Synthesis and *X*-Ray Structure of a Cobalt(II) Complex of a Negatively Charged Quinquedentate Macrocyclic Ligand †

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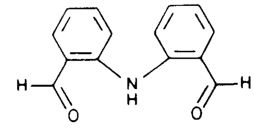
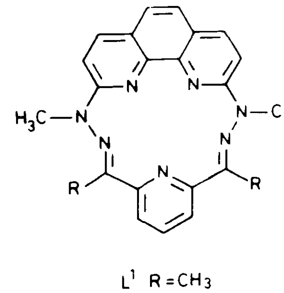
Reaction of 2,2′-iminobisbenzaldehyde with 2,9-di(1-methylhydrazino)-1,10-phenanthroline in the presence of cobalt(II) ions and pyridine leads to the formation of the spin-free title complex [CoL^3(py)$_2$]$^+$ (py = pyridine). The *X*-ray structure of the tetraphenylborate salt confirms a seven-co-ordinate, distorted pentagonal-bipyramidal geometry for the metal ion, which is bound equatorially by five nitrogens from the macrocycle and has two pyridine molecules in the axial sites. The complex crystallises in space group $P2_1/n$ with a = 16.786(4), b = 23.034(4), c = 13.546(3) Å, β = 97.09(3)°, and Z = 4. The structure was solved by Patterson and Fourier-difference techniques and refined to R = 0.097 and R' = 0.079 for 2 458 observed reflections.

Recent work in this laboratory has centred around the synthesis and characterisation of metal complexes of the macrocyclic ligand L^1 prepared by the template condensation reaction of 2,6-dicarbonylpyridines with 2,9-di(1-methylhydrazino)-1,10-phenanthroline in the presence of metal ions. *X*-Ray diffraction studies [1,2] have shown the resulting ligands to be quinquedentate to the metal *via* the phenanthroline, hydrazone, and pyridine donor atoms. A general conclusion from the work has been that it is the nature of the macrocycle that governs the bulk properties of the system, with axial ligands having only a relatively small effect.

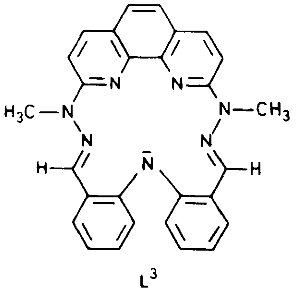
2,2′-Iminobisbenzaldehyde (1) has been successfully used by Rothnie and Black [3] as a ring-closing dicarbonyl in the synthesis of macrocyclic complexes. It deprotonates upon co-ordination to the metal ion to give a charged ligand system. As an extension to our work, compound (1) was investigated as a ring-closing dicarbonyl species with 2,9-di(1-methylhydrazino)-1,10-phenanthroline in the presence of a metal template, in an attempt to prepare complexes of the ligand L^3 for general comparison with those of L^1. We report here the successful synthesis of L^3 using Co^{II} as a template ion and the *X*-ray structure of [CoL^3(py)$_2$][BPh$_4$] (py = pyridine).



(1)



L^1 R = CH$_3$
L^2 R = H



L^3

Results and Discussion

Reaction of 2,2′-iminobisbenzaldehyde (1) with 2,9-di(1-methylhydrazino)-1,10-phenanthroline in the presence of pyridine and cobalt(II) ions gives [CoL^3(py)$_2$]$^+$, which may be precipitated in 60—70% yield by the addition of either NaBPh$_4$ (to give the BPh$_4^-$ salt) or NH$_4$PF$_6$ in methanolic pyridine (to give the PF$_6^-$ salt). In solution, the complex ion decomposes readily in the presence of trace amounts of acid but seems stable indefinitely under basic conditions. A determination of the magnetic moment of the PF$_6^-$ salt by the Gouy method gave μ = 4.60 B.M. (*ca.* 4.27 × 10^{-23} J T^{-1}), which is consistent with spin-free Co^{II} having a large orbital contribution to the moment. The conductivity in nitromethane solution of the BPh$_4$ salt (Λ = 61 ohm^{-1} cm^2 mol^{-1}) is in the range expected [4] for uni-univalent electrolytic behaviour in this solvent. Preliminary studies by cyclic voltammetry in MeCN (Ag–AgNO$_3$ reference electrode, 10^{-3} mol dm^{-3} solution of NBu$^n_4$BF$_4$ as supporting electrolyte) show that the complex exhibits a quasireversible wave at +0.11 V ($E_1 - E_2$ = 78 mV). The cobalt(II) complexes of L^1 show no wave in or near this region: indeed, they show no oxidation chemistry at all up to the solvent-decomposition point. A tentative assignment of the present wave is as due to the Co^{II} $\rightleftharpoons$ Co^{III} redox couple, observable in this complex because of the perturbation of the electrochemical environment of the metal ion by the deprotonated secondary amino-group.

