Inorganica Chimica Acta, 215 (1994) 151–157

Neutral transition metal complexes with the tridentate ligand 4-(5-methyl-4-imidazolyl)-3-thiabutanoic acid. A series of isostructural octahedral compounds

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(Received June 17, 1993; revised August 12, 1993)

Abstract

The synthesis and spectroscopic properties of the iron, cobalt, nickel and copper complexes with the ligand 4-(5-methyl-4-imidazolyl)-3-thiabutanoic acid (abbreviated Hitba) are described. The compound Co(itba)$_2$ (**A**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.600(1)$, $b = 7.697(1)$, $c = 8.2696(5)$ Å, $\alpha = 86.745(8)$, $\beta = 71.321(7)$, $\gamma = 69.538(12)°$, $V = 428.5$ Å^3, $D_x = 1.65$ g/cm^3 for $Z = 1$. The compound Cu(itba)$_2$ (**B**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.789(3)$, $b = 7.794(4)$, $c = 8.138(4)$ Å, $\alpha = 71.448(4)$, $\beta = 86.905(4)$, $\gamma = 67.805(4)°$, $V = 432.4$ Å^3, $D_x = 1.66$ g/cm^3 for $Z = 1$. In both structures the metal ion is located on the inversion centre because of symmetry considerations. The non-hydrogens were located using Fourier methods and the structures were refined by least-squares methods to residual R_w values of 0.089 (**A**) and 0.050 (**B**). The coordination geometry of the metal ion in both compounds **A** and **B** is octahedral with the donor atoms of the two ligands in mutual *trans* positions. The bond distances in the cobalt compound are significantly different from those in the Jahn–Teller distorted copper compound (Co–N = 2.109(7), Cu–N = 1.986(3), Co–O = 2.065(6), Cu–O = 1.988(2), Co–S = 2.501(2), Cu–S = 2.7146(8)). The geometry of the cobalt ion can be described as a rather regular octahedron compared with the elongated octahedral copper structure. The obtained compounds M(itba)$_2$ are all isostructural according to their X-ray powder patterns and IR spectra, and all show remarkably strong ligand field spectra.

Key words: Crystal structures, Cobalt complexes, Tridentate ligand complexes; Chelate complexes

Introduction

Coordination chemists worldwide try to find the best functional groups to mimic amino acid residues in binding metal ions at the active site. In most proteins the amino acid residues that need to be mimicked are histidine (imidazoles, pyrazoles, pyridines), methionine (thioether, thioketones), aspartic acid and glutamic acid (carboxylic acids), and cysteine (thiolates, thiophenolates, thioamides). We now report the synthesis of a ligand that combines three of the above mentioned functional groups and its coordination compounds. Therefore, the ligand can be used as a ligand to make model systems for various active sites as there is: the copper ion in azurin [1], the iron ion in hemerythrin [2], the zinc ion in alcohol dehydrogenase [3] and the nickel ion in CO-dehydrogenase [4]. The ligand 4-(5-methyl-4-imidazolyl)-3-thiabutanoic acid (abbreviated Hitba) is easily synthesized from 5-methyl-4-hydroxymethylimidazole hydrochloride and mercaptoacetic acid [5, 6]. It contains an imidazole group, a thioether function and a carboxylic acid in a tridentate chelating ligand.

Experimental

Starting materials

The starting materials 5-methyl-4-hydroxymethylimidazole hydrochloride, mercaptoacetic acid and the transition metal salts are commercially available and were used as received. Water is demineralized in house.

Synthesis of the ligand

The synthesis of the ligand Hitba was performed according to a published procedure [5]. The hydrochloride salt of the ligand has been synthesized by others, using a similar procedure [6].

