

References

- B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
- Curtis, M. D. & Butler, W. M. (1978). *J. Organomet. Chem.* **155**, 131–145.
- Klinger, R. J., Butler, W. M. & Curtis, M. D. (1978). *J. Am. Chem. Soc.* **100**, 5034–5038.
- Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- Song, L.-C., Dong, Q. & Hu, Q.-M. (1992). *Acta Chim. Sin.* **50**, 193–199.
- Song, L.-C., Wang, J.-Q., Hu, Q.-M., Wang, R.-J. & Wang, H.-G. (1993). *Polyhedron*, **12**, 259–261.
- Song, L.-C., Yang, H., Dong, Q. & Hu, Q.-M. (1991). *J. Organomet. Chem.* **414**, 137–143.

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Bis(1,3-benzothiazole-2-thiolato-*N,S'*)-(2,2'-bipyridine-*N,N'*)cadmium(II)

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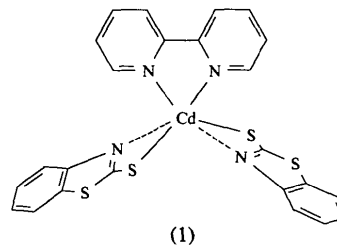
Abstract

The title tris-chelate complex [Cd(C₇H₄NS₂)₂-(C₁₀H₈N₂)] is monomeric, with a coordination sphere of the type N₄S₂. The Cd atom is linked to two thiazole N atoms and two exocyclic S atoms from two bidentate 1,3-benzothiazole-2-thiolate anions and two bipyridine N atoms. The Cd-atom coordination geometry is trigonal prismatic.

Comment

The 1,3-benzothiazole-2-thiolate (mbt⁻) anion, C₇H₄NS₂⁻, is a versatile ligand with more than one donor

atom potentially available for coordination to one or more metal centres in a variety of ways (Raper, 1985). Although extensively studied by spectroscopic methods, crystallographic investigations of zinc and cadmium complexes of this ligand have been limited (McCleverty *et al.*, 1982; Hursthouse, Khan, Mazid, Motevalli & O'Brien, 1990). We have recently reported the synthesis of the complexes [M(C₇H₄NS₂)₂(py)₂], [M(C₇H₄NS₂)₂(2,2'-bpy)] and [M(C₇H₄NS₂)₂(phen)] (py = pyridine, phen = phenanthroline, bpy = bipyridine, M = Zn or Cd) and the single-crystal structures of [Zn(C₇H₄NS₂)₂(py)₂], [Zn(C₇H₄NS₂)₂(2,2'-bpy)] and [Cd(C₇H₄NS₂)₂(py)₂] (Baggio, Garland & Perek, 1993). The three adducts were found to be monomeric, with distorted tetrahedral ZnN₂S₂ and distorted octahedral CdN₄S₂ cores, respectively.



This report presents results of the crystal structure determination of the tris-chelate complex [Cd(C₇H₄NS₂)₂-(2,2'-bpy)], (1). Fig. 1 presents the structural diagram and the atomic numbering scheme. The Cd atom lies on the twofold axis and its environment can be adequately described as trigonal prismatic, with no appreciable rotation (<1°) from the regular geometry of the two basal planes defined by N1, N2', S1 and N1', N2, S1', respectively (primes denote atoms generated by the twofold rotation). The intrachelate angles S—Cd—N and N—Cd—N are in the narrow range 62.5 (1)–69.2 (3)° and reflect the rigid chelate geometry in (1). In the complex [Cd(C₇H₄NS₂)₂(py)₂] already noted, the average intrachelate angle S—Cd—N is 62.1 (1)° and the N(py)—Cd—N(py) angle is 94.9 (2)°. Thus, substitution of the two pyridine N atoms by the bpy N atoms of the bidentate ligand leads to a configuration of three almost equivalent 'bites', with a mean normalized value of 1.05 (Kepert, 1977). Kepert's rules predict for this case a rather undistorted trigonal prismatic geometry as the most stable configuration, in accordance with the present results. Comparison of complex (1) with [Zn(C₇H₄NS₂)₂(2,2'-bpy)] noted above reveals that in the latter, the mbt⁻ ligands are bonded through the exocyclic S atom only, resulting in a distorted tetrahedral ZnN₂S₂ geometry. The larger size of the Cd atom allows S,N-bidentate bonding of the two mbt⁻ ligands. These structures illustrate the differences in coordination that can result in zinc(II) and cadmium(II) thiolates and may be relevant to their different biological activity (Reddy, Zhang, Schlemper & Schrauzer, 1992).

