Coordination compounds with the N_2S donor ligand 1,3-bis(5′-methyl-4′-imidazolyl)-2-thiapropane (sbi). The X-ray structure of $[ZnCl_2(sbi)]$

E. Bouwman, W. L. Driessen*, G. J. A. A. Koolhaas, A. C. van Steenbergen, J. Reedijk
Department of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden (The Netherlands)

M. Dartmann and B. Krebs
Anorganisch-Chemisches Institut der Universitat Münster, Wilhelm-Klemm-Strasse 8, D-4400 Münster (FRG)

(Received May 31, 1991; revised July 18, 1991)

Abstract

The synthesis, spectroscopy and structure of mononuclear transition-metal coordination compounds of the ligand 1,3-bis(5′-methyl-4′-imidazolyl)-2-thiapropane (sbi) are described. The ligand acts as a didentate N_2-ligand in the compounds $[ZnBr_2(sbi)]$, $[ZnCl_2(sbi)]$ and $[CoCl_2(sbi)]$, and the anions take part in the coordination of the metal ion, resulting in tetrahedral geometries with N_2X_2 chromophores. The ligand acts as a tridentate ligand in the compounds $[M(sbi)_2]X_2(H_2O)_n$ with $M = Co^{2+}$, Ni^{2+}; $X = Cl^-$, NO_3^-, BF_4^-; $n = 0-4$; and $[Co(sbi)_2](BF_4)_3$, resulting in octahedral geometries with an N_4S_2 chromophore. The latter compound formed by spontanious oxidation from a Co(II) solution. The compound $[ZnCl_2(sbi)]$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.357(2)$, $b = 8.935(3)$, $c = 10.600(3)$ Å, $\alpha = 75.25(2)$, $\beta = 83.45(2)$, $\gamma = 75.15(2)°$, $V = 738.9$ Å^3, $Z = 2$. The structure was solved with the Patterson map and refined by full-matrix least-squares methods to a residual R of 0.035 ($R_w = 0.041$) for 2824 significant reflections. The Zn(II) ion is tetrahedrally surrounded by two imidazole nitrogens of the ligand sbi and two chloride ions, with distances of 2.012(2), 2.019(2), 2.243(1) and 2.256(1) Å, respectively. The H atoms of the imidazole nitrogens are hydrogen bonded to the chloride anions of neighbouring molecules (N...Cl contacts are 3.213 and 3.323 Å).

Introduction

Valid models for the blue-copper site [1, 2] should contain at least two nitrogen donor atoms and two sulfur donors, i.e. most ideally two imidazolyl groups, a thioether sulfur and a thiolate donor atom, which should be able to accommodate both Cu(I) and Cu(II). Despite several attempts by many research groups [3, 4], so far such model systems have not been prepared [5]. The potentially tridentate N_2S-ligand 1,3-bis(5′-methyl-4′-imidazolyl)-2-thiapropane (abbreviated as sbi) might be a good building block for a blue-copper model. A schematic drawing of the ligand sbi is shown in Fig. 1. Copper complexes with the ligand sbi have already been described [6]. To investigate the coordination properties of the ligand sbi in more detail, coordination compounds with the transition metals, cobalt, nickel and zinc have been synthesized and the X-ray structure of $[ZnCl_2(sbi)]$ has been determined.

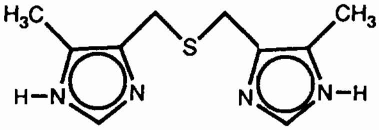

Fig. 1. Schematic drawing of the ligand 1,3-bis(5′-methyl-4′-imidazolyl)-2-thiapropane (sbi).

Experimental

Starting materials and syntheses

All chemicals were commercially available, of sufficient purity, and were used without further treatment. The synthesis of the ligand 1,3-bis(5′-methyl-4′-imidazolyl)-2-thiapropane (sbi) has been described elsewhere [7].