A solution of 7.5 g (50 mmol) 5-methyl-4-hydroxymethylimidazole hydrochloride and 4.6 g (50 mmol)

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0020-1693/94/\$07.00
SSDI 0020-1693(93)03681-Y

mercaptoacetic acid in 30 ml acetic acid was refluxed over a period of 6 h. The reaction mixture was then evaporated to dryness on a rotary evaporator yielding an off-white solid. This solid was dissolved in 50 ml water and the resulting clear solution was neutralized using solid $NaHCO_3$. The white precipitate was filtered, washed with water and acetone and dried in air. Partial evaporation of the filtrate yielded a second crop of white powder. Combined yields gave 6.9 g (75%) of Hitba. Melting point 245 °C. The compound is insoluble in the tried solvents, except for acidified solvents. NMR was therefore taken of the protonated ligand. The ^1H NMR spectrum of Hitba (solvent CD_3OD + a drop of 20% DCl in D_2O, internal standard $SiMe_4$) showed the following signals (ppm): 2.36 (s, 3H, methyl), 3.29 (s, 2H, SCH_2COO), 3.97 (s, 2H, $imCH_2S$), 8.75 (s, 1H, imidazole), 5.66 (OH, NH). *Anal.* Calc. for $C_7H_{10}N_2O_2S$: C, 45.15; H, 5.41; N, 15.04. Found: C, 44.68; H, 5.40; N, 14.59%. IR spectrum (KBr pellet): 3122(sharp, strong), 2500(vbroad), 1900(vbr), 1640(s), 1550(br), 1250(m), 1195(s), 1145(s), 870(br), 820(s), 720(s), 705(s), 652(m), 630(m), 600(s), 455(m), 343(w).

Synthesis of the complexes

Fe(itba)$_2$

The synthesis was performed in Schlenk type glassware in a nitrogen atmosphere. $[Fe(H_2O)_6](ClO_4)_2$ (1.5 g, 2 mmol) was dissolved in 8 ml water. A small amount of ascorbic acid was added to remove traces of Fe^{3+} from the starting salt. The ligand Hitba (0.75 g, 4 mmol) was suspended in 20 ml of 96% ethanol, and a few drops of triethylamine were added. Both the metal salt solution and the ligand suspension were deoxygenated by repeated evacuation and N_2 gas inlet. The iron perchlorate solution was added to the ligand suspension and the resulting reaction mixture was heated and stirred until most of the ligand had dissolved. The almost clear solution was filtered, the product crystallized as a metallic blue microcrystalline material, which was collected and washed with ether. Yield *c.* 50%. *Anal.* Calc. for $C_{14}H_{18}FeN_4O_4S_2$: C, 39.45; H, 4.26; N, 13.14; Fe, 13.1. Found: C, 39.33; H, 4.36; N, 12.77; Fe, 13.4%. IR spectrum (KBr pellet): 3180(s, br), 2955(m), 2900(w), 1620(vs, br), 1500(w), 1415(m), 1360(s), 1335(s), 1280(w), 1230(m), 1160(m), 1085(m), 970(m), 930(m), 915(s), 772(m), 720(m), 695(m), 665(m), 630(m), 550(w), 450(w), 430(w), 312(m).

Co(itba)$_2$

$[Co(H_2O)_6](NO_3)_2$ (0.29 g, 1 mmol) was dissolved in 5 ml water. The ligand Hitba (0.37 g, 2 mmol) was suspended in 10 ml water. Both the cobalt solution and the ligand suspension were heated on a hotplate and were mixed while hot. This mixture was heated for a short time to dissolve most of the ligand and was filtered whilst hot. Upon standing (and slow evaporation) the product appeared as a pink microcrystalline material. Yield *c.* 30%. *Anal.* Calc. for $C_{14}H_{18}CoN_4O_4S_2$: C, 39.16; H, 4.23; N, 13.05; Co, 13 7 Found: C, 39.04; H, 4.28; N, 12.85; Co, 13.6%. IR spectrum (KBr pellet): very similar to the Fe compound, with minor shifts in some bands.

Ni(itba)$_2$

The same procedure as for cobalt was followed. $[Ni(H_2O)_6]Cl_2$ (0.24 g, 1 mmol) was dissolved in 5 ml water, Hitba (0.37 g, 2 mmol) was suspended in 5 ml water. After filtration of the hot reaction mixture a lilac microcrystalline material was formed in approximately 30% yield. *Anal.* Calc. for $C_{14}H_{18}N_4NiO_4S_2$: C, 39.18; H, 4.23; N, 13.06; Ni, 13.7. Found: C, 38.76; H, 4.30; N, 12.77; Ni. 13.9% IR spectrum (KBr pellet): very similar to the Fe compound, with minor shifts in some bands.

