Synthesis, *X*-Ray Crystal Structure, and Reactivity of the Binuclear Copper(I) Complex [{Cu(3,5Me$_2$-pz)(CNR)}$_2$] (R = cyclohexyl, 3,5Me$_2$-pz = 3,5-dimethylpyrazolate) toward RNCO (R = cyclohexyl), PhNCS, COS, and CS$_2$. N,S Co-ordination of the 3,5-Dimethylpyrazolecarbodithioate Anion in [Cu{3,5Me$_2$-pz–C(S)–S}(CNR)$_2$]†

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The structure of the binuclear copper(I) complex [{Cu(3,5Me$_2$-pz)(CNR)}$_2$] (**1a**) (R = cyclohexyl, 3,5Me$_2$-pz = 3,5-dimethylpyrazolate) formed by reaction of cyclohexyl isocyanide with [{Cu(3,5Me$_2$-pz)}$_n$] has been solved by single-crystal *X*-ray analysis. The crystals are monoclinic, space group *C*2/*m* (no. 12), with a = 14.981(2), b = 12.553(2), c = 7.469(1) Å, β = 111.17(1)°, and Z = 2. Least-squares refinement gave final values for R and R' of 0.032 and 0.042. Each dimeric unit exhibits a Cu $\cdots$ Cu′ distance of 3.558(1) Å. The co-ordination around each Cu atom is planar trigonal, with the two 3,5-dimethylpyrazolate ligands bridging the metal centres and one cyclohexyl isocyanide ligand terminally bonded to each copper atom. Complex (**1a**) reacted with RNCO (R = cyclohexyl), PhNCS, and COS to form mononuclear derivatives of general formula [Cu{3,5Me$_2$-pz–C(Y)–Z}(CNR)] [Y = O, Z = NR, (**2**); Y = S, Z = NPh, (**3**); Y = O, Z = S, (**4**)]. Complexes (**2**)—(**4**) easily added a second isocyanide producing four-co-ordinated species. The reaction of CS$_2$ with (**1a**), in the presence of free RNC, gave [Cu{3,5Me$_2$-pz–C(S)–S}(CNR)$_2$] (**5**). A CuNS instead of CuS$_2$ co-ordination environment for this complex was deduced from its spectroscopic properties and confirmed by a preliminary *X*-ray crystal structure investigation.

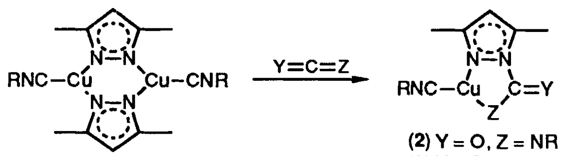
The polymeric copper(I) 3,5-dimethylpyrazolato complex [{Cu(3,5Me$_2$-pz)}$_n$] has been known since 1971,[1] but little attention has been devoted to its reactivity toward neutral ligands. We recently reported that its reaction with excess of 1,10-phenanthroline (phen) quantitatively yielded [{Cu(3,5Me$_2$-pz)(phen)}$_2$].[2] A dimeric structure was assigned to this species on the basis of its spectroscopic and chemical properties.[2] The reactions of RNC (R = cyclohexyl) with [{Cu(3,5Me$_2$-pz)}$_n$] and with the parent polymeric complex [{Cu(pz)}$_n$] (pz = pyrazolate) allowed the isolation of the dimeric copper(I) complexes [{Cu(3,5Me$_2$-pz)(CNR)}$_2$] (**1a**) and [{Cu(pz)(CNR)}$_2$] (**1b**), respectively.

The present paper reports the synthesis, structural characterization, and reactivity of (**1a**) towards heterocumulenes RNCO (R = cyclohexyl), PhNCS, COS, and CS$_2$.

