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Coordination compounds of the ligand 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh) with divalent nickel, cobalt and zinc salts. X-ray crystal structure of $Co(bddh)(NCS)_2$

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Abstract

The N_2S_2 ligand 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (abbreviated bddh) forms the coordination compounds (Co, Ni, Zn)(bddh)Cl_2, (Ni, Co)(bddh)$(NCS)_2$ and $[Ni(bddh)(NO_3)_2](H_2O)_2$. The X-ray crystal structure of Co(bddh)$(NCS)_2$ was determined at room temperature: tetragonal, space group $P4_12_12$, $a=b=9.083(1)$, $c=26.447(3)$ Å, $\alpha=\beta=\gamma=90.0°$, $Z=4$. The structure was solved by Patterson methods and refined by least-squares calculations to the residual R values of 0.038 (R) and 0.021 (R_w) and the goodness-of-fit of 2.27 for 4808 measured, 2313 independent and 1999 observed ($F>4.0\sigma(F)$) reflections. The cobalt(II) ion is in a distorted octahedral $CoN_2N'_2S_2$ geometry, in agreement with its ligand field spectrum. The ligand chelates through two pyrazole N atoms in *trans* position and the two sulfur atoms in *cis* position. The thiocyanate anions coordinate through the N atoms in a *cis* position. The Co–donor distances are 2.119(2) (N-pyrazole), 2.579(1) (S) and 2.026(3) (N-thiocyanate) Å. The ligand field spectra of the nickel compounds agree with octahedral coordination of the metal ion. IR spectroscopy of $[Ni(bddh)(NO_3)_2](H_2O)_2$ strongly suggests that both nitrate anions are monodentate and the water molecules are present in the crystal lattice. The compounds (Co, Zn)(bddh)Cl_2 are X-ray isomorphous and the ligand field spectrum of Co(bddh)Cl_2 shows a CoN_2Cl_2 chromophore.

Introduction

An increasing number of low-molecular weight coordination compounds are designed and synthesized to obtain a better insight into the structure and nature of the active sites of metalloproteins [1]. Even though such coordination compounds do not mimic all protein properties they can contribute to the greater understanding of certain topics, such as metal thioether interactions. In previous reports [2–4] the interesting coordination behaviour of the ligand 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) and 1,9-bis(3,5-dimethyl-1-pyrazolyl)-3,7-dithianonane (bddn), incorporating two pyrazole groups and two thioether functions, was described. These ligands, see Fig. 1, show a remarkable flexibility in their coordination behaviour towards first-row transition metal salts. The X-ray crystal structures of the compounds Zn(bddo)$(NCS)_2$ and the red and green modification of Cu(bddo)Cl_2 show that the thioether functions of the ligand bddo are not coordinated to the metal ion, whereas the X-ray crystal structures of the compounds Ni(bddo)$(NCS)_2$, $[Cu(bddn)(H_2O)](BF_4)_2$ and $Cd_2(bddo)(NCS)_4$ show that the thioether atoms are coordinated to the metal ion. To investigate the influence of the size of the bite between the pyrazole ring and the thioether

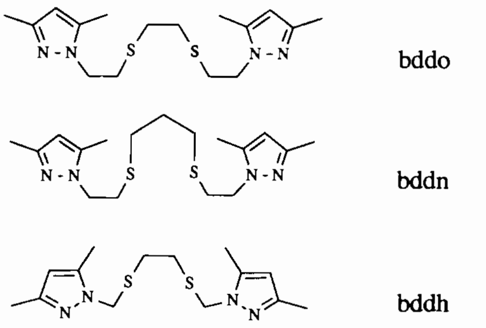

Fig. 1. The ligands bddo, bddn and bddh.

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function on the coordination behaviour of this ligand system, the ligand 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane, abbreviated as bddh, was synthesized. This new ligand bddh (Fig. 1) differs from bddo and bddn by having only one methylene unit between the pyrazole group and the thioether atom. In this report the coordination behaviour of the ligand bddh towards the divalent metal salts of nickel, cobalt and zinc using the anions chloride, nitrate, thiocyanate and tetrafluoroborate will be described. In a separate report the copper containing compounds will be described [5].

