Synthesis and Structure of [Hemiporphyrazinato(2 −)bis(1-methylimidazole)-cobalt(III)] Triiodide

By Armando Marzotto

Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Padova, Via Loredan 4, 35100 Padova, Italy

Giovanni Valle

Centro Studi del CNR sui Biopolimeri, Università di Padova, Via Marzolo 1, 35100 Padova, Italy

and Dore Augusto Clemente

Dipartimento di Scienza dei Materiali, Facoltà di Scienze, Università di Lecce, Via Monteroni, 73100 Lecce, Italy

Abstract. $[Co(C_{26}H_{14}N_8)(C_4H_6N_2)_2]I_3$, $M_r = 1042 \cdot 3$, triclinic, $P\bar{1}$, $a = 12 \cdot 721$ (3), $b = 9 \cdot 427$ (2), $c = 8 \cdot 440$ (2) Å, $\alpha = 62 \cdot 05$ (2)°, $\beta = 75 \cdot 02$ (2)°, $\gamma = 74 \cdot 58$ (2)°, $V = 851 \cdot 2$ (4) Å^3, $Z = 1$, $D_x = 2 \cdot 03$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 32 \cdot 40$ cm^{-1}, $F(000) = 500$, brown-green air-stable parallelepipeds elongated along **c**, $T = 294$ K, final $R = 0 \cdot 042$ for 2452 unique observed $[F_o > 5\sigma(F_o)]$ reflections. The hexacoordinate [(hemiporphy-razinato)bis(1-methylimidazole)cobalt(III)] triiodide was prepared by reacting a (hemiporphyrazinato)Co^{II} complex, $[Co(hp)(H_2O)_2]$, with pure 1-methylimidazole in the presence of molecular iodine. The Co^{III} atom lies at the crystallographic center of symmetry coincident with the center of the tetraaza ligand which is found to be nearly planar. The Co—N(isoindole) and Co—N(pyridine) bond lengths are 1·917 (5) and 2·115 (5) Å respectively, whereas that of Co—N(1-Meim) is 1·953 (4) Å, which indicates the low-spin state of the Co^{III} atom. The extended planarity of the hemiporphyrazine macrocycle is maintained because of the lack of strong crystal packing forces. The results are discussed in view of possible biological implications of the tetraaza–Co^{III} complexes as preferential binding sites for nitrogen donors of nucleobase derivatives and protein histidines.

Introduction. As part of an extensive investigation on the strength of the cobalt—nitrogen bond, the $[Co(hp)(H_2O)_2]$ complex (hpH$_2$ = hemiporphyrazine) was prepared and characterized and its axial reactivity towards nitrogen-donor ligand such as 1-methyl-imidazole was investigated (Marzotto & Clemente, 1988; Marzotto, Valle & Clemente, 1988). The interest of these studies lies in the ability of such metal

complexes to form a biologically and enzymatically stable metal–nitrogen bond similar to that known for vitamin B$_{12}$. Moreover, cobalt, an essential metal in biological systems, is coordinated to the corrinoid ring of vitamin B$_{12}$ and a very reduced toxicity is reported for the cobalt ion in humans (Martin, 1986).

The tetraazamacrocycle coordinated to the Co^{III} ion in a low-spin state may represent a model for studying the electronic and structural features of cobalt complexes and thus verify whether the Co^{III}—N(aromatic) is the strongest metal–N bond present in naturally occurring biological systems.

Experimental. $[Co(hp)(H_2O)_2]$ was prepared by refluxing for 4 h, in a dimethylformamide solution (60 ml), hemiporphyrazine (4·03 g, 9·1 mmol) with a slight excess of $Co(CH_3COO)_2.2H_2O$ (2·75 g, 11·0 mmol). After the mixture cooled to room temperature, the black precipitate was filtered, washed with dimethylformamide (DMF) and methanol and recrystallized from 1/1 DMF/MeOH solution. The crude product was dried at 353 K for 2 h. Analytical data: found: C 58·8; H 3·2; N 21·2%; calculated for $C_{26}H_{18}CoN_8O_2$: C 58·5; H 3·4; N 21·0%. A brown-green Co(hp)(H$_2$O) complex was prepared by other authors (Attanasio, Collamati & Cervone, 1983) with an analogous method in which the complex was purified by vacuum sublimation at 693 K, 1·33 Pa. The presence of the two molecules of H$_2$O in our black solid compound was checked both by thermo-gravimetry (TG and DTG) and by differential scanning calorimetry (DSC) measurements.

