Synthesis, crystal and molecular structure and magnetic properties of bis[(μ-hydroxo)bis(μ-2,5-diamino-1,3,4-thiadiazole-N^1,N^2)-chloroaqua(2,5-diamino-1,3,4-thiadiazole-N^1)cobalt(II)-O,N^1,N^1]-cobalt(II) dichloride dihydrate

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Abstract

The reaction product of cobalt(II) chloride and 2,5-diamino-1,3,4-thiadiazole was prepared and characterized by means of structural, magnetic and spectroscopic measurements. The crystals are monoclinic, space group $P2_1/c$, with $a=10.619(1)$, $b=12.503(1)$, $c=15.802(2)$ Å, $\beta=104.98(1)°$, and $Z=2$. The structure was solved by the heavy-atom method, and least-squares refinement of structural parameters led to a conventional R factor of 0.043 for 1236 independent reflections. The structure consists of centrosymmetric trimeric discrete molecules in which the central cobalt atom is coordinated in slightly distorted octahedral geometry by four nitrogen and two oxygen atoms, and the thermal cobalt atoms by three nitrogen, two oxygen and one chlorine atoms. The central cobalt atom is joined to each terminal cobalt ion by two planar triazole bridging molecules and one bridging hydroxide. The nearest-neighbor Co–Co distance is 3.360(2) Å. The magnetic susceptibility of the complex is compared with other trinuclear compounds bridged by triazolate ligands.

Introduction

1,3,4-Thiadiazoles have been investigated as versatile ligands which can yield mononuclear or polynuclear complexes [1, 2]. In particular it was found that 1,3,4-thiadiazoles can behave either as mono-coordinated ligands or as mono-protonated cations which involve hydrogen bonds with a highly condensed anion [1, 2]. Similar molecules, 1,2,4-triazoles, can yield polynuclear metal complexes with interesting magnetic properties [3–9]. In particular it was found that three 1,2,4-triazoles can bridge between two metal ions, yielding dimeric and trinuclear species [8–10]. We have recently found [11] that using 2,5-diamino-1,3,4-thiadiazole, a_2tz, as a ligand a compound of formula $Ni_3(SCN)_4(OH)_2(a_2tz)_4(OH_2)_2$ is formed, which has four a_2tz and two OH bridging groups between the internal and terminal nickel ions. Using cobalt(II) as metal ion a compound of formula $[Co_3(a_2tz)_6(OH)_2(OH_2)_2Cl_2]Cl_2 \cdot 2H_2O$ is formed and we wish to report here its crystal structure and magnetic properties in order to compare it to those with similar ligands [12–14]. Further interest in this compound is that it contains two pairs of metal ions bridged by two bidentate and one monodentate ligand, which seems to be a very diffuse type of arrangement. For instance iron atoms bridged by two carboxylates and an oxo or hydroxo group are known to be present in several metallo-enzymes [15, 16].

Experimental

Cobalt(II) chloride and 2,5-diamino-1,3,4-thiadiazole were used as the commercially available compounds.

Synthesis

The metal salt (1 mmol) dissolved in water (20 ml) was added to the ligand (3 mmol) dissolved in water (20 ml). A very slow evaporation gives pink crystals suitable for X-ray data collection. *Anal.* Calc. for $C_{12}H_{34}Co_3N_{24}O_6S_6Cl_4$: C, 12.85; H, 3.06; N, 29.97; S, 17.15. Found: C, 12.95; H, 3.03; N, 29.85; S, 17.05%. Carbon, hydrogen, and nitrogen and sulfur were determined with a Carlo Erba 1106 elemental analyzer.

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Spectral measurements

IR spectra were recorded in the solid state with a Bruker 113r FT-IR spectrophotometer. The spectra in the 4000–400 cm^{-1} range were measured in KBr discs; in the 400–50 cm^{-1} range they were measured in polyethylene discs. Atmospheric water was removed by flushing with dry nitrogen.

EPR spectra of the crystalline sample were recorded by using a Varian E9 spectrometer operating at X-band frequency and equipped with an Oxford Instruments ESR9 continuous-flow cryostat.

Magnetic susceptibility measurements

Magnetic susceptibilities were measured in the range 4.2–300 K with a fully automatized AZTEC DSM5 susceptometer equipped with an Oxford Instruments CF 1200S continuous flow cryostat and a Bruker BE15 electromagnet, operating at *c.* 1.2 T. Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal constants.