Results and Discussion

Synthesis of [{Cu(3,5Me$_2$-pz)(CNR)}$_2$] (**1a**) *and* [{Cu(pz)(CNR)}$_2$] (**1b**) (R = *cyclohexyl*).—By reaction of cyclohexyl isocyanide with the polymeric copper(I) complexes [{Cu(3,5Me$_2$-pz)}$_n$][1] and [{Cu(pz)}$_n$],[3] the binuclear copper(I) derivatives [{Cu(3,5Me$_2$-pz)(CNR)}$_2$] (**1a**) and [{Cu(pz)(CNR)}$_2$] (**1b**) were formed. The i.r. spectra of (**1a**) and (**1b**) showed ν(NC) at 2 164 and 2 165 cm^{-1}, respectively, quite close to the analogous absorption observed for binuclear copper(I) benzoato complexes binding isocyanides.[4] The structure of (**1a**) has been solved by single-crystal *X*-ray analysis (see later).

Reactions of Complex (**1a**) *with Heterocumulenes* Y=C=Z [Y = O, Z = NR (R = *cyclohexyl*); Y = S, Z = NPh; Y = O, Z = S].—Complex (**1a**) was recovered unchanged when treated with carbon dioxide at atmospheric pressure. Facile reactions were observed when (**1a**) was treated with heterocumulenes such as cyclohexyl isocyanate, phenyl isothiocyanate, and carbonyl sulphide [equation (1)].



(1)

(**1a**) R = cyclohexyl

(**2**) Y = O, Z = NR
(**3**) Y = S, Z = NPh
(**4**) Y = O, Z = S

Analytical and spectroscopic data support the formulations assigned to complexes (**2**)—(**4**) (see Experimental section and Table 1). The complexes result from *formal* nucleophilic addition of 3,5-dimethylpyrazolate anion to the central carbon atom of the heterocumulenes to give a new bidentate ligand.

For complex (**2**) the most striking feature of its i.r. spectrum is the presence of a significant band at 1 670 cm^{-1}, assignable to ν(C=O) of the five-membered ring. This absorption lies at lower frequency with respect to free 1-cyclohexylcarbamoyl-3,5-dimethylpyrazole (1 705 cm^{-1}).[5] A related lowering of the ν(C=O) band has been observed for urea complexes of formula [M(PPh$_3$)$_2$(RNCONR)] (M = Pd or Pt; R = *p*-MeC$_6$H$_4$-

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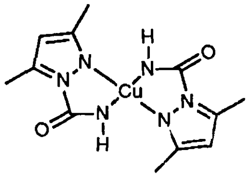
† Bis(μ-3,5-dimethylpyrazolato-1κ*N*^{1}:2κ*N*^{2})-bis[(cyclohexyl isocyanide)copper(I)].

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. I.r. and n.m.r. data

Compound	I.r. (Nujol, cm^{-1})	^{1}H N.m.r.[a]		^{13}C N.m.r.[a]				
		4-CH	3-, 5-CH$_3$	C^4	C^3,C^5	3-, 5-CH$_3$	NC	CO (or CS)
(1a)	2 164, ν(NC); 1 520[b]	5.85	2.35	102.8	148.5	13.98	141.3	
(1b)	2 165, ν(NC)	6.26	7.61[c]	107.4	139.4 146.1		*d*	
(2)	2 164, ν(NC); 1 670, ν(CO); 1 525[b]	5.86	2.21 2.58	107.8	143.4 145.9	13.60 13.93	141.8	156.6
(3)	2 158, ν(NC); 1 573,[b] 1 340, ν(CS)	6.04	2.31 2.64	109.8	146.9 151.3	14.32 16.20	143.4	162.9[e]
(4)[f]	2 185, ν(NC); 1 640, ν(CO)							
(5)	2 162, 2 140, ν(NC); 1 330, ν(CS); 1 577[b]	6.08	2.29 2.81	112.5	144.9 147.4	14.74 19.23	141.2	214.5[e]
(6)	2 155, 2 127, ν(NC); 1 670, ν(CO); 1 550[b]	5.86	2.19 2.53	107.5	143.7 146.1	13.51 13.84	141.5	156.5
(7)	2 172, 2 151, ν(NC); 1 640, ν(CO); 1 561[b]	5.93	2.24 2.51	107.1	151.5 157.3	12.44 14.51	140.8	166.4

[a] In CDCl$_3$ solutions, δ values. [b] Pyrazole-ring vibration. [c] 3-, 5-CH signals. [d] Not detected. [e] C=S signal. [f] Low solubility prevents solution n.m.r. measurements.



