

[Bis(3,5-dimethylpyrazol-1-yl- κN^2)-dithioacetato- κS](triphenylphosphine- κP)copper(I)

Lei-Lei Liu, Xiao-Yan Tang, Hong-Xi Li, Yong Zhang and Jian-Ping Lang*

Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, Jiangsu, People's Republic of China

Correspondence e-mail: jplang@suda.edu.cn

Received 2 September 2007

Accepted 22 September 2007

Online 13 October 2007

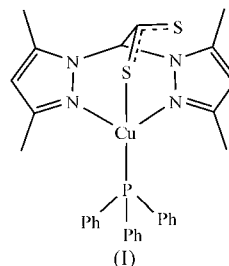
In the title compound, $[\text{Cu}(\text{C}_{12}\text{H}_{15}\text{N}_4\text{S}_2)(\text{C}_{18}\text{H}_{15}\text{P})]$, the copper(I) center is tetrahedrally coordinated by one S atom and two N atoms from one bis(3,5-dimethylpyrazol-1-yl)-dithioacetate ligand and one P atom from a triphenylphosphine ligand. In the crystal structure, adjacent pyrazole rings are involved in weak π - π interactions, thereby forming a one-dimensional zigzag chain running along the b axis.

Comment

In the past decades, much interest in metal complexes of the tris(pyrazolyl)borate or 'scorpionate' ligands (Trofimenko, 1967) has been motivated by their chemistry, their relevance in biological systems (Beck *et al.*, 2001) and their potential applications in advanced materials, such as single-molecule magnets (Li *et al.*, 2006), optoelectronic devices (Enomoto *et al.*, 2001) and catalysts (Noel *et al.*, 2006). Besides these 'scorpionate' ligands, several so-called 'heteroscorpionate' ligands, such as bis(3,5-dimethylpyrazol-1-yl)acetate (bdmpza), 2,2-bis(3,5-dimethylpyrazol-1-yl)ethoxide (bdmpze) and bis(3,5-dimethylpyrazol-1-yl)dithioacetate (bdmpzdta), in which one pyrazole group is replaced by a carboxylate, ethoxide or dithioacetate group, have been reported. A family of transition metal complexes of these 'heteroscorpionate' ligands has been prepared (Otero *et al.*, 2000, 2002, 2004, 2005; Beck *et al.*, 2001; Hammes *et al.*, 2003; Smith *et al.*, 2002, 2005; Ortiz *et al.*, 2004; Porchia *et al.*, 2006). Among them, only a few examples containing Ti^{VI} , Zr^{IV} , Hf^{IV} , Ru^{II} , Sc^{II} and Y^{III} involve the bdmpzdta ligand. There is no report of a cuprous complex of this ligand.

The title compound, (I), crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit contains a discrete $[\text{Cu}(\text{bdmpzdta})(\text{PPh}_3)]$ molecule with no crystallographically imposed symmetry. Compound (I) can be viewed as having a scorpionate-shaped structure in which the bdmpzdta ligand is

in an N,S,N' -tridentate coordination mode (Fig. 1). This coordination resembles that found in $[\text{Ti}(\text{bdmpzdta})\text{Cl}_2\{\text{O}(\text{CH}_2)_4\text{Cl}\}]$ (Otero *et al.*, 2002). The Cu center is tetrahedrally coordinated by two N atoms and one S atom from the



bdmpzdta ligand, and one P atom from the PPh_3 ligand. Tetrahedral Cu^{I} centers with three different donor atoms are only found in a limited number of complexes, such as $[\text{PtCu}_2(\text{bpy})_2(\text{tdt})(\text{dppm})_2](\text{ClO}_4)_2$ [bpy is 2,2'-bipyridine, tdt is 3,4-toluenedithiolate and dppm is bis(diphenylphosphino)methane; Chen *et al.*, 2004] and $[\text{Cu}_4(\text{SCN}_4\text{Me})_4(\text{PPh}_3)_3]$ (SCN_4Me is 1-methyl-1,2,3,4-tetrazole-5-thiolate; Nöth *et al.*, 1998). In (I), the dihedral angle between the two pyrazole rings in the bdmpzdta ligand is $49.83(3)^\circ$. The $\text{N}-\text{Cu}-\text{N}$ and $\text{N}-\text{Cu}-\text{S}$ angles range from $88.22(6)$ to $94.71(5)^\circ$ and are much smaller than the $\text{N}-\text{Cu}-\text{P}$ and $\text{P}-\text{Cu}-\text{S}$ angles [$120.68(5)$ – $128.91(2)^\circ$]. Such a difference may be due to the bite angles of the bdmpzdta ligand.

