[2,12-Di(2-pyridyl)-3,7,11-triazatrideca-2,11-diene-$N^{1'},N^{1''},N^3,N^7,N^{11}$]copper(II) Perchlorate

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Abstract. $C_{20}H_{27}CuN_5^{2+} . 2ClO_4^-$, [Cu($C_{20}H_{27}N_5$)](ClO$_4$)$_2$, monoclinic, $P2_1/n$, $a = 17.786$ (8), $b = 8.035$ (5), $c = 19.400$ (9) Å, $\beta = 111.49$ (5)°, $M_r = 599.6$, $Z = 4$; final $R = 0.113$ for 1832 counter reflections. The Cu atom of the cation has distorted trigonal-bipyramidal coordination involving the five N atoms of the quinquedentate ligand. The O atoms of one perchlorate anion and a bridging methylene C atom are disordered.

Introduction. The title compound [CuL^1](ClO$_4$)$_2$ forms part of a series of transition-metal complexes of macrocyclic quinquedentate nitrogen ligands whose properties are under study. [CoL^1Me]I$_2$.2H$_2$O and [MnL^1NO](ClO$_4$)$_2$ have already been determined (Stotter & Trotter, 1977, 1978), the N atoms of the ligand L^1 occupying square-pyramidal sites about the Co^{III} or Mn^{II} ion and the methyl or nitrosyl group completing the six coordination to give an approximate octahedral arrangement. Other Cu complexes of similar macrocyclic ligands have also been determined. The cationic moiety of [CuL^2](ClO$_4$)$_2$ crystallizes in a distorted square-pyramidal arrangement (Griggs, Hasan, Henrick, Matthews & Tasker, 1977), whilst the geometry of the cation in [CuL^3](PF$_6$)$_2$ is best described as a distorted trigonal bipyramid (Drew & Hollis, 1978).
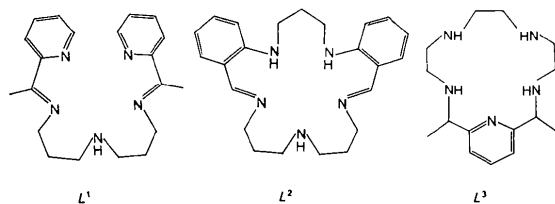
The compound was prepared by the method of Prince & Stotter (1974), and the crystals were grown from water. A crystal $0.3 \times 0.3 \times 0.3$ mm was used for data collection. The cell parameters were obtained by least squares from the settings of 25 reflections measured on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å, graphite

monochromated), and an ω–2θ scan mode [scan width $1.0°$ (θ), scan speed $0.03°$ (θ) s^{-1}]. 3450 reflections were collected in the range $3 < \theta < 22°$; 1832 unique reflections had $I_{(rel)} > 3.5\sigma I_{(rel)}$ and were considered observed. The intensities of three standard reflections measured every hour remained constant to within 1.3% of their mean values. Lorentz–polarization corrections were applied but no absorption correction was made. The structure was solved by the automatic centrosymmetric routine of *SHELX* (Sheldrick, 1978), in which an E map yielded the positions of 14 of the 36 heavy atoms. Subsequent refinement revealed that C(15) and the O atoms of one of the perchlorate anions were disordered. Consequently these atoms were omitted from a structure factor calculation and the ensuing difference map revealed two areas of electron density corresponding to each type of atom. For the perchlorate, the disorder could be interpreted as two distinct positions of the anion. Subsequent refinement of all the disordered atoms was carried out by placing them in two positions and varying their site-occupancy factors (s.o.f.'s), such that the sum of these factors was fixed at 1 for each atom. The s.o.f.'s refined to 0.52, 0.48 for C(15) and 0.56, 0.44 for the perchlorate O atoms. In the final refinement the heavy atoms whose thermal motion was small were refined anisotropically and the remainder isotropically. The two C(15) atoms were constrained to 1.50 ± 0.01 Å from their adjacent atoms and all the Cl—O lengths were constrained to 1.44 ± 0.01 Å. The H atoms were omitted. The refinement converged to $R_w = \sum w^{1/2}||F_o| - |F_c||/\sum w^{1/2}|F_o| = 0.114$ and $R = 0.113$ with $w = (\sigma^2 F)^{-1}$. Final atomic coordinates are given in Table 1, bond lengths and angles in Table 2.†