The crystal structure shows the macrocyclic nature of the product and the seven-co-ordinate, distorted pentagonal-bipyramidal geometry of the metal ion. The Figure shows a view of the cation, with hydrogen atoms omitted for clarity, and Tables 1 and 2 the atomic co-ordinates and selected bond parameters. The Co atom is bound by five N-donors of the macrocycle, and N(5) is bonded in the deprotonated form. Two pyridine molecules occupy the axial sites. The non-planarity of the aldehyde-derived segment is immediately apparent. Molecular models of the complex indicate that there is least strain in the conformation observed: the dialdehyde

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† [2,2′-Iminobis(benzaldehyde) *NN*′-dimethyl-*NN*′-1,10-phenanthroline-2,9-diylhydrazonato(1 −)]bis(pyridine)cobalt(II) tetrafluoroborate.

Supplementary data available (No. SUP 23418, 42 pp.): complete geometry, thermal parameters, least-squares planes, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Fractional atomic co-ordinates

Atom	*x*	*y*	*z*
Co	0.852 8(1)	0.105 9(1)	0.232 8(2)
N(1)	0.797 1(8)	0.023 3(6)	0.282 2(10)
N(2)	0.925 8(7)	0.028 8(6)	0.196 1(9)
N(3)	1.020 8(8)	0.090 2(6)	0.147 6(10)
N(4)	0.978 0(8)	0.132 0(6)	0.194 4(10)
N(5)	0.838 3(7)	0.195 5(5)	0.217 5(9)
N(6)	0.722 9(7)	0.117 0(6)	0.281 4(10)
N(7)	0.700 7(7)	0.076 1(6)	0.346 0(11)
N(8)	0.899 3(7)	0.117 0(6)	0.387 8(10)
N(9)	0.800 1(7)	0.098 0(5)	0.075 8(9)
C(1)	0.994 6(11)	0.036 5(8)	0.151 6(14)
C(2)	1.033 2(11)	−0.014 9(8)	0.118 7(13)
C(3)	1.002 1(10)	−0.069 2(8)	0.129 5(12)
C(4)	0.935 1(10)	−0.077 7(8)	0.176 6(13)
C(5)	0.899 0(11)	−0.024 4(8)	0.207 6(13)
C(6)	0.828 9(10)	−0.028 0(8)	0.260 0(12)
C(7)	0.798 7(9)	−0.083 1(7)	0.284 9(12)
C(8)	0.732 9(11)	−0.080 1(9)	0.336 8(14)
C(9)	0.702 4(11)	−0.031 0(8)	0.365 6(14)
C(10)	0.732 9(11)	0.023 1(9)	0.332 8(14)
C(11)	0.900 5(10)	−0.130 8(8)	0.199 7(13)
C(12)	0.835 7(10)	−0.134 3(7)	0.250 6(12)
C(13)	0.635 1(10)	0.084 2(8)	0.402 1(14)
C(14)	0.672 8(10)	0.156 9(7)	0.251 1(13)
C(15)	0.765 8(9)	0.219 3(7)	0.165 0(12)
C(16)	0.773 5(11)	0.261 7(8)	0.090 3(13)
C(17)	0.704 6(12)	0.280 7(8)	0.034 8(14)
C(18)	0.631 7(12)	0.264 0(8)	0.050 9(14)
C(19)	0.621 8(10)	0.224 4(7)	0.121 8(13)
C(20)	0.688 9(10)	0.202 0(7)	0.182 6(13)
C(21)	0.892 3(9)	0.237 9(7)	0.261 4(12)
C(22)	0.868 6(11)	0.288 4(7)	0.301 7(13)
C(23)	0.921 4(10)	0.329 4(8)	0.347 4(13)
C(24)	1.002 7(11)	0.319 5(8)	0.354 4(13)
C(25)	1.031 4(10)	0.271 5(7)	0.312 2(12)
C(26)	0.976 9(10)	0.226 6(7)	0.264 4(12)
C(27)	1.015 6(9)	0.178 1(7)	0.223 2(11)
C(28)	1.099 2(8)	0.105 4(8)	0.112 6(12)
C(29)	0.961 2(10)	0.086 3(7)	0.433 8(13)
C(30)	0.992 3(10)	0.093 6(8)	0.531 9(14)
C(31)	0.959 1(11)	0.133 9(7)	0.585 5(15)
C(32)	0.895 0(10)	0.167 6(8)	0.543 4(14)
C(33)	0.867 1(10)	0.155 9(7)	0.444 0(13)
C(34)	0.823 2(9)	0.134 4(7)	0.007 8(12)
C(35)	0.785 2(10)	0.139 1(8)	−0.087 7(14)
C(36)	0.721 3(10)	0.102 6(8)	−0.113 9(14)
C(37)	0.695 8(11)	0.062 0(8)	−0.049 1(14)
C(38)	0.738 0(9)	0.063 1(7)	0.046 9(13)
B	0.361 1(10)	0.114 4(8)	0.269 9(12)
C(101)	0.423 5(6)	0.118 5(3)	0.458 3(9)
C(102)	0.470 7(6)	0.144 1(3)	0.538 7(9)
C(103)	0.507 4(6)	0.197 6(3)	0.256 9(9)
C(104)	0.496 9(6)	0.225 4(3)	0.434 7(9)
C(105)	0.449 8(6)	0.199 8(3)	0.354 4(9)
C(106)	0.413 1(6)	0.146 3(3)	0.366 2(9)
C(201)	0.448 6(6)	0.017 2(5)	0.258 9(7)
C(202)	0.507 7(6)	−0.015 2(5)	0.220 1(7)
C(203)	0.546 4(6)	0.007 4(5)	0.143 2(7)
C(204)	0.526 0(6)	0.062 5(5)	0.105 1(7)
C(205)	0.467 0(6)	0.094 9(5)	0.143 9(7)
C(206)	0.428 2(6)	0.072 3(5)	0.220 1(7)
C(301)	0.280 7(7)	0.211 1(5)	0.222 3(7)
C(302)	0.235 4(7)	0.248 4(5)	0.156 5(7)
C(303)	0.220 4(7)	0.234 3(5)	0.055 8(7)
C(304)	0.250 6(7)	0.182 8(5)	0.020 9(7)
C(305)	0.296 0(7)	0.145 5(5)	0.086 8(7)
C(306)	0.311 0(7)	0.159 6(5)	0.187 5(7)
C(401)	0.267 2(7)	0.017 7(6)	0.268 2(7)
C(402)	0.204 0(7)	−0.012 9(6)	0.301 6(7)
C(403)	0.159 7(7)	0.021 1(6)	0.371 2(7)
C(404)	0.178 7(7)	0.067 7(6)	0.407 5(7)
C(405)	0.241 9(7)	0.098 4(6)	0.374 1(7)
C(406)	0.286 1(7)	0.073 4(6)	0.304 5(7)