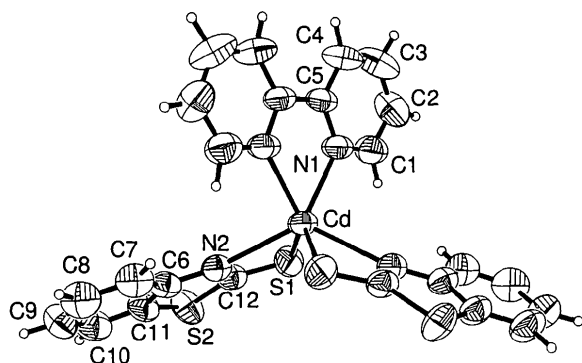


Fig. 1. Displacement ellipsoid plot of the molecule, showing the numbering scheme used.

The bpy group in (1) is bisected by the twofold axis. The resulting symmetry-related cycles are planar (r.m.s. deviation from the plane 0.007 Å), and slightly non-coplanar [dihedral angle 5.3 (3)°]. The mbt⁻ ligand is also planar (r.m.s. deviation 0.013 Å).

The Cd—S [2.618 (2) Å] and Cd—N [2.529 (5) Å] bond lengths of the bidentate mbt⁻ ligand are slightly shorter and longer, respectively, than the corresponding values in [Cd(C₇H₄NS₂)₃]⁻ [2.667 (6) and 2.42 (3) Å (McCleverty *et al.*, 1982)] and [Cd(C₇H₄NS₂)₂(py)₂] [2.706 (10) and 2.42 (1) Å (Baggio, Garland & Percec, 1993)]. The Cd—N(bpy) bond length of 2.349 (5) Å is similar to those reported for related six-coordinate complexes (Orpen *et al.*, 1989). The C—S and C—N bonds in the RN—C—S linkages of *ca* 1.72 and 1.32 Å are shorter than the single C—S (1.77 Å) and C—N (1.35 Å) bonds in 2-methylbenzothiazole (Wheatley, 1962) and benzothiazole-2-thione (Chesick & Donohue, 1971), respectively, suggesting electron delocalization in the RN—C—S groups.

Experimental

2,2'-Bipyridine (3.12 g, 0.02 mol) in chloroform–dimethylformamide (1:1, 20 cm³) was added to a suspension of polymeric [Cd(C₇H₄NS₂)₂]_n (2.22 g, 0.005 mol) in chloroform (10 cm³) at room temperature. After stirring for 2 h, a yellow solution formed, which was filtered to remove traces of solids and allowed to stand at room temperature. After 3 d, green–yellow crystals were collected by vacuum filtration and washed with acetone.

Crystal data

[Cd(C₇H₄NS₂)₂(C₁₀H₈N₂)]

M_r = 601.05

Monoclinic

*C*2/*c*

a = 19.411 (4) Å

b = 8.5580 (10) Å

c = 14.522 (2) Å

β = 93.21 (1)°

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 7.5–12.5°

μ = 1.274 mm⁻¹

T = 293 (2) K

Prism

V = 2408.6 (7) Å³

Z = 4

D_x = 1.658 Mg m⁻³

0.30 × 0.22 × 0.12 mm

Green–yellow

Data collection

Siemens R3m diffractometer

θ/2θ scans

Absorption correction:

empirical

T_{min} = 0.6250, *T_{max}* =

0.7899

1665 measured reflections

1586 independent reflections

1175 observed reflections

[*I* > 2σ(*I*)]

θ_{max} = 22.55°

h = -20 → 20

k = 0 → 9

l = 0 → 15

2 standard reflections

monitored every 98

reflections

intensity variation: none

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.041

wR(*F*²) = 0.0833

S = 1.059

1586 reflections

150 parameters

H-atom parameters not

refined

w = 1/[σ²(*F_o*²) + (0.0342*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.30 e Å⁻³

