A Convenient Method for the Preparation of 3-(2-Pyridyl)-triazolo[1,5-*a*]pyridine (L). Crystal Structures of L and $[CuL_2(OH_2)_2][NO_3]_2$*

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The compound 3-(2-pyridyl)triazolo[1,5-*a*]pyridine (L) was synthesized under mild conditions by refluxing equimolar amounts of hydrazine and di-2-pyridyl ketone in methanol–water. It has been characterized by X-ray diffraction and used as a ligand in two metal complexes, $[ML_2(OH_2)_2][NO_3]_2$ (M = Cu or Co). The crystal structure of the copper derivative, which is the first example of a triazolopyridine complex, has also been determined.

Pursuing our studies on the chelation behaviour of hydrazones[1] and in particular di-2-pyridyl ketone hydrazones,[2] we have investigated the reactivity of di-2-pyridyl ketone with hydrazine. An unexpected copper(II) triazolopyridine complex was obtained from an hydrolysis process involving an acylhydrazone of di-2-pyridyl ketone and copper nitrate and subsequent oxidation induced by molecular oxygen. In order to understand better the mechanism we have now studied the reaction of di-2-pyridyl ketone with hydrazine under different experimental conditions. The synthesis of triazole compounds by oxidative cyclization of hydrazones occurs in the presence of strong oxidants such as polyphosphoric acid, silver oxide, potassium hexacyanoferrate(III), manganese dioxide, iodine or lead(IV) acetate.[3,4] As far as we know, only 2-pyridyl-3-triazolo[1,5-*a*]-pyridyl ketone reacts with hydrazine to give, in the air, 3,3′-bi(triazolo[1,5-*a*]pyridine) in low yield (15%), 2-pyridyl-3-triazolo[1,5-*a*]pyridyl ketone hydrazone being the major product (51%).[5]

3-(2-Pyridyl)triazolo[1,5-*a*]pyridine (L) was previously synthesized by oxidation of di-2-pyridyl ketone hydrazone with nickel(II) peroxide in benzene at room temperature,[6] whereas we have isolated the compound under milder conditions by the reaction at reflux of equimolar amounts of hydrazine and di-2-pyridyl ketone in methanol–water.

The present paper deals with the synthesis and the spectroscopic characterization of L, and of the complexes $[CuL_2(OH_2)_2][NO_3]_2$ **1** and $[CoL_2(OH_2)_2][NO_3]_2$ **2**; the crystal structures of L and **1** are also reported. A preliminary account of complex **1** can be found in ref. 7.

Experimental

All reagents were of commercial quality used without further purification. Elemental analyses (C, H and N) were carried out on an automatic Carlo Erba CHNS-O EA1108 elemental analyser. Infrared spectra (4000–400 cm^{-1}) for KBr discs were recorded on a Nicolet 5PC FT-IR spectrometer, electron-impact (EI) mass spectra on a Finnigan SSQ710 spectrometer, electronic spectra (900–200 nm) on a Kontron UVIKON 860 spectrophotometer, and ^1H NMR spectra on a Bruker AMX 400 instrument; chemical shifts are given in ppm referred to tetramethylsilane. The thermogravimetric analyses were made with a Perkin-Elmer Delta series TGA 7 thermobalance from 30 to 400 °C at a rate of 20 °C min^{-1}. Melting points were obtained with a Gallenkamp MFB-595 apparatus in open capillaries and are uncorrected. The X-band EPR spectra of the powdered samples were recorded with a Varian E9 spectrometer, equipped with an Oxford Instruments liquid-helium continuous-flow cryostat.

Syntheses.—Compound L. To a methanol–water (1 : 1 v/v; 60 cm^3) solution of di-2-pyridyl ketone (0.5 g, 2.72 mmol) was added in the air an equimolar amount of hydrazine hydrate (80% aqueous solution). The solution was refluxed for about 4 h. Upon slow evaporation of the solvent colourless crystals were formed, the purity of which was checked by TLC [silica gel, ethyl acetate–hexane (9:1 v/v)], m.p. 123–125 °C, yield 85% (Found: C, 67.50; H, 5.40; N, 28.50. $C_{11}H_8N_4$ requires C, 67.35; H, 5.60; N, 28.55%). Mass spectrum: *m*/*z* 196 (40), 168 (100), 140 (30), 78 (40), 63 (40) and 51 (40%). UV (methanol): 317 (ε = 14 500), 305 (15 000) and 264 nm (11 500 dm^3 mol^{-1} cm^{-1}). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.72 (2 H, q), 8.65 (1 H, d), 8.34 (1 H, d), 7.78 (1 H, t), 7.35 (1 H, t), 7.20 (1 H, t) and 7.02 (1 H, t). When the reaction was carried out under nitrogen the product isolated after concentration was an oil, which did not contain compound L as indicated by TLC analysis. When the oil was refluxed in the presence of air compound L was again obtained.