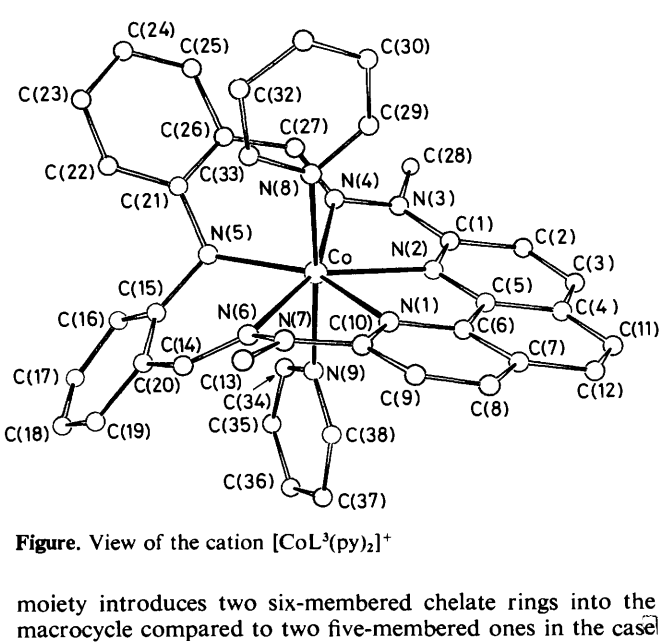

Figure. View of the cation $[\mathrm{CoL}^3(\mathrm{py})_2]^+$

moiety introduces two six-membered chelate rings into the macrocycle compared to two five-membered ones in the case of L^1, which results in extra strain. This strain is also apparent in the deviations of the N_5 donor set from coplanarity. Atom N(4) is *ca.* 0.2 Å to one side of this plane and N(2) is 0.24 Å on the other side; N(1) is also 0.16 Å out of the plane, on the same side as N(4). The mean plane of Co,N(5),C(21),C(15) is inclined at an angle of *ca.* 51° to the N-donor plane, and the sum of angles around the deprotonated atom is 360°, indicating its essentially sp^2 nature. The generally distorted nature of the macrocycle is also manifested in the orientation of the *N*-methyl groups. The angle sums around the nitrogen atoms N(3) and N(7) are 359 and 358° respectively, leading to their assignment as sp^2 hybridised. However, C(13) and C(28) are displaced either side of the Co/N-donor mean plane by 0.95 and 0.25 Å, respectively. The atoms of the phenanthroline unit deviate from coplanarity by less than 0.1 Å.