Crystal data

$C_{12}H_{34}Co_3N_{24}O_6S_6Cl_4$, $M = 1121.53$, monoclinic, space group $P2_1/c$ (No. 14), $a = 10.619(1)$, $b = 12.503(1)$, $c = 15.082(2)$ Å, $\beta = 104.98(1)°$, $U = 1934.38$ Å^3, $Z = 2$, $D_c = 1.92$ ($D_m = 1.90$ by flotation) g cm^{-3}, $F(000) = 547$, graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å), μ(Mo Kα) = 9.1 cm^{-1}, crystal dimensions *c.* 0.2×0.2×0.2 mm. Unit cell parameters were derived from least-squares fit to the setting angles of 20 intense reflections in the range θ: 8–13°.

TABLE 1. Final Positional Parameters of $[Co_3(a_2tz)_6(OH)_2(OH_2)_2Cl_2]Cl_2 \cdot 2H_2O$

Atom	*x/a*	*y/b*	*z/c*
Co(1)	0.0	0.0	1.0
Co(2)	0.0191(2)	−0.2159(1)	0.8714(1)
C1(1)	0.0111(3)	−0.2554(3)	0.7056(2)
C1(2)	0.5313(3)	0.2074(3)	0.4701(3)
O(1)	0.0221(7)	−0.1620(6)	0.9966(5)
O(2)	0.4810(9)	0.1919(8)	0.7021(8)
O(3)	0.1828(7)	0.6821(6)	0.9138(5)
S(1)	−0.3673(3)	−0.0258(3)	0.7503(2)
S(2)	0.3767(3)	0.0124(3)	0.8911(2)
S(3)	0.1503(3)	−0.0516(3)	0.5956(2)
N(1)	−0.1437(9)	−0.0164(8)	0.8697(6)
N(2)	−0.1462(8)	−0.1150(7)	0.8225(6)
N(3)	0.1553(8)	0.0001(8)	0.9299(6)
N(4)	0.1614(8)	0.9118(7)	0.8741(6)
N(5)	0.0936(9)	0.1426(8)	0.6211(7)
N(6)	0.191(1)	0.1475(8)	0.5723(7)
N(7)	0.278(1)	−0.1315(8)	0.1258(7)
N(8)	−0.2839(9)	−0.2180(9)	0.7075(7)
N(9)	0.286(1)	0.1453(8)	1.0002(7)
N(10)	0.3026(9)	−0.1670(8)	0.7949(7)
N(11)	−0.0201(9)	0.0169(8)	0.6881(6)
N(12)	0.317(1)	0.0324(9)	0.5063(7)
C(1)	0.252(1)	−0.035(1)	0.1594(8)
C(2)	−0.257(1)	−0.130(1)	0.7598(8)
C(3)	0.261(1)	0.059(1)	0.9456(8)
C(4)	0.271(1)	−0.0935(9)	0.8500(7)
C(5)	0.069(1)	0.0443(9)	0.6407(7)
C(6)	0.227(1)	0.053(1)	0.5541(8)

The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer with the (ω–2θ) scan technique in the range 2–28°, at a scan speed range of 1.0–3.3° min^{-1}, with a scan width 0.7° + 0.35 tgθ. Two standard reflections were measured every hour, and the intensities showed no significant changes. No. of collected reflections: 5047, no. of observed reflections: 1236, no. of unique reflections: 1189 with $I > 3.0\sigma(I)$ (after merge $R = 0.021$), no. of parameters: 160.

All data were corrected for Lorenz and polarization effects, and an empirical absorption correction, based on the Ψ scan, was applied [17] (max., min. transmission factor = 0.99, 0.91)

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares calculations, with $\Sigma_w(|F_o - F_c|)^2$ being minimized. Because of the relatively low number of reflections the cobalt, sulfur and oxygen atoms only were treated anisotropically, whereas the hydrogen atoms were treated as fixed contributors at located positions from difference Fourier maps, assuming a temperature factor 1 Å^2 greater than that of the attached nitrogen atoms.