The coordination compounds with general formula $[MX_2(sbi)]$ were prepared by dissolving the appropriate hydrated metal salt (3 mmol) in 20 ml of hot ethanol and adding this solution to a solution of the ligand sbi (1.5 mmol) in 20 ml of hot ethanol. After filtration of the reaction mixture, the complex crystallized on cooling. In some cases evaporation of

---

*Author to whom correspondence should be addressed.

some of the solvent was required before crystallization of the coordination compound occurred.

To synthesize the coordination compounds with general formula $[M(sbi)_2]X_2$ an analogous procedure was used with 6 mmol of the ligand sbi dissolved in 20 ml hot ethanol. For the preparation of the pink nickel compounds with the general formula $[Ni(sbi)_2]X_2$ larger volumes (35 ml) of solvent were used.

Characterization methods

Metal analyses were carried out complexometrically using EDTA as complexing agent. Chloride was determined potentiometrically with $AgNO_3$ as the precipitating agent [8]. C, H and N analyses were performed at University College, Dublin.

IR spectra (4000–200 cm^{-1}) were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a PE Data Station as Nujol mulls between KRS-5 discs or as KBr pellets.

Ligand-field spectra of the solids (300–2000 nm) were recorded on a Perkin-Elmer 330 spectrophotometer equipped with a diffuse reflectance attachment, using MgO as a reference.

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

X-ray methods and structure determination

A colourless needle ($0.14 \times 0.22 \times 0.4$ mm) of $[ZnCl_2(sbi)]$ was isolated and mounted in a glass capillary.

Crystal data: $C_{10}H_{14}Cl_2N_4SZn$, $M_r = 358.27$, triclinic, space group $P\bar{1}$, $a = 8.357(2)$, $b = 8.935(3)$, $c = 10.600(3)$ Å, $\alpha = 75.25(2)$, $\beta = 83.45(2)$, $\gamma = 75.15(2)°$, $V = 738.9$ Å^3. By least-squares refinement of 18 orientation reflections, $D_{calc} = 1.61$ g cm^{-3}, $Z = 2$.

Data collection: Siemens R3 diffractometer, operated in the 2ω–θ mode, using graphite-monochromatized Mo(Kα) radiation ($\lambda = 0.71073$ Å). Data collection range $4.0 < 2\theta < 54°$, $0 < h < 11$, $-12 < k < 12$, $-14 < l < 14$. A total of 3247 independent reflections was measured of which 2824 with $I > 2\sigma(I)$ were used for the structure solution and refinement. Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction by Ψ scans was applied ($\mu = 21.9$ cm^{-1}).

The structure was solved using the system SHELXTL-plus [9]. The position of the zinc atom was determined form a Patterson map. The atomic scattering factors were taken from ref. 10. The structure was refined by full-matrix least-squares refinement. The non-hydrogen atoms were refined anisotropically. The function minimized was $\Sigma w|F_o - F_c|^2$ with $w^{-1} = \sigma^2(F) + 0.0001F^2$. H atoms were placed at 0.96 Å from their parent atom. The positional parameters of the H atoms were coupled to their parent atoms during the refinement stages with fixed U values of 0.08 Å^2. At the final stage the conventional discrepancy index $R_F = \Sigma(|F_o - F_c|)/\Sigma F_o$ had been reduced to 0.035 and the weighted factor $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$ to 0.041. Maximum positive and negative densities in the final difference Fourier are 0.46 and -0.41 e Å^{-3}, respectively.

Results and discussion

Description of the structure of $[ZnCl_2(sbi)]$

The ligand-field spectra (*vide infra*) of $[CoCl_2(sbi)]$ and the similar IR spectral data for the Zn compound would suggest that the thioether is not coordinated in these compounds (*vide supra*). Therefore a crystal structure determination for a representive example was undertaken. A PLUTO drawing [11] of $[ZnCl_2(sbi)]$ is given in Fig. 2. The fractional coordinates of the non-hydrogen atoms are listed in Table 1. Bond distances and bond angles of the non-hydrogen atoms are listed in Table 2.