Experimental

Synthesis of the ligand bddh

The materials used in the synthesis were all commercially available and were used without purification. The synthesis of 1-hydroxymethyl-3,5-dimethylpyrazole (nhdp) is described elsewhere [6].

1-(Chloromethyl)-3,5-dimethyl-pyrazole (ncdp·HCl)

To a chilled solution ($T<5$ °C) of 30 g (0.24 mol) of nhdp in carefully dried chloroform 30.3 g (0.26 mol), thionyl chloride was added dropwise. The temperature of the reaction mixture was not allowed to exceed 10 °C. Stirring was prolonged for 30 min, while the reaction mixture was allowed to warm up to room temperature. The solvent was removed *in vacuo* and the resulting yellow oil was solidified by adding dry diethylether, while stirring vigorously. The product (yield 43 g) contains additional HCl (*c.* 5%), but the purity of the compound is sufficient for further use, as concluded by NMR spectroscopy. The compound hydrolyzes when exposed to air and must be stored under an inert atmosphere. ^{1}H NMR (solvent $CDCl_3$): 2.52 (s, 3H), 2.56 (s, 3H), 5.76 (s, 2H), 6.32 (s, 1H) ppm.

1,6-Bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (bddh)

A total of 46 g (190 mmol, 80% purity) ncdp·HCl was dissolved in 100 ml of dry dmf. To this solution was added dropwise 8 ml (95 mmol) of 1,2-ethanedithiol dissolved in about 10 ml of dmf. When the addition of the thiol was complete the reaction mixture was heated to 90–100 °C and after 15 min at this temperature 14 g KOH dissolved in 50 ml water was added. Heating was stopped and after 15 min 200 ml of water was added to the reaction mixture. After cooling to room temperature the reaction mixture was extracted four times with 100 ml of chloroform. The collected layers of chloroform were dried and removed *in vacuo*. The yellow oil (yield 22 g, 76%) was crystallized from thf. ^{1}H NMR (solvent $CDCl_3$): 2.20 (s, 6H), 2.28 (s, 6H), 2.76 (s, 4H), 5.04 (s, 4H), 5.80 (s, 2H) ppm.

When no base or water was added to the reaction mixture a small amount of white crystalline solid was obtained from the mixture. This product was the hydrochloric salt of the ligand bddh. ^{1}H NMR (solvent $CDCl_3$): 2.46 (s, 12H), 3.20 (s, 4H), 5.66 (s, 4H), 6.20 (s, 2H) ppm.

Synthesis of the coordination compounds

The coordination compounds based on the divalent metals nickel, cobalt, copper and zinc were prepared by dissolving 2 mmol of the appropriate hydrated metal salts in 7 to 10 ml of warm ethanol or methanol and adding this solution to a warm solution of the ligand in the same solvent. After cooling to room temperature mainly crystalline products were obtained. When the product was a powder or an oil, acetonitrile was used as solvent. If, with these methods, no solid compound could be obtained, cooling to −23 °C and addition of diethylether was tried to invoke precipitation. The compounds with thiocyanate as anion were prepared by adding ammonium thiocyanate to the corresponding ligand and metal nitrate solution. The presence of nitrate in the product was checked using IR spectroscopy.

Characterization

Metal contents were determined by EDTA titration, after destruction of the compound by heating with concentrated nitric acid [7]. C, H and N elements were analyzed at the Microanalytical Laboratory of University College (Dublin). IR spectra were recorded on a Perkin-Elmer 580 spectrophotometer, equipped with a P.E. data station. Samples were prepared as KBr pellets or as nujol mulls. Vis–NIR spectra were recorded on a Perkin-Elmer 330 spectrophotometer in the diffuse reflectance mode with MgO as reference. X-ray powder patterns were collected on a Guinier-De Wolff type camera, using Cu Kα radiation. ^{1}H NMR spectra were recorded on a Jeol JNM-FX 200 spectrometer (200 MHz, Fourier transform).