The pattern of bond lengths to the cobalt atom in this complex deviates from the trends observed [1] in the pyridine-containing species. For the seven-co-ordinate cobalt(II) complex of L^1 these bonds were divided into three classes: from the phenanthroline [2.116(6) and 2.113(5) Å], from the pyridine hydrazones [2.252(6) and 2.226(5) Å], and from the pyridine [2.095(6) Å]. Similar values were observed in the structure of the cobalt(II) complex of L^2. In the present structure the cobalt–phenanthroline bond lengths [2.258(14) and 2.250(14) Å] are significantly longer than in the complexes of L^2, and differ by only *ca.* 0.1 Å from the cobalt–hydrazone bond distances [2.308(13) and 2.366(13) Å]: this is close to the estimated standard deviations (e.s.d.s) for the structure. The bond between the cobalt atom and the deprotonated nitrogen N(5) is the shortest at 2.084(13) Å. The accommodation of a larger ring-closing dicarbonyl, leading to an increased ' hole

Table 2. Selected bond lengths (Å) and angles (°)

Co-N(1)	2.258(14)	Co-N(2)	2.250(14)	N(2)-Co-N(1)	69.9(5)	N(4)-Co-N(1)	135.1(5)
Co-N(4)	2.308(13)	Co-N(5)	2.084(13)	N(4)-Co-N(2)	67.6(5)	N(5)-Co-N(1)	144.8(5)
Co-N(6)	2.366(13)	Co-N(8)	2.163(13)	N(5)-Co-N(2)	145.0(5)	N(5)-Co-N(4)	79.5(5)
Co-N(9)	2.207(12)	N(1)-C(6)	1.344(22)	N(6)-Co-N(1)	65.2(5)	N(9)-Co-N(8)	176.9(5)
N(1)-C(10)	1.347(25)	N(2)-C(1)	1.379(24)	N(6)-Co-N(4)	158.6(5)	N(6)-Co-N(5)	79.7(5)
N(2)-C(5)	1.322(24)	N(3)-N(4)	1.398(20)	N(8)-Co-N(1)	85.8(5)	N(8)-Co-N(2)	99.6(5)
N(3)-C(1)	1.315(24)	N(3)-C(28)	1.495(20)	N(8)-Co-N(4)	87.6(5)	N(8)-Co-N(5)	90.2(5)
N(4)-C(27)	1.273(20)	N(5)-C(15)	1.441(19)	N(8)-Co-N(6)	87.3(5)	N(9)-Co-N(1)	94.9(5)
N(5)-C(21)	1.414(19)	N(6)-N(7)	1.370(20)	N(9)-Co-N(2)	83.5(5)	N(9)-Co-N(4)	94.1(5)
N(6)-C(14)	1.278(21)	N(7)-C(10)	1.357(25)	N(9)-Co-N(5)	87.6(5)	N(9)-Co-N(6)	90.2(5)
N(7)-C(13)	1.424(24)	C(5)-C(6)	1.45(3)	C(21)-N(5)-Co	125.6(9)	C(1)-N(3)-N(4)	116(1)
C(14)-C(20)	1.440(24)	C(21)-C(26)	1.439(23)	C(28)-N(3)-N(4)	120(1)	C(28)-N(3)-C(1)	123(1)
C(15)-C(20)	1.399(23)	C(26)-C(27)	1.439(23)	C(15)-N(5)-Co	120.5(9)	C(10)-N(7)-N(6)	113(1)
				C(21)-N(5)-C(15)	114(1)	C(13)-N(7)-C(10)	122(2)
				C(13)-N(7)-N(6)	123(1)		

size,' and/or electronic effects, reflecting the perturbation of the deprotonated nitrogen on the electronic environment of the metal ion, may be responsible for these differences.

Experimental

(*a*) *Precursors*.—The preparation of the substituted phenanthroline species has been described previously.[5] 2,2′-Iminobisbenzaldehyde (1) was prepared following the method of Rothnie.[6] Treatment of diazotised methyl anthranilate with potassium iodide gave * the iodo-substituted phenyl ester in 71% yield after distillation of the product. This was coupled with methyl anthranilate in the presence of copper powder to give [7] the 2,2′-iminobisbenzoate, which was converted into (1) in 32% overall yield using essentially the technique reported [8] for the preparation of 2,2′-(ethane-1,2-diyldi-imino)bisbenzaldehyde.