As indicated in Table 1, the mean $\text{Cu}-\text{N}$ bond distance in (I) is longer than those in $[\text{Cu}(\text{tdmpzb})(\text{PPh}_3)]$, $[\text{Cu}(\text{tdphzb})\text{Cl}]$ and $[\text{Cu}(\text{tdippzb})\text{Cl}]$. The $\text{Cu}-\text{P}$ bond length in (I) is longer than those observed in $[\text{Cu}(\text{tdmpzb})-$

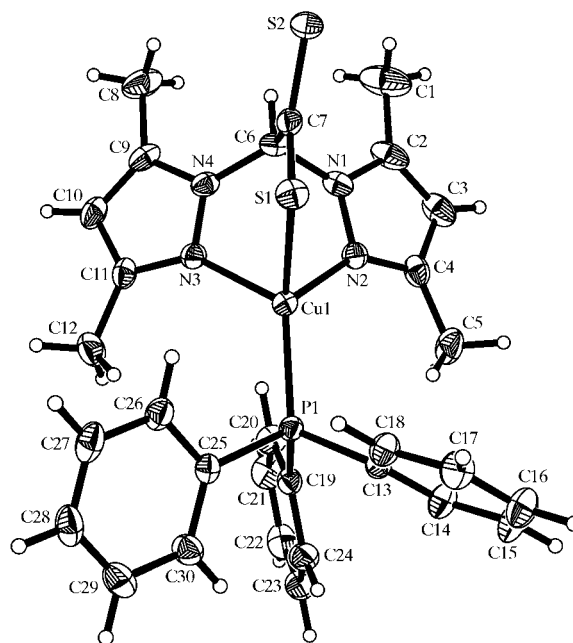


Figure 1

A view of the molecule of complex (I), with displacement ellipsoids drawn at the 30% probability level. H atoms are drawn as spheres of arbitrary radii.

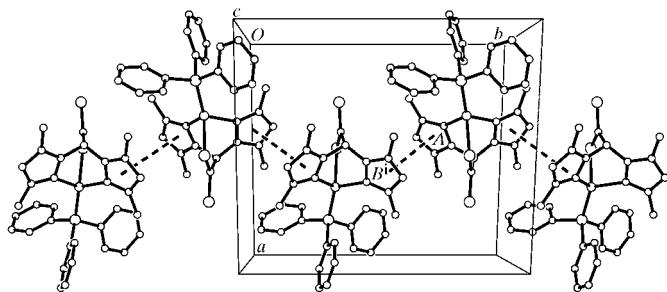


Figure 2
The packing of (I), viewed approximately down the *a* axis, showing the one-dimensional chain generated by π - π interactions. H atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$]

(PPh₃) and [Cu(tpms)(PPh₃)] but shorter than that in [Cu(PPh₃)₂(PhCOS)], while the Cu–S bond length in (I) is comparable to that found in [Cu(C₆H₁₁CN)₂(dmpzdtc)]. The average C–S bond length of (I) is comparable to that observed in [Li(THF)₄][ScCl₃(bdmpzdtc)], but much shorter than that in [Ti(bdmpzdtc)₂Cl₂], which may be ascribed to the different coordination mode of the CS₂ group in the latter complex.

In the crystal structure of (I), two pyrazole rings of neighboring molecules are partially overlapped, with a centroid–centroid separation of 4.139 (2) Å between rings *A* (atoms N1/N2/C2–C4) and *B*ⁱ [atoms N3/N4/C9–C11; symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$], indicating a weak intermolecular π - π interaction (Janiak, 2000; Tong *et al.*, 1999). If these interactions are considered, they imply the formation of a zigzag chain running along the *b* axis (Fig. 2).

Experimental

To a solution of Cu(PPh₃)Cl (0.181 g, 0.5 mmol) in CH₂Cl₂ (5 ml) was added a solution of [Li(bdmpzdtc)(H₂O)]₄ (0.606 g, 0.5 mmol) in MeCN (10 ml) (Otero *et al.*, 2002). The resulting red solution was stirred at room temperature for 10 h and then filtered. Diethyl ether was allowed to diffuse into the filtrate over a period of several days, forming red plates of (I), which were collected by filtration, washed with Et₂O and dried *in vacuo* (yield 0.527 g, 87% based on Cu). The crystal used for the crystal structure determination was obtained directly from the above preparation. Analysis found: C 59.39, H 5.08, N 9.11%; calculated for C₃₀H₅₀CuN₄PS₂: C 59.53, H 5.00, N 9.26%.

