	−746(4)	42(2)
C(8)	3426(5)	1368(3)	598(4)	46(2)
S(9)	3659(1)	180(1)	1077(1)	374(6)
C(10)	3405(4)	190(2)	2840(3)	563(7)
N(11)	−532(4)	1049(2)	3761(3)	37(2)
C(12)	−1200(4)	769(2)	2449(3)	35(2)
N(13)	81(3)	435(2)	1939(2)	31(2)
C(14)	1655(4)	524(2)	2979(3)	31(2)
C(15)	1279(4)	907(2)	4117(3)	34(2)
C(16)	2461(6)	1143(3)	5511(4)	50(3)
Cl	−1920(2)	2935(1)	1104(1)	563(7)
O	5508(5)	2670(4)	3185(4)	117(6)
[Co(memia)$_2$](BF$_4$)$_3$ (**C**)				
Co(10)	5000	0	5000	279(5)
Co(30)	10000	0	10000	296(5)
N(11)	6233(4)	3241(8)	6161(5)	40(1)
C(12)	5650(5)	2537(10)	6083(6)	37(2)
N(13)	5648(4)	1460(8)	5476(5)	31(1)
C(14)	6272(5)	1561(10)	5149(6)	35(2)
C(15)	6622(5)	2684(11)	5602(7)	40(2)
C(16)	7322(5)	3267(12)	5504(7)	75(3)
C(17)	6411(5)	558(10)	4418(7)	48(2)
S(18)	5829(1)	−987(3)	4336(2)	401(8)
C(19)	6203(5)	−2156(11)	5287(7)	52(2)
C(20)	6023(6)	−1679(13)	6149(7)	73(3)
N(21)	5317(4)	−1217(8)	6081(5)	35(1)
N(31)	8536(4)	2656(9)	8648(5)	43(1)
C(32)	9157(5)	2517(11)	9156(6)	40(2)
N(33)	9257(4)	1072(8)	9331(5)	28(1)
C(34)	8678(5)	356(10)	8900(6)	37(2)
C(35)	8237(5)	1379(11)	8489(7)	46(2)
C(36)	7520(5)	1152(12)	7895(7)	70(3)
C(37)	8662(5)	−1218(10)	8934(6)	48(2)
S(38)	9279(1)	−1907(2)	9861(2)	437(8)
C(39)	8889(4)	−1501(11)	10848(7)	66(3)
C(40A)	9285(10)	−741(36)	11543(5)	52(3)
C(40B)	9001(4)	−4(14)	11179(11)	52(3)
N(41)	9683(3)	513(8)	11143(5)	39(1)

[a] For **A** and **B**: $B_{eq}=\frac{1}{3}$ trace U; for **C**: $B_{eq}=\frac{8}{3}\pi^2$ trace U. [b] Atomic coordinates: Cu × 10^5, others × 10^4; equivalent thermal parameters: Cu Å^2 × 10^4, others Å^2 × 10^3. [c] Atomic coordinates: × 10^4; equivalent thermal parameters: Cu, S(9), Cl Å^2 × 10^4, others Å^2 × 10^3. [d] Atomic coordinates: × 10^4; equivalent thermal parameters: Co, S Å^2 × 10^2, others Å^2 × 10. Fractional coordinates of BF$_4$ anions not included.

The asymmetric unit consists of one molecule of [Cu(memia)Cl$_2$]. The copper(II) ion is surrounded by an imidazole nitrogen, an amine nitrogen and a thioether sulfur from the ligand and two chloride anions. Relevant bond distances and angles are given in Table 3(a). The nitrogen–copper distances are 1.99 and 1.96 Å for the amine nitrogen and the imidazole nitrogen, respectively. The sulfur–copper distance is 2.43 Å and the chloride–copper distances are 2.28 and 2.55 Å for Cl(2) and Cl(1), respectively. From the bond distances and angles it can be concluded that the coordination geometry around the copper(II) ion is intermediate between square pyramidal and trigonal bipyramidal ($\tau = 0.46$ [11]). The geometry can be described as square pyramidal with the two nitrogen atoms in *trans* positions (N–Cu–N = 166.4°) and the Cl(1) atom at the apex at a rather large distance of 2.55 Å. Alternatively, the geometry can be considered as trigonal bipyramidal, with the two nitrogen atoms at the axial positions at rather short distances and the sulfur and the chloride atoms in the equatorial plane. A weak intermolecular hydrogen bridge (N–Cl = 3.23 Å) exists between the imidazole N–H and one of the chloride anions of an adjacent molecule. The structure resembles the structure of the compound (1,3-bis(5-methyl-4-imidazolyl)-2-thiapropane)bis-(nitrato)copper(II) [12], which, however, possesses a coordination geometry closer to square pyramidal ($\tau = 0.24$ [11]).

