Crystal and Molecular Structure of *catena*-μ-Isothiocyanato-(*N'*-pyridylmethylene-*N''*-salicyloylhydrazinato-*NN'O*)copper(II)

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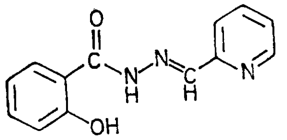
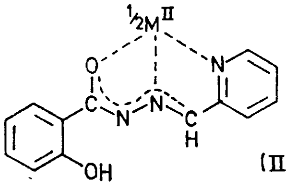
The crystal structure of the title compound has been determined by three-dimensional Patterson and Fourier methods from *X*-ray diffractometer data. Crystals are monoclinic, a = 16.46(1), b = 15.72(1), c = 5.63(1) Å, β = 92.4(1)°, Z = 4, space group $P2_1/n$. The structure was refined by least-squares to R 4.1 for 2 087 observed reflexions. Co-ordination around the metal is distorted square pyramidal and involves one organic anion, which chelates through the carbonyl oxygen [Cu–O 1.990(3) Å], a hydrazine nitrogen [Cu–N 1.925(4) Å], and a pyridine nitrogen [Cu–N 2.038(3) Å], and a thiocyanate nitrogen [Cu–N 1.930(5) Å] and sulphur [Cu–S 2.709(2) Å] from an adjacent thiocyanate group. This group bridges the co-ordination polyhedra in zig-zag chains along [001].

THE compound described in the present paper was obtained using as chelating ligand (I) the salicyloylhydrazone of picolinecarbaldehyde (Hsip) which co-ordinates to metal in the deprotonated form (sip) through the carbonyl oxygen, one hydrazine nitrogen, and the pyridine nitrogen as in (II). Crystal structure analysis of (IIb) has shown it to be polymeric since the thiocyanate group is in a bridging situation.



(I)



(II) a; M = Ni
b; M = Cu

EXPERIMENTAL

Preparation of (IIb). The ligand (I) was prepared as described in ref. 1. NaSCN (0.02 mol), dissolved in ethanol, was added to an ethanolic solution of $Cu(OAc)_2{\cdot}H_2O$ (0.01 mol) and (I) (0.01 mol), and the mixture heated under reflux for 20 min. A brown powder was formed and, from the filtered solution, deep green prismatic crystals were obtained by slow evaporation of the solvent (Found: C, 46.15; H, 2.70; Cu, 17.30; N, 15.20. $C_{14}H_{10}CuN_4O_2S$ requires C, 46.47; H, 2.79; Cu, 17.57; N, 15.49%).

TABLE 1

Fractional atomic co-ordinates (× 10^4 for the non-hydrogen atoms, × 10^3 for hydrogen atoms) and temperature factors,* with estimated standard deviations in parentheses