As is clear from Fig. 2 and Table 1, the thioether is not coordinated to the metal (shortest Zn–S distance is 4.341(1) Å) and only two imidazole nitrogens and two chloride ions bind to the zinc ion in a slightly distorted tetrahedral geometry. There are no other intermolecular distances shorter than the van der Waals distances. The imidazole rings are planar with distances to the least-squares planes of less than 0.02 Å and there is no stacking between the rings. So, the crystal packing is determined by the hydrogen bonding of the ligands to the anions and by normal van der Waals contacts.

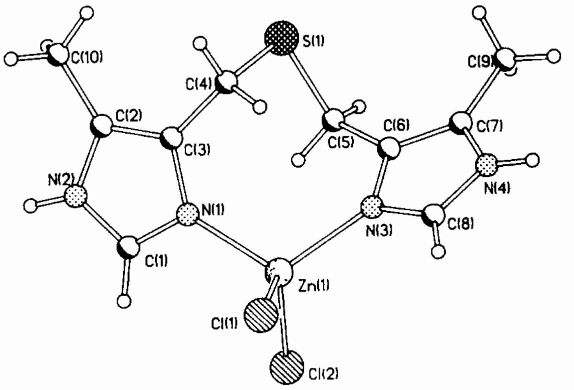

Fig. 2. PLUTO drawing [11] and atomic labelling of the molecular entity $[ZnCl_2(sbi)]$.

TABLE 1. Fractional coordinates and isotropic temperature factors of the non-hydrogen atoms in $[ZnCl_2(sbi)]$

	x	y	z	U_{eq}
Zn(1)	0.76528(4)	0.59308(4)	−0.28983(3)	0.0378(1)
Cl(1)	0.6080(1)	0.6621(1)	−0.4629(1)	0.0541(3)
Cl(2)	0.8758(1)	0.3286(1)	−0.2320(1)	0.0540(3)
S(1)	0.8962(1)	0.9098(1)	−0.0902(1)	0.0649(4)
N(1)	0.9655(3)	0.6860(3)	−0.3365(3)	0.0398(8)
N(2)	1.2140(3)	0.7043(3)	−0.4148(3)	0.052(1)
N(3)	0.6285(3)	0.6686(3)	−0.1384(3)	0.042(1)
N(4)	0.4189(3)	0.7250(3)	−0.0019(3)	0.054(1)
C(1)	1.1039(4)	0.6143(4)	−0.3914(3)	0.048(1)
C(2)	1.1449(4)	0.8421(4)	−0.3739(3)	0.046(1)
C(3)	0.9898(3)	0.8302(3)	−0.3259(3)	0.041(1)
C(4)	0.8628(4)	0.9406(3)	−0.2629(3)	0.052(1)
C(5)	0.8590(4)	0.7118(4)	−0.0289(3)	0.055(1)
C(6)	0.6839(4)	0.7058(3)	−0.0347(3)	0.043(1)
C(7)	0.5533(4)	0.7399(4)	0.0510(3)	0.052(1)
C(8)	0.4670(4)	0.6816(4)	−0.1142(3)	0.050(1)
C(9)	0.5442(5)	0.7917(6)	0.1763(4)	0.080(2)
C(10)	1.2331(4)	0.9709(4)	−0.3838(4)	0.066(2)

TABLE 2. Bond distances (Å) and bond angles (°) of the non-hydrogen atoms in $[ZnCl_2(sbi)]$

