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catena-Poly[[[[μ-bis(diphenylphosphino)amine-κ^2P:P']bis[acetonitrilecopper(I)]]-μ-(1,2-dicyanoethylene-1,2-dithiolato)-[(1,2-dicyanoethylene-1,2-dithiolato)molybdenate(IV)]-μ-1,2-dicyanoethylene-1,2-dithiolato] acetonitrile disolvate]

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Key indicators

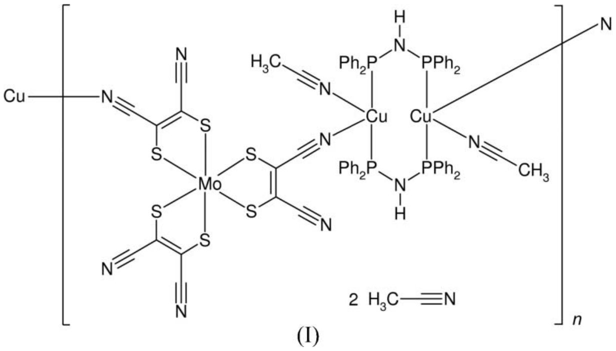
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.012 Å
R factor = 0.062
wR factor = 0.131
Data-to-parameter ratio = 15.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Reaction of $(Bu_4N)_2[Mo(mnt)_3]$ (mnt = *cis*-1,2-dicyanoethylene-1,2-dithiolate) with $[Cu_2(dppa)_2(MeCN)_4](ClO_4)_2$ [dppa = bis(diphenylphosphino)amine] yields the polymeric heterometallic title compound, $\{[Cu_2Mo(mnt)_3(\mu\text{-}dppa)_2(MeCN)_2]\cdot 2CH_3CN\}_n$ or $\{[Cu_2Mo(C_4N_2S_2)_3(C_{24}H_{21}NP_2)_2(C_2H_3N)_2]\cdot 2C_2H_3N\}$. The compound exhibits a polymeric zigzag structure formed from $[Mo(mnt)_3]^{2-}$ and $[Cu_2(dppa)_2(MeCN)_2]^{2+}$ units linked by coordination of the CN groups of the mnt ligands to the Cu^I centres.

Comment

The chemistry of metal–thiolate complexes is subject to intensive interest owing to their intriguing spectroscopic and optical properties (Paw *et al.*, 1998). Recent research has focused on the design of heteronuclear thiolate cluster complexes that can afford long-lived excited states and efficient photoluminescence (Chen *et al.*, 2004). One feasible synthetic approach for the preparation of these molecular materials is to combine metal thiolates with another metal component that has vacant or substitutable coordination sites (Chen *et al.*, 2005).



(I)

As a dithiolate-containing precursor with potential bridging character, $[Mo(mnt)_3]^{2-}$ (mnt = *cis*-1,2-dicaynoethylene-1,2-dithiolate) is useful for the preparation of heteronuclear complexes by combination with a metal diphosphine component. Reaction of $[Mo(mnt)_3]^{2-}$ with $[Ag_2(dppa)_2(MeCN)_4]^{2+}$ [dppa = bis(diphenylphosphino)amine] has been shown previously to afford an ionic salt $[Ag_2(dppa)_2(MeCN)_2]^{2+}$-$[Mo(mnt)_3]^{2-}$ (Xu *et al.*, 2002). A comparable reaction using $[Cu_2(dppa)_2(MeCN)_4]^{2+}$ yields the polymeric heterometallic title complex, $\{[Cu_2Mo(mnt)_3(\mu\text{-}dppa)_2(MeCN)_2]\cdot 2CH_3CN\}_n$, (I) (Fig. 1).

The polymeric complex (I) exhibits a zigzag structure formed from $[Mo(mnt)_3]^{2-}$ and $[Cu_2(dppa)_2(MeCN)_2]^{2+}$ units,

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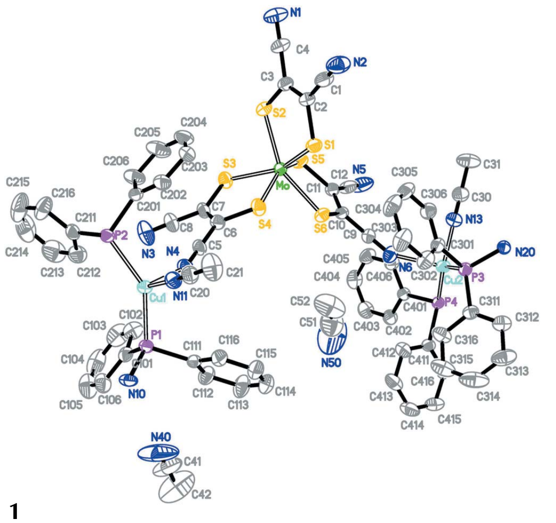

Figure 1

The asymmetric unit of (I), showing displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted.