SO$_2$)[6] [ν(C=O) 1 675—1 690 cm^{-1}; 1 750 cm^{-1} for free urea RNHCONHR].[6] Moreover, ν(C=O) observed for complex (**2**) parallels that of related copper(II) derivatives (see above) having chelate ligands formed by nucleophilic addition of 3,5-dimethylpyrazole to NCO$^-$ (*ca.* 1 690 cm^{-1}).[7]

Complex (**4**) is stable enough in the solid state but it extrudes COS at 60 °C under vacuum (10^{-2} Torr, *ca.* 1.33 Pa), restoring the starting complex (**1a**). In suspension, complex (**4**) remains unchanged only if free COS is present.

When the reaction of complex (**1a**) with COS [equation (1)] was carried out at low temperature (−20 °C) complex (**4**; Y = O, Z = S) was obtained always mixed with another product. The i.r. spectrum of this mixture in the region 2 100—1 600 cm^{-1}, besides ν(C=O) of complex (**4**) at 1 640 cm^{-1}, shows a significant absorption at 2 040 cm^{-1} (see Figure 1). We attribute this band to a S-bonded σ-co-ordinated COS ligand of the intermediate species [Cu(3,5Me$_2$-pz)(COS)(CNR)], from which (**4**) is formed, on the basis of the following observations.

(*i*) In some cases carbonyl derivatives have been obtained by treating transition-metal complexes with COS, *via* sulphur abstraction.[8] Assignment of the band at 2 040 cm^{-1} to the stretching of a terminally bonded carbonyl ligand was ruled out, as the starting complex (**1a**) and complex (**4**) itself were shown to be unreactive with respect to CO.

(*ii*) Repeated elemental analyses, including sulphur, carried out on different mixtures containing various amounts of complex (**4**) (evaluation based on the ratio of the band at 2 040 cm^{-1} to that at 1 640 cm^{-1}) always gave results consistent with those of (**4**) itself.

(*iii*) By stirring the mixture under a COS atmosphere, complex (**4**) was quantitatively recovered.

(*iv*) Finally, the i.r. spectrum of free COS (n-hexane solution) exhibits an absorption at 2 047 cm^{-1}.

Attempts are presently being made in order to isolate this intermediate species in an analytically pure form. To our knowledge, no previous examples of σ-co-ordinated COS complexes have been reported.

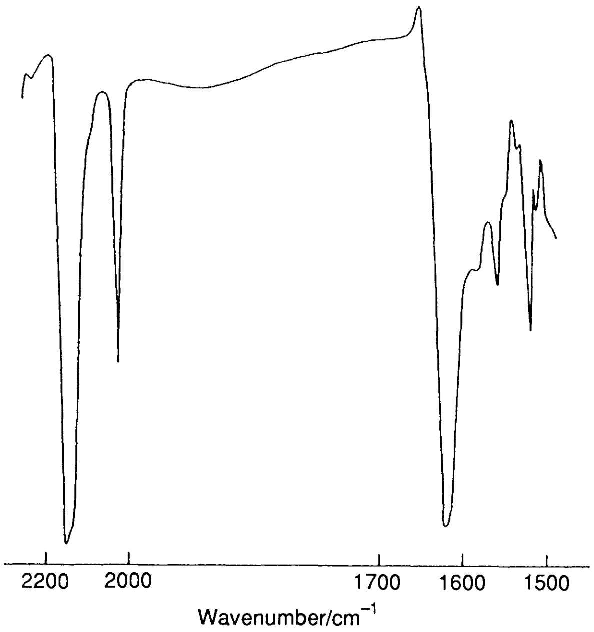


Figure 1. I.r. spectrum (2 200—1 500 cm^{-1}, Nujol mull) of the mixture obtained by treating complex (**1a**) with COS at −20 °C (see text)

Although there is no evidence as to whether formation of complexes (**2**)—(**4**) involves the binuclear complex (**1a**) itself or the mononuclear complex [Cu(3,5Me$_2$-pz)(CNR)], the results obtained above in the case of reaction of COS with (**1a**) seem to suggest that the reactions of (**1a**) with the CO$_2$-like molecules here reported may proceed *via* intermediate formation of a species having a unidentate 3,5-dimethylpyrazolato ligand and a σ-bonded heterocumulene. The subsequent nucleophilic addition of 3,5-dimethylpyrazolate anion to the carbon of the σ-bonded heterocumulene leads to the formation of the final products (**2**)—(**4**).