Cu(itba)$_2$

The same procedure as for cobalt was used. $[Cu(H_2O)_3(NO_3)_2]$ (0.24 g, 1 mmol) was dissolved in 10 ml water, Hitba (0.37 g, 2 mmol) was suspended in 10 ml water. After filtration of the hot reaction mixture a blue microcrystalline material was formed. Yield *c.* 40%. *Anal.* Calc. for $C_{14}H_{18}CuN_4O_4S_2$: C, 38.75; H, 4.18, N, 12.91; Cu, 14.64. Found: C, 38.85; H, 4.20; N, 12.70; Cu, 14.4%.

Characterization methods

Metal analyses were carried out complexometrically with ethylenediaminetetraacetate (Na_2H_2edta) as the complexing agent [7]. C, H and N analyses were carried out at the University of Groningen, Netherlands.

IR spectra in the range 4000–200 cm^{-1} were recorded on a Perkin-Elmer 580 spectrophotometer. The samples were pelleted in KBr or Nujol mulls were made. Ligand field spectra (300–2000 nm) were recorded on a Perkin-Elmer 330 spectrophotometer, equipped with a PE data station, MgO was used as reference. EPR spectra were recorded on a Jeol Esprit 330 spectrophotometer with DPPH as internal standard. X-ray powder diffractograms were made with a Guinier-de Wolff camera using Cu Kα radiation. NMR spectra were taken with a 200 MHz Jeol FX-200, equipped with a Tecmag data station.

Crystallographic data collection and structure refinement

The diffraction data for $[Co(itba)_2]$ (**A**) and $[Cu(itba)_2]$ (**B**) were collected at room temperature on a CAD4 diffractometer, using Cu Kα radiation. The crystal data and refinement data of both structures are given in Table 1

TABLE 1. Crystal and refinement data of the compounds Co(itba)$_2$ (**A**) and Cu(itba)$_2$ (**B**)

	A	**B**
Formula	$CoC_{14}H_{18}N_4O_4S_2$	$CuC_{14}H_{18}N_4O_4S_2$
Formula weight	429.37	433.99
a (Å)	7.600(1)	7.789(3)
b (Å)	7.697(1)	7.794(4)
c (Å)	8.2696(5)	8.138(4)
α (°)	86.745(8)	71.448(4)
β (°)	71.321(7)	86.905(4)
γ (°)	69.538(12)	67.805(4)
V (Å^3)	428.52	432.42
F(000)	221	223
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Z	1	1
D_x (g/cm^3)	1.65	1.66
μ Cu Kα (cm^{-1})	106.7	42.1
Crystal dimensions (mm)	0.36×0.36×0.08	0.35×0.15×0.05
h Values	−9 to 9	0 to 9
k Values	0 to 9	−9 to 9
l Values	−10 to 10	−9 to 9
Scan range, θ	2.5–70.0	2.5–70.0
No. measured reflections	1633	1648
No. unique	1631	1646
No. used in refinement[a]	1197	1404
R_f[b]	0.064	0.043
R_w[c]	0.089	0.050
Max., min. $\Delta\rho$ excursions (e/Å^3)	0.91, −0.91	0.40, −0.46

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

The intensities of the reflections were corrected for Lorentz and polarization effects. Absorption correction was applied on both structures since the absorption coefficient are $\mu = 106.7$ and 42.1 cm^{-1} for compound **A** and **B**, respectively. An empirical absorption correction was carried out on both structures using the program DIFABS [8], whereas an additional Monte Carlo method absorption correction [9] was carried out for structure **A** because of the very high linear absorption coefficient resulting from the use of copper radiation. The calculations were performed on the Leiden University Amdahl mainframe using a local set of computer programs. Scattering factors were taken from ref. 10. In both structures the position of the heavy atom was deduced from symmetry considerations. The other non-hydrogen atoms were located with the program DIRDIF [11].

