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Crystal structure and chemical properties of $[Cu(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S)(CNR)_2]$ (R = cyclohexyl; $3,5Me_2$-pz = 3,5-dimethylpyrazolate)

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Abstract

The binuclear copper(I) complex $[Cu(3,5Me_2\text{-}pz)(CNR)]_2$ (R = cyclohexyl; $3,5Me_2$-pz = 3,5-dimethylpyrazolate) (**A**) reacts with CS_2 in the presence of free RNC, yielding the 3,5-dimethylpyrazolecarbodithioate derivative $[Cu(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S)(CNR)_2]$ (**I**). In the absence of free RNC, **A** gives $[Cu_2(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S)_2(CNR)]$ (**II**). The action of an excess of RNC on **II** afforded **I**. One RNC ligand in complex **I** is easily replaced by PPh_3 producing $[Cu(3,5Me_2\text{-}pzC(S)\text{-}S)(CNR)(PPh_3)]$ (**III**). The crystal and molecular structure of **I** has been elucidated by single crystal X-ray analysis. Its unit cell has dimensions $a = b = 9.806(1)$, $c = 23.734(6)$ Å, space group $P4_1$. The structure was solved with conventional Patterson and difference Fourier methods, and refined to $R = 0.040$ for 1134 reflections having $I > 3\sigma(I)$. By treating **I** with ethyl bromide, the pyrazole carbodithioate anion is displaced and recovered as the corresponding ethyl ester, $3,5Me_2\text{-}pzCS_2Et$.

Introduction

The polymeric copper(I) 3,5-dimethylpyrazolato complex $[Cu(3,5Me_2\text{-}pz)]_n$ has been known since 1971 [1], but little attention has been devoted to its reactivity towards neutral ligands. We recently reported its reaction with molecular oxygen; $[Cu_8(3,5Me_2\text{-}pz)_8(OH)_8]$ was obtained and its X-ray structure determined [2]. The latter represents the first example of a copper complex containing a planar cycle of eight metal atoms. Moreover, the action of RNC (R = cyclohexyl) on $[Cu(3,5Me_2\text{-}pz)]_n$ allowed the isolation of the dimeric copper(I) complex, $[Cu(3,5Me_2\text{-}pz)(CNR)]_2$ (**A**), which has also been structurally characterized [3]. We also reported the reactivity of **A** towards some heterocumulenes [3]. In particular, the reaction of **A** with CS_2 in the presence of free RNC yielded $[Cu(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S)(CNR)_2]$ (**I**) whose preliminary crystal data have been published [3].

The present paper reports the full structural characterization of **I**, which substantiated the N,S coordination of the pyrazolecarbodithioate anion to the metal center, together with its chemical behaviour.

Results and discussion

$Cu(3,5Me_2\text{-}pz)(CNR)]_2$ (**A**) (R = cyclohexyl) reacts with carbon disulfide in the presence of free RNC giving the copper(I) complex (**I**), eqn. (1).

$$A + CS_2 \xrightarrow{\text{RNC}} \underset{\textbf{I}}{[Cu(3,5Me_2\text{-}pz\text{-}C((S)\text{-}S)(CNR)_2]} \qquad (1)$$

Complex I exhibits ν(NC) at 2162 and 2140 cm^{-1}, together with an absorption at 1330 cm^{-1}, which we assign to $\nu(C{=}S)$.

In 1968 Trofimenko [4] reported the synthesis of some metal(II) pyrazolecarbodithioates, suggesting that the coordination properties of the ambidentate pyrazolecarbodithioate anion produced MN_2S_2 (**A**), instead of MS_4 (**B**), coordination environments.

