Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Synthesis and Structure of a Tetracopper(II) Complex of a Pyrrole-Containing Unsymmetrical Binucleating Ligand: [$Cu_2L(NCS)_2$]$_2$

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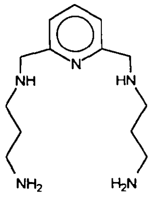
Abstract

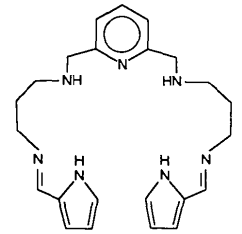
The unsymmetrical binucleating ligand H_2L (L = $C_{23}H_{29}N_7$) was formed *in situ* from the condensation of two equivalents of 2-pyrrolecarboxaldehyde with one equivalent of 2,6-bis[N-(3-aminopropyl)aminomethyl]pyridine. Subsequent addition of two equivalents of copper acetate followed by two equivalents of sodium thiocyanate yielded [$Cu_2L(NCS)_2$]$_2$, bis{[7,7′-pyridine-2,6-diylbis(2,6-diazahept-1-en-1-yl)di-2-pyrrolato]bis(thiocyanato)dicopper(II)}. The complex exists as a dimer of dicopper(II) units held together by two 1,3-thiocyanate ion bridges.

Comment

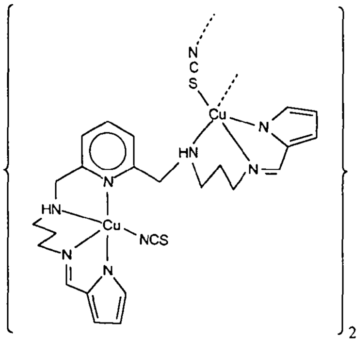
During our development of a general route into unsymmetrical macrocycles providing two distinct types of metal-binding environments for two or more metal ions (Brooker & Croucher, 1993), a range of 'two-armed' precursors was prepared, including 2,6-bis[N-(3-aminopropyl)aminomethyl]pyridine, (I). In addition to studying unsymmetrical macrocycles based on this precursor (Brooker & Simpson, unpublished results), the unsymmetrical binucleating acyclic ligand H_2L, (II), was prepared and complexed with copper(II). The resulting complex, [$Cu_2L(NCS)_2$]$_2$, (III), is reported.



(I)



(II)



(III)

The structure determination reveals that the complex is a dimer of dicopper units, related to each other by a centre of inversion, and held together by two 1,3-thiocyanate ion bridges (Fig. 1). A second type of thiocyanate ion binding mode is also observed, that is, N-terminal coordination to Cu1, which is consistent with the infrared spectrum (C≡N str. 2105, 2077 cm^{-1}). Both independent copper(II) ions are five-coordinate; both exhibit very distorted geometries. On complexa-

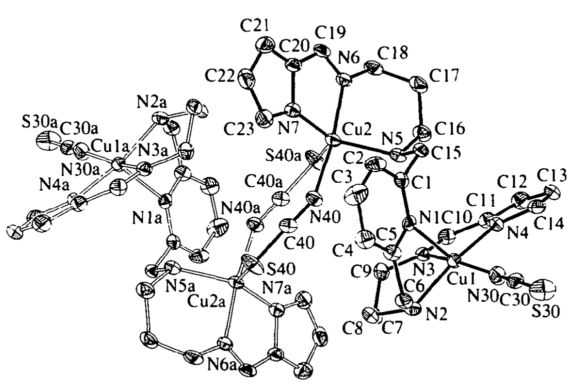


Fig. 1. View of [$Cu_2L(NCS)_2$]$_2$. Displacement ellipsoids are drawn at the 50% probability level.

tion, the tridentate 2,6-bis(aminomethyl)pyridine portion of L^{2-} has folded back on itself so that, uncharacteristically, it acts as only a bidentate donor (N1, N2) to Cu1, with the remaining N atom donor (N5) coordinating to Cu2. Both 2-iminomethylpyrrole arms (C=N str. 1588 cm^{-1}) are found to have deprotonated and coordinated, giving similar geometrical parameters to those found in a related dicopper complex (Bertrand & Kirkwood, 1972).

The facile deprotonation and coordination of H_2L is encouraging. Further work with pyrrole-containing ligands is underway.

