

研究简报

双(3-对甲苯基-2-硫代咪唑-1-基)-(3-甲基-5-苯基吡唑-1-基) 硼氢酸根的镉及钴配合物的合成与结构表征

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Syntheses and Crystal Structures of Cadmium(II) and Cobalt(II) Complexes with Hydro[bis(3-*p*-tolyl-2-thioimidazol-1-yl)-(3-phenyl-5-methyl-pyrazol-1-yl)] Borate

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Abstract: Two new complexes CdL₂ (**1**) and CoL₂ (**2**) were synthesized by reactions of L {L = hydro[bis(3-*p*-tolyl-2-thioimidazol-1-yl)-(3-phenyl-5-methyl-pyrazol-1-yl)]borate} with cadmium(II) and cobalt(II) acetate respectively, and structurally characterized. The title complexes feature distorted trigonal dipyramidal geometries with a S₄H donor set defined by the sulphur and hydrogen atoms of two tripodal sulfur-rich ligands. CCDC: 235514, **1**; 244021, **2**.

Key words: tripodal ligand; cadmium; cobalt; crystal structure

0 Introduction

Thiolate ligands show very high tendency to bridge metal centers and form polymeric structures^[1]. In contrast, coordination polymers with tripodal S₃ ligands of the tris(mercaptoimidazolyl)hydroborato type are less common^[2]. A number of mononuclear complexes of tris(mercaptoimidazolyl)hydroborato ligands with main group metals^[3] and transition metal ions^[4,5] have been published since the first reported by Reglinski^[6]. Due to their tetrahedral coordination potential, the ligands have also been successfully employed in the

syntheses of structural models of zinc containing liver alcohol dehydrogenase in both research groups of Parkin^[7] and Vahrenkamp^[8]. Considering its structural similarity with tris(pyrazolyl)borates, both groups designed the tripodal S₂N-coordinating, bis(mercaptoimidazolyl)(pyrazolyl)borate ligands^[9-11] to mimic the S₂NZnX coordination in alcohol dehydrogenase. With this S₂N ligand, Vahrenkamp and his coworkers have reported the best structural model^[10] for alcohol dehydrogenase. Furthermore the coordination chemistry with other S₂N ligands has also attracted attention^[12,13]. Here we report the syntheses and crystal structures of cadmium(II) and

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cobalt(II) complexes with hydro[bis(3-*p*-tolyl-2-thioimidazol-1-yl)-(3-phenyl-5-methyl-pyrazol-1-yl)] borate.

1 Experimental

1.1 Materials and measurements

All chemicals used were of analytical grade. Solvents were purified by conventional methods. Potassium hydro[bis(4-methyl-phenyl-2-thioimidazol)-(3-phenyl-5-methyl-pyrazol)] borate was prepared according to the published procedures^[10,11]. ¹H NMR spectra were recorded on a Varian Mercuryplus-400 spectrometer. ¹H chemical shifts are reported in ppm relative to SiMe₄ ($\delta=0$) and were referenced internally with respect to the solvent impurity. All coupling constants are reported in Hz. IR spectra were recorded as KBr pellets on an AWATAR 360-FT spectrophotometer in the range of 4 000~400 cm⁻¹. C, H, and N elemental analyses were measured using a Perkin-Elmer 2400 elemental analyser.

1.2 Synthesis of CdL₂ (1)

0.086 g (0.11 mmol) of 3CdSO₄·8H₂O was dissolved in methanol (5 mL), to which 0.196 g (0.33 mmol) potassium hydro[bis(3-*p*-tolyl-2-thioimidazol-1-yl)-(3-phenyl-5-methyl-pyrazol-1-yl)]borate in 5 mL dichloromethane was added dropwise. The resulting clear colorless solution was stirred at room temperature for 2 hours. The solvent was removed by reducing pressure. Extracted with dichloromethane and layered with petroleum ether carefully. Colorless crystals suitable for structure analysis were obtained after three weeks. Yielded 0.165 g (82% based on the ligand). Anal. Found (calc.) (%) for C₆₀H₅₆B₂CdN₁₂S₄ (1 207.45): C 59.92(59.68); H 4.83(4.67); N 13.67(13.92); S 10.42(10.62). IR data (cm⁻¹): 2 482, 2 512(B-H). ¹H NMR (CDCl₃, at 298 K, Internal TMS): $\delta=2.38$ [s, 6H, Me (tol)], 2.43 [s, 3H, H(pz)], 6.33 [s, 1H, H(pz)], 6.81

[(d, $J=6.0$ Hz, 2H, H(im)), 7.20 [(d, $J=2.2$ Hz, 2H, H(im)), 7.10~7.39 [m, 11H, Ar], 7.74 [d, $J=8.4$ Hz, 2H, Ph] (ppm). IR (cm⁻¹, KBr pellets): ν (B-H) 2 482(w).