Zn(1)–Cl(1)	2.243(1)	Cl(1)–Zn(1)–Cl(2)	112.5(1)
Zn(1)–Cl(2)	2.256(1)	Cl(1)–Zn(1)–N(1)	109.9(1)
Zn(1)–N(1)	2.012(2)	Cl(2)–Zn(1)–N(1)	103.3(1)
Zn(1)–N(3)	2.019(2)	Cl(1)–Zn(1)–N(3)	109.3(1)
S(1)–C(4)	1.823(4)	Cl(2)–Zn(1)–N(3)	110.4(1)
S(1)–C(5)	1.816(4)	N(1)–Zn(1)–N(3)	111.3(1)
N(1)–C(1)	1.321(4)	Zn(1)–N(1)–C(1)	122.9(3)
N(1)–C(3)	1.388(4)	Zn(1)–N(1)–C(3)	130.7(2)
N(2)–C(1)	1.334(5)	C(1)–N(1)–C(3)	106.3(3)
N(2)–C(2)	1.373(4)	N(1)–C(1)–N(2)	110.2(3)
C(2)–C(3)	1.358(4)	C(1)–N(2)–C(2)	109.0(2)
C(2)–C(10)	1.496(5)	N(2)–C(2)–C(3)	105.4(3)
C(3)–C(4)	1.478(4)	N(2)–C(2)–C(10)	123.9(3)
C(4)–S(1)	1.823(4)	C(3)–C(2)–C(10)	130.7(3)
S(1)–C(5)	1.816(4)	C(2)–C(3)–N(1)	109.1(3)
C(5)–C(6)	1.486(5)	C(4)–C(3)–N(1)	121.8(3)
N(3)–C(6)	1.384(4)	C(2)–C(3)–C(4)	128.9(3)
N(3)–C(8)	1.325(4)	C(3)–C(4)–S(1)	112.1(2)
C(6)–C(7)	1.361(4)	C(4)–S(1)–C(5)	99.9(2)
C(7)–C(9)	1.502(6)	S(1)–C(5)–C(6)	113.8(2)
C(7)–N(4)	1.361(5)	C(5)–C(6)–N(3)	122.4(3)
N(4)–C(8)	1.333(4)	C(5)–C(6)–C(7)	128.7(3)
C(8)–N(3)	1.325(4)	N(3)–C(6)–C(7)	108.9(3)
C(7)–C(8)	1.362(5)	C(6)–C(7)–N(4)	105.8(3)
		C(6)–C(7)–C(9)	130.7(4)
		N(4)–C(7)–C(9)	123.5(3)
		C(7)–N(4)–C(8)	108.9(3)
		N(4)–C(8)–N(3)	110.3(3)
		C(8)–N(3)–C(6)	106.1(3)
		C(8)–N(3)–Zn(1)	126.1(2)
		C(6)–N(3)–Zn(1)	127.7(2)

Moderate strong hydrogen bonds are observed between the imidazole N–H groups and the Cl^- anions from neighbouring molecules. The N–Cl distances (3.213 and 3.323 Å, respectively) are correlated with the position of the N–H vibrations in accordance with the relationship of Bellamy and Owen [12].

Spectroscopic characterization

In Table 3 the spectroscopic data of the coordination compounds of the ligand sbi are given. Analytical results of the coordination compounds with the ligand sbi were all satisfactory (see 'Supplementary material').

With cobalt and zinc some 1:1 sbi compounds have been obtained: $[CoCl_2(sbi)]$ is a blue–green compound with a Vis–NIR spectrum typical for C_{2v}-distorted tetrahedral cobalt(II) with an N_2Cl_2Co chromophore [13], indicating that the thioether sulfur is not coordinated to the metal ion. X-ray Guinier de Wolff and IR spectra showed $[CoCl_2(sbi)]$ and $[ZnCl_2(sbi)]$ to be structurally isomorphous. The Vis–NIR spectrum of a cobalt-doped sample of $[ZnBr_2(sbi)]$ indicates that the zinc atom has a tetrahedral geometry, as was the case for the zinc ion in $[ZnCl_2(sbi)]$, confirmed by X-ray crystallography (*vide supra*). X-ray Guinier de Wolff spectra showed the two zinc complexes not to be structurally isomorphous.