Experimental

H_2L was not isolated but formed *in situ* from 2-pyrrolecarboxaldehyde (4 mmol) (Silverstein, Ryskiewicz & Willard, 1956) and 2,6-bis[*N*-(3-aminopropyl)aminomethyl]-pyridine (2 mmol) (Brooker & Simpson, unpublished results). Subsequent dropwise addition of copper acetate monohydrate (4 mmol) in dry CH_3OH (100 cm^3) to an orange dry CH_3OH (30 cm^3) solution of H_2L caused an immediate colour change to intense green. Dropwise addition of sodium thiocyanate (4 mmol) in dry CH_3OH (20 cm^3) resulted in the immediate precipitation of a green powder which, after stirring for a further 30 min, was filtered off and dried *in vacuo*. Yield: 0.93 g (72%). Single crystals of $[Cu_2L(NCS)_2]_2$ were obtained by vapour diffusion of diethyl ether into dry *N*,*N*-dimethylformamide (DMF) solutions. Analysis: found C 46.2, H 4.9, N 19.6, S 9.7, Cu 19.2%; calculated for $C_{50}H_{58}N_{18}S_4Cu_4$ C 46.4, H 4.5, N 19.5, S 9.9, Cu 19.6%. FAB MS: cluster at 589 a.m.u. corresponding to $[Cu_2L(NCS)]^+$. Λ_m(DMF) = 17 Ω^{-1}mol^{-1}cm^2.

Crystal data

$[Cu_4(NCS)_4(C_{23}H_{29}N_7)_2]$
$M_r = 1293.54$
Triclinic
$P\bar{1}$
$a = 10.527\,(3)$ Å
$b = 12.163\,(3)$ Å
$c = 12.653\,(5)$ Å
$\alpha = 107.36\,(3)°$
$\beta = 104.31\,(3)°$
$\gamma = 108.60\,(2)°$
$V = 1356.5\,(7)$ Å^3
$Z = 1$
$D_x = 1.583$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 4–13°$
$\mu = 1.755$ mm^{-1}
$T = 133$ K
Block
0.60 × 0.38 × 0.12 mm
Green

Data collection

Siemens *P*4 four circle diffractometer
ω scans
Absorption correction: ψ scan
$T_{\min} = 0.691$, $T_{\max} = 0.991$
4809 measured reflections
4533 independent reflections
3244 observed reflections [$I > 2\sigma(I)$]