*[Cu(memia)$_2$]Cl$_2$(H$_2$O)$_2$ (**B**)*

The structure of the cation [Cu(memia)$_2$]$^{2+}$ is represented in a PLUTO [10] drawing (Fig. 3), together with the atomic labelling scheme. The asymmetric unit consists of half a molecule of [Cu(memia)$_2$]Cl$_2$(H$_2$O)$_2$. The copper ion is surrounded by two memia ligands, each tridentately coordinated to the metal ion with an amine nitrogen, an imidazole nitrogen and a thioether sulfur. Relevant bond distances and angles are given in Table 3(b).

TABLE 3. Selected bond lengths (Å) involving non-hydrogen atoms, selected bond angles (°) and H bond distances (Å) for compounds **A–C**

(a) [Cu(memia)Cl_2] (**A**)	
Cu–N(6)	1.987(4)
Cu–N(13)	1.958(4)
Cu–Cl(1)	2.553(2)
Cu–Cl(2)	2.275(2)
Cu–S(9)	2.428(2)
Cl(1)–Cu–N(6)	87.5(2)
Cl(1)–Cu–Cl(2)	118.1(2)
Cl(2)–Cu–N(6)	95.9(2)
S(9)–Cu–N(6)	85.7(2)
N(6)–Cu–N(13)	166.4(3)
Cl(1)–Cu–N(13)	91.0(2)
Cl(1)–Cu–S(9)	103.2(2)
Cl(2)–Cu–N(13)	96.7(2)
S(9)–Cu–N(13)	81.6(2)
Cl(2)–Cu–S(9)	138.7(2)
Cl(1)–N(11)^a	3.232(5)
Cl(1)–N(11)H^a	2.36(5)
(b) [Cu(memia)$_2$]$Cl_2(H_2O)_2$ (**B**)	
Cu–N(6)	2.034(3)
Cu–N(13)	2.018(3)
Cu–S(9)	2.774(2)
N(6)–Cu–N(13)	90.5(2)
N(6)–Cu–S(9)	79.3(2)
N(13)–Cu–S(9)	82.8(2)
Cl–O^b	3.200(6)
Cl–N(11)^c	3.183(5)
Cl–N(11)H^c	2.48(5)
(c) [Co(memia)$_2$]$(BF_4)_3$ (**C**)	
Co(10)–N(13)	1.91(1)
Co(10)–S(18)	2.245(4)
Co(10)–N(21)	1.97(1)
Co(30)–N(33)	1.90(1)
Co(30)–S(38)	2.246(4)
Co(30)–N(41)	1.96(1)
N(13)–Co(10)–S(18)	87.0(3)
N(13)–Co(10)–N(21)	89.7(4)
N(13)–Co(10)–N(13)′	180.0
N(13)–Co(10)–S(18)′	93.0(3)
N(13)–Co(10)–N(21)′	90.3(4)
S(18)–Co(10)–N(21)	88.3(3)
S(18)–Co(10)–S(18)′	180.0
S(18)–Co(10)–N(21)′	91.7(3)
N(21)–Co(10)–N(21)′	180.0
N(33)–Co(30)–S(38)	85.9(3)
N(33)–Co(30)–N(41)	89.6(4)
N(33)–Co(30)–N(33)″	180.0
N(33)–Co(30)–S(38)″	94.1(3)
N(33)–Co(30)–N(41)″	90.4(4)
S(38)–Co(30)–N(41)	88.5(3)
S(38)–Co(30)–S(38)″	180.0
S(38)–Co(30)–N(41)″	91.5(3)
N(41)–Co(30)–N(41)″	180.0

Symmetry positions: $^a = 0.5+x,\ 0.5-y,\ 0.5+z$; $^b x-1,\ 0.5-y,\ z-0.5$; $^c x,\ 0.5-x,\ z-0.5$; $' = 1-x,\ -y,\ 1-z$; $'' = 2-x,\ -y,\ 2-z$.