Crystal data

[Cu(C ₁₂ H ₁₅ N ₄ S ₂)(C ₁₈ H ₁₅ P)]	<i>V</i> = 2945.9 (12) Å ³
<i>M_r</i> = 605.24	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 13.051 (3) Å	μ = 0.96 mm ⁻¹
<i>b</i> = 14.256 (3) Å	<i>T</i> = 193 (2) K
<i>c</i> = 17.100 (3) Å	0.46 × 0.45 × 0.20 mm
β = 112.19 (3)°	

Data collection

Rigaku Mercury diffractometer	26346 measured reflections
Absorption correction: multi-scan (Jacobson, 1998)	6583 independent reflections
<i>T</i> _{min} = 0.666, <i>T</i> _{max} = 0.831	5364 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$	347 parameters
$wR(F^2) = 0.089$	H-atom parameters constrained
<i>S</i> = 1.07	$\Delta\rho_{\max} = 0.27 \text{ e \AA}^{-3}$
6583 reflections	$\Delta\rho_{\min} = -0.34 \text{ e \AA}^{-3}$

Table 1

Comparative bond distances (Å) for (I) and some related complexes.

Complex	Cu–N	Cu–P	Cu–S	C–S
[Cu(dmpzdtc)(PPh ₃)] ^d	2.0844 (14)	2.1809 (7)	2.3295 (11)	1.673 (2)
[Cu(tdmpzb)(PPh ₃)] ^b	2.075 (2)	2.156 (2)	–	–
[Cu(tdphpbz)Cl] ^c	2.046 (3)	–	–	–
[Cu(tdippzb)Cl] ^d	1.984 (3)	–	–	–
[Cu(tpms)(PPh ₃)] ^e	–	2.147 (2)	–	–
[Cu(PPh ₃) ₂ (PhCOS)] ^f	–	2.263 (2)	–	–
[Cu(C ₆ H ₁₁ CN) ₂ (dmpzdtc)] ^g	–	–	2.327 (2)	–
[Li(THF) ₄][ScCl ₃ (bdmpzdtc)] ^g	–	–	–	1.658 (3)
[Ti(bdmpzdtc) ₂ Cl ₂] ^h	–	–	–	1.736 (2)

Notes: (a) this work; (b) Lobbia *et al.* (2004) [tdmpzb is hydridotris(3,5-dimethylpyrazol-1-yl)borate]; (c) Higashimura *et al.* (2000) [tdphpbz is hydridotris(3,5-diphenylpyrazol-1-yl)borate]; (d) Kitajima *et al.* (1990) [tdippzb is hydridotris(3,5-diisopropylpyrazol-1-yl)borate]; (e) Santini *et al.* (2002) [tpms is tris(pyrazolyl)methanesulfonate]; (f) Deivaraj *et al.* (2000); (g) Arduzozia *et al.* (1991) [dmpzdtc is 3,5-dimethylpyrazole-1-dithioacetate]; (h) Otero *et al.* (2002).

Methyl H atoms were constrained to an ideal geometry [C–H = 0.98 Å and *U*_{iso}(H) = 1.5*U*_{eq}(C)] but were allowed to rotate freely about the parent C–C bonds. All other H atoms were placed in geometrically idealized positions (C–H = 1.0 Å for methine groups and C–H = 0.95 Å for aromatic groups) and constrained to ride on their parent atoms [*U*_{iso}(H) = 1.2*U*_{eq}(C)].

Data collection: *CrystalClear* (Rigaku/MSK, 2001); cell refinement: *CrystalClear*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Natural Science Foundation of China (grant No. 20525101) and the NSF of Jiangsu Province (grant No. BK2004205).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3041). Services for accessing these data are described at the back of the journal.