Discussion. Fig. 1 shows a perspective view of the cation with the atomic nomenclature. The Cu atom has distorted trigonal-bipyramidal coordination, the five N

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† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34197 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. Fractional atomic coordinates ($\times 10^4$) of the heavy atoms

	x	y	z		x	y	z
Cu	4834 (1)	7221 (3)	2413 (1)	C(19)	6452 (12)	6550 (27)	4653 (10)
N(1)	4685 (12)	9642 (28)	2283 (11)	C(20)	5148 (12)	5207 (25)	3717 (12)
N(5)	3911 (10)	6730 (23)	1474 (11)	C(22)	3916 (11)	4360 (28)	2871 (12)
N(9)	5374 (10)	5547 (19)	1884 (8)	C(23)	3856 (14)	3106 (27)	3335 (14)
N(17)	5778 (8)	7456 (21)	3361 (9)	C(24)	4489 (16)	2891 (29)	3983 (14)
N(21)	4546 (8)	5417 (18)	3049 (8)	C(25)	5164 (14)	3962 (27)	4227 (12)
C(2)	3884 (14)	10381 (26)	1877 (12)	Cl(1)	1503 (4)	3503 (8)	1057 (4)
C(3)	3200 (16)	9296 (39)	1440 (15)	Cl(2)	6896 (6)	−1100 (11)	1028 (5)
C(4)	3113 (14)	7594 (35)	1324 (13)	O(11)	782 (9)	3753 (27)	1207 (11)
C(6)	4002 (14)	5685 (27)	1004 (13)	O(12)	1441 (12)	4521 (24)	428 (8)
C(7)	3342 (11)	5267 (28)	282 (11)	O(13)	2111 (12)	4121 (34)	1706 (10)
C(8)	4833 (11)	4966 (27)	1262 (12)	O(14)	1547 (10)	1797 (14)	874 (10)
C(10)	6135 (11)	4982 (26)	2126 (12)	O(21)	6445 (23)	−651 (52)	274 (10)
C(11)	6356 (14)	3740 (30)	1756 (15)	O(22)	7549 (17)	−1877 (50)	869 (22)
C(12)	5786 (15)	3137 (31)	1074 (14)	O(23)	7249 (28)	384 (35)	1426 (23)
C(13)	4992 (14)	3738 (27)	808 (12)	O(24)	6548 (25)	−2722 (28)	992 (24)
C(14)	5346 (13)	10753 (27)	2617 (12)	O(212)	7217 (32)	−2543 (47)	1479 (27)
C(15a)	6149 (17)	9896 (46)	2823 (18)	O(222)	6896 (33)	−820 (77)	1762 (14)
C(15b)	6020 (21)	10438 (36)	3343 (16)	O(232)	6028 (9)	−1184 (73)	789 (31)
C(16)	6405 (12)	8754 (27)	3477 (13)	O(242)	7184 (37)	574 (34)	1033 (31)
C(18)	5808 (10)	6431 (27)	3867 (11)				

Table 2. Bond lengths (Å) and angles (°)