The copper ion lies on a center of symmetry, implying that the ligands are facially coordinated to the copper ion with the thioether sulfurs in *trans* positions. The coordination geometry around the copper ion is elongated octahedral with the amine nitrogens and the imidazole nitrogens in the equatorial plane (Cu(II)–N(amine) = 2.03; Cu(II)–N(imidazole) = 2.02 Å) and the thioether sulfurs at the axial positions at rather large distances, e.g. 2.77 Å. The Cl^- anions and the water molecules are not coordinated. The chloride anions form weak hydrogen bridges with both the water molecules (Cl–O = 3.20 Å) and the imidazole N–H (Cl–N = 3.18 Å). The structure of the cation of **B** is similar to the structure of the cation of bis(1,3-bis(5-methyl-4-imidazolyl)-2-thiapropane)copper(II) bis(tetrafluoroborate) bis(ethanol) [12].

[Co(memia)$_2$]$(BF_4)_3$ (C)

A PLUTO [10] projection of the cation [Co(memia)$_2$]$^{3+}$ is given in Fig. 4, together with the atomic numbering scheme. The asymmetric unit of the monoclinic cell consists of two half molecules of bis(4-(5-methyl-4-imidazolyl)-1-amino-3-thiabutane)cobalt(III) tris(tetrafluoroborate). The cobalt(III) ions lie on centres of symmetry and are facially coordinated by two tridentate ligands, with the imidazole nitrogens, the thioether sulfurs, and the amino nitrogens mutually in *trans* positions. The cobalt(III) ion is in an elongated octahedral symmetry. Relevant bond distances and bond angles are given in Table 3(c). The imidazole and the amine nitrogens are situated in the equatorial plane (Co–N(imidazole) = 1.91; Co–N(amine) = 1.99 Å) and the thioether sulfurs in the axial positions (Co–S = 2.25 Å). This Co–S distance is short when compared to distances between divalent metals and thioether sulfurs in similar compounds (2.5–2.8 Å), however, such short distances have been found before in cobalt(III)–thioether complexes [13, 14]. The cobalt-imidazole nitrogen distance (1.91 Å) is also rather short compared to those in other cobalt(III) imidazole compounds (1.95–2.05 Å) [14–16], which may be the result of the chelating nature of the ligand. The imidazole rings are planar, with deviations from the least-square planes being less than 0.02 Å. The bond distances and bond angles in the ligand are normal.

The BF_4^- anions are not coordinated, and are strongly disordered positionally. Although some F...H–N distances were found to be short enough for hydrogen bridges, the disorder of the BF_4^- anions suggests that they are very weak. The BF_4^- anions have been refined in three or four positions with varying occupation factors. However, additional par-

TABLE 4. Colours and spectroscopic data (ligand field ($\times 10^3$ cm^{-1}) and EPR) of the compounds with the ligand memia

Compound	Colour LF ($\times 10^3$ cm^{-1})	EPR (at room temperature)
$[Cu(memia)Cl_2]$	green 12.9	g_1 2.19, g_2 2.11, g_3 1.99
$[Cu(memia)_2]Cl_2(H_2O)_2$	purple 11.8, 15.2(sh), 18.9	g 2.05
$[Cu(memia)_2](BF_4)_2$	purple 12.1, 15.2(sh), 18.9	g 2.21, g 2.05
$[Cu(memia)_2](NO_3)_2$	purple 12.0, 15.6(sh), 18.9	g 2.20, g 2.02
$[Co(memia)Cl_2](H_2O)_2$	green 6.6, 14.8, 15.6(sh), 19.8	
$[Co(memia)_2](NO_3)_3$	orange 20.9	
$[Co(memia)_2](BF_4)_3$	orange 20.9	
$[Ni(memia)Cl_2](H_2O)$	green 8.6, 15.1, 24.4	
$[Ni(memia)_2](BF_4)_2$	purple 11.2, 16.1, 20.0, 29.9	

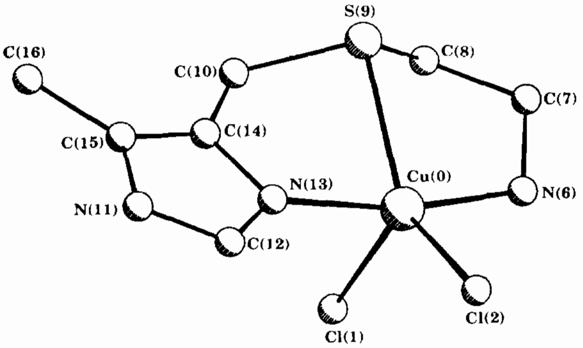

Fig. 2. PLUTO projection and atomic labelling of the compound $[Cu(memia)Cl_2]$. For clarity the hydrogen atoms are omitted.