This model converged to $R = 0.043$ and $R_w = 0.041$, $w = 1.2/[\sigma^2(F) + 0.00035F_o^2]$. The residual electron density in the final difference Fourier map was −0.49 to 0.50 e Å^{-3}. During refinement zero weights were assigned to four low-order reflections, which may be affected by secondary extinction. Complex neutral-atom scattering factors [18] were employed throughout; major calculations were carried out on a Vax 6210 computer, using the SHELX 76 [19] program package and the ORTEP [20] plotting program.

Final fractional coordinates for non-hydrogen atoms are given in Table 1. Bond distances and bond angles are given in Table 2. See also 'Supplementary material'.

Results and discussion

Crystal structure

The structure of $[Co_3(a_2tz)_6(OH)_2(OH_2)_2Cl_2]Cl_2 \cdot 2H_2O$ consists of discrete trimeric, centrosymmetric, complex molecules (Fig. 1) and hydrogen bonded lattice water molecules. One of the two crystallograpically independent cobalt atoms is in a special position, and they all have slightly distorted octahedral coordination geometries.

TABLE 2. Bond distances (Å) and angles (°) of $[Co_3(a_2tz)_6(OH)_2(OH_2)_2Cl_2]Cl_2\cdot 2H_2O$ with e.s.d.s in parentheses

Co(1)–O(1)	2.042(7)	Co(1)–N(1)	2.163(9)	Co(1)–N(3)	2.177(8)
Co(2)–O(1)	1.998(8)	Co(2)–O(3)	2.118(8)	Co(2)–Cl(1)	2.529(3)
Co(2)–N(2)	2.132(9)	Co(2)–N(4)	2.191(9)	Co(2)–N(5)	2.155(9)
C(1)–N(1)	1.30(1)	C(1)–S(1)	1.76(1)	C(1)–N(7)	1.36(1)
C(2)–N(2)	1.31(1)	C(2)–S(1)	1.73(1)	C(2)–N(8)	1.35(1)
C(3)–N(3)	1.31(1)	C(3)–S(2)	1.75(1)	C(3)–N(9)	1.35(1)
C(4)–N(4)	1.31(1)	C(4)–S(2)	1.74(1)	C(4)–N(10)	1.34(1)
C(5)–N(5)	1.31(1)	C(5)–S(3)	1.72(1)	C(5)–N(11)	1.37(1)
C(6)–N(6)	1.30(1)	C(6)–S(3)	1.74(1)	C(6)–N(12)	1.36(1)
N(1)–N(2)	1.42(1)	N(3)–N(4)	1.40(1)	N(5)–N(6)	1.41(1)

N(4)–N(3)–Co(1)	116.8(6)	C(3)–N(3)–Co(1)	129.2(8)
C(3)–N(3)–N(4)	112.4(9)	N(3)–N(4)–Co(2)	116.5(6)
C(4)–N(4)–Co(2)	128.1(8)	C(4)–N(4)–N(3)	112.9(9)
C(5)–N(5)–N(6)	112(1)	C(6)–N(6)–N(5)	111(1)
N(2)–C(2)–S(1)	114.6(9)	N(8)–C(2)–S(1)	121.9(9)
N(8)–C(2)–N(2)	123(1)	N(3)–C(3)–S(2)	113.8(9)
N(9)–C(3)–S(2)	120.2(9)	N(9)–C(3)–N(3)	126(1)
N(4)–C(4)–S(2)	113.5(8)	N(10)–C(4)–S(2)	120.3(9)
N(10)–C(4)–N(4)	126(1)	N(5)–C(5)–S(3)	114.4(8)
N(11)–C(5)–S(3)	121.3(9)	N(11)–C(5)–N(5)	124(1)
N(6)–C(6)–S(3)	114.3(9)	N(12)–C(6)–S(3)	120(1)
N(12)–C(6)–N(6)	125(1)	C(4)–S(2)–C(3)	87.3(5)
N(1)–Co(1)–O(1)	86.7(3)	N(3)–Co(1)–O(1)	83.2(3)
N(3)–Co(1)–N(1)	90.2(3)	N(2)–Co(2)–Cl(1)	87.7(2)
N(2)–Co(2)–O(1)	86.5(3)	N(2)–Co(2)–O(3)	177.4(3)
N(2)–Co(2)–N(5)	94.9(3)	N(2)–Co(2)–N(4)	94.5(3)
N(4)–Co(2)–Cl(1)	90.4(2)	N(4)–Co(2)–O(1)	83.9(3)
N(4)–Co(2)–O(3)	85.7(3)	N(4)–Co(2)–N(5)	170.6(3)
O(3)–Co(2)–Cl(1)	89.8(2)	O(3)–Co(2)–O(1)	96.1(3)
O(3)–Co(2)–N(5)	85.0(3)	O(1)–Co(2)–Cl(1)	171.5(2)
O(1)–Co(2)–N(5)	95.8(3)	N(5)–Co(2)–Cl(1)	90.8(3)
Co(2)–O(1)–Co(1)	112.6(3)	C(6)–S(3)–C(5)	87.3(6)
N(2)–N(1)–Co(1)	117.1(6)	N(1)–N(2)–Co(2)	115.7(6)
C(2)–N(2)–Co(2)	132.0(8)	C(2)–N(2)–N(1)	112.2(9)
C(2)–S(1)–C(1)	86.5(5)	C(1)–N(1)–Co(1)	127.2(8)
C(1)–N(1)–N(2)	111.5(9)	N(1)–C(1)–S(1)	114.9(9)