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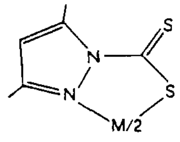
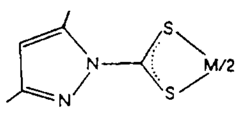


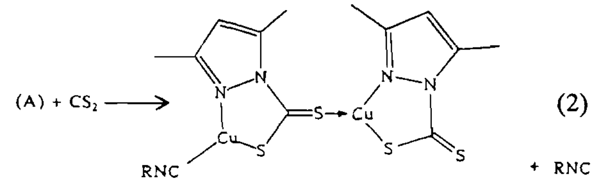
A



B

The MN_2S_2 coordination, in the case of bis(3,5-dimethylpyrazolecarbodithioato)copper(II), was substantiated by Bereman *et al.* [5] in 1978 on the basis of IR, visible and ESR spectra.

The presence of free RNC was shown to be essential in order to obtain **I** as an analytically pure product. When reaction (1) was carried out in the absence of an excess of RNC, the displacement of one mole of RNC per mole of **A** was observed and complex **II** was isolated, eqn. (2).



(2)

The formulation assigned to complex **II** is based on its chemical analysis, including sulfur determination and IR data. Its IR spectrum exhibits the ν(NC) absorption at 2173 cm^{-1}; moreover, two significant bands are present at 1313 and 1240 cm^{-1}. We tentatively attribute the 1240 cm^{-1} absorption to the ν(C=S) of the C=S group S-bonded to the copper(I) center. Molecular weight measurements and NMR spectra were prevented by the low solubility of **II** in the common organic solvents. A polymeric formulation, in which **II** is present as the repeating unit, however, cannot be ruled out [4].

Complex **II** readily reacted with RNC or PPh_3 in the presence of RNC, complex **I** or $[\overline{\mathrm{Cu(3,5Me_2\text{-}pz\text{-}C(S)S}}\mathrm{(CNR)(PPh_3)}]$ (**III**) being formed respectively (see 'Experimental').

Complex **III** can be alternatively obtained by reacting **I** with PPh_3 in acetone. It is worth noting that even in the presence of an excess of triphenylphosphine, only one RNC ligand can be displaced. The IR spectra of **III** and **I** showed high similarities in the region in which bands assignable to the five-membered ring are found; this seems to indicate that the ancillary ligands on the metal center do not significatively affect the nature of the ring.

Description of the structure of *$[Cu(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S)(CNR)_2]$ (R = cyclohexyl)*

The crystal structure of compound **I** consists of discrete $[\overline{\mathrm{Cu(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S}}\mathrm{)(CNR)_2}]$ molecules, held together by normal van der Waals interactions. The refined fractional coordinates of the non-hydrogen atoms are reported in Table 1, while the relevant bond distances and angles are collected in Table 2. An ORTEP view of compound **I** is shown in Fig. 1.

TABLE 1. Positional parameters with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Cu	0.2475(1)	0.1114(1)	0.000
S1	0.4175(2)	−0.0508(3)	0.0138(1)
S2	0.6109(3)	−0.0707(3)	0.1076(2)
N1	0.2896(6)	0.1571(6)	0.0824(3)
N2	0.3915(6)	0.0865(6)	0.1097(3)
C	0.4707(8)	−0.0091(9)	0.0788(4)
C1	0.2294(8)	0.2336(8)	0.1209(4)
C2	0.3926(7)	0.1215(8)	0.1662(3)
C3	0.2912(9)	0.2104(9)	0.1731(3)
C4	0.106(1)	0.321(1)	0.1053(4)
C5	0.480(1)	0.065(1)	0.2122(4)
N3	−0.0508(7)	0.0278(9)	−0.0198(3)
C30	0.0610(9)	0.0534(9)	−0.0112(4)
C31	−0.192(1)	−0.005(1)	−0.0315(4)
C32	−0.206(1)	−0.149(1)	−0.0451(5)
C33	−0.174(2)	−0.183(1)	−0.0987(7)
C34	−0.241(1)	−0.101(1)	−0.1449(5)
C35	−0.208(2)	0.047(1)	−0.1301(6)
C36	−0.245(1)	0.092(1)	−0.0787(6)
N4	0.3361(8)	0.2944(8)	−0.0980(3)
C40	0.3061(9)	0.233(1)	−0.0586(4)
C41	0.372(1)	0.371(1)	−0.1484(4)
C42	0.494(1)	0.458(1)	−0.1397(5)
C43	0.536(1)	0.527(1)	−0.1907(5)
C44	0.554(1)	0.443(1)	−0.2375(5)
C45	0.441(1)	0.349(1)	−0.2486(5)
C46	0.392(1)	0.272(1)	−0.1955(5)