The structures were refined by full-matrix least-squares. The thermal parameters of the non-hydrogen atoms of both structures were refined anisotropically. The function minimized was $\Sigma w|F_o - F_c|^2$ with $w^{-1} = \sigma^2(F)$. All hydrogen atoms of structure **B** and almost all hydrogen atoms of structure **A** were located in difference Fourier maps; three hydrogen atoms of the ligand in **A** were placed at 0.95 Å from their parent atoms.

The positional parameters of the H atoms were coupled to their parent atoms during the isotropic refinement stages, with their B values coupled to one another; the final values for B_{iso} are 5.48 and 6.06 Å^2 for **A** and **B**, respectively. The fractional coordinates of the non-hydrogen atoms of **A** and **B** are listed in Table 2. Bond distances, bond angles and hydrogen bond data are given in Table 3. See also 'Supplementary material'.

Results

General considerations

A listing of spectroscopic characteristic data is given in Table 4. The elemental analyses of the compounds were satisfactory, see 'Experimental'. All coordination compounds show similar IR spectra, with only small shifts in some of the vibrations. All compounds have nearly identical X-ray powder patterns, indicating similar coordination geometries for each of the complexes. The details of the spectroscopic data will be discussed after the description of the structures.

Description of the structures of Co(itba)$_2$ (A) and Cu(itba)$_2$ (B)

PLUTON [12] projections of the structures of Co(itba)$_2$ (**A**) and Cu(itba)$_2$ (**B**) with the atomic labelling

TABLE 2. Fractional coordinates and equivalent temperature parameters of the non-hydrogen atoms of Co(itba)$_2$ (**A**) and Cu(itba)$_2$ (**B**)

Atom	x/a	y/b	z/c	B_{eq}[a]
Co(itba)$_2$ (**A**)[b]				
Co(1)	0	0	0	206(8)
O(5)	−1304(8)	−1882(9)	1190(7)	22(2)
O(6)	−3503(11)	−2484(10)	3421(8)	37(3)
C(7)	−234(1)	−166(1)	276(1)	22(3)
C(8)	−204(1)	−42(1)	396(1)	31(4)
S(9)	−1059(3)	1336(4)	2990(2)	253(9)
C(10)	−326(1)	319(1)	292(1)	33(4)
N(11)	−5892(11)	2692(12)	82(10)	30(3)
C(12)	−400(1)	172(1)	−80(1)	28(3)
N(13)	−2858(9)	1792(10)	83(8)	22(2)
C(14)	−406(1)	277(1)	161(1)	19(3)
C(15)	−600(1)	337(1)	158(1)	26(3)
C(16)	−791(1)	454(2)	287(1)	44(5)
Cu(itba)$_2$ (**B**)[c]				
Cu(1)	0	0	0	253(2)
O(5)	1820(4)	1162(4)	−1109(2)	311(9)
O(6)	2594(4)	3278(4)	−3207(4)	398(11)
C(7)	1702(5)	2209(5)	−2680(4)	271(11)
C(8)	501(5)	2140(5)	−4064(5)	313(13)
S(9)	−1359(1)	1318(1)	−3363(1)	289(3)
C(10)	−3140(5)	3490(6)	−3089(5)	321(13)
N(11)	−2633(5)	5594(5)	160(5)	400(14)
C(12)	−1690(6)	3679(6)	922(5)	381(15)
N(13)	−1694(4)	2692(4)	−119(4)	290(10)
C(14)	−2712(5)	4064(5)	−1631(4)	263(11)
C(15)	−3296(5)	5886(5)	−1478(5)	321(12)
C(16)	−4416(8)	7865(6)	−2687(7)	48(2)

[a] $B_{eq} = 8/3\ \pi^2$ trace U. [b] Atomic coordinates: Co × 1, C atoms × 10^3, others × 10^4, equivalent thermal parameters Co, S × 10^2, others × 10 Å^2. [c] Fractional coordinates: Cu × 1, others × 10^4, equivalent thermal parameters C(16) × 10, others × 10^2 Å^2.