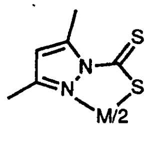
The binuclear copper(I) complex (**1a**) readily reacts with CS$_2$; the presence of free RNC (R = cyclohexyl) was shown to be essential in order to obtain an analytically pure product, [Cu{3,5Me$_2$-pz–C(S)–S}(CNR)$_2$](**5**). The 3,5-dimethylpyrazole-carbodithioate complex (**5**) exhibits ν(NC) at 2 162 and 2 140 cm^{-1}, together with an absorption at 1 330 cm^{-1} which is assigned to ν(C=S), thus suggesting a NS co-ordination of the

Table 2. Selected bonding distances (Å) and angles (°) for complex (**1a**)

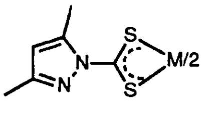
Cu–N(1)	1.960(2)	N(2)–C(4)	1.159(5)
N(1)–N(1′)	1.396(3)	N(2)–C(5)	1.446(4)
N(1)–C(1)	1.342(4)	C(5)–C(6)	1.472(4)
C(1)–C(2)	1.367(4)	C(6)–C(7)	1.530(4)
C(1)–C(3)	1.503(4)	C(7)–C(8)	1.480(5)
Cu–C(4)	1.853(4)		
N(1)–Cu–N(1″)	113.0(1)	C(1)–C(2)–C(1′)	106.5(5)
N(1)–Cu–C(4)	123.46(6)	Cu–C(4)–N(2)	177.2(4)
Cu–N(1)–N(1′)	123.43(6)	C(4)–N(2)–C(5)	179.7(5)
Cu–N(1)–C(1)	129.3(2)	N(2)–C(5)–C(6)	109.6(2)
N(1′)–N(1)–C(1)	107.2(1)	C(5)–C(6)–C(7)	111.1(3)
N(1)–C(1)–C(2)	109.5(3)	C(6)–C(7)–C(8)	112.5(4)
N(1)–C(1)–C(3)	121.9(3)	C(7)–C(8)–C(7″)	110.9(5)
C(2)–C(1)–C(3)	128.5(3)	C(6)–C(5)–C(6″)	113.3(5)

The symbols ′ and ″ indicate the symmetry transformations of $\bar{x},y,\bar{z}$ and $x,\bar{y},z$, respectively.

dithiocarboxylate anion. In 1968 Trofimenko[9] reported the preparation of a series of metal(II) pyrazolecarbodithioates (M = Mn, Fe, Co, Ni, Cu, or Zn), suggesting that the co-ordination properties of the ambidentate pyrazolecarbodithioate anion produced MN_2S_2, (**A**), instead of MS_4, (**B**), co-



(A)



(B)

ordination environments. The N_2S_2 co-ordination, in the case of bis(3,5-dimethylpyrazolecarbodithioato)copper(II), was substantiated by Bereman *et al.*[10] in 1978 on the basis of i.r., visible, and e.s.r. spectra.

A preliminary *X*-ray analysis confirmed the presence in complex (**5**) of a five-membered ring.*

Complexes (**2**) and (**4**) easily added a second isocyanide unit thereby producing a tetrahedral stereochemistry about the copper(I) centre [complexes (**6**) and (**7**)].

The three- and four-co-ordinated complexes (**2**) and [Cu{3,5Me$_2$-pz–C(O)–NR}(CNR)$_2$] (**6**) were confirmed to be stable to water alone, under an inert atmosphere. When excess of RNC (R = cyclohexyl) was added to solutions containing (**2**) or (**6**) and water a reaction was observed, free 3,5Me$_2$-pz–CONHR being the only characterizable product. We were unable to isolate and identify the copper(I)-containing species formed in this decomposition reaction.