	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	−41(1)	1 976(1)	2 032(1)	4.04(2)	4.38(2)	3.14(2)	0.06(2)	−0.02(2)	−0.45(2)
S	346(1)	3 347(1)	9 396(2)	4.36(5)	3.64(5)	2.22(4)	−0.80(4)	−0.35(3)	−0.24(3)
O(1)	1 073(2)	1 483(2)	2 249(4)	3.55(12)	3.84(13)	2.88(11)	0.65(10)	−0.52(9)	−0.71(10)
O(2)	1 642(2)	−13(2)	−3 675(5)	4.60(15)	5.27(16)	3.66(13)	0.88(13)	−0.07(11)	−1.62(12)
N(1)	3(2)	2 592(2)	4 998(6)	3.98(15)	4.58(17)	2.39(13)	0.16(14)	0.12(11)	−0.19(12)
N(2)	−1 255(2)	2 032(2)	1 173(5)	3.13(13)	3.21(14)	2.89(13)	−0.36(12)	0.25(10)	0.04(11)
N(3)	−92(2)	1 188(2)	−586(5)	3.22(14)	2.75(14)	2.96(14)	−0.17(11)	0.23(11)	−0.19(11)
N(4)	617(2)	800(2)	−1 187(5)	3.10(14)	3.34(15)	3.08(14)	−0.08(12)	0.04(11)	−0.66(11)
C(1)	155(2)	2 911(2)	6 802(6)	2.73(15)	3.44(17)	2.42(15)	0.02(13)	0.19(12)	0.37(13)
C(2)	−1 845(3)	2 464(3)	2 204(7)	3.98(19)	3.70(19)	3.98(19)	−0.23(16)	0.47(15)	−0.35(15)
C(3)	−2 645(3)	2 451(3)	1 304(8)	3.50(19)	4.14(21)	5.58(24)	0.11(16)	0.64(17)	−0.13(18)
C(4)	−2 873(3)	1 988(3)	−697(8)	3.21(18)	4.05(20)	5.76(24)	−0.37(17)	−0.47(16)	0.51(18)
C(5)	−2 233(3)	1 540(3)	−1 781(8)	3.72(18)	3.53(19)	4.07(19)	−0.67(15)	−0.38(15)	−0.07(15)
C(6)	−1 449(2)	1 565(2)	−808(7)	3.14(16)	2.94(16)	2.97(16)	−0.75(13)	−0.09(13)	0.10(13)
C(7)	−773(2)	1 096(3)	−1 758(7)	3.51(17)	3.34(18)	3.07(16)	−0.55(14)	0.06(13)	−0.62(14)
C(8)	1 200(2)	1 009(2)	454(7)	3.61(17)	2.57(16)	3.03(16)	−0.04(14)	0.17(13)	0.22(13)
C(9)	2 022(2)	674(2)	67(6)	3.94(16)	2.72(16)	2.86(16)	0.11(13)	0.32(13)	0.05(13)
C(10)	2 646(3)	843(3)	1 760(8)	3.62(18)	3.68(20)	4.26(20)	−0.06(15)	−0.22(15)	−0.24(16)
C(11)	3 432(3)	571(3)	1 447(8)	3.76(20)	4.97(24)	5.06(23)	0.01(18)	−0.40(17)	0.12(19)
C(12)	3 605(3)	123(3)	−600(8)	3.71(20)	4.85(23)	5.28(23)	0.91(18)	0.79(17)	−0.11(19)
C(13)	3 012(3)	−55(3)	−2 277(8)	4.56(22)	4.43(22)	4.28(21)	0.96(18)	0.94(17)	−0.30(17)
C(14)	2 208(3)	205(3)	− 1975(7)	4.17(19)	3.08(18)	3.51(18)	0.30(15)	0.28(15)	0.10(14)

				$B/\text{Å}^2$					$B/\text{Å}^2$
H(1) †	114(3)	20(3)	−316(8)	6.27(1.12)	H(7)	−83(3)	72(3)	−300(7)	4.77(1.01)
H(2)	−167(2)	279(2)	364(6)	3.24(84)	H(10)	251(3)	120(3)	332(7)	5.23(1.14)
H(3)	−303(3)	275(3)	213(8)	5.74(1.17)	H(11)	386(3)	68(3)	260(8)	5.98(1.18)
H(4)	−336(3)	198(3)	−126(7)	4.98(1.05)	H(12)	416(3)	−9(3)	−84(8)	5.51(1.10)
H(5)	−233(2)	123(3)	−312(7)	4.15(97)	H(13)	313(3)	−36(3)	−374(8)	6.14(1.16)

* Anisotropic thermal parameters are in the form: $\exp -0.25(h^2\beta_{11}a^{*2} + \cdots + 2kl\beta_{23}b^*c^*)$. † Hydrogen atoms are numbered according to the carbon atoms to which they are attached, except H(1) which is on O(2).