are given in the Figs. 1 and 2, respectively. The unit cell appeared to be so small that only one molecule of M(itba)$_2$ could be fitted into the cell. In a first attempt the metal ion was placed on the center of symmetry of the primitive cell $P\bar{1}$. This appeared to be the right choice, as the other non-hydrogen atoms were easily found in the first run of a Fourier program. The cobalt and copper ion are surrounded by two ligands in an octahedral fashion. All like atoms are in *trans* positions as expected due to the symmetry restrictions. The cobalt ion is in the center of a rather regular octahedron in which no special axis can be found. This is in contrast to the copper compound, where a significant elongation is found in the copper to sulfur direction as is accounted for by the Jahn–Teller effect. The cobalt to ligand distances (Co–N 2.11; Co–S 2.50; Co–O 2.07 Å) are all comparable to similar complexes with *trans* geometry [13], whereas the cobalt to sulfur distances are shorter than those for *cis* bound thioether sulfurs (Co–S > 2.6 Å) [14]. The copper to ligand distances (Cu–N 1.99; Cu–S 2.71; Cu–O 1.99 Å)

TABLE 3. Bond distances (Å), bond angles (°) and hydrogen bond data in Co(itba)$_2$ (**A**) and Cu(itba)$_2$ (**B**) with e.s.d.s in parentheses

A		**B**	
Co(1)–O(5)	2.065(6)	Cu(1)–O(5)	1.988(2)
Co(1)–S(9)	2.501(2)	Cu(1)–S(9)	2.7146(8)
Co(1)–N(13)	2.109(7)	Cu(1)–N(13)	1.986(3)
O(5)–C(7)	1.271(9)	O(5)–C(7)	1.265(4)
O(6)–C(7)	1.231(9)	O(6)–C(7)	1.241(4)
C(7)–C(8)	1.53(1)	C(7)–C(8)	1.529(4)
C(8)–S(9)	1.798(9)	C(8)–S(9)	1.793(4)
S(9)–C(10)	1.79(1)	S(9)–C(10)	1.808(4)
C(10)–C(14)	1.50(1)	C(10)–C(14)	1.488(5)
N(11)–C(12)	1.34(1)	N(11)–C(12)	1.335(5)
N(11)–C(15)	1.34(1)	N(11)–C(15)	1.374(5)
C(12)–N(13)	1.31(1)	C(12)–N(13)	1.314(4)
N(13)–C(14)	1.37(1)	N(13)–C(14)	1.383(4)
C(14)–C(15)	1.39(1)	C(14)–C(15)	1.363(5)
C(15)–C(16)	1.50(1)	C(15)–C(16)	1.489(6)
O(5)–N(11)″	2.911(9)	O(5)–N(11)‴	3.146(4)
O(5)–H(11)″	2.091(9)	O(5)–H(11)‴	2.58(5)
O(6)–N(11)″	3.10(1)	O(6)–N(11)‴	2.887(4)
O(6)–H(11)″	2.50(1)	O(6)–H(11)‴	2.30(5)
O(5)–Co(1)–S(9)	83.3(2)	O(5)–Cu(1)–S(9)	80.99(7)
O(5)–Co(1)–N(13)	87.3(2)	O(5)–Cu(1)–N(13)	86.9(1)
O(5)–Co(1)–S(9)′	96.7(2)	O(5)–Cu(1)–S(9)′	99.01(7)
O(5)–Co(1)–N(13)′	92.7(2)	O(5)–Cu(1)–N(13)′	93.1(1)
S(9)–Co(1)–N(13)	83.2(2)	S(9)–Cu(1)–N(13)	81.37(8)
S(9)–Co(1)–N(13)′	96.8(2)	S(9)–Cu(1)–N(13)′	98.63(8)
Co(1)–O(5)–C(7)	122.2(6)	Cu(1)–O(5)–C(7)	125.8(2)
O(5)–C(7)–O(6)	124.0(8)	O(5)–C(7)–O(6)	123.0(3)
O(5)–C(7)–C(8)	118.9(7)	O(5)–C(7)–C(8)	121.0(3)
O(6)–C(7)–C(8)	116.9(8)	O(6)–C(7)–C(8)	116.0(3)
C(7)–C(8)–S(9)	116.7(6)	C(7)–C(8)–S(9)	117.9(2)
Co(1)–S(9)–C(8)	94.6(3)	Cu(1)–S(9)–C(8)	90.8(1)
Co(1)–S(9)–C(10)	97.1(3)	Cu(1)–S(9)–C(10)	92.0(1)
C(8)–S(9)–C(10)	101.7(5)	C(8)–S(9)–C(10)	101.8(2)
S(9)–C(10)–C(14)	111.9(6)	S(9)–C(10)–C(14)	114.7(3)
C(12)–N(11)–C(15)	109.7(7)	C(12)–N(11)–C(15)	108.5(3)
N(11)–C(12)–N(13)	109.1(8)	N(11)–C(12)–N(13)	110.9(3)
Co(1)–N(13)–C(12)	130.8(6)	Cu(1)–N(13)–C(12)	128.6(3)
Co(1)–N(13)–C(14)	116.6(5)	Cu(1)–N(13)–C(14)	122.7(2)
C(12)–N(13)–C(14)	107.9(7)	C(12)–N(13)–C(14)	106.0(3)
C(10)–C(14)–N(13)	122.9(7)	C(10)–C(14)–N(13)	122.0(3)
C(10)–C(14)–C(15)	129.4(8)	C(10)–C(14)–C(15)	128.4(3)
N(13)–C(14)–C(15)	107.5(8)	N(13)–C(14)–C(15)	109.5(3)
N(11)–C(15)–C(14)	105.6(8)	N(11)–C(15)–C(14)	105.1(3)
N(11)–C(15)–C(16)	123.2(8)	N(11)–C(15)–C(16)	122.6(4)
C(14)–C(15)–C(16)	131.2(9)	C(14)–C(15)–C(16)	132.3(4)