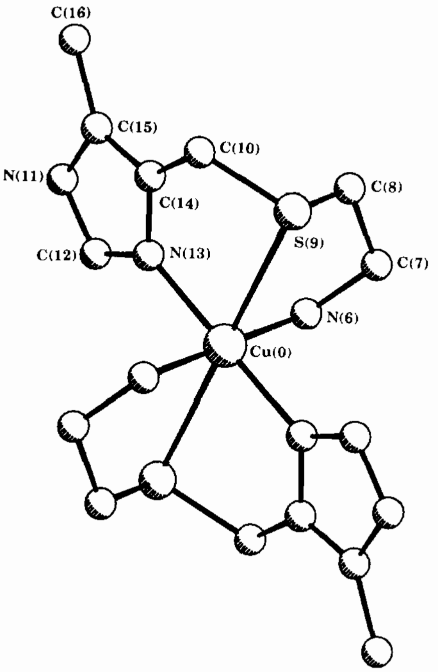

Fig. 3. PLUTO projection and atomic labelling of the cation $[Cu(memia)_2]^{2+}$. For clarity the hydrogen atoms and the chloride anions are omitted.

tially occupied sites are present, as the final difference Fourier map still contains some rather high peaks. One of these peaks has been attributed to a water molecule with an occupancy of 1/3. No attempts to further resolve this phenomenon were undertaken.

Spectroscopic results

In Table 4 the colours and LF and EPR data of the complexes with memia are given. In the IR spectra the characteristic vibrations of the anions NO_3^- (1350 cm^{-1}) and BF_4^- (1050 cm^{-1}) are easy to recognize.

Two types of metal(II) compounds, i.e. 1:1 and 1:2 complexes, were formed. In the 1:1 complexes with the general formula $[M(memia)Cl_2](H_2O)_n$, with M = Cu, Co, Ni, both the ligand and the anions are coordinated to the metal ion. With NO_3^- and BF_4^- no 1:1 complexes could be synthesized, probably due to the fact that these anions are weaker donors than Cl. van Steenbergen *et al.* [12] found similar results with the imidazole-thioether ligand 1,3-bis(5-methyl-4-imidazolyl)-2-thiapropane (sbi), in which the primary amine of memia has been substituted by an imidazole ring. With sbi 1:2 complexes could be obtained with a large variety of anions, while attempts to synthesize a 1:1 complex with BF_4^- as the only anion were unsuccessful, although the mixed-anion compound, $Cu(sbi)Cl(BF_4)$, could be obtained [12]. The 1:2 complexes of copper(II) and nickel(II) with memia have the general formula $[M(memia)_2]X_2 \cdot (H_2O)_n$ (M = Cu, Ni; X = Cl, NO_3, BF_4), while the 1:2 cobalt(III) complexes have the general formula $[Co(memia)_2]X_3$ (X = NO_3, BF_4). In these compounds only the memia ligands are coordinated to the metal ions.

Copper(II) complexes

Two types of copper(II) compounds, i.e. 1:1 and 1:2 (M:memia) complexes, were formed with the

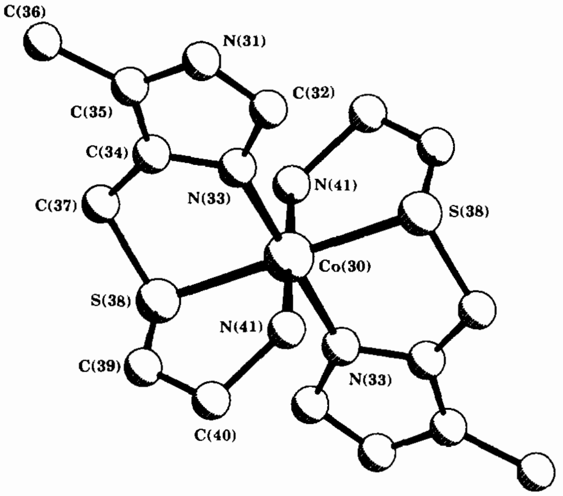

Fig. 4. PLUTO projection and atomic labelling of the cation $[Co(memia)_2]^{3+}$. For clarity the hydrogen atoms and the tetrafluoroborate anions are omitted.

anion Cl^-. The ligand field spectrum and the rhombic EPR spectrum of the compound $[Cu(memia)Cl_2]$ (Table 4) suggest square pyramidal or trigonal bipyramidal geometry [17], which was confirmed by the crystal structure.