With cobalt and nickel also some 1:2 complexes could be prepared. The nickel compounds all analyze as $[Ni(sbi)_2]X_2(H_2O)_n$ with $n = 0$–5. The crystal structure of the purple compound $[Ni(sbi)_2](SiF_6)(H_2O)_5$ has been solved [14]. In this compound, the nickel ion appeared to be in an octahedral environment with two ligands coordinating, with, suprisingly, the two thioether sulfur atoms *cis* coordinated, in contrast to the *trans* coordination observed for the copper compounds [6].

TABLE 3. Spectroscopic data of the coordination compounds with the ligand sbi

Compound	Colour	Vis–NIR (10^3 cm^{-1})
$CoCl_2(sbi)$	blue	15.9, 7.3
$ZnCl_2(sbi)$	white	
$ZnBr_2(sbi)$	white	
$Co(sbi)_2Cl_2$	brown	22.9, 18.3, 10.9
$Co(sbi)_2(NO_3)_2(H_2O)_2$	brown	22.9, 18.2, 11.3
$Co(sbi)_2(BF_4)_3$	orange	22.1
$Ni(sbi)_2(SiF_6)(H_2O)_5$	purple	27.8, 17.6, 11.0
$Ni(sbi)_2Cl_2(H_2O)_4$	purple	28.5, 18.0, 11.2
$Ni(sbi)_2Cl_2(H_2O)_4$	pink	20.2, 14.3, 12.0, 10.3
$Ni(sbi)_2(BF_4)_2$	purple	27.8, 17.6, 11.0
$Ni(sbi)_2(NO_3)_2(H_2O)_2$	purple	28.1, 17.6, 11.9
$Ni(sbi)_2(NO_3)_2(H_2O)_2$	pink	20.2, 14.3, 11.7, 10.5

The nickel compounds all show a remarkably strong ligand field (see Table 3). For the nickel compounds two different types of Vis–NIR spectra are encountered (Fig. 3). The first type of spectra are obtained from purple coloured nickel compounds and the second type of spectra are obtained from the pink coloured compounds. With the anion BF_4^- only the purple compound was obtained. With the anions NO_3^- and Cl^- both the purple and the pink species could be obtained, depending upon the conditions used. The Vis–NIR spectra of the purple nickel compounds indicate an octahedral ligand field. The geometry of the nickel ion in all these complexes is therefore probably also *cis*-distorted octahedral, analogous to $[Ni(sbi)_2](SiF_6)(H_2O)_5$ [14]. For the pink nickel nitrate and the pink nickel chloride compounds, the Vis–NIR spectra indicate significant splitting in agreement with a C_{4v}-coordination, apparently arising from the *trans*-NiN_4S_2 chromophore with the weak sulfur donor atoms on the axial positions. Unfortunately, no single crystals could be obtained to confirm this coordination geometry.

Two 1:2 cobalt(II) compounds have been prepared and characterized, namely $[Co(sbi)_2](NO_3)_2(H_2O)_2$ and $[Co(sbi)_2]Cl_2$. The compounds have nearly identical Vis–NIR spectra, indicating a distorted octahedral geometry of the cobalt ion [13], possibly with the sulfur atoms at a rather large distance from the metal ion. X-ray Guinier de Wolff and IR spectra showed $[Co(sbi)_2](NO_3)_2$ and the pink modification of $[Ni(sbi)_2](NO_3)_2$ to be structurally isomorphous. No cobalt compounds isomorphous with the purple nickel compounds could be isolated.

Surprisingly, a cobalt compound, with stoichiometry $[Co(sbi)_2](BF_4)_3$, was obtained, starting from a solution containing cobalt(II). The analytical data and the Vis–NIR spectrum show it to be a cobalt(III) compound. With the imidazole-thioether ligand 4-(2′-aminoethylthiomethyl)-5-methylimidazole (memia) [15] also a spontaneous oxidation of cobalt(II) to cobalt(III) occurred during the preparation. These are the only thioether coordinated cobalt compounds known in which such a spontaneous oxidation takes place. For the compound $[Co(sbi)_2](BF_4)_3$ an octahedral coordination geometry with Co–N and Co–S distances similar to those in $[Co(memia)_2](BF_4)_3$ are envisaged [15].