′ $-x, -y, -z$; ″ $-1-x, -y, -z$; ‴ $-x, 1-y, -z$.

TABLE 4. Ligand field data (× 10^3 cm^{-1}) and EPR data for the itba complexes

Fe(itba)$_2$	15.0, 8.5
Co(itba)$_2$	25.9, 19.4, 10.8
Ni(itba)$_2$	27.8, 18.3, 14.4, 10.7
Cu(itba)$_2$	16.2, 12.7, 10.8
	$g_\perp$ 2.07, $g_\parallel$ 2.32 (solid, room temperature)
	$g_\perp$ 2.08, $g_\parallel$ 2.35, $A_\parallel$ 13.8 mT (H_2O/glycol, 77 K)

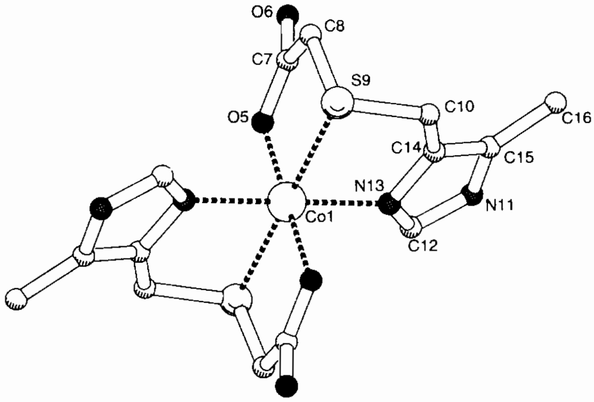

Fig. 1 PLUTON [12] projection of the compound Co(itba)$_2$. Hydrogen atoms are omitted for clarity.

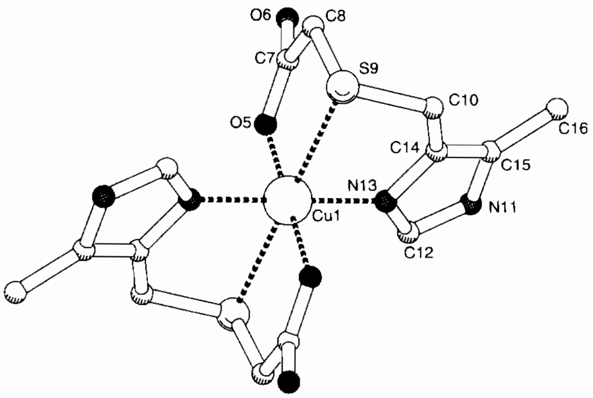

Fig 2 PLUTON [12] projection of the compound Cu(itba)$_2$. Hydrogen atoms are omitted for clarity.

are also to be considered normal, although the copper to sulfur distance falls in the shorter range for axially bound, semi-coordinated sulfur atoms [15, 16].