The central cobalt atom is coordinated by four N (thiadiazole) and two oxygen atoms while the terminal cobalt atoms are coordinated by three N (thiadiazole), two oxygen and one chlorine. The four unique Co–N bond distances (2.163(9), 2.177(8), 2.132(9), 2.191(9) Å) are quite similar one another and similar to the Co–N distances found in the literature: 2.12(2)–2.18(2) Å in $Co(triazole)_2(NCS)_2$ [21].

The distortion from ideal octahedral geometry of the coordination polyhedra involves both the dihedral angles between planes and the bond angles; the deviations from the ideal values are lower around the terminal Co atoms (max. 2.4 and 2.9°) than those around the central metal atom (max. 6.8 and 7.6°).

The nearest-neighbor Co–Co distance within the trimeric molecule is 3.360(2) Å close to the 3.320(4) observed in a similar Ni complex $Ni_3(SCN)_4(OH)_2(a_2tz)_4(OH_2)_2$ [11] and to the 3.39(1) observed in $Ni_3(detrH)_6(SCN)_6\cdot 2H_2O$ [8] in which two triazole and one thiocyanate groups bridge two nickel atoms.

The triazole rings are found to be almost planar. Bond distances and angles of the ring compare well with those found by other authors [6, 8]. The dihedral angles between internal ring planes are 55.1 and 48.0°; the dihedral angles between Co(1)O(1)Co(2) and Co(1)O(1)'Co(2) and the internal ring planes are 61.66 and 61.71°, respectively.

Intermolecular hydrogen-bond contacts, on which the crystal packing mainly depends, occur between the NH_2 groups and the chlorine ion, and the oxygen atoms, between the oxygen atoms and the chlorine ion, and the sulfur atoms of the 2,5-diamino-triazole molecule.

Magnetic properties

The EPR spectra are so broad even at 4.2 K, that no obvious assignment of *g* values can be performed. Although fast relaxation is expected for high spin cobalt(II) it is presumably the trinuclear nature of the complex which determines the unusually broad absorption.