Crystal Data.—$C_{14}H_{10}CuN_4O_2S$, $M = 361.9$, Monoclinic, $a = 16.46(1)$, $b = 15.72(1)$, $c = 5.63(1)$ Å, $\beta = 92.4(1)°$, $U = 1455.5$ Å^3, $D_m = 1.62$ g cm^{-3}, $Z = 4$, $D_c = 1.65$ g cm^{-3}, $F(000) = 732$. Cu-K_α radiation, $\lambda = 1.5418$ Å; $\mu(\text{Cu-}K_\alpha) = 35.5$ cm^{-1}. Space group $P2_1/n$ (from systematic absences). Cell constants were determined from rotation and Weissenberg photographs and single-crystal diffractometry.

Crystallographic Measurements.—*X*-Ray intensity data were collected on a Siemens single-crystal automated diffractometer on-line to an Olivetti Elea-6001/S computer. The Ni-filtered Cu-K_α radiation and the ω—2θ (2θ max 140°) technique were used. In this way the intensities of 2761 independent reflexions were measured, of which 2087 having $I > 2\sigma(I)$ were considered observed and were employed in the analysis. After Lorentz and polarization corrections had been applied, the absolute scale was determined, first by Wilson's method and then by comparison of the observed and calculated structure amplitudes.

Structure Analysis.—The structure was solved by the heavy-atom method, the initial set of co-ordinates for copper being deduced from a three-dimensional Patterson map. The final value of 0.041 for R was achieved by refining the non-hydrogen atoms with anisotropic unweighted least squares and by adding the contributions of the hydrogen atoms, located on a difference map and refined isotropically. Atomic scattering factors used throughout the calculations were from ref. 2 for non-hydrogen and from ref. 3 for hydrogen atoms. Final positional and thermal parameters with their estimated standard deviations are given in Table 1. Observed and calculated structure factors, details of i.r. and electronic spectra, and

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[1] P. Domiano, A. Musatti, M. Nardelli, and C, Pelizzi, *J.C.S. Dalton*, 1975, **295**.

[2] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

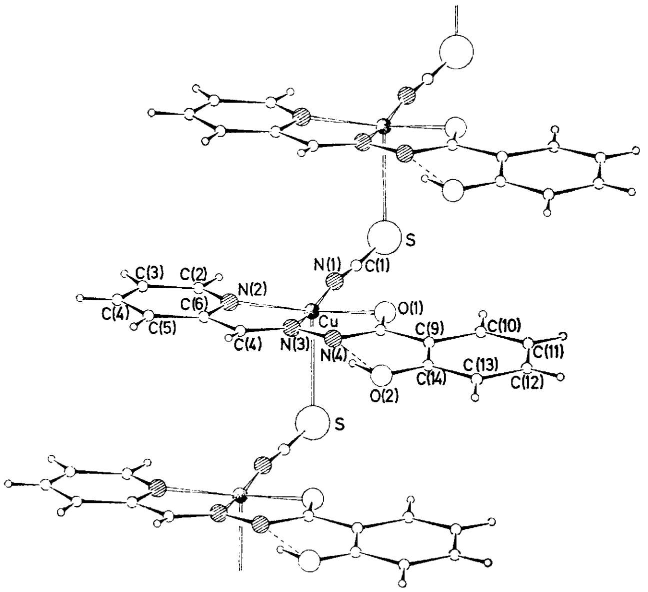
[3] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

magnetic properties are listed in Supplementary Publication No. SUP 21282 (17 pp., 1 microfiche).*

All calculations were performed on a CDC 6600 computer at the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Bologna) with programs of Immirzi.[4]

RESULTS AND DISCUSSION

As shown in the Figure, the co-ordination is more strictly square planar and is determined by the terdentate behaviour of the organic ligand which co-ordinates to the metal through its carbonyl oxygen, one hydrazine nitrogen, and the pyridine nitrogen, and by the thiocyanate nitrogen, to form two nearly coplanar chelation rings; the dihedral angle between them is 172.7°. The metal–nitrogen distances involving the thiocyanate [N(1)] and hydrazine [N(3)] nitrogen atoms are equal, and significantly shorter than that involving pyridine [N(2)]. This is probably due to the excess of negative charge both on N(1) and N(3). The Cu–O distance agrees well with those generally found in five-co-ordinate copper(II) complexes.