$R_{\rm int} = 0.0384$
$\theta_{\max} = 25.00°$
$h = 0 \rightarrow 12$
$k = -13 \rightarrow 12$
$l = -15 \rightarrow 14$
3 standard reflections monitored every 97 reflections
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0450$
$wR(F^2) = 0.0966$
$S = 1.052$
4531 reflections
343 parameters
H atoms riding; $U_{\rm iso} = 1.2 \times U_{\rm eq}$(carrying atom)
$w = 1/[\sigma^2(F_o^2) + (0.0390P)^2 + 0.4546P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.456$ e Å^{-3}
$\Delta\rho_{\min} = -0.424$ 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* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu1	0.04992 (6)	0.40451 (5)	0.08913 (5)	0.0224 (2)
Cu2	0.35027 (6)	0.23857 (5)	0.34829 (5)	0.0243 (2)
N1	0.0131 (4)	0.3035 (3)	0.2145 (3)	0.0209 (8)
C1	0.0232 (5)	0.1981 (4)	0.2191 (4)	0.0212 (10)
C2	−0.0188 (5)	0.1481 (5)	0.2954 (5)	0.0318 (12)
C3	−0.0707 (6)	0.2101 (5)	0.3729 (5)	0.0412 (14)
C4	−0.0824 (5)	0.3176 (5)	0.3675 (4)	0.0317 (12)
C5	−0.0421 (5)	0.3612 (4)	0.2866 (4)	0.0237 (11)
C6	−0.0582 (5)	0.4758 (4)	0.2744 (4)	0.0261 (11)
N2	0.0504 (4)	0.5395 (4)	0.2323 (3)	0.0254 (9)
C7	0.1895 (5)	0.6254 (4)	0.3364 (4)	0.0297 (12)
C8	0.3158 (5)	0.6796 (4)	0.3030 (4)	0.0282 (11)
C9	0.3728 (5)	0.5841 (4)	0.2531 (4)	0.0280 (11)
N3	0.2662 (4)	0.4835 (3)	0.1386 (3)	0.0231 (9)
C10	0.3060 (5)	0.4456 (4)	0.0513 (4)	0.0264 (11)
C11	0.1994 (5)	0.3492 (5)	−0.0586 (4)	0.0257 (11)
C12	0.1950 (6)	0.2855 (5)	−0.1711 (4)	0.0330 (12)
C13	0.0530 (6)	0.1987 (5)	−0.2405 (4)	0.0334 (12)
C14	−0.0262 (5)	0.2108 (4)	−0.1681 (4)	0.0294 (12)
N4	0.0627 (4)	0.3029 (3)	−0.0573 (3)	0.0237 (9)
C15	0.0886 (5)	0.1399 (4)	0.1368 (4)	0.0251 (11)
N5	0.2451 (4)	0.2198 (4)	0.1783 (3)	0.0228 (9)
C16	0.3026 (6)	0.1776 (5)	0.0851 (4)	0.0305 (12)
C17	0.3235 (6)	0.0574 (5)	0.0719 (4)	0.0309 (12)
C18	0.4404 (5)	0.0707 (5)	0.1790 (4)	0.0309 (12)
N6	0.4001 (4)	0.0963 (4)	0.2823 (3)	0.0261 (9)
C19	0.3898 (5)	0.0244 (4)	0.3384 (4)	0.0269 (11)
C20	0.3458 (5)	0.0541 (4)	0.4364 (4)	0.0264 (11)
C21	0.3170 (5)	0.0016 (5)	0.5152 (5)	0.0350 (13)
C22	0.2739 (5)	0.0789 (5)	0.5896 (4)	0.0346 (13)
C23	0.2789 (5)	0.1763 (5)	0.5530 (4)	0.0324 (12)
N7	0.3219 (4)	0.1624 (4)	0.4610 (3)	0.0257 (9)
N30	−0.1599 (5)	0.3470 (4)	0.0072 (4)	0.0337 (10)
C30	−0.2832 (6)	0.3058 (5)	−0.0193 (4)	0.0290 (12)
S30	−0.45692 (15)	0.25082 (14)	−0.05797 (14)	0.0437 (4)
N40	0.3253 (4)	0.3880 (4)	0.4332 (3)	0.0256 (9)
C40	0.3500 (4)	0.4751 (4)	0.5170 (4)	0.0214 (10)
S40	0.38416 (14)	0.59966 (13)	0.63359 (12)	0.0404 (4)

Table 2. *Selected geometric parameters* (Å, °)

Cu1—N4	1.960 (4)	Cu2—N7	1.951 (4)
Cu1—N30	1.973 (4)	Cu2—N40	1.951 (4)
Cu1—N3	2.010 (4)	Cu2—N6	1.974 (4)
Cu1—N2	2.048 (4)	Cu2—N5	2.068 (4)
Cu1—N1	2.310 (4)	Cu2—S40$^{\rm i}$	2.765 (2)
N4—Cu1—N30	91.5 (2)	N7—Cu2—N40	94.2 (2)
N4—Cu1—N3	81.3 (2)	N7—Cu2—N6	82.5 (2)
N30—Cu1—N3	164.0 (2)	N40—Cu2—N6	172.0 (2)
N4—Cu1—N2	168.7 (2)	N7—Cu2—N5	141.2 (2)
N30—Cu1—N2	90.1 (2)	N40—Cu2—N5	96.0 (2)
N3—Cu1—N2	94.4 (2)	N6—Cu2—N5	91.1 (2)
N4—Cu1—N1	114.76 (15)	N7—Cu2—S40$^{\rm i}$	124.57 (12)

N30—Cu1—N1	92.1 (2)	N40—Cu2—S40^i	88.42 (12)
N3—Cu1—N1	103.92 (14)	N6—Cu2—S40^i	87.49 (12)
N2—Cu1—N1	76.34 (14)	N5—Cu2—S40^i	93.12 (12)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The structure was solved by Patterson methods (Sheldrick, 1990) and refined against all F^2 using the gamma-test version of *SHELXL*93 (Sheldrick, 1993).

