

Dibromido(dimethyl sulfoxide- κ O)- (1,10-phenanthroline- κ^2 N,N')- copper(II)

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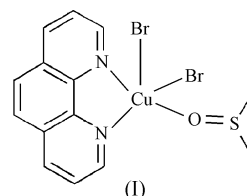
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The solvent effect on the molecular structures of copper(II) complexes produced from the reaction between CuBr_2 and 1,10-phenanthroline is evident. The monomeric title compound, $[\text{CuBr}_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_2\text{H}_6\text{OS})]$, which consists of discrete units, is produced from this reaction in dimethyl sulfoxide (DMSO), whereas a polymeric copper(II) compound is known to be produced from the same reaction in the poor coordinating solvent ethanol. The geometry around the copper(II) ion in the title compound is best described as trigonal-bipyramidal distorted square-based pyramidal, with a τ value of 0.37. The two phenanthroline N atoms, the DMSO O atom and one of the Br atoms occupy the four basal positions, while the second Br atom occupies the axial position. The magnetic susceptibility data also indicate that the title compound is monomeric, but there is still a weak antiferromagnetic interaction between paramagnetic copper(II) centers *via* the intermolecular 'Cu—Br...Br—Cu' contact pathway.

Comment

Polymeric $[\text{CuBr}_2(\text{phen})]_\infty$ (phen is 1,10-phenanthroline) is produced when anhydrous CuBr_2 is reacted with an equimolar amount of 1,10-phenanthroline in ethanol. This polymer consists of chains linked by Cu—Br bonds, in which the Cu atom displays tetragonally elongated (4+2)-coordination (Garland *et al.*, 1988). However, the same reaction carried out in dimethyl sulfoxide (DMSO), a coordinating solvent, produces the monomeric and five-coordinate title Cu^{II} complex, $[\text{CuBr}_2(\text{phen})(\text{DMSO})]$, (I). In this work, we report the preparation of (I) and the determination of its single-crystal structure. Selected bond distances and angles for (I) are listed in Table 1.

The coordination geometry around the Cu atom is best described as trigonal-bipyramidal distorted square-based pyramidal, with a τ value of 0.37 (Addison *et al.*, 1984; Harrison *et al.*, 1981; Nagle *et al.*, 1990); the two N atoms of the phen molecule, one Br atom and the O atom of DMSO occupy the four basal positions, while the other Br atom occupies the axial position (Fig. 1). The basal Cu—Br2 bond distance is



considerably shorter than the axial Cu—Br1 bond distance, but both distances are longer than the terminal Cu—Br distances observed in the polymeric $[\text{CuBr}_2(\text{phen})]_\infty$ compound. The unequal Cu—N bond distances (Table 1) and the distortion of the normally symmetric phen ligand in (I) are attributable to the coordination of the large DMSO molecule to the Cu atom. The Cu—O_{DMSO} (Cu—O15) distance in (I) is similar to those in $[\text{Cu}(\text{DMSO})_4](\text{ClO}_4)_2$ [1.934 (6)–1.954 (6) Å; Blake *et al.*, 1996], but is significantly shorter than those in $[\text{Cu}(\text{C}_9\text{H}_5\text{N}_2\text{O}_3)(\text{DMSO})_2]$ [2.336 (5) or 2.418 (7) Å; Popović *et al.*, 2007] or the Zn—O_{DMSO} distances in a similar Zn—DMSO complex [2.045 (5) and 2.066 (5) Å; Che *et al.*, 2006]. The intermolecular distance between the two parallel aromatic rings N1/C2—C5/C14 and C5ⁱ—C8ⁱ/C13ⁱ/C14ⁱ [symmetry code: (i) $-x + 1, -y + 2, -z$] of the coordinated phen ligands in the packing structure (3.4 Å) is much shorter than 4.11 Å, indicating the existence of significant π – π interactions between them (Fig. 2).

Magnetic data of (I) were collected as a function of temperature (2–300 K). Fig. 3 shows a plot of magnetic susceptibility *versus* temperature. The room-temperature magnetic moment of (I), estimated from $\mu_{\text{eff}} = 2.828(\chi_{\text{M}})^{1/2}$, is 1.9 B.M. (B.M. = Bohr magneton = $9.274 \times 10^{-24} \text{ J T}^{-1}$) and the Neel temperature T_{N} is observed at 4.0 K, indicating the

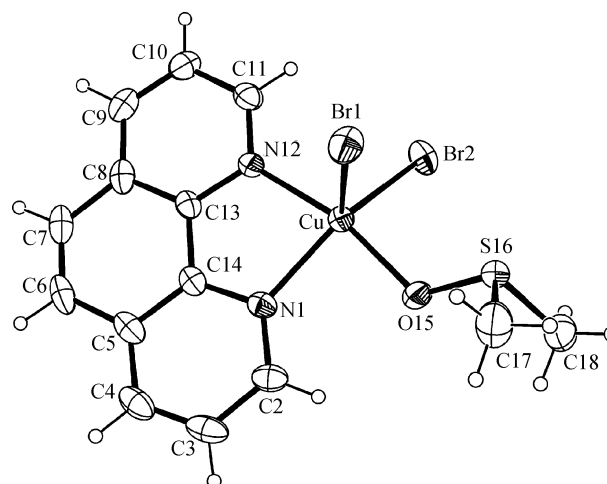


Figure 1
An ORTEP-3 (Farrugia, 1997) diagram of (I), showing the atom-numbering scheme and 30% probability displacement ellipsoids.