Δρ_{min} = -0.36 e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992),

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^*$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cd	0	0.10704 (7)	1/4	0.0528 (3)
S1	-0.05433 (9)	-0.0195 (2)	0.09865 (13)	0.0683 (5)
S2	-0.19428 (9)	-0.1587 (2)	0.13181 (12)	0.0744 (6)
N1	0.0327 (3)	0.3330 (6)	0.1716 (4)	0.0618 (15)
N2	-0.1165 (3)	-0.0230 (6)	0.2583 (4)	0.0546 (13)
C1	0.0651 (4)	0.3260 (9)	0.0931 (6)	0.079 (2)
C2	0.0882 (4)	0.4565 (12)	0.0490 (5)	0.093 (3)
C3	0.0753 (5)	0.5977 (11)	0.0873 (7)	0.109 (3)
C4	0.0407 (4)	0.6076 (9)	0.1660 (6)	0.089 (2)
C5	0.0191 (3)	0.4740 (7)	0.2077 (4)	0.060 (2)
C6	-0.1762 (3)	-0.0682 (6)	0.3005 (5)	0.056 (2)
C7	-0.1899 (4)	-0.0443 (8)	0.3918 (5)	0.072 (2)
C8	-0.2519 (4)	-0.0945 (9)	0.4217 (5)	0.083 (2)
C9	-0.3011 (4)	-0.1656 (8)	0.3632 (6)	0.079 (2)
C10	-0.2876 (4)	-0.1917 (8)	0.2725 (6)	0.079 (2)
C11	-0.2254 (3)	-0.1437 (7)	0.2413 (4)	0.060 (2)
C12	-0.1187 (3)	-0.0605 (6)	0.1700 (5)	0.056 (2)

Table 2. Selected geometric parameters (Å, °)

Cd—N1	2.349 (5)	N2—C6	1.396 (7)
Cd—N1 ⁱ	2.349 (5)	C1—C2	1.375 (10)
Cd—N2	2.529 (5)	C2—C3	1.359 (11)
Cd—N2 ⁱ	2.529 (5)	C3—C4	1.360 (10)
Cd—S1	2.618 (2)	C4—C5	1.371 (9)
Cd—S1 ⁱ	2.618 (2)	C5—C5 ⁱ	1.470 (12)
S1—C12	1.704 (7)	C6—C7	1.381 (8)
S2—C11	1.737 (7)	C6—C11	1.407 (8)
S2—C12	1.754 (6)	C7—C8	1.371 (9)
N1—C1	1.335 (8)	C8—C9	1.383 (9)
N1—C5	1.347 (7)	C9—C10	1.375 (9)
N2—C12	1.320 (7)	C10—C11	1.375 (8)

N1—Cd—N1 ⁱ	69.2 (3)	C6—N2—Cd	155.4 (4)
N1—Cd—N2	130.7 (2)	N1—C1—C2	122.8 (7)
N1 ⁱ —Cd—N2	94.2 (2)	C3—C2—C1	117.4 (8)
N1—Cd—N2 ⁱ	94.2 (2)	C2—C3—C4	120.6 (8)
N1 ⁱ —Cd—N2 ⁱ	130.7 (2)	C3—C4—C5	119.8 (8)
N2—Cd—N2 ⁱ	127.8 (2)	N1—C5—C4	120.2 (6)
N1—Cd—S1	92.34 (14)	N1—C5—C5 ⁱ	116.4 (4)
N1 ⁱ —Cd—S1	129.79 (13)	C4—C5—C5 ⁱ	123.4 (5)
N2—Cd—S1	62.55 (13)	C7—C6—N2	126.1 (6)
N2 ⁱ —Cd—S1	95.57 (12)	C7—C6—C11	119.6 (7)
N1—Cd—S1 ⁱ	129.79 (13)	N2—C6—C11	114.3 (6)
N1 ⁱ —Cd—S1 ⁱ	92.34 (14)	C8—C7—C6	118.5 (7)
N2—Cd—S1 ⁱ	95.57 (12)	C7—C8—C9	122.1 (7)
N2 ⁱ —Cd—S1 ⁱ	62.55 (13)	C10—C9—C8	119.8 (7)
S1—Cd—S1 ⁱ	131.15 (8)	C9—C10—C11	119.0 (7)
C12—S1—Cd	81.3 (2)	C10—C11—C6	120.9 (6)
C11—S2—C12	90.2 (3)	C10—C11—S2	129.5 (5)
C1—N1—C5	119.0 (6)	C6—C11—S2	109.6 (5)
C1—N1—Cd	122.0 (5)	N2—C12—S1	123.8 (5)
C5—N1—Cd	119.0 (5)	N2—C12—S2	113.9 (5)
C12—N2—C6	112.1 (5)	S1—C12—S2	122.4 (4)
C12—N2—Cd	92.3 (4)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