N(1)—Cu	1·97 (2)	C(10)—N(9)	1·34 (2)	C(7)—C(6)	1·50 (3)	C(15a)—C(16)	1·50 (1)
N(5)—Cu	1·99 (2)	C(16)—N(17)	1·48 (2)	C(8)—C(6)	1·49 (3)	C(15b)—C(16)	1·50 (1)
N(9)—Cu	2·12 (2)	C(18)—N(17)	1·27 (2)	C(13)—C(8)	1·42 (3)	C(19)—C(18)	1·54 (2)
N(17)—Cu	1·99 (1)	C(20)—N(21)	1·36 (2)	C(11)—C(10)	1·37 (3)	C(20)—C(18)	1·48 (3)
N(21)—Cu	2·09 (2)	C(22)—N(21)	1·35 (2)	C(12)—C(11)	1·42 (3)	C(25)—C(20)	1·40 (3)
C(14)—N(1)	1·43 (3)	N(1)—C(2)	1·48 (3)	C(13)—C(12)	1·40 (3)	C(23)—C(22)	1·38 (3)
C(4)—N(5)	1·51 (3)	C(3)—C(2)	1·48 (3)	C(15a)—C(14)	1·50 (1)	C(24)—C(23)	1·36 (3)
C(6)—N(5)	1·29 (2)	C(4)—C(3)	1·39 (3)	C(15b)—C(14)	1·50 (1)	C(25)—C(24)	1·41 (3)
C(8)—N(9)	1·32 (2)						

N(1)—Cu—N(5)	93·0 (8)	C(4)—N(5)—C(6)	121 (2)	C(7)—C(6)—N(5)	123 (2)	C(16)—C(15b)—C(14)	118 (2)
N(1)—Cu—N(9)	128·9 (7)	C(6)—N(5)—Cu	120 (2)	C(8)—C(6)—N(5)	112 (2)	C(15a)—C(16)—N(17)	109 (2)
N(1)—Cu—N(17)	93·0 (8)	C(8)—N(9)—Cu	111 (1)	C(8)—C(6)—C(7)	125 (2)	C(15b)—C(16)—N(17)	110 (2)
N(1)—Cu—N(21)	135·4 (8)	C(10)—N(9)—Cu	129 (1)	C(6)—C(8)—N(9)	118 (2)	C(19)—C(18)—N(17)	122 (2)
N(9)—Cu—N(5)	78·5 (7)	C(10)—N(9)—C(8)	120 (2)	C(13)—C(8)—N(9)	125 (2)	C(20)—C(18)—N(17)	118 (2)
N(17)—Cu—N(5)	174·0 (7)	C(16)—N(17)—Cu	123 (1)	C(13)—C(8)—C(6)	117 (2)	C(20)—C(18)—C(19)	119 (2)
N(17)—Cu—N(9)	97·4 (6)	C(16)—N(17)—C(18)	122 (2)	C(11)—C(10)—N(9)	121 (2)	C(18)—C(20)—N(21)	113 (2)
N(21)—Cu—N(5)	96·1 (7)	C(18)—N(17)—Cu	116 (1)	C(12)—C(11)—C(10)	119 (2)	C(25)—C(20)—N(21)	125 (2)
N(21)—Cu—N(9)	95·6 (6)	C(20)—N(21)—Cu	112 (1)	C(13)—C(12)—C(11)	120 (2)	C(25)—C(20)—C(18)	122 (2)
N(21)—Cu—N(17)	80·0 (7)	C(22)—N(21)—Cu	130 (1)	C(12)—C(13)—C(8)	115 (2)	C(23)—C(22)—N(21)	123 (2)
C(2)—N(1)—Cu	122 (2)	C(22)—N(21)—C(20)	117 (2)	C(15a)—C(14)—N(1)	112 (3)	C(24)—C(23)—C(22)	117 (2)
C(14)—N(1)—Cu	121 (2)	N(1)—C(2)—C(3)	120 (2)	C(15b)—C(14)—N(1)	124 (3)	C(25)—C(24)—C(23)	123 (2)
C(14)—N(1)—C(2)	118 (2)	C(4)—C(3)—C(2)	134 (3)	C(16) C(15a)—C(14)	118 (2)	C(24)—C(25)—C(20)	114 (2)
C(4)—N(5)—Cu	119 (2)	C(3)—C(4)—N(5)	112 (2)				

atoms of the quinquedentate ligand occupying the coordination sites. The two pyridyl N atoms and the protonated N coordinate equatorially. Although the N—Cu—N angles in the equatorial plane vary between 95·6 and 135·4°, their sum totals 359·9° and Cu lies only 0·005 Å from the plane defined by the three N atoms in question. A square-pyramidal structure had been predicted (although with some reservations) for this complex on the basis of reflectance and ESR spectra (Prince & Stotter, 1974; Stotter, 1974).