TABLE 2. Relevant bond distances (Å) and angles (°) with e.s.d.s. in parentheses

Cu–S1	2.327(2)	Cu–N1	2.048(6)
Cu–C30	1.934(11)	Cu–C40	1.917(11)
S1–C	1.678(7)	S2–C	1.650(8)
C–N2	1.422(9)	N1–N2	1.378(8)
N1–C1	1.321(9)	C1–C3	1.398(11)
C2–C3	1.333(11)	N2–C2	1.383(9)
C30–N3	1.143(9)	C40–N4	1.153(10)
S1–Cu–N1	82.6(2)	S1–Cu–C30	119.7(3)
S1–Cu–C40	108.1(3)	N1–Cu–C30	112.7(3)
N1–Cu–C40	119.7(3)	C30–Cu–C40	111.4(3)
Cu–S1–C	100.7(3)	S1–C–S2	123.4(5)
S1–C–N2	117.8(5)	S2–C–N2	118.8(5)
C–N1–N2	118.9(6)	Cu–N1–N2	119.1(5)
Cu–C30–N3	175.1(8)	C30–N3–C31	179.2(9)
Cu–C40–N4	172.3(8)	C40–N4–C41	178.6(9)

Each $[\overline{\mathrm{Cu(3,5Me_2\text{-}pz\text{-}C(S)S}}\mathrm{)(CNR)_2}]$ molecule consists of a monomeric Cu(I) complex showing a pseudotetrahedral arrangement of the ligands, i.e. two RNC units and a chelating $3,5Me_2\text{-}pz\text{-}CS_2$ moiety. The presence of a bidentate $3,5Me_2\text{-}pz\text{-}CS_2$ ligand

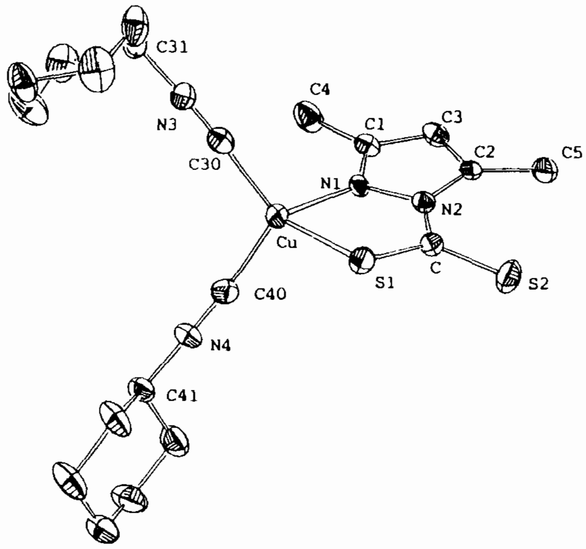


Fig. 1. ORTEP drawing of the $[\overline{\mathrm{Cu(3,5Me_2pz\text{-}C(S)\text{-}S}})\mathrm{(CNR)_2}]$ molecule, with partial labelling scheme; thermal ellipsoids have been drawn at 30% probability. For sake of clarity, hydrogen atoms have been omitted.

creates a five-membered cycle ($\overline{\mathrm{Cu-N-N-C-S}}$), which represents the first structurally characterized example of an N,S coordination of a CS_2 derivative, if compared to the most common $\mathrm{R-C}\Big\langle{}^{\mathrm{S}}_{\mathrm{S}}$ chelating mode of dithiocarbamates and xanthates.