$[Co(hp)(1-Meim)_2]I_3$ was obtained by reacting $[Co(hp)(H_2O)_2]$ (2·13 g, 4 mmol) in pure 1-methyl-imidazole in the presence of molecular iodine (1·39 g,

11 mmol). From the solution, brown-green crystals slowly precipitated and were recrystallized from acetone/chloroform. Analytical data: found: C 39·1; H 2·6; N 16·0; I 36·4%; calculated for $C_{34}H_{26}CoI_3N_{12}$: C 39·2; H 2·5; N 16·1; I 36·5%.

A brown-green crystal of $[Co(hp)[1\text{-Meim}]_2]I_3$, approximately 0·1 × 0·1 × 0·4 mm, was mounted on a Philips PW1100 diffractometer, using Mo $K\alpha$ graphite-monochromated radiation. Accurate lattice and orientation parameters were obtained by least-squares treatment of 25 symmetry-related reflections. Intensity data were collected by the ω–2θ scan method with individual profile analysis (Lehmann & Larsen, 1974). The intensities of three standard reflections displayed no observable trend; random variations were in the range ±3%. Of 2971 reflections measured $(2\cdot0 < \theta < 25°)$ only 2452 unique reflections with $F_o > 5\sigma(F_o)$ were used in the subsequent structure determination and refinement. −13 $\leq h \leq$ 14, −9 $\leq k \leq$ 10, 0 $\leq l \leq$ 10. The intensities were corrected for Lorentz and polarization effects and absorption corrections were made following the empirical method of North, Philips & Mathews, (1968); min., max. relative transmission coefficients 0·761, 1·00. The I_3^- moiety was located from a three-dimensional Patterson map. A series of Fourier and difference Fourier maps revealed the positions of the Co atom and successively of all non-H atoms. The structure was refined on F by full-matrix least-squares method using the $SHELX76$ package of programs (Sheldrick, 1976), $w = 1$ for all the reflections. At the beginning, displacement parameters were anisotropic for I_3^- and Co atoms, but when the conventional residual R reached 0·15 all non-H atoms were assigned anisotropic displacement parameters. This brought R to 0·10 and no further significant improvement could be made. At this point using a weighting scheme $w = 1/\sigma^2(F_o)$ and including all the H atoms in calculated positions, after three cycles of refinement convergence was obtained (maximum shift/e.s.d. < 1·6, maximum shift 0·008 Å). The final conventional R value was 0·040 for 2452 reflections with a slightly higher discrepancy for five strong reflections; three of these (002; 102; 202) are underestimated, probably for uncorrected extinction effects. The final Fourier difference synthesis showed peaks as high as 0·4 e Å^{-3} near the Co atom and peaks of 0·8 e Å^{-3} in the neighbourhood of the I atoms. This may be due to some crystallographic disorder of the I_3^- moiety. In fact, when no crystallographic symmetry is imposed, this anion is bent by up to 5° and shows a difference in the I—I distances of up to 0·06 Å (see e.g. Runsink, Swen-Walstra & Migchelsen, 1972; Biagini Cingi, Manotti Lanfredi, Tiripicchio, Bandoli & Clemente, 1981). When I_3^- lies on a symmetry center, it must appear linear with two identical I—I distances. Although

Table 1. *Positional parameters and equivalent isotropic thermal parameters $(U_{eq} \times 10^2)$ and their standard deviations for* $[Co(hp)(1\text{-Meim})_2]I_3$