However, the nine angles about the Cu atom (Table 2) show that the coordination can be best described as distorted trigonal bipyramidal. The pyridyl and five-membered rings are essentially planar. The two pyridyl rings are almost orthogonal (mean planes through the rings subtend an angle of 96·1°) analogous to the $[CoL^1Me]I_2.2H_2O$ complex. The six-membered chelate rings in this cation differ conformationally from those reported for the Co complex where they are both in chair conformations. The ring Cu—N(5)—C(4)—C(3)—
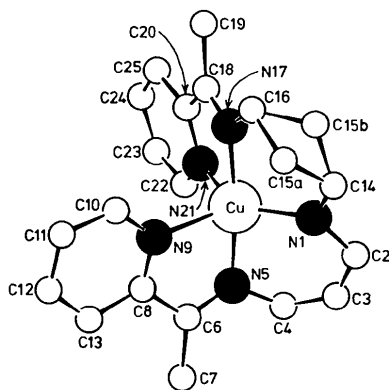
Fig. 1. Perspective view of the cation with the atomic nomenclature.

C(2)—N(1) is in a distorted half-chair conformation where N(5) and to a lesser extent Cu are the out-of-plane atoms. Since C(15) is disordered there are two possible conformations for the remaining six-membered ring. The ring containing C(15a) has a distorted boat conformation, Cu and C(15a) being the apices of the boat. Alternately the ring containing C(15b) lies almost midway between an envelope [C(16) out-of-plane] and a half-chair [C(16) and N(17) out-of-plane]. In the two similar six-membered chelate rings in $[CuL^2](ClO_4)_2$

there is disorder of five methylene C atoms in addition to two independent ClO_4^- groups for each central Cl atom.

The cation is well separated from the ClO_4^- anions with no intermolecular or interionic close contacts.

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Structure of μ-[1,6-Bis(trifluoro)-3,4-bis(trifluoromethyl)hexene-2-thionato]-tetracarbonyldicobalt, a Product of the Reaction between Hexacarbonyltetrakis-(pentafluorobenzenethiolato)dicobalt and Hexafluoro-2-butyne

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Abstract. $Co_2(C_8F_{12}S)(CO)_4$, $C_{12}Co_2F_{12}O_4S$, orthorhombic, $P2_12_12_1$, $a = 9.635$ (6), $b = 10.497$ (6), $c = 17.411$ (8) Å, $U = 1760.9$ Å^3, $Z = 4$, $D_c = 2.21$ Mg m^{-3}, $F(000) = 1128$, μ(Mo $K\alpha$) = 2.22 mm^{-1}. The structure was refined to an R of 0.033 for 2049 reflections. The complex has a flyover structure, with a C_4S bridge between the Co atoms. The bridge is bound to one Co atom through the S atom and an η^3-allyl function and to the other Co atom through the CS group and the terminal C atom. The Co—Co separation is 2.552 (1) Å.

Introduction. Hexafluoro-2-butyne reacts with hexacarbonyltetrakis(pentafluorobenzenethiolato)dicobalt

to give several complexes, one of which has the composition $[Co_2(CO)_4\{C_4(CF_3)_4S\}]$ (Davidson & Sharp, 1975). We undertook an X-ray analysis of this complex to elucidate the molecular structure.

A crystal 0.4 × 0.4 × 0.3 mm was selected for the intensity measurements on a Hilger & Watts four-circle diffractometer with Zr-filtered Mo $K\alpha$ radiation. Intensities were measured by the ω–2θ step-scan procedure and of the 2657 independent reflections surveyed, 2049 satisfied the criterion $I > 3\sigma(I)$.

Initial coordinates for the Co atoms were deduced from a Patterson synthesis and the remaining atoms located in electron-density distributions. The atomic parameters were then adjusted by least-squares cal-