$[CuL_2(OH_2)_2][NO_3]_2$ **1**. To a methanol solution (70 cm^3) of compound L (0.1 g, 0.51 mmol) was added an equimolar amount of $Cu(NO_3)_2{\cdot}3H_2O$; after slow evaporation of the solvent at room temperature pale green crystals were isolated, decomp. 240–245 °C, yield 82% (Found: C, 43.00; H, 3.20; N, 22.75. $C_{22}H_{20}CuN_{10}O_8$ requires C, 42.90; H, 3.15; N, 22.75%). Compound **1** was also isolated by refluxing for 4 h di-2-pyridyl ketone, hydrazine and the copper salt (2:2:1 molar ratio) in methanol solution (yield 40%).

$[CoL_2(OH_2)_2][NO_3]_2$ **2**. Pale red crystals of the complex were obtained following the same procedure described for compound **1**; decomp. about 280 °C, yield 70% (Found: C, 43.00; H, 3.05; N, 22.30. $C_{22}H_{20}CoN_{10}O_8$ requires C, 43.20; H, 3.25; N, 22.90%). TGA analysis: both water molecules lost at *ca.* 120 °C (5.8% weight loss from 100 to 160 °C).

X-Ray Crystallography.—Diffraction measurements were carried out at room temperature using a Siemens AED diffractometer with nickel-filtered Cu-Kα radiation (λ 1.5418 Å) for compound L and a Philips PW1100 diffractometer with

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

monochromatized Mo-Kα radiation (λ 0.7107 Å) for complex **1**. Crystal data and relevant details concerning data collection and refinement for both compounds are in Table 1. The reflections were processed with the peak-profile analysis procedure and corrected for Lorentz and polarization effects.

The structure of compound L was solved by direct methods, while that of complex **1** was solved by the conventional heavy-atom method. Refinement was in each case by full-matrix least squares based on F with anisotropic thermal parameters for all non-hydrogen atoms. All the hydrogen atoms including those of the water molecule in **1** were located from a ΔF map and introduced in the last refinement cycle with isotropic thermal parameters. The nitrate ion in **1** is disordered with the oxygen atoms statistically distributed over two sites with an occupancy factor ratio of 0.8:0.2. Atomic scattering factors were taken from ref. 8. All the calculations were performed on a Gould 6040 computer using SHELX 76,[9] ORTEP[10] and PARST[11] programs. Final atomic coordinates for non-hydrogen atoms are given in Tables 2 and 3, selected bond distances and angles in Table 4.

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

Results and Discussion

As reported,[3] most syntheses of triazolopyridines start from pyridines rather than triazoles. Moreover, the majority of triazolo[1,5-*a*]pyridines have been prepared by oxidation of the hydrazone of a pyridine-2-carbaldehyde or -ketone. In the present case the oxidation is due to molecular oxygen, present in the air, and is probably favoured by the basic medium produced by the hydrazine. On the other hand, under similar conditions, 2-benzoylpyridine reacts with hydrazine to give the corresponding hydrazone, which only after oxidation with silver oxide leads to the formation of 3-phenyltriazolo[1,5-*a*]pyridine.[4] It can be therefore concluded that in the one-step formation of compound L the electron-withdrawing character of the two pyridine rings plays a significant role.

The structure of compound L is shown in Fig. 1. The molecule, as a whole, has a planar configuration, the angle between the pyridine and triazolopyridine rings being only 0.9(1)°. The H atoms bonded to C(8) and C(4) are suitably positioned for internal bonding with N(1) and N(4), respectively [C(8)···N(1) 3.149(4) Å, C(8)–H(5)···N(1) 108(2)°; C(4)···N(4) 2.899(5) Å, C(4)–H(4)···N(4) 105(2)°], so contributing to locking the two rings in the same plane. As shown by the X-ray analysis of the copper complex, during complexation these bonds are broken and the pyridine rotates 180° so as to be able to co-ordinate the copper atom. A similar behaviour was found for di-2-pyridyl ketone [phenyl(semicarbazono)acetyl]hydrazone in its copper complex.[2] A search carried out by means of the Cambridge Crystallographic Database indicated that this is the first triazolo[1,5-*a*]pyridine

Table 1 Experimental data* for the crystallographic analyses of compound L and complex **1**