X-ray data collection and structure refinement of Co(bddh)(NCS)$_2$

A suitable crystal, red squared column with dimensions 0.08×0.08×0.27 mm, was isolated from the reaction mixture. The data was collected on an Enraf-Nonius CAD4 diffractometer. Scattering factors and anomalous dispersion corrections were taken from the literature [8].

Crystal data: $C_{16}H_{22}N_6S_4Co$, $M_w=485.6$, tetragonal, space group $P4_12_12$, $a=b=9.083(1)$, $c=26.447(3)$ Å,

$\alpha=\beta=\gamma=90.0°$, cell volume $=2181.9(4)$ Å^3, $Z=4$, $D_{calc}=1.47$ g cm^{-3}, radiation λ(Mo Kα) $=0.71073$ Å, μ(Mo Kα) $=11.6$ cm^{-1}.

The structure was solved by Patterson methods and refined by least-squares calculations, using the program SHELXTL [9]. The position of all atoms were taken from Fourier difference maps. The positional parameters of the hydrogen atoms were refined with the atoms coupled to their parent atom. With 4808 measured, 2313 independent and 1999 observed ($F>4.0\sigma(F)$) reflections the residual R values were 0.038 (R) and 0.021 (R_w) and the goodness-of-fit 2.27. Largest electron densities in the final Fourier difference map were 0.81 and -0.47 e Å^{-3}. A list of relevant bond lengths and angles is presented in Table 1 and the fractional coordinates are collected in Table 2.

Results and discussion

General

The coordination compounds obtained with the ligand bddh using the metal salts (Ni, Co, Zn)(NO_3, Cl, NCS, BF_4)$_2$ are listed in Table 3. The compounds are formulated as M(bddh)A_2 (A = coordinating anion), except for the nickel nitrate compound, which is formulated as [Ni(bddh)(NO_3)$_2$](H_2O)$_2$. Colour, melting point, electronic absorption maxima and elemental analyses are given in Table 3. The IR spectra and the X-ray powder diffraction patterns of Co(bddh)Cl_2 and Zn(bddh)Cl_2 are almost identical, indicating a very similar structure for these compounds.

TABLE 1. Relevant bond lengths (Å) and angles (°) for Co(bddh)(NCS)$_2$, with e.s.d.s. in parentheses

Co(1)–N(21)	2.026(3)
Co(1)–N(12)	2.119(2)
Co(1)–S(31)	2.579(1)
Co(1)–N(21)–C(22)	175.2(3)
Co(1)–N(12)–N(11)	119.3(2)
Co(1)–N(12)–C(13)	135.3(2)
Co(1)–S(31)–C(32)	99.0(1)
Co(1)–S(31)–C(18)	93.6(1)
N(21)–Co(1)–N(21)′	97.3(2)
N(21)–Co(1)–N(12)	101.5(1)
N(21)–Co(1)–S(31)	89.6(1)
N(12)–Co(1)–N(12)′	160.7(1)
N(12)–Co(1)–S(31)	87.4(1)
N(12)–Co(1)–N(21)′	91.2(1)
S(31)–Co(1)–N(21)′	173.1(1)
S(31)–Co(1)–N(12)′	78.2(1)
S(31)–Co(1)–S(31)′	83.5(1)
S(23)–C(22)–N(21)	179.6(4)

′ = y, x, −z.

The IR spectra of thiocyanate containing compounds clearly show the presence of the thiocyanate anion and the absence of nitrate anions [10]. The C–N stretching frequencies of the thiocyanate anion occur below 2100 cm^{-1} (Ni and Co: 2090 and 2080 cm^{-1}, respectively) indicating that the thiocyanate anion coordinates through the nitrogen atom.