We are grateful to Professor W. T. Robinson for the X-ray data collection and to B. M. Clark for the FAB mass spectrum (University of Canterbury, New Zealand).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1024). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$[M_2(CO)_{10}(\mu\text{-dppp}_e)]$ [M = Cr, W; dppp$_e$ = $Ph_2P(CH_2)_5PPh_2$]

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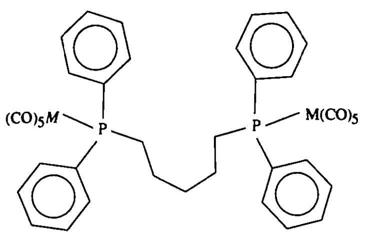
Abstract

The dppp$_e$ monobridged bimetallic complexes μ-1,5-bis(diphenylphosphino)pentane-P:P'-bis(pentacarbonylchromium), $[Cr_2(CO)_{10}\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}]$, (I), and μ-1,5-bis(diphenylphosphino)pentane-P:P'-bis(pentacarbonyltungsten), $[W_2(CO)_{10}\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}]$, (II), are isomorphous and isostructural. In each molecule, a crystallographic twofold axis passes through the central methylene C atom of the dppp$_e$ pentane chain. The torsion angles P—C$_\alpha$—C$_\beta$—C$_\gamma$ and C$_\alpha$—C$_\beta$—C$_\gamma$—C$_\delta$ are 169.1 (2) and 59.0 (2)°, respectively, for (I), and 169.5 (7) and 60.6 (5)°, respectively, for (II).

Comment

There are several reports of syntheses of Group 6 metal–carbonyl derivatives containing the long-backbone diphosphine ligand dppp$_e$. The monobridged dinuclear complexes $[M_2(CO)_{10}(\mu\text{-dppp}_e)]$ have been prepared from $[M(CO)_6]$ and dppp$_e$ under reflux in $EtOCH_2CH_2OCH_2CH_2OH$ solution (M = Mo) (Dietsche, 1966) and from the same starting materials with Me_3NO as initiator in CH_3CN (M = Cr, Mo and W) (Hor, 1989). $[Mo(CO)_4(\text{dppp}_e)]$, which contains an eight-membered chelate ring, was synthesized from $[Mo(CO)_4(NBD)]$ (NBD = norborna-2,5-diene) and dppp$_e$ (Ueng & Hwang, 1994*a*). The structure of the doubly bridged 16-membered bimetallacycle *trans*-$[Mo_2(CO)_8(\mu\text{-dppp}_e)_2]$, synthesized from $[Mo(CO)_6]$ and dppp$_e$ (mole ratio 1:1), has been described (Ueng & Hwang, 1994*b*). For comparison, the crystal structures of the title compounds, (I) and (II), which contain only a single dppp$_e$ bridge, have been determined.



(I) M = Cr
(II) M = W

The molecules consist of two metal atoms each bonded to five carbonyls and one P atom from the diphosphine ligand. The coordination around each metal is distorted octahedral with the deviation of the metal from the equatorial least-squares plane formed by C(1), C(2), C(4) and C(5) being −0.029 (2) Å for the Cr complex and −0.023 (6) Å for the W complex. In each

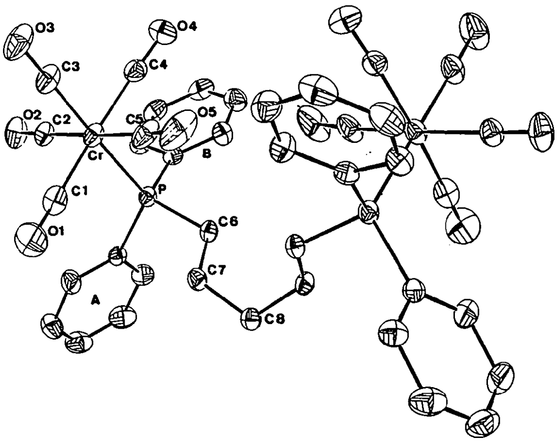


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the molecular structure of $[Cr_2(CO)_{10}(\mu\text{-dppp}_e)]$ with H atoms omitted for clarity. Displacement ellipsoids are shown at the 30% probability level.

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