Compound	L	**1**
Formula	$C_{11}H_8N_4$	$C_{22}H_{20}CuN_{10}O_8$
M	196.21	616.01
a/Å	7.159(3)	7.084(2)
b/Å	10.675(3)	12.110(4)
c/Å	12.523(4)	14.662(5)
β/°	99.10(5)	99.10(1)
U/Å^3	945.0(6)	1242.0(7)
Z	4	2
D_c/g cm^{-3}	1.379	1.647
D_m/g cm^{-3}	1.31	1.66
θ range/° for lattice parameters	20.3–40.0	9.1–15.5
F(000)	408	630
Crystal size/mm	0.29 × 0.33 × 0.71	0.28 × 0.37 × 0.55
μ/cm^{-1}	7.14	9.50
θ range/°	3–65	3–24
Standard reflection	1 −5 0	0 6 4
Maximum intensity variation (%)	4.2	4.0
No. of reflections measured	1792	2247
No. of reflections used in the refinement	1272 [$I > 3\sigma(I)$]	1172 [$I > 2\sigma(I)$]
No. of refined parameters	162	241
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$	0.0510	0.0337
$R' = [\Sigma w(\Delta F^2)/\Sigma wF_o^2]^{\frac{1}{2}}$	0.0567	0.0335
k, g in $w = k/[\sigma^2(F_o) + gF_o^2]$	10.6, 5.2 × 10^{-5}	0.43, 8.97 × 10^{-4}
Maximum, minimum height in final ΔF map/e Å^{-3}	0.08, −0.05	0.25, −0.18

* Details in common: space group $P2_1/c$; 25 reflections for lattice parameters; scan speed 3–12° min^{-1}; scan mode ω–2θ.

Table 2 Atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for non-hydrogen atoms of compound L

Atom	X/a	Y/b	Z/c
C(1)	6185(6)	−1223(4)	2901(4)
C(2)	6060(5)	−2481(4)	3100(4)
C(3)	6531(5)	−2862(4)	4140(4)
C(4)	7124(4)	−1998(3)	4931(4)
C(5)	7218(3)	−748(3)	4663(2)
C(6)	7813(3)	188(3)	5482(2)
C(7)	7987(3)	1483(3)	5379(2)
C(8)	7692(4)	2375(3)	4544(2)
C(9)	8034(5)	3594(3)	4786(3)
C(10)	8641(5)	3986(3)	5863(3)
C(11)	8912(4)	3153(3)	6662(3)
N(1)	6736(4)	−344(3)	3644(2)
N(2)	8587(3)	1905(2)	6408(2)
N(3)	8812(4)	946(3)	7121(2)
N(4)	8325(4)	−96(3)	6547(2)

Table 3 Atomic coordinates (× 10^4) with e.s.d.s in parentheses for non-hydrogen atoms of complex **1**

Atom	X/a	Y/b	Z/c
Cu	0	0	0
N(1)	1 592(5)	1 394(3)	68(2)
N(2)	−4 188(5)	1 949(3)	−1 476(2)
N(3)	−3 667(5)	923(3)	−1 188(2)
N(4)	−1 892(5)	1 029(3)	−742(2)
C(1)	3 430(7)	1 503(4)	463(3)
C(2)	4 365(8)	2 501(4)	535(3)
C(3)	3 391(8)	3 423(4)	187(3)
C(4)	1 509(8)	3 327(4)	−234(3)
C(5)	658(6)	2 303(3)	−291(3)
C(6)	−1 296(6)	2 082(3)	−736(3)
C(7)	−2 781(7)	2 706(3)	−1 212(3)
C(8)	−3 162(9)	3 818(4)	−1 460(4)
C(9)	−4 891(11)	4 077(6)	−1 939(4)
C(10)	−6 291(11)	3 275(6)	−2 183(4)
C(11)	−5 945(8)	2 229(6)	−1 962(4)
N(5)	9 158(9)	1 239(5)	6 683(4)
O(1)[a]	10 335(10)	535(5)	7 012(5)
O(2)[a]	8 115(7)	983(4)	5 939(4)
O(3)[a]	9 189(13)	2 161(5)	6 996(5)
O(1)[b]	8 626(105)	2 127(65)	6 604(43)
O(2)[b]	10 199(75)	1 045(42)	7 357(33)
O(3)[b]	8 312(83)	804(48)	6 678(40)
O(4)	−1 271(7)	611(5)	1 337(3)

[a] Occupancy factor 0.8. [b] Occupancy factor 0.2.