The ligand field spectra of the compounds $[Cu(memia)_2]X_2(H_2O)_n$, where X = Cl, NO_3 or BF_4, were found to be nearly identical. Similar spectra were obtained for the compounds $[Cu(sbi)_2]X_2(H_2O)_n$, with X = Cl, Br, NO_3, BF_4, CF_3SO_3 [12]. The low energy parts of the spectra are consistent with an elongated octahedral geometry, as confirmed by the crystal structure determination of $[Cu(memia)_2]Cl_2(H_2O)_2$ (**B**) and $[Cu(sbi)_2](BF_4)_2$ [12]. An additional absorption is found in the spectra of the compounds with memia and sbi at about 19×10^3 cm^{-1}, which is rather high for a copper d–d transition. A similar high-energy transition has been observed before in the compound $[Cu(L)_2](ClO_4)_2$, where L = 1,3-(5-phenyl-2-imidazolyl)-2-thiapropane [18]. The EPR spectra of $[Cu(memia)_2](NO_3)_2$ and $[Cu(memia)_2](BF_4)_2$ appear as axial and are very similar; however, in the spectrum of $[Cu(memia)_2]Cl_2$ $g_\parallel$ was not observed. From the ligand field and EPR spectra it may be concluded that the coordination geometry around the copper(II) ion in the compounds $[Cu(memia)_2]X_2(H_2O)_n$ (X = Cl, NO_3, BF_4) is essentially the same. The different X-ray powder patterns, however, imply that the compounds are not structurally isomorphous, which can be ascribed to packing differences, due to the presence of different anions.

Cobalt(II) and cobalt(III) complexes

With cobalt(II) the blue–green amorphous 1:1 complex $[Co(memia)Cl_2](H_2O)_2$ was formed. The ligand field spectrum is typical for a tetrahedral Co(II) ion [17], which suggests that memia coordinates bidentately to the metal ion using both its imidazole nitrogen and its amine nitrogen, the coordination sphere being completed by two chloride anions. This would result in a $Co(II)N_2Cl_2$ chromophore.

Two similar 1:2 cobalt(III) complexes have been prepared, i.e. $[Co(memia)_2](NO_3)_3$ and $[Co(memia)_2](BF_4)_3$. The ligand field spectra of these coordination compounds are identical and contain a low-spin d–d transition at 20.9×10^3 cm^{-1}, suggesting the presence of Co(III). This was confirmed by the elemental analyses and the crystal structure determination of $[Co(memia)_2](BF_4)_3$ (see above). The oxidation of Co(II) to Co(III) is spontaneous and occurs immediately after the addition of the Co(II) solutions to the ligand solutions. Even under dinitrogen atmosphere no compounds of the type $[Co(memia)_2]X_2$ could be synthesized. With sbi a similar Co(III) complex with the formula $[Co(sbi)_2](BF_4)_3$ could be synthesized [12], however, in this case the colour change only occurred after a few days. In contrast with the present observations for memia, two 1:2 Co(II) compounds could be isolated with sbi, i.e. $[Co(sbi)_2](NO_3)_2(H_2O)_4$ and $[Co(sbi)_2]Cl_2$. Apparently the Co(II) complexes with sbi are less sensitive towards oxidation to Co(III), than are the Co(II) compounds with memia. The complexes $[Co(memia)_2](BF_4)_3$, $[Co(memia)_2](NO_3)_3$ and $[Co(sbi)_2](BF_4)_3$ are the only thioether-coordinated cobalt compounds known, in which such a spontaneous oxidation takes place. No attempts were undertaken to detect the reduction products.

Nickel(II) complexes

A green 1:1 nickel(II) complex with the formula $[Ni(memia)]Cl_2(H_2O)$ has been isolated. The ligand field spectrum of this compound suggests an octahedral coordination geometry around the Ni(II) ion. In addition to one tridentately coordinating molecule of memia and two coordinating chloride anions, the coordination sphere is probably completed by one molecule of water, resulting in a $Ni(II)NNSCl_2O$ chromophore. No 1:1 Ni(II) complexes have been obtained with the ligand sbi [12].