A similar topological sequence of Cu, N, C and S atoms has been previously found in dithiocarbazones and dithiosemicarbazones, although their formal distribution of single and double bonds is far from what assumed in the present case; in particular, the C–N bond of compound **I** is a formal, although partially conjugated, single bond. Nevertheless, the bite angle of the 3,5Me$_2$-pz-CS$_2$ ligand (82.6(2)°) is only slightly lower that those observed in other N,S chelates (83.2–85.3°) [6a–d]. All the other L–Cu–L′ angles (108.1(3)–119.7(3)°), therefore, reflect the slight distortion from ideal tetrahedral symmetry determined by the presence of the chelating ligand. The Cu-S1 distance (2.327(2) Å), however, is among the highest values observed so far in $\overline{\mathrm{Cu-N-N-C-S}}$ five-membered rings, (longer distances have been found only in (sulfato-*O*)-bis(thiosemicarbazide-*N,S*)copper(II), showing two independent C,S interactions of 2.367 and 2.347 Å, [7]), and is counterparted by the very short S1–C distance (1.678(7) Å), only slightly longer than the 'exocyclic' sulfur-to-carbon interaction of 1.650(7) Å. Within the assumption that bond distances and bond orders are inversely correlated, evidence for a highly delocalized π system within the CS_2 fragment is therefore given.

Furthermore, the π conjugation with the pyrazole ring might also be of some importance, owing to the fact that the best planes through the 3,5-dimethylpyrazole and NCS_2 fragments are at an angle of only 12.9° (strict planarity of the pyrazole ring was observed, the maximum displacement measured being 0.009(9) Å for C3 atom) and that the carbon atom of the original CS_2 molecule lies in plane (within 1σ) with the N2,S1 and S2 atoms. On the other hand, the pattern of bond distances and angles of the pyrazole unit is slightly distorted, with aromatic unique C–C bond distances of 1.40(1) and 1.33(1) Å. If this is not due to misplacement of the lighter carbon atoms by poor convergence of the least-squares refinement in the non-centric (polar) space group, an intramolecular S...H repulsion between the exocyclic sulfur atom and the adjacent, possibly rotating, methyl group, might be invoked, the estimated H...S2 interaction being of the order of 2.7 Å.

Both RNC ligands, whose bonding parameters closely match those found in the parent [Cu(3,5Me$_2$-pz)(RNC)]$_2$ compound, are, in the solid state, in a chair conformation, and show strict (within 2 e.s.d.s) linearity of the CN–R systems.

Experimental

3,5-Dimethylpyrazole, cyclohexylisocyanide and carbon disulfide were used as supplied. Solvents were dried and distilled by standard methods. All the reactions were carried out under an atmosphere of dry nitrogen gas.

IR spectra were recorded on a Perkin-Elmer 783 instrument; NMR spectra in $CDCl_3$ solutions with a Bruker WP80 spectrometer. Elemental analyses were carried out at the microanalytical laboratory of this University (C, H, N) and at Mikroanalytisches Labor Pascher, Remagen (F.R.G.) (S). [Cu(3,5Me$_2$-pz)(CNR)]$_2$ was prepared as already described [3].

$[\overline{\mathrm{Cu(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S}})\mathrm{(CNR)_2}]$ (I)

To a solution of CS_2 (0.5 ml) and cyclohexylisocyanide (90 mg, 0.83 mmol) in acetone (10 ml), [Cu(3,5Me$_2$-pz)(CNR)]$_2$ (300 mg, 0.56 mmol) was added under stirring. The starting material dissolved and after 4 h the orange solution was evaporated to *c*. 1 ml and n-pentane (10 ml) was added. Complex **I** separated as an orange product which was filtered off, washed with n-pentane and dried under vacuum. Complex **I** can be alternatively obtained by treating suspensions of **II** with a slight excess of cyclohexylisocyanide. Crystals suitable for X-ray analysis were obtained by slow diffusion of n-pentane into an acetone solution of the complex containing traces of cyclohexylisocyanide.

