

Bis(*O,O'*-diisopropyl dithiophosphato-*S,S'*)(1,10-phenanthroline-*N,N'*)-metal(II) complexes with cadmium(II) and iron(II)

Qingli Hao,^a Xujie Yang,^a Fangfang Jian,^a Lude Lu,^a
Xin Wang,^a Ibrahim Abdul Razak,^b Suchada
Chantrapromma^{b†} and Hoong-Kun Fun^{b*}

^aMaterials Chemistry Laboratory, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China, and ^bX-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

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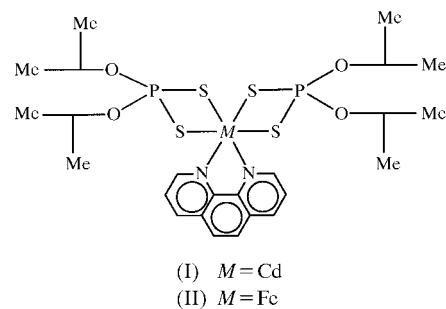
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The two title compounds, $[M(C_6H_{14}O_2PS_2)_2(C_{12}H_8N_2)]$, where $M = Cd^{II}$ and Fe^{II} , are isomorphous. Each compound has a crystallographic twofold axis of symmetry through the metal atom and the 1,10-phenanthroline molecule. The central metal atom is coordinated to four S atoms from the two dithiophosphate groups and two N atoms from the 1,10-phenanthroline ligand. The environment of the metal atom is a distorted octahedron.

Comment

Metal dialkyl dithiophosphates (dtp) and their derivatives have been widely employed both as antioxidant and antiwear additives in rubber and as lubricating oils (Harrison & Kikabhai, 1987; Kovtun *et al.*, 1992). Adducts and their formation reactions have also been found to be useful in a variety of ways, such as with biological systems (Livingstone & Mihkelson, 1970). Metal complex ions of the type $[M(LL)_3]$, where LL is either 1,10-phenanthroline (phen) or a modified phen ligand, are particularly attractive species for developing new diagnostic and therapeutic agents which can recognize and cleave DNA (Barton, 1986; Naing *et al.*, 1995). Furthermore, cadmium is often substituted into the proteins and used to aid the determination of the coordination environment of the native metal, primarily because of the usefulness of Cd NMR. Also, a series of potential models, $[M(SR)_x(N-donor)_{(4-x)}]$ ($M = Zn, Co, Cd$), have been reported for cysteine-containing zinc metalloproteins (Santos *et al.*, 1990). The original $Co^{II}(dtp)_2$ is easily oxidized. However, similar complexes are very stable in air. $Fe^{II}(dtp)_2$ and its adducts are also expected to have this property. The title adducts, (I) and

(II), were prepared and the structures determined so that the determination of the equilibrium constants can be performed to confirm the property.



In complex (I), the Cd–N bond length is comparable with the complexes of $[Cd^{II}(tBuS_2CS)_2(bipy)]$ [bipy is bipyridine; 2.368 (3) Å; Black *et al.*, 1986]. It is, however, shorter than those of $[Cd^{II}(Et)_2NCS_2](bipy)$ [2.434 (6) Å; Glinskaya *et al.*, 1992], but longer than those of $[Cd(C_{24}H_{18}O_4)(bipy)]$ [2.342 (5) and 2.355 (5) Å; Annan *et al.*, 1990]. The Fe–N bond length in complex (II) is comparable with those of the complex $[Fe(phen)_2(PhCOO)]_2OCl_2 \cdot 7H_2O$ [2.221 (4), 2.168 (3), 2.139 (3) and 2.270 (3) Å; Li *et al.*, 1995].

The Cd–S distances in (I) are in good agreement with $[Cd^{II}(Et-dtp)_2(hex)_2]$ [Et-dtp is diethyl dithiophosphate; 2.682 (1) and 2.704 (1) Å; Shimoi *et al.*, 1982]. However, the Cd–S bond lengths are longer than those found in the tetrahedral configuration, $[Cd^{II}(iPr-dtp)_2]$ [*iPr*-dtp is diisopropyl dithiophosphate; 2.486 (7) and 2.590 (8) Å; Lawton & Kokotailo, 1969], but shorter than those in $[Cd^{II}(iPr-dtp)_2(NMe_4)]$ [2.659 (1) and 2.777 (2) Å; McCleverty *et al.*, 1982]. In (II), the Fe^{II} –S distances are longer than Fe^{III} –S