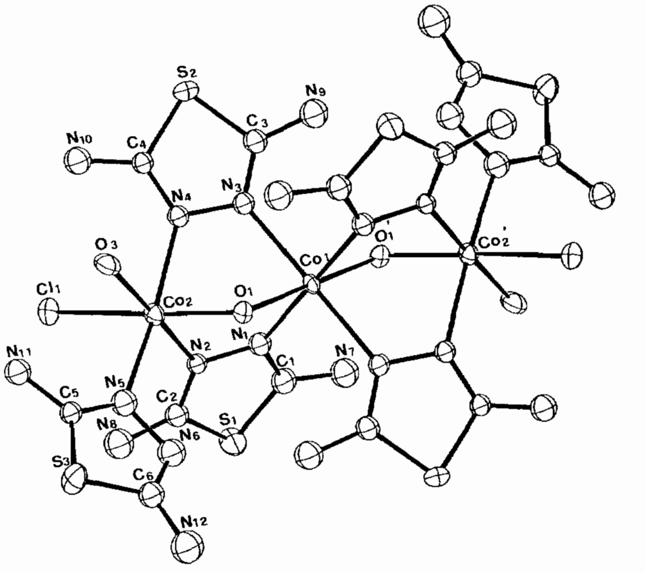

Fig. 1. ORTEP view of the bis[(μ-hydroxo)bis(μ-2,5-diamino-1,3,4-thiadiazole-N^1,N^2)chloroaqua(2,5-diamino-1,3,4-thiadiazole-N^1)cobalt(II)-O,N^1,N^1)cobalt(II) dichloro dihydrate complex showing the atom numbering and the thermal motion ellipsoids (50%) for Co, O, S and Cl. The hydrogen atoms are not represented for clarity.

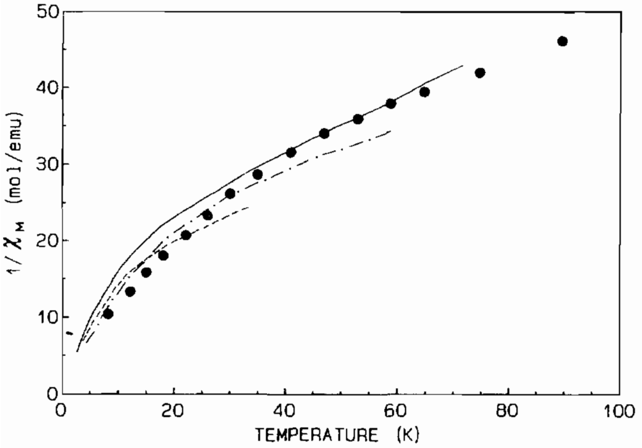

Fig. 2. Plot of the temperature dependence of the reciprocal magnetic susceptibility, per cobalt ion, observed for $[Co_3(a_2tz)_6(OH)_2(H_2O)_2Cl_2]Cl_2\cdot 2H_2O$ (filled circles); $[Co_3(mtbtz)_7(H_2O)_5](CF_3SO_3)_6\cdot 4H_2O$ [12] (solid line); $[Co_3(detrH)_6F_2(NCS)_4]\cdot 2H_2O$ [14] (dotted line); $[Co_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2\cdot 9H_2O$ [22] (broken-dotted line).

In Fig. 2 we show the temperature dependence of the reciprocal magnetic susceptibility of $[Co_3(a_2tz)_6(OH)_2(OH_2)_2Cl_2]Cl_2\cdot 2H_2O$, and for comparison purposes those of three other cobalt(II) trinuclear compounds bridged by triazolate ligands [12, 14, 22].

The analysis of the magnetic susceptibility of polynuclear cobalt(II) complexes is made difficult by the orbital degeneracy of the ground state of the octahedral metal ion. In fact the analysis of the previously reported trinuclear complexes has been performed using an Ising approach, and showed that the coupling is substantially similar for all of them. The visual comparison of the χ^{-1} versus T plot of our compound indicates a rather similar behaviour. However the uncertainties associated with the orbital degeneracy of octahedral cobalt(II) do not allow any significant analysis of the magnetic data. If we stay to the similar behaviour we may conclude that for cobalt(II) the substitution of one trz bridge with an OH bridge does not substantially alter the extent of the magnetic coupling. This is in agreement with the analogous conclusion reached for the nickel(II) complex [11].

Vibration spectra

The contemporary presence of OH and OH_2 coordinated species complicates the interpretation of the IR spectrum of the present compound. An OH band is observed at 3572 cm^{-1}, and the characteristic bridging OH bending mode near 1000 cm^{-1} is obscured by the presence of the ligand. In the far-IR spectrum, the new bands with respect to the free ligand molecule spectrum found at *c.* 400, 339 and 255 cm^{-1} can be attributed, as in other similar compounds to Co–O [23], Co–Cl [24–27] and Co–N [28–30].

Supplementary material

Positional and thermal parameters for hydrogen atoms (Table S1); bond distances and angles involving hydrogen atoms, and hydrogen bonding interactions (Table S2); isotropic thermal parameters of carbon and nitrogen atoms (Table S3); anisotropic thermal parameters (Table S4); selected least-squares planes (Table S5, 2 pages); and observed and calculated structure factors (Table S6, 7 pages) are available from the authors on request.

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