The presence of water in the molecule [Ni(bddh)(NO_3)$_2$](H_2O)$_2$ is deduced from the elemental analysis and the IR spectra of a nujol and KBr mull. The very broad O–H stretching vibration (3230 cm^{-1}) of the water molecules indicates that the water molecules are not coordinating and only involved in a very weak hydrogen bridge [10]. The N–O stretching vibrations ν_1 and ν_4 of the nitrate anion are split by approximately 100 cm^{-1}, which is according to Nakamoto [10] in agreement with monodentate coordination of this anion [10]. The IR pattern (nujol mull) of Ni(L)(NO_3)$_2$(H_2O)$_2$ in the nitrate $\nu_1+\nu_4$ overtone region (1700–1800 cm^{-1}) is very similar to the pattern found for a cobalt(II) containing coordination compound with monodentate nitrate anions [11]. These findings strongly suggest that both nitrate anions of [Ni(L)(NO_3)$_2$](H_2O)$_2$ are coordinating in a monodentate fashion and the water molecules are present in the crystal lattice and only weakly hydrogen bridged to, most likely, the nitrate anions. The ligand field spectrum of [Ni(bddh)(NO_3)$_2$](H_2O)$_2$ shows typical octahedral features [12], leading to a proposed $NiN_2S_2O_2$ chromophore for this compound.

The ligand field spectra of the nickel(II) compounds and of the cobalt(II) thiocyanate compound clearly show octahedral features [12]. The ligand field spectrum of Co(bddh)Cl_2 shows typical tetrahedral features [12], suggesting an MN_2CL_2 chromophore for the compounds Co(bddh)Cl_2 and Zn(bddh)Cl_2.

Description of the structure of Co(bddh)(NCS)$_2$

The cobalt atom is in a distorted octahedral $CoN_2N'_2S_2$ geometry (see Fig. 2). The cobalt atom and the centre of the ethylene bridge between the two thioether functions lie on a crystallographic two-fold axis, so the asymmetric unit consists of half the formula unit. The ligand coordinates through two pyrazole N atoms *in trans* position and the two sulfur atoms in *cis* position. The thiocyanate anions coordinate through the N atoms in a *cis* position. The Co–N(pyrazole) (2.119(2) Å), Co–S (2.579(1) Å) and Co–N(thiocyanate) (2.026(3) Å) distances can be regarded as normal [14].

The angles at the cobalt atom clearly show that the coordination geometry is not a perfect octahedron. The distortion is the result of the small

TABLE 2. Fractional coordinates of the non-hydrogen atoms with isotropic thermal parameters (Å^2) for structure of $Co(bddh)(NCS)_2$

Atom	x	y	z	U_{eq}[a]
Co(1)	0.80475(5)	0.80475	0	0.0364(1)
S(23)	0.3378(1)	0.7516(1)	0.0824(1)	0.0651(4)
C(22)	0.4954(3)	0.7763(3)	0.0553(1)	0.040(1)
N(21)	0.6081(3)	0.7930(3)	0.0359(1)	0.050(1)
N(11)	0.8412(3)	0.9151(3)	−0.1076(1)	0.044(1)
N(12)	0.7469(3)	0.9178(3)	−0.0672(1)	0.041(1)
C(13)	0.6258(3)	0.9844(3)	−0.0845(1)	0.040(1)
C(14)	0.6424(4)	1.0192(4)	−0.1353(1)	0.047(1)
C(15)	0.7801(4)	0.9759(4)	−0.1489(1)	0.047(1)
C(16)	0.4975(5)	1.0147(6)	−0.0518(2)	0.061(2)
C(17)	0.8597(6)	0.9849(8)	−0.1979(2)	0.079(2)
C(18)	0.9873(4)	0.8499(5)	−0.1037(1)	0.057(1)
S(31)	0.8503(1)	1.0588(1)	0.0406(1)	0.0480(3)
C(32)	1.0461(4)	1.0760(4)	0.0278(2)	0.063(2)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Colours, melting points (°C), and electronic absortion absorption maxima of the coordination compounds with bddh