Projection of the structure illustrating the copper co-ordination arrangement and the bridging interactions of the thiocyanate ions. The atom numbering system used in the analysis is also shown

The co-ordination polyhedron is completed to a nearly regular tetragonal pyramid by the sulphur atom of an adjacent thiocyanate group [Cu-S^I 2.709(2) Å; the angle between the Cu–S^I bond and the mean plane through the other four co-ordinated atoms is 88.8°], such that the complex molecules are linked in chains parallel to [001] by thiocyanate bridges. Copper is out of the co-ordination plane by 0.18 Å in the direction of the top of the pyramid. The Cu–S distance is longer by *ca.* 0.4 Å than that observed when sulphur lies in the main co-ordination plane (2.26—2.41 Å).[5,6] A longer Cu–S distance (2.93 Å) has been observed in copper(II)-picolinate complexed with thiourea,[7] where co-ordination is elongated tetragonal bipyramidal.

TABLE 2

Bond distances (Å) and angles (°), with standard deviations in parentheses

(*a*) In the co-ordination polyhedron

Cu–O(1)	1.990(3)	N(1)–Cu–N(2)	100.7(1)
Cu–N(1)	1.930(5)	N(1)–Cu–N(3)	170.1(1)
Cu–N(2)	2.038(3)	N(2)–Cu–N(3)	80.5(1)
Cu–N(3)	1.925(4)	O(1)–Cu–S(^{I})	96.1(1)
Cu–S(^{I})	2.709(2)	N(1)–Cu–S(^{I})	94.3(1)
O(1)–Cu–N(1)	98.1(1)	N(2)–Cu–S(^{I})	94.9(1)
O(1)–Cu–N(2)	157.4(1)	N(3)–Cu–S(^{I})	95.5(1)
O(1)–Cu–N(3)	78.9(1)		

(*b*) In the organic ligand

C(6)–N(2)	1.363(5)	N(2)–C(6)–C(5)	121.6(3)
N(2)–C(2)	1.338(5)	N(3)–C(7)–C(6)	114.7(3)
C(2)–C(3)	1.391(6)	N(3)–N(4)–C(8)	108.1(3)
C(3)–C(4)	1.368(7)	O(1)–C(8)–N(4)	123.4(3)
C(4)–C(5)	1.381(6)	C(8)–C(9)–C(10)	118.9(3)
C(5)–C(6)	1.381(6)	C(10)–C(9)–C(14)	118.5(4)
C(6)–C(7)	1.455(6)	C(10)–C(11)–C(12)	119.2(4)
C(7)–N(3)	1.285(5)	C(12)–C(13)–C(14)	120.6(4)
N(3)–N(4)	1.372(5)	O(2)–C(14)–C(13)	117.8(4)
N(4)–C(8)	1.345(5)	N(2)–C(2)–C(3)	121.8(4)
C(8)–O(1)	1.281(5)	C(3)–C(4)–C(5)	119.3(4)
C(8)–C(9)	1.477(6)	C(5)–C(6)–C(7)	123.8(4)
C(9)–C(10)	1.398(6)	N(2)–C(6)–C(7)	114.7(3)
C(10)–C(11)	1.381(6)	N(4)–N(3)–C(7)	123.8(3)
C(11)–C(12)	1.391(7)	N(4)–C(8)–C(9)	116.3(3)
C(12)–C(13)	1.359(7)	O(1)–C(8)–C(9)	120.3(3)
C(13)–C(14)	1.402(6)	C(8)–C(9)–C(14)	122.6(3)
C(14)–O(2)	1.352(5)	C(9)–C(10)–C(11)	121.3(4)
C(14)–C(9)	1.411(6)	C(11)–C(12)–C(13)	121.0(4)
C(2)–N(2)–C(6)	118.7(3)	C(9)–C(14)–C(13)	119.3(4)
C(2)–C(3)–C(4)	119.4(4)	O(2)–C(14)–C(9)	122.9(4)
C(4)–C(5)–C(6)	119.2(4)		