Studies are in progress in order to clarify the factors that favour the σ-co-ordination of the heterocumulene molecules in transition-metal pyrazolato complexes (*i.e.* the mode of co-ordination of the pyrazolato group, the nature of the substituents on the pyrazolato ring, and the neutral ligand bonded to the metal). Further studies involving the reactivity of the polymeric copper(I) complexes [{Cu(3,5Me$_2$-pz)}$_n$] and [{Cu(pz)}$_n$] will deal with the oxidation reactions of these systems.

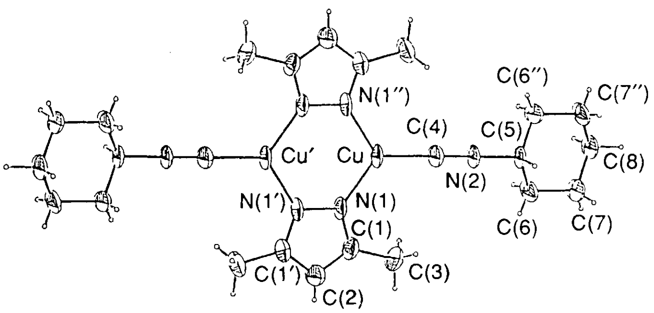


Figure 2. ORTEP view of the dimeric molecule (**1a**) located on a 2/*m* crystallographic position

Description of the Structure of [{Cu(3,5Me$_2$-pz)(CNR)}$_2$] (**1a**).—The crystal structure of complex (**1a**) consists of discrete dimeric units with normal van der Waals contacts. The molecules are located on crystallographic 2/*m* positions (*a* in Wyckoff notation), with the 3,5-dimethylpyrazolate and the cyclohexyl isocyanide ligands lying on a two-fold axis and on a mirror plane, respectively. Figure 2 shows an ORTEP view of compound (**1a**); relevant bond parameters are collected in Table 2.

The dimeric molecule contains two copper(I) centres linked by 3,5-dimethylpyrazolate bridging ligands; each metal centre also bears a cyclohexyl isocyanide ligand terminally bonded. The distance between the two copper atoms [3.558(1) Å] is significantly longer than that found in the previously reported [{Cu(Hpz)$_2$Cl}$_2$] (Hpz = pyrazole) [3.401(1) Å],[11] and consistent with the presence of a bulkier bridging ligand (3,5Me$_2$-pz *vs.* Cl). The co-ordination around the copper atoms is planar trigonal with Cu 0.026(1) Å from the plane defined by N(1), N(1″), and C(4) (see Table 2 for symmetry operations). The N(1)–Cu–C(4) angle [and the equivalent N(1″)–Cu–C(4)] is greater than N(1)–Cu–N(1″) [123.46(6) and 113.0(1)°, respectively], probably because of the steric and electronic requirements of the six-membered planar ring defined by the two copper and four 3,5-dimethylpyrazolate nitrogen atoms [the absolute values of the deviations from the least-squares plane through the atoms are 0.014(1) and 0.018(3) Å for the copper and the nitrogen atoms, respectively]; as a result, the four Cu–N(pyrazole) (symmetry-related) distances [1.960(2) Å] appear slightly elongated with respect to those found in [{Cu(Hpz)$_2$Cl}$_2$][1.935(2) and 1.943(2) Å].

The distances from Cu to atoms in neighbouring molecules exclude long-range interactions.

As normally observed, the N–N distance is longer in complexes containing the pyrazolate ion (normal range 1.33—1.39 Å) than in compounds binding neutral pyrazoles.[12] The value found in complex (**1a**) [1.396(3) Å] lies slightly outside this range. A possible explanation for this trend was suggested by Chong *et al.*[12] for a nearly planar 3,5-dimethylpyrazolate-bridged nickel dimer which shows an exceptionally long [1.463(4) Å] N–N bond; because of the near planarity of this dimeric molecule d_π(metal)–p_π(pyrazolate) interactions are allowed, with back donation from the metal into antibonding π* orbitals of the pyrazolate moiety.

The cyclohexyl isocyanide ligands are terminally bonded to the copper atoms with a nearly perfect linear arrangement of the Cu–C(4)–N(2)–C(5) fragment [Cu–C(4)–N(2) 177.2(4) and C(4)–N(2)–C(5) 179.7(5)°].