Another significant difference in both structures (apart from the Jahn–Teller elongation for Cu) is found in the hydrogen bond interactions. Both the coordinating and the non-coordinating oxygen atoms of the carboxylate groups in the cobalt and the copper structure are more or less involved in a hydrogen bond interaction with the imidazole hydrogens. In the cobalt structure the O5 to H11 distance is the shortest (2.09 Å, O6–H11 2.5 Å) whereas in the copper compound the distance of the non-coordinating O6 to H11 is shorter (2.30 Å, O5–H11 2.58 Å). The differences probably result from packing effects.

The imidazole rings are planar with deviations being smaller than 0.01 Å. All distances and angles within the organic ligands are as expected.

Spectroscopic data of the coordination compounds

The IR spectra of the M(itba)$_2$ complexes are all very similar and show a very characteristic pattern in the region 1090–1250 cm^{-1} (three sharp peaks) and in the region 600–800 cm^{-1} (six sharp peaks).

The compound Fe(itba)$_2$ shows two distinct bands in its LF spectrum (at 15.0 and 8.5×10^3 cm^{-1}) in agreement with a tetragonal high-spin iron complex [17].

The ligand field spectrum of Co(itba)$_2$ is in agreement with an octahedral geometry and resembles the spectra of other imidazole–thioether complexes with *trans* sulfur coordination [13]. In the case of octahedral cobalt compounds with *cis* sulfur coordination, the ligand field spectra show severe distortions from octahedral and will even resemble tetrahedral species [14, 18].

For the tridentate N$_2$S ligand 1,3-bis(5-methyl-4-imidazolyl)-2-thiapropane, two isomers were formed with nickel salts, namely a purple compound with a very strong LF spectrum of which a crystal structure determination showed (surprisingly) the two sulfur atoms to be *cis* coordinated [19] and a pink compound in which an all *trans* conformation was postulated [20]. The ligand field spectrum of the present lilac Ni(itba)$_2$ strongly resembles that of the pink $[Ni(N_2S)_2]^{2+}$ complexes; taking together the found isomorphism within the itba compounds, the above postulation seems to be proved.

The LF spectrum of the copper compound Cu(itba)$_2$ shows a rather sharp peak with a maximum at 16.3×10^3 cm^{-1} and a broad peak with a maximum at 12.7 and a shoulder at 10.8×10^3 cm^{-1}. This pattern is in good agreement with the observed elongated octahedron and resembles that of other imidazole thioether copper compounds [15]. In this case no clear distinction can be made between *cis* and *trans* thioether coordination. However, close inspection can perhaps discriminate whether the *trans* thioethers form the axial, elongated axis (as described in this paper) or form one of the equatorial shorter axes [13], but this postulation needs to be confirmed using other data. The EPR spectrum is axial, but hyperfine splitting is not observed. Attempts were made to synthesize copper dopes in zinc and cadmium, but no pure, isomorphous compounds could be obtained.

Discussion

From the analytical data, the identical IR spectra and the X-ray data, it can be readily deduced that the metal ions in all compounds M(itba)$_2$ are in a similar *trans* octahedral geometry.

In one attempt it even seemed possible to synthesize the cadmium complex Cd(itba)$_2$, having a similar IR as the other compounds. However, this product could not be reproduced and successive attempts yielded mixtures of Cd(itba)$_2$ and Hitba or just the pure ligand as crystalline material. Also, attempts to synthesize the manganese and zinc analogs did not result in the respective itba complexes. With copper chloride another compound could be isolated: when copper chloride and Hitba were combined in ethanol a gelatinous mass was formed, which after filtration dried up to a powder. IR spectroscopy showed the presence of the ligand and analysis indicated the compound to be [Cu(itba)Cl]. The ligand field spectrum of this compound showed one maximum at 12.7×10^3 cm^{-1}, indicating a square planar geometry of the copper ion. However, the compound could not be crystallized in a pure form and therefore it will not be further discussed.