The data were collected using a variable scan speed of 4.19–29.3° min⁻¹ (Siemens, 1991). The structure was solved through a combination of direct methods and difference Fourier synthesis, using the *SHELXTL* program package (Sheldrick, 1991). Refinement was performed with *SHELXL93* (Sheldrick, 1993) on *F*² using the whole data set. H atoms were included at their expected positions, with fixed displacement parameters.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: AB1143). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Baggio, R. F., Garland, M. T. & Pereg, M. (1993). *J. Chem. Soc. Dalton Trans.* In the press.
- Chesick, J. P. & Donohue, J. (1971). *Acta Cryst.* B27, 1441–1444.
- Hursthouse, M. B., Khan, O. F. Z., Mazid, M., Motevalli, M. & O'Brien, P. (1990). *Polyhedron*, 9, 541–544.
- Kepert, D. L. (1977). *Proc. Inorg. Chem.* 23, 1–65.
- McCleverty, J. A., Gill, S., Kowalsky, R. S. Z., Bailey, N. A., Adams, H., Lumbard, K. W. & Murphy, M. A. (1982). *J. Chem. Soc. Dalton Trans.* pp. 493–503.
- Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* SI.
- Raper, E. S. (1985). *Coord. Chem. Rev.* 61, 115–139.
- Reddy, H. K., Zhang, C., Schlemper, E. O. & Schrauzer, G. N. (1992). *Inorg. Chem.* 31, 1673–1677.
- Sheldrick, G. M. (1991). *SHELXTL/PC*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1993). *SHELXL93. Program for Crystal Structure Refinement*. Univ. of Göttingen, Germany.
- Siemens (1991). *P3/P4-PC Diffractometer Program*. Version 4.27. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Wheatley, P. J. (1962). *J. Chem. Soc.* pp. 3636–3638.

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On the Structure of the Mixed Ligand Complex of [VO]²⁺ with Hydrotris(3,5-dimethylpyrazolyl)borato and 1,3-Diphenyl-1,3-propanedionato Ligands

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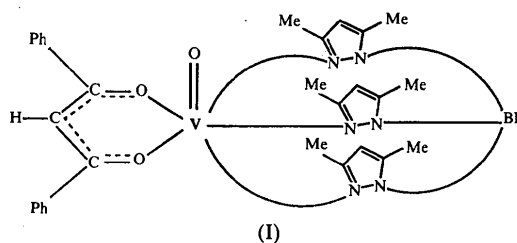
(Received 17 January 1994; accepted 19 April 1994)

Abstract

The structure of (1,3-diphenyl-1,3-propanedionato- κ^2O,O')oxo[tris(3,5-dimethyl-1-pyrazolyl- κN^2)hydroborato]vanadium(IV) methyl cyanide, [VO(C₁₅H₂₂BN₆)(C₁₅H₁₁O₂)]·xCH₃CN, has recently been described and refined [Beddoes, Eardley, Mabbs, Moorcroft & Passand (1993). *Acta Cryst.* C49, 1923–1926] in space group *Pna*2₁ (orthorhombic; *a* = 15.960 (1), *b* = 12.447 (1), *c* = 17.044 (1) Å, *Z* = 4). It is better described in *Pnma* (conventional setting of *Pnam*). Revised coordinates are given and the anomalous bond lengths reported earlier are revised.

Comment

In their report of the structure of [VO(C₁₅H₂₂BN₆)(C₁₅H₁₁O₂)]·xCH₃CN, (I), described and refined in space group *Pna*2₁, the authors (Beddoes, Eardley, Mabbs, Moorcroft & Passand 1993; hereinafter,



BEMMP) reported that the two, presumably equivalent, C—O bonds in the propanedionato group have very different lengths, 1.183 (12) and 1.382 (14) Å, as do the C—C bonds in these groups, 1.287 (18) and 1.472 (17) Å; C—N distances in the pyrazolyl groups (not all are listed by BEMMP) range from 1.26 to 1.45 Å. They also noted 'suspect bond lengths in the regions of the phenyl groups', which prompted them to collect data from two separate crystals and, even-

† Contribution No. 8918.