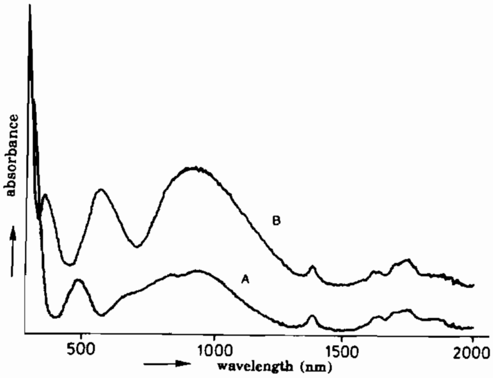

Fig. 3. Vis–NIR spectra of the pink (A) and the purple (B) modification of $[Ni(sbi)_2](NO_3)_2$.

Conclusions

In all 1:2 complexes the thioether sulfur coordinates to the metal ions with distances of 2.79 Å in $[Cu(sbi)_2](BF_4)_2(C_2H_5OH)_2$ and of 2.513 and 2.496 Å in $[Ni(sbi)_2](SiF_6)(H_2O)_5$. Two types of chromophores seem to be possible for the 1:2 compounds, a *cis*-MS_2N_4 chromophore for the purple nickel compounds and a *trans*-MS_2N_4 chromophore for the pink nickel compounds and the cobalt and copper 1:2 compounds.

Supplementary material

Tables containing: a structure determination summary, the atomic coordinates, the bond lengths and valence angles, the non-hydrogen anisotropic thermal parameters, the observed and calculated structure factors, and the analytical data of the compounds are available from Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, D-7514 Eggenstein, Leopoldshafen 2, on quoting the depository number CSD 55409, the name of the authors and the journal citation.

References

1 J. M. Guss, P. R. Harrowell, M. Murata, V. A. Norris and H. C. Freeman, *J. Mol. Biol., 192* (1986) 361.
2 W. E. B. Shepard, B. F. Anderson, D. A. Lewandoski, G. E. Norris and E. N. Baker, *J. Am. Chem. Soc., 109* (1990) 7817.
3 L. Cassella, M. Gullotti and E. Suardi, *J. Chem. Soc., Dalton Trans.,* (1990) 2843.
4 J. S. Thompson, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc., 101* (1979) 4181.
5 E. Bouwman, W. L. Driessen and J. Reedijk, *Coord. Chem. Rev., 104* (1990) 143.
6 A. C. van Steenbergen, E. Bouwman, W. L. Driessen, J. Reedijk and P. Zanello, *J. Chem. Soc., Dalton Trans.,* (1990) 3175.
7 E. Bouwman and W. L. Driessen, *Synth. Commun., 18* (1988) 1581.
8 A. I. Vogel, *Quantitative Inorganic Analyses*, Longmans, London, 1961.

9 SHELXTL program package, NICOLET XRD Corporation, Madison, WI.

10 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch, Birmingham, UK, 1974.

11 W. D. S. Motherwell and W. Clegg, *PLUTO*, a program for plotting molecular and crystal structures, University of Cambridge, UK, 1978.

12 L. J. Bellamy and A. J. Owen, *Spectrochim.. Acta, Part A, 25* (1969) 329.

13 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1986.

14 A. L. Spek, A. J. M. Duisenberg, E. Bouwman, W. L. Driessen and J. Reedijk, *Acta Crystallogr., Sect. C, 44* (1988) 1569.

15 P. D. Verwey, S. Sital, E. Bouwman, W. L. Driessen, J. Reedijk and J. S. Wood, *Inorg. Chim. Acta, 182* (1991) 187.