Compound	Colour	Melting point (°C)	Ligand field maxima (10^3 cm^{-1})
$Ni(L)Cl_2$[a]	green	250d	23.4, 14.1, 8.6
$[Ni(L)(NO_3)_2](H_2O)_2$[b]	blue	220d	26.0, 15.4, 9.7
$[Ni(L)(NCS)_2]$[c]	blue	>250	26.0, 16.7, 10.1
$Co(L)Cl_2$[d]	blue	228	15.6, 8.4, 6.9, 5.9
$[Co(L)(NCS)_2]$[e]	purple	236	19.8, 9.0
$Zn(L)Cl_2$[f]	white	226	

[a]%M = 13.2(13.3), %Cl = 17(16.1), calculated values between parentheses. [b]%M = 11.6(11.5), %C = 30.96(31.77), %H = 5.17(4.95), %N = 15.53(15.88), %O = 23.45(24.18). [c]%M = 12.0(12.1). [d]%M = 13.3(13.4), %Cl = 17(16.1). [e]%M = 11.9(12.1). [f]%M = 14.6(14.6). %Cl = 17(15.9).

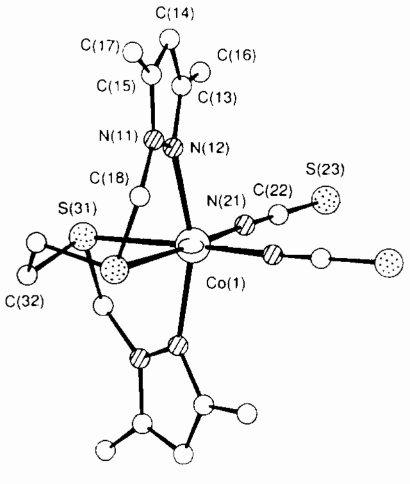

Fig. 2. PLUTO [13] drawing of $Co(bddh)(NCS)_2$ with the atom labeling scheme. Hydrogen atoms have been omitted for clarity.

ligand bites. The packing of the molecules in the crystal lattice proceeds via normal van der Waals contacts. The structure of $Co(bddh)(NCS)_2$ resembles the X-ray crystal structure of $Co(bidhp)(NCS)_2$, described by van Rijn *et al.* [15]. The N_2S_2 donor ligand bidhp differs from bddh by incorporating imidazole groups instead of pyrazole groups and a propyl fragment, instead of an ethylene fragment, between the two thioether sulfurs. The coordination geometry of $Co(bidhp)(NCS)_2$ shows a greater S–Co–S bite (92.16(8) versus 83.5(1)°), but a smaller N(azole)–Co–S bite (77.6(2) versus 87.4(1)°). The Co–S distances are slightly but significantly, smaller for bddh (Co–S: 2.579(1) Å) than for bidhp (Co–S: 2.656(2) and 2.618(2) Å), but the Co–N(azole) distances for $Co(bddh)(NCS)_2$ are greater (Co–N: 2.119(2) Å) than for $Co(bidhp)(NCS)_2$ (Co–N: 2.058(6) and 2054(6) Å). The Co–N(thiocyanate) bond lengths are similar (bddh: 2.026(3) Å; bidhp: 2.067(7) and 2.043(7) Å).

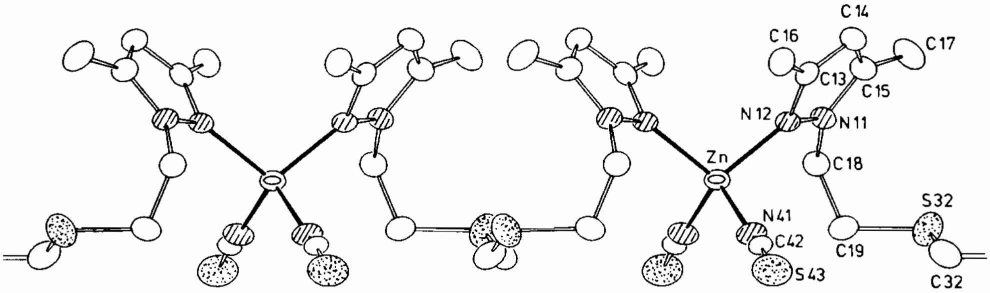

Fig. 3. PLUTO [13] drawing of $Zn(bddo)(NCS)_2$ with the atom labeling scheme. Hydrogen atoms have been omitted for clarity.