(*c*) In the thiocyanate group

C(1)–S	1.633(5)	Cu–N(1)–C(1)	169.0(3)
C(1)–N(1)	1.152(5)	Cu–S^I–C(1^I)	98.3(4)
N(1)–C(1)–S	178.2(3)		

(*d*) Involving hydrogen atoms

O(2)–H(1)	0.95(5)	N(3)–C(7)–H(7)	122(3)
C(2)–H(2)	0.99(4)	C(11)–C(10)–H(10)	120(2)
C(3)–H(3)	0.93(5)	C(12)–C(11)–H(11)	119(3)
C(4)–H(4)	0.90(4)	C(13)–C(12)–H(12)	118(3)
C(5)–H(5)	0.91(4)	C(14)–C(13)–H(13)	118(3)
C(7)–H(7)	0.92(4)	N(2)–C(2)–H(2)	115(2)
C(10)–H(10)	1.07(4)	C(2)–C(3)–H(3)	118(3)
C(11)–H(11)	0.95(5)	C(3)–C(4)–H(4)	119(3)
C(12)–H(12)	0.99(5)	C(4)–C(5)–H(5)	122(3)
C(13)–H(13)	0.98(5)	C(6)–C(7)–H(7)	123(3)
C(14)–O(2)–H(1)	106(3)	C(9)–C(10)–H(10)	119(2)
C(3)–C(2)–H(2)	123(2)	C(10)–C(11)–H(11)	122(3)
C(4)–C(3)–H(3)	123(3)	C(11)–C(12)–H(12)	121(3)
C(5)–C(4)–H(4)	122(3)	C(12)–C(13)–H(13)	122(3)
C(6)–C(5)–H(5)	118(3)	O(2)–H(1) · · · N(4)	149(4)

Dimensions, π delocalization (Table 2), and planarity in the organic ion are not essentially different from those

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

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[5] I. D. Brown, C. P. Weiss, and K. K. Wu, Bond Index to the Determinations of Inorganic Crystal Structures (BIDICS), Institute for Material Research, McMaster University, Hamilton, Ontario, 1969—71.

[6] I. D. Brown and W. L. K. Ho, Bond Index to the Determinations of Inorganic Crystal Structures (BIDICS), Institute for Material Research, McMaster University, Hamilton, Ontario, 1972.

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Table 3

van der Waals contacts <3.6 Å

$C(3) \cdots O(1^{II})$	3.48(1)	$C(4) \cdots O(1^{II})$	3.19(1)
$O(1) \cdots S(^{I})$	3.53(1)	$N(2) \cdots S(^{I})$	3.53(1)
$N(1) \cdots S(^{I})$	3.44(1)	$N(3) \cdots S(^{I})$	3.47(1)
$O(2) \cdots O(1^{I})$	3.39(1)	$N(3) \cdots N(1^{I})$	3.33(1)
$C(7) \cdots N(1^{I})$	3.27(1)	$N(3) \cdots C(1^{I})$	3.12(1)
$O(2) \cdots C(10^{I})$	3.39(1)	$C(7) \cdots O(2^{III})$	3.35(1)

Roman numeral superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x, y, z - 1$ II $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$
III $-x, -y, -z - 1$

observed in (IIa)[1] and in (I).[8] The main difference in the deprotonated ion, with respect to the unco-ordinated molecule, concerns the pyridine ring, in which, in the metal complexes, the nitrogen atom is *syn* with respect to the amide C=O group, whereas, in the free molecule, it is *anti*, thus enabling terdentate co-ordination of the metal.

Bond distances and angles involving the thiocyanate group are in agreement with those generally found in other complexes.[9–15] van der Waals contacts <3.6 Å are listed in Table 3.

[4/1576 *Received, 25th November*, 1974]

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[14] G. D. Andreetti, L. Cavalca, and P. Sgarabotto, *Gazzetta*, 1971, **101**, 483.

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