Table 4 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for compound L and complex **1**

	L	**1**		L	**1**
C(1)–C(2)	1.372(7)	1.375(7)	C(1)–N(1)	1.336(5)	1.345(6)
C(2)–C(3)	1.354(7)	1.368(7)	C(3)–C(4)	1.371(6)	1.382(8)
C(4)–C(5)	1.380(4)	1.375(7)	C(5)–C(6)	1.447(4)	1.459(6)
C(5)–N(1)	1.339(4)	1.348(5)	C(6)–C(7)	1.395(4)	1.390(6)
C(6)–N(4)	1.360(4)	1.343(5)	C(7)–C(8)	1.406(4)	1.409(7)
C(7)–N(2)	1.369(3)	1.365(6)	C(8)–C(9)	1.350(5)	1.349(9)
C(9)–C(10)	1.413(5)	1.39(1)	C(10)–C(11)	1.330(5)	1.32(1)
C(11)–N(2)	1.381(4)	1.376(7)	N(2)–N(3)	1.351(4)	1.346(5)
N(3)–N(4)	1.341(4)	1.329(5)	Cu–N(1)		2.024(3)
Cu–N(4)		2.018(3)	Cu–O(4)		2.400(5)
C(2)–C(1)–N(1)	125.6(4)	122.7(5)	C(1)–C(2)–C(3)	117.0(4)	118.7(5)
C(2)–C(3)–C(4)	119.7(5)	119.5(5)	C(3)–C(4)–C(5)	119.7(3)	119.0(5)
C(4)–C(5)–N(1)	121.9(3)	121.9(4)	C(4)–C(5)–C(6)	121.0(3)	124.7(4)
C(6)–C(5)–N(1)	117.1(3)	113.4(4)	C(5)–C(6)–N(4)	123.0(3)	116.9(4)
C(5)–C(6)–C(7)	129.7(2)	135.5(4)	C(7)–C(6)–N(4)	107.3(2)	107.5(3)
C(6)–C(7)–N(2)	105.0(2)	103.7(4)	C(6)–C(7)–C(8)	137.3(3)	138.4(4)
C(8)–C(7)–N(2)	117.7(2)	117.8(4)	C(7)–C(8)–C(9)	119.0(3)	118.5(6)
C(8)–C(9)–C(10)	121.2(3)	121.5(7)	C(9)–C(10)–C(11)	120.4(3)	120.6(7)
C(10)–C(11)–N(2)	118.2(3)	118.7(6)	C(1)–N(1)–C(5)	116.1(3)	118.1(4)
C(7)–N(2)–C(11)	123.4(2)	122.8(4)	C(11)–N(2)–N(3)	125.5(3)	124.8(4)
C(7)–N(2)–N(3)	111.1(2)	112.4(4)	N(2)–N(3)–N(4)	106.2(2)	104.8(3)
C(6)–N(4)–N(3)	110.4(2)	111.5(3)	N(4)–Cu–O(4)		87.0(2)
N(1)–Cu–O(4)		88.9(2)	N(1)–Cu–N(4)		80.1(1)
Cu–N(1)–C(5)		115.3(3)	Cu–N(1)–C(1)		126.6(3)
Cu–N(4)–N(3)		134.5(3)	Cu–N(4)–C(6)		113.7(2)

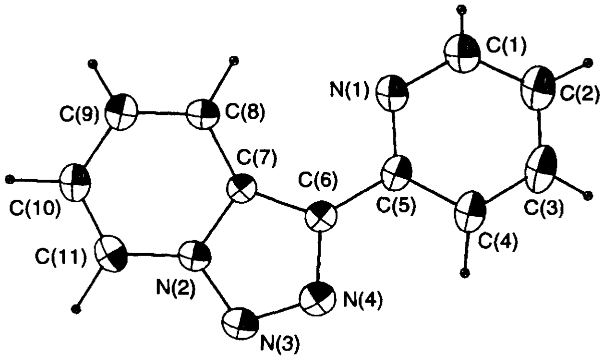

Fig. 1 An ORTEP drawing and numbering scheme for compound L. Thermal ellipsoids are drawn at the 50% probability level