Discussion

The X-ray crystal structure of $Co(bddh)(NCS)_2$ shows that the cobalt atom is coordinated in a distorted octahedral $CoN_2N'_2S_2$ fashion (see Fig. 2). Comparison of the X-ray crystal structure of $Co(bddh)(NCS)_2$ with the X-ray crystal structure of $Co(bidhp)(NCS)_2$ [15] (with the same chromophore, bidhp = 1,7-bis(5-methyl-4-imidazolyl)-2,6-dithiaheptane) shows that the S–Co–N(azole) angle, S–Co–S angle, the Co–S bond lengths and the Co–N bond lengths differ. The only differences between the two ligands are the azole heterocycle (pyrazole versus imidazole) and the length of the $-(CH_2)_n-$bridge ($n = 2,3$) between the two thioether atoms. The five-membered S–Co–S chelate ring of $Co(bddh)(NCS)_2$ versus the six-membered chelate ring of the corresponding bidhp compound clearly accounts for the S–Co–N(azole) angle of $Co(bddh)(NCS)_2$ being smaller than for $Co(bidhp)(NCS)_2$. The S–Co–N(azole) angles differ almost 10°, which is remarkable considering that both S–Co–N(azole) chelate rings are five-membered. The difference in the Co–N(azole) distances (bddh: 2.119(2) Å; bidhp: 2.058(6) and 2.054(6) Å) may force the ligand bddh to stretch the S–Co–N(azole) angles to be able to reach both nitrogen positions. The difference in the Co–N(azole) distances in combination with the size of the S–Co–S chelate ring is likely to be the origin of the differences in the Co–S bond lengths.

The nickel-containing compounds and the compound $Co(bddh)(NCS)_2$ clearly show octahedral coordination of the metal ions, which can be related to $MN_2S_2X_2$ chromophores.

A different coordination geometry for the metal ion is observed for the (X-ray) isomorphous compounds $Co(bddh)Cl_2$ and $Zn(bddh)Cl_2$. The ligand field spectrum of the cobalt compound shows tetrahedral features, which agrees with a CoN_2Cl_2 chromophore. This chromophore has been encountered frequently in the study of pyrazole containing N_2S_2 ligands. In previous studies of the ligand bddo [2, 4] it was demonstrated that such a chromophore was found in polymeric type of compounds. The structure of two examples have been determined [2, 4], i.e. $Zn(bddo)(NCS)_2$ (see Fig. 3) and the red modification of $Cu(bddo)Cl_2$ [4]. The metal ions of these polymeric type compounds are coordinated by two pyrazole nitrogen atoms from different ligands and two anions in a tetrahedral fashion. The sulfur atoms of the ligand bddo do not participate in the coordination. Because of the very similar ligand field spectra of $Co(bddh)Cl_2$ and $Co(bddo)(NCS)_2$ (X-ray isomorphous with $Zn(bddo)(NCS)_2$) a chain like structure of the compounds $Co(bddh)Cl_2$ and $Zn(bddh)Cl_2$ is proposed.

In a previous study [2, 4] it was suggested that the non-coordinating behaviour of the thioether functions is partly due to the long and flexible connection between pyrazole group and thioether function of the ligand bddo. The occurrence of non-coordinating thioethers for bddh, with a smaller connection between pyrazole ring and thioether, in the present study shows that this influence is smaller than was suggested. Thus it is demonstrated that the weak donor capabilities of thioether functions towards first-row transition metals and crystal packing effects favouring polymeric type structures, play important roles in the formation of the observed coordination geometries.

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