(*b*) *Macrocyclic Complex of* L^3.—50% Aqueous ethanol (50 cm^3) was brought to reflux under an atmosphere of nitrogen. 2,9-Di(1-methylhydrazino)-1,10-phenanthroline (31 mg, 10^{-4} mol) was added, followed by $Co[BF_4]_2 \cdot 6H_2O$ (34 mg, 10^{-4} mol). The solution was heated under reflux for 5 min before 2 equivalents of pyridine were added, followed by (1) (22 mg 10^{-4} mol). The solution was refluxed for 2 h during which time it became deep red. An excess of pyridine was then added to the solution. After brief stirring, a concentrated solution of $NaBPh_4$ in ethanol (5 cm^3) was added to precipitate the product. After cooling, the brick-red microcrystalline complex (as the BPh_4^- salt) was collected and dried *in vacuo*. Yield 72 mg, 72%. For the PF_6^- salt, ammonium hexafluorophosphate in methanolic pyridine was used as the precipitating agent {Found: C, 74.1; H, 5.5; N, 12.8. $[CoL^3(py)_2][BPh_4]$ requires C, 74.3; H, 5.3; N, 12.6. Found: C, 54.9; H, 3.7; N, 15.0. $[CoL^3(py)_2][PF_6]$ requires C, 55.1; H, 4.0; N, 15.2%}.

(*c*) *Crystal-structure Determination*.—Large dark red crystals of the title complex were grown from nitromethane solution by slow evaporation. 5 391 Reflections were collected on a Stöe four-circle diffractometer using a 140-step ω—θ scan technique, graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å), and a crystal of dimensions $0.42 \times 0.38 \times 0.31$ mm. After data collection, intensities were corrected for Lorentz and polarisation effects to leave 2 458 unique intensity data, $F > 4\sigma(F)$.

Crystal data. $[CoL^3(py)_2][BPh_4]$, $M = 992$, Monoclinic, space group $P2_1/n$, $a = 16.786(4)$, $b = 23.034(4)$, $c = 13.546(3)$ Å, $\beta = 97.09(3)°$, $U = 5\,197.4$ Å^3, $D_c = 1.27$ g cm^{-3}, $Z = 4$, $F(000) = 2\,076$, μ(Mo-K_α) = 3.48 cm^{-1}, $R = 0.097$, $R' = 0.079$.

The cobalt atom was located from a Patterson map and all remaining non-hydrogen atoms from subsequent difference maps. In the later stages of refinement the weighting scheme $w = 1/[\sigma^2(F)]$ was introduced. Neutral atom scattering factors were used throughout. The phenyl rings of the counter ion were refined as regular hexagons of C-C bond distance 1.395 Å. The hydrogen atoms were constrained to lie in geometrically idealised sites 1.08 Å from the parent carbon atom. The methyl groups were treated as rigid bodies. Anisotropic thermal parameters were assigned to the cobalt and all nitrogen atoms.

Acknowledgements

We thank the S.E.R.C. for financial support and ICI Ltd. for a C.A.S.E. award (both to C. W. G. A.).

References

1 M. M. Bishop, J. Lewis, T. O'Donoghue, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1980, 1390; J. Lewis and T. O'Donoghue, *ibid.*, p. 1383; C. W. G. Ansell, J. Lewis, P. R. Raithby, and J. N. Ramsden, *ibid.*, 1982, 2127.
2 C. W. G. Ansell, J. Lewis, M. C. Liprot, P. R. Raithby, and M. Schroder, *J. Chem. Soc., Dalton Trans.*, 1982, 1593.
3 N. Rothnie and D. St. C. Black, *Tetrahedron Lett.*, 1978, **31**, 2835.
4 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
5 J. Lewis and T. O'Donoghue, *J. Chem. Soc., Dalton Trans.*, 1980, 736.
6 N. Rothnie, Ph.D. Thesis, Monash University, 1978.
7 D. Hellwenkel and M. Melan, *Chem. Ber.*, 1971, **104**, 1001.
8 M. Green, J. Smith, and P. A. Tasker, *Inorg. Chim. Acta*, 1971, **5**, 17.

Received 4*th May* 1982; *Paper* 2/724

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* The method used was essentially that of Heaney and Millar for the preparation of *o*-bromoiodobenzene: see *Org. Synth.*, 1960, **40**, 105.