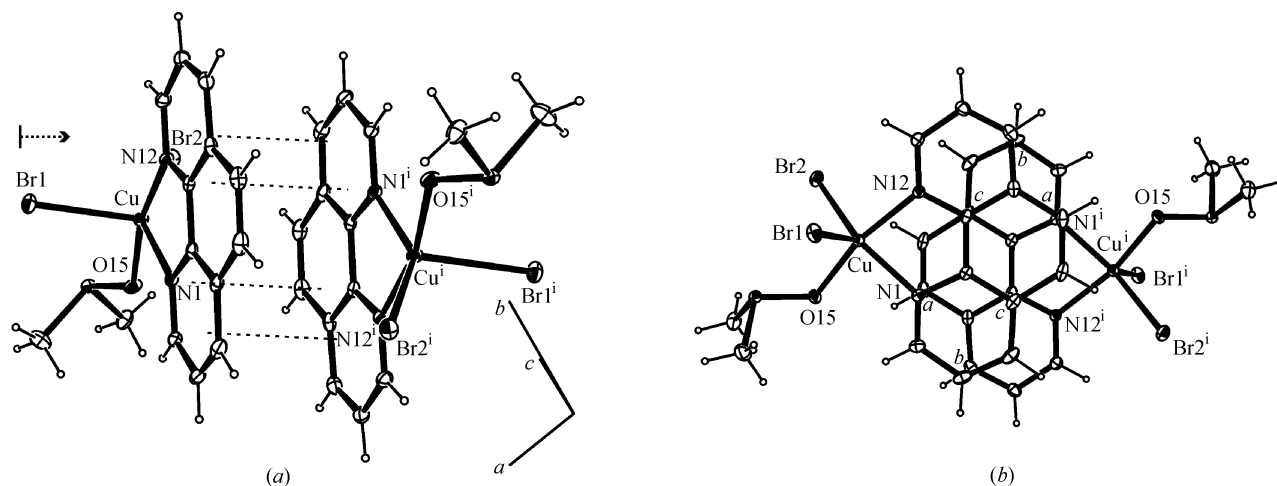


Figure 2
 The π - π stacking interactions between two phen ligands of (I), viewed (a) parallel and (b) perpendicular to the π - π stacking interactions [$a = \text{N1} \cdots \text{C7}^i = 3.411(7) \text{ \AA}$, $b = \text{C3} \cdots \text{C9}^i = 3.414(8) \text{ \AA}$ and $c = \text{C5} \cdots \text{C13}^i = 3.466(7) \text{ \AA}$; symmetry code: (i) $-x + 1, -y + 2, -z$].

presence of a very weak antiferromagnetic interaction between paramagnetic Cu^{II} centers. The distance between the two nearest Cu atoms in the packing structure is $7.228(1) \text{ \AA}$, which is too long for a pair of Cu^{II} centers to interact magnetically. In view of the magnetic exchange mechanism of the monomeric copper(II)-bromide system, the 'bromide-bromide contact' or $\text{Cu}-\text{Br} \cdots \text{Br}-\text{Cu}$ contact is known to be an important pathway for antiferromagnetic interaction (Dyrek *et al.*, 1987; Bond *et al.*, 1995). The $\text{Br} \cdots \text{Br}$ intermolecular contact distance in (I) is $5.180(1) \text{ \AA}$. This contact distance is considerably longer than the sum of the van der Waals radii of two Br atoms (3.90 \AA), but is in the range of the typical $\text{Br} \cdots \text{Br}$ contact distances (3.90 – 5.61 \AA) observed for many di- and tetrabromidocuprate compounds that exhibit antiferromagnetism at low temperature (Kang *et al.*, 2004; Van der Bilt *et al.*, 1981). The observed weak antiferromagnetism of the title compound in the crystalline state is most probably due to magnetic exchange *via* the ' $\text{Cu}-\text{Br} \cdots \text{Br}-\text{Cu}$ ' pathway.