References

- Arduzozia, G. A., Angaroni, M., Monica, G. L., Moret, M. & Masciocchi, N. (1991). *Inorg. Chim. Acta*, **185**, 63–67.
- Beck, A., Weibert, B. & Burzlaff, N. (2001). *Eur. J. Inorg. Chem.* pp. 521–527.
- Chen, Y. D., Qin, Y. H., Zhang, L. Y., Shi, L. X. & Chen, Z. N. (2004). *Inorg. Chem.* **43**, 1197–1205.
- Deivaraj, T. C., Lai, G. X. & Vittal, J. J. (2000). *Inorg. Chem.* pp. 1028–1034.
- Enomoto, M., Kishimura, A. & Aida, T. (2001). *J. Am. Chem. Soc.* **123**, 5608–5609.
- Hammes, B. S., Kieber-Emmons, M. T., Letizia, J. A., Shirin, Z., Carrano, C. J., Zakharov, L. N. & Rheingold, A. L. (2003). *Inorg. Chim. Acta*, **346**, 227–238.
- Higashimura, H., Kubota, M., Shiga, A., Fujisawa, K., Moro-oka, Y., Uyama, H. & Kobayashi, S. (2000). *Macromolecules*, **33**, 1986–1995.
- Jacobson, R. (1998). Private communication to the Rigaku Corporation, Tokyo, Japan.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

- Kitajima, N., Fujisawa, K. & Morooka, Y. (1990). *J. Am. Chem. Soc.* **112**, 3210–3212.
- Li, D. F., Parkin, S., Wang, G. B., Yee, G. T., Clérac, R., Wernsdorfer, W. & Holmes, S. M. (2006). *J. Am. Chem. Soc.* **128**, 4214–4215.
- Lobbia, G. G., Hanna, J. V., Pellei, M., Pettinar, C., Santini, C., Sketton, B. W. & White, A. H. (2004). *J. Chem. Soc. Dalton Trans.* pp. 951–958.
- Noel, G., Roder, J. C., Dechert, S., Pritzkow, H., Bolk, L., Mecking, S. & Meyer, F. (2006). *Adv. Synth. Catal.* **348**, 887–897.
- Nöth, H., Beck, W. & Burger, K. (1998). *Eur. J. Inorg. Chem.* pp. 93–99.
- Ortiz, M., Díaz, A., Cao, R., Otero, A. & Fernández-Baeza, J. (2004). *Inorg. Chim. Acta*, **357**, 19–24.
- Otero, A., Fernández-Baeza, J., Antinolo, A., Carrillo-Hermosilla, F., Tejada, J., Lara-Sánchez, A., Sanchez-Barba, L., Fernandez-Lopez, M., Rodriguez, A. M. & Lopez-Solera, I. (2002). *Inorg. Chem.* **41**, 5193–5202.
- Otero, A., Fernández-Baeza, J., Antinolo, A., Tejada, J., Lara-Sánchez, A., Sanchez-Barba, L., Fernandez-Lopez, M. & Lopez-Solera, I. (2004). *Inorg. Chem.* **43**, 1350–1358.
- Otero, A., Fernández-Baeza, J., Antinolo, A., Tejada, J., Lara-Sánchez, A., Sánchez-Barba, L., Martínez-Caballero, E., Rodríguez, A. N. & López-Solera, I. (2005). *Inorg. Chem.* **44**, 5336–5344.
- Otero, A., Fernández-Baeza, J., Tejada, J., Antinolo, A., Carrillo-Hermosilla, F., Díez-Barra, E., Lara-Sánchez, A. & Fernández-López, M. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2367–2374.
- Porchia, M., Papini, G., Santini, C., Lobbia, G. G., Pellei, M., Tisato, F., Bandoli, G. & Dolmella, A. (2006). *Inorg. Chim. Acta*, **359**, 2501–2508.
- Rigaku/MS (2001). *CrystalClear*. Version 1.30. Rigaku/MS, The Woodlands, Texas, USA.
- Rigaku/MS (2004). *CrystalStructure*. Version 3.6.0. Rigaku/MS, The Woodlands, Texas, USA.
- Santini, C., Pellei, M., Lobbia, G. G., Cingolani, A., Spagna, R. & Camalli, M. (2002). *Inorg. Chem. Commun.* **5**, 430–433.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Smith, J. N., Hoffman, J. T., Shirin, Z. & Carrano, C. J. (2005). *Inorg. Chem.* **44**, 2012–2017.
- Smith, J. N., Shirin, Z. & Carrano, C. J. (2002). *J. Am. Chem. Soc.* **125**, 868–869.
- Tong, M. L., Lee, H. K., Chen, X. M., Huang, R. B. & Mak, T. C. W. (1999). *J. Chem. Soc. Dalton Trans.* pp. 3657–3659.
- Trofimenko, S. (1967). *J. Am. Chem. Soc.* **89**, 3170–3177.