The nickel complex with Hitba was only formed in a *trans* geometry, no *cis* conformation was observed, as for the nickel compounds with the tridentate N_2S ligand L_1 [19, 20]. A schematic drawing of the discussed ligands is given in Fig. 3. Other tridentate ligands containing an ONS coordination bite include some Schiff base type ligands with *S*-alkyldithiocarbazate or thiophenolate sulfur groups and phenolate or pyridine-*N*-oxide oxygen functions. An octahedral nickel complex with two NOS ligands L_2 has been reported by Zimmer *et al.* [21]. Unlike in the itba compounds, the tridentate ligands in this compound are meridionally coordinated. Square planar nickel compounds with L_3 and pyridine [22] or L_4 and benzenethiolate [23] have been reported Square planar dinuclear nickel compounds have also been obtained with L_2, in which the phenolate oxygen bridges the two nickel ions [24, 25]. Unfortunately, it did not seem possible to make analogous four-coordinated compounds with Hitba, with the exception of the ill-defined copper compound described above. A crystal structure of a nickel complex with the $N_2S_2O_2$ ligand L_5, with two amines, two thioether groups and two carboxylate functions has recently been reported [26] Due to the restrictions of the ligand, the amine-N and thioether-S atoms are *cis* coordinated. The nickel to ligand distances are, however, such as would be expected for our [Ni(itba)$_2$] compound.

Unfortunately, due to the extremely low solubility of the complexes in all tried solvents, no other measurements and studies could be undertaken.

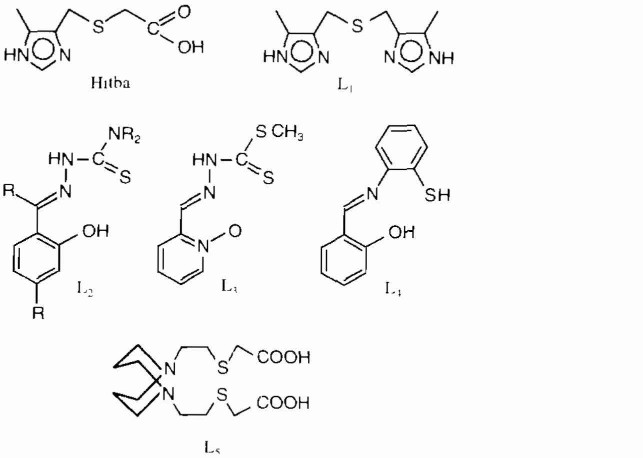

Fig 3 Schematic drawings of the ligands discussed in the text

Conclusions

This paper describes a new tridentate ligand which combines three biologically relevant functional groups, namely an imidazole, a thioether and a carboxylate group. The coordinating behavior of this ligand towards the transition metals iron, cobalt, nickel, copper and zinc has been investigated. In all cases (except for zinc) extremely stable and insoluble compounds with general formula M(itba)$_2$ were formed. Despite the general interest of these octahedral compounds, their extreme stability unfortunately prevented further studies regarding biologically more relevant model systems. Several attempts to obtain complexes with a ligand to metal ratio of 1 1, thus creating reactive sites where (for example) thiolate groups could bind, have failed. Further studies to obtain model systems relevant for nickel hydrogenases will be undertaken.

Supplementary material

Lists of the fractional coordinates of the hydrogen atoms, anisotropic temperature factors, and lists of observed and calculated structure factors of **A** and **B** are available from the authors upon request.

Acknowledgements

We are indebted to Dr R.A.G. de Graaff for his assistance in the processing of the diffraction data, to Ms I Y Koopmans for some experimental work, and to Mr J F van Lent and Mr N M. van der Pers of Delft Technical University for taking the Guinier-de Wolff X-ray powder pictures The research of Dr E. Bouwman has been made possible by a fellowship of the Royal Netherlands Academy of Arts and Sciences.

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