The Cu–C(4) and C(4)–N(2) distances [1.853(4) and 1.159(5) Å, respectively] fall within the range of values reported for copper(I) isocyanide compounds so far structurally characterized.[4] Among them, bis(cyclohexyl isocyanide)(*NNN′N′*-tetramethylethylenediamine)copper(I) tetraphenylborate is the only cyclohexyl isocyanide derivative in which the Cu–C bond

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* Crystal data for $C_{20}H_{29}CuN_4S_2$: tetragonal, space group $P4_1$ (no. 76), a = 9.794(2), c = 23.697(5) Å, U = 2 273(1) Å^3, M = 453.15, Z = 4, D_c = 1.324 g cm^{-3}, $F(000)$ = 952, λ(Mo-K_α) 0.710 73 Å, R = 0.054 for 1 132 observed reflections having $I > 3\sigma(I)$.

Table 3. Crystal data and intensity-collection parameters for complex (**1a**)

Formula	$C_{24}H_{36}Cu_2N_6$
M	535.67
Crystal system	Monoclinic
a/Å	14.981(2)
b/Å	12.553(2)
c/Å	7.469(1)
β/°	111.17(1)
U/Å^3	1 309.8
Z, D_c/g cm^{-3}	2, 1.358
Space group	$C2/m$ (no. 12)
F(000)	560
μ(Mo-K_α)/cm^{-1}	16.49
2θ range/°	$6 \leqslant 2\theta \leqslant 50$
Scan method	ω
Scan interval/°	1.00 + 0.35 tanθ
Scan speed/° min^{-1}	2.0
Collected octants	$\pm h,k,l$
No. of data collected (at room temperature)	1 207
No. of data used [$I > 3\sigma(I)$]	924
Maximum, minimum transmission factors	1.00, 0.95
Crystal size/mm	0.11 × 0.10 × 0.05
Weighting factor p	0.045
R	0.0321
R'	0.0421
E.s.d.	1.430
No. variable parameters	109
Maximum peak in final Fourier difference map/e Å^{-3}	0.336

E.s.d. = $[\Sigma w(F_o - k|F_c|)^2/(N_o - N_v)]^{\frac{1}{2}}$ where N_o, N_v = number of observations and variables; $w = 4F_o{}^2/\sigma^2(F_o{}^2)$ where $\sigma(F_o{}^2) = [\sigma^2(I) + (pI)^2]^{\frac{1}{2}}/L_p$; $R = \Sigma(F_o - k|F_c|)/\Sigma F_o$; $R' = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o{}^2]^{\frac{1}{2}}$.

distances [1.897 Å (mean)] are longer than those in (**1a**),[13] probably because of the more crowded pseudo-tetrahedral co-ordination around the copper atom. The cyclohexyl rings exhibit a chair conformation with normal bond distances and angles.

Experimental

Pyrazole, 3,5-dimethylpyrazole, cyclohexyl isocyanide, cyclohexyl isocyanate (RNCO), phenyl isothiocyanate, carbonyl sulphide, and carbon disulphide were used as supplied (Aldrich Chemical Co.). Solvents were distilled and dried before use. Reactions were carried out under an atmosphere of dry dinitrogen gas.

I.r. spectra were recorded on a Perkin-Elmer 783 instrument, n.m.r. spectra in $CDCl_3$ solutions with a Bruker WP80 spectrometer operating at 80.13 (^1H) and 20.15 MHz (^{13}C). Elemental analyses were carried out at the microanalytical laboratory of this University.

I.r. and n.m.r. (^1H, ^{13}C) data are reported in Table 1.

Syntheses.—[{Cu(3,5Me$_2$-pz)(CNR)}$_2$] (**1a**). To an acetone solution (10 cm^3) of RNC (0.6 cm^3) was added [{Cu(3,5Me$_2$-pz)}$_n$] (3.15 mmol) and the white suspension stirred for 4 h at room temperature. Complex (**1a**) was collected by filtration, washed with acetone and n-hexane, and dried under vacuum; yield ≈94%. Crystals suitable for *X*-ray analysis were obtained by slow diffusion of n-hexane into a dichloromethane solution of the complex, m.p. 232 °C (decomp.) (Found: C, 53.95; H, 6.85; N, 15.45. $C_{24}H_{36}Cu_2N_6$ requires C, 53.85; H, 6.75; N, 15.70%).