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq} (Å^2)
I(1)	0·0000	0·0000	0·0000	4·49 (3)
I(2)	0·0399 (1)	0·3050 (1)	0·0353 (1)	6·95 (3)
Co	0·5000	0·5000	1·0000	2·18 (4)
N(1)	0·5621 (4)	0·2937 (5)	0·9444 (6)	2·6 (2)
N(2)	0·3984 (4)	0·5788 (5)	0·8323 (6)	2·4 (2)
N(3)	0·6090 (4)	0·6216 (5)	0·8071 (6)	2·6 (2)
N(4)	0·4421 (4)	0·3714 (6)	0·7232 (7)	3·5 (3)
N(5)	0·6954 (4)	0·1663 (6)	1·1570 (7)	3·1 (2)
N(6)	0·7659 (4)	0·6955 (6)	0·6432 (7)	3·2 (3)
C(1)	0·5241 (5)	0·2703 (7)	0·8241 (7)	2·8 (3)
C(2)	0·5649 (5)	0·1326 (7)	0·7859 (8)	3·5 (3)
C(3)	0·6447 (5)	0·0117 (7)	0·8767 (9)	3·6 (3)
C(4)	0·6827 (5)	0·0306 (7)	0·9993 (9)	3·5 (3)
C(5)	0·6431 (5)	0·1699 (7)	1·0331 (7)	2·7 (2)
C(6)	0·3880 (5)	0·5044 (7)	0·7322 (7)	2·9 (3)
C(7)	0·2995 (5)	0·6031 (7)	0·6202 (8)	3·0 (3)
C(8)	0·2591 (6)	0·5814 (8)	0·4984 (9)	4·0 (3)
C(9)	0·1750 (7)	0·7008 (10)	0·4113 (10)	4·0 (4)
C(10)	0·1337 (6)	0·8361 (9)	0·4500 (10)	3·9 (4)
C(11)	0·1738 (6)	0·8547 (9)	0·5752 (10)	3·5 (3)
C(12)	0·2590 (6)	0·7374 (8)	0·6568 (9)	2·9 (3)
C(13)	0·3219 (5)	0·7213 (7)	0·7881 (8)	2·6 (3)
C(14)	0·7177 (5)	0·5866 (8)	0·7971 (9)	3·0 (3)
C(15)	0·6846 (6)	0·8065 (9)	0·5491 (10)	3·5 (3)
C(16)	0·5878 (6)	0·7609 (8)	0·6510 (9)	3·4 (3)
C(17)	0·8855 (7)	0·6914 (11)	0·5836 (12)	5·2 (4)

such a situation may be due to static or dynamic disorder, it is now accepted (Dong, Hendrickson, Pierpont & Moore, 1986) that the vibrational motion interconverts the I_3^- anion between the two limiting forms [I(1)—I(2)···I(3)] and [I(1)···I(2)—I(3)]. X-rays 'see' a symmetric I_3^- ion probably because the vibrations are slow with respect to the X-ray diffraction time scale.

Scattering factors are those incorporated in the $SHELX$ package. The final atomic coordinates are listed in Table 1.*

Discussion. The structure consists of well separated monomeric $[Co(hp)(1\text{-Meim})_2]^+$ cations and I_3^- anions. Each cation and anion has a crystallographically imposed center of symmetry, coincident with the Co atom and with the central I atom, respectively. Table 2 reports bond distances and angles and Figs. 1 and 2 indicate the numbering scheme adopted. The Co^{III} atom is six-coordinated and lies in the plane of the four equatorial N atoms, as imposed by symmetry. The two apical positions are occupied by two N(3) atoms of the axially bound 1-methylimidazole (1-Meim). The difference of

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Table 2. *Selected bond distances* (Å) *and angles* (°) *in* [Co(hp)(1-Meim)$_2$]I$_3$

Hemiporphyrazinato–Co^{III}

Co—N(1)	2·115 (5)	C(6)—N(4)	1·286 (8)
Co—N(2)	1·917 (5)	N(2)—C(6)	1·373 (10)
Co—N(3)	1·953 (4)	N(2)—C(13)	1·383 (7)
N(1)—C(1)	1·354 (10)	C(6)—C(7)	1·482 (9)
N(1)—C(5)	1·387 (7)	C(7)—C(8)	1·374 (13)
C(1)—C(2)	1·416 (10)	C(8)—C(9)	1·394 (10)
C(2)—C(3)	1·373 (8)	C(9)—C(10)	1·398 (14)
C(3)—C(4)	1·347 (13)	C(10)—C(11)	1·381 (15)
C(4)—C(5)	1·401 (10)	C(11)—C(12)	1·381 (9)
C(5)—N(5)	1·361 (10)	C(12)—C(13)	1·459 (12)
C(1)—N(4)	1·375 (8)	N(5)—C(13^i)	1·292 (10)
N(1)—Co—N(2)	89·8 (2)	C(1)—N(1)—C(5)	115·1 (5)
N(1)—Co—N(2^i)	90·2 (2)	Co—N(2)—C(6)	126·4 (4)
N(1)—Co—N(3)	91·6 (2)	Co—N(2)—C(13)	126·8 (4)
N(2)—Co—N(3)	90·7 (2)	C(6)—N(2)—C(13)	106·8 (5)
Co—N(1)—C(1)	122·8 (4)	C(1)—N(4)—C(6)	124·0 (6)
Co—N(1)—C(5)	122·0 (4)	C(5)—N(5)—C(13^i)	125·6 (6)