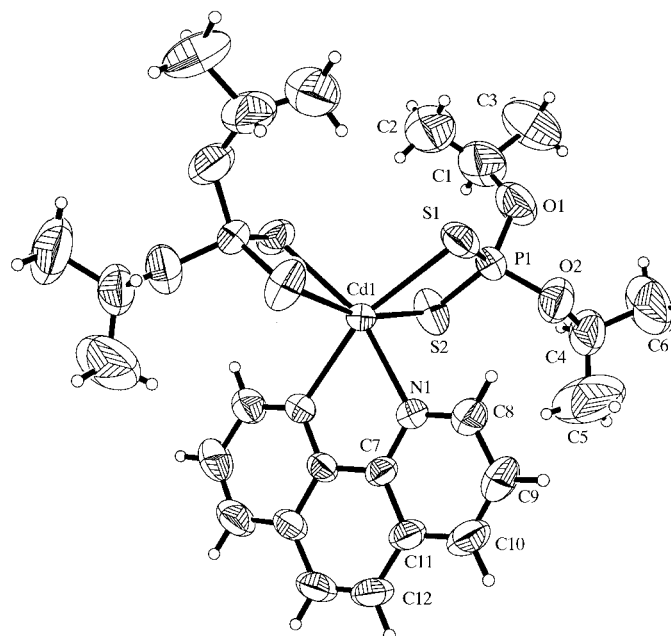


Figure 1

The structure of compound (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

[†] Permanent address: Department of Chemistry, Prince of Songkla University, Hat-Yai, Songkhla 90112, Thailand.

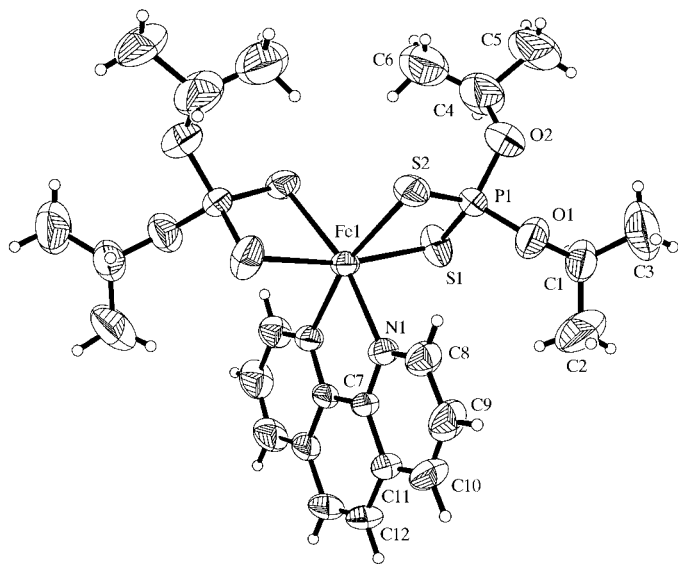


Figure 2
The structure of compound (II) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

distances reported by Drew *et al.* (1986) [2.461 (2), 2.492 (2) and 2.473 (2) Å].

The P—S distances in the dtp groups in (I) and (II) are nearly identical, and are intermediate between the single-bond (2.09 Å) and double-bond (1.87 Å) values.

In (I), the S1—Cd1—S2 bond angle is larger than those found in [Cd(ⁱPr-dtp)₂(NMe₄)] [74.9 (5)°] and [Cd{(Et)₂-NCS₂}(bipy)] [67.3 (1) and 68.5 (2)°]. The N1—Cd1—N1A bond angle is in good agreement with those of [Cd(phen)₃](ClO₄)₂ [71.7 (1)°; Xiong *et al.*, 1997]. In (II), the S1—Fe1—S2 bond angle is 79.8 (7)°. The N1—Fe1—N1A bond angle [75.1 (2)°] is similar to that of the six-coordinate compound [Fe(phen)₂(PhCOO)]₂OCl₂·7H₂O [75.1 (1)°; Li *et al.*, 1995].