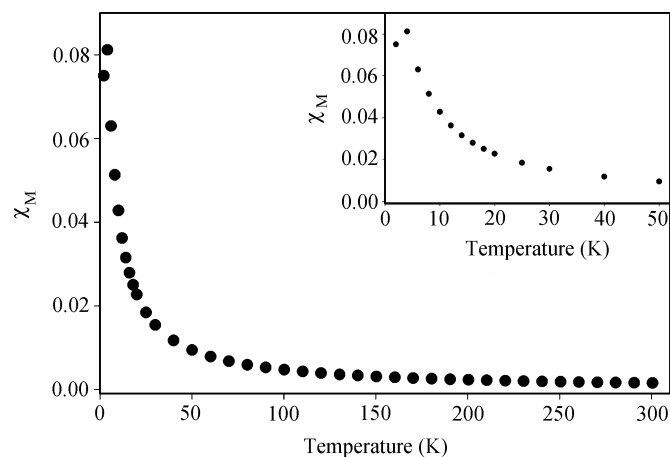


Figure 3
 A plot of magnetic susceptibilities *versus* temperature in the temperature region 2–300 K for (I).

Experimental

Dibromido(1,10-phenanthroline)copper(II), $[\text{CuBr}_2(\text{phen})]$, was prepared according to the method described by Garland *et al.* (1988). The chocolate-colored precipitates (0.5 mmol) were dissolved in DMSO. Green single crystals of (I) were obtained by slow evaporation of $[\text{CuBr}_2(\text{phen})]$ in a DMSO solution for 3 d. Analysis calculated for $\text{C}_{14}\text{H}_{14}\text{Br}_2\text{CuN}_2\text{O}$: C 34.91, H 2.93, N 5.82%; found: C 34.79, H 2.61, N 5.81%.

Crystal data

$[\text{CuBr}_2(\text{C}_{12}\text{H}_8\text{N}_2)(\text{C}_2\text{H}_6\text{OS})]$	$V = 1643.29(6) \text{ \AA}^3$
$M_r = 481.69$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.3984(2) \text{ \AA}$	$\mu = 6.32 \text{ mm}^{-1}$
$b = 14.0857(3) \text{ \AA}$	$T = 295(2) \text{ K}$
$c = 14.5004(3) \text{ \AA}$	$0.15 \times 0.09 \times 0.06 \text{ mm}$
$\beta = 106.667(2)^\circ$	

Data collection

Bruker SMART CCD area-detector diffractometer	22691 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	3778 independent reflections
$T_{\text{min}} = 0.511, T_{\text{max}} = 0.685$	2381 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$	190 parameters
$wR(F^2) = 0.127$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.53 \text{ e \AA}^{-3}$
3778 reflections	$\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cu—N1	2.071(4)	Cu—Br2	2.4692(8)
Cu—N12	2.003(4)	Cu—O15	1.933(4)
Cu—Br1	2.5769(8)		
N1—Cu—N12	80.84(16)	N12—Cu—Br2	93.71(12)
N1—Cu—Br1	107.20(11)	N12—Cu—O15	165.55(16)
N1—Cu—Br2	143.48(11)	Br1—Cu—O15	95.93(13)
N1—Cu—O15	86.51(17)	Br2—Cu—O15	92.31(13)
N12—Cu—Br1	94.47(12)	Br2—Cu—Br1	109.22(3)

H atoms were positioned geometrically and constrained to ride on their attached atoms, with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINTE* (Bruker, 2002); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3138). Services for accessing these data are described at the back of the journal.

References

- Addison, A. W., Rao, T. N., Reedjik, J., Van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Blake, A. J., Grimditch, R. S., Parsons, S. & Schröder, M. (1996). *Acta Cryst. C52*, 514–516.
- Bond, M. R., Place, H., Wang, Z. & Willett, R. D. (1995). *Inorg. Chem.* **34**, 3134–3141.
- Bruker (2002). *SADABS* (Version 2.03), *SAINTE* (Version 6.02) and *SMART* (Version 5.62). Bruker AXS Inc., Madison, Wisconsin, USA.
- Che, X.-Q., Gao, Y.-X. & Wang, J.-W. (2006). *Acta Cryst. C62*, m440–m442.
- Dyrek, K., Goslar, J., Hodorowicz, S. A., Hoffmann, S. K., Oleksyn, B. J. & Weselucha-Bircaynska, A. (1987). *Inorg. Chem.* **26**, 1481–1487.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Garland, M. T., Grandjean, D., Spodine, E., Atria, A. M. & Manzur, J. (1988). *Acta Cryst. C44*, 1547–1549.
- Harrison, W. D., Kennedy, D. M., Power, M., Sheahan, R. & Hathaway, B. J. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1556–1564.
- Kang, S. K., Lee, Y.-M., Kim, Y. I., Kim, Y., Seff, K. & Choi, S.-N. (2004). *Inorg. Chim. Acta*, **357**, 2602–2608.
- Nagle, P., O'Sullivan, E., Hathaway, B. J. & Muller, E. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3339–3406.
- Popović, Z., Pavlović, G. & Kukovec, B.-M. (2007). *Acta Cryst. C63*, m181–m183.
- Sheldrick, G. M. (2008). *Acta Cryst. A64*, 112–122.
- Van der Bilt, A., Joung, K. O., Carlin, R. L. & De Jongh, L. J. (1981). *Phys. Rev. B*, **24**, 445–449.