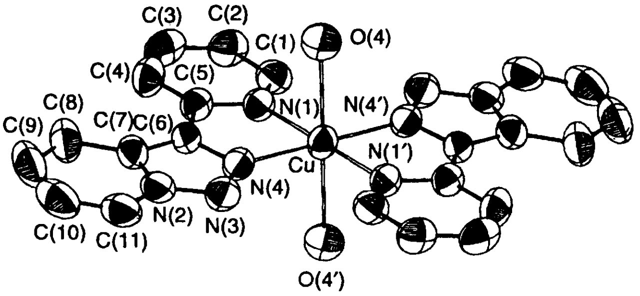

Fig. 2 An ORTEP drawing and numbering scheme for complex **1**. Thermal ellipsoids are drawn at the 50% probability level. The primed atoms are related to the unprimed ones by the symmetry operation $-x, -y, -z$

to be structurally characterized. The bond distances agree well with those previously reported for similar bonds in triazolopyridinium ylides,[12,13] while small but significant differences occur in the angles, probably because in the latter compounds N(4) is positively charged. The crystalline cohesion is ensured by normal van der Waals contacts, the shortest being C(11) ··· N(4) $(2 - x, y + \frac{1}{2}, \frac{3}{2} - z)$ 3.322(4) Å.

Complex **1** is built up of $[CuL_2(OH_2)_2]^{2+}$ cations and NO_3^- anions. The structure of the cation is shown in Fig. 2. As the space group $P2_1/c$ has four general positions, the presence of two molecules in the unit cell requires the compound to have a crystallographically imposed $\bar{1}$ symmetry. Accordingly, the copper atom lies on an inversion centre and has a tetragonally elongated octahedral co-ordination involving the N(1) and N(4) ligand atoms in the basal plane [Cu–N(1) 2.024(3), Cu–N(4) 2.018(3) Å] and the water molecules in the axial positions [Cu–O(4) 2.400(5) Å]. The N(1)–Cu–N(4) angle is forced to be remarkably smaller [80.1(1)°] than the expected 90° by the short ligand bite; the N(1)C(5)C(6)N(4)Cu chelate ring is almost planar, the maximum deviation being 0.06 Å. As can be seen from Table 4, which enables a comparison between L and **1**, the dimensions of the organic molecule are almost the same in the two compounds. The only significant differences involve exocyclic angles at C(5) and C(6) and they are due to the co-ordination. The Cu–N distances are similar to the corresponding equatorial distances found in bipyridyl or 1,10-phenanthroline copper complexes.[14] The nitrate anion shares the packing through hydrogen bonds involving as donors the water molecules [O(4) ··· O(1$^{\mathrm{I}}$) 2.777(8) Å, O(4)–H(1w) ··· O(1$^{\mathrm{I}}$) 165(6)°, I $1 - x, -y, 1 - z$; O(4) ··· O(3$^{\mathrm{II}}$) 2.867(8) Å, O(4)–H(2w) ··· O(3$^{\mathrm{II}}$) 167(5)°, II $x - 1, \frac{1}{2} - y, z - \frac{1}{2}$].

The IR spectrum of compound L is characterized by a medium band at 1635 cm^{-1} attributable to the ν(C=N) absorption[4,15] and by a pattern in the 800–690 cm^{-1} region typical for a ring system. The spectra of complexes **1** and **2** are quite similar. The more significant bands concern the ν(C=N) absorption, which undergoes a positive shift to 1643 cm^{-1}, and the strong absorption at 1385 cm^{-1} due to the nitrate group in its ionic form. The similar spectroscopic pattern, identical stoichiometry and, in the cobalt derivative, the loss of both water molecules at 120 °C suggesting they are co-ordinated, lead us to conclude that the two complexes have similar co-ordination geometries and ligand behaviours.

The EPR room-temperature powder spectrum of the copper compound shows an axial pattern, with $g_{\parallel} = 2.08$ and $g_{\perp} = 2.27$; these values are normal for a copper(II) ion in a tetragonally elongated octahedral environment.[16] The spectrum recorded at 4.2 K did not show any meaningful variation from the room-temperature one, either in the principal g values or in the shape, indicating that no exchange interaction larger than about 3 cm^{-1} is present. For the cobalt complex the spectrum recorded at 4.2 K is clearly rhombic, with $g_1 = 5.92, g_2 = 3.57$ and $g_3 = 2.01$; one component of the hyperfine splitting is observable, $A_3 \approx 200$ G (0.02 T). The correlation between g values and chemical structure is problematic, since the former strongly depend on any distortion which decreases the site symmetry of the cobalt ion.[17,18] An unusual feature is the temperature dependence of the g values, which at ≈ 60 K are $g_1 = 5.33, g_2 = 3.27$, while the resonance corresponding to g_3 is no longer observable because it becomes too large. A possible explanation could be derived from some motion of the axial water molecules, presumably librations, frozen at 4.2 K and activated when the temperature rises. This would be consistent with the large influence of both axial and equatorial π-bonding interactions on the g values of high-spin cobalt(II).

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