Anal. Found: C, 52.95; H, 6.50; N, 12.16; S, 13.78. Calc. for $C_{20}H_{29}CuN_4S_2$: C, 53.04; H, 6.41; N, 12.38; S, 14.14%. IR (cm^{-1}, nujol): 2162, 2141, ν(NC); 1330, (C=S). ^{1}H NMR (δ, $CDCl_3$): 6.08, 4-CH; 2.29, 2.81, 3-,5-CH_3. ^{13}C NMR (δ, $CDCl_3$): 112.5, C4; 144.9, 147.4, C3,C5; 141.2, NC; 214.5, C=S. m.p. 128 °C (dec.).

$[Cu_2(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S)_2(CNR)]$ *(II)*

To a solution of CS_2 (0.5 ml) in acetone (10 ml), $[Cu(3,5Me_2\text{-}pz)(CNR)]_2$ (300 mg, 0.56 mmol) was added under stirring. The white suspension slowly turned brown. After 8 h the brown solid was filtered off, washed with CH_2Cl_2 and n-pentane and dried under vacuum.

Anal. Found: C, 39.43; H, 4.23; N, 11.96; S, 21.88. Calc. for $C_{19}H_{25}Cu_2N_5S_2$: C, 39.45; H, 4.33; N, 12.11; S, 22.15%. IR (cm^{-1}, nujol): 2173, ν(NC); 1313, 1240 (C=S). m.p. 163 °C (dec.).

$[\overline{Cu(3,5Me_2\text{-}pz\text{-}C(S)\text{-}S})(CNR)(PPh_3)]$ *(III)*

(a) To a suspension of complex **II** (250 mg, 0.43 mmol) in acetone (5 ml), RNC (R = cyclohexyl) (70 mg, 0.65 mmol) and PPh_3 (170 mg, 0.65 mmol) were added under stirring. A yellow solution formed. After 2 h, the solution was concentrated to *c.* 1 ml and Et_2O (10 ml) was added. Complex **III** crystallized as a yellow solid which was filtered, washed with diethyl ether and dried under vacuum.

(b) To a solution of PPh_3 (472 mg, 1.8 mmol) in acetone (10 ml) complex **I** (271 mg, 0.60 mmol) was added. After 30 min the yellow solution was treated as described in (a).

Anal. Found: C, 61.02; H, 5.77; N, 7.12; S, 10.38. Calc. for $C_{31}H_{33}CuN_3PS_2$: C, 61.44; H, 5.45; N, 6.94; S, 10.57%. IR (cm^{-1}, nujol): 2148 ν(NC); 1332 ν(C=S). ^{1}H NMR (δ, $CDCl_3$): 5.94, 4-CH; 1.88, 2.83, 3-,5-CH_3. ^{13}C NMR (δ, $CDCl_3$): 108.3, C4; 142.3, 148.5, C3, C5; 141.9, NC; 214.7, C=S. m.p. 146 °C (dec.).

Reaction of I with EtBr

To a solution of ethyl bromide (1 ml) in tetrahydrofuran (10 ml), complex **I** (500 mg) was added. The solution was stirred overnight at r.t., then evaporated to dryness and the residue extracted with n-pentane. The extract was evaporated giving a pale yellow oil. IR and mass spectrum confirmed the nature of the oil as the ester $3,5Me_2\text{-}pz\text{-}CS_2Et$.

X-ray intensity measurements

The crystal data for compound **I** are summarized in Table 3, together with some experimental details. Auto-indexing procedures and least-squares fitting of the setting angles of 25 randomly distributed intense reflections having $9 < \theta < 11°$ gave accurate refined cell dimensions and their standard deviations. A total of 2336 independent reflections was then collected by the ω-scan technique in the $6 < 2\theta < 50°$ range ($+h$, $+k$, $+l$ octant). The intensities of three standard reflections, monitored at 3600 s intervals, showed no systematic decay. The raw intensity data were corrected for Lorentz-polarization effects (including the polarization of the crystal monochromator) and then for absorption. The empirical method developed by North *et al.* [8] was used with the aid of psi-scans (psi = 0–360°, every 10°) of three reflections having χ near 90°.