The complex [{Cu(pz)(CNR)}$_2$] (**1b**) was prepared by using similar experimental conditions to those for (**1a**); m.p. 183 °C (decomp.) (Found: C, 50.20; H, 5.90; N, 17.45. $C_{20}H_{28}Cu_2N_6$ requires C, 50.10; H, 5.85; N, 17.55%).

[Cu{3,5Me$_2$-pz–C(O)–NR}(CNR)] (**2**). To a n-pentane solution (5 cm^3) of RNCO (0.44 mmol) was added complex (**1a**) (0.18 mmol) with stirring. After 2 h the white product was filtered off, washed with n-pentane, and dried under reduced pressure, m.p. 196 °C (decomp.) (Found: C, 58.20; H, 7.45; N, 14.10. $C_{19}H_{29}CuN_4O$ requires C, 58.10; H, 7.40; N, 14.25%).

[Cu{3,5Me$_2$-pz–C(S)–NPh}(CNR)] (**3**). To a n-pentane solution (10 cm^3) of PhNCS (0.84 mmol) was added complex (**1a**) (0.64 mmol) with stirring. The white suspension turned slowly to yellow. After 18 h the pale yellow solid was filtered off, washed with n-pentane, and dried *in vacuo*, m.p. 165 °C (decomp.) (Found: C, 56.45; H, 5.75; N, 13.80. $C_{19}H_{23}CuN_4S$ requires C, 56.65; H, 5.70; N, 13.90%).

[Cu{3,5Me$_2$-pz–C(O)–S}(CNR)] (**4**). Gaseous COS was bubbled for 5 min through n-hexane (10 cm^3) maintained at −70 °C, and complex (**1a**) (0.85 mmol) was added. The temperature was gradually raised to 0 °C and the suspension stirred for 5 h. The brown product (**4**) was recovered by filtration, washed with n-hexane, and dried *in vacuo*, m.p. 145 °C (decomp.) (Found: C, 47.30; H, 5.70; N, 12.45. $C_{13}H_{18}CuN_3OS$ requires C, 47.65; H, 5.50; N, 12.80%).

In a typical experiment, the suspension obtained was filtered at −20 °C. The i.r. spectrum of the pale brown solid showed absorptions associated with the presence of complex (**4**) together with a significant band which can be attributed to the formation of a σ-co-ordinated COS complex (see text). When this mixture was stirred under a COS atmosphere and at room temperature, complex (**4**) was obtained as the only product.

[Cu{3,5Me$_2$-pz–C(S)–S}(CNR)$_2$] (**5**). To an acetone solution (10 cm^3) containing CS_2 (0.5 cm^3) and RNC (0.3 cm^3) was added complex (**1a**) (0.70 mmol). The orange solution was stirred for 5 h and concentrated to *ca.* 1 cm^3, after which n-hexane (15 cm^3) was added. Complex (**5**) was recovered as an orange product by filtration, washed with n-hexane, and dried under vacuum, m.p. 128 °C (decomp.) (Found: C, 52.95; H, 6.50; N, 12.30. $C_{20}H_{29}CuN_4S_2$ requires C, 53.05; H, 6.40; N, 12.40%).

[Cu{3,5Me$_2$-pz–C(O)–NR}(CNR)$_2$] (**6**). To a n-pentane solution (10 cm^3) of RNC (0.85 mmol) was added complex (**2**) (0.76 mmol). The suspension was stirred for 0.5 h, then the white product was collected by filtration, washed with n-pentane, and dried under vacuum.

Complex (**6**) can be directly obtained by treating (**1a**) with a solution of RNCO and RNC in n-pentane [ratio (**1a**):RNCO:RNC = 1:2:2], m.p. 82 °C (Found: C, 62.60; H, 7.90; N, 13.70. $C_{26}H_{40}CuN_5O$ requires C, 62.20; H, 8.00; N, 13.95%).