1.3 Synthesis of CoL₂ (2)

0.084 g (0.33 mmol) of Co(CH₃COO)₂·2H₂O was suspended in acetonitrile (5 mL), to which 0.196 g (0.33 mmol) potassium hydro[bis(*N*-*p*-tolyl-2-thioimidazol-1-yl)-(3-phenyl-5-methyl-pyrazol-1-yl)]borate in 5 mL dichloromethane was added dropwise. The mixture was stirred at room temperature for 3 hours, resulting a clear green solution. The solvent was removed by reducing pressure. Recrystallized from acetonitrile, the complex was isolated as green microcrystals, yielded 0.131 g (68 % based on the ligand). Green crystals suitable for structure analysis were obtained from dichloromethane solution of the complex layered by petroleum ether. Anal. Found (calc.) (%) for C₆₀H₅₆B₂CoN₁₂S₄ (1 153.98): C 62.68(62.45); H 5.05(4.89); N 14.39(14.57); S 10.87(11.11). IR (cm⁻¹, KBr pellets): ν (B-H) 2 470(w).

1.4 X-ray structure analyses

All measurements were performed with Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm) on a Bruker Smart Apex CCD area detector equipped with graphite monochromator. Data of the two title complexes were collected by the ω/ϕ scan technique. The structures were solved by direct method and refined by the full-matrix least-squares on F^2 by using the SHELXTL-97 program. The non-hydrogen atoms were refined anisotropically. Hydrogens adjacent boron atoms were obtained from Fourier-difference maps and the other hydrogens positions were calculated by using idealized geometries. Full details of the data collection and structure refinement are given in Table 1. The selected bond lengths and angles are listed in Table 2.

CCDC: 235514, **1**; 244021, **2**.

Table 1 Crystal data and structure refinement for complexes **1** and **2**

Complex	1	2
Formula	C ₆₀ H ₅₆ B ₂ N ₁₂ S ₄ Cd	C ₆₀ H ₅₆ B ₂ N ₁₂ S ₄ Co
Formula weight	1 207.43	1 153.96
Temperature / K	293(2)	293(2)
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$

Continued Table 1

<i>a</i> / nm	1.093 8(3)	1.083 28(13)
<i>b</i> / nm	1.614 2(5)	1.613 48(18)
<i>c</i> / nm	1.896 5(6)	1.909 1(2)
α / (°)	106.188(6)	106.540(3)
β / (°)	105.147(7)	104.025(3)
γ / (°)	104.585(6)	105.521(2)
Volume / nm ³	2.907 4(16)	2.893 1(6)
<i>Z</i>	2	2
Density (calculated) / (Mg·m ⁻³)	1.379	1.325
Absorption coefficient / mm ⁻¹	0.570	0.492
<i>F</i> (000)	1 244	1 202
Crystal size / mm	0.321 × 0.279 × 0.233	0.201 × 0.138 × 0.049
θ range for data collection / (°)	1.98 to 25.00	1.19 to 25.50
Index ranges	-13 ≤ <i>h</i> ≤ 12, -19 ≤ <i>k</i> ≤ 16, -14 ≤ <i>l</i> ≤ 22	-12 ≤ <i>h</i> ≤ 13, -19 ≤ <i>k</i> ≤ 15, -20 ≤ <i>l</i> ≤ 23
Reflections collected	14 771	15 425
Independent reflections	10 101 [<i>R</i> _{int} =0.046 2]	10 630 [<i>R</i> _{int} =0.119 9]
Data / restraints / parameters	10 101 / 42 / 712	10 630 / 4 / 720
Goodness-of-fit on <i>F</i> ²	1.078	0.866
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ =0.048 4, <i>wR</i> ₂ =0.066 7	<i>R</i> ₁ =0.092 9, <i>wR</i> ₂ =0.164 9
<i>R</i> indices (all data)	<i>R</i> ₁ =0.072 0, <i>wR</i> ₂ =0.069 6	<i>R</i> ₁ =0.266 1, <i>wR</i> ₂ =0.238 8
Largest diff. peak and hole/ (e·nm ⁻³)	754 and -614	417 and -399