The ligand field spectra of the Ni(II) 1:2 compounds $[Ni(memia)_2](BF_4)_2$ (a) and $[Ni(sbi)_2](SiF_6)_2(H_2O)_5$ (b) [19] are redrawn in Fig. 5. Both spectra are in accordance with an octahedral geometry around the nickel ion. The crystal structure of the sbi compound was solved and showed that the ligands in $[Ni(sbi)_2](SiF_6)_2(H_2O)_5$ are facially bound to the Ni(II) ion with the two sulfurs in *cis* positions. For the memia compound the splittings of both σ_1 and

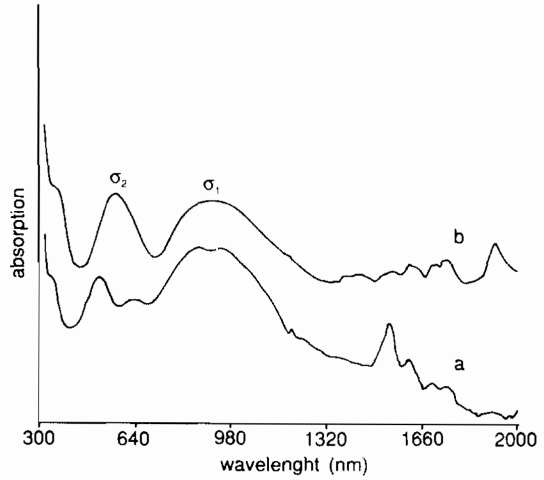

Fig. 5. Ligand field spectra of $[Ni(memia)_2](BF_4)_2$ (a) and $[Ni(sbi)_2](SiF_6)_2(H_2O)_5$ (b) [19].

σ_2 suggest a tetragonal distortion in the structure [17]. Therefore, it is expected that the structure of $[Ni(memia)_2](BF_4)_2$ is *trans*-octahedral, the ligands coordinating either facially or meridionally to the Ni(II) ion. Because of steric hindrance considerations the former possibility is expected to be the most probable one.

Conclusions

This investigation has shown that both 1:1 and 1:2 (metal:ligand) complexes can be synthesized with the tridentate ligand memia. When Cl^- was used as the anion 1:1 compounds were found with copper(II), cobalt(II) and nickel(II), i.e. $[Cu(memia)Cl_2]$, $[Co(memia)Cl_2](H_2O)_2$ and $[Ni(memia)Cl_2](H_2O)$, respectively. The coordination geometry in these complexes was found to depend on the particular metal ion. The ligand field and EPR spectra of $[Cu(memia)Cl_2]$ are compatible with both a square pyramidal and a trigonal bipyramidal surrounding of the Cu(II) ion in a $CuNN'SCl_2$ chromophore. The crystal structure determination of $[Cu(memia)Cl_2]$ confirmed that the geometry is intermediate between square pyramidal and trigonal bipyramidal with the nitrogen atoms at *trans* positions. The coordination geometry in the cobalt(II) complex is tetrahedral, as indicated by the ligand field spectrum. A $CoNN'Cl_2$ chromophore is expected, which would imply that the thioether sulfur of memia does not coordinate. The ligand field spectrum of the nickel(II) compound is consistent with a distorted octahedral coordination geometry. The coordination sphere probably consists of one tridentately coordinating ligand, two chloride anions and one water molecule, resulting in a $NiNN'SCl_2O$ chromophore.

The 1:2 complexes with copper(II) and nickel(II) have the general formula $[M(memia)_2]X_2(H_2O)_n$, with X = Cl, NO_3, BF_4, while cobalt(III) complexes with the general formula $[Co(memia)_2]X_3$ (X = NO_3, BF_4) were obtained. In both the copper(II) and the cobalt(III) compounds the metal ions are surrounded by two tridentately chelating ligands, resulting in $MN_2N'_2S_2$ chromophores with the sulfur atoms in *trans* positions, as confirmed by the crystal structure determinations of $[Cu(memia)_2]Cl_2(H_2O)_2$ and $[Co(memia)_2](BF_4)_3$ and the spectroscopic data. The ligand field spectrum of $[Ni(memia)_2](BF_4)_2$ suggests a similar coordination geometry around the nickel(II) ion with the sulfur atoms in *trans* positions.

The coordination behaviour of memia is very similar to that of the thioether-imidazole ligand sbi [12]. A remarkable feature of both ligands is the spontaneous oxidation of Co(II) to Co(III) during the attempted synthesis of their Co(II) compounds.

Supplementary material

List of the atomic coordinates of the hydrogen atoms, the non-hydrogen anisotropic temperature factors, bond distances and bond angles, observed and calculated structure factors, and elemental analyses are available from the authors upon request.

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