[Cu{3,5Me$_2$-pz–C(O)–S}(CNR)$_2$] (**7**). This product can be obtained by treating complex (**4**) with RNC in n-hexane. Alternatively, it was prepared directly by adding (**1a**) to a n-hexane solution of RNC, previously saturated with COS; m.p. 96 °C (decomp.) (Found: C, 54.75; H, 6.60; N, 12.50. $C_{20}H_{29}CuN_4OS$ requires C, 55.00; H, 6.65; N, 12.85%).

Reaction of Complex (**2**) *or* (**6**) *with* RNC *in Wet Media.*—To wet CH_2Cl_2 solutions of complex (**2**) or (**6**) was added RNC and the i.r. spectrum of the solution registered. In a few minutes the ν(C=O) absorption present in the i.r. spectrum of (**2**) or (**6**) (1 670 cm^{-1}) disappeared. This behaviour was not observed in the absence of excess of RNC. The CH_2Cl_2 solution was evaporated to dryness, treated with n-hexane in order to remove RNC, and then with diethyl ether. The presence of 3,5Me$_2$-pz–CONHR in the ether solution was confirmed by spectroscopy.

X-*Ray Crystal Structure Determination of Complex* (**1a**).—Crystallographic data and experimental conditions are reported in Table 3. The diffraction data were collected at room temperature on an Enraf-Nonius CAD4 computer-controlled

Table 4. Fractional atomic co-ordinates for complex (**1a**)

Atom	x	y	z
Cu	0.062 75(4)	0.000	0.252 68(6)
N(1)	0.026 1(2)	−0.130 2(2)	0.098 6(3)
N(2)	0.153 9(3)	0.000	0.684 1(5)
C(1)	0.040 8(2)	−0.232 4(3)	0.154 8(4)
C(2)	0.000	−0.297 6(4)	0.000
C(3)	0.096 8(3)	−0.262 8(3)	0.359 5(5)
C(4)	0.121 1(4)	0.000	0.517 8(6)
C(5)	0.194 3(3)	0.000	0.891 5(5)
C(6)	0.250 3(3)	−0.098 0(3)	0.959 5(4)
C(7)	0.300 1(3)	−0.097 1(3)	1.178 0(5)
C(8)	0.358 2(4)	0.000	1.248 5(6)
H(2)	0.000	−0.360(3)	0.000
H(51)	0.133(4)	0.000	0.935(9)
H(61)	0.223(3)	−0.149(4)	0.915(5)
H(62)	0.293(3)	−0.098(4)	0.908(6)
H(71)	0.331(2)	−0.151(3)	1.216(5)
H(72)	0.258(3)	−0.111(3)	1.239(6)
H(81)	0.388(4)	0.000	1.396(8)
H(82)	0.417(4)	0.000	1.201(9)

diffractometer, using graphite-monochromatized Mo-K_α radiation (λ = 0.710 73 Å).

A least-squares fit of the setting angles of 25 randomly oriented reflections with θ ranging from 10 to 12° provided the unit-cell parameters. Intensities were collected using a variable scan range with a 25% extension at each end for background determination. Three standard reflections were measured at regular intervals during the data collection and no decay was observed. Correction for Lorentz and polarization effects was applied. An empirical absorption correction was performed based on ψ scans[14] (ψ 0—360°, every 10°) of suitable reflections with χ values close to 90°. Anomalous dispersion corrections for atomic scattering factors were taken from ref. 15.

The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares using the Enraf-Nonius structure determination package (SDP)[16] on a PDP 11/23 computer. Anisotropic thermal factors were assigned to all non-hydrogen atoms, while the hydrogens, except those belonging to the methyl groups, were refined with isotropic thermal parameters. The methyl groups were found to be disordered; the disorder was interpreted in terms of two models, having equal populations, with the hydrogen atoms rotated about the C(1)–C(3) bond by *ca.* 60°, in the staggered position. These atoms were located in their ideal positions (C–H 0.95 Å, B 10.0 Å^2) and not refined.

The final values of the agreement indices are reported in Table 3, the final positional parameters in Table 4. The final Fourier-difference map was flat, showing only small residual peaks not exceeding 0.35 e Å^{-3}.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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