1-Meim

N(3)—C(14)	1·323 (8)	N(6)—C(15)	1·366 (8)
N(3)—C(16)	1·381 (7)	N(6)—C(17)	1·470 (10)
N(6)—C(14)	1·338 (7)	C(15)—C(16)	1·352 (10)
Co—N(3)—C(14)	127·4 (4)	C(14)—N(3)—C(16)	105·9 (6)
Co—N(3)—C(16)	126·6 (5)		
I(1)—I(2)	2·917 (1)		

Symmetry code: (i) 1 − *x*, 1 − *y*, 2 − *z*.

0·198 (5) Å between the cobalt—hemiporphyrazine nitrogen bond lengths [Co^{III}—N(isoindole) = 1·917 (5) and Co^{III}—N(pyridine) = 2·115 (5) Å] is mainly due to the asymmetry of the free hp ligand [C_t—N(isoindole) = 1·927 (5) and C_t—N(pyridine) = 2·246 (6) Å, C_t = center of symmetry] as discussed by Attanasio, Collamati & Daul (1985) and Agostinelli, Attanasio, Collamati & Fares (1984) for Nihp(py)$_2$ (py = pyridine) [Ni^{II}—N(isoindole) = 1·96 (1), Ni^{II}—N(pyridine) = 2·16 (1) Å]. This asymmetry is also caused by the interruption of the π conjugation in the hp ligand that enhances the isoindole nitrogen basicity (Bossa, Cauletti, Grandinetti & Nota, 1987; Hiller, Strahle, Datz, Hanack, Hatfield, ter Haar & Gutlich, 1984). Moreover, such an interpretation is supported by: (i) the short C(6)—N(4) [1·286 (8) Å] and the long C(1)—N(4) [1·375 (8) Å] bond distances; (ii) the Co^{III}—N-(isoindole) distance, shorter than the usual values occurring in the 1·948–1·985 Å range as found for [Co^{III}(tpp)] complexes (tpp = tetraphenyl-porphyrinato) (Iimura, Sakurai & Yamamoto, 1988); (iii) the Co^{III}—N(pyridine) distance, much longer than the normal value of 1·91 (1) Å, found for example in [(η^5-C$_5$H$_5$)CoINC$_5$H$_4$—C(CH$_3$)=N—CH(CH$_3$)(C$_6$H$_5$)]$^+$.I$^-$ (Bernal, Riesner, Brunner & Riepl, 1985). The introduction of a Co^{III} ion in the hole of the hemiporphyrazinato anion reduces the C_t—N distances as for Fe^{IV} [where Fe—N(isoindole) = 1·910 (3) and Fe—N(pyridine) = 2·135 (3) Å;

Hiller *et al.* (1984)], suggesting an interaction between the empty $d_{x^2-y^2}$ metal orbital and the nitrogen lone pair of the hp ligand (Attanasio *et al.*, 1985).

Another point of interest in this structure is the planarity of the hemiporphyrazinato–Co^{III} group (mean deviation from plane 0·022 Å); the maximum deviation is for the C(4) atom (−0·057 Å). Among the few metal–hp derivatives that have been structurally characterized so far, only the Ge(hp)L_2 complex (L = 2-ethoxyethanol) has been found to be completely planar (Hecht & Luger, 1974), whereas the other complexes exhibit a strong distortion, the isoindole units and the pyridine rings being twisted above the mean plane by 30°, Fe^{IV}Ohp (Hiller *et al.*, 1984); 27°, Co^{II}hp and Ni^{II}hp (Speakman, 1953); 9°, Ni^{II}hp(py)$_2$ (Agostinelli *et al.*, 1984). These features, as suggested by Speakman (1953), could be interpreted by considering that such a distortion increases with the size of the metal ion. This view was also invoked to explain the behavior of iron–porphyrin complexes (Fleisher, 1970; Perutz, 1970; Hoard,
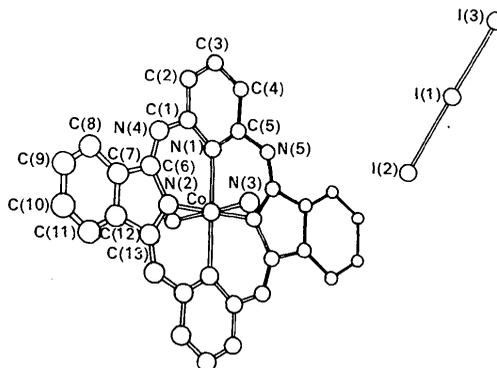
Fig. 1. Drawing of [Co(hp)(1-Meim)$_2$]I$_3$ with numbering scheme for non-H atoms. For clarity only the N(3) atoms of the two axial *N*-methylimidazole groups are shown.
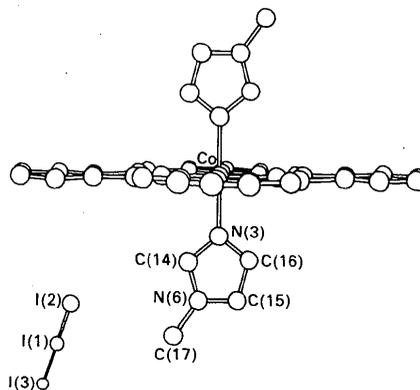
Fig. 2. View of the molecule projected on the methylimidazole plane showing the Co^{III}—N(3) bonding.