**Table 2 Selected bond lengths (nm) and angles (°)
for complexes 1 and 2**

	M=Cd	M=Co
M-S(1)	0.252 55(13)	0.236 2(3)
M-S(2)	0.256 71(12)	0.233 1(3)
M-S(3)	0.252 05(13)	0.236 7(3)
M-S(4)	0.254 71(11)	0.232 1(3)
M-H(1)	0.255 5	0.227 4
S(1)-M-S(2)	105.42(3)	109.60(10)
S(1)-M-S(3)	128.22(4)	104.74(10)
S(1)-M-S(4)	107.10(3)	106.36(11)
S(2)-M-S(3)	104.22(4)	98.26(11)
S(2)-M-S(4)	111.10(4)	103.75(10)
S(3)-M-S(4)	100.37(4)	103.93(11)

2 Results and discussion

The space group and cell parameters of two complexes are similar to each other as listed in Table 1. It indicates that two complexes are isomorphous and isostructural, and thus only the structure of complex 1 is described here in detail. Fig.1 shows the ellipsoid

representation of the structure of **1** with the atom numbering scheme. Complex **1** is a neutral bis(ligand) complex with CdS₄H coordination core. The four sulphur atoms from two tripodal ligands coordinate to the cadmium(II) ion, meanwhile the nitrogen atoms of the pyrazole rings are un-coordinated. This is the similar observation to some of their zinc complexes^[11]. The Cd-S distances vary from 0.252 05(13) to 0.256 71(11) nm. Cd-H(1) distance is 0.255 5 nm, while Cd-H(31) distance is 0.413 38 nm. Therefore cadmium(II) ion is considered to be five-coordinated with a S₄H donor set. The geometric parameter τ of the polyhedral CoS₄H, calculated by using the literature method^[12], is 0.678. Therefore, the coordination geometry of Cd atom in **1** can be regarded as a distorted trigonal dipyramid since the τ value is equal to zero for a perfectly tetragonal geometry while it becomes unity for a perfectly trigonal-bipyramidal geometry. The atoms S(1), S(2) and S(4) form the trigonal plane of the Cd sites, H(1) and S(3) occupy the corresponding apical positions. The average cadmium-sulphur bond length is 0.254 0 nm. The structure is different from the that of cadmium hy-

dro[bis (mercaptoimidazolyl)-(pyrazolyl)]borate^[13], in which the cadmium atom is coordinated by both sulphur and a hydrogen donors from each hydro[bis(mercaptoimidazolyl)-(pyrazolyl)]borate ligand forming a octahedral CoS_4H_2 coordination core.

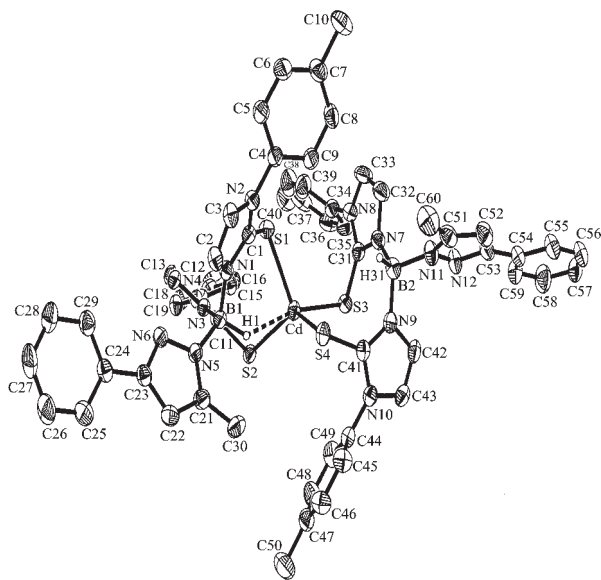


Fig.1 Ellipsoid diagram with atomic labelling of **1**, H atoms attached to the carbon atoms are omitted for clarity

3 Conclusion

The results indicate that the sulphur atoms in sulphur-rich ligand hydro[bis(3-*p*-tolyl-2-thioimidazol-1-yl)-(3-phenyl-5-methyl-pyrazol-1-yl)] borate show low tendency to bridge transition metal ions and can be used to prepare mononuclear complexes with transition metals. The reactions between cobalt (II) or cadmium (II) with the ligand resulted mononuclear complexes with a S_4H_2 donor set defined by the sulphur and hydrogen atoms of two tripodal ligands.

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