Determination and refinement of the structure

The position of the single independent copper atom was determined from the three-dimensional Patterson function, calculated from all intensity data. The coordinates of the remaining non-hydrogen atoms were located by successive least-squares refinements and difference Fourier maps. The hydrogen atoms were added in the last cycles of refinement in calculated positions (C–H 0.95 Å, B 10.0 Å^2). Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Full matrix least-squares refinement was based on F, the minimized function being $\Sigma w(|F_o|-k|F_c|)^2$. Weights were assigned as: $w = 1/\sigma^2(F_o)$, where $\sigma(F_o) = \sigma(F_o^2)/2F_o$, $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{1/2}/LP$, and p, the ignorance factor, set at 0.04. A total of 1134 reflections with $I > 3\sigma(I)$ was used in the final refinement of the structural parameters. The atomic scattering factors, corrected for real and imaginary dispersion terms, were taken from ref. 9.

The handness of the crystal was determined by refining both enantiomeric models (in their suitable $P4_1$ and $P4_3$ space groups) [10]; owing to the small value of the anomalous scattering of a single Cu atom, $f'' = 1.2$ electrons (and the almost negligible values for the remaining atoms), their contribution to the imaginary part of the structure factors is also small, and resulted in very similar agreement values for the two enantiomeric models ($R = 0.0404$, $R_w = 0.0475$ and $GOF = 1.721$ in one case, $R = 0.0404$, $R_w = 0.0478$ and $GOF = 1.730$ in the other). Nevertheless, we assumed that the lowest R,R_w and GOF factors were those of the actual enantiomeric crystal measured; therefore, Tables 1–3, together with the crystal structure discussion, have been based on that model. All computations were performed on a PDP 11/73 microcomputer using the Structure Determination Package [11] and the physical constants tabulated therein.

TABLE 3. Crystal data and intensity collection parameters

Compound	[Cu(3,5Me$_2$-pz-C(S)-S)(CNR)$_2$]
Formula	$C_{20}H_{29}CuN_4S_2$
Formula weight (g mol^{-1})	453.15
Color, shape	orange, tetragonal bipyramid
Crystal size (mm^3)	0.25 × 0.25 × 0.30
Crystal system	tetragonal
$a = b$ (Å)	9.806(1)
c (Å)	23.734(6)
V (Å^3)	2282(1)
Z, D_{calc} (g cm^{-3})	4, 1.319
Space group	$P4_1$ (No. 76)
$F(000)$	952
Radiation (graphite monocr.) (Å)	Mo Kα, $\lambda = 0.71073$
Diffractometer	Enraf Nonius CAD4
μ (Mo Kα) (cm^{-1})	11.46
2θ range (°)	6–50
Scan method	ω
Scan interval (°)	$0.9 + 0.347 \tan \theta$
Prescan speed (° min^{-1})	16
Prescan acceptance, $\sigma(I)/I$	1.0
Required, $\sigma(I)/I$	0.01
Max. time for 1 reflection measurement (s)	60
Collected octants	$+h, +k, +l$
No. data collected at r.t.	2336
No. data used ($I > 3\sigma(I)$)	1134
No. azimut reflections for absorption correction	3
Transmission factors: max., min.	1.00, 0.96
R	0.040
R_w	0.048
GOF	1.721
No. variable parameters	243
Max peak in final difference Fourier (e/Å^3)	0.20(5)

$R = [\Sigma|F_o - kF_c|/\Sigma F_o]$; $R_w = [\Sigma w(F_o - kF_c)^2/wF_o^2]^{1/2}$; $GOF = [\Sigma w(F_o - kF_c)^2/(N_{obs} - N_{var})]^{1/2}$.

Supplementary material

Additional material available from the Cambridge Crystallographic data Centre comprises thermal parameters, positional parameters of hydrogen atoms, full list of bond lengths and angles and table of observed and calculated structure factors.

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