1973; Little & Ibers, 1974a; Hoard, 1975; Scheidt, 1977) which is due to the larger size of the high-spin Fe^{II} ion ($r = 0.77$ Å) compared to the low-spin Fe^{II} ($r = 0.61$ Å) or Fe^{III} [$r = 0.55$(LS)–0.645 Å(HS)] ions (Shannon, 1976).

Nevertheless, such a simple explanation cannot justify the deviation from planarity of the metal–hp derivatives. In fact, the octahedral covalent (Pauling, 1960) and ionic (Shannon, 1976) radii of Co^{III} ($r_c = 1.22$; $r_i = 0.545$ Å) and Fe^{IV} ($r_c = 1.20$; $r_i = 0.585$ Å) and the square-planar covalent and ionic radii of the Ni^{II} ion ($r_c = 1.20$; $r_i = 0.55$ Å) are practically identical.

It has been demonstrated on quantum-mechanical grounds (Bossa et al., 1987) that the hp ligand is easily deformable, being essentially a nonaromatic system with 20 π non-delocalized electrons and thus should be regarded as formed by two pyridine rings connected by single bonds to the rest of the molecule. We therefore believe that deviations from planarity of the hp complexes may occur when there are strong intermolecular interactions. In fact, FeOhp exhibits strong intermolecular contacts with the axial oxygen ions; Nihp seven short contacts in the 3.37–3.45 Å range; Nihp(py)$_2$ six short contacts in the 3.38–3.48 Å range. In contrast, Ge^{IV}hp shows only one relatively short contact, 3.463 (6) Å, and the present Co^{III}hp complex only three contacts: $C(8)\cdots N(6^i) = 3.450$ (12), $C(15)\cdots N(5^{ii}) = 3.459$ (8) and $I(2)\cdots C(17^i) = 3.598$ (12) Å which is probably the only true hydrogen bond [(i) $1 - x$, $1 - y$, $1 - z$; (ii) x, $1 + y$, $-1 + z$].

The Co^{III}—N(imidazole) bond length of 1.953 (4) Å is only slightly longer than 1.90 Å, that is the sum of the covalent radii of the Co^{III} ion with $t_{2g}^6 e_g^0$ configuration (1.22 Å) and of an N(sp^2) atom (0.68 Å) (Lauher & Ibers, 1974; Little & Ibers, 1974b). In fact, for a cobalt ion with an unpaired electron in the e_g orbitals, this bond length becomes 2.15 (1) Å, an increase of 0.25 Å. Little & Ibers (1974b), suggested that the Co—N(imidazole) distance is governed not only by the spin state of the Co atom, but also by the steric interaction of H(14) and H(16) with the hp ligand. In our case, the non-bonded contacts less than 2.6 Å are $H(14)\cdots N(2^i) = 2.576$ and $H(16)\cdots C(13) = 2.577$ Å. Following Collins, Countryman & Hoard (1972), if the dihedral angle between the imidazole plane and the plane passing through N(3), Co and N(2) is 45°, these steric interactions are minimized and the imidazole H atoms will point towards the —N= bridging atom. In our case, this angle is 26.4 (2)°, which could explain the elongation of the Co—N(imidazole) distance from 1.90 to 1.953 (4) Å. In any case, such a bond length is one of the shortest axial metal–nitrogen bonds so far known and this is interesting in view of possible biological applications.

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