The coordination around the Cd1 atom in (I) and the Fe1 atom in (II) is distorted octahedral, with bond angles ranging from 70.7 (2) to 164.2 (1)° and from 75.1 (2) to 168.2 (1)°, respectively. The central metal atom is coordinated to four S atoms from the two dtp groups and two N atoms from the 1,10-phenanthroline ligand. In both complexes, the four-membered ring formed by the M1, S1, S2 and P1 atoms is almost planar. This plane and the plane through the M1, N1, C7, N1A and C7A atoms make dihedral angles of 86.5 (1) and 86.9° for (I) and (II), respectively.

Experimental

Compound (I) was prepared by mixing an EtOH solution (50 ml) of bis(*O,O'*-diisopropyl dithiophosphate)cadmium(II) (0.1 mmol) and phen (0.1 mmol) with heating. After cooling to room temperature and filtration, colourless single crystals suitable for X-ray analysis were obtained on slow evaporation of the solvent. Complex (II) was prepared from bis(*O,O'*-diisopropyl dithiophosphate)iron(II) and phen in acetone using the method given for complex (I). Dark-red single crystals suitable for X-ray analysis were obtained on slow evaporation of the solvent.

Compound (I)

Crystal data

[Cd(C₆H₁₄O₂PS₂)₂(C₁₂H₈N₂)]
M_r = 719.13
 Orthorhombic, *Pbcn*
a = 11.7493 (1) Å
b = 19.0809 (3) Å
c = 14.6006 (2) Å
V = 3273.27 (7) Å³
Z = 4
D_x = 1.459 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 6966 reflections
 θ = 2.04–28.32°
 μ = 1.050 mm⁻¹
T = 293 (2) K
 Block, colourless
 0.46 × 0.42 × 0.36 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
 T_{\min} = 0.644, T_{\max} = 0.704
 21 589 measured reflections
 4054 independent reflections

2965 reflections with $I > 2\sigma(I)$
 R_{int} = 0.078
 θ_{max} = 28.35°
 h = -15 → 12
 k = -16 → 25
 l = -19 → 18
 Intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)]$ = 0.054
 $wR(F^2)$ = 0.168
 S = 1.07
 4054 reflections
 168 parameters
 H atoms: see text

$w = 1/[\sigma^2(F_o^2) + (0.0962P)^2 + 1.5469P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 1.03 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.02 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °) for (I) and (II).

	(I) <i>M</i> = Cd	(II) <i>M</i> = Fe
<i>M</i> —N1	2.368 (3)	2.209 (4)
<i>M</i> —S1	2.719 (1)	2.581 (2)
<i>M</i> —S2	2.640 (1)	2.513 (2)
P1—S1	1.970 (2)	1.966 (2)
P1—S2	1.969 (2)	1.969 (2)
N1— <i>M</i> —N1 ⁱ	70.73 (15)	75.1 (2)
S2— <i>M</i> —S1	76.40 (4)	79.86 (6)

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

Compound (II)

Crystal data

[Fe(C₆H₁₄O₂PS₂)₂(C₁₂H₈N₂)]
M_r = 662.58
 Orthorhombic, *Pbcn*
a = 11.5761 (2) Å
b = 18.8015 (1) Å
c = 14.7098 (2) Å
V = 3201.56 (7) Å³
Z = 4
D_x = 1.375 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 6556 reflections
 θ = 2.07–28.36°
 μ = 0.863 mm⁻¹
T = 293 (2) K
 Block, dark red
 0.32 × 0.28 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
 T_{\min} = 0.770, T_{\max} = 0.846
 8551 measured reflections
 2834 independent reflections

1686 reflections with $I > 2\sigma(I)$
 R_{int} = 0.089
 θ_{max} = 25.00°
 h = -7 → 13
 k = -22 → 13
 l = -12 → 17
 Intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.074$
 $wR(F^2) = 0.127$
 $S = 0.97$
 2834 reflections
 168 parameters

H atoms: see text
 $w = 1/[\sigma^2(F_o^2) + (0.1222P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.02 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.61 \text{ e } \text{Å}^{-3}$

After checking their presence in the difference map, all H atoms were placed at idealized positions and were allowed to ride on their parent C atoms. Due to the large fraction of weak data at higher angles in (II), the 2θ maximum for (II) is limited to 50° . The maximum and minimum electron-density peaks are located 1.11 Å from H4A and 0.90 Å from Cd1, respectively, for (I) and 1.09 and 1.23 Å , respectively, from Fe1 for (II).

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1016). Services for accessing these data are described at the back of the journal.

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