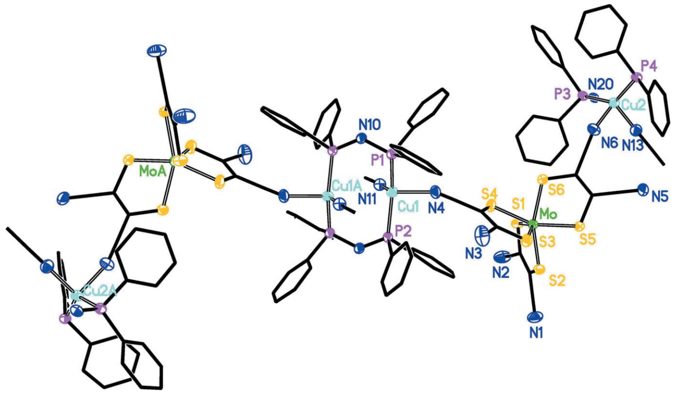

Figure 2

A section of the polymeric complex in (I), illustrating the zigzag structure. H atoms have been omitted. Atoms with the suffix A are related by the symmetery operation $(1 - x, -y, 1 - z)$.

linked by coordination of the CN groups of the mnt ligands to the Cu^I centres (Fig. 2). Each Cu^I centre exhibits an N_2P_2 coordination environment with a distorted tetrahedral geometry (Table 1). The Mo^{IV} centre is coordinated by six S-atom donors in a distorted octahedral arrangement (Table 1) comparable to that found in the parent complex $(Bu_4N)_2[Mo(mnt)_3]$ (Brown & Stiefel, 1973) and the ionic salt $[Ag_2(dppa)_2(MeCN)_2][Mo(mnt)_3]$ (Xu *et al.*, 2002). The Cu⋯Cu distances across the bridging dppa ligands are $Cu1\cdots Cu1^i$ = 3.3188 (14) and $Cu2\cdots Cu2^{ii}$ = 3.5107 (15) Å [symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $1 - x, 2 - y, -z$], similar to that found in the parent compound $[Cu_2(dppa)_2(MeCN)_4](PF_6)_4$ (Liu *et al.*, 2002). The Mo⋯Cu separations through the bridging mnt ligands are 7.8272 (9) and 7.8191 (9) Å for Mo⋯Cu1 and Mo⋯Cu2, respectively.

Experimental

The starting compounds $(Bu_4N)_2[Mo(mnt)_3]$ (Stiefel *et al.*, 1970) and $[Cu_2(dppa)_2(MeCN)_2](ClO_4)_2$ (Liu *et al.*, 2002) were prepared by literature procedures. The title compound was then synthesized by the following procedure. To a dichloromethane (3 ml) solution of $[Cu_2(\mu\text{-dppa})_2(MeCN)_4](ClO_4)_2$ (34 mg, 0.03 mmol) was added $[Bu_4N]_2[Mo(mnt)_3]$ (30 mg, 0.03 mmol); the colour changed to black in a few minutes. After the solution had been stirred at room temperature for 12 h, the solvent was removed *in vacuo*, and the resulting residue was extracted with acetonitrile (3 ml). Diffusion of diethyl ether into the acetonitrile solution afforded brown crystals of (I).

Crystal data

$[Cu_2Mo(C_4N_2S_2)_3(C_{24}H_{21}NP_2)_2(C_2H_3N)_2]\cdot 2C_2H_3N$
M_r = 1572.44
Triclinic, $P\overline{1}$
a = 12.6197 (6) Å
b = 12.8711 (6) Å
c = 23.497 (1) Å
α = 82.079 (1)°
β = 79.725 (1)°
γ = 88.113 (1)°
V = 3719.4 (3) Å^3
Z = 2
D_x = 1.404 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 1.03 mm^{-1}
T = 293 (2) K
Prism, brown
0.50 × 0.45 × 0.40 mm

Data collection

Siemens SMART CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.516, T_{max} = 0.661
19485 measured reflections
13031 independent reflections
9643 reflections with $I > 2\sigma(I)$
R_{int} = 0.030
θ_{max} = 25.1°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.131
S = 1.23
13031 reflections
838 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.01P)^2 + 10.4674P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Mo—S1	2.3768 (17)	Cu1—P2	2.2689 (17)
Mo—S2	2.3990 (16)	Cu1—N4	2.176 (5)
Mo—S3	2.3696 (17)	Cu1—N11	2.033 (6)
Mo—S4	2.3716 (16)	Cu2—P3	2.2693 (16)
Mo—S5	2.3980 (16)	Cu2—P4	2.2523 (15)
Mo—S6	2.3916 (16)	Cu2—N6	2.171 (6)
Cu1—P1	2.2590 (16)	Cu2—N13	2.022 (6)
S1—Mo—S2	81.74 (6)	S5—Mo—S6	81.45 (5)
S1—Mo—S3	147.56 (6)	P1—Cu1—P2	140.00 (7)
S1—Mo—S4	80.92 (6)	P1—Cu1—N4	95.21 (15)
S1—Mo—S5	120.19 (7)	P1—Cu1—N11	112.36 (16)
S1—Mo—S6	86.21 (6)	P2—Cu1—N4	96.02 (15)
S2—Mo—S3	84.39 (6)	P2—Cu1—N11	102.91 (16)
S2—Mo—S4	123.34 (6)	N4—Cu1—N11	101.0 (2)
S2—Mo—S5	82.94 (6)	P3—Cu2—P4	134.42 (6)
S2—Mo—S6	151.98 (6)	P3—Cu2—N6	100.43 (15)
S3—Mo—S4	82.52 (6)	P3—Cu2—N13	105.12 (16)
S3—Mo—S5	86.76 (6)	P4—Cu2—N6	101.58 (15)
S3—Mo—S6	117.66 (6)	P4—Cu2—N13	112.63 (16)
S4—Mo—S5	150.11 (6)	N6—Cu2—N13	93.8 (2)
S4—Mo—S6	79.06 (6)		

H atoms were positioned geometrically, with C—H = 0.93 (CH) or 0.96 Å (CH_3) and N—H = 0.86 Å, and allowed to ride during subsequent refinement, with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}$(methyl C).

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Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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